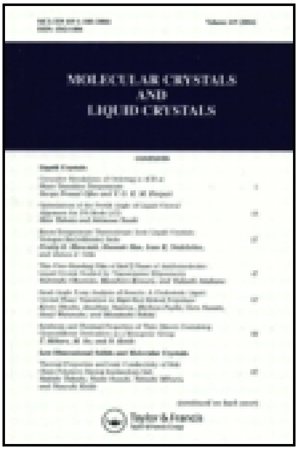

Molecular Crystals

Positron Annihilation in Irradiated Organic Crystals

Y. Tabata [a] , Y. Ito [a] & K. Oshima [a]

[a] Faculty of Engineering, University of Tokyo, Tokyo, Japan

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Positron Annihilation in Irradiated Organic Crystals

Y. TABATA, Y. ITO, and K. OSHIMA

Faculty of Engineering
University of Tokyo,
Tokyo, Japan

Abstract—It is well known that " positron e^+ " interacts with matter and forms a positronium ($e^+ - e^-$) with the electrons of matter. Both the probability of the positronium formation and the lifetime of positronium are profoundly affected not only by the physical state of molecular substances, such as amount of defects, crystallinity, the size and other properties of crystals, but also by the presence of ions, radicals and excited species, produced in the system. Therefore, one can follow solid state reactions by the measurement of lifetime of positronium and the probability of the formation in the reaction system without any degradative analysis. By applying this method to the radiation-induced reaction in organic crystalline state, polymerization of several monomers such as acrylonitrile, methacrylonitrile, acetoaldehyde and N-vinyl-carbazole, in the crystalline state has been studied in our laboratory. In this paper, the radiation-induced solid state polymerizations N-vinyl-carbazole are reported.

Introduction

It is well known that positrons, e^+, interact with matter and can form positronium ($e^+ - e^-$) with the electrons of matter. Both the probability of positronium formation and the lifetime of positronium are profoundly affected not only by the physical state of molecular substances, such as the defect population, the crystallinity, the size and other properties of crystals, but also by the presence of species, such as ions, radicals and other excited species, produced in the system.[1,2,3,4,5] Therefore, one can analyze radiation-induced solid state reactions by the measurement of the lifetime of positronium and the probability of its formation in the reaction system. By applying this method to radiation-induced reactions in the organic crystalline state, solid state polymerization of various monomers has been studied in our laboratory.[6] In this paper, the radiation-induced polymerization of N-vinyl-carbazole is reported.

Positron Annihilation

The behavior of positron in matter is presented schematically in Fig. 1.

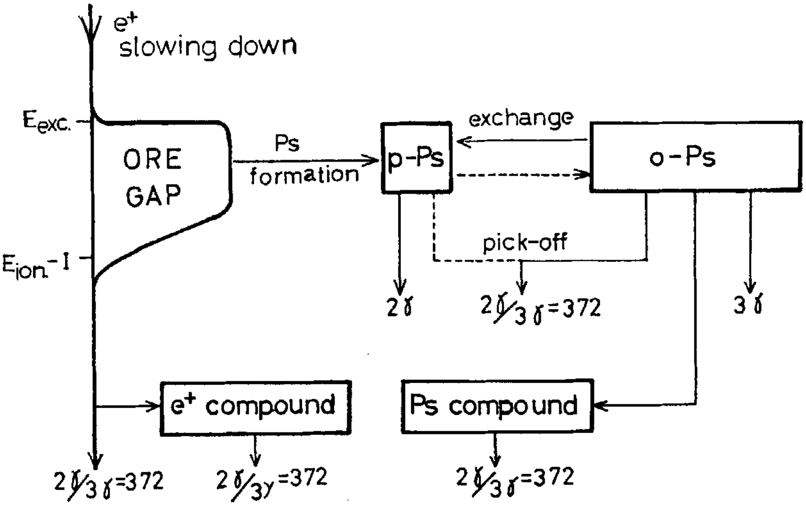


Figure 1. Schematic diagram for positron annihilation.

High energy positrons lose the energy rapidly by ionization collisions and are slowed down to several tens of eV in about 10^{-10} sec. Positronium, ($e^- - e^+$), which is very similar to hydrogen atoms, is formed in the intermediate positron energy range between $E_{\text{ion}} - I$ and E_{exc}.

$$E_{\text{ion}} - I < E < E_{\text{exc.}}$$

where E_{ion} is the ionization potential of the molecules, $E_{\text{exc.}}$ the lowest excitation energy of molecules and I is the bonding energy of positronium. The intermediate energy region is called the " Ore gap ". If a positron lands in the Ore gap, it will have a good chance of forming positronium. Triplet and singlet positroniums are formed, in the ratio of 3 : 1, and annihilate via 3γ and 2γ processes, respectively. However, the annihilation is profoundly affected by interactions of positronium with surrounding substances.

