NOTES

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Vinyl Polymerization. 239.[*1] Polymerization of Methyl Methacrylate with Cellulose Triacetate in Presence of Various Solvents

Kanemitsu KUBUSHIRO, Kiichi TAKEMOTO[*2] and Minoru IMOTO

Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sumiyoshi-ku, Osaka

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Recently, fibrous cellulose triacetate (CTA) was found to initiate the polymerization of methyl methacrylate (MMA) in the presence and absence of water.[1)] The present paper concerns a further study on the polymerization of MMA initiated with CTA in the presence of various solvents. The initiation of polymerization seems to be referred to an interaction of some active sites on CTA with MMA, but the essential feature of the polymerization remains uncertain.

Experimental

All of the procedures were the same as in the previous paper.[1)] The degree of swelling of CTA was measured in the following way: CTA was dissolved at first in dichloromethane and ethanol mixture (9 : 1 in vol.), and the solution was spread onto a glass plate. The cast film obtained after drying was transparent and colorless, and of 0.208 mm in thickness. 0.1 g of the CTA film was placed in a test tube, with a mixture of methyl isobutyrate with other solvents. The tube was sealed off and kept at 30°C for 24 hr, and thereafter, the weight increase of the CTA films was measured.

Results and Discussion

Effect of Solvents on the Rate of Polymerization. Figure 1 shows examples of time-conversion curves, where polymerization was carried out in the presence of various solvents. As shown in Fig. 1, a small amount of ethyl acetate acted to decrease the rate of polymerization, while *n*-hexane to accelerate it considerably.

Figure 2 shows the initial rates of polymerization calculated from the initial slopes of time-conversion curves. This figure shows that the value of the rate of polymerization (percent per hour) divided by the monomer concentration is constant, regardless of the monomer concentration, except the cases where *n*-hexane, dichloromethane and ethyl acetate were used. This result means that benzene, ethanol, dimethylformamide and carbon tetrachloride acted only as diluents.

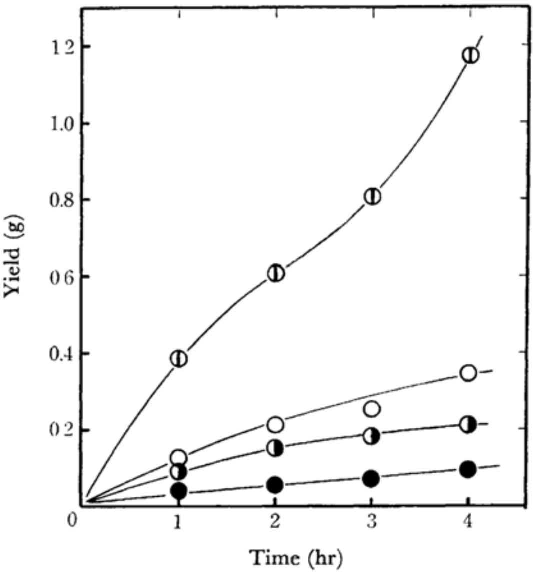

Fig. 1. Polymerization of MMA in the presence of various solvents. Total volume 5 m*l*, CTA 0.5 g, at 85°C.

⦶ *n*-hexane 3 m*l* ○ MMA in bulk

◑ carbon tetrachloride ● ethyl acetate

The relation between the degree of swelling and the solvent composition is shown in Fig. 3. The solvents consisted of methyl isobutyrate and other organic solvents which were used for polymerization. Methyl isobutyrate was chosen instead

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[*1] Part 238 of the series: T. Nakaya, Y. Maki and M. Imoto, *Makromol. Chem.*, **125**, 161 (1969)

[*2] Present address: Department of Petr ochemistry, Faculty of Engineering, Osaka University, Yamada-Kami, Suita, Osaka.

1) K. Kubushiro, K. Takemoto and M. Imoto, *Makromol. Chem.*, **120**, 39 (1968).

