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Vinyl Polymerization. 393. Radical Polymerization of Vinyl Monomer Initiated by Aliphatic Aldehyde

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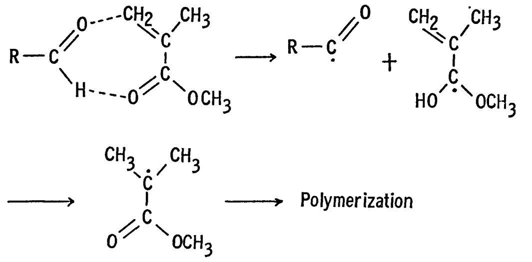
The homogeneous polymerization of methyl methacrylate (MMA) initiated with butanal (PrCHO), pentanal (BuCHO), and hexanal ($C_5H_{11}CHO$) was carried out in dioxane. It was found that the rate of polymerization can be expressed by $R_p=k[MMA]^{1.5}[RCHO]^{0.5}$. The polymerization was confirmed to proceed through a radical mechanism. Overall activation energies, when PrCHO, BuCHO, and $C_5H_{11}CHO$ were used, were estimated to be 37.2, 36.3, and 36.0 kJ mol^{-1}, respectively. Instead of MMA, many kinds of vinyl monomer were applied. Various methacrylates and acrylates could be polymerized, but not styrene and acrylonitrile. The effect of solvent on the rate of polymerization was studied.

Imoto, Oishi, and Ouchi found that poly(acrylaldehyde-co-styrene)(AL/St)[1] and poly(methyl vinyl ketone-co-styrene)[2] can initiate the radical polymerization of methyl methacrylate (MMA). When the CHO group of AL/St was hydrogenated with $NaBH_4$ to CH_2OH group, the polymerization activity of AL/St was lost. It was thus concluded that the active center of AL/St is the pendent CHO group. Imoto, Maeda, and Ouchi reported that not only macromolecular aldehyde compounds, such as poly(formylstyrene)(*m*-:*p*-, 68:30)[3] and vanacryl,[4] but also low-molecular aldehydes of vanillin[4] or benzaldehyde (PhCHO)[5] can initiate the radical polymerization of MMA, the following mechanism of initiation being proposed.[4,5]



(1)

The present paper deals with the radical polymerization of vinyl monomers, particularly MMA, initiated by aliphatic aldehydes.

Experimental

Materials. Propanal (EtCHO, bp 49 °C), butanal (PrCHO, bp 74.8 °C), pentanal (BuCHO, bp 51.2 °C/121 mmHg), hexanal ($C_5H_{11}CHO$, bp 48 °C/40 mmHg) and benzaldehyde (PhCHO, bp 51 °C/5 mmHg), all of commercial special grade, were used. They were dried over anhydrous Na_2SO_4, distilled twice in a nitrogen atmosphere and furthermore distilled before use. No peroxyl group was found by the KI-method.

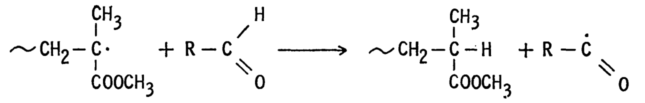
Vinyl monomers were purified by the usual methods. Dioxane was passed through a column filled with alumina and distilled, other solvents being purified by the usual methods.

Procedures. Vinyl monomer and aldehyde were dissolved in solvent and placed in a tube. The tube was thawed by nitrogen and sealed in a vacuum. The tube was shaken in a thermostat. After a certain time, the contents of the tube were poured into a large amount of methanol in order to precipitate the polymer produced. The conversion of the monomer was calculated from the weight of the polymer. Number-average degree of polymerization, $\overline{P}_n$, of poly(MMA) was estimated by GPC-method (Type 501, ALC/GPC of Waters Ltd.).

ESR Measurement. The ESR spectrum was measured at room temperature by using a JES-FE 1X spectrometer with 100 kHz field modulation.

Results and Discussion

Effect of the Concentration of Aldehyde on the Polymerization of MMA. Polymerization of MMA was carried out by keeping the concentration of MMA constant at 2.79 mol dm^{-3} and varying the concentration of aldehyde (Fig. 1). The formyl group retards the radical polymerization by the following chain-transfer reaction:



$$\sim CH_2-\overset{CH_3}{\underset{COOCH_3}{\overset{|}{\underset{|}{C}}}}\cdot + R-C\overset{H}{\underset{O}{\lessgtr}} \longrightarrow \sim CH_2-\overset{CH_3}{\underset{COOCH_3}{\overset{|}{\underset{|}{C}}}}-H + R-\dot{C}=O \tag{2}$$

Thus with increase in the concentration of RCHO, the rate of chain-transfer reaction of MMA-radical to the aldehyde becomes greater, the conversion of MMA tending to decrease. The chain length of the alkyl group of RCHO remarkably affects conversion and rate of polymerization. The conversion increases, according to the order $C_2H_5<C_3H_7<C_4H_9$, but C_5H_{11} shows a lower activity than C_3H_7 or C_4H_9. EtCHO may have much higher activity for the chain-transfer reaction than the initiating reaction.

