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VINYL POLYMERIZATION. 302. POLYMERIZATION OF METHYL METHACRYLATE WITHOUT SHAKING WITH THE SYSTEM OF STARCH, WATER AND CARBON TETRACHLORIDE

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Polymerization of methyl methacrylate(MMA) initiated with aquous starch solution in the presence of carbon tetrachloride was carried out on standing. The rate of polymerization and the molecular weight of the polymer obtained were faster and higher than those under shaking. It was found that the polymerization initiated and proceeded in the water layer. The rate of polymerization(R_p) was concluded to be expressed by the equation: R_p = const.[starch]$^{1.0}$

1. Introduction

Recently$^{1)}$, the polymerization of methyl methacrylate(MMA) initiated with soluble starch(DP:30), water and carbon tetrachloride was carried out under shaking. The rate of polymerization(R_p) was concluded to be proportional to the 0.5 power of the amount of starch added.

$$\text{Under shaking:} \quad R_p = \text{const.}[\text{starch}]^{0.5} \qquad (1)$$

In the present letter, we would like to report the polymerization of MMA without shaking. The method of polymerization on standing gave us some interesting results. (i) Strange to say, the rate of polymerization is faster about four times than that in the case under shaking, and is expressed by the following Equation (2) which is different from Equation (1).

$$\text{On standing:} \quad R_p = \text{const.}[\text{starch}]^{1.0} \qquad (2)$$

(ii) The number-average degree of polymerization($\bar{P}_n$) of the poly-MMA obtained on standing is much higher than that of the poly-MMA obtained under shaking.

(iii) The polymerization proceeds in a water layer containing starch.

2. Experimental

Materials: Soluble starch was purified by the reprecipitation from water by ethyl alcohol. MMA was purified by the conventional method. Water was ion-exchanged and distilled. Carbon tetrachloride was passed through an alumina column and distilled under vacuum in the stream of nitrogen.

Procedure: In a tube, carbon tetrachloride, aquous starch solution and MMA were placed successively. The tube was degassed carefully using nitrogen and sealed in vacuo and was allowed to stand without shaking in a thermostat at 50°C. The content consisted of three layers, as shown in Fig. 1(a). As the polymerization proceeded, the water layer became turbid by the generation of polymerized MMA, as shown in Fig. 1(b).

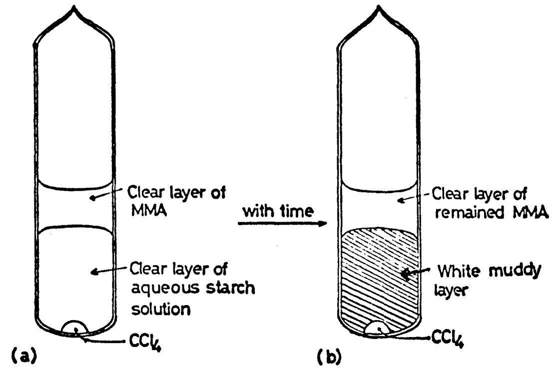

Fig. 1 Appearance in the tube.

After definite time, the content in the tube was poured into a large amount of methanol to precipitate the poly-MMA formed.

Determination of the number-averge degree of polymerization($\bar{P}_n$): $\bar{P}_n$ of poly-MMA was determined from the viscosity of the benzene solution, using the following equation[2)]:

$$\log \bar{P}_n = 3.346 + 1.32 \log [\eta] \qquad (3)$$

3. Results and Discussion

3.1. Location in where the polymerization occurs.

As the figure 1(b) suggested, it seemed that the polymerization proceeded in the water layer. This consideration was confirmed by the following two experiments. (i) After 5 hrs of polymerization, 2 ml of the MMA layer was pipetted out and poured into methanol. No precipitation was observed. Furthermore, 2 ml of the MMA layer was evaporated under vacuum to dryness and only a trace of the residue was obtained. Accordingly, the polymerization occurred scarcely in the layer of MMA. (ii) 1,3,5-triphenyl verdazyl was dissolved in MMA and the polymerization was carried out as described above in Fig. 1. The water layer became cloudy with the formation of poly-MMA. However, a green color of triphenyl verdazyl in MMA layer remained unchanged apparently. Thus the location of the polymerization was concluded to be in the aquous starch layer.

3.2. Rate of polymerization on standing.

As compared of R_p and $\bar{P}_n$ in the case under shaking with those in the case on standing, the results obtained were listed in Table 1.