" Pick-off quenching " is an important process of annihilation. *Triplet*-positronium interacts with electrons of surrounding substances and free annihilation takes place.[7] Another important interaction is called " exchange collision " or " conversion ".[8] This process is a kind of paramagnetic quenching and *triplet*-positronium converts to *singlet*-positronium by exchanging its electron with that of paramagnetic atoms, molecules and radicals.

A third kind of interaction is the formation of positronium compounds[9] by the interaction of positronium with atoms, paramagnetic molecules and radicals. Finally, oxidation or reduction process of positronium[10] by ions can not be neglected. However, the contribution of this may be small or neglegible in our cases.

The pick-off process is influenced to a great extent by the size and amount of the free volumes in the system. On the other hand, exchange collision and positronium compound formation are profoundly affected by radicals produced in irradiated organic solid systems. Therefore, it is quite probable that these processes are influenced by both active species and polymers produced in solid monomers during polymerization.

In order to investigate the mechanism of radiation-induced solid state polymerization, we have measured the rate of positronium annihilation in the system of irradiated monomers where the reaction is taking place in the solid state. In the irradiated system, either the change of the long lifetime component of *triplet*-positronium to τ_2 or the change in its intensity I_2 would be caused by; (1) free annihilation originating from pick-off quenching of *triplet*-positronium in free volumes, (2) triplet to singlet conversion originating from exchange collision with unpaired electron spins, and (3) formation of positronium compounds by capture of the positronium atom by the active species in the system.

The crystalline structure of monomers changes with the formation of polymers and the amount of defects and dislocations increases with polymerization. Such kind of phenomena, including the expansion of lattice constant, result in the increase of free volume in the system. Positronium can have comparatively longer lifetimes in the free volume in such deformed lattices. Then the pick-off rate of positronium would be decreased resulting in the lengthening of τ_2.

Measurement of Lifetime

The lifetime measurements were made by a conventional fast-slow coincidence system, with MB–10 plastic scintilators, 56 AVP photomultipliers, a Weisberg type time to amplitude converter, and a TMC 100 channel analyzer. The resolving time calibrated with γ-rays from a Co^{60} source was 1.1 n sec. The accumulated data were analyzed by a HITAC 5020 A computer.

Radiation-Induced Solid State Polymerization of N-Vinyl-Carbazole

The monomers were purified by re-crystallization from *n*-hexane solution and about 15μCi of ^{22}Na was added to 1 gm of monomer. Irradiation was carried out at 20 °C at a dose rate of 7.2×10^4 r/hr. The measurement of the lifetime spectrum was made over a range of temperatures by regulating temperature with the devices shown in Fig. 2.

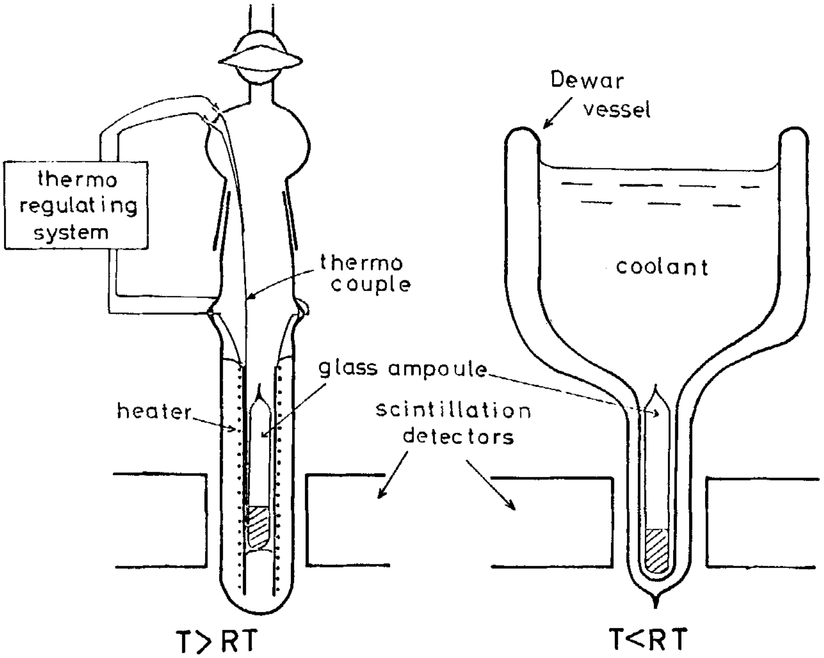


Figure 2. Experimental arrangements for measurement of lifetime of positrons at various temperatures.

A typical lifetime spectrum is shown in Fig. 3.

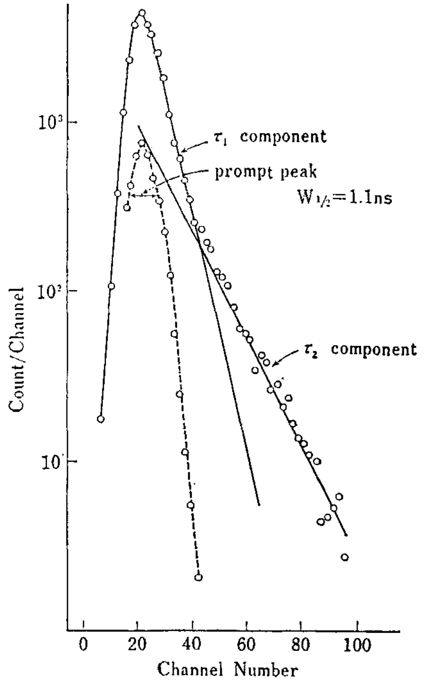


Figure 3. Lifetime spectrum of positrons in liquid N-vinyl-carbazole at 65 °C, and that of prompt γ from Co^{60} for calibration.