Figure 2 shows the decrease in $\overline{P}_n$ of poly(MMA)

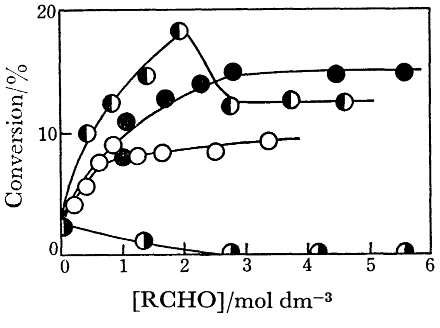


Fig. 1. Conversion of MMA *vs.* concentration of RCHO. [MMA]=2.79 mol dm^{-3}, in dioxane; 85 °C, 3 h. (◑) EtCHO, (●) PrCHO, (◐) BuCHO, (○) $C_5H_{11}CHO$.

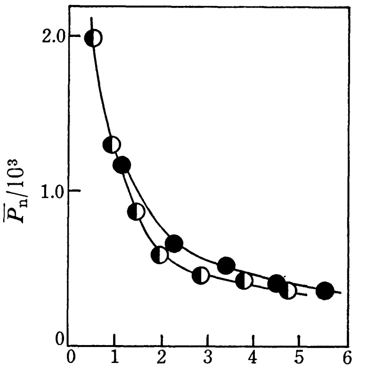


Fig. 2. Decrease of $\overline{P}_n$ of poly(MMA) with RCHO. [MMA]=2.79 mol dm^{-3}, in dioxane; 85 °C, 3 h. (●) PrCHO, (◐) BuCHO.

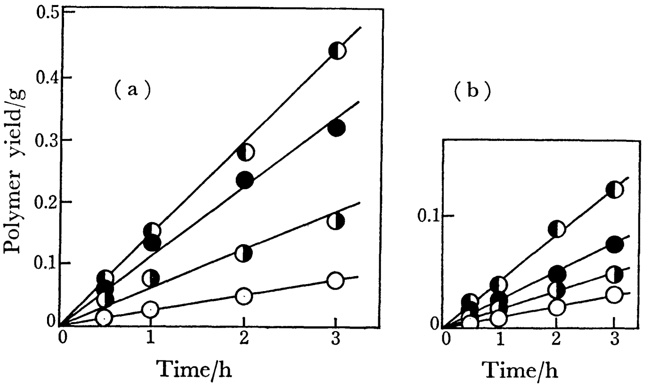


Fig. 3. Time-conversion curves.
(a) Overall conversion obtained in the presence of BuCHO *vs.* time. (b) Thermal conversion obtained in the absence of BuCHO *vs.* time. [BuCHO]= 0.94 mol dm^{-3}, in dioxane; 85 °C.
(○) [MMA]=0.93 mol dm^{-3}, (◑) [MMA]=1.86 mol dm^{-3}, (●) [MMA]=2.79 mol dm^{-3}, (◐) [MMA]= 3.72 mol dm^{-3}.

produced. This is due to the chain transfer reaction.

Reaction Orders with Respect to MMA and RCHO. Figures 3(a) and 3(b) show the time-conversion curves of MMA in the presence and absence, respectively, of BuCHO. From the straight lines in Fig. 3(a), the overall rate of polymerization, R_p(overall), can be calculated by dividing conversion by time. R_p(thermal) is the rate of polymerization in the absence of BuCHO. Accordingly, the polymerization initiated with RCHO, R_p, was calculated by the equation.

$$R_p^2 = R_p^2(\text{overall}) - R_p^2(\text{thermal}) \tag{3}$$

The relationship between R_p and [MMA] or [RCHO] is shown in Figs. 4 and 5. From the slopes of the straight lines, the reaction orders with respect to MMA and RCHO were calculated (Table 1).

Table 1. Reaction order[a)]

RCHO	*m*	*n*
PrCHO	—	0.45
BuCHO	1.41	0.44
$C_5H_{11}CHO$	1.50	0.50

a) $R_p=k[\text{MMA}]^m[\text{RCHO}]^n$.

