Polymerization of Methyl Methacrylate Initiated by a Combined Action of p-Tolyl Methyl Sulfone, Dimethylaniline and Oxygen in Air

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p-Tolyl methyl sulfone first reported by Knoevenagel⑴ is a compound prepared from sodium *p*-toluenesulfinate and methyl iodide, and an isomer of methyl *p*-toluenesulfinate. The effect of *p*-toluenesulfinic acid for the polymerization of methyl methacrylate has been noted by several authors⑵ and that of *p*-tolyl hydroxymethyl sulfone has been reported by Bredereck⑶, but about the effect of *p*-tolyl methyl sulfone nothing has been reported up to the present.

It has been found by the present author that the polymerization of methyl methacrylate was initiated by a combined action of *p*-tolyl methyl sulfone, dimethylaniline and oxygen in air. The fact that the system of *p*-toluenesulfinic acid, dimethylaniline and oxygen lost the ability to initiate the polymerization by changing the sulfinic acid to its esters has been reported in a previous paper by the present author⑷. So, it appears of interest that the isomer of the methyl ester initiates the polymerization in combination with dimethylaniline and oxygen. In the present paper, some experimental results concerning the relation between the per cent conversion of the polymerization and the concentrations of the initiating reagents, and effects of various amines on the initiating ability of the system are given. In Fig. 1, per cent conversions versus time of the bulk polymerization of methyl methacrylate in air at 70°C are shown. The concentrations of *p*-tolyl methyl sulfone (TMS) and dimethylaniline (DMA) were respectively 3.01×10^{-2} and 2.98×10^{-2} mol./l. In the case when *p*-tolyl methyl sulfone alone was used

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1) E. Knoevenagel, *Ber.*, **21**, 1349 (1888).
2) For example, H. Bredreck et. al., ibid., **89**, 731 (1956).
3) H. Bredereck et. al., *Makromol. Chem.*, **12**, 100 (1954).
4) R. Uehara, This Bulletin, **32**, 1079 (1959).

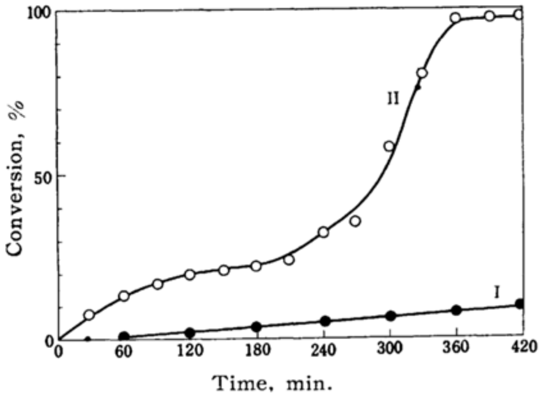

Fig. 1. Conversion versus time relationships of the bulk polymerization at 70°C in air.
([TMS]$=3.01\times10^{-2}$, [DMA]$=2.98\times10^{-2}$ mol./l., I. TMS alone, II. TMS and DMA).

under air, an induction period appeared and then the polymerization took place at a very small rate. When dimethylaniline was used alone, trace of polymethyl methacrylate was formed after 3 hr. By means of *p*-tolyl methyl sulfone and dimethylaniline, the polymerization proceeded at a fairly rapid rate under air. In that case, the time-conversion curve shows an *S*-form which appears usually in the bulk polymerization of methyl methacrylate. The polymerization was completely inhibited by the addition of 0.10×10^{-2} mol./l. of hydroquinone. Under nitrogen the polymerization did not take place.

When equimolar mixture of *p*-tolyl methyl sulfone and dimethylaniline were used in air, per cent conversion after 1 hr. at 60°C were linearly proportional to the initial concentration of *p*-tolyl methyl sulfone or dimethylaniline. At 70°C, the linear dependence of the per cent conversion upon the concentration of *p*-tolyl methyl sulfone can be seen in case the initial concentration of *p*-tolyl methyl sulfone is less than 3.0×10^{-2} mol./l. Those correlations are shown in Fig. 2.

