

Radical polymerization and copolymerization of methyl 2-(acyloxymethyl)acrylate as hindered 2-substituted acrylate

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Methyl 2-(acyloxymethyl)acrylates [$\text{CH}_2=\text{C}(\text{CH}_2\text{OCOR})\text{COOCH}_3$; $\text{R}=\text{CH}_3$, $\text{CH}_2\text{CH}_2\text{CH}_3$, $\text{CH}(\text{CH}_3)_2$ and $\text{C}(\text{CH}_3)_3$] were prepared by nucleophilic substitution of methyl 2-(bromomethyl)acrylate with the desired carboxylic acid in the presence of triethylamine at ambient temperature. These particular monomers homopolymerize faster than methyl methacrylate (MMA) despite the presence of large 2-substituents. Propagating radicals of the acyloxymethylacrylates in benzene in a homogeneous system were detected and quantified. The rate constants of propagation (k_p) and termination (k_t) for methyl 2-(acetoxymethyl)acrylate (MAcMA) at 60°C, which were determined based on the quantification of propagating radical, are smaller than those of MMA by factors of 1.5 and 20, respectively. The steric hindrance of the 2-substituent reduced k_t more significantly than k_p , leading to polymerization to a higher molecular weight. The 2-(acyloxymethyl)acrylates can be noted to yield homopolymers through *steric hindrance-assisted polymerization*. Slightly higher reactivities for MAcMA than MMA were estimated in the copolymerization with styrene because of the effect of the electronegative character of the oxygen atom on the acetoxyl group.

(Keywords: 2-(substituted methyl)acrylate; radical polymerization; e.s.r. study)

INTRODUCTION

The radical polymerizability of vinyl monomers is governed by resonance, polar and steric factors. It has been revealed that 2-alkylacrylic esters and acids, except methacrylic ester and acid, were reluctant to polymerize extensively because of the steric hindrance of the 2-substituent^{1,2}. However, Baldwin and Reed have reported that 2-substituted acrylates bearing hydroxymethyl, ethoxymethyl, acetoxymethyl, carboethoxymethyl and fluoromethyl groups as 2-substituents polymerize to a higher molecular weight³. The sequence of tedious reactions⁴ used to synthesize 2-(hydroxymethyl)acrylic esters, which are common precursors of 2-(ethoxymethyl)-, 2-(acetoxymethyl)- and 2-(halomethyl)acrylates, prevented a detailed study of the polymerization behaviour of 2-(substituted methyl)acrylate.

A base-catalysed reaction developed in the last decade^{5,6} can be adopted to conveniently prepare 2-(hydroxymethyl)acrylic esters from acrylic esters with formaldehyde. Among 2-(substituted methyl)acrylates derived directly or indirectly from 2-(hydroxymethyl)acrylates, 2-(alkoxy-methyl)-^{7–9}, 2-(fluoroalkoxymethyl)-^{10–13}, 2-(acyloxy-methyl)-^{14,17} and 2-(fluoromethyl)acrylates¹⁸ have recently been reinvestigated as highly polymerizable monomers. The propagating polymer radicals from some

2-(substituted methyl)acrylates were easily detected by electron spin resonance (e.s.r.) spectroscopy. The concentration of the polymer radical was estimated directly. Based on the absolute values of the propagation (k_p) and termination (k_t) rate constants for methyl 2-(butoxymethyl)acrylate⁷ and methyl 2-(benzyloxymethyl)acrylate⁹, it has been shown that the steric hindrance due to the 2-substituent results in a slightly smaller k_p and a considerably smaller k_t than those for methyl methacrylate (MMA). Considerably smaller k_p and k_t values for itaconic esters^{19–24} than those of MMA reveal that the absolute values of the rate constants for the polymerizable 2-(substituted methyl)acrylates are variable over wide ranges.

On the other hand, 2-(alkylthiomethyl)acrylates^{25–27} and 2-(bromomethyl)acrylates^{27–30}, which are reluctant to polymerize and copolymerize, have drawn attention as efficient chain-transfer agents through the addition-fragmentation mechanism. Furthermore, we have shown that 2-(chloromethyl)acrylates^{18,31} and 2-(phenoxy-methyl)acrylates^{32,33} yield low molecular weight polymers bearing 2-carboalkoxyallyl groups at the ω -end as a result of competition of propagation and β -fragmentation of the propagating radicals.

