

VINYL POLYMERIZATION. 347. A FORMATION OF FREE RADICAL  
BY THE REACTION OF BENZIDINE WITH METHYL METHACRYLATE IN  
THE PRESENCE OF Fe(III)-ION AND WATER

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Benzidine, a carcinogenic compound, was found to be able to initiate the polymerization of methyl methacrylate in the presence of water and Fe(III)-ion. The reaction proceeded through a radical mechanism.

Introduction

The present letter concerns with a formation of free radical by the reaction of benzidine with methyl methacrylate(MMA) in the presence of aqueous solution of FeCl<sub>3</sub>. Literatures revealed already that a combined system of amine and metallic ion could initiate a radical polymerization of MMA. Imoto, Ouchi et al.<sup>1)</sup> reported on the polymerization of MMA by the complex of ethylenediamine and cupric acetate in bulk or in benzene, where water was proved to be a strong inhibitor. El-Rafie and Hebeish<sup>2)</sup> carried out a graft-polymerization of MMA onto nylon with dimethylaniline and Cu(II)-ion in the presence of water. Inaki, Takemoto et al. found that the Cu(II)-complexes of amine,<sup>3)</sup>  $\alpha$ -amino acid esters,<sup>4)</sup> imidazole derivatives<sup>5)</sup> and NH<sub>2</sub>-(CH<sub>2</sub>)<sub>n</sub>-NH<sub>2</sub> (n=2~6)<sup>6)</sup> could initiate radical polymerization of MMA and acrylonitrile in DMSO.

Benzidine(BD) is known as a compound which shows a carcinogenic activity. Accordingly, the fact that BD and Fe(III)-ion can initiate a radical polymerization of MMA in the presence of water, suggests a interesting meaning as to a problem of pollution.

Experimental and Discussions

Materials: BD was purified by repeated recrystallization from alcohol; m.p. 127°C.

MMA was purified by usual method and redistilled just before use. Water was ion-exchanged and distilled. Metallic salts were of high pure commercial grade.

Procedures: Reagents and MMA were placed in a tube. The tube was flushed with nitrogen, frozen, evacuated at 0.1 mmHg, and sealed. BD dissolved in MMA and water at 85°C. The tube was shaken in a thermostat. After reaction, the contents in the tube were poured into a large amount of methanol to precipitate the polymer. To separate BD from poly-MMA, the precipitate was washed thoroughly with methanol.

#### 1. Promoting Activity of Metallic Ion.

Five ml of MMA was reacted with 0.1 g of BD and  $3.62 \times 10^{-5}$  mol of metallic salt in the absence or in the presence of 3 ml of water. The results were listed in Table 1.

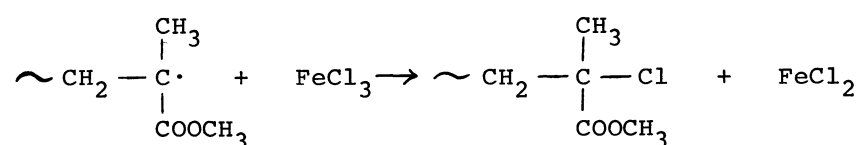
Table 1. Polymerization of MMA initiated with benzidine  
(H<sub>2</sub>O 3 ml, MMA 5 ml; 85°C, 5 hr)

BD (g)	Metal chloride $3.62 \times 10^{-5}$ mol	H <sub>2</sub> O (ml)	Conversion (%)
0	None	0	1.8
0	None	3	1.4
0	FeCl <sub>3</sub> ·6H <sub>2</sub> O	0	0
0	FeCl <sub>3</sub> ·6H <sub>2</sub> O	3	1.3
0	CuCl <sub>2</sub> ·2H <sub>2</sub> O	0	0
0	CuCl <sub>2</sub> ·2H <sub>2</sub> O	3	1.0
0	NiCl <sub>2</sub> ·6H <sub>2</sub> O	3	0.8
0	MnCl <sub>2</sub> ·4H <sub>2</sub> O	3	0.7
0.1	None	0	0
0.1	None	3	0
0.1	FeCl <sub>3</sub> ·6H <sub>2</sub> O	0	1.5
0.1	FeCl <sub>3</sub> ·6H <sub>2</sub> O	3	6.7
0.1	CuCl <sub>2</sub> ·2H <sub>2</sub> O	0	1.6
0.1	CuCl <sub>2</sub> ·2H <sub>2</sub> O	3	1.1
0.1	NiCl <sub>2</sub> ·6H <sub>2</sub> O	3	2.5
0.1	MnCl <sub>2</sub> ·4H <sub>2</sub> O	3	0

From Table 1, the following conclusions were obtained. (1) In the absence of BD, no polymerization took place. (2) Using metallic ion in such an amount of  $3.62 \times 10^{-5}$  mol for 0.1 g of BD,  $\text{FeCl}_3$  showed the most favorable activity.

