An Electron Spin Resonance Study of Irradiated Polymethylacrylate

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The decaying behavior of free radicals in irradiated polymers has been studied by the electron spin resonance (ESR) method with polymethylmethacrylate,[1,2] polyvinylchloride,[3,4] polyvinylalcohol,[5] polyoxymethylene[6] and polypropylene.[7] In most cases, free radicals follow a first-order or a second-order decay reaction, depending on the polymer and temperature range studied. It has been reported, in addition, that free radicals in many irradiated polymers, such as polyethylene,[8] polyvinylalcohol,[5,9] polytrifluorochloroethylene[8] and polycarbonate,[10] decay readily near the glass transition temperature. In order to study the decaying behavior of free radicals, the glass transition temperature should thus be taken into account.

For the convenience of experimental procedures, polymethylacrylate (PMA), with the glass transition temperature of +3°C, was used in the present investigation. First, ESR spectra of irratiated PMA were recorded at various temperatures and then interpreted. Irradiated methacrylate and polyethylacrylate were also studied for the sake of comparison. Quantitative studies of the decaying behavior of the free radicals in PMA were made below and above the glass transition temperature. The results obtained were then discussed in terms of molecular motion in the polymer and in terms of the structure of the free radicals.

Experimental

The PMA samples were prepared by the bulk polymerization of commercial methylacrylate after the usual purification. The polymer obtained was precipitated twice from an acetone solution with water and dried in vacuo.

The irradiations were carried out with 1.5 MeV. electrons from a Van de Graaff accelerator (dose rate: 1.5×10^5 rad./sec.) at −196°C. The PMA samples were irradiated in glass tubes which were sealed under a vacuum better than 10^{-4} mmHg.

ESR spectra were observed with a reflection-type x-band spectrometer using low-frequency field modulation (80 c. p. s.). Most observations were made at −196°C or at 12°C, using a TE_{011} cylindrical and a TE_{102} rectangular sample cavity respectively.

Results and Discussion

Observed Spectra and Their Interpretation.— PMA, irradiated and measured at −196°C, gave ESR spectra of the shape shown in Fig. 1 (a), with the irradiation dose of 3×10^7 rad. The spectra had no distinct hyperfine structure. With successive warming of the samples to −78°C, −45°C, −10°C and +18°C, the spectra changed from a singlet with the half-height width of 36 oerst. into a triplet, as Fig. 1 shows. Irradiated PMA gave the triplet spectrum at 12°C shown in Fig. 2 (a) immediately after warming to that temperature. This spectrum is the same as that reported by Ormerod and Charlesby.[2] The separation of the triplet

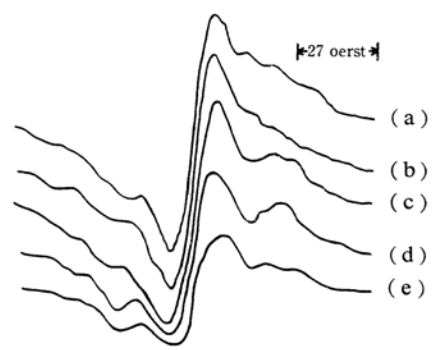

Fig. 1. ESR spectra of PMA irradiated and observed at −196°C (irradiation with 3×10^7 rad.): (a) without warming, (b) after warming to −78°C for 82 min., (c) after warming to −45°C for 87 min., (d) after warming to −10°C for 57 min., (e) after warming to +18°C for 8 min.

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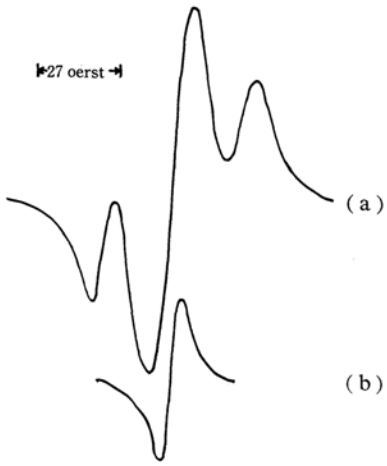

Fig. 2. ESR spectra of PMA irradiated at −196°C with the dose of 3×10^7 rad. and observed at 12°C: (a) immediately after warming to 12°C, (b) after 20 hr. at 12°C.

hyperfine components was 22 oerst. The central peak was a little more intense than the expected intensity distribution of 1:2:1. This may be due to an overlapping with a singlet spectrum, which showed ΔH_{mse} of 22 oerst. and was still observed after standing 20 hours at room temperature. The change of the spectra from a singlet at a low temperature to a triplet at room temperature was irreversible.

