Polymerization of Methyl Methacrylate Initiated by a Combined Action of Trichloroacetic Acid and Dimethylaniline

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(Received May 27, 1958)

The author[1] preliminarily reported that polymerization of methyl methacrylate could be initiated, even at room temperature, by a combined action of trichloroacetic acid and dimethylaniline. Neither trichloroacetic acid nor dimethylaniline alone was responsible for the initiation, but, when they were dissolved together in methyl methacrylate, the polymerization was initiated. Recently, Lal[2] and others, in their paper concerning initiating actions of saccharine amine salts for polymerization of vinyl monomers, have reported that some combinations of carboxylic acids and dimethylaniline act as initiators for methyl methacrylate. But, in their report, only a brief mention of per cent yields of polymethyl methacrylate after 1 hr., at 58.6°C, was given.

This paper presents the results of experiments about the dependence of the initial rate of polymerization of methyl methacrylate upon the concentrations of both trichloroacetic acid and dimethylaniline, and a bimolecular reaction between trichloroacetic acid and dimethylaniline to form radicals is suggested as the initial reaction of the polymerization.

Experimental

Materials.—Methyl methacrylate was washed with 5% aqueous sodium carbonate and water, then distilled with steam, dried over anhydrous sodium sulfate, and carefully distilled in oxygen-free nitrogen under reduced pressure through a fractionating column. A fraction boiling at 46°C/12 mmHg was used immediately after the distillation. Dimethylaniline was distilled under nitrogen and a fraction boiling at 110°C/12 mmHg was used. Trichloroacetic acid was prepared from chloral and nitric acid, and a fraction boiling at 196°∼197°C was employed. Thiophene-free benzene was dried over anhydrous sodium sulfate and distilled. Hydroquinone was dissolved in ether, decolorized by means of active carbon, and then precipitated by adding dry benzene, m.p. 174°C.

Determination of Initial Rate of Polymerization.—Polymerization of methyl methacrylate was carried out in sealed test tubes which were 15 mm. in diameter and 10 cm. in height and made of hard glass. The test tubes were cleaned by immersing them in 1% aqueous hydrofluoric acid for 12 hr., then washed with pure water and steam, and dried. Trichloroacetic acid and dimethylaniline were dissolved separately in methyl methacrylate. Both solutions were cooled in a methanol-dry ice bath, and measured amounts of both solutions were placed in a test tube and mixed. When hydroquinone was used, it was dissolved in methyl methacrylate together with dimethylaniline. In case of solution-polymerization, benzene was added to test tubes from a burette. The volume of the contents of one test tube was limited, not to exceed 5 cc. The test tubes were flashed for 10 minutes with dry nitrogen, which had been deoxygenated according to the procedure described by Fieser[3], then evacuated to 1 mmHg, and sealed. They were kept in a cooling bath for 30 minutes in order to ensure uniformity of temperature. The polymerization was effected by shaking the test tubes in a thermostat. The time of polymerization was measured from the beginning of the shaking. The yields of the polymer were measured at intervals of 15 minutes. Two tubes were picked up for one measurement, chilled in a cooling bath, and then opened. The contents of the tube were diluted with 5 cc. of acetone and taken out. The tube was then washed with 5 cc. of acetone. The contents and the washing were combined, and poured into 200 cc. of methanol so as to precipitate the polymer formed. The precipitated polymer was collected on a glass filter, washed three times with 10 cc. of methanol, then dried to a constant weight at 50°C under reduced pressure. The average weight of the samples of polymer from the two test tubes was taken as its yield. The initial rate of polymerization was determined from a linear part of the time-conversion curve in the initial stage of the polymerization, and expressed in a unit of per cent per minute.

Results and Discussion

Fig. 1 shows the relation between the initial rate of polymerization (R) and the concentration of trichloroacetic acid ([TCA]). In this case the equimolar

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[1] R. Uehara, Kagaku-no-Ryoiki, **7**, 295 (1953).

[2] J. Lal et al., *J. Polymer Sci.*, **24**, 81 (1957).

[3] L. Fieser, "Experiments in Organic Chemistry", D. C. Heath Co., New York (1941) p. 395.

amounts of trichloroacetic acid and dimethylaniline were used. So, the dependence of the initial rate of polymerization upon the concentration of dimethylaniline ([DMA]) was the same as that of Fig. 1. From Fig. 1, it can be seen that the initial rate is linearly dependent upon the concentration of trichloroacetic acid at temperatures of 25°, 35° and 55°C, respectively.

