Polymerization of Methyl Methacrylate Initiated by a Combined Action of Di-p-tolylsulfonylhydroxylamine and Oxygen in Air

By Ryoichi UEHARA

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Di-*p*-tolylsulfonylhydroxylamine was first prepared by Koenigs[1] through the reaction of nitrous acid on *p*-toluenesulfinic acid:

$$2CH_3C_6H_4SO_2H + HNO_2 = H_2O + (CH_3C_6H_4SO_2)_2NOH$$

It has been found by the present author that di-*p*-tolylsulfonylhydroxylamine initiates the polymerization of methyl methacrylate by a combined action with oxygen in air, and this effect is accelerated by the addition of dimethylaniline[2]. Although some compounds related to di-*p*-tolylsulfonylhydroxylamine such as *p*-toluenesulfinic acid[3] and di-*p*-tolylsulfonylmethylamine[4] are noted as components of the initiating system for the polymerization of methyl methacrylate, nothing has been reported up to the present about the effect of di-*p*-tolylsulfonylhydroxylamine for the polymerization.

In the present paper, experimental results concerning the polymerization of methyl methacrylate intiated by the combined action of di-*p*-tolylsulfonylhydroxylamine and oxygen in air, with or without dimethylaniline, are given.

Fig. 1 shows the per cent conversion versus time of the bulk polymerization of methyl methacrylate in air. The polymerization proceeded at a moderate rate by means of 1.86×10^{-2} mol./l. of di-*p*-tolylsulfonylhydroxylamine (DTSH) alone. By the addition of 2.0×10^{-2} mol./l. of dimethylaniline (DMA) the polymerization proceeded fairly rapidly. 3.1×10^{-2} mol./l. of hydroquinone (HQ) retarded the polymerization initiated with 1.86×10^{-2} mol./l. of di-*p*-tolylsulfonylhydroxylamine, i.e., the rate of polymerization was not affected until the conversion reached approximately 5%, but after that the reaction hardly proceeded at all. In the atmosphere of nitrogen, the polymerization occured with difficulty by means of di-*p*-tolylsulfonylhydroxylamine and dimethylaniline. So, it is evident that oxygen is necessary for the initiation of the polymerization.

Copolymerization of methyl methacrylate

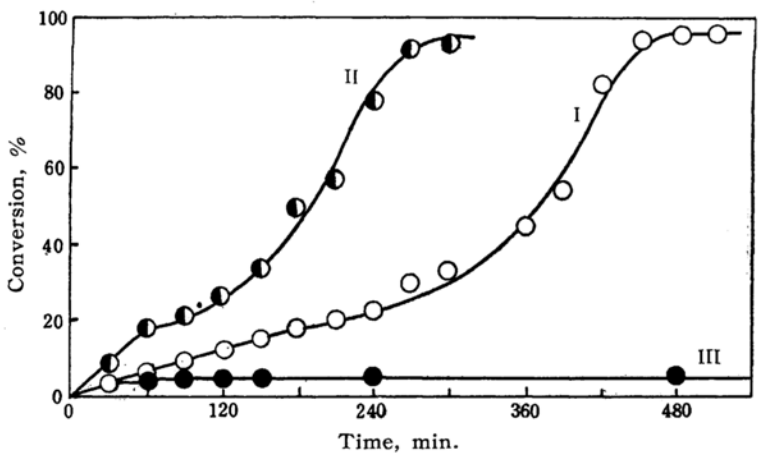

Fig. 1. Per cent conversion versus time of bulk polymerization of methyl methacrylate at 70°C in air. I. DTSH 1.86×10^{-2} mol./l., II. DTSH 1.86×10^{-2} and DMA 2.0×10^{-2} mol./l., III. DTSH 1.86×10^{-2} and HQ 3.1×10^{-2} mol./l.

1) P. Koenigs, *Ber.*, **11**, 616 (1878).
2) R. Uehara, *J. Japan. Chem.* (*Kagaku-no-Ryoiki*), **7**, 291 (1953).
3) For example, H. Bredereck et al., *Ber.*, **89**, 731 (1956).
4) H. Bredereck et. al., *Makromol. Chem.*, **12**, 100 (1954).

and styrene was examined by the initiating system of di-*p*-tolylsulfonylhydroxylamine, oxygen and dimethylaniline. An equimolar mixture of methyl methacrylate and styrene containing 1.7×10^{-2} mol./l. each of di-*p*-tolylsulfonylhydroxylamine and dimethylaniline was heated at 70°C in air. After 2 hr., 9.1% by weight of the copolymer was obtained. Analysis of the copolymer shows that a copolymer in the molar ratio of 1 : 1 has been formed; i. e., found: C, 76.31 and H, 8.03%, calculated for the copolymer in the molar ratio of 1 : 1, $(C_{13}H_{16}O_2)_n$: C, 76.47 and H, 7.84%, respectively. This fact indicates that the polymerization proceeds through a free radical mechanism[5].

