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Vinyl Polymerization. 254.* Polymerization of Methyl Methacrylate by the System Cellulose-Water-Carbon Tetrachloride

M. Imoto[a]; M. Kinoshita[a]; Y. Iki[a]
[a] Osaka City University Faculty of Engineering Sugimoto-cho, Osaka, Japan

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Vinyl Polymerization. 254.* Polymerization of Methyl Methacrylate by the System Cellulose-Water-Carbon Tetrachloride

M. IMOTO, M. KINOSHITA, and Y. IKI

Osaka City University
Faculty of Engineering
Sugimoto-cho, Sumiyoshi-ku
Osaka, Japan

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SUMMARY

Radical polymerization of methyl methacrylate initiated by the system cellulose-water-carbon tetrachloride was kinetically studied. Results obtained are: 1) The amounts of water, carbon tetrachloride, and cellulose affected the conversion. Michaelis-Menten's equation was applied to the relationship between the rate of polymerization and the amount of MMA. 2) Other methacrylates and acrylates were also polymerized by this system. 3) When methanol or ethanol was used instead of water, some weak polymerization activity was observed. 4) Initiating ability depended on the kind of cellulose used. 5) The activity of cellulose was not changed by washing with boiling water or by solvent extraction. 6) Polymerization was inhibited by the presence of air. 7) Heating in the presence of water and carbon tetrachloride markedly decreased the activity of the cellulose.

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*253 of the series: K. Takemoto, Y. Maki, T. Matsumiya, R. Fujita, and M. Imoto, *Sci. Int. J.* (Rumania), In Press.

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INTRODUCTION

In a series of our papers, cellulose and water were found to be able to initiate the polymerization of methyl methacrylate (MMA). However, large differences were observed in the initiating ability of cellulose depending on the kind of cellulose used. Some kinds showed considerable initiation ability and others did not.

In 1967, Imoto, Takemoto, and Sutoh [1] found that a small amount of carbon tetrachloride could greatly increase the rate of polymerization of MMA initiated by the system cellulose-water. Regardless of the ability of the cellulose used, carbon tetrachloride gave the system cellulose-water great initiation ability [2]. Thus, Imoto, Ueda, and Takemoto, using cupra-rayon, which has no activity for initiation, made a study of the polymerization of MMA [3] in the presence of carbon tetrachloride and water and on the grafting efficiency of MMA onto cupra-rayon [4].

This paper is concerned with a kinetic study of the polymerization of some acrylates and methacrylates by the cellulose-water-carbon tetrachloride system, with particular attention paid to the kinds of cellulose and solvents used and to the polymerization atmosphere.

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EXPERIMENTAL

Reagents

MMA, MA (methyl acrylate), BMA (butyl methacrylate), BA (butyl acrylate), and other vinyl monomers were washed thrice by a combination of steps with saturated Na_2SO_3 aqueous solution, 5% aqueous solution of NaOH, and 20% aqueous solution of NaCl, dried with anhydrous Na_2SO_4, and distilled under nitrogen in vacuo. They were redistilled just before use.

Table 1.[a]

Linter pulp (g)	Water (ml)	CCl_4 (ml)	Conversion (%)
0	10	0.2	1.1, 1.6
0.2	0	0.2	2.1, 2.5
0.2	10	0	2.5, 2.6
0.2	10	0.2	24.0, 36.1

[a] MMA, 2 ml; 85°; 4 hr.

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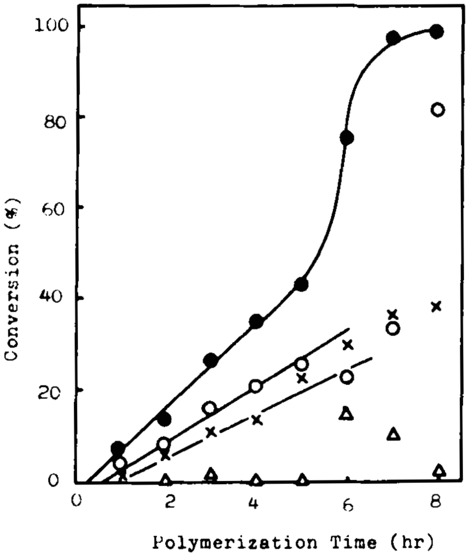

Fig. 1. Time-conversion curves. Cellulose, 0.2 g; water, 10 ml; carbon tetrachloride, 0.2 ml; MMA, 2 ml. ●: 85°, ○: 75°, X: 65°, △: 55°.