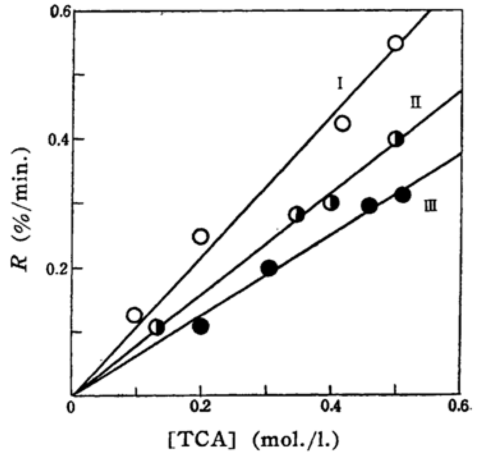

Fig. 1. Relation between R and [TCA] ([TCA] = [DMA]) I, at 55°; II, at 35°; III, at 25°C.

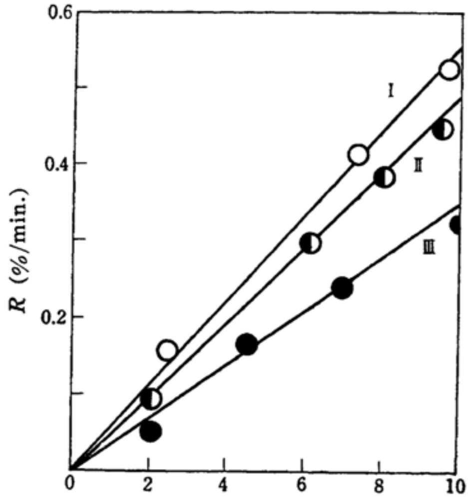

Fig. 2. Correlation of R with square-root of [DMA] at 35°C, I, [TCA] = 0.50; II, [TCA] = 0.42; III, [TCA] = 0.21 mol./l.

When the concentration of trichloroacetic acid was held constant and that of dimethylaniline was varied, the initial rate of polymerization was linearly dependent upon the square root of the concentration of dimethylaniline, i. e., the so-called square-root dependence was observed as shown in Fig. 2. From this figure, the square-root dependence can be seen to hold for each case, in which 0.21, 0.42 and 0.50 mol./l., respectively, of trichloroacetic acid was used at 35°C. The fact that each of the straight lines in Fig. 2 is brought to a focus at the origin shows that trichloroacetic acid alone is not responsible for the initiation of polymerization.

In Fig. 3, initial rates of polymerization

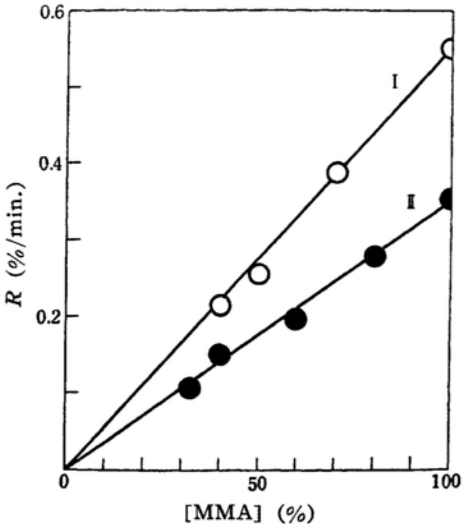

Fig. 3. Correlation of R with [MMA] at 55°C ([TCA] = [DMA]).
I, 0.50 mol./l. of TCA
II, 0.34 mol./l. of TCA

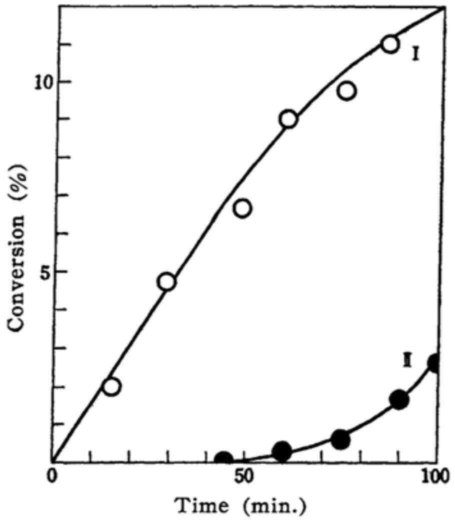

Fig. 4. Time conversion curves of bulk polymerization at 35°C ([TCA] = [DMA] = 0.20 mol./l.).
I, without hydroquinone
II, with 0.026 mol./l. of hydroquinone

in benzene are plotted against the concentration of methyl methacrylate ([MMA]). Two cases, in which 0.34 and 0.50 mol./l. of trichloroacetic acid with equimolar amounts of dimethylaniline were used, are shown. The initial rate of polymerization was proportional to the concentration of methyl methacrylate.

