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POLYMERIZATION OF METHYL METHACRYLATE INITIATED WITH POLY(FORMYLSTYRENE)*

Minoru IMOTO, Takamasa MAEDA, Noriyuki MURAYAMA, and Tatsuro OUCHI
Department of Applied Chemistrym Faculty of Engineering,
Kansai University, Suita Osaka 564

The polymerization of methyl methacrylate(MMA) initiated by poly(formylstyrene)(PFS) was carried out in p-dioxane at 85°C. The rate of polymerization was expressed by the following equation: R_p = const. $[PFS]^{0.43}[MMA]^{1.31}$. The polymerization proceeded homogeneously through a radical mechanism. The initiating ability of PFS was found to be larger than that of benzaldehyde indicating a macromolecular effect on the polymerization.

Introduction

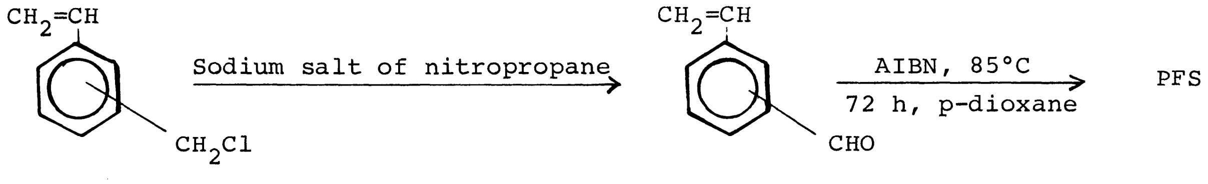
Gaylord et al.[1)] and Imoto et al.[2)] found that cellulose containing CHO group had somewhat strong promoting ability for the polymerization of methyl methacrylate (MMA). Švec et al.[3)] could polymerize MMA, using a crosslinked terpolymer having pendent CHO groups, as an initiator. And we found that aldehyde compounds such as benzaldehyde(PhCHO)[4)] and vanillin[5)] could initiate the radical polymerization of methyl methacrylate(MMA) in the absence of usual initiators or metal ions. Furthermore, in the hope for the macromolecular promoting effect, the polymerization of MMA was carried out using vanacryl (poly(4-formyl-2-methoxy)phenyl methacrylate)[5)] as a macromolecular initiator having vanillin units. However, the initiating ability of vanacryl was only slightly larger than that of vanillin. This was explained by the participation of the ester carbonyl group of vanacryl in the initiation step.

The present paper deals with the polymerization of MMA initiated by poly(formylstyrene)(PFS) having no ester carbonyl group.

Experimental

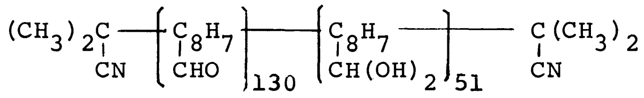
Materials

PFS was prepared by the following scheme, according to the method of Satomura.[6)]



(m- : p- , 68 : 30)   Bp. 74.5-75.5°C / 2.5 mmHg

PFS was purified twice by reprecipitation from p-dioxane and methanol. Number-average mol. wt. was 25000 (GPC). IR (KBr): 2830, 2730, 1695 cm^{-1}(CHO); 3450 cm^{-1} (hydrated CHO). Found: C% 78.82, H% 6.43. Assuming that PFS has the following copolymer structure, the values of the elemental analysis and mol. wt. agree with those calculated.



$$(CH_3)_2\underset{CN}{C}-\left[\underset{CHO}{C_8H_7}\right]_{130}-\left[\underset{CH(OH)_2}{C_8H_7}\right]_{51}-\underset{CN}{C}(CH_3)_2$$

PFS

$C_{1637}H_{1562}N_2O_{232}$
Mol. wt. 24948, DP 181
Calcd. C% 78,81, H% 6.31

PhCHO, MMA, Styrene(St) and acrylonitrile(AN) were purified by usual methods. p-Dioxane was passed through a column filled with alumina, and distilled.

