Polymerization of Methyl Methacrylate Initiated by the System of p-Toluenesulfinic Acid, Dimethylaniline and Oxygen

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Polymerization of vinyl monomers initiated by some sulfinic acids was first reported by Hagger[1]. The present author[2] has reported a self-curing method of methyl methacrylate by the combined action of *p*-toluenesulfinic acid and dimethylaniline in the presence of air. Hagger considered that sulfinic acids by themselves could initiate the polymerization of vinyl monomers and reported an equation representing a relation between the initial rate of polymerization of methyl methacrylate and the concentration of *p*-toluenesulfinic acid.

Recently, Bredereck and others[3] found that absolutely pure *p*-toluenesulfinic acid could not initiate the polymerization of methyl methacrylate, and that for the initiation of the polymerization, the coexistence of oxygen and an "oxygen-acceptor" such as amines or chloide ions was necessary. The polymerization-initiating action of sulfinic acid found by Hagger was explained by Bredereck to be due to the combined action of the sulfinic acid, oxygen in air, and chloride ions containd in the sulfinic acid as an impurity. Moreover, Bredereck[4] has postulated a mechanism for the initiation of the polymerization of methyl methacrylate with an initiating system consisting of oxygen, *p*-toluenesulfinic acid, and an "oxygen-acceptor"; i. e., a peroxide was formed from oxygen and the sulfinic acid, and then a radical was produced from the peroxide and the "oxygen-acceptor" to initiate the polymerization. But no experimental evidence was given by him for this mechanism.

The present author has studied the polymerization of methyl methacrylate initiated by the system of *p*-toluenesulfinic acid, oxygen in air and dimethylaniline from the standpoint of chemical kinetics. In the present paper, correlations of the initial rate of polymerization of methyl methacrylate with the concentration of the components of the inititating system are given, and the initial step of the polymerization is discussed.

The polymerization was carried out in open test tubes under atmospheric pressure of air for the study of the dependence of the initial rate (R) of polymerization upon concentrations of *p*-toluenesulfinic acid (TSA), dimethylaniline (DMA), and methyl methacrylate (MMA). When the effect of the initial pressure of oxygen was tested, the polymerization was carried out in sealed test tubes under various initial pressures of air.

When the concentration of *p*-toluenesulfinic acid was held constant and that of dimethylaniline was varied under atmospheric pressure of air, the initial rate of the bulk polymerization of methyl methacrlate

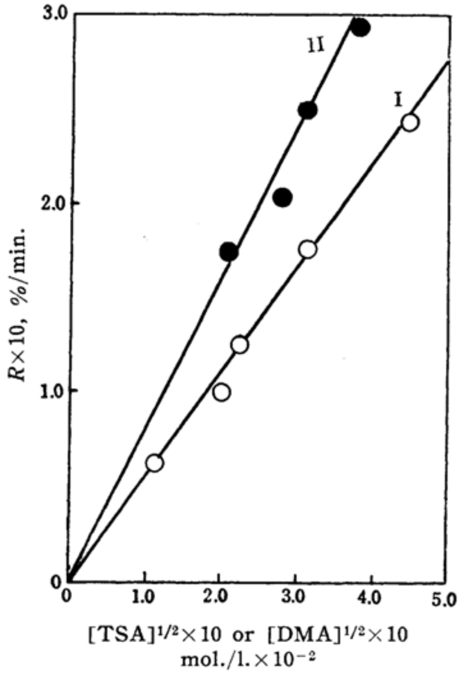

Fig. 1. Correlations of R with $[TSA]^{1/2}$ and $[DMA]^{1/2}$ at 30°C in air.
Line I. $[TSA]=5.1\times10^{-2}$ mol./l.
Line II. $[DMA]=10.0\times10^{-2}$ mol./l.

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[1] O. Hagger, *Helv. Chim. Acta.*, **31**, 1629 (1948).

[2] R. Uehara, *Dental Practice* (*Rinsho Shika*), **196**, 24 (1952).

[3] H. Bredereck et al., *Ber.*, **89**, 731 (1956).

[4] H. Bredereck et. al., *Angew. Chem.*, **68**, 306 (1956).

was linearly proportional to the square root of the concentration of dimethylaniline. This correlation is shown by line I in Fig. 1, in which 5.01×10^{-2} mol./l. of *p*-toluenesulfinic acid was used at 30°C.

When the concentration of dimethylaniline was kept constant and that of *p*-toluenesulfinic acid was varied, the initial rate of polymerization was linearly dependent upon the square root of the concentration of *p*-toluenesulfinic acid. This relationship is shown by line II in Fig. 1, in which 10×10^{-2} mol./l. of dimethylaniline was used at 30°C. Straight lines I and II in Fig. 1 are brought to a focus at the origin. This fact indicates that neither *p*-toluenesulfinic acid nor dimethylaniline alone can initiate the polymerization in combination with oxygen in air.