Table 1. Polymerization of MMA at 50°C.
(Starch 0.3g, Water 10ml, CCl_4 0.25ml; 5hrs)

	MMA(ml)	Poly-MMA	
		Yield(g)	$\bar{P}_n \times 10^{-4}$
Under shaking	1	0.0710	1.44
	2	0.0561	1.65
	3	0.0616	—
On standing	1	0.2653	2.74
	2	0.2601	2.68
	3	0.2515	3.16

The yields of poly-MMA were constant at 0.06g and 0.26g under shaking and on standing respectively, using 1, 2 and 3 ml of MMA. A fact has been repeatedly reported that when the amount of MMA exceedes a certain limit, the yield of poly-MMA is independent of the amount of MMA. It was astonishing that the yields of the polymer on standing were higher about four times than those under shaking. And also $\bar{P}_n$ obtained in the case without shaking were much higher than those under shaking. Accordingly, it was considered that the rate of termination decreased by standing still, thus $\bar{P}_n$ and the yieleds increased.

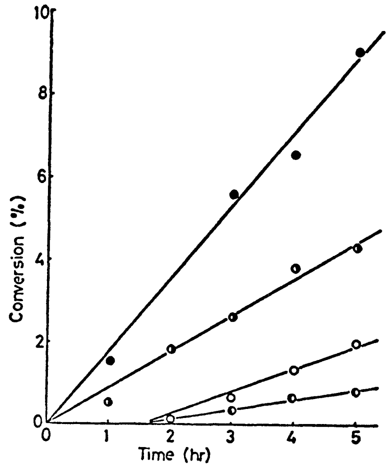

Fig. 2 Time-conversion curves in the polymerization on standing.

MMA 3ml, H_2O 10ml, CCl_4 0.25ml; 50°C
Starch: ● 0.3g, ◑ 0.2g, ○ 0.1g, ◐ 0.05g

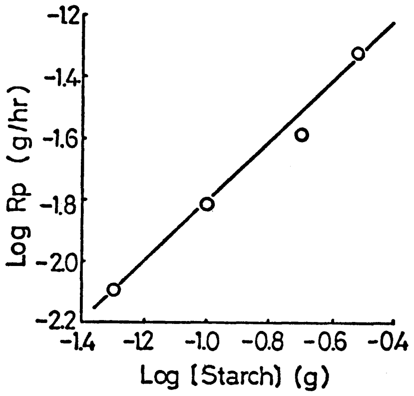

Fig. 3 Log R_p vs. Log [Starch].

In order to determine the effect of the concentration of starch in the water layer on the rate of polymerization, the polymerizations were carried out by keeping the amount of MMA, water and CCl_4 constant at 3 ml, 10 ml and 0.25 ml, respectively. The results obtained were shown in Fig. 2. From the inclinations of the lines, R_p were calculated, giving Fig. 3. Thus R_p can be expressed by Equation (2). The cause of the difference between Equations (1) and (2) can not be clearly explained here. However, it may be able to assume that in the polymerization on standing, a monomolecular termination proceeds in the aquous layer, but in the case under shaking, a bimolecular termination occurs in the MMA layer. The monomolecular termination means here that a propagating chain terminates by occlusion of the radical end or by the reaction with solvent or monomer, etc. Experiments in order to confirm this assumption are going on.

The degrees of polymerization of poly-MMA obtained in the experiments drawn in Fig. 2 were measured to give the result as shown in Fig. 4. As can be seen from the figure, when the larger amount of starch was used, the smaller value of $\overline{P}_n$ was observed.

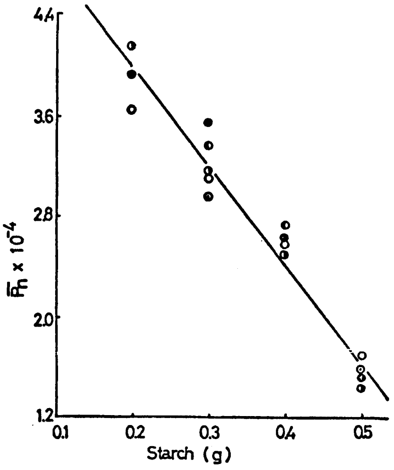

Fig. 4 $\overline{P}_n$ of poly-MMA vs. amount of starch.

Polymn. Time: ⊙ 1hr, ● 2hrs, ◐ 3hrs, ◑ 4hrs, ○ 5hrs

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