One channel corresponds to 0.13×10^{-9} sec. τ_2 can be easily obtained from the gradient of the longer lifetime component.

In another experiment, the yield of polymer and its viscosity were measured. Polymer was separated from the irradiated monomers by acetone. The degree of polymerization was determined by using following formula.[11]

$$\overline{DP} = 4.61 \times 10^3 (\eta)^{1.72}$$

The lifetime spectra for various irradiation doses are shown in Figs. 4 and 5.

τ_2 and I_2 can be obtained from these lifetime spectra and the variation with the irradiation dose are shown in Fig. 6.

The relation between conversion and irradiation dose at 28 °C is

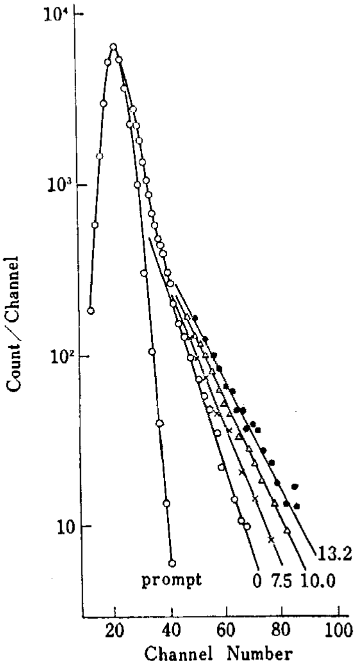


Figure 4. Lifetime spectra of positrons in solid N-vinyl-carbazole for various irradiation doses in Mrad at 23 °C.

shown in Fig. 7. The degree of polymerization is also known in the same figure.

Experimental results at 20 °C obtained by Chapiro and Hardy are also cited in this figure.[12]

The polymerization process may be divided into four stages of the polymerization, as shown in Fig. 6. Regions I and II are the induction period of polymerization, region III is the period in which the propagation proceeds very rapidly, and, finally, region IV indicates the period of saturation in the polymerization yield. In the region I, the rate of annihilation does not change at all as shown in Fig. 6. However, since the rate of annihilation of positronium is profoundly affected by trapped radicals and the lifetime is shortened by the interaction with the radicals, there seems to exist another effect of such nature that the effect due to radicals is cancelled. In the region II, the polymerization yield is less than several % and the lifetime of positronium, τ_2, begins to be longer. This may be due to the

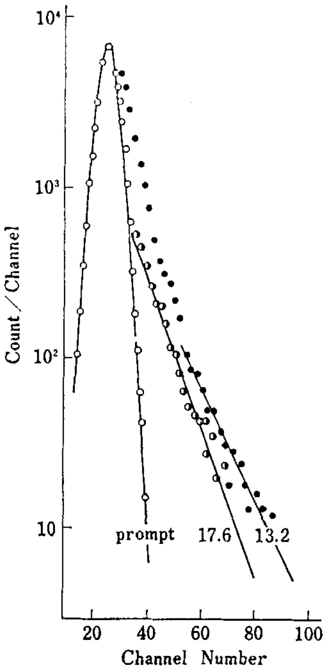


Figure 5. Lifetime spectra of positrons in solid N-vinyl-carbazole for various irradiation doses in Mrad at 23 °C.

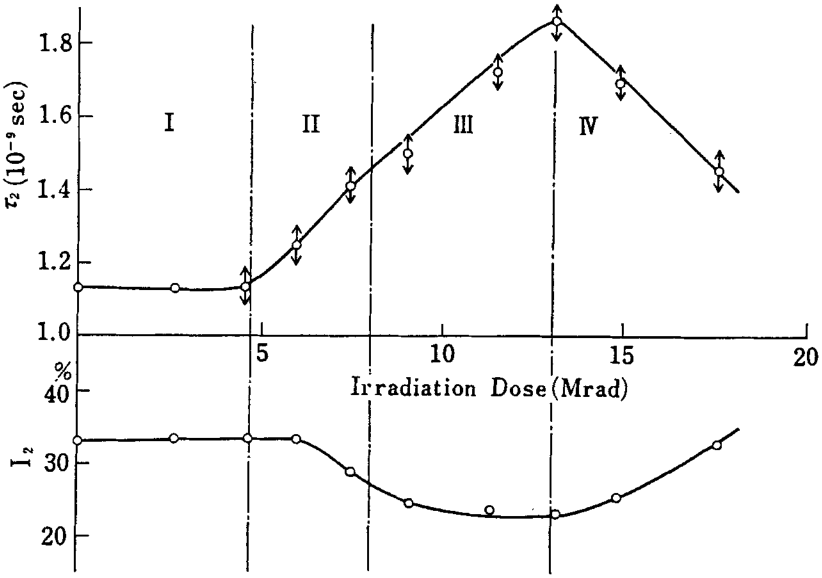


Figure 6. τ_2 and I_1 as a function of irradiation dose at 23 °C.