For comparison with the triplet spectra of irradiated PMA mentioned above, the ESR spectra of irradiated methylacrylate and irradiated polyethylacrylate were also studied.

Methylacrylate (MA) was solidified at −196°C and was irradiated at the same temperature under a vacuum. Irradiated MA gave a triplet spectrum with a separation of 22 oerst. at −196°C, as Fig. 3 shows. With an increase in the temperature, the spectrum became weaker, without changing its shape, until it disappeared completely below −78°C. On the other hand, MA which had been irradiated at −196°C with 5×10^7 rad. and warmed to −78°C gave white precipitates when dissolved at −78°C in petroleum ether. Apparently

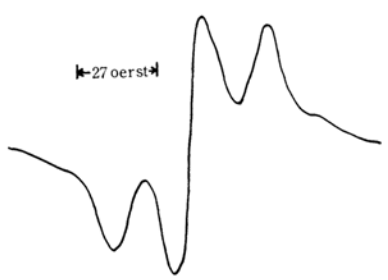

Fig. 3. ESR spectrum of methylacrylate irradiated and observed at −196°C, with the dose of 5×10^7 rad.

polymerization occurs in MA irradiated at −196°C and warmed to −78°C. It is probable that the free radicals giving a triplet spectrum are propagating end groups which disappear with the termination of the propagating chains.

Polyethylacrylate (PEA) was prepared, and its spectra were examined in the same way as those of PMA. PEA irradiated at −196°C gave the quintet spectrum shown in Fig. 4 (a), as has been reported previously.[2] With an increase in the temperature the spectrum changed irreversibly, to a triplet with the separation of 22 oerst. The triplet spectrum of irradiated PEA was much less stable than that of PMA.

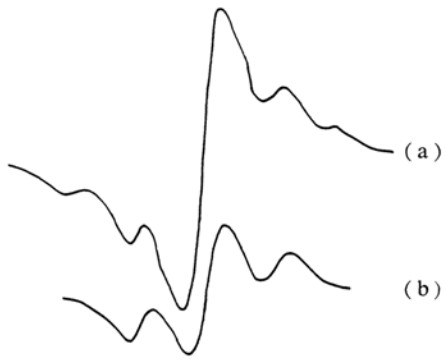

Fig. 4. ESR spectra of PEA irradiated at −196°C with the dose of 3×10^7 rad.: (a) observed at −196°C without warming, (b) observed at about −26°C immediately after warming to this temperature.

It has been reported that propagating radicals in vinyl polymerizations give triplet spectra.[11-15] It is not unreasonable to interpret the triplet spectrum of irradiated PMA as being due to propagating radicals, ~~~CH_2-$\dot{C}H(COOCH_3)$, as in the case of irradiated MA. With both PMA and MA, the separation between triplet hyperfine components was the same.

An alternative interpretation would be that the triplet spectrum of PMA is due to the radical structure, -CH_2-$CH(COO\dot{C}H_2)$-CH_2-, but this is not probable because irradiated PEA gave the same triplet.

The Formation and Decay of Free Radicals in PMA.—The concentration of free radicals in PMA increased with the irradiation dose, as

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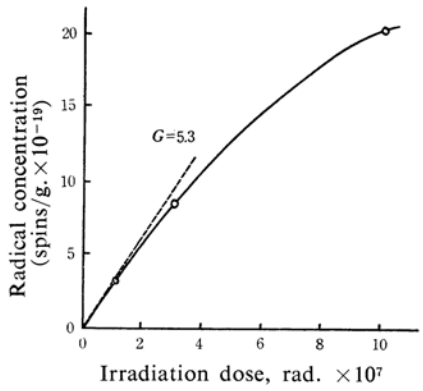

Fig. 5. Formation of free radicals in PMA irradiated at −196°C with the dose rate of 1.5×10^5 rad./sec. and observed at the same temperature.

is shown in Fig. 5. Irradiations and measurements were carried out at −196°C. From the initial slope of the curve in Fig. 5, the G value is calculated to be 5.3, with reference to the formation of free radicals which are stable at −196°C. The absolute value is correct within a 50% range of experimental error, and it is in accordance with that reported by Ormerod and Charlesby.[2]

