BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 567—569 (1970)

Initiation of Vinyl Polymerization with Tertiary Amines/Alkylating Agents

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(Received August 18, 1969)

It has been reported that the binary system of such tertiary amines as dimethylaniline and such organic halides as benzyl chloride initiates the radical polymerization of methyl methacrylate.[1,2] In this case, a quaternary salt is formed, and then it decomposes at the N^+–C bond into radicals which react with the monomer to initiate the polymerization.[1,3]

On the other hand, several workers[4-6] have found that vinyl pyridine is polymerized in the presence of some alkylating agents, such as methyl iodide and dimethyl sulfate, through a quaternary pyridinium salt. The present paper will describe

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[1] T. Fueno, H. Okamoto, T. Tsuruta and J. Furukawa, *J. Polym. Sci.*, **36**, 407 (1959).

[2] T. Otsu, S. Aoki and K. Itakura, *ibid.*, *Part A-1*, in press.

[3] T. Otsu, T. Sato and M. Ko, *ibid.*, in press.

[4] V. A. Kabanov, K. V. Aliev and V. A. Kargin, *Vysokomol. Soedin.*, **A**, **10**, 1618 (1968).

[5] S. Iwatsuki, T. Kokubo, K. Motomura and Y. Yamashita, *Makromol. Chem.*, **120**, 154 (1968).

[6] T. Otsu, M. Ko and T. Sato, *J. Polym. Sci.*, *Part A-1*, in press.

Table 1. Polymerizations of some vinyl monomers with DMA/alkylating agents at 60°C: [DMA] = 0.2 mol/l, [DMS] = 0.2 mol/l, [MTS] = 0.2 mol/l, [Monomer]/[Solvent] = 6/4 in volume

Alkylating Agent	Solvent	MMA		St		VAc	
		Time hr	Yield %	Time hr	Yield %	Time hr	Yield %
DMS	C_6H_6	7	0.9	30	2.1	—	—
DMS	C_2H_5OH	7	12.8	30	1.6	20	0.4
MTS	C_6H_6	7	5.0	30	3.7	—	—
MTS	C_2H_5OH	7	11.5	30	6.1	20	3.0

the results of the polymerization of vinyl monomers with the binary system and the quaternary salt of several dialkylanilines, especially dimethylaniline (DMA), and dimethyl sulfate (DMS) or methyl *p*-toluenesulfonate (MTS).

Experimental

The tertiary amines and vinyl monomers were purified in the usual manner from the reagent-grade materials. The commercial DMS and MTS were distilled prior to use.

The quaternary salts of DMA with DMS and MTS were prepared by reacting an equimolar mixture of the two materials in water, followed by recrystallization from water: mp 126 and 167—168°C respectively.

Polymerizations were carried out in a sealed tube in the absence of light with shaking at 60°C.

Results and Discussion

Table 1 shows the results of the polymerizations of methyl methacrylate (MMA), styrene (St), and vinyl acetate (VAc) with the binary initiator system of DMA and DMS or MTS at 60°C.

From Table 1, these binary systems may be seen to have been effective as the initiator of the MMA polymerization in the presence of ethanol, but they showed rather weak activity for the St and VAc ploymerizations. A similar tendency was found in the polymerization with the DMA-benzyl chloride system.$^{1)}$ From Table 1, these binary systems may be seen to show a lower activity in benzene than in ethanol, for the quaternary salts, which were formed concurrently, were insoluble in benzene and were precipitated in the polymerizing mixture.

Table 2. Polymerization of MMA with quarternary salts of DMA-DMS and of DMS-TMS at 60°C for 22 hr

Quaternary salts	Solvent	Yield %
DMA-DMS	none	1.1
DMA-DMS	C_2H_5OH**	2.3
DMA-MTS	none	1.5
DMA-MTS	C_2H_5OH**	2.1

* The concentration was kept at 2×10^{-2} mol/l.

** MMA (5 ml) and C_2H_5OH (5 ml) were used.

However, the quaternary salts of DMA with DMS and MTS showed very weak activity for the MMA polymerization in ethanol, as is shown in Table 2. This result might indicate that the initiating radical was produced from the unstable intermediate formed through the quaternary reaction.

