Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Vinyl Polymerization. 371. Polymerization of Methyl Methacrylate Initiated by the System of Polyvinylferrocene and Carbon Tetrachloride

Tatsuro Ouchi[a]; Hiromu Taguchi[a]; Minoru Imoto[a]
[a] Department of Applied Chemistry, Faculty of Engineering Kansai University, Osaka, Japan

To cite this Article Ouchi, Tatsuro , Taguchi, Hiromu and Imoto, Minoru(1978) 'Vinyl Polymerization. 371. Polymerization of Methyl Methacrylate Initiated by the System of Polyvinylferrocene and Carbon Tetrachloride', Journal of Macromolecular Science, Part A, 12: 5, 719 — 730

To link to this Article: DOI: 10.1080/00222337808066587

URL: http://dx.doi.org/10.1080/00222337808066587

J. MACROMOL. SCI.–CHEM., A12(5), pp. 719-730 (1978)

Vinyl Polymerization. 371. Polymerization of Methyl Methacrylate Initiated by the System of Polyvinylferrocene and Carbon Tetrachloride

TATSURO OUCHI, HIROMU TAGUCHI, and MINORU IMOTO

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

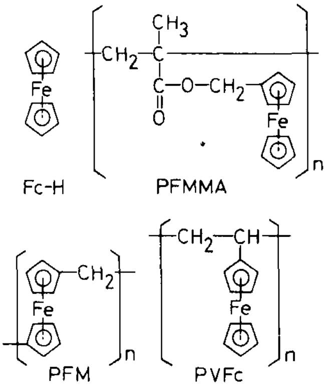
ABSTRACT

The polymerization of vinyl monomers initiated with the system of polyvinylferrocene (PVFc) and carbon tetrachloride (CCl_4) was carried out in dark. Methyl methacrylate (MMA) and acrylonitrile (AN) could be polymerized, while styrene (St) was hardly polymerized under the conditions used. The polymerization proceeded through a free-radical mechanism and was concluded to be initiated by attack of vinyl monomer, having a polarized vinyl group, on the charge-transfer complex of PVFc/CCl_4. In the polymerization of MMA, the initiating ability of PVFc was much larger than that of ferrocene (Fc-H) or poly(ferrocenylmethyl methacrylate) (PFMMA) and was comparable to that of polyferrocenylenemethylene (PFM). The overall activation energy was estimated to be 34.2 kJ/mole.

INTRODUCTION

The homogeneous solution polymerization of vinyl monomers initiated by ferrocene (Fc-H) and carbon tetrachloride (CCl_4) in the dark was already reported [1]. The following results were obtained: (1) methyl methacrylate (MMA) and acrylonitrile (AN) could be polymerized but styrene (St) could not; (2) CCl_4 was necessary for the reaction; (3) a charge-transfer complex (CT complex) of Fc-H/CCl_4 was involved in the initiation; (4) the rate of polymerization of MMA in benzene solution was proportional to $[\text{Fc-H}]^{0.5}[CCl_4]^{0.5}[\text{MMA}]^{1.5}$; and (5) the polymerization proceeded through a free-radical mechanism. We therefore presumed that the radical species was formed by the attack of vinyl monomer having a polarized vinyl group on the CT complex.

Moreover, the macromolecular effect on the polymerization was investigated, by using poly(ferrocenylmethyl methacrylate) (PFMMA) [2] or polyferrocenylenemethylene (PFM) [3] instead of Fc-H. The initiating activity increased in the order PFM ≫ PFMMA > Fc-H. The following two considerations were made to explain why the initiating ability of PFMMA was smaller than that of PFM: (1) the PFMMA unit has a pendent ferrocenyl group and (2) the PFMMA unit has a carbonyl group which can interact with positively charged iron atom.

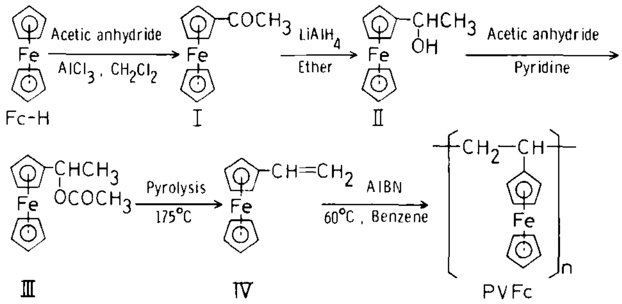


The present paper is concerned with the polymerization of vinyl monomers with the system of CCl_4 and polyvinylferrocene (PVFc) whose unit has a pendent ferrocenyl group and no carbonyl group.