As for the effect of amount of Fe(III)-ion, Fig. 1 was obtained. At the point A in Fig. 1, the molar ratio of BD to Fe(III)-ion was 15:1.

The amount of  $\text{FeCl}_3$  showed remarkable effects on the rate of polymerization and on the degree of polymerization ( $\bar{P}_n$ ) of poly-MMA.<sup>7)</sup> After exceeding a certain amount,  $\text{FeCl}_3$  became to inhibit the polymerization. The inhibition mechanism can be expressed as follows:



The inhibition was verified also from the rapid decrease of  $\bar{P}_n$  with the increase of the concentration of  $\text{FeCl}_3$ , as shown in Fig. 1.

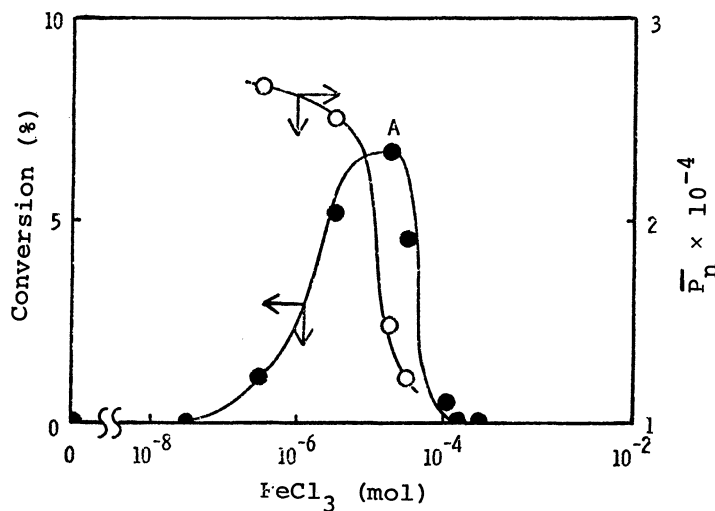


Fig. 1. Conversion of MMA and degree of polymerization of poly-MMA vs. amount of Fe(III)-ion.  
MMA 5 ml, BD 0.1 g,  $\text{H}_2\text{O}$  3 ml;  
85°C, 5 hr

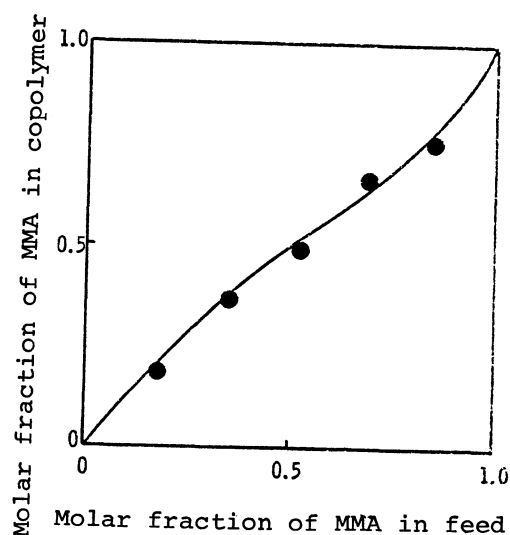


Fig. 2. Composition curve of the copolymer of MMA and styrene.  
MMA + styrene 6 ml, BD 0.1 g,  
 $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$   $3.62 \times 10^{-5}$  mol,  
 $\text{H}_2\text{O}$  3 ml; 85°C, 5 hr

## 2. Selectivity for Vinyl Monomer.

Five ml of vinyl monomer,  $3.62 \times 10^{-5}$  mol of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 0.1 g of BD were reacted at  $85^\circ\text{C}$  for 5 hr in the presence of 3 ml of water. The yields of polymer were as follows:

Styrene 3.5%, Acrylonitrile  $\sim 0\%$ , MMA 6.7%

The yield of polystyrene by the system of BD,  $\text{Fe(III)}$ -ion and water was the same as that by thermal polymerization.

Accordingly, it is clear that only MMA is polymerized by the present system of initiator.

## 3. Proof of Radical Mechanism.

In a mixture of 5 ml of MMA and an aqueous solution of  $3.62 \times 10^{-5}$  mol of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in 3 ml of water, diphenylpicrylhydrazyl was added in an amount of 0.1 g as a radical scavenger. Another polymerization was carried out in air. In both cases, formation of poly-MMA was not observed. Further, a copolymerization of MMA and styrene was carried out as shown in Fig. 2. The polymerization of MMA was proved to proceed through a radical mechanism.

## References

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- 7)  $\bar{P}_n$  of poly-MMA was estimated by the following Welch's equation from  $[\eta]$  measured at  $30^\circ\text{C}$  in benzene;  $\log \bar{P}_n = 3.346 + 1.32 \log [\eta]$ .

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