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### Vinyl Polymerization. 354. Polymerization of Methyl Methacrylate Initiated with the System Polyferrocenylenemethylene and Carbon Tetrachloride

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## **Vinyl Polymerization. 354. Polymerization of Methyl Methacrylate Initiated with the System Polyferrocenylenemethylene and Carbon Tetrachloride**

TATSURO OUCHI, SHIGERU HARAI, and MINORU IMOTO

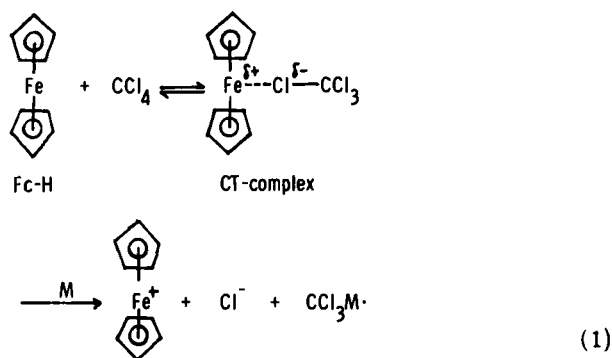
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### **ABSTRACT**

The polymerization of vinyl monomers with the system of polyferrocenylenemethylene (PFM) and carbon tetrachloride ( $\text{CCl}_4$ ) was carried out in dark. Methyl methacrylate (MMA) and acrylonitrile could be polymerized, while styrene was hardly polymerized under the conditions used. The polymerization was concluded to be initiated by attack of vinyl monomers, having an electron-attracting vinyl group on the CT-complex of PFM/ $\text{CCl}_4$ . In the polymerization of MMA in the presence of  $\text{CCl}_4$ , the initiating ability of PFM was much larger than that of ferrocene(Fc-H); the macromolecular effect of the initiator was very remarkable. The polymerization proceeded through a free-radical mechanism. The overall activation energy and entropy were estimated to be 77.7 kJ/mole and  $-127 \text{ J}^\circ \text{ K-mole}$ , respectively.

## INTRODUCTION

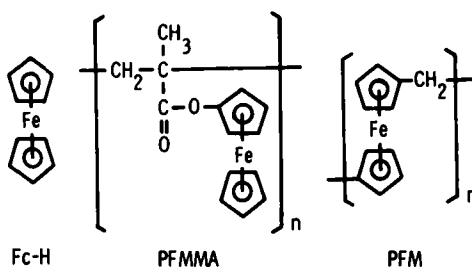
The homogeneous solution polymerization of vinyl monomers initiated by ferrocene (Fc-H) and carbon tetrachloride (CCl<sub>4</sub>) in the dark was recently reported [1]. The following results were obtained: (1) methyl methacrylate (MMA) and acrylonitrile (AN) could be polymerized; (2) carbon tetrachloride necessary for the reaction; (3) a charge-transfer complex (CT-complex) of Fc-H/CCl<sub>4</sub> was involved in the initiation; (4) the rate of polymerization of MMA in benzene solution was proportional to [Fc-H]<sup>0.6</sup>[CCl<sub>4</sub>]<sup>0.5</sup>[MMA]<sup>1.5</sup>; and (5) the polymerization proceeded through a free-radical mechanism. We therefore presumed that the initiating species is formed by the attack of vinyl monomers M, having electron-attracting vinyl groups, on the CT-complex as shown in Eq. (1).



When cellulose (a regular bright-type staple rayon) was present in the polymerization, the conversion of MMA increased from 28% to 100% [2]. This was a dramatic effect of cellulose. However, as cellulose is insoluble in benzene, the polymerization became to a heterogeneous reaction. Accordingly, in order to ascertain the macromolecular effect on the homogeneous polymerization of MMA, the initiator of Fc-H itself was converted to a macromolecular compound, i.e., poly(ferrocenylmethyl methacrylate) (PFMMA) [3]. It was concluded that PFMMA could give higher conversion than Fc-H, although the macromolecular effect was not so remarkable as cellulose. As mentioned above, the initiation step contains a reaction of MMA with CT-complex. Considering that PFMMA is a macromolecular analog of monomeric MMA, the radical initiation reaction of MMA may

compete with the reaction of PFMMA with CT-complex. Accordingly, it seemed reasonable that PFMMA could not have a marked macromolecular effect on the polymerization.

