Polymerization of Methyl Methacrylate Initiated by Phenylazo p-Tolyl Sulfone

By Ryoichi UEHARA

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Phenylazo *p*-tolyl sulfone was first prepared by Koenigs[1] through the reaction of benzenediazonium chloride with sodium *p*-toluenesulfinate:

$$C_6H_5N_2Cl + CH_3C_6H_4SO_2Na = C_6H_5N_2SO_2C_6H_4CH_3 + NaCl$$

Copolymerization of butadiene and styrene (GR-S rubber) by the use of various arylazo aryl sulfones as initiators have been carried out by Brown[2]. It has been reported by Theobold[3] that solution-polymerization of acrylonitrile in ethanol takes place very smoothly at 40°C by means of phenylazo *p*-tolyl sulfone and a very small amount of cupric chloride. The present author has examined the effect of phenylazo *p*-tolyl sulfone upon the polymerization of methyl methacrylate. Phenylazo *p*-tolyl sulfone was an efficient initiator of the polymerization, but it was not suitable for use in manufacture of polymethyl methacrylate, because the polymer formed was dark orange in color. On the other hand, it appears of interest that dimethylaniline acted as an accelerator for this polymerization. In the present paper, results of experiments about the

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[1] P. Koenigs, *Ber.*, **10.**, 1531 (1877).

[2] R. S. Brown, U. S. Pat., 2,527,393 (1950); *Chem. Abstr.*, **45**, 383 (1951).

[3] C. W. Theobold, U. S. Pat., 2,584,306 (1952); *Chem. Abstr.*, **46**, 3798 (1952).

relation between the initial rate of polymerization and the concentrations of phenylazo *p*-tolyl sulfone, dimethylaniline and methyl methacrylate are given, and the nature of the initiating reaction is discussed from the standpoint of the reaction kinetics.

The dependence of the initial rate of polymerization (*R*) upon the concentration of phenylazo *p*-tolyl sulfone ([AZS]) in the solution-polymerization in benzene (concentration of methyl methacrylate, 30%) were studied at 41, 51 and 60°C. As are shown in Fig. 1, the square root dependence of the rate upon the concentration was observed at each temperature. When the logarithms of the initial rates (phenylazo *p*-tolyl sulfone 1.1×10^{-2} mol./l.) were plotted against the reciprocals of the temperatures, a straight line was obtained (Fig. 2). The overall activation energy of the polymerization calculated from the slope of the straight line in Fig. 2 was found to be 12.2 kcal./mol.

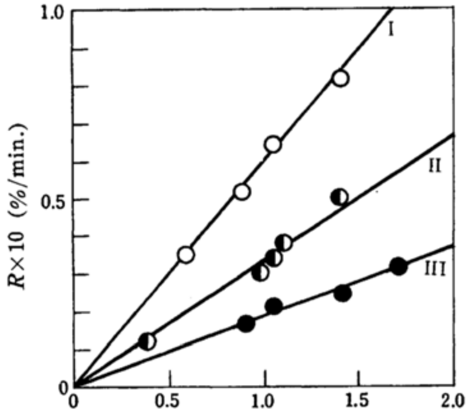

Fig. 1. Dependences of *R* upon $[\text{AZS}]^{1/2}$ at 60 (I), 51 (II) and 41°C (III) ([MMA]=30% in benzene).

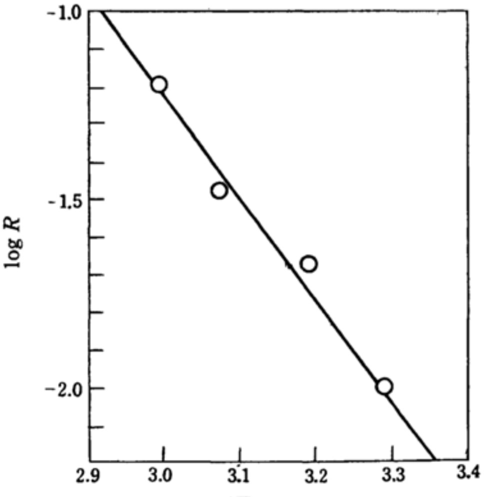

Fig. 2. Relationship between log *R* and $1/T$ ($[\text{AZS}]=1.1\times10^{-2}$ mol./l. and [MMA]=30% in benzene).