EXPERIMENTAL

Materials

PVFc was prepared by the scheme (1), according to the method of Arimoto et al. [4].



(1)

Vinylferrocene. Ferrocenyl methyl ketone (I) was prepared as described in the literature [5]. I was obtained as orange colored needlelike crystals; theoretical yield 56%; mp 95.8-96.9°C. The IR showed $\nu_{C=O}$ 1660 cm^{-1}.

Analysis Calcd for $C_{12}H_{12}OFe$: C, 63.20%; H, 5.30%. Found: C, 63.15%; H, 4.95%.

Ferrocenylmethylcarbinol (II) was prepared by the method of Arimoto and Haven [4]. II was obtained as orange-red needlelike crystals; theoretical yield 92%; mp 79.2-79.8°C. The IR showed ν_{OH} 3190-3250 cm^{-1}.

Analysis: Calcd for $C_{12}H_{14}OFe$: C, 62.64%; H, 6.13%. Found: C, 62.52%; H, 5.81%.

Ferrocenylmethylcarbinyl acetate (III) was prepared by the method of Arimoto and Haven [4]; theoretical yield 93%; mp 69.3-90.4°C. The IR spectrum showed $\nu_{C=O}$ 1710 cm^{-1}, $_{C-O}$ 1220 cm^{-1}. The crude acetate was distilled under reduced pressure into a glass tube packed with glass wool. As the tube was heated to 175°C, the acetate was decomposed to crude vinylferrocene (IV). The theoretical yield was 73%. IV obtained (IR, $\nu_{C=C}$ 1630 cm^{-1}) was a viscous liquid and was used without further purification.

Polyvinylferrocene (PVFc). Polymerizations of the two kinds of VFc were carried out at 60°C with 2,2'-azobisisobutyronitrile as an initiator, as described in the literature [4, 6-8]. Each polymer was purified two times by reprecipitation from benzene and methanol. They were yellow powders. $\overline{P}_n$ measured by vapor pressure osmometry method in benzene at 37°C were 15 and 22, respectively.

Carbon tetrachloride was passed through a column filled with alumina and distilled at atmospheric pressure. MMA, St, AN, benzene, and dimethylformamide (DMF) were purified by the usual methods.

Procedures

The polymerization of vinyl monomer was carried out in a sealed glass ampoule. Monomer, ferrocenyl compound, CCl_4, and solvent were placed in the ampoule. The ampoule was flushed with nitrogen, frozen, and sealed in vacuo. The order to carry out the homogeneous solution polymerization, benzene was used as solvent for MMA and St, and DMF for AN. The polymerization was carried out with shaking in a thermostat. After the reaction, the contents were poured into a large amount of methanol to precipitate the polymer formed. The polymer was filtered, washed thoroughly with methanol, and dried under vacuum at 80°C. The conversion of the monomer was calculated by Eqs. (2) and (3) for PVFc and Fc-H, respectively.

$$\text{Conversion (PVFc) (\%)} = \frac{[\text{Total precipitates}]\ (\text{g}) - [\text{PVFc}]\ (\text{g})}{\text{Monomer}} \times 100 \qquad (2)$$

$$\text{Conversion (Fe-H) (\%)} = \frac{\text{Precipitate (g)}}{\text{Monomer (g)}} \times 100 \qquad (3)$$

RESULTS AND DISCUSSION

Selectivity of Vinyl Monomer

A mixture of 5 cm^3 of monomer, 3.52×10^{-2} mole/dm^3 of ferrocenyl unit (F. U.), 0.2 cm^3 of CCl_4, and 5 cm^3 of solvent was heated under vacuum at 85°C for 5 hr. The results, listed in Table 1, show clearly that MMA and AN could be polymerized with the PVFc/CCl_4 system, while St was hardly polymerized. The presence of CCl_4 was indispensable. These results were the same as those of the cases of Fc-H, PFMMA, and PFM. The promoting effects of the ferrocenyl compounds on the polymerization rate increased in the order, PFM, PVFc $\gg$ PFMMA $>$ Fc-H. The reason why St could not be polymerized is its nonpolarizing property, which will be discussed in the last section of the present paper.

