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VINYL POLYMERIZATION. 303. MEASUREMENT OF THE INITIATION RATE OF THE POLYMERIZATION OF METHYL METHACRYLATE BY THE SYSTEM OF SOLUBLE STARCH, WATER, AND CARBON TETRACHLORIDE

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The polymerization of methyl methacrylate initiated with soluble starch, water, and carbon tetrachloride was carried out without shaking. The rate of initiation was measured, using hydroquinone as an inhibitor, and was found to be proportional to the concentration of starch in the water phase.

In the preceding letter$^{1)}$, we have confirmed that the polymerization of methyl methacrylate(MMA) initiated with starch, water and carbon tetrachloride occurs in the aquous phase. Following this confirmation, in this letter we would like to report a measurement of the rate of initiation (R_i).

The measurement of R_i was made dilatometorically, using an apparatus shown in Fig. 1. A round flask of ca. 16 ml (A) was attached to the capillary by the ground glass joint. A solution of purified starch (the degree of polymerization: 30-35) in α ml of water was placed in the tube (B), and a solution of hydroquinone in 2 ml of water in the tube (C). The portions of (D) and (E) were sealed off. The whole apparatus was cooled to -20°C and degassed carefully. Then the tube (B) was coold in a dry ice-methanol bath. After the water in the tube (C) was distilled under vacuum into the tube (B), the portion (E) was opened. β ml of MMA and 0.25 ml of carbon tetrachloride were charged into the tube (C). The whole volume (αml + 2ml + βml + 0.25ml) becomes 16 ml. The portion (E) was sealed off again. The whole apparatus was degassed. The solution in the tube (C) was transfered into the tube (B) to dissolve hydroquinone. Finally, the whole solution was transfered into the dilatometer (A). The inner pressure of (A) was adjusted to 30-40 mmHg with nitrogen. The portion (F) was sealed off. The dilatometer (A) was warmed at 50°C in a thermostat.

Measurement of concentration of MMA in aquous starch solution: From the aquous layer, 1 ml was pipetted out and diluted up to 625 ml with water. The concentration of MMA was determined by the absorption at 2050Å of UV-spectrum.

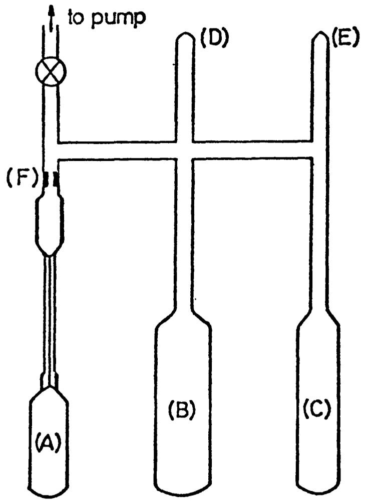

Fig. 1 Apparatus.

The major part of MMA exists separately on the layer of water solution, and the initiating reaction proceeds in the water layer$^{1)}$ (Fig. 2).

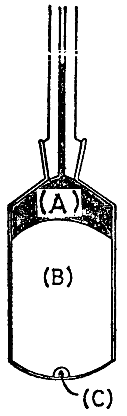

Fig. 2 Appearance of the tube (A).

(A) MMA, Hydroquinone

(B) H_2O, Starch, Hydroquinone, MMA and polymer

(C) CCl_4

For example, the polymerization proceeded, as shown in Fig. 3.

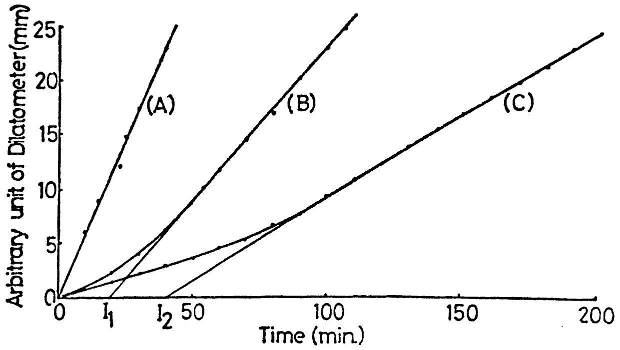

Fig. 3 Effect of hydroquinone. (MMA 3ml, CCl_4 0.25ml, Starch 0.3g, H_2O 12.75ml: 50°C)

Hydroquinone: 0.0g(A), 10.1mg(B), 20.2mg(C)

The points of I_1 and I_2 denote the induction period(IP). Granting that one molecule of hydroquinone can react with one propagating chain, R_i can be easily calculated, as listed in Table 1. A part of added hydroquinone may dissolve in the upper MMA layer (Fig. 2). Accordingly, the calculated values of R_i were not absolute, but only apparent. However, as the amount of MMA is constant, these values of R_i may be considered to be proportional linearly to the absolute values of the rate of initiation.