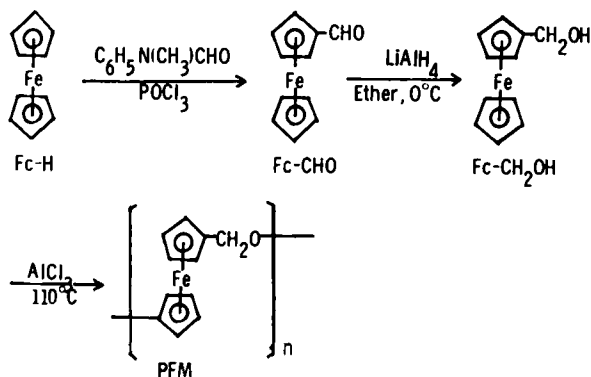
In the present paper, the homogeneous polymerization of MMA initiated with the system  $\text{CCl}_4$ -polyferrocenylmethylene (PFM) containing no carbonyl group, was carried out in benzene, and the macromolecular effect on the polymerization was investigated. As expected, the polymerization was found to be strongly promoted by PFM.



## EXPERIMENTAL

### Materials

PFM was prepared by the reaction sequence summarized in Eq. (2).



(2)

### Formylferrocene (Fc-CHO)

To a mixture of 112 g of Fc-H and 107 g of phosphorus oxychloride, 81 g of N-methylformamide was dropped at 50°C under stirring for 2 hr and allowed to stand for 3 hr at room temperature in a nitrogen stream [4]. The mixture was poured on 500 g of ice, and the product was extracted with diethyl ether. On distilling off the diethyl ether, crude aldehyde was obtained as a black, oily residue. Upon recrystallization from n-heptane-methylene chloride (3:1 by volume), Fc-CHO was obtained as red-brown scaly crystals. Yield 35.7%; IR,  $\nu_{\text{C=O}}$  1660  $\text{cm}^{-1}$ ,  $\nu_{\text{C-H}}$  2850-2750  $\text{cm}^{-1}$ . Analysis. Calcd for  $\text{C}_{11}\text{H}_{10}\text{OFe}$ : C, 61.81%; H, 4.68%. Found: C, 62.44%; H, 4.68%.

### Hydroxymethylferrocene (Fc-CH<sub>2</sub>OH)

Fc-CH<sub>2</sub>OH was prepared by the reduction of Fc-CHO with lithium aluminum hydride at 0°C in a nitrogen atmosphere [5]. Long, yellow needlelike crystals were obtained by recrystallization from n-hexane/chloroform (6:1 by volume). Yield 79.3%; mp 77.2-78.5°C (lit. 74-76°C). Analysis. Calcd for  $\text{C}_{11}\text{H}_{12}\text{OFe}$ : C, 61.24%; H, 5.57%. Found: C, 61.93%; H, 5.57%.

### PFM

PFM was obtained from heating a mixture of 5.02 g of Fc-CH<sub>2</sub>OH and 3.56 g of anhydrous aluminum chloride at 110°C in a nitrogen atmosphere for 1 hr [6]. Yellow-brown polymer was reprecipitated from benzene with petroleum ether. Yield 71.0%; IR,  $\nu_{\text{C-H}}$  1110-800  $\text{cm}^{-1}$ . Analysis. Calcd for  $(\text{C}_{11}\text{H}_{10}\text{Fe})_n$ : C, 66.71%; H, 5.08%. Found: C, 67.78%; H, 5.22%. The number-average degree of polymerization ( $\bar{P}_n$ ) measured by vapor pressure osmometry in benzene at 37°C was 53.

PFMMA was prepared according to the method of Pittman [7, 8]. Into a mixture of 6.3 g of Fc-CH<sub>2</sub>OH, 3 cm<sup>3</sup> of pyridine, 50 cm<sup>3</sup> dried diethyl ether, and several milligrams of hydroquinone, 3.9 g of methacryloyl chloride was dropped under stirring at 0°C. Ferrocenyl-methyl methacrylate (FMMA) was obtained from the ethereal layer. After recrystallization from n-hexane, the yield of yellow needles was 3.8 g [7]; mp 62.8-65.8°C (lit. mp 52-54°C); IR,  $\nu_{\text{C=C}}$  1630  $\text{cm}^{-1}$ . Analysis. Calcd for  $\text{C}_{15}\text{H}_{16}\text{O}_2\text{Fe}$ : C, 63.41%; H, 5.68%. Found C, 63.52%; H, 5.65%.