Effect of the Concentration of PVFc

The polymerizations of MMA were carried out with varying concentration of PVFc as shown in Fig. 1. As can be clearly seen, the rate

TABLE 1. Vinyl Polymerization Initiated with PVFc or Fc-H[a]

Monomer	Solvent	Ferrocenyl compound	CCl_4 (cm^3)	Conversion (%)
MMA	Benzene	-	0	1.39
		-	0.2	1.37
		Fc-H	0	3.21
		Fc-H	0.2	4.09
		PVFc	0	7.22
		PVFc	0.2	39.76
AN	DMF	-	0	0
		-	0.2	0
		Fc-H	0	0
		Fc-H	0.2	4.76
		PVFc	0	0.12
		PVFc	0.2	32.68
St	Benzene	-	0	1.61
		-	0.2	1.55
		Fc-H	0	1.59
		Fc-H	0.2	0.58
		PVFc	0	2.48
		PVFc	0.2	4.09

[a] Polymerization conditions: monomer, 5 cm^3; ferrocenyl compound, 3.52×10^{-2} mole/dm^3 of F. U.; solvent, 5 cm^3; 85°C; 5 hr.

of polymerization initiated by PVFc is comparable to that by PFM and is much larger than that by PFMMA or Fc-H.

Effect of the Amount of MMA

Polymerizations of MMA were carried out in benzene at 85°C for 3 hr on varying [MMA] and keeping [PVFc] and [CCl_4] constant. The results obtained are shown in Fig. 2. Figure 2 shows also that

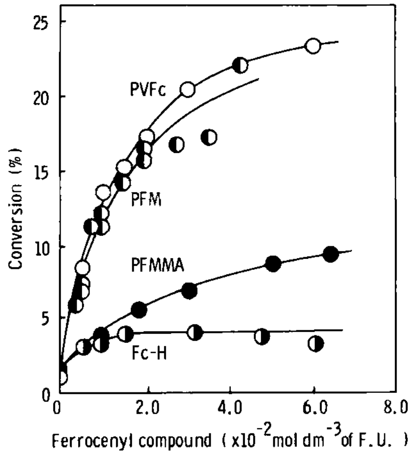


FIG. 1. Effects of the concentration of ferrocenyl compound on the polymerization of MMA. MMA, 5 cm^3; CCl_4, 0.2 cm^3; total volume, 10 cm^3 (benzene); 85°C; 3 hr.

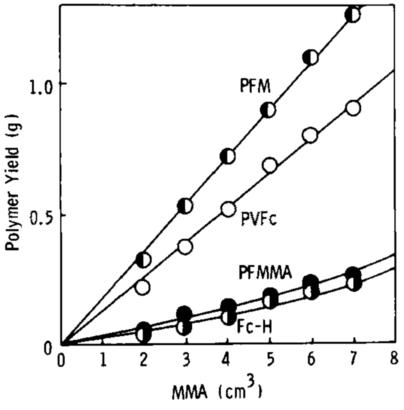


FIG. 2. Effects of the amount of MMA on the polymerization. Ferrocenyl compound, 1.01×10^{-2} mole/dm^3 F. U.; CCl_4, 0.2 cm^3; total volume 10 cm^3 (benzene); 85°C; 3 hr.

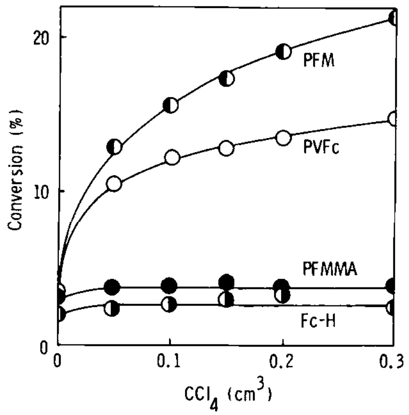


FIG. 3. Effects of the amount of CCl_4 on the polymerization of MMA. Ferrocenyl compound, 1.01×10^{-2} mole/dm^{-3} F. U.; MMA, 5 cm^3; total volume 10 cm^3 (benzene); 85°C; 3 hr.

the rate of polymerization of MMA with the PVFc/CCl_4 and PFM/CCl_4 systems were very much larger than those with the PFMMA/CCl_4 and Fc-H/CCl_4 systems. The promoting effects increased in the order PFM $>$ PVFc $\gg$ PFMMA $>$ Fc-H.

