# *Decay of Free Radicals in $\gamma$-Irradiated Polymethyl Methacrylate*

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Recently, many investigations have been carried out for polymers by using the electron spin resonance (ESR) technique. Especially the polymethyl methacrylate (PMMA) is one of the most comprehensively investigated ones, and the properties of the radicals produced by $\gamma$-irradiation have been clarified fairly well[1,2]. In the present communication, a preliminary work on the decay of radicals in $\gamma$-irradiated PMMA above and below the transition point by the ESR spectrometer will be reported, while a similar work by Ohnishi and Nitta was recently carried out independently of ours only below the transition point[3].

The samples used were PMMA plates (a section $0.2\times0.2\,\mathrm{cm}^2$ : columnar-shaped ; Acrylite, Mitsubishi Rayon Co., Ltd.) and the irradiations were carried out $3\times10^6$ r. at room temperature with $\gamma$-ray from a $^{60}$Co source (dose rate $2.2\times10^5$ r./hr.). The radicals produced were detected by the ESR spectrometer (JEP-1 E.P.R. Spectroscope; Japan Electron Optics Laboratory Co., Ltd., X-band, bridge-type). The resonance pattern thus obtained is the same as in the case of fine powdered samples sealed in vacuo, and also similar to those by Schneider[1] and by Abraham et al.[2], and no appreciable change by the influence of oxygen was detected in the present experiment, in spite of a considerable change observed in the powdered sample exposed to air. So the experiments were carried out by using plated samples only, to avoid color centers resulting from irradiation in the glass which was used to seal the samples in vacuo.

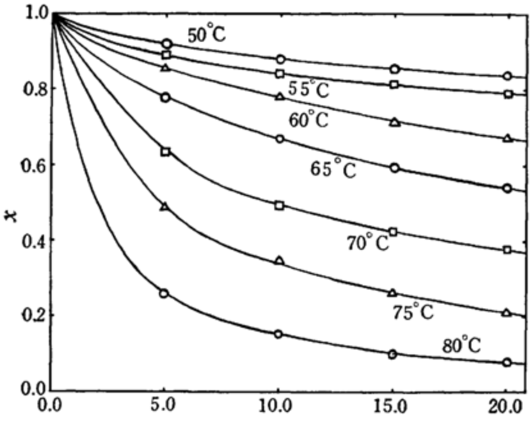

Fig. 1. Relative concentration of free radicals $x$ aginst time $t$.

Decay of the free radicals was investigated at temperatures between 50 and 80°C. In detection, the samples (stored in dry ice after irradiation) kept at the reaction temperature were taken out every five minutes and suddenly cooled to the room temperature by dry ice in order to interrupt the reaction rapidly, because

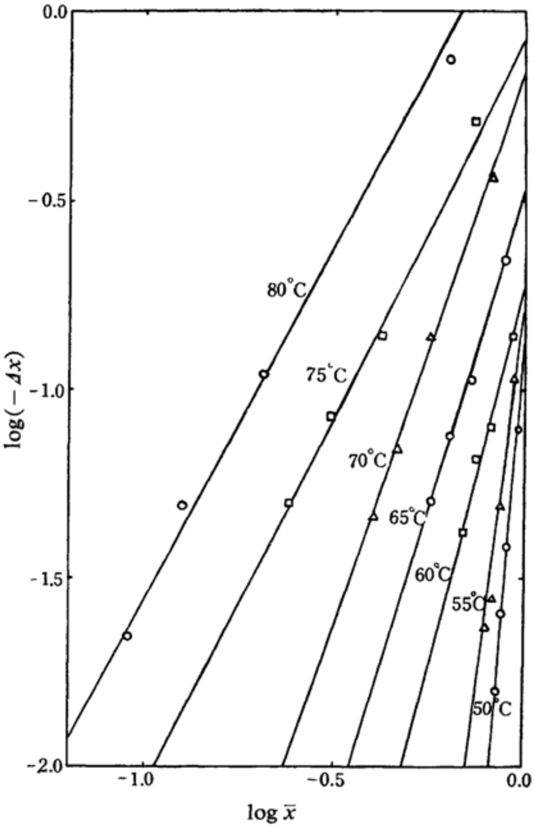

Fig. 2. Logarithm of the change of the relative concentration in five minutes $\log(-\Delta x)$ against logarithm of the mean value of the relative concentration $\log\bar{x}$.