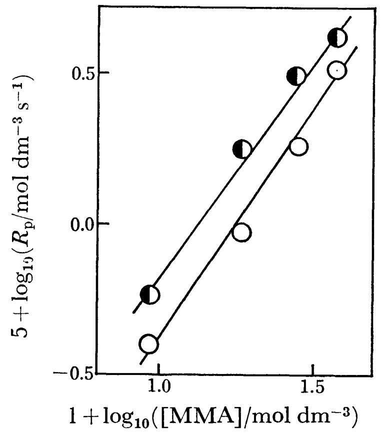


Fig. 4. Relationship between R_p and [MMA]. (◐) [BuCHO]=0.94 mol dm^{-3}, (○) [$C_5H_{11}CHO$]= 0.72 mol dm^{-3}, in dioxane; 85 °C.

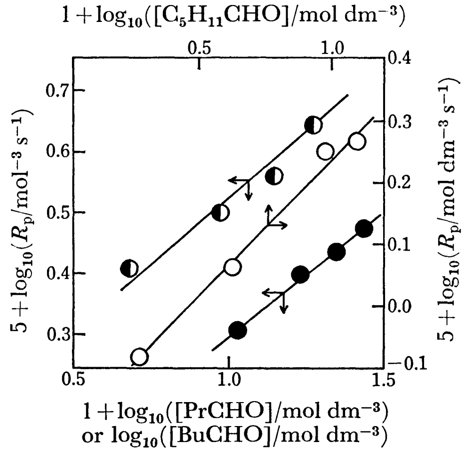


Fig. 5. Relationship between R_p and [RCHO]. [MMA]=2.79 mol dm^{-3}, in dioxane; 85 °C. (●) PrCHO, (◐) BuCHO, (○) C_5H_{11}CHO.

Table 2. Values of r_1 and r_2

RCHO	r_1	r_2
PrCHO	0.59	0.53
BuCHO	0.56	0.46
$C_5H_{11}CHO$	0.51	0.49

In the case of benzaldehyde, the rate equation was found to be $R_p=k[\text{MMA}]^{1.5}[\text{PhCHO}]^{0.5}$. Similarly in the present case of RCHO, the rate equation of the polymerization obeys the equation.

$$R_p = k[\text{MMA}]^{1.5}[\text{RCHO}]^{0.5} \tag{4}$$

Proofs of Radical Mechanism. That the polymerization of MMA initiated with RCHO proceeds through a radical mechanism was confirmed by two methods, (a) complete inhibition of the polymerization by 2,2-diphenyl-1-picrylhydrazyl (DPPH) (Fig. 6) and (b) copolymerization of MMA and St (Fig. 7). The calculated values of r_1 and r_2 are given in Table 2.

From these two experiments it was confirmed that the polymerization of MMA initiated with RCHO proceeds through a radical mechanism.

Selectivity of Vinyl Monomers. Instead of MMA, many kinds of methacrylate were used in the polymeri-

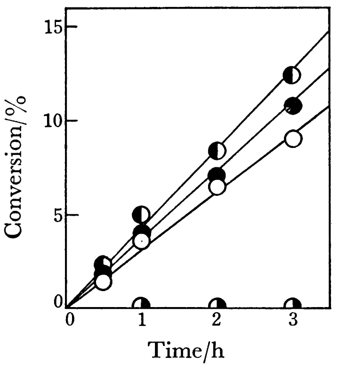


Fig. 6. Inhibition of the polymerization by DPPH. MMA 3 cm³, RCHO 1 cm³, in dioxane; 85 °C. (●) PrCHO, (◐) BuCHO, (○) $C_5H_{11}CHO$. The symbol ◑ includes the three results obtained by BuCHO, PrCHO or $C_5H_{11}CHO$.

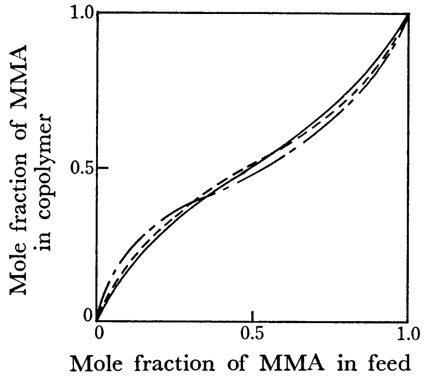


Fig. 7. Copolymerization of MMA(M_1) with St(M_2). (St+MMA) 3 cm³, RCHO 1 cm³, in dioxane; 85 °C, 3 h.
----: PrCHO, ——: BuCHO, ——: $C_5H_{11}CHO$.