Effect of the Concentration of Carbon Tetrachloride

On maintaining the total volume at 10 cm^3, various amounts of CCl_4, 5 cm^3 of MMA, and 1.0×10^{-2} mole/dm^3 of F. U. of ferrocenyl compound were heated in benzene at 85°C for 3 hr. The results shown in Fig. 3 were obtained. The presence of CCl_4 is necessary for the polymerization, and the rate of polymerization of MMA increased in the order PFM $>$ PVFc $\gg$ PFMMA $>$ Fc-H.

As Figs. 1, 2, and 3 show, in all cases the polyferrocenyl compounds have larger initiating activities than monomeric ferrocene (Fc-H). This is the macromolecular effect. Macromolecules can incorporate the reacting substances and promote the reaction.

Proof of Radical Mechanism

To a mixture of 5 cm^3 of MMA, 1.01×10^{-2} mole/dm^3 of F. U. of PFVc, and 0.2 cm^3 of CCl_4, and benzene (to a total volume of 10 cm^3), was added 0.1 g of diphenylpicrylhydrazyl (DPPH) as a radical

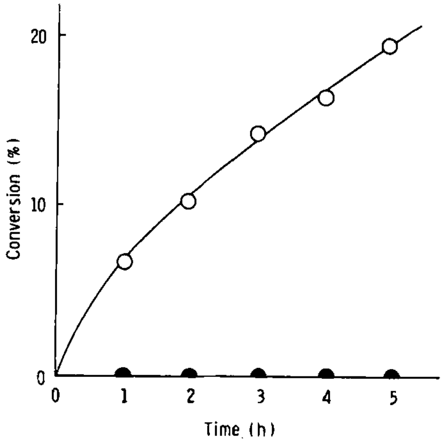


FIG. 4. Inhibition of the polymerization by DPPH: (○) no DPPH; (●) 0.1 g DPPH. MMA, 5 cm^3; PVFc, 0.0211 g (1.01×10^{-2} mole/dm^3 F. U.); CCl_4, 0.2 cm^3; total volume 10 cm^3 (benzene); 85°C.

scavenger. As can be seen in Fig. 4, the polymerizations were completely inhibited. Therefore the polymerization of MMA initiated with PVFc and CCl_4 was found to proceed through a radical mechanism.

Effect of Temperature

In order to estimate the overall activation energy, the polymerizations of MMA were carried out at 65-90°C. As shown in Fig. 5, after about 1 hr, the time-conversion relationship can be expressed by a straight line. The slopes of the lines were considered to be the rate of polymerization R_p, and the Arrhenius equation was applied. The plots were obtained as a straight line (Fig. 6). From the line, the overall activation energy was estimated to be 34.2 kJ/mole.

Comparison of Overall Activation Energy

Overall activation energies of four kinds of ferrocenyl compound/CCl_4/MMA systems are shown in Table 2. PFMMA and PVFc, which have a ferrocenyl group in the side chain, had small activation energies, while PFM, having a ferrocenyl group in the main chain, had a higher activation energy. As stated above, PFM and PVFc had almost the

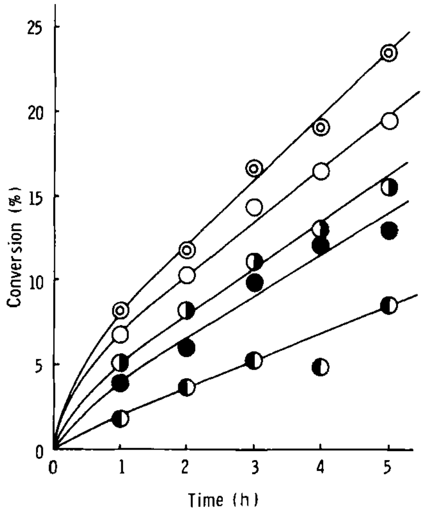


FIG. 5. Effect of temperature on the polymerization of MMA with PVFc/CCl_4 system: (◐) 65°C; (●) 75°C; (◑) 80°C; (○) 85°C; (◎) 90°C. PVFc, 1.01×10^{-2} mole/dm^3 F. U.; MMA, 5 cm^3; CCl_4, 0.2 cm^3; total volume 10 cm^3 (benzene).