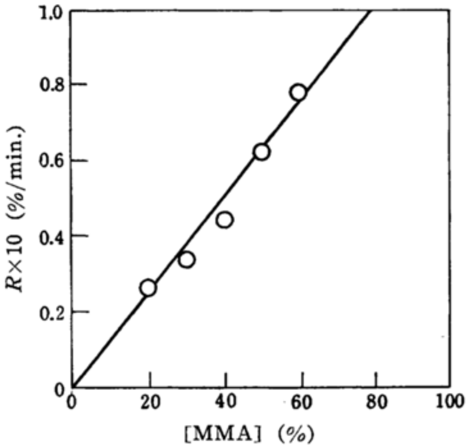

Fig. 3. Correlation of *R* with [MMA] at 51°C ($[\text{AZS}]=1.1\times10^{-2}$ mol./l.).

Fig. 3 shows a relationship between the initial rate and the concentration of methyl methacrylate ([MMA]) in benzene (at 51°C and phenlazo *p*-tolyl sulfone 1.1×10^{-2} mol./l.). The rate was linearly proportional to the concentration of methyl methacrylate.

Relationships shown in Figs. 1 and 3 are represented by Eq. 1:

$$R=k_0[\text{AZS}]^{1/2}[\text{MMA}] \qquad (1)$$

where k_0 is a constant. This equation is quite similar to that which is usually known to hold in the polymerization of vinyl monomers initiated by benzoyl peroxide or α,α'-azo-bis-isobutyronitrile[4]. Eq. 1, therefore, suggests a unimolecular first order decomposition of phenylazo *p*-tolyl sulfone as the initiating reaction of the polymerization.

The polymerization of methyl methacrylate initiated by phenylazo *p*-tolyl sulfone is accelerated by addition of dimethylaniline. When the concentration of phenylazo *p*-tolyl sulfone was kept constant and various amounts of dimethylaniline were added, the initial rate of polymerization was linearly dependent upon the square root of the concentration of dimethylaniline ([DMA]). Fig. 4 shows

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[4] P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N. Y. (1953), p. 116.

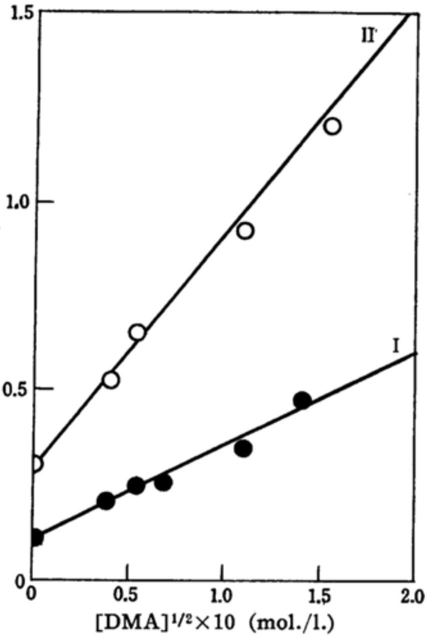

Fig. 4. Correlations of R with $[\mathrm{DMA}]^{1/2}$ at 51°C ($[\mathrm{MMA}]=30\%$, $[\mathrm{AZS}]=0.15\times 10^{-2}$ for line I and 0.96×10^{-2} mol./l. for line II).

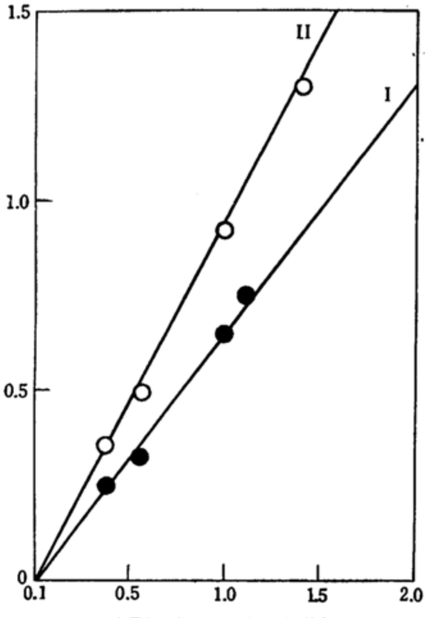

Fig. 5. Correlations of R with $[\mathrm{AZS}]^{1/2}$ at 51°C ($[\mathrm{MMA}]=30\%$, $[\mathrm{DMA}]=0.29\times 10^{-2}$ for line I and 1.2×10^{-2} mol./l. for line II).

examples of this relationship (concentration of methyl methacrylate 30%; concentration of phenylazo *p*-tolyl sulfone 0.15×10^{-2} and 0.95×10^{-2} mol./l. at 51°C).

