Polymerization of Methyl Methacrylate Initiated by a Combined Action of p-Tolylsulfonylacetic Acid and Dimethylaniline

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It has been first reported by Lal et al.1), that the polymerization of methyl methacrylate is initiated by mixtures of dimethylaniline and various carboxylic acids. In a previous paper by the present author2), results of studies on the kinetics of the polymerization of methyl methacrylate initiated by a combined action of trichloroacetic acid and dimethylaniline have been reported, and a bimolecular reaction between these two compounds has been suggested as the initial reaction of the polymerization. In the report of Lal, per-cent-conversions after 1 hr. in the bulk polymerization of methyl methacrylate at 58.6°C by using nine carboxylic acids have been given briefly, and six acids, i. e., mono-, di- and trichloroacetic, mercaptoacetic, phenoxyacetic and 1, 4-dichlorobenzoic acids, were found to be effective.

The present author has found that *p*-tolylsulfonylacetic acid, which has been prepared by Gabriel3) from sodium *p*-toluenesulfinate and monochloroacetic acid, is also effective as a component of the polymerization-initiating system.

$$CH_3C_6H_4SO_2Na + ClCH_2COOH$$
$$= CH_3C_6H_4SO_2CH_2COOH + NaCl$$

In the present paper, per-cent-conversion of the bulk polymerization of methyl methacrylate initiated by the system of *p*-tolylsulfonylacetic acid and dimethylaniline is given, and the effects of *p*-substituted groups in dimethylaniline upon the polymerization-initiating efficiencies of the two systems, trichloroacetic acid-dimethylaniline and *p*-tolylsulfonylacetic acid-dimethylaniline, are compared.

The polymerization was carried out in the atmosphere of nitrogen. In Table I, per-cent-conversion of the bulk polymerization at 60°C is given. Each of *p*-tolylsulfonylacetic acid, and dimethylaniline alone was not responsible for the initiation of the polymerization. In Fig. 1, per-cent-conversion after 1 hr., in the bulk polymerization, by means of equimolar amounts of *p*-tolylsulfonylacetic acid and dimethylaniline at temperatures of 51, 60 and 70°C are plotted against the concentration of the acid. It is observed that the per-cent-conversion after 1 hr. is linearly dependent upon the concentration of the acid. This fact indicates that, in this polymerization, the linear dependence of the rate of polymerization upon the initial concentration of *p*-tolylsulfonylacetic acid or dimethylaniline holds, as in the case of the

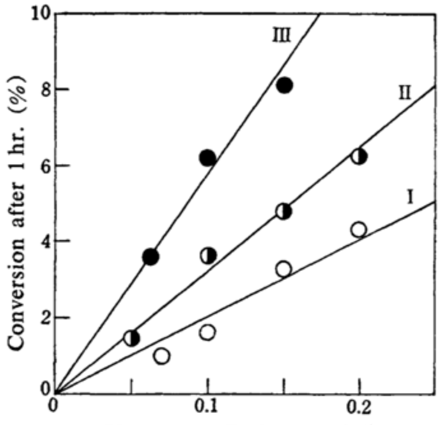

Fig. 1. Correlations of per-cent-conversion after 1 hr. with the concentration of *p*-tolyl-sulfonylacetic acid or dimethyl aniline.
I at 51°C, II at 60°C, III at 70°C

TABLE I. PER-CENT-CONVERSION (C) AND AVERAGE DEGREE OF POLYMERIZATION (DP) IN THE BULK POLYMERIZATION OF METHYL METHACRYLATE AT 60°C BY MEANS OF *p*-TOLYLSULFONYLACETIC ACID (TSAA) AND DIMETHYLANILINE (DMA)

mol./l.		Time, hr.	C, %	DP
TSAA	DMA			
0.15	0.15	1	4.8	
〃	〃	2	10.9	2120
〃	〃	3	15.3	2470
〃	〃	4	21.0	2500
〃	〃	5	27.8	
〃	〃	6	33.6	3900
〃	〃	10	97.3	
0.36	0	1	0	
〃	0	8	trace	
0	0.18	1	0	
0	0.30	10	0	

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1) J. Lal et al., *J, Polymer Sci.*, **24**, 81 (1957).
2) R. Uehara, This Bulletin., 31, 685 (1958).
3) S. Gabriel, *Ber.*, **14**, 834 (1881).

polymerization initiated by equimolar amounts of trichloroacetic acid and dimethylaniline[2], because per-cent-conversion after 1 hr., can be considered to be proportional to the initial rate of polymerization.

p-Substituted groups in dimethylaniline significantly affect the polymerization-initiating efficiencies of the two systems, *p*-tolylsulfonylacetic acid-dimethylaniline and trichloroacetic acid-dimethylaniline. Table II shows per-cent-conversions after 1 hr. by using various dimethylanilines in bulk polymerizations of methyl methacrylate, in which *p*-tolylsulfonylacetic and trichloroacetic acids were used respectively. Electron-donating groups such as methyl and methoxyl promote, and electron-withdrawing groups such as chloro, bromo and nitroso reduce the efficiencies of the polymerization-initiating systems. In Table II, C/C_0 are also shown, where C_0 and C are per-cent-conversions in the polymerizations by using dimethylaniline and *p*-substituted dimethylaniline, respectively.