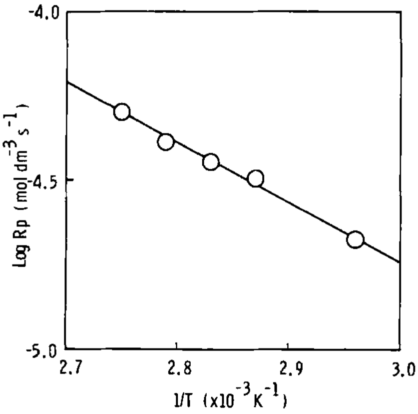


FIG. 6. Arrhenius plot.

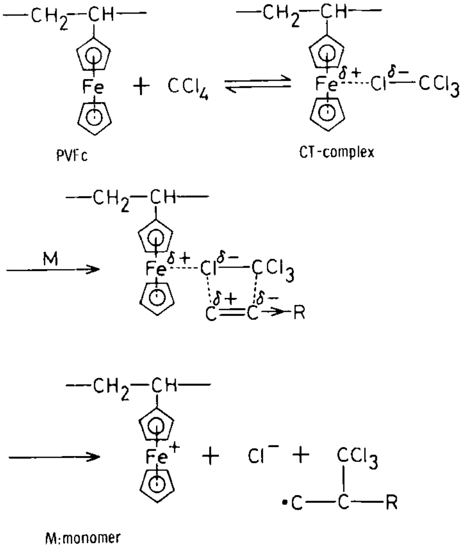
TABLE 2. Overall Activation Energies

Ferrocenyl compound	Activation energy (kJ/mole)
Fc-H	54.3
PFMMA	39.4
PFM	77.7
PVFc	34.2

same activities. Accordingly, the overall activation entropy in the case of PFM is more convenient to the initiating reaction than that in the case of PVFc. At the present time, the exact reason is not clear.

Initiation Mechanism

Formation of the CT complex of ferrocene with CCl_4 was reported [9-11]. The initiating species (CCl_3-M·) was considered to be formed

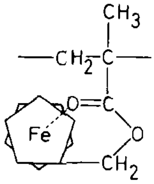


(4)

from the CT complex by the attack of vinyl monomers having electron-attracting vinyl groups. Thus, the mechanism of initiation can be expressed by Eq. (4), as in the cases of PVFc, PFMMA and Fc-H.

In Eq. (4) MMA or AN forms a complex with PVFc and CCl_4, by its polarized structure, white St is a weakly polarized molecule and forms hardly the complex.

As Figs. 1-3 show, the initiating ability of PFMMA was very small. Nevertheless, the overall activation energy was only 39.4 kJ/mole. Therefore, the low activity of PFMMA is due to the interaction of ferrocenyl group with carbonyl group, to form an intramolecular



complex. In other words, the most reaction sites of PFMMA were blocked by the carbonyl group.

REFERENCES

[1] M. Imoto, T. Ouchi, and T. Tanaka, Nippon Kagaku Kaishi, 1974, 775.

[2] T. Ouchi, T. Ogawa, and M. Imoto, Kobunshi Ronbunshu, 33, 585 (1976).

[3] T. Ouchi, S. Harai, and M. Imoto, J. Macromol. Sci.–Chem., A11, 295 (1977).

[4] F. S. Arimoto and A. C. Haven, Jr., J. Amer. Chem. Soc., 77, 6295 (1955).

[5] K. L. Rinehart, Jr., K. Motz, and S. Moon, J. Amer. Chem. Soc., 79, 2749 (1957).

[6] Y. Sasaki, L. L. Walker, E. L. Hurst, and C. U. Pittman, Jr., J. Polym. Sci. Polym. Chem. Ed., 11, 1213 (1973).

[7] A. J. Tinker, M. H. George, and J. A. Barrie, J. Polym. Sci. Polym. Chem. Ed., 13, 2133 (1975).

[8] M. H. George and G. F. Hayes, J. Polym. Sci. Polym. Chem. Ed., 13, 1049 (1975); Ibid., 14, 475 (1976).

[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).

Accepted by editor November 6, 1977
Received for publication December 10, 1977