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Polymerization of Methyl Methacrylate by Amide-Carbon Tetrachloride System

Kyoji KAERIYAMA

Research Institute for Polymers and Textiles, Sawatari, Kanagawa-ku, Yokohama

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Some systems consisting of amide and halide, dimethylaniline - benzyl chloride[1] and pyridine-carbon tetrachloride in liquid sulfur dioxide,[2] for example, are known to initiate the polymerization of vinyl monomers. It has been found that the amide-carbon tetrachloride system induces the polymerization of vinyl monomers.

The results of the polymerization of methyl methacrylate (MMA) in the presence of various components are shown in Table 1. It can be seen from Table 1 that the acetamide-carbon tetrachloride system initiates the polymerization of MMA. Other chlorides, such as *n*-butyl chloride and chloroform, can not take the place of carbon tetrachloride. Pyridine has little effect on polymerization. DPPH and benzoquinone inhibit the polymerization. This suggests that the polymerization proceeds according to a radical mechanism.

Polymerization was carried out in the presence of various amides. It can be seen from Table 2 that formamide, acetamide, and urea are active as initiators, but that dimethylated amide, dimethyl acetamide, dimethylformamide are inactive.

Table 3 summarizes the data on the polymerisation of several vinyl monomers. The initiator system is selective for monomers. It can initiate the polymerization of acryl ester and amide, but it can not polymerize styrene. This characteristic is

TABLE 1. POLYMERIZATION OF MMA

Acetamide (g)	Carbon tetrachloride (m*l*)	DMSO* (m*l*)	Other additives: Additive	Other additives: Amount	Conversion (%)
1.0	1.0	6.0			35.0
1.0	1.0	3.0	Pyridine	3.0 m*l*	32.8
	1.0	7.0			6.2
1.0		6.0	*n*-Butyl chloride	1.0 m*l*	6.2
1.0		6.0	Chloroform	1.0 m*l*	11.0
1.0		3.5	Pyridine	3.5 m*l*	3.1
1.0	1.0	6.0	DPPH**	0.50 g	0
1.0	1.0	6.0	Benzoquinone	0.50 g	1.5

MMA: 2.0 m*l*
Polymerization: at 60°C for 20 hr.
*DMSO=dimethyl sulfoxide
**DPPH=diphenyl picryl hydrazyl

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

[2] M. Matsuda and T. Hirayama, *ibid.*, **5**, 2769 (1967).

TABLE 2. EFFECT OF VARIOUS AMIDE

Amide		Carbon tetrachloride (m*l*)	Conversion (%)
Amide	Amount		
Formamide	0.72 m*l*	0.88	30.7
Acetamide	1.0 g	1.0	35.0
Urea	0.55 g	0.88	24.6
Dimethylformamide	1.0 m*l*	1.0	4.6
Dimethylacetamide	1.0 m*l*	1.0	7.1

DMSO: 6.0 m*l*; MMA: 2.0 m*l*
Polymerization: at 60°C for 20 hr

TABLE 3. POLYMERIZATION OF VARIOUS VINYL MONOMERS

Monomer	Acetamide (g)	Carbon tetrachloride (m*l*)	Conversion (%)
Methyl methacrylate	1.0	1.0	32.8
Acrylonitrile	0.805	1.32	16.7
Styrene	0.805	1.32	3.5
Methyl acrylate	0.805	1.32	61.2
Acrylamide*		0.92	64.3

Monomer: 2.0 m*l*
Solvent: 3.0 m*l* DMSO+3.0 m*l* pyridine
Polymerization: at 60°C for 20 hr
* 1.4 g acrylamide
Solvent: 2.5 m*l* DMSO+2.5 m*l* pyridine

similar to that of the dimethylaniline - benzyl chloride system.[1]

Figure 1 shows the conversion of the monomer as a function of the mole fraction of amide to carbon tetrachloride. In the case of acetamide, the maximum conversion is observed at the mole fraction of 0.667. In the case of malonamide, it is at the equimolar fraction. This implies that two amide groups and one carbon tetrachloride molecule participate in the initiation of the polymerization of MMA.

Grafting onto polyacryl amide, which had been polymerized by potassium persulfate as an initiator, was attempted. The polymerizing mixture, which consisted of 1.90 g of polyacryl amide, 14.0 m*l* of DMSO, 1.0 m*l* of carbon tetrachloride, and 5.0 m*l* of MMA, was maintained at 60°C for 20 hr. The conversion amounted to 27.7%, but polymethyl methacrylate was completely extracted from the product with acetone. No graft-copolymer was obtained by these means. It is clear that polymerization is not initiated by a radical which has been formed by the cleavage of a bond in the amide molecule.

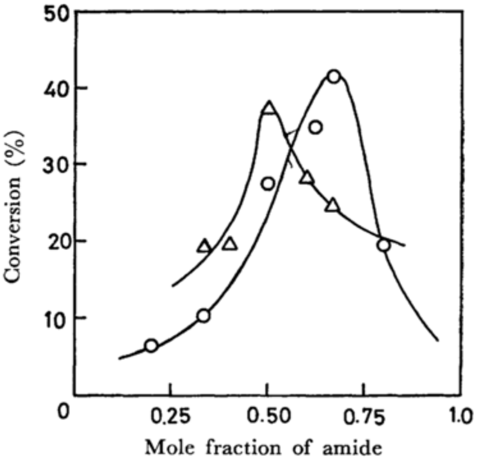

Fig. 1. Dependence of conversion on mole fraction of amide.
—○— Acetamide+CCl_4=27.3 mmol
DMSO: 6.0 m*l*; MMA: 2.0 m*l*
Polymerization: at 60°C for 20 hr
—△— Malonamide+CCl_4=18.2 mmol
DMSO: 14 m*l*; MMA: 4.0 m*l*
Polymerization: at 70°C for 20 hr

Experimental

Acetamide and acrylamide were recrystallized from a hot benzene solution. Malonamide was purified by pouring an aqueous solution into tetrahydrofuran. Urea was purified by pouring an aqueous solution into dioxane. Dimethyl sulfoxide, formamide, dimethylformamide, dimethylacetamide, and monomers were distilled under reduced pressure just prior to use. Polymerization was carried out in the dark according to the procedure described previously.[3]

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[3] K. Kaeriyama, This Bulletin, **42**, 1342 (1969).