SHORT COMMUNICATIONS

Polymerization of Methyl Methacrylate Initiated by a Combined Action of Di-p-tolyl Disulfoxide, Dimethylaniline and Oxygen in Air

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The effects of *p*-toluenesulfinic acid (TSA) upon polymerization of vinyl monomers have been noted by Hagger[1] and Bredereck[2]. In a previous paper by the present author[3], results of studies on the kinetics of the polymerization of methyl methacrylate (MMA) initiated by the system of TSA, dimethylaniline (DMA) and oxygen in air have been reported. The polymerization was initiated at room temperature by means of this system. TSA is not so stable even at room temperature, and by being left in air changes into *p*-toluenesulfonic acid (TSOA), di-*p*-tolyl disulfoxide (DTDS) and water through the following reaction[4]:

$$3CH_3C_6H_4SO_2H = CH_3C_6H_4SO_3H + (CH_3C_6H_4SO)_2 + H_2O$$

Owing to this deterioration, the activity of TSA as a component of the initiating system of the room-temperature polymerization of MMA is reduced gradually[5]. The present author has examined the effects of TSOA and DTDS upon the polymerization of MMA at various temperatures, and found that the polymerization was initiated by a combined action of DTDS, DMA and oxygen in air at above 60°C. TSOA could not initiate the polymerization in combination with DMA and oxygen. It has been found by the present author that several compounds related to TSA, e.g., *p*-tolyl methyl sulfone[6] and di-*p*-tolylsulfonylhydroxylamine[6], initiated the polymerization of MMA in combination with DMA and oxygen. DTDS is a new material which belongs to this group of compounds. In the present communication, some results of experiments are given. The nature of the effects of the polymerization-initiating system will be discussed in future.

In Table I, per cent conversions after 1 hr. at various temperatures are given (DTDS 2.34×10^{-2} mol./l. and DMA 2.58×10^{-2} mol./l. in air). For the initiation of the polymerization, the coexistence of the three components of the initiating system was necessary. Namely, in the cases when MMA was heated at 70°C with DTDS 2.51×10^{-2} mol./l. and DMA 2.52×10^{-2} mol./l. in the atmosphere of nitrogen or with DTDS 2.48×10^{-2} mol./l. alone in air, no polymerization took place, and when DMA 2.52×10^{-2} mol./l. alone was employed in air, only trace of polymethyl methacrylate (PMMA) was obtained after 3 hr. at 70°C. In Fig. 1, per cent conversions of the bulk polymerization of MMA at 70°C in air (DTDS 2.16×10^{-2} mol./l. and DMA 2.20×10^{-2} mol./l.) are plotted against the time of polymerization. A time conversion curve of the polymerization by means of benzoyl peroxide (BPO, 2.0×10^{-2} mol./l.) in nitrogen is shown by the dotted line in the figure. From the beginning of

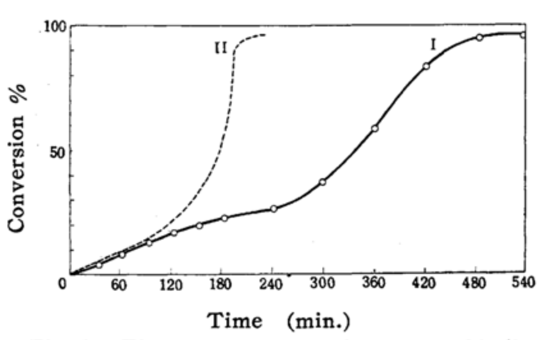

Fig. 1. Time versus conversion curve of bulk polymerization of MMA at 70°C in air. I, DTDS 2.16×10^{-2} mol./l. and DMA 2.20×10^{-2} mol./l. II, BPO 2.0×10^{-2} mol./l. (under nitrogen).

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[1] O. Hagger, *Helv. Chim. Acta*, **31**, 1629 (1948).
[2] H. Bredereck et al., *Ber.*, **89**, 731 (1956).
[3] R. Uehara, Submitted to this Bulletin for publication., **32**, No. 9 or 10 (1959).
[4] C. Pauly and R. Otto, *Ber.*, **10**, 2128 (1877).
[5] C. E. Schildknecht, "Polymer Processes", Interscience, New York, (1956), p. 61.
[6] R. Uehara, Submitted to this Bulletin for publication, **32**, No. 9 or 10 (1959).

the polymerization until the conversion reached to 15%, the rate of polymerization initiated by the system of DTDS, DMA and oxygen was only slightly smaller than that of the polymerization by BPO. After this period, the polymerization initiated by the system of DTDS, DMA and oxygen proceeded at a moderate rate and somewhat acceleratively in the final period, while the polymerization by BPO run quite acceleratively and almost explosively at the final stage. In the polymerization initiated by the system of DTDS, DMA and oxygen, the conversion reached to 90% after 450 min. from the beginning of the reaction, but in case of the polymerization by BPO the conversion reached to the same extent after 190 min. In the bulk polymerization of MMA, gelation of the reacting system occurs when the conversion reaches to 20～30%. So, it is very probable that the polymerization initiated by the system of DTDS, DMA and oxygen does not proceed so acceleratively owing to the fact that the rate of diffusion of oxygen from air into the reacting system is reduced due to the gelation. On the other hand, DTDS alone did not affect upon the polymerization of MMA initiated by BPO under nitrogen, i. e., per cent conversion after 1 hr. and the degree of polymerization (DP) of PMMA were not changed by the addition of DTDS (Table I).

TABLE I. RESULTS OF THE BULK POLYMERIZATION OF METHYL METHACRYLATE

Atmosphere	Initiator (mol./l. $\times 10^2$)	°C	% Conversion after 1 hr.	DP
Air	DTDS (2.34) DMA (2.58)	40	0	
Air	DTDS (2.34) DMA (2.58)	50	1.5	
Air	DTDS (2.34) DMA (2.58)	60	3.7	4900
Air	DTDS (2.34) DMA (2.58)	70	8.7	2850
Air	DTDS (2.34) DMA (2.58)	80	17.4	1390
Air	DTDS (2.48)	70	0*	
Air	DMA (2.52)	70	trace*	
Nitrogen	DTDS (2.51) DMA (2.52)	70	0*	
Nitrogen	BPO (2.0)	70	10.3	3900
Nitrogen	BPO (2.0) DTDS (2.51)	70	10.9	3780

* After 3 hr.

Experimental — DTDS was prepared by heating TSA (20 g.) with water (60 cc.) in a boiling water bath. TSA was dissolved and then an oily material separated gradually. After 5 hr., the oil was washed with 5% aqueous sodium hydroxide and pure water, and cooled. Crude DTDS was recrystallized three times from a mixture of methanol and ether (1 : 1 by volume), and pure DTDS (6.5g.) was obtained, m.p. 78.5°C. Purification of MMA and DMA have been mentioned in a previous paper⁷⁾. The polymerization in air and under nitrogen were carried out respectively in open test tubes³⁾ and sealed tubes⁷⁾. DTDS and DMA were dissolved in MMA cooled in an ice-salt bath. The solution (5 cc.) was placed in a test tube and heated with shaking. Per cent conversion of the polymerization was estimated from the weight of PMMA. Details of the procedures have been given previously⁷⁾. DP of PMMA was calculated from the intrinsic viscosity in chloroform by using the equation of Sakurada⁸⁾.

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

8) I. Sakurada, *Chem. High Polymers* (*Kobunshi Kagaku*), 2, 253 (1945).