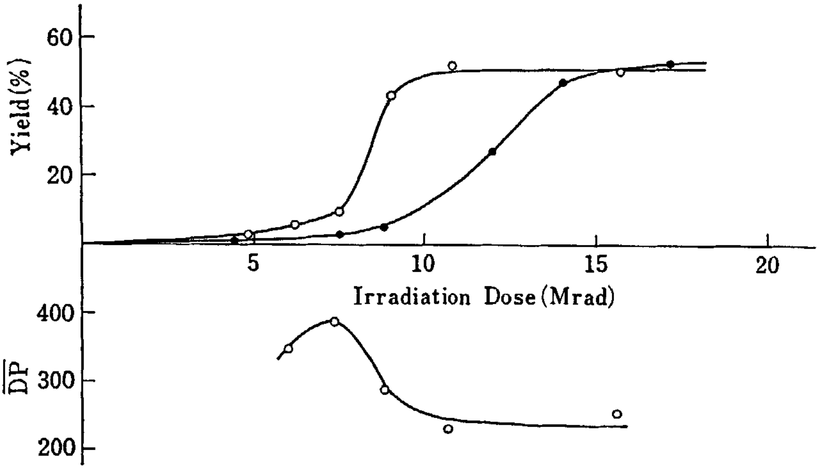


Figure 7. Yield (%) and degree of polymerization (*DP*) as a function of irradiation dose at 28 °C. (●) Chapiro's and Hardy's data, (○) our data.

increase of free volume originating from the expansion of lattice constant and the deformation of crystals in the system. In the period III, τ_2 increases linearly with the polymerization yield. This is due to formation of polymer having an amorphous structure in the crystalline monomer.

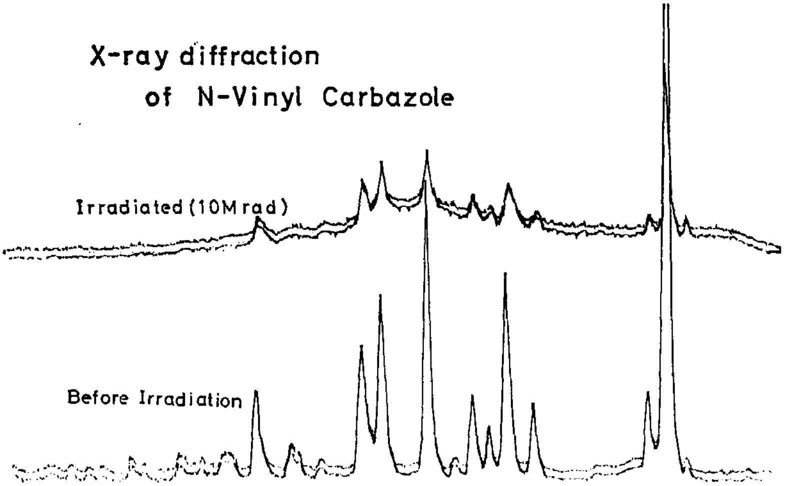


Figure 8. X-ray diffraction curves of non-irradiated and irradiated (10 Mrads) solid monomers at room temperature.

To determine the state of crystallinity in monomers during polymerization, X-ray diffraction measurements were carried out at 25 °C. X-ray diffraction curves for non-irradiated and 10 Mrad irradiated monomers are shown in Fig. 8.

The halo intensity which corresponds to the amount of amorphous material was plotted as a function of irradiation dose. The relation is shown in Fig. 9.

