Pulse Radiolysis Applied to Polymerization Reactions: The Intermediate in the Radiation-Induced Polymerization of α-Methylstyrene*

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A reaction intermediate of radiation-induced polymerization has been observed for the first time in extremely dried α-methylstyrene by means of pulse radiolysis. The indication that an anion radical plays an important role in the γ-ray-induced polymerization arose during the study of sodium-dried α-methylstyrene at room temperature,[1] in which a G(-monomer) value as high as 36500 was obtained. The main bases on which the intermediate was postulated were; 1) a radical scavenger such as DPPH practically inhibited the reaction, as did an ion scavenger, water, and 2) no copolymer was found in the mixture of α-methylstyrene and isobutylene which is known to polymerize through a cationic intermediate, while a copolymer had been found in the mixture of α-methylstyrene and methylmethacrylate,[2] which is known to polymerize through a radical intermediate.

There has been a dispute about the reaction mechanism for some time. It seems that much of the discussion has been concerned with the radical and the cationic intermediates; the importance of the anion radical has been overlooked entirely. Although in only a few cases is the anion radical suggested in the radiation-induced polymerization, there are several examples of such an intermediate in such cases as the so-called anionic polymerization initiated by alkali metal.[3] The present investigation has had the purpose of confirming the anion radical mechanism in the radiation-induced polymerization[1] and of obtaining quantitative rate data by the direct observation of the reaction intermediate.

The experimental method is only briefly explained below, because the details will be published elsewhere. The monomer, dried by passing it through a sodium-potassium alloy,** and sealed into a high-purity quartz cell provided with optically-flat windows, was irradiated by a 1.6 μsec. electron pulse from a Fuji Denki lineac modified to give a single pulse, the energy of which was 4 MeV.; the peak current was 7.5×10^{-2} amp. The electron beam was collimated on the wall of the cell with a diameter of about 1 cm. In the determination of spectra, the cell was irradiated cross-wise. The light source, a quartz tube equipped with tungsten electrodes, containing 75 mmHg xenon, was flashed by discharging a 2 μf condenser charged to 6 kV. by means of a 2G22P hydrogen thyratron.[4] It was triggered by a signal from the lineac at any delayed time designed by utilizing the delayed trigger circuit of a synchroscope. The duration of the flash was estimated to be 20 μsec.

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[1] K. Hirota and M. Katayama, *Annual Report of JARRP*, 5, 205 (1963—64).

[2] K. Hirota and F. Takemura, This Bulletin, 35, 1037 (1962).

[3] K. Hirota, K. Kuwata and K. Morigaki, ibid., 31, 538 (1958).

** A novel technique for drying the monomer has been developed in the Chemistry Lab. of Hokkaido University. It was found quite satisfactory for drying styrene; details will be given in a coming publication.

[4] J. H. Callomon and D. A. Ramsay, *Can. J. Phys.*, 35, 129 (1957).

The spectra was taken on a spectroscopic process-type Fuji plate by means of a Shimadzu quartz spectrograph. The plate was developed and subsequently fixed according to the recommendations of the manufacturer.

It has been reported[5] that when α-methylstyrene is brought in contact with sodium metal, it turns pale yellow and has an absorption maximum at 3275Å, while after a long time has elapsed or when it is heated it turns red, with the maximum shifting to 5100Å.

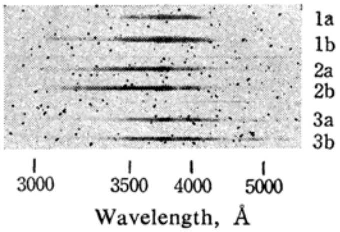

Fig. 1. Absorption spectra of transient species at room temperature.
a: 1.6 μsec. after the pulse and b: without it.
1: extremely dried α-methylstyrene
2: in the presence of trace of water
3: in the presence of DPPH

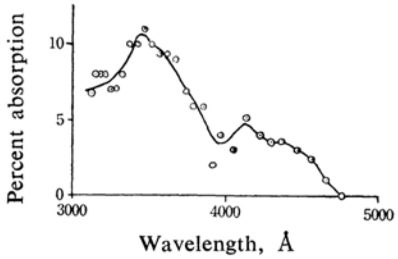

Fig. 2. Absorption spectrum of transient species in extremely dried α-methylstyrene.

In the present investigation, a broad transient absorption below 3500Å was observed in the dried α-methylstyrene. 1a and 1b in Fig. 1 show spectra typical of such investigations. The 1a is the spectrum taken 1.6 μsec. after the irradiation of a pulse, while 1b is the spectrum taken without irradiation. The difference in the densitometer reading between 1a and 1b shows (Fig. 2) an absorption maximum at 3500Å, as was visually observed in 1a with a shoulder at about 4200Å. The lower the beam current of the pulse, the weaker became the absorption, and it practically disappeared after a few tenths of a millisecond. We believe that this maximum is in good correspondence with that of 3275Å observed in the sodium-α-methylstyrene system, considering the possible solvent effects, ion pair formation, etc., in the latter system, and that this constitutes a support for the existence of an anion radical in the radiation-induced polymerization of α-methylstyrene.

There still is uncertainty, however, that the absorbing species might not be the one which leads to the polymerization. Since it is known, as has been stated above, that the reaction is practically inhibited by the addition of a small amount of water or DPPH, the transient absorption observed in the dried monomer should diminish upon the addition of these compounds if it is caused by the reaction intermediate. This point has been tested, and this has been found to be the case. 2a and 2b in Fig. 1 show the effect of added water. The spectrum 2a in the figure was obtained 1.6 μsec. after the pulse, and 2b, without it. A visual comparison of these spectra shows that there is hardly any absorption. The densitometer reading also showed only a very weak absorption at the lower wavelength. In the experiment, water was added by the equilibration of the dried monomer with atmospheric moisture. 3a and 3b show the effect of added DPPH in less than 10^{-4} M. The notations a and b correspond to those used with the earlier pairs. The densitometer reading revealed that the absorption was greatly diminished, as can be seen by a visual comparison.

In conclusion, new support for the postulated anion radical mechanism in the radiation-induced polymerization of α-methylstyrene has been obtained by the present investigation.

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[5] K. Hirota, K. Kuwata, H. Togawa and S. Ishida, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zassi)*, **79**, 602 (1958).