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VINYL POLYMERIZATION. 292. A MACROMOLECULAR EFFECT OBSERVED BY THE POLYMERIZATION OF METHYL METHACRYLATE INITIATED WITH THE SYSTEM OF CELLULOSE, Cu(II)-ION AND WATER

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The system of cellulose, water and Cu(II)-ion can polymerize MMA through a radical mechanism. The rate of polymerization, Rp, is expressed by the equation,

$$Rp = k\ [\text{Cellulose}]^{n}[\text{MMA}]^{1\longrightarrow 0}$$

The value of n decreases from 1.0 to 0.5 with the decrease of the degree of polymerization of the cellulose.

In a series of the papers, we have established that some kinds of macromolecules or oligomers can polymerize methyl methacrylate (MMA) in the presence of water through a radical mechanism. The active center for the initiation was concluded to be a chelate of copper ion or an inclusionscompound of carbon tetrachloride with the macromolecules or with the oligomers.[1)]

Kinetic studies showed that the rate of polymerization (Rp) was proportional to the amount of macromolecules, when the degree of polymerization (DP) was high. For example, linter-pulp[2)] or nylon[3)] gave the following equations:

$$Rp = k\ [\text{Cellulose}]^{1.0}[\text{MMA}]^{1.0\longrightarrow 0.0} \quad (1)$$

$$\text{and } Rp = k\ [\text{Nylon}]^{1.0}[\text{MMA}]^{1.0\longrightarrow 0.0} \quad (2)$$

The reaction order of $1.0\longrightarrow 0.0$ of MMA in the Eq.(1) and Eq.(2) means that when the amount of MMA([MMA]) used is small, the rate is proportional to the [MMA]; however, after [MMA] exceeds some amount, the rate becomes to be independent of [MMA].

When soluble starch[4)] or low moleculer weight polyvinylalcohol ($DP < 9$)[5)] was used, the rate was expressed by Eq.(3) or Eq.(4).

$$Rp = k\ [\text{Soluble Starch}]^{0.5}[\text{MMA}]^{1.0\longrightarrow 0.0} \quad (3)$$

$$\text{and } Rp = k\ [\text{Low mol. wt. PVA}]^{0.5}[\text{MMA}]^{1.0} \quad (4)$$

The difference of the reaction orders of the macromolecules and of the oligomers between 1.0 and 0.5 in Eqs.(1)$\sim$(4) offers an interesting problem. The present paper concerns with the determination of the reaction order of the low molecular weight cellulose in the polymerization of MMA initiated with the system of cellulose, Cu(II)-ion and water.

(1) Experimental. Five kinds of low mol. wt. cellulose were prepared by treating about 7 g of the viscose-type staple rayon (DP 300) with 250 ml of 0.5N- or 2N-HCl aq. solution at 80°C during 2～30 hr. The degree of polymerization (DP) was calculated by Staudinger's equation, Eq. (5), measuring the viscosity in Schweizer's solution.[6]

$$\frac{\eta_{sp}}{c} = 5.0 \times 10^{-3}(DP) \qquad (c = 0.6\ g/dl) \qquad (5)$$

The procedure for the polymerization was as follows; first, cellulose and 10 ml of water containing 10^{-3}g of copper ion ($CuCl_2 \cdot 2H_2O$ was used) were placed in a tube. The tube was flushed with nitrogen, stoppered tightly and stood at room temperature for 40 hr. Then MMA was added and the tube was sealed in vacuo, after flushing with nitrogen. The tube was warmed at 85°C. After a definite interval, the content of the tube was poured into a large amount of methanol to precipitate the polymer formed.

(2) Results and Discussion. In order to determine the reaction order of the cellulose, the polymerizations of MMA were carried out in the presence of various amount of cellulose. The result was shown in Fig.1.

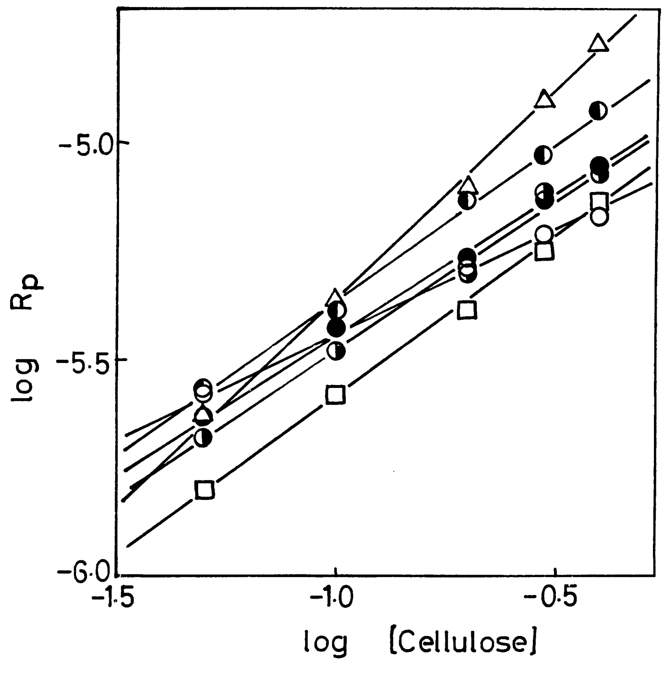

Fig. 1 The Rate of Polymerization of MMA, Rp, vs. the Amounts of Cellulose. (MMA 2 ml, H_2O 10 ml, Cu(II) 10^{-3}g; 85°C)

DP of Cellulose:

○ 25, ◑ 36, ◐ 40, ● 48, □ 66, △ 300

The slopes of the straight lines in the figure gave the reaction orders of the celluloses as listed in Table 1.

Table 1. The Reaction Order of the Cellulose in the Polymerization of MMA. (MMA 2 ml, H_2O 10 ml, Cu(II) 10^{-3}g, Cellulose 0.05 ~ 0.40 g; 85°C)

DP of Cellulose	The Reaction Order of Cellulose
300[a)]	0.95
66	0.73
48	0.64
40	0.71
36	0.67
25	0.48

a) Rayon (TOHO-Regular Type Rayon Staple without TiO_2 was purified by extracting with a mixture of acetone and benzene)

The effects of the degree of polymerization of the cellulose on the yield of the polymerized MMA and the degree of polymerization of homopolymer of MMA were shown in Table 2.

Table 2. Yield and DP of poly-MMA. (MMA 2 ml, H_2O 10 ml, Cu(II) 10^{-3}g, Cellulose 0.40 g; 85°C, 6 hr)

DP of Cellulose	Yield (%)	DP[a)] of homopoly-MMA
300	27.1	17800
66	12.1	26200
48	12.9	24700
40	15.9	30600
36	12.7	31100
25	10.7	28700

a) DP was calculated by the following equation.[7)]

$$\log \bar{P}_n = 3.346 + 1.32 \log[\eta]$$

From the Table 1, it was concluded that the reaction order of cellulose reached to 0.5 from 1.0 by decreasing the degree of polymerization of the cellulose.

Accordingly the difference of the reaction order between 1.0 and 0.5 in the rate equations (1)~(4) was due to the difference of the degree of polymerization of the macromolecule, but not to the kind of the macromolecule. The reason of the difference of the reaction order by the degree of polymerization of the cellulose is not clear.

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