The Transient Absorption of Irradiated α-Methylstyrene

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A new transient absorption was observed at 5461Å in extremely dried α-methylstyrene by means of pulse radiolysis.

We have proposed previously[1,2] that the important intermediate in the radiation-induced polymerization of α-methylstyrene was the anion radical, which exhibited an absorption maximum at about 3500Å which was observed by a photographic method of pulse radiolysis.

It has been reported[3] that an absorption at 5100Å, as well as one at 3275Å, usually assigned to the anion radical, appeared when α-methylstyrene was brought into contact with alkalimetals. Therefore, irradiated α-methylstyrene may be expected to show an absorption maximum anywhere between 5000 to 6000 Å, in addition to that at 3500Å, if our proposal is correct.

The experimental details may be briefly explained as follows: An electron linear accelerator was used as the source of radiation. It provided a 1.6 μsec. pulse. A mercury lamp was used as the source of analytical light for spectroscopy. For recording the absorption, the photoelectric method was employed. The monomer was eventually dried by using a mirror of alkali metal. All the measurements were conducted at 15°C.

A typical synchroscope trace for the decay of absorption in dried α-methylstyrene is shown in Fig. 1. The arrow in the figure indicates the time of the irradiation of the sample with a pulse. The rate of the decay of the intermediate obeyed the first-order reaction kinetics (Fig. 2.) and had a half-life of about 25 μsec.

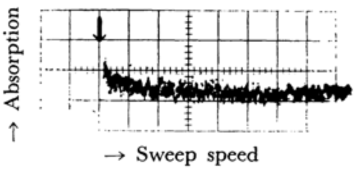

Fig. 1. Decay of absorption in extremely dried α-methylstyrene at 5461 Å (mean dose of 3 k. rads). Absorption: 1.6% per large division Sweep speed: 50 μ sec. per large division

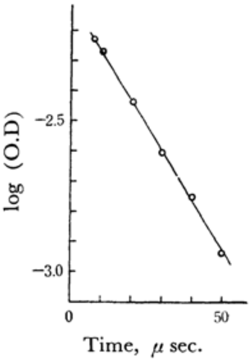

Fig. 2. The first-order plot of the decay of the absorption at 5461 Å (mean dose of 3 k. rads).

The transient absorption observed here at 5461Å behaves exactly like the one at 3500Å previously reported.[1] Thus, the addition of water or DPPH in a minute amount caused the intermediate to decay at a much faster rate. The decays with the additives were, actually, both too fast to be measured* with the same time scale as in Fig. 1. This is in conformity with the fact[2] that the polymerization is practically inhibited by the addition of these compounds. The first-order decay of the intermediate strongly suggests that it is reacting with the monomer molecules:

$$(\alpha\text{-MS})^{\ominus} + \alpha\text{-MS} \rightarrow \text{Polymerization}$$

It should be mentioned that the rate of the decay observed at 5461Å in the dried monomer quantitatively agreed with that at 3500Å.[4]

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

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[1] M. Katayama, M. Hatada, K. Hirota, H. Yamazaki and Y. Ozawa, This Bulletin, **38**, 851 (1965).

[2] K. Hirota and M. Katayama, *Annual Report of Japanese Association for Rad. Res. Polymers*, **5**, 205 (1963—64).

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

* The momentary effects of Cerenkov radiation, make it difficult to observe the decays quantitatively with a shorter time scale.

[4] M. Katayama, et al., to be published in *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), January (1966).