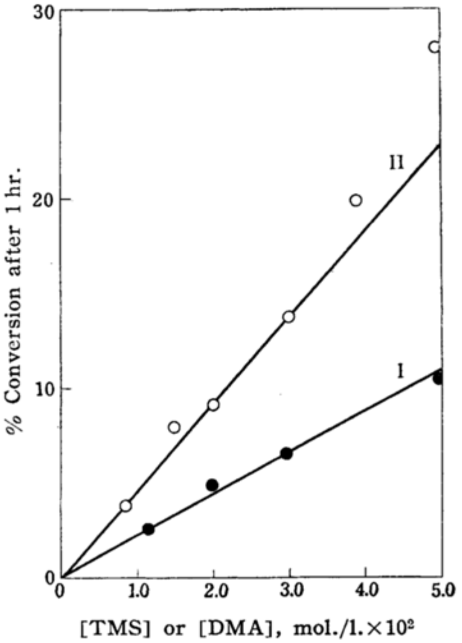

Fig. 2. Correlations of % conversion after 1 hr. with concentration of the initiating reagent.
(I, at 60°C, II, at 70°C)

TABLE I. THE PER CENT CONVERSIONS AFTER 1 HR. AT 70°C IN AIR

Amine*	% Conversion
Dimethylaniline	14.5
N,N-Dimethyl-*p*-anisidine	31.3
N,N-Dimethyl-*p*-toluidine	26.9
N,N-Dimethyl-*p*-chloroaniline	6.03
N,N-Dimethyl-*p*-bromoaniline	5.86
N,N-Dimethyl-*p*-nitrosoaniline	0
N,N-Dimethyl-*p*-nitroaniline	0
N,N-Dimethyl-*p*-phenylazoaniline	0
Aniline	0
N-Methylaniline	0
Diphenylamine	Trace
Quinoline	0
Pyridine	0
Triethylamine	0

* 3.0×10^{-2} mol./l. of each amine and *p*-tolyl methyl sulfone were used.

In Table I, per cent conversions after 1 hr. (at 70°C) in the bulk polymerization of methyl methacrylate initiated by equimolar mixtures of *p*-tolyl methyl sulfone and various amines are shown. The mixtures containing heterocyclic, aliphatic, primary and secondary amines were not responsible for the initiation of the polymerization. Only aromatic tertiary amines were effective as the component of the polymerization-initiating system. *p*-Substitution in dimethylaniline influenced significantly its efficiency as a component of the initiating system. Electron-donating groups such as methyl and methoxy increased the yield of the polymer, while electron-withdrawing groups such as chlorine and bromine reduced the yield. When a strongly electron-withdrawing group such as nitro, nitroso, or phenylazo was present in the para position of dimethylaniline, no polymerization occurred even after 3 hr. The nature of the effects of dimethylaniline will be discussed in future.

Copolymerization of styrene and methyl methacrylate with this initiating system has been examined. To an equimolar mixture of styrene and methyl methacrylate 3.0×10^{-2} mol./l. of each of *p*-tolyl methyl sulfone and dimethylaniline were added, and the polymerization was carried out in air at 70°C for 2 hr. A portion (5.7% by weight) of the copolymer was obtained. *Analysis* found: C, 76.09 and H, 8.13%, 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. It was evident that a copolymer containing styrene and methyl methacrylate in a molar ratio of approximately 1 : 1 was obtained.

Experimental results mentioned above suggest that the polymerization is initiated by a combined action of *p*-tolyl methyl sulfone, dimethylaniline, and oxygen. The facts that the polymerization is inhibited with hydroquinone, and a copolymer in a molar ratio of 1 : 1 is formed from styrene and methyl methacrylate indicate that the polymerization proceeds through a free radical mechanism[5]. So, it is probable that radicals to initiate the polymerization are produced from *p*-tolyl methyl sulfone, dimethylaniline and oxygen, though the details of the reaction forming the radical are not made clear at present.

Experimental

p-Tolyl methyl sulfone was prepared from sodium *p*-toluenesulfinate and methyl iodide in aqueous methanol[1]. The crude product was carefully washed with 10% aqueous solution of sodium carbonate and distilled water, then recrystallized from ethanol, m. p. 87°C. Purification of methyl methacrylate, dimethylaniline, and hydroquinone were given in a previous paper[6]. Styrene was washed with 10% aqueous solution of sodium hydroxide and pure water, dried over anhydrous sodium sulfate and carefully distilled under a reduced pressure in nitrogen through a fractionating column, b. p. 46°C/20 mmHg. Amines were distilled under reduced pressure of 3 mmHg, or recrystallized from ethanol.

Polymerization was carried out in open test tubes as mentioned in the preceding paper[4]. The procedures of the polymerization and the determination of per cent conversions have been reported in a previous paper[6].

Summary

The polymerization of methyl methacrylate is initiated by a combined action of *p*-tolyl methyl sulfone, dimethylaniline, and oxygen. The efficiency of the initiating system is increased by using dimethylanilines substituted with electron-donating groups in the para position. The fact that the 1 : 1 copolymer of styrene and methyl methacrylate is formed by means of this initiating system suggests the formation of radicals to initiate the polymerization from the initiating system.

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

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