In the case when the concentration of dimethylaniline was held constant and that of phenylazo *p*-tolyl sulfone was varied, the initial rate of polymerization was proportional to the square root of the concentration of phenylazo *p*-tolyl sulfone. Examples of this correlation are shown in Fig. 5 (methyl methacrylate 30%, and dimethyl- aniline 0.29×10^{-2} and 1.2×10^{-2} mol./l. at 51°C). It is evident from Figs. 1 and 4 that the polymerization takes place at measurable rates at 51°C by means of phenylazo *p*-tolyl sulfone alone. Therefore, in the case where the concentration of methyl methacrylate is kept constant, the correlations shown in Figs. 4 and 5 can be represented by the following equation:

$$R=k[\mathrm{AZS}]^{1/2}+k'[\mathrm{AZS}]^{1/2}[\mathrm{DMA}]^{1/2} \qquad (2)$$

where k and k' are constants.

Eq. 2 suggests that the polymerization of methyl methacrylate by means of phenylazo *p*-tolyl sulfone and dimethylaniline is initiated by two reactions, i. e., a unimolecular first order decomposition of phenylazo *p*-tolyl sulfone and a bimolecular reaction between phenylazo *p*-tolyl sulfone and dimethylaniline, k and k' being the rate constants respectively. From Eq. 2, the following equation is derived:

$$R=k[\mathrm{AZS}]^{1/2}(1+k'/k[\mathrm{DMA}]^{1/2}) \qquad (3)$$

k'/k, the ratio of the rate constants of the two initiating reactions of the polymerization, can be calculated from the slops of the straight lines in Fig. 4. It was found to be 2.00 from line I and 2.18 from line II (at 51°C and methyl methacrylate 30% in benzene).

Imoto and others[5] have reported a rate-concentration equation similar to Eq. 2 or 3 for the polymerization of methyl methacrylate initiated with benzoyl peroxide and dimethylaniline, and suggested a similar mechanism to that mentioned above.

Experimental

Materials.—Purification of methyl methacrylate, dimethylaniline and benzene have been mentioned in a previous paper by the present author[6]. Phenylazo *p*-tolyl sulfone was obtained by addition of sodium *p*-toluenesulfinate (21 g.) into an aqueous solution of benzenediazonium chloride which was prepared from aniline (10 g.), 30%

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[5] M. Imoto et al., *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **58**, 451 (1955).

[6] R. Uehara, This Bulletin, **31**, 685 (1958).

aqueous HCl (40 cc.) and $NaNO_2$ (8 g.). The crude product was recrystallized three times from pure methanol, giving pure phenylazo *p*-tolyl sulfone (17.5 g.), m. p. 87.5°C with decomposition (83.5°C by Brown[2]). This compound was not quite stable at room temperature under sunlight. In a colorless, transparent glass vessel, it changed into a resinous meterial during several weeks in summer.

Polymerization. — Polymerization was carried out in sealed test tubes which were 15 mm. in diameter and 10 cm. in height and made of brown-colored glass so as to reduce the effects of sunlight upon the polymerization. Phenylazo *p*-tolyl sulfone was dissolved in benzene. Methyl methacrylate was cooled in an ice-salt bath. Measured amounts of the benzene-solution and methyl methacrylate were placed in a test tube and mixed. The test tube was immersed in a dry ice-methanol bath and flushed with nitrogen and sealed. The extent of the polymerization was estimated from the weight of polymethyl methacrylate, and the rate of polymerization was expressed in unit of per cent per minute. Details of the procedures of the polymerization and the determination of the initial rate of polymerization have been reported previously[6].

Summary

The effects of phenylazo *p*-tolyl sulfone upon the polymerization of methyl methacrylate were examined. In the solution-polymerization in benzene, the initial rate of polymerization was linearly dependent respectively upon the square root of the concentration of phenylazo *p*-tolyl sulfone and upon the concentration of methyl methacrylate. A unimolecular first order decomposition of phenylazo *p*-tolyl sulfone is suggeted as the initiating reaction of the polymerization. Dimethylaniline acted as an accelerator for this polymerization. In this case, the initial rate of polymerization was linearly proportional to the square root of each of the concentrations of phenylazo *p*-tolyl sulfone and dimethylaniline. A bimolecular reaction between phenylazo *p*-tolyl sulfone and dimethylaniline has been proposed for the acceleration of the polymerization.

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Tama Kagaku Kogyo Co.
2–28 *Minamirokugo*
Ota-ku, Tokyo