TABLE II. RELATIVE EFFICIENCY OF *p*-SUBSTITUTED DIMETHYLANILINE IN THE POLYMERIZATIONS INITIATED RESPECTIVELY BY SYSTEMS, *p*-TOLYLSULFONYLACETIC ACID-DIMETHYLANILINE AND TRICHLOROACETIC ACID-DIMETHYLANILINE

Substituent	% Conversion* (TSAA and DMA)	C/C_0	% Conversion** (TCA and DMA)	C/C_0
OCH_3	11.3	2.35	11.4	1.752
CH_3	8.7	1.81	8.9	1.37
H	4.8	1.0	6.5	1.0
Cl	2.9	0.604	4.2	0.646
Br	2.4	0.500	4.1	0.630
NO	0	0	0	0

* 0.15 mol./l. of each of TSAA and DMA were used at 60°C.

** 0.20 mol./l. of each of TCA and DMA were used at 25°C.

For each of the substituted groups, the value of C/C_0 in the polymerization by using *p*-tolylsulfonylacetic acid is substantially similar to that in the polymerization, in which trichloroacetic acid was employed, i. e., the relative efficiency of *p*-substituted dimethylaniline is substantially the same in the initiating systems. When the logarithms of C/C_0 are plotted against σ (substitutent constant of Hammett) of each substituted groups, good straight lines are obtained as are shown in Fig. 2. It is evident that Hammett's rule holds in the two cases.

As has been mentioned above, the dependence of the initial rate of polymerization upon the concentration of *p*-tolylsulfonylacetic acid (or dimethylaniline) and the relative efficiency of the substituted dimethylaniline in the polymerization of methyl methacrylate initiated by the system of *p*-tolylsulfonylacetic acid and dimethylaniline are quite similar to those in the polymerization initiated by a combined action of trichloroacetic acid and dimethylaniline. Therefore, it is conceivable, that the polymerization initiated by *p*-tolylsulfonylacetic acid and dimethylaniline proceeds through the same mechanism as that which has been postulated previously for the polymerization initiated by trichloroacetic acid and dimethylaniline[2].

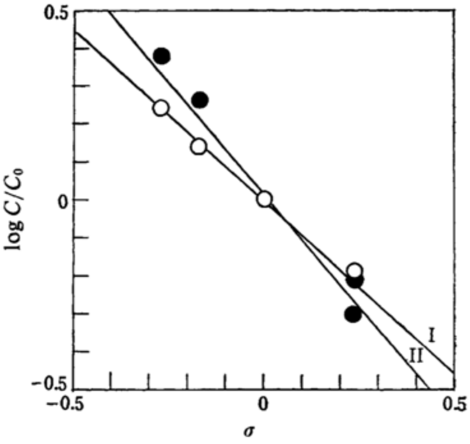

Fig. 2. Correlations of $\log C/C_0$ with σ.
I for TCA and DMA (○)
II for TSAA and DMA (●)

Experimental

The polymerization and the purification of methyl methacrylate were carried out as mentioned previously[2]. *p*-Tolylsulfonylacetic acid was prepared by the following procedures; sodium *p*-toluenesulfinate (43 g.) and monochloroacetic acid (19 g.) were mixed with methanol (100 cc.), and sodium hydroxide (8 g.) which was dissolved in water (100 cc.) was added. The mixture was refluxed for 4 hr., and then methanol was distilled off. By treating the residue of the distillation with 30% aqueous hydrochloric acid (50 cc.), an oily material separated. The oil was cooled in an ice salt-bath until it changed into crystalline solids. They were washed with aqueous methanol (1 : 1 by volume) and recrystallized from pure methanol, giving pure *p*-tolylsulfonylacetic acid (17.5 g.), m. p. 86°C. Dimethylaniline and *p*-substituted dimethylaniline were distilled under reduced pressure in the atmosphere of nitrogen or recrystallized from methanol: dimethylaniline b. p. 56°C/5 mmHg, $-CH_3$ b. p. 73.5°C/5 mmHg, $-Cl$ b. p. 86°C/5 mmHg, $-Br$ b. p. 101°C/5 mmHg, $-OCH_3$ m. p. 48.5°C, and $-NO$ m. p. 85°C.

Summary

It has been found that the polymerization of methyl methacrylate is initiated by the system of *p*-tolylsulfonylacetic acid and dimethylaniline.

In the polymerization initiated by equimolar amounts of *p*-tolylsulfonylacetic acid and dimethylaniline, the initial rate of polymerization is linearly dependent upon the initial concentration of the acid (or dimethylaniline). Hammett's rule holds for the relative efficiency of *p*-substituted dimethylaniline as the component of the polymerization-initiating system. These relationships are quite similar to those which are observed in the polymerization of methyl methacrylate, initiated by trichloroacetic acid and dimethylaniline. It is conceivable that the two polymerization reactions proceed through the same mechanism.

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