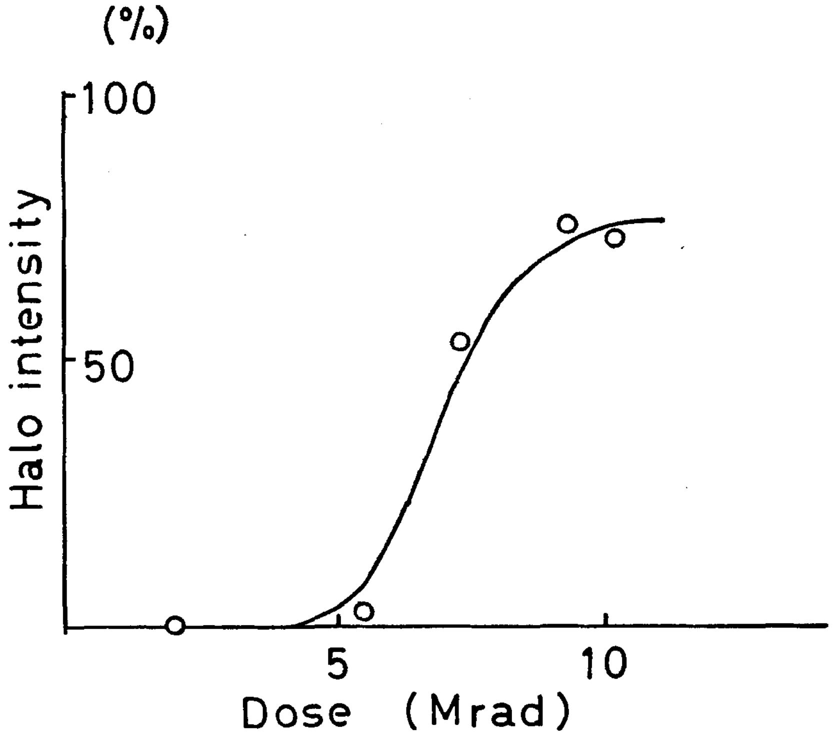


Figure 9. Intensity of halo against irradiation dose.

From these experimental results, it is obvious that the crystalline structure begins to be destroyed rapidly by polymerization after a definite period of induction. This corresponds well with the relations between irradiation dose and conversion.

Since the effect due to increase of free volume on the lifetime of positronium is considered to be more important in comparison with the effect due to the formation of radicals in region II, the pick-off annihilation rate, λ_p, can be written as

$$\lambda_p = p\lambda_v + (1 - p)\lambda_n \tag{1}$$

$$\tau_2 \simeq \frac{1}{\lambda_p} \tag{2}$$

where λ_n is the annihilation rate in the free volume at a normal site in the crystal and λ_v is the rate in free volume at vacancy sites produced by the polymerization. p is the probability with which annihilation at the rate λ_v takes place. The probability p may be represented as,

$$\frac{p}{1-p} = \frac{(\text{vacancy sites})}{(\text{normal sites})} e^{\frac{\Delta E}{kT}} \tag{3}$$

The first term is the ratio of free volume at the vacancy and normal sites and ΔE is the difference between energies of positronium in the both sites.

In the region II, where the conversion is less than a few %, the polymer produced is considered to be still suspended in the crystal matrix of the monomer. The phase separation may not yet have taken place. On the other hand, the molecular weight of the polymer is shown to be rather high from the viscosity measurement and the free volume is considered to be considerably larger in this region. Then the energy difference ΔE becomes large enough. Therefore a decrease in the rate of annihilation λ_p is expected.

In the region III, the polymer yield increases rapidly, but the molecular weight of polymers decreases sharply with irradiation dose. The number of sites with free volume is high in this region, compared with the region II. However, the size of the free volume at a given site may become rather smaller in the region III than in the region II. This may result in the decrease of ΔE. Although the number of vacancy sites and the energy difference ΔE are changing with the irradiation dose, the probability, p, may increase in a definite rate through the II and III regions as a result of the combined effects due to the two factors.

In region IV, it is obvious that the lifetime decreases with irradiation dose. Since the formation of polymer does not take place in this region, the free volume in the system may remain unchanged from the saturation point of yield. Therefore active species trapped by further irradiation may be responsible to the shortening of lifetime τ_2.

An electron spin resonance spectrum of irradiated monomer crystals is shown in Fig. 10. This is a double triplet with coupling constants of 21 gauss for α proton and 25 gauss for β protons. The spectrum can be assigned to the propagating radical.

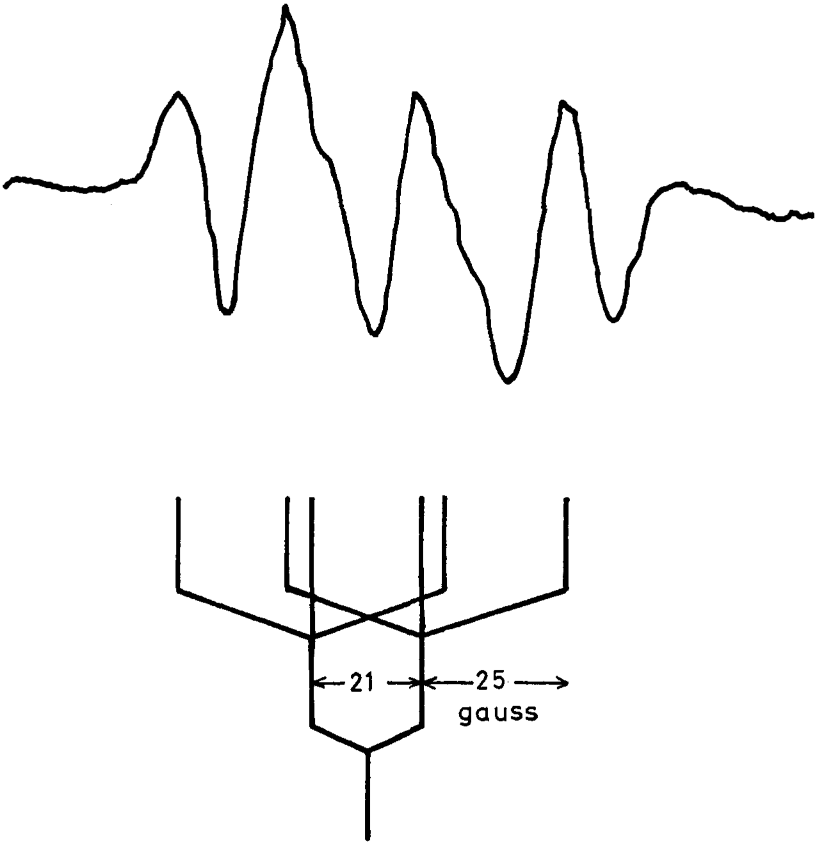
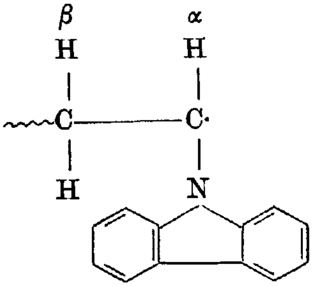