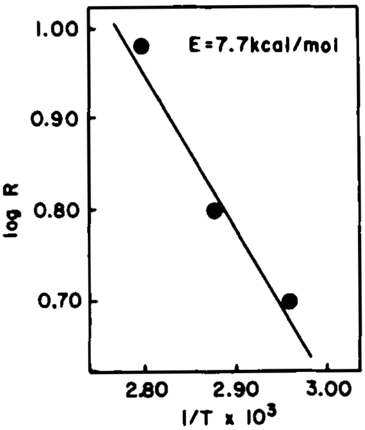

Fig. 2. Over-all activation energy (R is % conversion/hr).

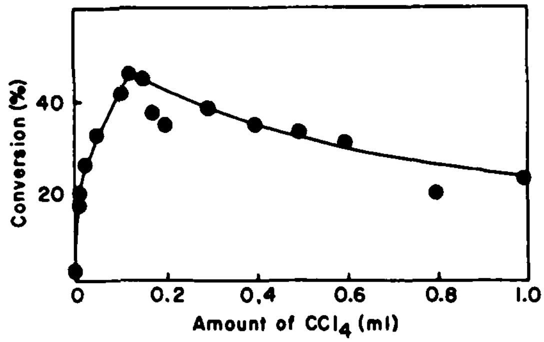

Fig. 3. Effect of the amount of carbon tetrachloride. MMA, 2 ml; water, 10 ml; cellulose, 0.2 g; 85°; 4 hr.

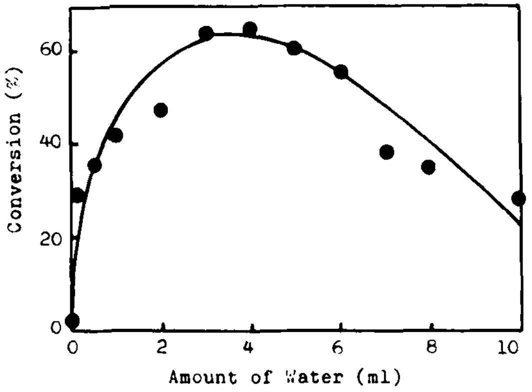

Fig. 4. Effect of the amount of water. MMA, 2 ml; carbon tetrachloride, 0.2 ml; cellulose, 0.2 g; 85°; 4 hr.

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Solvents were purified by the usual methods. Carbon tetrachloride was purified by washing with a 1% aqueous solution of NaOH and then with water. It was dried over anhydrous Na_2SO_4 and distilled. It was passed through a column packed with active alumina before use. The water used was ion-exchanged. Linter pulp or wood pulp was boiled in a large amount of water for 20 hr and dried in a vacuum desiccator.

Procedures

Cellulose, water, carbon tetrachloride, and monomer were introduced into a tube by a glass pipet. The contents of the tube were thrice frozen

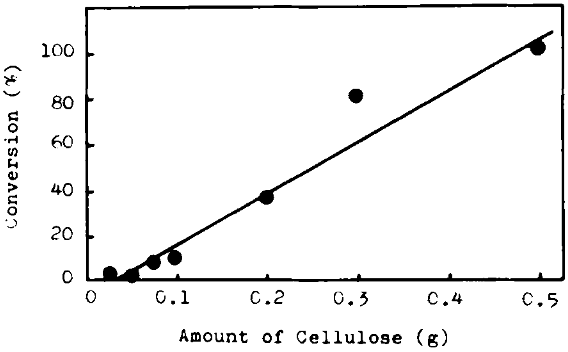

Fig. 5. Effect of the amount of cellulose. MMA, 2 ml; water, 10 ml; carbon tetrachloride, 0.2 ml; 85°; 4 hr.