Thus, a considerable number of studies have been made of the radical polymerization of 2-(substituted methyl)acrylates. However, what seems to be lacking is a

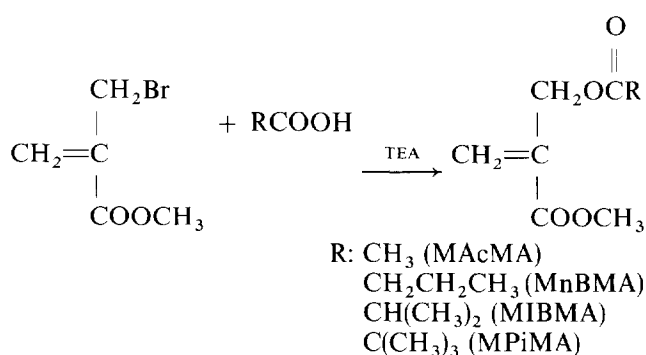
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relationship between the k_p and k_t values and the size of the 2-substituent of 2-(substituted methyl)acrylate. For this purpose, the synthesis and polymerization of a variety of 2-(substituted methyl)acrylates were required.

In our previous studies, some of the 2-(substituted methyl)acrylates were prepared by reaction of methyl 2-(bromomethyl)acrylate (MBMA) with alcohols in the presence of triethylamine (TEA) in high yields^{7-9,11}. Similarly, the 2-(chloromethyl)acrylate was allowed to react with an alcohol in the presence of TEA^{10,13}. Recently, we have also reported the radical polymerization of methyl 2-[2,2-bis(carboalkoxy)ethyl]acrylates, which were prepared by reaction of MBMA with dialkyl malonates in the presence of TEA³⁴. We thought that acidic compounds including carbon acids may react with MBMA in the presence of TEA to yield the 2-(substituted methyl)acrylate.

The 2-(acyloxymethyl)acrylic esters can be synthesized¹⁵⁻¹⁷ by reaction of 2-(hydroxymethyl)acrylates with an acid anhydride or acyl chloride in yields of 40–80%. Recently, Avci *et al.* have reported the synthesis of 2-(acyloxymethyl)acrylates by the reaction of the chloromethylacrylate with sodium salts of carboxylic acids using a phase-transfer catalyst such as quaternary ammonium chloride in high yields¹⁷. We found that the reaction of MBMA with carboxylic acids in the presence of TEA at room temperature also affords 2-(acyloxymethyl)acrylates in high yields.

The present work deals with the synthesis and radical polymerization of methyl 2-(acyloxymethyl)acrylates because these compounds have been noted as monomers yielding high molecular weight polymers with the fastest rate among the 2-(substituted methyl)acrylates examined. The k_p and k_t for these monomers were evaluated by the e.s.r. method for further study of the steric hindrance in the polymerization of the 2-(substituted methyl)acrylates.



EXPERIMENTAL

Materials

Methyl 2-(acetoxymethyl)acrylate (MAcMA) was prepared by reacting MBMA³⁵ (26.5 g; 0.148 mol) with acetic acid (15.0 g; 0.250 mol) in the presence of TEA (20.0 g; 0.198 mol) in benzene with stirring overnight at room temperature. MAcMA (20.4 g; 87%) was obtained after distillation under reduced pressure. Methyl 2-(n-butyroxymethyl)acrylate (MnBMA), methyl 2-(isobutyroxymethyl)acrylate (MIBMA) and methyl 2-(pivaroxymethyl)acrylate (MPiMA) were also synthesized from MBMA and the corresponding carboxylic acid at room temperature. All the monomers were obtained in ~90% yield and were purified by distillation under reduced pressure. The

structures of the monomers were verified by ¹H and ¹³C n.m.r. spectroscopy.

MAcMA: b.p. 58°C/3 mmHg; ¹H n.m.r. (CDCl₃): δ = 2.11 (s, 3H, OCOCH₃), 3.79 (s, 3H, COOCH₃), 4.81 (s, 2H, C=CCH₂O), 5.86 (s, 1H, CH=), 6.36 (s, 1H, CH=); ¹³C n.m.r. (CDCl₃): δ = 20.5 (OCOCH₃), 51.7 (COOCH₃), 62.1 (C=CCH₂O), 127.2 (CH₂=C), 135.0 (CH₂=C), 165.3 (COOCH₃), 170.0 (OCOCH₃).

