Radiation-induced Polymerization of α-Methylstyrene.
II. Reply to the Criticism of Bates et al.

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In radiation-induced polymerization, there are now a number of examples which can be explained by ionic mechanisms. However, these experiments were carried out at much lower temperatures than 0°C, and the monomers irradiated were all, except isobutene, of a solid state[1]. On the other hand, α-methystyrene (αMS) is known to be hardly polymerizable by ordinary peroxide initiators. Therefore, it would be interesting from the point of view of the reaction mechanism to investigate the radiation-induced polymerization of liquid αMS at room temperature[2].

In former reports[3], we came to the conclusion that the mechanism would be a radical one by taking the following experimental facts into consideration: 1) Besides such radical inhibitors as oxygen and *p*-benzoquinone, the reaction was retarded or inhibited by the presence of naphthalene or nitrobenzene respectively, which would make it likely for the polymerization to occur by an ionic mechanism. 2) Radical initiators produced photochemically or by a redox-reagent[4] had the power to polymerize αMS at room temperature. 3) Though the amount of polymerized product increased in proportion to the dose rate, this could be explained if the degradative chain transfer were considered in the reaction scheme, taking the existence of a low ceiling temperature for this monomer (60~70°C) into consideration. 4) The activation energy was found to be 4.1 kcal., which was a reasonable value for radical polymerizations initiated photochemically or by irradiation.

However, Bates et al.[5] recently proposed a cationic mechanism for this reaction based on the fact that its G (-monomer) increased up to 10000 from 10 if the monomer was pretreated with silica gel. Their theory is slightly contradictory to ours, because the monomer used in our experiment was dehydrated more severely with evaporated sodium film, while our G (-monomer) was smaller (200~600) than that of the Bates experiment. Such being the situation, further experiments were carried out by the use of three different methods of research in order to decide the mechanism.

Experimental and Results

The method of preparation of the samples was quite similar to that used in a former report; i. e., the monomer was deaerated and sealed in a glass ampule. Dehydration was carried out with calcium hydride instead of metallic sodium.

Experiment 1. The Effect of Zinc Oxide.—In order to study the effect of dehydration on the polymerization, the effect of zinc oxide was investigated, according to the suggestion of Bates et al. For the sake of comparison, styrene was irradiated as well as αMS. All the samples in the systems to be compared were irradiated for 18 hr. under the same dose rate. The results are shown in Table I.

In the case of αMS without dehydration, the yield of polymer rather decreased in the presence of zinc oxide, but it increased twofold when αMS was deaerated and dehydrated with calcium hydride. It is noteworthy that no such accelerating effect was observed in the case of styrene, which is a well-known monomer polymerizable by the radical mechanism.

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[1] E. Collinson, F. S. Dainton and H. A. Gills, *J. Phys. Chem.*, **63**, 909 (1959).

[2] K. Hirota, K. Kuwata and K. Makino, *Isotopes and Radiation*, **1**, 104 (1958).

[3] K. Hirota, K. Makino, K. Kuwata and G. Meshitsuka, This Bulletin, **33**, 251 (1960).

[4] G. G. Lowry, *J. Polymer Sci.*, **31**, 187 (1958).

[5] T. H. Bates, J. V. F. Best and T. F. Williams, *Nature*, **188**, 469 (1960).

TABLE I. THE EFFECT OF ZnO ON THE POLYMERIZATION

Run No.	Sample		Monomer used g.	Total dose r	Polymer obtained %	G (-monomer)
3	αMS	ZnO	3.77	1.6×10^5	0.093	50
4		—	1.75	1.6×10^5	0.11	60
1′	αMS	ZnO	3.11	2×10^5	0.16	80
2′	Dehydrated	—	2.34	2×10^5	0.09	50
10	Styrene	ZnO	3.64	3.6×10^4	6.07	1.69×10^3
11	Dehydrated	—	1.74	3.6×10^4	5.58	1.55×10^3

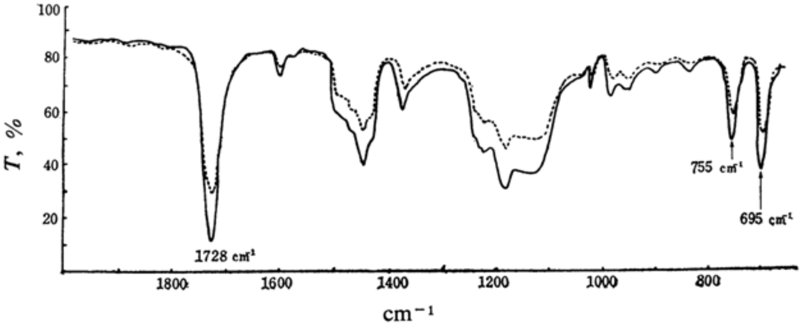

Fig. 1. Infrared spectra of the polymers obtained from the mixture of αMS and MMA.
—— Product polymerized by irradiation
---- Product polymerized by ABIN
1728 cm⁻¹ stretching vibration of C=O group
755 and 695 cm⁻¹ out-of-plane bending vibrations of CH of C_6H_5 group