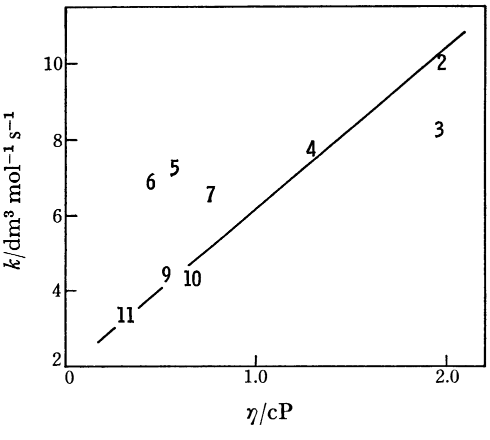


Fig. 8. k *vs.* η of solvent. The number refer to the experiments in Table 5.

Table 3. Polymerization of methacrylates initiated with BuCHO[a)]

Monomer	Conversion/%	
	None[b)]	BuCHO[c)]
Methyl methacrylate	2.4	12.4
Ethyl methacrylate	1.9	10.3
Isopropyl methacrylate	3.0	7.4
Butyl methacrylate	2.6	12.0
Isobutyl methacrylate	8.9	16.1
t-Butyl methacrylate	5.8	11.2
Benzyl methacrylate	2.9	14.8
2-Hydroxyethyl methacrylate	11.2	17.9

a) Monomer 3 cm³, total volume 10 cm³, in dioxane; 85 °C, 3 h. b) None indicates the absence of BuCHO. c) BuCHO 1 cm³.

Table 4. Polymerization of vinyl monomers initiated with BuCHO[a)]

Monomer	Conversion/%	
	None[b)]	BuCHO[c)]
Methyl acrylate	27.0	49.9
Ethyl acrylate	9.8	51.7
Styrene	1.4	2.4
α-Methylstyrene	0.0	0.0
Acrylonitrile	0.2	1.7
Methacrylonitrile	0.0	0.6
Acrylamide[d)]	3.7	30.0
Methacrylamide[d)]	1.8	8.3
Methacrylic acid	0.2	2.3

a) Monomer 3 cm³, total volume 10 cm³, in dioxane; 85 °C, 3 h. b) Absence of BuCHO. c) BuCHO 1 cm³. d) Monomer 3 g.

Table 5. Effect of solvent on R_p[a)]

No.	Solvent	$k\times10^5$ / $dm^3\ mol^{-1}\ s^{-1}$	ε[6)]	η/cP[6)]
1	Chloroform	10.10	4.9	0.563
2	DMSO	9.96	48.9	1.996
3	Ethyl benzoate	8.25	5.89	1.956
4	Dioxane	7.58	2.2	1.3
5	Benzene	7.16	2.28	0.6010
6	Ethyl acetate	6.94	6.02	0.449
7	DMF	6.46	36—71	0.802
8	H_2O[b)]	4.98	80.10	1.0019
9	THF	4.35	7.58	0.55
10	Isobutyl acetate	4.26	5.29	0.697
11	Acetone	3.39	20.70	0.316
12	Methyl isobutyrate	3.00	—	—

a) MMA 3 cm³, BuCHO 1 cm³, solvent 6 cm³; 85 °C.
b) H_2O 10 cm³; Heterogeneous polymerization.

zation initiated with BuCHO. Methacrylates were always easily polymerized (Table 3).

Vinyl monomers other than methacrylate were also examined (Table 4).

We see that acrylates and acrylamide can be more easily polymerized than methacrylates. Styrene, α-methylstyrene and acrylonitrile could not be polymerized. The results are in line with the proposed mechanism (1). Styrene and acrylonitrile form no adequate complex with RCHO.

Effect of Solvent on Polymerization. Twelve solvents were used in the polymerization of MMA initiated with BuCHO. The results obtained are given in Table 5, where k is calculated from the conversion of

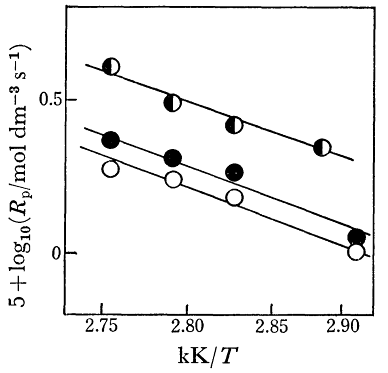


Fig. 9. Arrhenius plots.
[MMA]=2.79 mol dm^{-3}, (●) [PrCHO]=1.11 mol dm^{-3}, (◐) [BuCHO]=0.94 mol dm^{-3}, (○) [C_5H_{11}-CHO]=0.72 mol dm^{-3}, in dioxane; 70—90 °C.