MnBMA: b.p. 73°C/2 mmHg; ¹H n.m.r. (CDCl₃): δ = 0.96 (t, 3H, CH₂CH₂CH₃), 1.68 (sext, 2H, CH₂CH₂CH₃), 2.34 (t, 2H, CH₂CH₂CH₃), 3.79 (s, 3H, COOCH₃), 4.82 (s, 2H, C=CCH₂O), 5.85 (s, 1H, CH=), 6.36 (s, 1H, CH=); ¹³C n.m.r. (CDCl₃): δ = 13.5 (CH₂CH₂CH₃), 18.3 (CH₂CH₂CH₃), 35.9 (CH₂CH₂CH₃), 51.8 (COOCH₃), 62.1 (C=CCH₂O), 127.2 (CH₂=C), 135.3 (CH₂=C), 165.5 (COOCH₃), 172.8 (OCOCH₂CH₂CH₃).

MIBMA: b.p. 65°C/2 mmHg; ¹H n.m.r. (CDCl₃): δ = 1.19 (d, 6H, CH(CH₃)₂), 2.61 (sept, 1H, CH(CH₃)₂), 3.79 (s, 3H, COOCH₃), 4.81 (s, 2H, C=CCH₂O), 5.84 (s, 1H, CH=), 6.36 (s, 1H, CH=); ¹³C n.m.r. (CDCl₃): δ = 18.9 (CH(CH₃)₂), 33.9 (CH(CH₃)₂), 51.9 (COOCH₃), 62.1 (C=CCH₂O), 127.1 (CH₂=C), 135.4 (CH₂=C), 165.6 (COOCH₃), 176.4 (OCOCH(CH₃)₂).

MPiMA: b.p. 63°C/0.5 mmHg; ¹H n.m.r. (CDCl₃): δ = 1.23 (s, 9H, C(CH₃)₃), 3.79 (s, 3H, COOCH₃), 4.80 (s, 2H, C=CCH₂O), 5.82 (s, 1H, CH=), 6.35 (s, 1H, CH=); ¹³C n.m.r. (CDCl₃): δ = 27.0 (C(CH₃)₃), 38.7 (C(CH₃)₃), 51.8 (COOCH₃), 62.2 (C=CCH₂O), 126.6 (CH₂=C), 135.5 (CH₂=C), 165.5 (COOCH₃), 177.6 (OCO-t-Bu).

Commercial styrene (St) and MMA were distilled under reduced pressure before use. Dimethyl 2,2'-azobis(isobutyrate) (MAIB) and 2,2'-azobis(isobutyronitrile) (AIBN) were recrystallized from n-hexane and methanol, respectively. 1,3,5-Triphenylverdazyl (TPV) was synthesized as described in the literature³⁶ and recrystallized from methanol.

Polymerization procedure

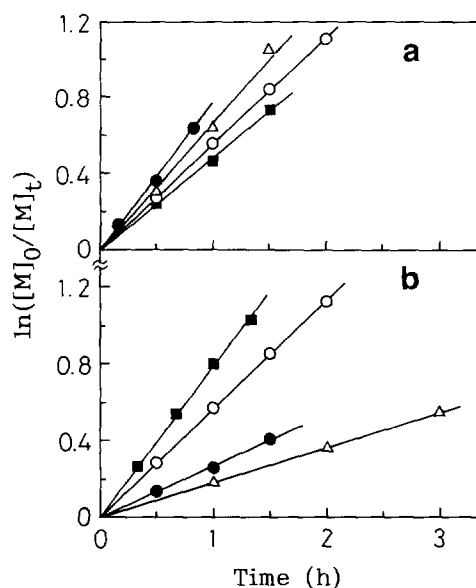
All polymerizations and copolymerizations were carried out in glass tubes sealed off under vacuum. After polymerization for a prescribed time, the contents of the ampoule were poured into a large amount of n-hexane or aqueous methanol to isolate the respective polymers and copolymers. The overall rate of polymerization (R_p) was calculated from the slope of the first-order kinetic plot with respect to monomer and the monomer concentration. Compositions of the copolymers of MAcMA with MMA were calculated from the intensity ratio of the resonances of COOCH₃ and CH₂O protons at 3.0–4.5 ppm to the resonances of CH₂, CH₃ and OCOCH₃ protons at 0.5–2.5 ppm in the ¹H n.m.r. spectra of the copolymers. Compositions of the MAcMA–St copolymers were also determined by n.m.r. spectroscopy based on the intensity ratios of the resonances of phenyl protons at 6.5–7.5 ppm to the remaining resonances at 1.0–4.5 ppm. The monomer reactivity ratios (r_1 and r_2) were evaluated by a non-linear least-squares procedure³⁷.