Table 1. Measurement of R_i of the polymerization of MMA by starch, water and CCl_4 at 50°C.
(MMA 3ml, CCl_4 0.25ml, Water 12.75ml: Total Volume 16ml)

Hydroquinone ($\times 10^{-4}$mole)	Starch (g)	IP (min)	R_i ($\times 10^{-6}$mole/min)
1.92	0.1	108	1.77
1.92	0.2	74	2.59
1.83	0.3	41	4.46
1.90	0.4	38	5.01
2.85	0.5	40	7.08

Fig. 4 shows that the rate of initiation is a linear reletionship with the amount of starch dissolved in water, which is able to be expressed by Equation (1).

$$R_i = \text{const. [amount of starch added]}^{1.0} \qquad (1)$$

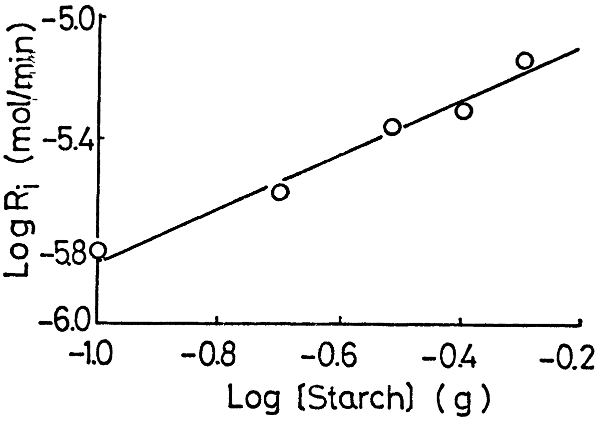

Fig. 4 Rate of initation vs. the concentration of starch.
(MMA 3ml, CCl_4 0.25ml, H_2O 12.75ml: 50°C)

Although a part of water dissolves into MMA-layer, the amount of starch is assumed to be proportional almost linearly to its concentration, because the amount of water used is constant at 12.75 ml. Accordingly, the equation (1) may be rewritten as Equation (2).

$$R_i = \text{const. } [\text{starch}]^{1.0} \qquad (2)$$

Next, the amounts of CCl_4 and starch were kept at constant and the amount of MMA (also the amount of water) were varied. The results was shown in Fig. 5.

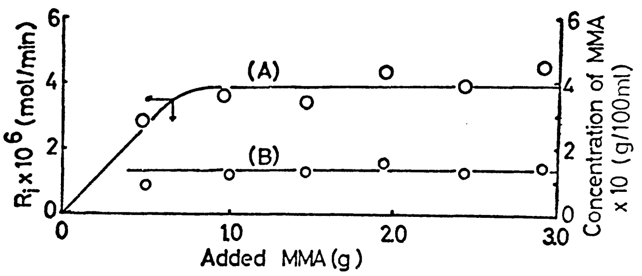

Fig. 5 (A) Rate of initiation vs. amount of MMA added.
(B) Concentration of MMA in the water layer vs. amount of MMA added.
(Starch 0.3g, CCl_4 0.25ml, H_2O 12.75–15.25ml; Total Volume 16ml: 50°C)

From the line (A), R_i is considered to be constant, even if the amount of MMA is changed in the range of 1 to 3 ml. In the preceding paper, we have reported that Rp was independent of the amount of MMA in the same range. The results on R_p obtained in the preceeding paper coincides well with those obtained here on R_i.

According to the line (B) in Fig. 5, the concentration of MMA in the water layer may be considered to be independent of the amount of MMA.

Those results support reasonablly our assumption that the initiation center is a complex of starch with carbon tetrachloride, water and MMA.

Reference

1) M.Imoto, K.Ree and T.Ouchi, preceding letter.

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