Table 3 shows the effects of the tertiary amines on the MMA polymerization with these binary initiator systems. From this table, it can be seen

Table 3. Polymerization of MMA with a system of various amines and alkylating agents at 60°C*

Alkylating agent	Amine	Time hr	Yield %
DMS	$C_6H_5N(CH_3)_2$	5.0	15.1
MTS	$C_6H_5N(CH_3)_2$	5.0	13.3
DMS	$C_6H_5N(CH_3)(CH_2C_6H_5)$	5.0	6.9
MTS	$C_6H_5N(CH_3)(CH_2C_6H_5)$	5.0	5.9
DMS	$C_6H_5N(CH_2C_6H_5)_2$	5.0	4.2
MTS	$C_6H_5N(CH_2C_6H_5)_2$	5.0	3.8
DMS	$C_6H_5CH_2N(CH_3)_2$	8.3	2.6
MTS	$C_6H_5CH_2N(CH_3)_2$	8.3	1.1

* Polymerization conditions:
[Amine] = [Alkylating agent] = 0.2 mol/l
[MMA] = [C_2H_5OH] = 5 ml.

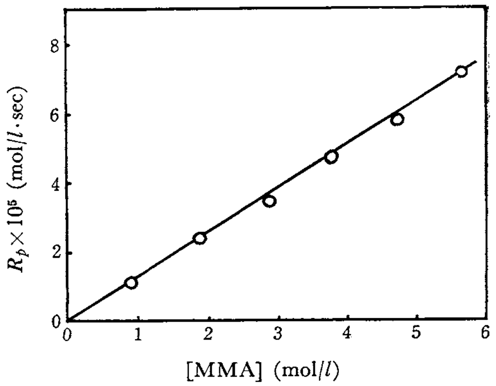

Fig. 1. Relationship between R_p and [MMA] in the polymerization of MMA with DMA/DMS at 60°C: [DMA] = [DMS] = 0.2 mol/l, [C_2H_5OH] = 6.87 mol/l in benzene.

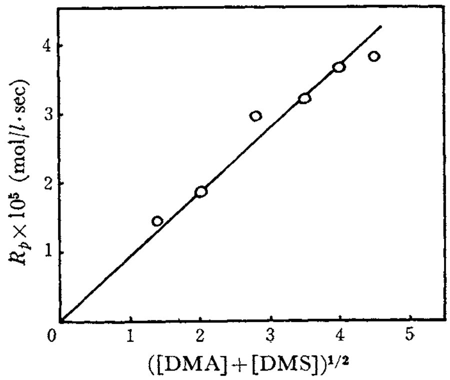

Fig. 2. Relationship between R_p and initiator concentration in the polymerization of MMA with DMA/DMS at 60°C: [MMA]=4.7 mol/l, $[C_2H_5OH]$=8.58 mol/l in benzene.

that, when the methyl group in DMA was replaced with the benzyl group, the initiator activity of the binary system decreased. The aliphatic tertiary amine, benzyldimethylamine, formed a very weak initiator system with DMS and MTS. This result was the same as that reported in a previous paper.[6]

The polymerization of MMA with an equimolar mixture of DMA and DMS was then investigated kinetically at 60°C. The effects of the monomer and the total initiator concentrations on the rate of polymerization (R_p) are shown in Figs. 1 and 2. From these figures, the following rate equation was obtained:

$$R_p = k([\mathrm{DMA}] + [\mathrm{DMA}])^{1/2}[\mathrm{MMA}]$$

A similar rate equation was observed with the binary system of DMA and MTS at 60°C. It was also found that the copolymers obtained from the copolymerization of an equimolar mixture of MMA and St with DMA-DMS and DMA-TMS contained 49.7 and 47.7 mol% of the St unit respectively; this finding agrees with those reported with azobisisobutyronitrile as the initiator. These findings might suggest that the polymerization proceeded *via* a radical mechanism.