Polystyrene(PSt) having a degree of polymerization(DP) of 155 (GPC) was prepared by the usual fractional precipitation of the polystyrene which was obtained by the radical polymerization of St initiated with AIBN. DP of PSt is near to DP(181) of PFS.

PhCHO, PFS, PSt and vanacryl (mol. wt. 5×10^5) were found not to contain peroxide groups by KI method.

Procedure

The polymerization was carried out in a tube sealed under vacuum, with shaking at 85°C in dark. After a given time, the content of tube was poured into methanol to precipitate the polymer. The conversion of MMA was calculated from the weight of the polymer produced. The rate of polymerization, R_p, was calculated by the following equation.

$$R_p^2 = R_p^2 \text{ overall} - R_p^2 \text{ thermal} \qquad (1)$$

Here, R_p overall and R_p thermal denote the rates of polymerization in the presence and absence of PFS, respectively.

Results and Discussion

Selectivity of Vinyl Monomer

The polymerization of vinyl monomers with PFS was carried out in p-dioxane at 85°C for 3 h. The results obtained were shown in Table I. The polymerization of MMA was specifically initiated with PFS, while those of St and AN were not.

Comparison of Initiating Ability of PFS with those of PhCHO and Vanacryl

The initiating ability of PFS for the polymerization of MMA was compared with those of PhCHO and vanacryl, and the results obtained are shown in Fig. 1. From this figure, it was clear that PFS had the larger initiating activity than PhCHO. This can be regarded as the macromolecular effect.

In order to investigate the nature of the macromolecular effect, the polymerization of MMA by PhCHO was carried out in the presence of PSt. If the effect by PFS is only related to the increased viscosity of the polymerization system, then the conversion of MMA by PhCHO in the presence of PSt should be near to that by PFS.

Table I

Polymerization of Vinyl Monomer with PFS[a]

Monomer	PFS(g)	Conversion(%)
MMA	0	0.9
	0.2	3.1
St	0	0.7
	0.2	1.0
AN	0	0
	0.2	0.7

[a] Monomer 3 cm^3, dioxane 7 cm^3; 85°C, 3 h.

Because, DP of PSt is 155 which is near to 181 of DP of PFS. The results obtained were shown in Fig. 2. The viscosity effect of PSt was observed as the vertical difference between the curves A and B. Also the effect could be seen in the increasing thermal conversion of the curve C. In these cases, the viscosity effects were not so large. Accordingly, the macromolecular effect of PFS was concluded to be other than the viscosity effect.

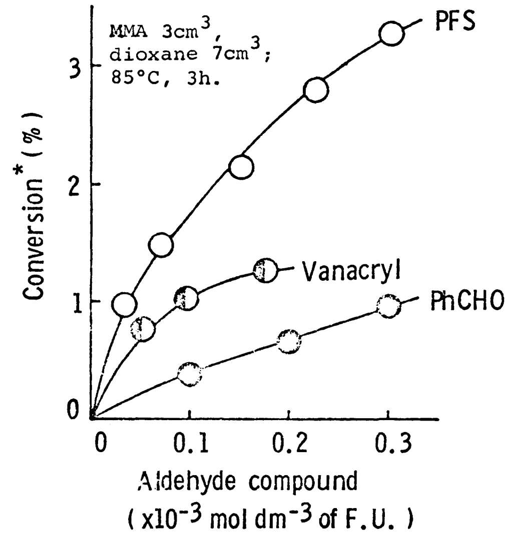


Fig. 1. Comparison of the initiating activity of PFS with those of PhCHO and vanacryl.

* Thermal conversion of MMA was subtracted.

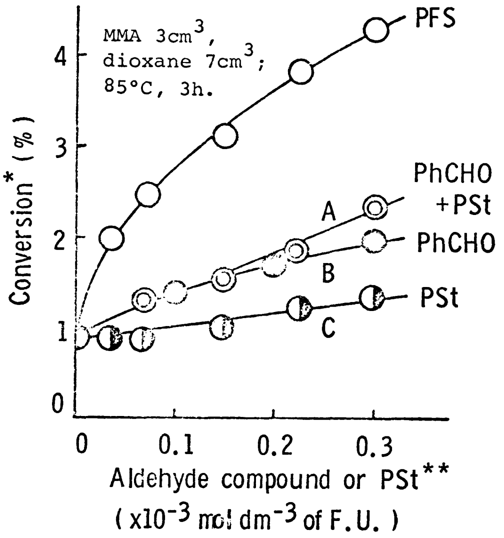


Fig. 2. Effect of viscosity on the conversion of MMA.

