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POLYMERIZATION OF METHYL METHACRYLATE INITIATED WITH VANILLIN[*]

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Vanillin was found to initiate the polymerization of methyl methacrylate(MMA) in benzene at 85°C. The effects of the concentrations of vanillin and MMA on the rate of polymerization and on the degree of polymerization of poly-MMA were investigated. A probable initiation mechanism proposed. The polymerization is assumed to proceed through a radical mechanism. The polymeric effect of the polymer containing vanillin units was also studied.

Introduction

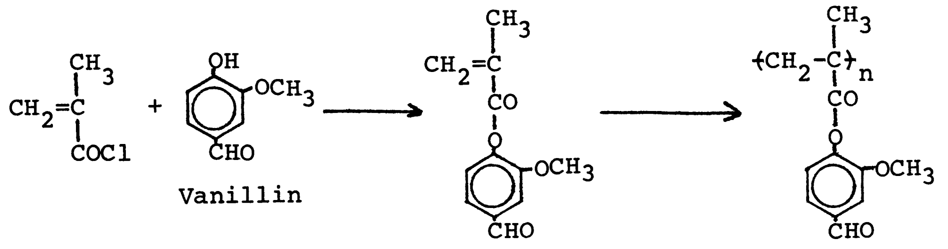
We have interests in the study of the radical polymerization initiated with aldehyde groups. Imoto, Oishi and Ouchi[1,2] reported that poly(styrene-co-acrolein) and poly(styrene-co-methyl vinyl ketone) can initiate the radical polymerization of MMA in dioxane in the absence of usual initiator or metallic salt. Also, Imoto, Maeda and Ouchi[3] found that benzaldehyde behaves as a radical initiator for the polymerization of MMA in benzene.

The present paper concerns with the vinyl polymerization with vanillin. MMA was polymerized, while styrene(St) and acrylonitrile(AN) were not. Furthermore, the polymerization of MMA with vanacryl(poly-(4-formyl-2-methoxy)phenyl methacrylate), which is a macromolecule having vanillin as pendent groups, was dealt.

Experimental

Materials

Vanillin was purified by repeated recrystallization from water; mp 82.3-82.8°C. Vanacryl was prepared by the method of Brown et al.[4]



Vanacryl

Twenty grams of vanillin, 24.2 cm^3 of triethylamine and 90 cm^3 of benzene were placed in a three-necked flask equipped with a stirrer and a condenser. A mixture of 10 cm^3 of benzene and 14 cm^3 of methacryloyl chloride containing 0.16 g of benzoquinone was dropped into the above solution, maintaing the reaction temperature at 5°C. After 1 h, the reaction mixture was extracted with benzene. After benzene was evaporated under a reduced pressure, (4-Formyl-2-methoxy)phenyl methacrylate was recrystallized from petroleum ether; mp 56.5-58.0°C (56-58°C); the yield was 85%. Then, a mixture of 10.8 g of (4-formyl-2-methoxy)phenyl methacrylate, 12.4 mg of α,α'-azobisisobutylonitrile and 80 cm^3 of dioxane was placed in a sealed tube, and the polymerization was carried out under vacuum in dark at 60°C, after thawing in nitrogen. After 24 h, the content of the tube was poured into a large amount of methanol to precipitate the polymer. The polymer was purified by repeated reprecipitation with dioxane-methanol system; the yield was 95%. Number-average molecular weight of vanacryl estimated by GPC method was 5×10^5. The purity of vanillin was confirmed by the one peak in high liquid chromatograph, using methanol as elute. Moreover, vanillin and vanacryl were confirmed to have no peroxide group by KI-method. Monomers and solvents were purified by the usual methods.

Procedure

Reactants and benzene were placed in a tube and sealed under vacuum after thawing in nitrogen. The tube was shaked at 85°C in dark. After a definite time, the contents of the tube was poured into a large amount of methanol to precipitate the polymer. The number-average degree of polymerization($\bar{P}_n$) of poly-MMA was calculated by Welch's equation⁵⁾ on the basis of the viscosity measured in benzene at 30°C. The conversion was calculated by following equations.

In the case of vanillin

$$\text{Conversion}(\%) = \frac{\text{Weight of precipitate (g)}}{\text{Weight of monomer (g)}} \times 100$$

In the case of vanacryl

$$\text{Conversion}(\%) = \frac{\text{Weight of precipitate(g)} - \text{Initial weight of vanacryl(g)}}{\text{Weight of monomer(g)}} \times 100$$

Results and Discussion

Selectivity of Vinyl Monomer

The polymerizations of vinyl monomers with vanillin were carried out in benzene at 85°C for 3 h. The results obtained were shown in Table I. The polymerization of MMA was initiated by vanillin successfully, while those of St and AN did not occur.

Table I

Polymerization of Vinyl Monomer with Vanillin[a]

Monomer	Vanillin (g)	Conversion (%)
MMA	0	0.4
	2	3.9
St	0	0.6
	2	0.6
AN	0	0
	2	trace

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

Effect of the Concentration of Vanillin

In order to investigate the effects of concentration of vanillin on the rate of polymerization (R_p) and on the degree of polymerization of poly-MMA, the polymerizations were carried out, keeping the concentration of MMA constant and varing the concentration of vanillin. From the results shown in Fig. 1, R_p and $\bar{P}_n$ can be expressed by Eqs.(1) and (2), respectively.

$$R_p = k[\text{Vanillin}]^{1/2} \quad (1) \qquad 1/\bar{P}_n = A[\text{Vanillin}]^{1/2} + B \quad (2)$$