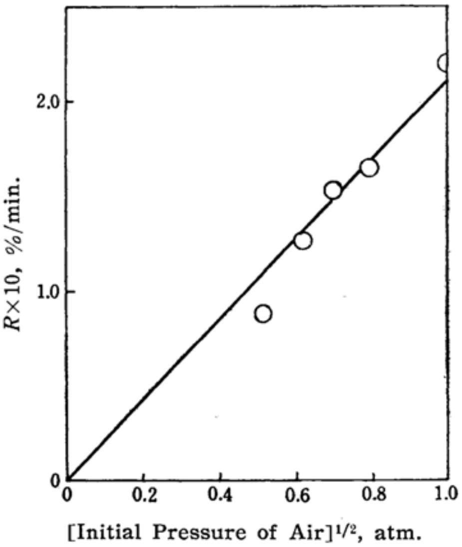

Fig. 2. Correlation of R with the initial pressure of air at 30°C
[TSA] = [DMA] = 8.8×10^{-2} mol./l.

In Fig. 2 the correlation of the initial rate of polymerization with the initial pressure of air in the sealed test tubes is shown. The initial rate of polymerization is linearly proportional to the square root of the initial pressure of air. In this case 8.8×10^{-2} mol./l. of both *p*-toluenesulfinic acid and dimethylaniline were used. The straight line in Fig. 2 gose through the origin. This fact indicates that the polymerization can not be initiated without air. The pressure of air is proportional to that of oxygen, so Fig. 2 shows that the initial rate of polymerization is linearly dependent upon the square root of the initial pressure of oxygen.

In the case of the solution-polymerization in benzene, the initial rate of polymerization was linearly dependent upon the concentration of methyl methacrylate. This correlation is shown in Fig. 3, in which 5.10×10^{-2} mol./l. of both *p*-toluenesulfinic acid and dimethylaniline were used at 40°C, under air of atmospheric pressure.

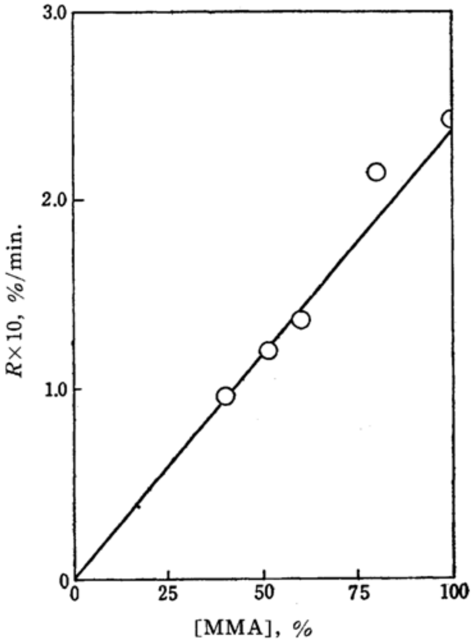

Fig. 3. Relationship between R and [MMA] in case of solution-polymerization in benzene at 40°C.
[TSA] = [DMA] = 5.10×10^{-2} mol./l.

Correlations shown in Figs. 1—3 can be represented by the following equation:

$$R=k[O_2]^{1/2}[TSA]^{1/2}[DMA]^{1/2}[MMA] \quad (1)$$

where k is a constant.

Eq. 1 suggests that oxygen, *p*-toluenesulfinic acid and dimethylaniline, all three, take part in the formation of a radical to initiate the polymerization, but methyl methacrylate is not concerned in the radical formation at the initiation reaction. Moreover, Eq. 1 suggests that there may be several reactions forming the radical from the initiating system. As mentioned above, Bredereck[4] has postulated the formation of a peroxide from oxygen and *p*-toluenesulfinic acid as the first step of the initiation. In another paper, however, Bredereck[3] has reported very briefly without any details of experiments that salts of *p*-toluenesulfinic acid and some aromatic amines initiated the polymerization of methyl methacrylate under air. In addition, it has been reported by

Bredereck[5] and Brauer[6] that salts of the sulfinic acid and amines were efficient accelerators for the polymerization of methyl methacrylate initiated with benzoyl peroxide. Formation of a salt from an amine and *p*-toluenesulfinic acid takes place very smoothly in organic solvent[6]. So, in the case of the combination of *p*-toluenesulfinic acid and dimethylaniline, formation of a salt from the sulfinic acid and the amine is more probable than the formation of a peroxide from the sulfinic acid and oxygen in air. The initiating system, *p*-toluenesulfinic acid-oxygen-chloride ions, must be considered separately from the initiating system under discussion.

To get support for this idea from another point of view, the present author has examined the effects of anhydride, and methyl and ethyl esters of *p*-toluenesulfinic acid for the initiation of the polymerization. The per cent conversions of bulk polymerization by means of equimolar mixtures of these compounds and dimethylaniline are shown in Table I.