Figure 10. Electron spin resonance spectrum of irradiated crystal N-vinylcarbazole at 24 °C.



The concentration of radicals was determined by using DPPH in benzene as a standard. The result is shown in Fig. 11. The concentration increases linearly with irradiation dose under our experimental conditions.

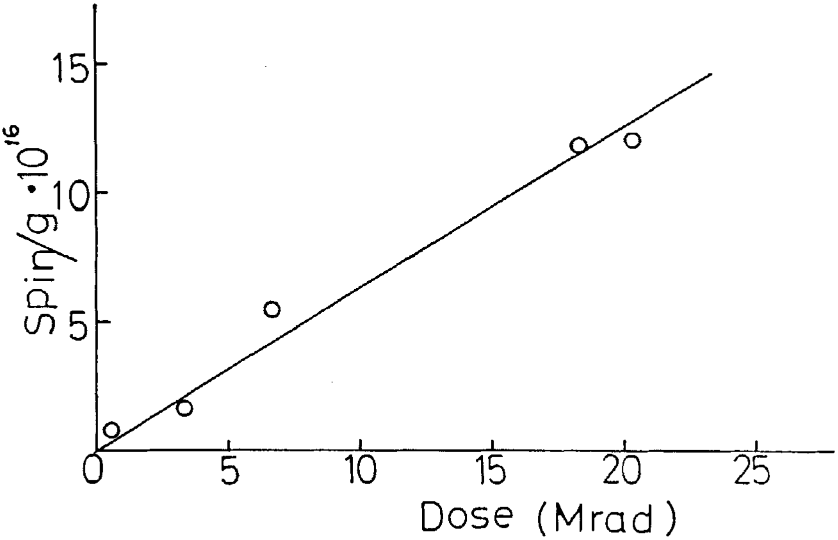


Figure 11. Radical concentration as a function of irradiation dose.

From the measurement of the irradiated monomer with electron spin resonance, it may be concluded that positronium interacts with the trapped radicals and the lifetime is shortened.

The dose dependency of I_2 is also very interesting. Decrease in I_2 in the region III may be explained by the formation of positron compounds or the narrowing of Ore gap due to the reduction of average ionization potential or an increase in the average excitation potential of the system.

The rate of annihilation λ_2 can be divided into several components,

$$\lambda_2 = \lambda_T + \lambda_{p1} + \lambda_{p2} + k_m \tag{4}$$

where λ_T is the rate of triplet decay, λ_{p1} the rate of pick-off in the normal sites of the crystals (free volumes in crystals), λ_{p2} the rate of pick-off in the vacancy sites produced by polymerization and k_m the rate of interaction of positronium with trapped radicals.

Since $\lambda_T(\simeq 7 \times 10^6\,\text{sec}^{-1}) \ll \lambda_p(\simeq 10^9\,\text{sec}^{-1})$, then

$$\lambda_2 \simeq \lambda_p + k_m \tag{5}$$

$$\lambda_p = \lambda_{p1} + \lambda_{p2} \tag{6}$$

Since λ_p is considered to be constant after the saturation in polymer yield, the shortening of the lifetime of positronium in this region may be due to the interaction of positronium with trapped radicals produced by further irradiation. The rate constant k_m is described by

$$k_m = N\sigma_m v \tag{7}$$

where N is the number of radicals per unit volume, v is velocity of positronium in the system and σ_m is the cross-section of the interaction of positronium with the trapped radicals. Since

$$\lambda_p \simeq \text{constant}, \tag{8}$$

$$\Delta\lambda_2 = \Delta k_m = \sigma_m v \Delta N \tag{9}$$

From Figs. 6 and 11, Δk_m and ΔN are estimated to be 0.037×10^9 sec^{-1}/Mrad and 0.76×10^{16} spins/cm^3/Mrad (0.62×10^{16} spins/gr/Mrad).

$$\sigma_m v = \frac{\Delta k_m}{\Delta N} = 4.87 \times 10^{-9}\,\text{cm}^3/\text{sec} \tag{10}$$