Average degrees of polymerization of polymethyl methacrylate formed by means of the initiating system are shown in Table I. In a course of the bulk polymerization by means of 1.86×10^{-2} mol./l. of di-*p*-tolylsulfonylhydroxylamine, the average degrees were approximately constant until the conversion reached 20% (after about 240 min.), while, after that period, they increased gradually corresponding to the extent of the polymerization. Fig. 2 shows the correlation of the average degree of polymerization of polymethyl methacrylate formed during the course of the first 30 min. of the polymerization with the initial concentration of di-*p*-tolylsulfonylhydroxylamine. It is seen that the reciprocal of the average degree of polymerization is linearly dependent upon the square root of the intial concentration of di-*p*-tolylsulfonylhydroxylamine. This fact also indicates the radical character of the polymerization.

TABLE I. AVERAGE DEGREE OF POLYMERIZATION, $\bar{P}$, OF POLYMETHYL METHACRYLATE FORMED BY MEANS OF DTSH AT 70°C IN AIR

DTSH (mol./l.×10²)	Time (min.)	Conversion (%)	$\bar{P}$
1.86	30	3.1	2280
〃	60	6.1	2540
〃	90	9.8	2570
〃	120	13.0	2580
〃	240	23.1	2880
〃	300	33.5	3820
〃	360	45.1	3910
〃	420	79.6	3940
〃	480	95.8	3990
〃*	60	16.2	1310
〃*	120	26.8	1560
〃*	180	49.5	1830
3.13	30	4.5	1760
4.50	〃	4.8	1490
5.12	〃	5.0	1310
6.30	〃	6.0	1280
7.19	〃	6.3	1110
8.20	〃	6.5	1080
9.00	〃	6.6	940

* With an equimolar amount of dimethylaniline.

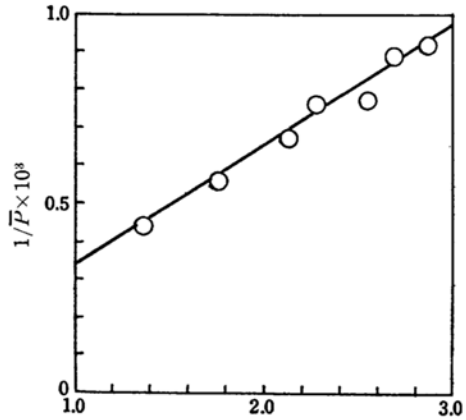

Fig. 2. Correlation of the average degree of polymerization of polymethyl methacrylate with the initial concentration of DTSH at 70°C in air.

The relation between the initial rate of polymerization and concentrations of di-*p*-tolylsulfonylhydroxylamine and dimethylaniline has been investigated. The correlation of the initial rate of polymerization in air with the concentration of di-*p*-tolylsulfonylhydroxylamine is shown in Fig. 3 by line I. The initial rate of polymerization is linearly proportional to the square root of the initial concentration of di-*p*-tolylsulfonylhydroxylamine. When the concentration of di-*p*-tolylsulfonylhydroxylamine was kept constant and various amounts of dimethylaniline were added, the initial rate of polymerization was linearly dependent upon the square root of the initial concentration of dimethylaniline. Line II in Fig. 3 shows this relation in a case when 1.2×10^{-2} mol./l. of di-*p*-tolylsulfonylhydroxylamine was used. It is evident that the so-called square root dependence which is typically seen in the radical polymerization of vinyl monomers holds between the initial rate of polymerization and the initial concentration of both di-*p*-tolylsulfonylhydroxylamine and dimethylaniline. This fact can be regarded as supporting the

5) C. Walling, F. R. Briggs, W. Cummings and F. R. Mayo, *J. Am. Chem. Soc.*, 72, 48 (1950).