Polymerization of FMMA was carried out in vacuo at 60°C, with 2,2'-azobisisobutyronitrile (AIBN) as an initiator [8]. The polymer

was purified three times by reprecipitation with benzene and petroleum ether. It was a yellow-colored solid.  $\bar{P}_n$  measured by vapor pressure osmometry in benzene at 37° C was 80.

Carbon tetrachloride was distilled in vacuo under a stream of nitrogen and passed through a column filled with alumina. MMA, styrene (St), AN, benzene, and N, N-dimethylformamide (DMF) were purified by the usual methods.

### Polymerization of Vinyl Monomer

The polymerization was carried out in a sealed glass ampoule. Monomer, ferrocenyl compound, CCl<sub>4</sub>, and solvent were placed in the ampoule, and then it was flushed with nitrogen, frozen, and sealed in vacuo. The reaction system was homogeneous. After the polymerization was carried out under shaking in a thermostat at 85° C, the ampoule was broken and the contents were poured into a large amount of petroleum ether to precipitate the polymer formed. The polymer was filtered, washed thoroughly with petroleum ether, and dried under vacuum. The monomer conversions were calculated from the following relationships.

For PFM and PFMA:

Conversion (%)

$$= \frac{[\text{Total precipitates}] \text{ (g)} - [\text{PFM or PFMA}] \text{ (g)}}{\text{Monomer (g)}} \times 100$$

For Fc-H:

$$\text{Conversion (\%)} = \frac{\text{Precipitate (g)}}{\text{Monomer (g)}} \times 100$$

## RESULTS AND DISCUSSION

### Selectivity of Vinyl Monomer

A mixture of 5 cm<sup>3</sup> of monomer, 3.52 × 10<sup>-2</sup> mole/dm<sup>3</sup> of ferrocenyl unit (FU), and 5 cm<sup>3</sup> of solvent were heated under vacuum at 85° C for 5 hr. The polymerization proceeded homogeneously and

TABLE 1. Vinyl Polymerizations Initiated with PFM, PFMMA or Fc-H<sup>a</sup>

Monomer	Ferrocenyl compound	CCl <sub>4</sub> (cm <sup>3</sup> )	Conversion (%)
MMA	—	0	1.20
	—	0.2	1.83
	PFM	0	2.07
	PFM	0.2	51.32
	PFMMA	0	4.20
	PFMMA	0.2	8.07
	Fc-H	0	2.14
	Fc-H	0.2	6.02
AN	—	0	0
	—	0.2	0
	PFM	0	trace
	PFM	0.2	32.04
	PFMMA	0	trace
	PFMMA	0.2	7.08
	Fc-H	0	trace
	Fc-H	0.2	0.90
St	—	0	1.65
	—	0.2	1.59
	PFM	0	2.20
	PFM	0.2	3.17
	PFMMA	0	2.58
	PFMMA	0.2	2.90
	Fc-H	0	1.88
	Fc-H	0.2	2.06

<sup>a</sup>Polymerization conditions: Monomer, 5 cm<sup>3</sup>; ferrocenyl compound,  $3.52 \times 10^{-2}$  mole/dm<sup>3</sup> of FU; Solvent, 5 cm<sup>3</sup>, benzene (MMA, St) or DMF (AN); time, 5 hr; 85° C.

gave the results listed in Table 1. The data in this table show clearly that MMA and AN could be polymerized with the system of PFM and  $\text{CCl}_4$ , while St was hardly polymerized. The presence of  $\text{CCl}_4$  was indispensable. These results were the same as those of cases of PFMMA and Fc-H. The promoting effect on the polymerization rate increased in order  $\text{PFM} > \text{PFMMA} > \text{Fc-H}$ .