Since positronium is considered to be thermalized (0.023 eV), the velocity v may be given, as a rough approximation;

$$v \simeq 0.63 \times 10^7\,\text{cm/sec} \tag{11}$$

Therefore, the cross-section may be easily estimated,

$$\sigma_m = 7.66 \times 10^{-16}\ \mathrm{cm}^2 \tag{12}$$

It is known that the cross-section of exchange collision of positronium is in a region of 10^{-17} to 10^{-18} cm^2 from both theoretical considerations and experiments. On the other hand, it is believed from the measurements of pick-off rate and angular distribution of 2γ that positronium compounds are formed in benzene solutions of DPPH and the cross-section is found to be 8×10^{-16} cm^2.[13]

Therefore, the shortening of lifetime of positronium τ_2 in the region IV, may be due to the formation of positronium compounds with trapped radicals.

Since the rate of the formation of positronium compounds is proportional to the concentration of trapped radicals, the overall rate of pick-off λ_2 can be divided into two components, k_m and λ_p, as shown in Fig. 12.

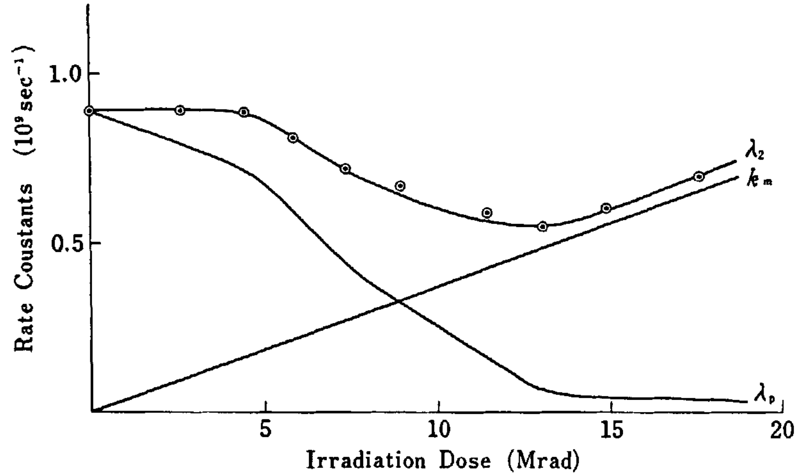


Figure 12. λ_2 and it's components of k_m and λ_p as a function of irradiation dose.

The free volume effect on the lifetime in the regions I and II is discussed in some detail. The potential curve shown in Fig. 13 is postulated as a first approximation.[14] It is assumed that positronium atoms are thermalized and are in the ground state in the potential well.

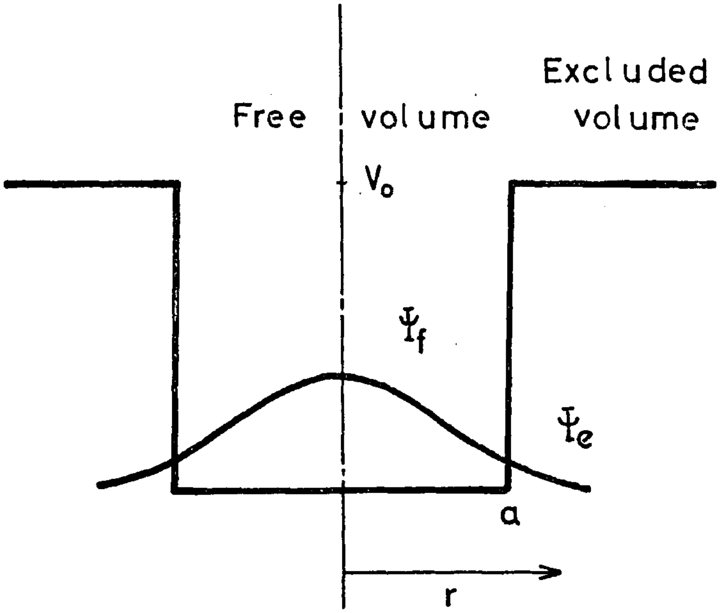


Figure 13. Schematic potential of free volume. V_0 depth of the potential; *a*, radius of the potential well.

Let Ψ_{e^+} be the wave function of a positron bound as *triplet*-positronium in the lattice.

$$\Psi_{e^+} = \alpha(\bar{r})\Psi_{ps} \qquad \text{for } \vec{K}_{ps} \simeq 0 \tag{13}$$

where $\alpha(\bar{r})$ is the polarization function and is unity as a first approximation. $\vec{K}_{ps}$ is the wave vector of positronium. The spin averaged pick-off annihilation rate can be written as;

$$\begin{aligned}\lambda_p = \lambda_2 - \lambda_T - k_m &= \pi r_0^2 c \int_{\text{lattice}} |\Psi_{e^+}|^2 \cdot |\Psi_{e^-}|^2 d\tau \\ &= \pi r_0^2 \rho_0 c \int_{v_e} |\Psi_{e^+}|^2 d\tau \\ &= \pi r_0^2 \rho_0 c \int_{v_e} |\Psi_{ps}|^2 d\tau \end{aligned} \tag{14}$$