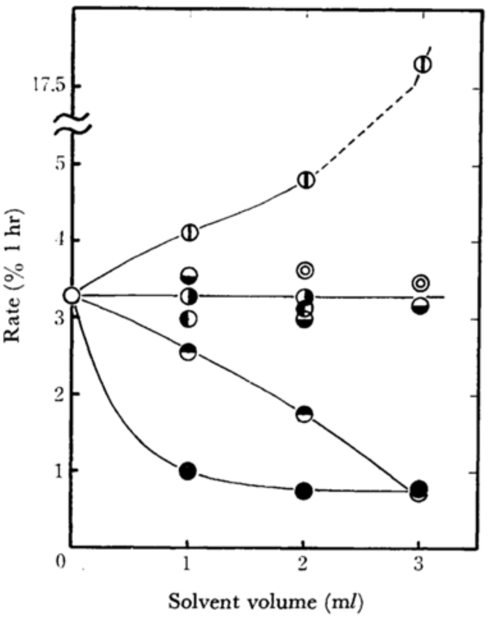

Fig. 2. Rate of Polymerization in various solvents. Total volume 5 ml, CTA 0.5 g, at 85°C.

⊖ *n*-hexane ◒ benzene
◑ carbon tetrachloride ◐ dimethylformamide
◓ dichloromethane ● ethyl acetate
◎ ethanol

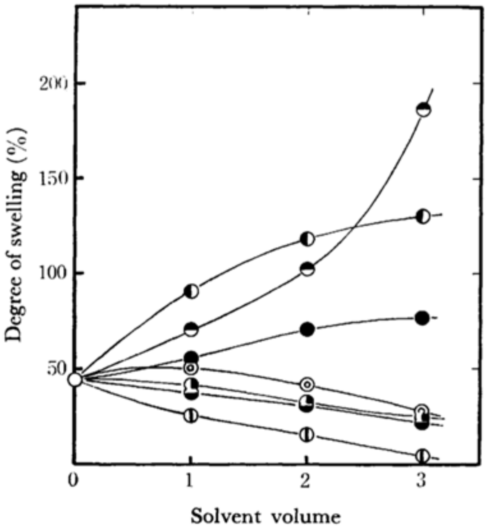

Fig. 3. Degree of swelling of CTA in methyl isobutyrate and various solvents. Total volume 5 ml, CTA 0.1 g, 30°C for 24 hr.

◓ dichloromethane ◐ dimethylformamide
● ethyl acetate ◎ ethanol
◑ carbon tetrachloride, ◒ benzene
⦶ *n*-hexane

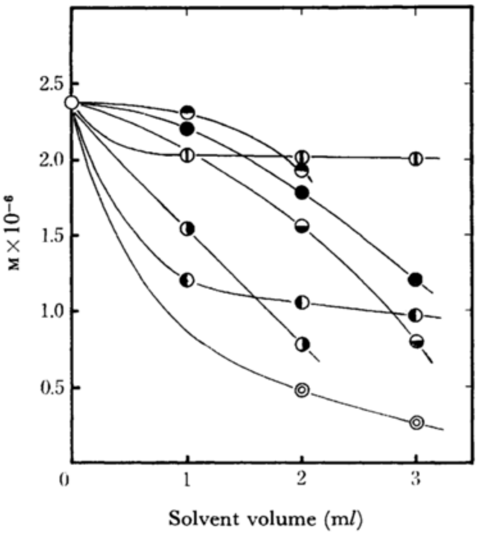

Fig. 4. Molecular weight of extracted PMMA polymerized in various solvents. Total volume 5 ml, CTA 0.5 g at 85°C.

◓ dichloromethane ● ethyl acetate
⦶ *n*-hexane ◒ benzene
◑ carbon tetrachloride ◐ dimethylformamide
◎ ethanol

of MMA, because their structures are similar. The effect of solvents on the rate of polymerization seems to show no parallelism with the swelling ability of these solvents for CTA.

From Figs. 2 and 3, in which different solvents are given, we see that polymerization preceeds not only inside CTA, but also outside it. This consideration agrees with that reported in a previous paper,[1] *viz.*, the rate of polymerization is proportional to the square root of CTA and to the monomer concentration.

