Vinyl Polymerization. 327. Determination of the Initiating Radical Species in Polymerization with a Dimethylmercury and Copper(II)-Ion System

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Dimethylmercury was found to give a methyl radical $(\cdot CH_3)$ by the reaction with Cu(II)-ion in the presence of water. Generation of $\cdot CH_3$ 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

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 3	0.7 1.0	trace trace	4.6 4.2
2		0 3	$\begin{array}{c} 2.4 \\ 7.3 \end{array}$	$\substack{1.2\\7.1}$	$\begin{array}{c} 5.3 \\ 6.7 \end{array}$
3	$\begin{cases} \mathrm{FeCl_3}\!\cdot\!6\mathrm{H_2O} \\ \mathrm{FeCl_3}\!\cdot\!6\mathrm{H_2O} \end{cases}$	0 3	$^0_{11.3}$	$\begin{array}{c} 1.4 \\ 7.6 \end{array}$	$\frac{0.5}{7.1}$
4	$ \begin{pmatrix} \text{NaCl} \\ \text{NiCl}_2 \cdot 6\text{H}_2\text{O} \\ \text{NiCl}_2 \cdot 6\text{H}_2\text{O} \\ \text{CuCl} \\ \text{FeCl}_2 \cdot n\text{H}_2\text{O} \\ \text{SnCl}_4 \cdot n\text{H}_2\text{O} \\ \text{CrCl}_3 \cdot 6\text{H}_2\text{O} \\ \text{HgCl}_2 \end{pmatrix} $	3 0 3 3 3 3 3 3	4.2 1.0 1.2 1.9 0.6 4.5 0.4 2.0	trace trace trace trace trace trace 0.2 3.5	4.4 4.8 4.8 5.3 5.2 4.5 5.0 4.8

a) Blank experiments

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.

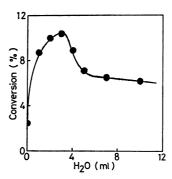


Fig. 1. Effect of the amount of water on the polymerization of MMA.
MMA 5 ml, DM-Hg 0.1 ml, Cu(II)-ion 1.5×10⁻⁵ mol; 85 °C, 6 hr

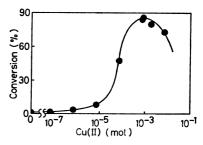


Fig. 2. Effect of the amount of Cu(II)-ion on the polymerization of MMA.

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

Effect of Amount of Metallic Salt on Polymerization. Keeping the amounts of water and monomer constant and varying the amount of cupric chloride, the polymerization of MMA was carried out at 85 °C for 6 hr (Fig. 2).

Maximum conversion was attained at 1.3×10^{-3} mol of Cu(II)-ion. 0.1 ml of DM-Hg corresponds to 1.28×10^{-3} mol, viz., maximum conversion was obtained when the molar quantity of DM-Hg was equal to that of Cu(II)-ion. This suggests that the initiation proceeds through the bimolecular reaction of DM-Hg with Cu(II)-ion. No formation of a complex of DM-Hg with Cu(II)-ion could be observed from its electronic spectrum.

Excess Cu(II)-ion might act as an inhibitor of the propagation by the following reaction:

 $\cdots M \cdot + CuCl_2 \rightarrow \cdots M \cdot Cl + CuCl$

Proof of the Radical Mechanism. In order to confirm the radical mechanism of the polymerization, the copolymerization of St and MMA was carried out (Fig. 3).

Determination of Initiating Radical Species. We have assumed that the initiating species is the methyl radical from DM-Hg. If this is the case, the methyl radical should be captured TPV and become colorless methyl-TPV.

 $2.56\times10^{-3}\,\mathrm{mol}$ (2 ml) of DM–Hg, $1.4\times10^{-3}\,\mathrm{mol}$ (2.16 g) of $\mathrm{CuCl_2\cdot 2H_2O}$, $9.57\times10^{-4}\,\mathrm{mol}$ (0.300 g) of TPV and 8 ml of benzene were placed in a tube, evacuated, sealed and warmed at 85 °C for 2 hr under shaking. The content turned almost colorless from a deep green. The reacted system was fractionated into three portions: Residue, Fractions I and II (Fig. 4).

Fraction I: Recrystallization of Fraction I from

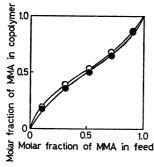


Fig. 3. Composition curves in the copolymerization of MMA with St.

Monomer 5 ml, DM–Hg 0.1 ml, $\rm H_2O$ 3 ml; 85 °C, 3 hr

 \bigcirc : Cu(II)-ion 1.5×10^{-5} mol

 \bullet : Fe(III)-ion 1.5×10^{-5} mol

Reaction Mixture

| Filtration |
| Residue | Filtrate |
| Separation by silica-column chromatography |
| (Benzen was used as solvent) |
| Fraction I |
| Fraction II

Fig. 4. Separation of products obtained from the reaction of DM-Hg with Cu(II) and TPV.

methanol gave pale yellow powder-like crystals (0.21 g). mp 138—139 °C, mol wt 328.6 (by VPO-method, using benzene as a solvent at 37 °C); cf. the values by Kuhn and Trischmarm, 5 mp of methyl-TPV 138—139 °C, mol wt of methyl-TPV 328.4.

Found: C, 76.89; H, 6.12; N, 16.99%.

Calcd for $C_{21}H_{20}N_4$: C, 76.80; H, 6.14; N, 17.06%. The yield (0.21 g) corresponds to 6.39×10^{-4} mol of methyl-TPV, corresponding to 67% of the theoretical value. IR-spectrum of TPV showed no definite absorption of C=N at 1660 cm⁻¹ by resonance of π -electrons. Fraction I had a strong absorption of ν C=N at 1660 cm⁻¹.

Fraction II: Fraction II gave white plate crystals. By successive recrystallization from methanol and water. Yield 2.41 g; mp 170—171 °C; mol wt 251.4 (VPO). The reported melting point of chloromethylmercury (MC-Hg) is 170 °C⁶) and its mol wt 251.5. The mixed melting point of the crystals with an authentic sample was also 170—171 °C. Thus Fraction II was found to be consistent with MC-Hg.

Residue: The residue, yellow green, was washed thoroughly with benzene, methanol and water, yield 1.23 g. Its solution in dilute aqueous nitric acid gave a white precipitate of AgCl with AgNO₃ solution. The washed residue contained 76.36% copper.

Calcd for CuCl: Cu, 79.88%; calcd for CuCl₂: Cu, 41.68% Thus the residue mainly consists of cuprous chloride.

The reaction was thus concluded to proceed as follows:

$$(CH_3)_2Hg + CuCl_2 \longrightarrow CH_3HgCl + CuCl + \cdot CH_3$$

$$(DM-Hg) \qquad (MC-Hg)$$

$$Ph \qquad CH_3 \qquad Ph$$

$$N-N \qquad N-N$$

$$CH_3 + Ph-C \qquad CH_2 \rightarrow Ph-C \qquad CH_2$$

$$N-N \qquad N-N \qquad N-N$$

$$Ph \qquad Ph \qquad (TPV) \qquad (methyl-TPV)$$

It can be concluded that the initiating species is the methyl radical.

Polymerization of MMA with MC-Hg and Cu(II)-ion. 5 ml of MMA, 1.5×10^{-5} mol of CuCl₂·2H₂O, 0.2 g of MC-Hg and 3 ml of water were shaken under vacuum at 85 °C for 6 hr to obtain a trace of poly-MMA. MC-Hg is thus found to be unable to initiate the polymerization of MMA, even in the presence of cupric chloride and water.

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