where r_0 is the classical electron radius, c the velocity of light, ρ_0 the averaged electron density in the excluded volume $|\Psi_{e-}|^2$ and v_e

the excluded volume. The wave function of positronium is described as;

$$\left.\begin{aligned} \Psi_f &= \frac{A \sin \alpha r}{\alpha r} \quad \text{for } r \leqq a \text{ in the free volume} \\ \Psi_e &= \frac{B e^{-\beta r}}{\beta r} \quad \text{for } r \geqq a \text{ in the excluded volume} \end{aligned}\right\} \tag{15}$$

$$\text{where } \alpha = \sqrt{\frac{2m}{\hbar^2} E} \qquad \beta = \sqrt{\frac{2m}{\hbar^2}(V_0 - E)}$$

From the boundary condition at $r = a$, one can get

$$\alpha a \cot \alpha a = -\beta a$$

Therefore, λ_p can be described as follows;

$$\lambda_p = \pi r_0^2 c \rho_0 \frac{\int_{v_e} |\Psi_e|^2 d\tau}{\int_{v_e} |\Psi_e|^2 d\tau + \int_{v_f} |\Psi_f|^2 d\tau} \tag{16}$$

$$\lambda_p = \frac{\pi r_0^2 c}{1 + F}$$

$$F = \frac{\int_{v_f} |\Psi_f|^2}{\int_{v_e} |\Psi_e|^2} = \frac{\beta}{\alpha} \cdot \frac{2\alpha a - \sin 2\alpha a}{1 - \cos 2\alpha\beta} = \frac{\beta\alpha}{\alpha^2 a^2}\left(\beta a + \frac{2m}{\hbar^2} V_0 a^2\right)$$

From these relations the energy of positronium, E, can be obtained for a definite combination of V_0 and a.

The free volume of N-vinyl-carbazole can be estimated from the measurement of specific volume as a function of temperature. The specific volume ϕ at 0 °K was estimated to be 0.570 by extrapolation. If the monomer molecule is assumed to be spherical, the following relation is derived.

$$v_e = \frac{\pi}{2\sqrt{3}} \phi \tag{17}$$

Therefore, the excluded volume v_e is easily determined as

$$v_e = \frac{\pi}{2\sqrt{3}} 0.570 = 0.518 \text{ cm}^3/\text{gr} \tag{18}$$

The free volume as a function of temperature is shown in Fig. 14.

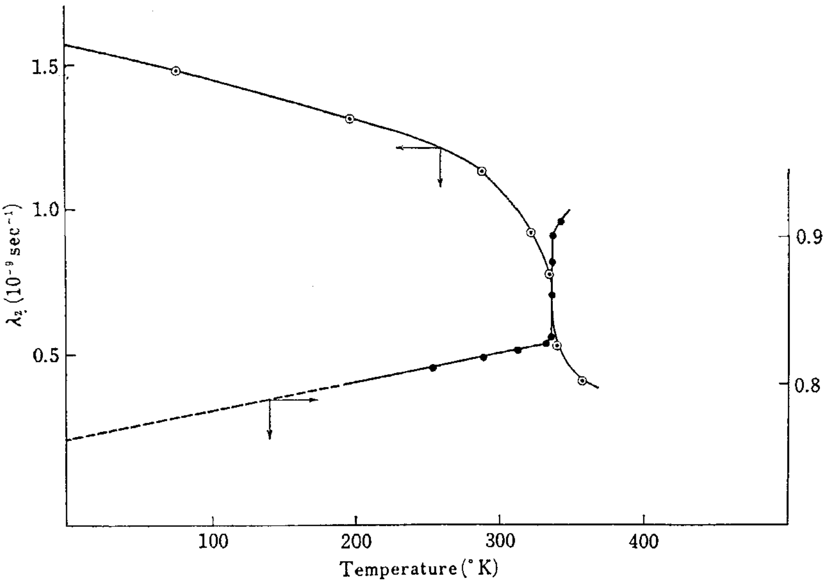


Figure 14. Lifetime of positrons τ_2 and specific volume ϕ as a function of temperature.

Using these data mentioned above, the potential energy V_0 is found to be 6.8 eV. In the calculation, $\lambda_p = \pi r_0^2 c \rho_0$ was taken as $2.9 \times 10^9 \mathrm{sec}^{-1}$, according to Brandt.[14] If the energy difference ΔE between normal and vacancy sites is known, one can estimate the size of the sites by using V_0. For irradiated N-vinyl-carbazole in region I, one can get the sizes of vacancy and normal sites as $a^v = 3.7$ Å and $a^n = 2.8$ Å, assuming that low molecular weight polymers are produced from radicals.

Conclusion

It was shown from the investigation that information about both nucleation process and radicals trapped in the radiation-induced solid state polymerization can be obtained by the measurement of lifetime of positronium in irradiated organic monomers. This method is suggested to be one of the new techniques to investigate solid state polymerization.

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