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1) E. E. Schnider, *Disc. Faraday Soc.*, **19**, 158 (1955).

2) R. J. Abraham, H. W. Melville, D. W. Overnall, and D. H. Whiffen, *Trans. Farady Soc.*, **54**, 1133 (1958).

3) S. Ohnishi and I. Nitta, *J. Polymer Sci.*, **38**, 451 (1959). In this paper, our result quoted should be corrected.

the change in the room temperature is very slow. Thus the relative concentrations in these samples were obtained by the ESR spectra at the room temperature comparing with the reference sample which was irradiated under the same condition and stored in dry ice. Under these circumstances, no appreciable change of the resonance pattern was observed.

The variation of the radical concentration so obtained is given in Fig. 1. To determine the order of the reaction, the logarithm of the change of the relative concentration in five minutes $\varDelta t$, $\log(-\varDelta x)$, was plotted against the logarithm of the mean value of the relative concentration, $\log \bar{x}$, as shown in Fig. 2, since the order $n$ is obtainable from the slope by using the following relation:

$$\log(-\varDelta x)=n \log \bar{x}+(\log k+\log \varDelta t)$$

From Fig. 2, one can easily find the interesting feature that above 70°C the reaction is of the second order while below 70°C the apparent order is greater than the second and increases with decreasing temperature. Since the PMMA is amorphous and its transition point is considered to be about 70°C, the mechanism of the decay of the radical is considered to be different above and below the transition point taken as the border. That is, above the transition point the motion of the chain segment is rather unrestricted so that the reaction rate is proportional to the concentrations of each radical recombined, because the radicals are considered to be independent for the dose rate used, whereas below the point, the decaying process becomes complicated because of relaxation. This is also consistent with the result by Ohnishi and Nitta[3] in which below the transition point the reaction was the second order except in the beginning range (several hours). The activation energy obtained in the present work is $3\times 10$ kcal./mol., which is also consistent with their result, although it is rather difficult to obtain accurately because of the aforementioned mechanism.

The present work is preliminary and includes many points requiring improvements as follows: (1) The error due to the fact that the samples were taken out from the reaction temperature and the ESR spectrum was observed at the room temperature. (The decay at the room temperature could not be absolutely negligible. This can be improved by the use of a cavity which can be used at various temperatures in question.) (2) A little influence of oxygen because of the experiment carried out in air. (This can be improved by sealing the sample in vacuo.) (3) The inconsistency of the experimental conditions; i. e. the $\gamma$-irradiation due to the $^{60}$Co irradiation apparatus, and in the change of temperatures.

Although the present experiment encounters the above-mentioned problems, the result gives the following interesting suggestion: investigation of the decay of radicals in the $\gamma$-irradiated polymer gives information concerning the knowledge of the motion of polymers. Although it is not a direct method and the change of the mechanism bordering the transition point has already been observed in the crosslinking of polyethylene and of polyvinyl chloride[4], the present phenomenon is rather simple and favorable to the investigation of the motion of polymers. Though the present PMMA is amorphous, similar investigations can also be carried out for partially crystalline polymers. In this case, it is possible to observe separately the motion of polymers in the crystalline and amorphous regions since the resonance patterns for these regions can not always be the same because of the steric effect of the radical produced. In fact, including the case of PMMA, a more preçise investigation is absolutely necessary, especially for the points aforementioned, in order to obtain more conclusive result.

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[4] A. N. Pravednikov, Y. S. Kan, and S. S. Medvedev, *Proc. United Nations International Conference on the Peaceful Uses of Atomic Energy*, No. 2294, 192 (1958); See, S. Okamura, *Chemistry (Kagaku)*, 5, 7 (1960).