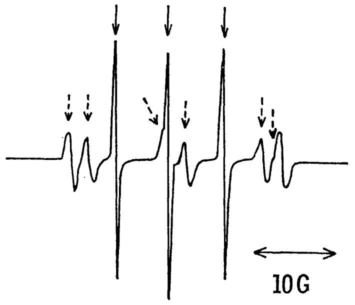


Fig. 10. ESR spectrum of the system of BuCHO/MA/BNO after reaction at 30 °C. [BuCHO]=9.4×10^{-1} mol dm^{-3}, [MA]=2.6 mol dm^{-3}, [BNO]=5.5×10^{-2} mol dm^{-3}, in benzene. ——→: (**3a**), - - -→: (**4**).

MMA by the rate equation, $R_p=k[\text{BuCHO}]^{0.5}[\text{MMA}]^{1.5}$.

The effect of solvent on R_p could not be interpreted in terms of dielectric constants (ε). However, as Fig. 8 shows, R_p increased with the viscosity of the solvent, except in the cases of water (unhomogeneous polymerization) and chloroform (high chain transfer constant, 4.54×10^{-5}).

Estimation of Overall Activation Energy. The polymerization of MMA initiated with three kinds of RCHO was carried out in dioxane at 70—90 °C. The logarithms of the calculated R_p were correlated with the reciprocals of the polymerization temperature. The results obtained are shown in Fig. 9. The overall activation energy E_a was calculated from the slopes of the lines (Table 6).

Spin Trapping of Free Radicals with 2-Methyl-2-nitrosopropane (BNO). Attempts were made to detect the radicals produced in the polymerizing system of aldehyde and methyl acrylate (MA) by spin trapping technique.

Figure 10 shows the ESR spectrum observed from the system of BuCHO/MA/BNO in benzene at 30 °C. Two sets of ESR signals were observed; a triplet with A_N=8.0 G and a sextuplet with A_N=14.3 G, A_H^β=2.7 G. The former is considered to be due to (**3a**) and the latter to (**4**), which are derived from the reaction of BNO with acyl radical (**1a**) or 1-(methoxycarbonyl)ethyl radical (**2**), respectively.

When PhCHO was used instead of BuCHO, a similar spectrum was obtained; a triplet with A_N=8.2 G and a sextuplet with A_N=14.4 G, A_H^β=2.7 G.

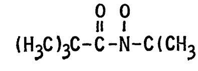
The coupling constants of nitroxyl radicals obtained by the addition of acyl radicals and 1-(methoxycarbonyl)ethyl derivative radicals to BNO are summarized in Table 7.

Table 6. Overall activation energies

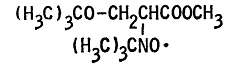
RCHO	Solvent	E_a/kJ mol^{-1}
PrCHO	Dioxane	37.2
BuCHO	Dioxane	36.3
$C_5H_{11}CHO$	Dioxane	36.0

Table 7. Reported values of coupling constant of spin adduct

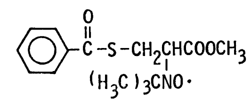
Spin adduct	$\frac{A_N}{G}$	$\frac{A_H^\beta}{G}$	Ref.
5	8.1	—	7
3b	8.05	—	8
6	13.9	2.4	9
7	14.0	2.6	10


$(H_3C)_3C-\overset{O}{\overset{\|}{C}}-\overset{\dot{O}}{\overset{|}{N}}-C(CH_3)_3$

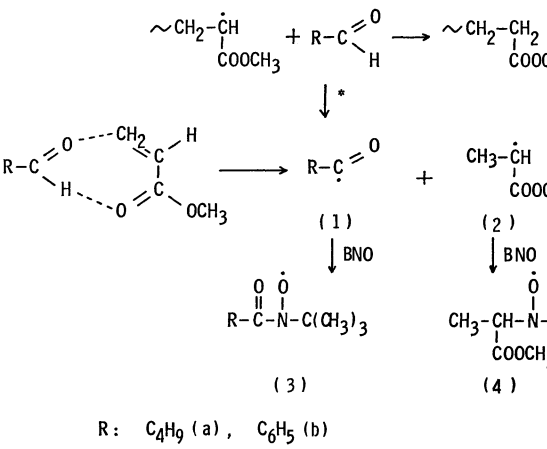
(**5**)


$(H_3C)_3CO-CH_2\underset{(H_3C)_3CN\dot{O}}{\underset{|}{C}}HCOOCH_3$

(**6**)



(**7**)



(5)

* Chain transfer reaction of propagating radical of MA onto aldehyde.

The values obtained above are close to those reported. Thus, our asignment for ESR signals is reasonable.

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