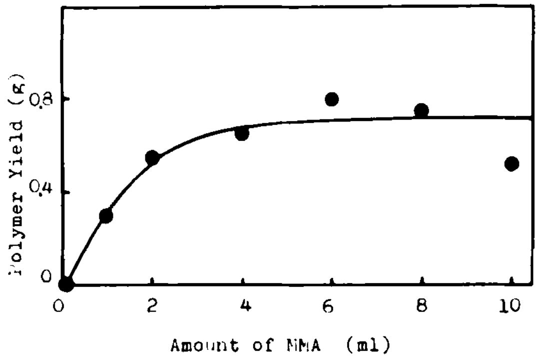

Fig. 6. Effect of the amount of monomer. Water, 10 ml; carbon tetrachloride, 0.2 ml; cellulose, 0.2 g; 85°; 4 hr.

and evacuated. Then the tube was sealed in vacuo, and shaken in the dark in a thermostat. After a definite time, the content was poured into a large amount of methanol to precipitate the polymers.

RESULTS

Indispensability of Cellulose, Water, or Carbon Tetrachloride

As stated above, even with cellulose having no ability for initiation, carbon tetrachloride is able to give the cellulose initiation ability. Water is always necessary. The relation is shown in Table 1.

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Effect of Temperature

Polymerization was carried out between 55-85°C. Figure 1 shows the results. No reproducibility was obtained at 55°C. The over-all activation energy was estimated as 7.7 kcal/mole from the straight lines obtained at 65-85°C (Fig. 2).

Effect of the Amounts of Reagents

Figures 3, 4, and 5 show the relationships between the conversion of MMA and the amounts of carbon tetrachloride, water, and cellulose, respectively. It is also clear from these figures that water and carbon tetrachloride are necessary for polymerization. Conversion was linearly proportional to the amounts of cellulose.

Figure 6 shows the relationship between the yield of polymer and the amount of MMA added.

From the results shown in Figs. 5 and 6, the initiation of polymerization may be considered to proceed through the formation of a complex between cellulose ($-CCl_4$) and MMA. If the rate of formation of free radical is assumed to be proportional to the rate of polymerization, R_p, the relationship between R_p and the amount of MMA may be shown by the following equation, which is rewritten from the Michaelis-Menten equation:

$$\frac{1}{R_p} = \frac{K}{k[\text{cellulose}]}\,\frac{1}{[\text{MMA}]} + \frac{1}{k[\text{cellulose}]}$$

Assuming the amount of MMA to be applicable instead of the concentration of MMA, the value of $1/R_p$ was plotted against the reciprocal of the amount of MMA and a straight line was obtained, as shown in Fig. 7. From this line the Michaelis constant, K, was calculated as 2.8 ml, and $1/k[\text{cellulose}]$ as 0.85 (0.2 g cellulose/g polymer).

Effect of the Kind of Cellulose

Different kinds of cellulose were purified by boiling in water. Table 2 shows the results obtained. Except for cupra-rayon, the other kinds of cellulose polymerized MMA at 17-36% conversion. As to the quantitative conversion by cupra-rayon, it may be considered that a mutual interaction of copper ion, which is contaminated in the fiber, and carbon tetrachloride enhanced the initiation. In order to study the effect of any impurities existing in the linter pulp, the purifications listed in Table 3 were carried out. However, no remarkable changes were observed.

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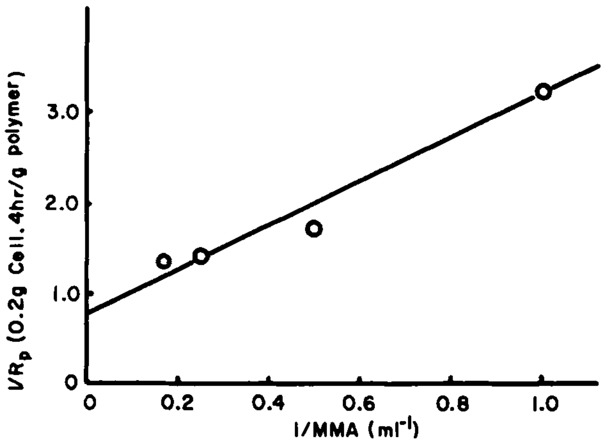

Fig. 7. Michaelis-Menten plot for the polymerization of MMA by the sytem cellulose-water-carbon tetrachloride (85°C).