* Including the thermal conversion.

** The dissolved unit moles of PSt correspond to those of PFS.

Proof of Radical Mechanism

Into a mixture of 3 cm^3 of MMA, 0.2 g of PFS and 7 cm^3 of p-dioxane, 0.1 g of 1,1-diphenyl-2-picrylhydrazyl(DPPH) was added. The polymerization was completely inhibited by DPPH. Thus, the polymerization was suggested to proceed through a radical mechanism.

Effects of Concentrations of PFS and MMA

In order to investigate the influence of the concentrations of PFS and MMA, the plots of log R_p vs. log[PFS] and log[MMA] were made in Fig. 3. From the slopes of these straight lines, R_p was found to be expressed by Eq. (2).

$$R_p = k[\mathrm{PFS}]^{0.43}[\mathrm{MMA}]^{1.31} \qquad (2)$$

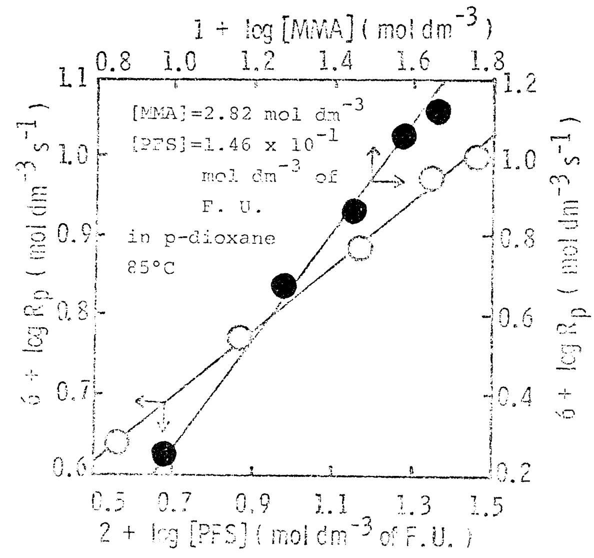


Fig. 3. Effects of the concentrations of PFS and MMA on the rate of polymerization.

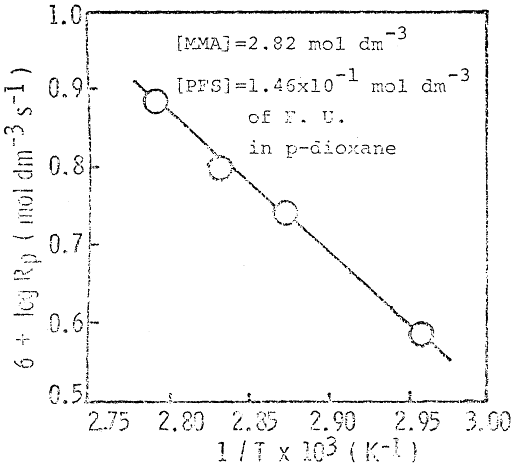


Fig. 4. Arrhenius plot.

In the case of PhCHO, R_p was found to be proportional to $[PhCHO]^{0.5}[MMA]^{1.5}$. Accordingly, the polymerization mechanism with PFS is assumed to be the same as that with PhCHO, which was proposed in the previous paper.[1)]

Estimation of Overall Activation Energy

Keeping the feeded concentrations of reactants at constant, the polymerization of MMA was carried out at 65-85°C. The Arrhenius plot was made as shown in Fig. 4. From the slope of the straight line obtained, the overall activation energy was estimated to be 36.3 kJ mol^{-1}. This value was smaller than 56.3 kJ mol^{-1} obtained for the polymerization in benzene, initiated by PhCHO.

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* Part 384 of Studies on Vinyl Polymerization.

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