#### Effect of the Amount of Ferrocenyl Compound

Various amounts of ferrocenyl compound,  $5 \text{ cm}^3$  of MMA and  $0.2 \text{ cm}^3$  of  $\text{CCl}_4$  were heated in benzene solution (total volume was  $10 \text{ cm}^3$ ) at  $85^\circ \text{C}$  for 3 hr. The results obtained are shown in Fig. 1. When the concentration of ferrocenyl compound was not so large, the rate of polymerization increased with the concentration of ferrocenyl compound, but gradually the rate became independent of the concentration of ferrocenyl compound. As can be seen in Fig. 1, the initiating activity increased in the order,  $\text{PFM} > \text{PFMMA} > \text{Fc-H}$ .

#### Effect of the Amount of Carbon Tetrachloride

On maintaining the total volume at  $10 \text{ cm}^3$ , various amounts of  $\text{CCl}_4$ ,  $5 \text{ cm}^3$  of MMA, and  $1.0 \times 10^{-2} \text{ mole/dm}^3$  of FU of ferrocenyl

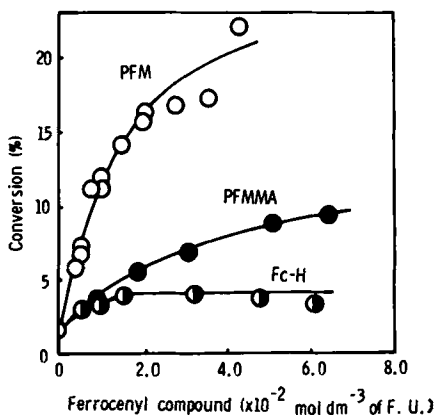


FIG. 1. Effects of the amount of ferrocene compounds on the polymerization of MMA. MMA,  $5 \text{ cm}^3$ ;  $\text{CCl}_4$ ,  $0.2 \text{ cm}^3$  in benzene; total volume,  $10 \text{ cm}^3$ ;  $85^\circ \text{C}$ ; 3 hr.



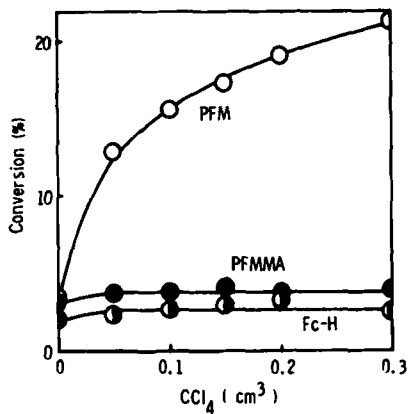


FIG. 2. Effects of the amount of  $\text{CCl}_4$  on the polymerization of MMA. Ferrocene compound,  $1.01 \times 10^{-2}$  mole/ $\text{dm}^3$  of FU; MMA,  $5 \text{ cm}^3$  in benzene; total volume,  $10 \text{ cm}^3$ ;  $85^\circ \text{C}$ ; 3 hr.

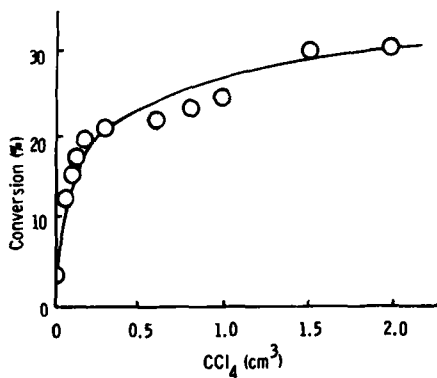


FIG. 3. Effects of the amount of  $\text{CCl}_4$  on the polymerization of MMA. MMA,  $5 \text{ cm}^3$ ; PFM,  $1.01 \times 10^{-2}$  mole/ $\text{dm}^3$  of FU in benzene; total volume,  $10 \text{ cm}^3$ ;  $85^\circ \text{C}$ ; 3 hr.

compound in benzene were heated at 85°C for 3 hr. The results shown in Fig. 2 were obtained. As can be seen clearly, the presence of  $\text{CCl}_4$  is necessary for the polymerization to occur, and the rate of polymerization of MMA increased in the order  $\text{PFM} > \text{PFMMA} > \text{Fc-H}$ . In the cases of Fc-H and PFMMA, the rate of polymerization (conversion) became independent of the amount of  $\text{CCl}_4$  after exceeding a certain amount. However, in the case of PFM, the rate increased with the amount of  $\text{CCl}_4$ . This increasing effect by  $\text{CCl}_4$  is also shown in Fig. 3, where larger amount of  $\text{CCl}_4$  was used.