Table 2. Effect of Various Kinds of Cellulose[a]

Cellulose	Conversion of MMA (%)
Wood pulp	24, 36
Tissue paper	18, 21
Filter paper	17, 22
Cupra-rayon	100
Viscose rayon	23, 36

[a] Cellulose, 0.2 g; MMA, 2 ml; water, 10 ml; CCl_4, 0.2 ml; 85°; 4 hr.

Effect of the Kind of Solvent on Conversion

Some other solvents were used instead of water, as shown in Table 4. As can be seen, water is the most powerful solvent, while methanol or ethanol, having OH group, revealed some activity.

Effect of Atmospheric Oxygen on Conversion

As Table 5 shows, atmospheric oxygen inhibited polymerization.

Table 3. Effect of Washing Commercially Purified Linter Pulp

	Treatment	Conversion (%)
A.	Boiled in water for 8 hr	43, 49
B.	Boiled in water for 20 hr	24, 36
C.	Boiled in water for 100 hr	26, 28
D.	A was extracted with ethanol for 8 hr	29, 39
E.	D was extracted with ether for 8 hr	33, 39
F.	E was boiled in 1% NaOH solution for 3 hr and washed with water	36, 39
G.	F was immersed in 1% $NaBH_4$ solution for 24 hr and washed with water	29, 39

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Table 4. Conversion and Solvent[a]

Solvent	Conversion (%)
Water	24, 36
Acetone	2.0, 1.9
Benzene	0.9, 1.1
Methanol	6.5, 6.8
Ethanol	8.0, 8.5
Dioxane	2.0, 2.1
n-Hexane	0

[a] Solvent, 10 ml; cellulose, 0.2g; CCl_4, 0.2 ml; MMA, 2 ml; 85°; 4 hr.

Polymerization of Other Monomers than MMA

Table 6 shows the polymerization results of some vinyl monomers other than MMA. Acrylates and methacrylates, especially MMA, MA, and BA, show excellent polymerizability with this system.

Effect of Preheating the Cellulose-Water-Carbon Tetrachloride System

When the cellulose (linter pulp) was heated in the presence of water and

Table 5. Effect of Atmospheric Oxygen

	Treatment	Conversion (%)
A.	Sealed in air (atm)	0
B.	Freezing and degassing were carried out 1 time before sealing in vacuo	25, 26
C.	Freezing and degassing were repeated 3 times before sealing in vacuo	24, 30
D.	First, cellulose was degassed at 10^{-3} mm Hg at room temperature and the other reagents were placed by distillation in vacuo	19, 20
E.	The same as D. However, cellulose was degassed at 100-120°C	19, 34
F.	The same as D. However, cellulose was degassed at 150-170°C	100

Table 6. Polymerization of Several Vinyl Monomers[a]

Monomer	Total conversion (%)	Thermal conversion (%)
MMA	23, 46	1.1, 1.6
MA	49, 49	0
BMA	16, 17	2.1
BA	37, 38	4.1
Styrene	3.1, 3.2	2.4
Acryronitrile	0, 0	0

[a] Monomer, 2 ml; linter pulp, 0.2 g; water, 10 ml; carbon tetrachloride, 0.2 ml; 85°C; 4 hr.

carbon tetrachloride before the addition of monomer, its initiating ability was reduced markedly (Table 7). When this treatment was carried out only with carbon tetrachloride, there was no change in its initiating ability. The ability was the same as in the case in which the cellulose was washed with boiling water.

These results show that the above treatments decompose the active groups or the active centers of the cellulose, and that the formation of

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Table 7. Change of the Initiating Ability of Cellulose by Preheating

Treatment	Conversion (%)
None	24, 36
85°C, 30 hr with CCl_4	36, 37
85°C, 30 hr with $CCl_4 + H_2O$	14, 16
85°C, 100 hr with $CCl_4 + H_2O$	5.0, 5.9

active species is through the reaction of cellulose, water, and carbon tetrachloride in the polymerization system.

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