As can be seen from Fig. 2, in the case of *n*-hexane, the rate of polymerization increases with the decrease in the concentration of monomer. When the concentration is 3.74 mol/*l*, the rate is about six times larger than that obtained in the other normal solvents. This result seems to be in line with the following consideration: *n*-hexane dose not swell CTA but dissolves MMA, while a part of MMA swells CTA and the rest of MMA remains in *n*-hexane. Thus, MMA is divided between CTA and *n*-hexane, and CTA swells with MMA. Accordingly, the interior of the fiber becomes a viscous polymerizing system for MMA, that is, an effect similar to the gel effect arises even in the initial stage of polymerization. As MMA is consumed by polymerization in the interior of the fiber, MMA is supplied successively from the *n*-hexane solution.

Next, we may consider the retardation effect of ethyl acetate. The structure of ethyl acetate is like that of MMA and ethyl acetate also can swell CTA. If ethyl acetate has some interaction with active sites on CTA, the interaction of MMA with these sites may be hindered and then the formation of radical is retarded.

On the other hand, a thermal polymerization of MMA in ethyl acetate was carried out in the absence of CTA. The time-conversion curve obtained was similar to that in the Fig. 1. Accordingly, the corresponding curve in the figure seems to be the one caused by thermal polymerization.

The mechanism of initiation remains still to be clarified, which will be dealt with more exactly in the near future.

Molecular Weight of Poly-MMA obtained in the Presence of Solvents. The molecular weight of homopolymer of MMA obtained in the presence of various solvents, with the exception of *n*-hexane, was found to decrease gradually with an increase in the amount of the solvent. The results are shown in Fig. 4. The decrease may be due to the chain transfer effect on the solvents. The reason why the molecular weight is not affected by the presence of *n*-hexane, would come from the following view: CTA has only little affinity for *n*-hexane, so that only a very minor amount of *n*-hexane would be present in the interior of CTA, even when a larger amount of *n*-hexane was added in the reaction system.

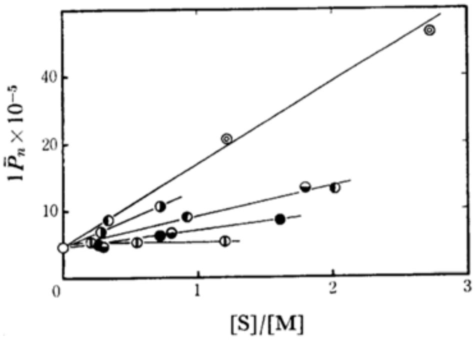

Fig. 5. Relationship between $1/\bar{P}_n$ and [S]/[M].

◎ ethyl
◑ carbon tetrachloride
◒ benzene
◐ dimethylformamide
● ethyl acetate
⦶ *n*-hexane

In the presence of solvent, number average molecular weight of the polymers can be expressed by the following equation:

$$1/\bar{P}_n = C_m + C_s[\mathrm{S}]/[\mathrm{M}] + k_t/k_p \cdot \frac{[\mathrm{M}\cdot]}{[\mathrm{M}]} \qquad (1)$$

In this equation, the value of $k_t/k_p \cdot [\mathrm{M}\cdot]/[\mathrm{M}]$ would be very much smaller as compared with C_m, as was reported in the previous paper,[1] so it can be simplified to

$$1/\bar{P}_n = C_m + C_s \frac{[\mathrm{M}]}{[\mathrm{S}]} \qquad (2)$$

From the data in Fig. 4, a linear relationship between $1/P_n$ and [S]/[M] is obtained as shown in Fig. 5. The C_s value calculated is of the same order as that reported in literature,[2] where number average molecular weight of the polymers was estimated according to the following relationship, assuming that the molecular weight distribution of each polymer is identical and obeys Schulz's equation.[3]

$$M_n = 1/2 \cdot \bar{M}_w \qquad (3)$$

C_s values obtained in the experiment are shown in Table 1.

TABLE 1. C_s VALUES OF VARIOUS SOLVENTS TO POLY-MMA RADICAL

Solvent	$C_s \cdot 10^5$
Ethanol	14.6
Carbon tetrachloride	8.2
Dimethylformamide	4.6
Ethyl acetate	2.6
n-Hexane	0.0

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2) "Polymer Handbook," ed. by J. Brandrup and E. H. Immergut, Interscience Publ., New York (1966), II-101.

3) G. V. Schulz, *Z. physik. Chem.*, **B30**, 379 (1935); *Chem. Abstr.*, **30**, 2460 (1936).