### Effect of the Amount of MMA

Polymerization of various amounts of MMA,  $1.01 \times 10^{-2}$  mole/ $\text{dm}^3$  of FU of ferrocenyl compound,  $0.2 \text{ cm}^3$  of  $\text{CCl}_4$  in benzene, at a constant total volume at  $10 \text{ cm}^3$ , was carried out at 85°C for 3 hr. The results obtained are shown in Fig. 4. This figure shows also that the rate of polymerization of MMA with the system  $\text{PFM}/\text{CCl}_4$  was very much larger than the rates with the systems  $\text{PFMMA}/\text{CCl}_4$  and  $\text{Fc-H}/\text{CCl}_4$ . Evidently, the polymerization of MMA initiated by the system of ferrocenyl compound and  $\text{CCl}_4$  was promoted by conversion of the ferrocenyl compound to a macromolecule.

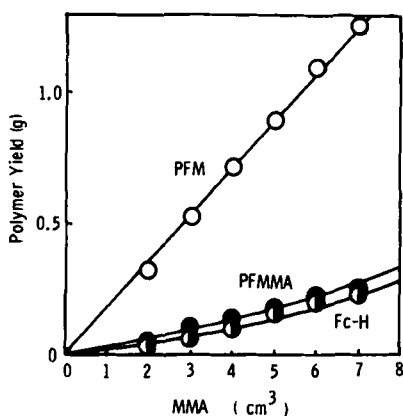


FIG. 4. Effects of the amount of MMA on the polymerization. Ferrocene compound,  $1.01 \times 10^{-2}$  mole/ $\text{dm}^3$  of FU;  $\text{CCl}_4$ ,  $0.2 \text{ cm}^3$  in benzene; total volume,  $10 \text{ cm}^3$ ; 85°C; 3 hr.

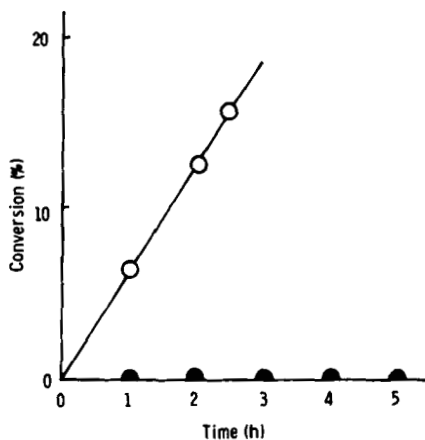


FIG. 5. Inhibition of the polymerization by DPPH: (○) no DPPH; (●) 0.1 g DPPH. MMA, 5 cm<sup>3</sup>; PFM, 0.02 g; CCl<sub>4</sub>, 0.2 cm<sup>3</sup> in benzene; total volume, 10 cm<sup>3</sup>; 85° C.

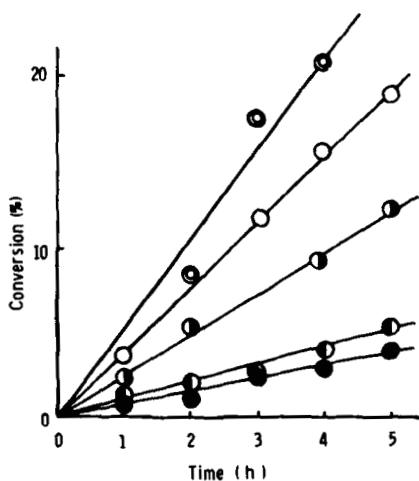


FIG. 6. Effect of temperature on the polymerization of MMA with the system PFM-CCl<sub>4</sub>: (●) 65° C; (◐) 75° C; (◑) 80° C; (○) 85° C; (⊙) 90° C. MMA, 5 cm<sup>3</sup>; CCl<sub>4</sub>, 0.2 cm<sup>3</sup>; PFM, 0.02 g in benzene; total volume, 10 cm<sup>3</sup>.