Effect of the Concentration of MMA

The polymerizations were carried out by keeping the concentration of vanillin constant and varing the concentration of MMA. The plots of log R_p vs. log [MMA] and the plots of the amount of MMA vs. $\bar{P}_n$ of poly-MMA were shown in Fig. 2. As can be seen in this figure, R_p can be expressed by Eqs.(3) and (4), respectively.

$$R_p = k'[\text{MMA}]^{3/2} \quad (3) \qquad 1/\bar{P}_n = A'[\text{MMA}]^{-1/2} + B' \quad (4)$$

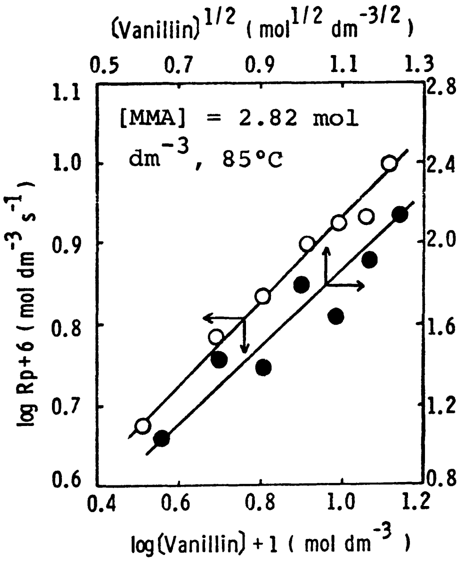


Fig. 1. Effects of the amount of vanillin on the rate of polymerization and $\bar{P}_n$ of poly-MMA

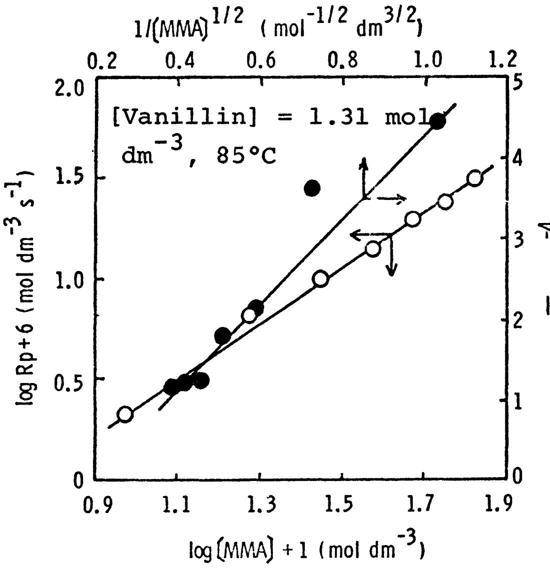


Fig. 2. Effects of the amount of MMA on the rate of polymerization and $\bar{P}_n$ of poly-MMA

Proof of Free-radical Mechanism

Into a mixture of 3 cm^3 of MMA, 2 g of vanillin and 7 cm^3 of benzene, 0.1 g of 1,1-diphenyl-2-picrylhydrazyl (DPPH) was added. The results obtained were listed in Table II. As can be seen, the polymerization was inhibited by DPPH. Thus, it was suggested that the polymerization proceeded through a free radical mechanism.

Table II

Effect of DPPH on the Polymerization of MMA[a].

MMA (cm^3)	Vanillin (g)	DPPH (g)	Conversion (%)
3	2	0	3.9
3	2	0.1	0

[a] Benzene 7 cm^3; 85°C, 3 h.

Polymerization of MMA in the Presence of Vanacryl

In order to study the macromolecular effect on this polymerization, vanacryl was used as an initiator, instead of vanillin. The results were shown in Table III. Comparing with Table I, it is clear that the rate of polymerization was smaller than that in the case of vanillin.

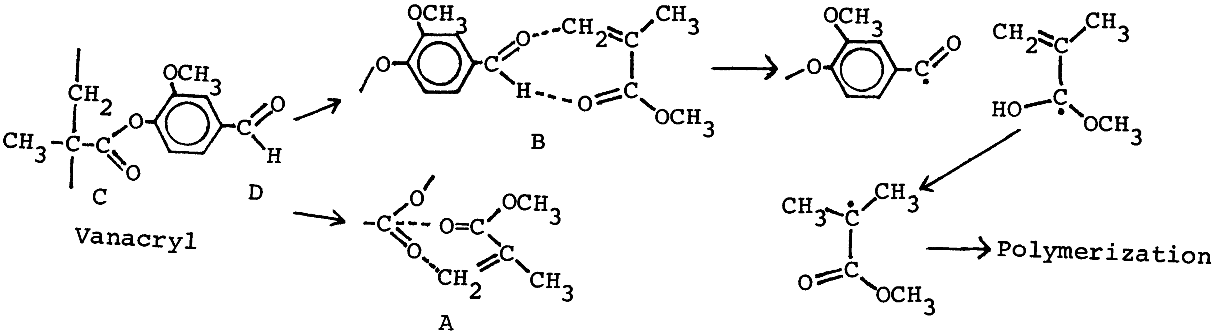
Table III

Polymerization of MMA in the Presence of Vanacryl[a]

Vanacryl (g)	Dioxane (cm^3)	H_2O (cm^3)	Conversion (%)
0	7	0	1.2
0.1	7	0	2.5

[a] MMA 3 cm^3; 85°C, 4 h.

This could be explained by assuming the participation of the carbonyl group of ester unit on the initiation. Monomeric MMA could form two kinds of complex with vanacryl, as shown in the following scheme. One is the complex A involving the site C and the other the complex B involving the site D. As reported in the preceeding paper[3)], the complex B can initiate the polymerization of MMA. However, the complex A can generate no effective radical. In the present case, since the site C may be more active than the site D, the complex A is assumed to be formed easier than the complex B.



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