Figure 6 shows the decaying behavior of free radicals in irradiated PMA when warmed

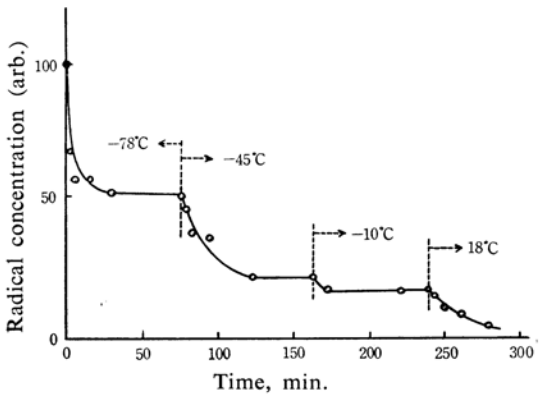

Fig. 6. Decay of free radicals in PMA irradiated at −196°C with the dose of 3×10^7 rad. with successive warming at several temperatures.

successively to a series of temperatures. At temperatures below the glass transition point of PMA, the radical concentration decreased rapidly at the beginning of warming, but it readily attained a final value at each temperature. At temperatures of transition point, the free radicals disappeared following a 2nd order decay process.

The same decaying behavior as that observed for PMA below the glass transition temperature was also reported for polymethylmethacrylate.[2] A possible interpretation for the behavior—in rigid PMA below its glass transition point—is that the thermal activation process which causes the disappearance of free radicals has a wide distribution of activation energies. A similar interpretation was applied by Semenov to the decaying behavior of free radicals in a mixture of *n*-octylalcohol, water and hydroperoxide which was solidified and irradiated at −196°C.[16]

The decay of free radicals in PMA was examined at different temperatures above the glass transition point. As Fig. 7 shows, the observed results fitted well to a 2nd-order decay process, $-d[R\cdot]/dt=k[R\cdot]^2$, except at the beginning of warming. Free radicals which disappeared in this range of warming temperature gave a triplet spectrum. The deviation from the 2nd-order decay at the beginning may be caused by free radicals which disappeared at the transient temperature from −196°C to each warming temperature. The rate constant, k, was obtained from the diagram

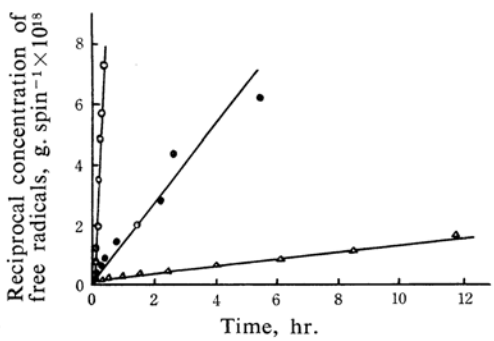

Fig. 7. Decay of free radicals in PMA, irradiated at −196°C with the dose of 3×10^7 rad. and measured at different temperatures.
○ 30°C ● 20°C △ 12°C

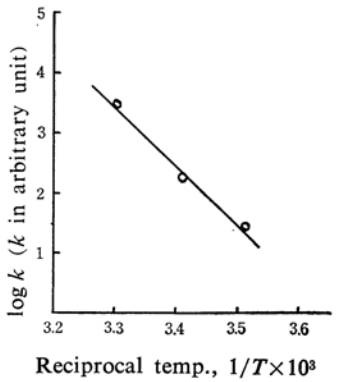

Fig. 8. Rate constants for radical recombination vs. reciprocal temperatures.

16) N. Semenov, Private communication (1962).

in Fig. 7; it is plotted as a function of the reciprocal temperatures in Fig. 8. The activation energy for k was 44 kcal./mol.

The activation energy for segmental motion in PMA has been reported to be 40 kcal./mol. from mechanical dispersion measurements.[17] The good agreement between the activation energies obtained from the mechanical measurements and from the decay of free radicals suggests that the free radicals in PMA giving a triplet spectrum disappear through recombination caused by segmental motion in the polymer. The assignment of the triplet spectrum as being due to the radical structure ~~~$-CH_2-\dot{C}H(COOCH_3)$ is not in contradiction to the previously-discussed decaying mechanism of the free radicals.

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