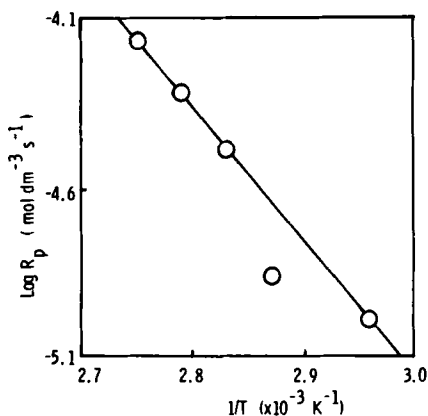


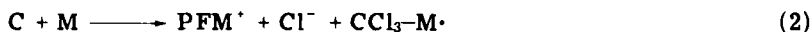
FIG. 7. Arrhenius plot. MMA, 5 cm<sup>3</sup>; PFM, 0.02 g; CCl<sub>4</sub>, 0.2 cm<sup>3</sup> in benzene; total volume, 10 cm<sup>3</sup>; 65-90°C.

### Proof of Radical Mechanism

To a mixture of 5 cm<sup>3</sup> of MMA, 0.02 g of PFM, and 0.2 cm<sup>3</sup> of CCl<sub>4</sub> in benzene, at a constant total volume of 10 cm<sup>3</sup>, 0.1 g of diphenylpicrylhydrazyl (DPPH) was added as a radical scavenger. As can be seen in Fig. 5, the polymerization was completely inhibited. Therefore the polymerization of MMA initiated with PFM and CCl<sub>4</sub> was found to proceed through a radical mechanism.

### Initiation Mechanism

Formation of the CT-complex of ferrocene with CCl<sub>4</sub> was reported in many papers [1, 9-11]. The initiating species was considered to be formed from the CT-complex by the attack of vinyl monomers having electron-attracting vinyl groups. Thus, the mechanism of polymerization may be expressed by Eqs. (1)-(4), as in the case of Fc-H, CCl<sub>4</sub>, and MMA [1].



Here C is the CT-complex, M is a monomer, P is the polymer, and  $M\cdot$  is a propagating radical.

### Effect of Temperature

In order to determine the rate of polymerization  $R_p$ , the polymerizations of a system composed of 5 cm<sup>3</sup> of MMA, 0.02 g of PFM, 0.2 cm<sup>3</sup> of CCl<sub>4</sub> in benzene, to a total volume of 10 cm<sup>3</sup>, were carried out at 65-90°C. As shown in Fig. 6, straight lines were obtained. From the slopes of the lines,  $R_p$  were calculated and applied to the Arrhenius equation. The plots were obtained as a straight line (Fig. 7). The overall activation energy and entropy were estimated to be 77.7 kJ/mole and -127 J/°K-mole, respectively.

### REFERENCES

- [1] M. Imoto, T. Ouchi, and T. Tanaka, Nippon Kagaku Kaishi, 1974, 775.
- [2] M. Imoto, T. Ouchi, and T. Tanaka, J. Polym. Sci. Polym. Letters Ed., 12, 21 (1974).
- [3] T. Ouchi, T. Ogawa, and M. Imoto, Kobunshi Ronbunshu, in press.
- [4] P. J. Graham, R. V. Lindsey, and G. W. Parshall, J. Amer. Chem. Soc., 79, 3416 (1957).
- [5] G. B. Broadhead, J. M. Osgerby, and P. L. Pauson, J. Chem. Soc., 1958, 650.
- [6] E. W. Neuse and D. S. Trifan, J. Amer. Chem. Soc., 85, 1952 (1963).
- [7] C. U. Pittman, Macromolecules, 3, 746 (1970).
- [8] C. U. Pittman, Macromolecules, 4, 291 (1971).
- [9] J. C. D. Brand and W. Suedden, Trans. Faraday Soc., 53, 894 (1957).
- [10] L. Kaplan, W. L. Kester, and J. J. Katz, J. Amer. Chem. Soc., 74, 5531 (1952).
- [11] K. Tsubakiyama and S. Fukisaki, J. Polym. Sci. Polym. Letters Ed., 10, 344 (1972).

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