In Fig. 4, the time-conversion curves for the bulk polymerization at 35°C, in which 0.20 mol./l. of each of trichloroacetic acid and dimethylaniline were used with or without hydroquinone, are shown. In the presence of 0.025 mol./l. of hydroquinone, a considerably long induction period was observed, therefore, it was clear that hydroquinone acted as an inhibitor for this reaction.

The relation between the initial rate and the concentration shown in Figs. 1, 2 and 3, can be represented by the following equation:

$$R=k[\mathrm{TCA}]^{1/2}\,[\mathrm{DMA}]^{1/2}\,[\mathrm{MMA}] \qquad (1)$$

where k is a constant. This equation suggests a bimolecular reaction between trichloroacetic acid and dimethylaniline to form radicals as the initial reaction of the polymerization:

$$\mathrm{TCA}+\mathrm{DMA} \xrightarrow{k_1} \mathrm{R}\cdot \qquad (2)$$

where k_1 is the rate constant and R· represents the radical, the chemical identity of which will be the subject for further investigation. Reaction 2 is followed by the usual series of reactions of polymerization, i. e., initiation, propagation and termination:

$$\mathrm{TCA}+\mathrm{DMA} \xrightarrow{k_1} \mathrm{R}\cdot$$

$$\mathrm{R}\cdot+\mathrm{M} \xrightarrow{k_2} \mathrm{P}_1\cdot$$

$$\mathrm{P}_m\cdot+\mathrm{M} \xrightarrow{k_3} \mathrm{P}_{m+1}\cdot$$

$$\mathrm{P}_m\cdot+\mathrm{P}_n\cdot \xrightarrow{k_4} \mathrm{P}_{m+n} \text{ or } \mathrm{P}_m+\mathrm{P}_n$$

where $\mathrm{P}_1\cdot$, $\mathrm{P}_m\cdot$, $\mathrm{P}_n\cdot$ and $\mathrm{P}_{m+1}\cdot$ represent polymer radicals, P_m, P_n and P_{m+n} polymer molecules, M is MMA, and k_2, k_3 and k_4 are rate constants, respectively, for initiation, propagation and termination. By assuming a stationary state for each of R· and P·, the following equation can be deduced for the initial rate of polymerization:

$$R=k_3(k_1/k_4)^{1/2}[\mathrm{TCA}]^{1/2}[\mathrm{DMA}]^{1/2}[\mathrm{M}] \qquad (3)$$

Although the chemical identity of R· is unknown at present, equation 3 perfectly coincides with equation 1.

The rate-concentration relation represented by equation 1 or 3 is quite similar to that of Imoto[4] and others for the polymerization of vinyl monomers initiated by a combined action of benzoyl peroxide and dimethylaniline. They also postulated a bimolecular reaction between benzoyl peroxide and dimethylaniline for the initial reaction of the polymerization.

Summary

The polymerization of methyl methacrylate is initiated even at room temperature by a combined action of trichloroacetic acid and dimethylaniline. In case of bulk polymerization, the initial rate of polymerization is proportional to each of the square roots of the concentrations of trichloroacetic acid and dimethylaniline. In case of polymerization in benzene, the initial rate depends upon the concentration of methyl methacrylate. These relationships can be reasonably explained by assuming a bimolecular reaction between trichloroacetic acid and dimethylaniline to form radicals as the initial reaction of the polymerization. Hydroquinone acts as an inhibitor for this reaction.

The author thanks Professor Osamu Simamura of University of Tokyo for his kind guidance and also Mr. Tsurahide Cho, the President of Tama Kagaku Kogyo Co., for permission to undertake this work.

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[4] M. Imoto and K. Takemoto, *Chem. High Polymers* (*Kobunsi Kagaku*), **12**, 120 (1955).