Experiment 2. Copolymerization with Methyl Methacrylate.— Six cc. of an equivolume mixture of αMS and MMA (methyl-methacrylate) which was sealed and deaerated in a glass ampule was irradiated with γ-rays for 376 hr. at room temperature. The dose rate was 0.73×10^4 r/hr., the total dose therefore amounting to 2.7×10^6 r. In the infrared spectrum of the polymer thus obtained, characteristic bands corresponding to the carbonyl group at 1728 cm⁻¹ and to the phenyl group at 755 cm⁻¹ and 695 cm⁻¹ appeared, as is shown by the full curve in Fig. 1. Moreover, this spectrum was quite similar to the spectrum (dotted curve) of the product copolymerized from the same mixture of αMS and MMA with azo-bis-isobutylonitril. Therefore, the product obtained by irradiation may be a copolymer of both monomers.

Experiment 3. Turbidometry of the Copolymer.—Strictly speaking, there is yet a possibility in Exp. 2 that the product might be a mixture of poly-αMS and poly-MMA. In order to investigate this possibility, turbidometry was adopted on the product by use of a self-recording apparatus manufactured by Shimadzu. By dropping a mixture of methanol-water (50% : 50%) into the acetone solution (100 cc.) of the polymer, a turbidity-time curve was obtained, as is shown in Fig. 2. It was found by the shape of the curve that the product was composed of two polymers. The major part (90%) of the polymer is established as copolymer, while the remaining, more insoluble part (10%) as poly-αMS, in the following discussion.

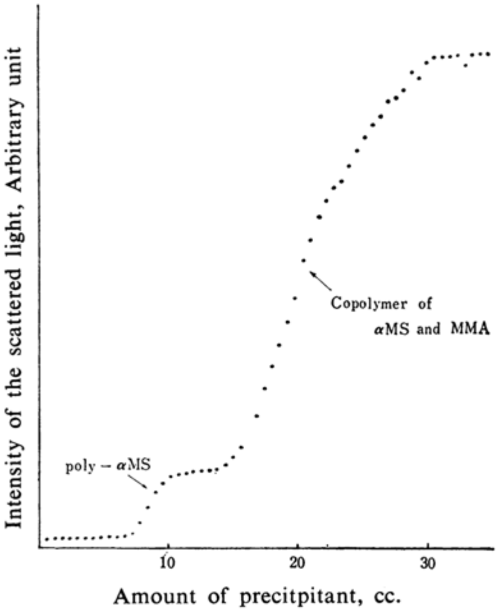

Fig. 2. Turbidity-time curve of the polymer obtained by irradiating the mixture of αMS and MMA.
Sample : 100 cc. of acetone solution (0.01%)
Precipitant : Water-methanol (50% : 50%)
Apparatus : Shimadzu PG-21.

Discussion

Generally, there exists no reliable report on radiation-induced polymerization which is explained by an anionic mechanism, in a case when no solvent is used and the polymerization is carried out at room temperature. The present polymerization, therefore, must be explained by radical or cationic mechanisms, or by both. According to Exp. 2, the polymerization may be explained at least by a radical mechanism for the following reasons. First, MMA is only with difficulty copolymerizable with αMS by a cationic catalyst, such as iodine[6]. Second, it is hardly conceivable that the radical ends of both poly-αMS and poly-MMA coexist in the solution. Therefore, the polymer here obtained must be a copolymer, produced by a radical mechanism.

However, according to Exp. 1, the presence of zinc oxide seems to accelerate the polymerization, though the effect was not so marked. This result can be explained by the cationic mechanism, if zinc oxide plays the role of an electrontrap, which would help the formation of cation, though Bates et al. attributed its dehydrating action to the origin of the accelerating effect. It may therefore be reasonable to conclude that the polymerization did not necessarily always occur according to one and the same mechanism. If this is so, the product of Exp. 2 will include not only the copolymer but also the homopolymer. Such a possibility is actually confirmed by Exp. 3. Now the minor part of the product confirmed by Exp. 3 must be the homopolymer of αMS, considering that it is less soluble than the major part and also that the homopolymer of MMA may not be produced under the present conditions.

In short, the above results teach us that γ-ray-induced polymerization of αMS occurs simultaneously as a result of both radical and cationic initiators produced by irradiation, the fraction of the polymer produced by the radical initiator, however, being much larger. By assuming such a coexistence of two mechanisms during the process of the present polymerization, the data of Bates et al. and those of present authors, regarding this reaction, can be explained without any contradiction.

Summary

Gamma-ray-induced polymerization of α-methylstyrene occurs mostly according to the radical mehanism, as had been concluded by one of the present authors, but simultaneously it occurs to some extent according to the cationic mechanism, as had been asserted by Bates et al.

In conclusion, we wish to express our deep thanks to Dr. Keiji Kuwata and Mr. Junichi Matuura of Osaka University for their discussions and help in the measurement of the turbidometry.

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[6] K. Hirota, G. Meshitsuka, F. Takemura and T. Tanaka, This Bulletin, 33, 1316 (1960).

[7] Cf. K. Hayashi, *Isotopes and Radiation*, 3, 109 (1960).