TABLE I. THE PER CENT CONVERSIONS OF THE BULK POLYMERIZATION OF METHYL METHACRYLTE UNDER ATMOSPHERIC PRESSURE OF AIR

Initiator*	Conversions, %			
	at 30°C		at 70°C	
	3 hr.	6 hr.	1 hr.	3 hr.
p-Toluenesulfinic acid	22.1	98.7	43.8	96.2
Anhydride	0	0	trace	3.8
Methyl ester	0	0	trace	8.4
Ethyl estr	0	0	trace	4.3

* 5.0×10^{-2} mol./l. of each was used together with equimolar amount of dimethylaniline

Polymerizations were carried out at 30 and 70°C under atmospheric pressure of air. At 30°C, *p*-toluenesulfinic acid was the only material which was responsible for the initiating action. At 70°C, the effect of *p*-toluenesulfinic acid was much greater than those of its derivatives. Namely, the polymerization-initiating action of the sulfinic acid was lost by changing it to its anhydride or esters. Therefore, it appears to be conclusive that the formation of a salt from the sulfinic acid and dimethylaniline is the first step of the polymerization.

By considering the formation of the salt, the following reactions of polymerization are derived:

$$\mathrm{TSA}+\mathrm{DMA}\overset{K}{\rightleftarrows}\mathrm{S}$$

$$\mathrm{S}+\mathrm{O_2}\xrightarrow{k_1}\mathrm{R}\cdot$$

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

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

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

where S is the salt, $\mathrm{R}\cdot$ the radical formed from the salt and oxygen, $\mathrm{P}_1\cdot$, $\mathrm{P}_m\cdot$, $\mathrm{P}_n\cdot$, $\mathrm{P}_{m+1}\cdot$ are polymer radicals, P_m, P_n, P_{m+n} polymer molecules, K is the euqilibrium constant, and k_1, k_2, k_3, k_4 are respectively rate constants for each of the reactions.

From these reactions the follwing equation can be deduced by the usual method of chemical kinetics for radical polmerization:

$$R=k_3(Kk_1/k_4)^{1/2}[\mathrm{O_2}]^{1/2}[\mathrm{TSA}]^{1/2}[\mathrm{DMA}]^{1/2}[\mathrm{MMA}] \qquad (2)$$

Eq. 2 completely coincides with Eq. 1.

Experimetal

Materials.—Purification of methyl methacrylate, dimethylaniline and benzene have been reported in a previous paper by the present author[7]. *p*-Toluenesulfinic acid was prepared from *p*-toluenediazonium sulfate by using sulfur dioxide and copper[8]. The crude product was washed with distilled water until ions of heavy metals, chloride and sulfate were not detected in the washing then recrystallized from benzene and methanol, and dried under reduced pressure, m.p. 81°C. The crystallization and the drying of the sulfinic acid were carried out as rapidly as possible, and the purified sulfinic acid was used immediately after drying to avoid deterioration. Anhydride of the sulfinic acid was obtained by treating the acid with acetic anhydride in the presence of a small amount of sulfuric acid, m.p. 75.0°C[9]. Methyl and ethyl esters of the sulfinic acid were prepared from sodium *p*-toluenesulfinate and metyl or ethyl chlorocarbonate, respectively[10]. The esters were used without any purification because of their instability.

Polymerization.—Polymerization under atmospheric pressure of air was carried out in test tubes, each of which was open to the atmosphere

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5) H. Bredereck et. al., *Makromol. Chem.*, **12**, 100 (1954).

6) G. M. Brauer and F. R. Burns, *J. Polymer Sci.*, **19**, 311 (1956).

7) R. Uehara, This Bulletin, **31**, 685 (1958).

8) L. Gattermann, *Ber.*, **32**, 1136 (1899).

9) E. Knoevenagel, ibid., **41**, 3326 (1908).

10) R. Otto et. al., ibid., **18**, 2506 (1885).

through a capillary at the top. The test tubes were 15 mm. in diameter and 20 cm. in height, and the capillary was 1 mm. in inner diameter and 4 cm. in length, and fitted to the test tube with a ground glass joint. When the effect of the initial pressure of the air was examined, sealed test tubes, each of which was 20 cc. in capacity, were used in place of the above mentioned open tubes. *p*-Toluenesulfinic acid and dimethylaniline were dissolved separately in methyl methacrylate. Both solutions were chilled in a dry ice-methanol bath for 30 min. Measured amounts of each chilled solution were placed in a test tube and mixed. The polymerization was effected by shaking the tubes in a thermostat. The yield of the polymer was measured at intervals of 10 min. Details of the procedures of polymerization and the determination of the initial rate of polymerization have been reported previously[7].

Summary

Initiation of the polymerization of methyl methacrylate with the initiating system, *p*-toluenesulfinc acid-oxygen-dimethylaniline, has been investigated from the standpoint of chemical kinetics. The initial rate of polymerization of methyl methacrylate was linearly proportional to the square roots of the concentrations of each component of the initiating system, and methyl methacrylate. The polymerization initiating action of the initiating system is lost by changing the sulfinic acid to its anhydride or esters. The formation of a salt from the sulfinic acid and dimethylaniline was suggested as the first step of the initiation of the polymerization.

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