

Vinyl Polymerization. 327.¹⁾ Determination of the Initiating Radical Species in Polymerization with a Dimethylmercury and Copper(II)-Ion System

Minoru IMOTO, Yoshiaki NAKAMURA, and Tatsuro OUCHI

Department of Applied Chemistry, Faculty of Engineering, Kansai University, Suita-shi, Osaka 564

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Dimethylmercury was found to give a methyl radical ($\cdot\text{CH}_3$) by the reaction with Cu(II)-ion in the presence of water. Generation of $\cdot\text{CH}_3$ was proved by scavenging with 1,3,5-triphenylverdazyl. Radical polymerization of methyl methacrylate and acrylonitrile was carried out with the system dimethylmercury/water/Cu(II)- or Fe(III)-ion.

Koton²⁾ found that dialkylmercury could initiated the polymerization of vinyl monomer and that the stronger the bond strength of C-Hg of dialkylmercury, the slower the rate of polymerization, *i.e.* dimethylmercury(DM-Hg) was the weakest promoter. Inoue³⁾ *et al.* and Razubaev⁴⁾ *et al.* carried out vinyl polymerization initiated by dibutylmercury or diisopropylmercury in the presence of various metallic salts, using appropriate organic solvents. However, the initiating mechanism remains unclarified.

We have carried out the polymerization using DM-Hg as an initiator in the presence of metallic salts, water being used instead of organic solvent. The initiating species for the polymerization was determined by reaction of DM-Hg with 1,3,5-triphenylverdazyl(TPV) and cupric chloride in benzene.

Experimental

Materials: All metallic salts, DM-Hg and methylmercury chloride (MC-Hg) of special grade were used without further purification. TPV was synthesized by Kuhn's method.⁵⁾ Methyl methacrylate(MMA), styrene(St), acrylonitrile(AN) and solvents were purified, according to the usual method.

Procedure: Polymerization was carried out in a 30 cm³ tube. Monomer, mercury compound, metallic salt and solvent were placed in the tube which was cooled to -78°C and thawed thrice with nitrogen and sealed under vacuum. After the tube had been shaken in a thermostat at 85°C for 6 hr, the contents of the tube were poured into a large

amount of methanol to precipitate the polymer.

Results and Discussion

Polymerization in the Presence of Metallic Salt and Water. The effects of metallic salt and water on the polymerization of MMA, AN and St are given in Table 1. It can be seen that cupric chloride and ferric chloride in groups 2 and 3 are active promoters for the polymerization of MMA and AN, the presence of water being necessary. NaCl, NiCl₂, SnCl₄, CrCl₃, HgCl₂ and the lower valency salts of iron and copper(group 4) can not be regarded as promoters in such small amount as 1.5×10^{-5} mol.

Effect of Amount of Water on Polymerization. In order to confirm the effect of water on the polymerization of MMA initiated with DM-Hg and Cu(II)-ion, polymerization was carried out, varying the amount of water and keeping the amounts of DM-Hg and MMA constant. The results are shown in Fig. 1. It was confirmed that the presence of water is indispensable.

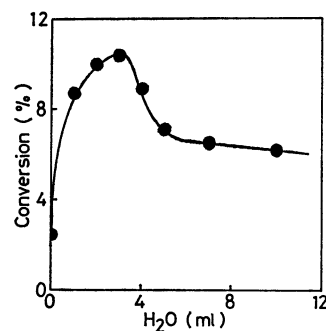


Fig. 1. Effect of the amount of water on the polymerization of MMA.

MMA 5 ml, DM-Hg 0.1 ml, Cu(II)-ion 1.5×10^{-5} mol; 85°C , 6 hr

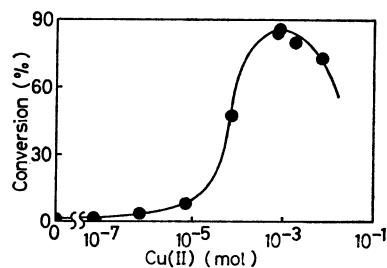


Fig. 2. Effect of the amount of Cu(II)-ion on the polymerization of MMA.

MMA 5 ml, DM-Hg 0.1 ml, H₂O 3 ml; 85°C , 6 hr

TABLE 1. POLYMERIZATION OF VINYL MONOMERS INITIATED WITH DM-Hg (metallic salt 1.5×10^{-5} mol, DM-Hg 0.1 ml, monomer 5 ml; 85°C , 6 hr)

Group	Salts	H ₂ O (ml)	Conversion (%)		
			MMA	AN	St
1a)	0	0	0.7	trace	4.6
	0	3	1.0	trace	4.2
2	CuCl ₂ ·2H ₂ O	0	2.4	1.2	5.3
	CuCl ₂ ·2H ₂ O	3	7.3	7.1	6.7
3	FeCl ₃ ·6H ₂ O	0	0	1.4	0.5
	FeCl ₃ ·6H ₂ O	3	11.3	7.6	7.1
4	NaCl	3	4.2	trace	4.4
	NiCl ₂ ·6H ₂ O	0	1.0	trace	4.8
	NiCl ₂ ·6H ₂ O	3	1.2	trace	4.8
	CuCl	3	1.9	trace	5.3
	FeCl ₂ ·nH ₂ O	3	0.6	trace	5.2
	SnCl ₄ ·nH ₂ O	3	4.5	trace	4.5
	CrCl ₃ ·6H ₂ O	3	0.4	0.2	5.0
	HgCl ₂	3	2.0	3.5	4.8

a) Blank experiments