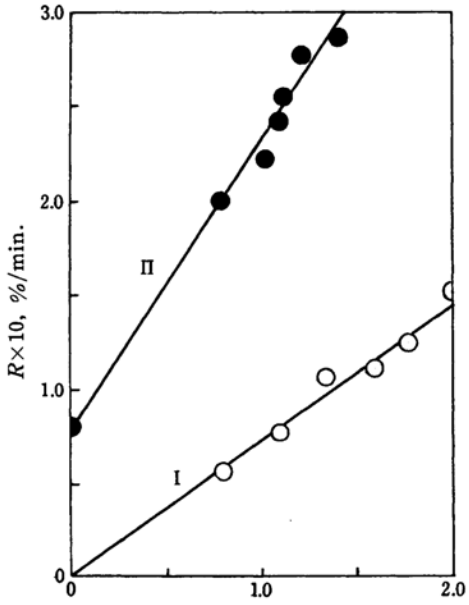

Fig. 3. Correlations of the initial rate of polymerization with concentrations of DTSH and DMA at 70°C in air.

radical character of the polymerization reaction.

The accelerating effect of dimethylanilne is significantly influenced by groups substituted in its para position. The per cent conversions of the polymerization after 1 hr. at 70°C accelerated by using various amines are compared in Table II. Electron-donating groups such as methyl and methoxy promote, and electron-withdrawing groups such as chloro and bromo reduce the efficiency of the initiating system. By strongly electron-withdrawing groups such as nitro and nitroso, the polymerization-initiating action of the initiating system is completely lost.

TABLE II. EFFECTS OF *p*-SUBSTITUTED DIMETHYLANILINE ON THE EFFICIENCY OF THE INITIATING SYSTEM

Substituted group	% Conversion after 1 hr.
CH_3O	30.4
CH_3	23.5
H	16.0
Cl	8.1
Br	7.3
NO	0
NO_2	0

Di-*p*-tolylsulfonylhydroxylamine (1.86×10^{-2} mol./l.) and the amine (2.0×10^{-2} mol./l.) were used at 70°C in air.

From the above mentioned experimental results, it is evident that the polymerization of methyl methacrylate initiated by a combined action of di-*p*-tolylsulfonylhydroxylamine and oxygen, with or without dimethylaniline as an accelerator, proceeds through a free radical mechanism. Therefore, it is very probable that a radical to initiate the polymerization is produced from the initiating system, though the nature of the initiating reactions will be the subject of further investigations.

Experimental

Purification of methyl methacrylate, dimethylaniline, and hydroquinone have been reported in a previous paper by the present author[6]. Di-*p*-tolylsulfonylhydroxylamine was prepared from sodium *p*-toluenesulfinate, sodium nitrite, and hydrochloric acid at 0°C[1]. The crude product was washed with distilled water until no ions of chloride and heavy metals were detected in the washing to eliminate water soluble impurities, and recrystallized from benzene and methanol, m. p. 127°C, with decomposition.

Polymerizations were carried out in open test tubes which have been mentioned in a previous paper by the author[7]. Di-*p*-tolylsulfonylhydroxylamine and dimethylaniline were dissolved in methyl methacrylate cooled in an ice-salt bath. The solution (2 cc.) was placed in each of the tubes and heated in a thermostat bath with shaking. The procedures of the polymerization and determination of the initial rate of polymerization have been given previously[6]. The initial rate was expressed in unit of per cent per minute. The average degree of polymethyl methacrylate was estimated from its intrinsic viscosity in chloroform by using the equation of Sakurada[8].

Summary

The polymerization of methyl methacrylate is initiated by a combined action of di-*p*- tolylsulfonylhydroxylamine and oxygen. The polymerization is accelerated with dimethylaniline and retarded with hydroquinone. The initial rate of polymerization is linearly dependent upon the square roots of concentrations of di-*p*-tolylsulfonylhydroxylamine and dimethylaniline in air. The reciprocal of the average degree of polymerization of the

6) R. Uehara, This Bulletin, 31, 685 (1958).
7) R. Uehara, This Bulletin 32, 1079 (1959).
8) I. Sakurada, *Chem. High Polymers* (*Kobunshi Kagaku*), 2, 253 (1945).

polymethyl methacrylate formed by means of the present initiating system is proportional to the square root of the initial concentration of di-*p*-tolylsulfonylhydroxylamine. A copolymer (1 : 1) is obtained from an equimolar mixture of styrene and methyl methacrylate. These facts suggest that the polymerization is initiated by a radical produced from the initiating system.

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