Measurements

The number- and weight-average molecular weights (\bar{M}_n and \bar{M}_w) of the resultant polymers were determined with a Tosoh 8000 series high performance liquid chromatograph equipped with columns for gel permeation chromatography (g.p.c.) packed with TSK Gel G7000HHR, G6000HHR, G4000HHR and G2000HHR

Table 1 Radical polymerization of MAcMA in benzene at 60°C

[MAcMA] (mol l ⁻¹)	[MAIB] × 10 ² (mol l ⁻¹)	$R_p \times 10^4$ (mol l ⁻¹ s ⁻¹)	$\nu \times 10^{-2a}$	$\bar{M}_n \times 10^{-4}$ (g.p.c.)	\bar{M}_w/\bar{M}_n (g.p.c.)
0.50	5.0	0.69	1.6	1.8	1.9
1.0	5.0	1.6	3.6	3.7	2.0
2.0	5.0	3.7	8.3	7.9	1.8
4.0	5.0	8.6	19	17	1.9
1.0	0.50	0.51	12	11	1.8
1.0	1.0	0.73	8.2	7.0	2.1
1.0	10	2.2	2.5	2.8	1.9

^aThe kinetic chain length calculated from equation (1)**Figure 1** First-order plots for radical polymerization of MAcMA in benzene at 60°C: (a) [MAIB] = 5.0×10^{-2} mol l⁻¹; [MAcMA] = 4.0 (●), 2.0 (△), 1.0 (○), 0.50 (■) mol l⁻¹, and (b) [MAcMA] = 1.0 mol l⁻¹; [MAIB] = 0.10 (■), 0.050 (○), 0.010 (●), 0.0050 (△) mol l⁻¹

connected in this order at 38°C. Tetrahydrofuran was used as the eluent and standard polystyrene was employed for calibration.

¹H and ¹³C n.m.r. spectra were recorded on a Jeol JNM-A400 spectrometer at 400 and 100 MHz, respectively. Deuteriochloroform and tetramethylsilane were used as the solvent and internal standard, respectively.

The viscosities of the polymerization mixture (η) before polymerization were measured using an Ubbelohde viscometer at 30°C. Benzene was used as the reference: $\eta^{30} = 0.5621$ cP, $d^{30} = 0.8683$ g ml⁻¹.

The e.s.r. spectra of the polymer radical were taken by a Bruker ESP-300 spectrometer at X band (~9.5 GHz) with 100 kHz field modulation at the microwave power of 15.9 mW and the modulation amplitude was 8 G. The spectra were recorded over a magnetic field of 150 G width divided into 1024 points, and the conversion time of each point and time constant were 40.96 and 655.36 ms, respectively. Having been sealed off under vacuum, a 5 mm o.d. quartz tube containing the polymerization mixture was heated at the polymerization temperature in the cavity. The change in the sensitivity of the cavity of the e.s.r. spectrometer with polymerization time was

monitored with Mn²⁺/MnO in capillary tubing attached to the e.s.r. tube containing the polymerization mixture. The concentration of the propagating polymer radical was calibrated by the signal intensity of TPV dissolved in the polymerization mixture except for the initiator.

RESULTS AND DISCUSSION

Homopolymerization

Radical polymerization of MAcMA in benzene was initiated with MAIB at 60°C. Figure 1 shows the first-order plots of the MAcMA polymerization. Table 1 lists the R_p estimates and the \bar{M}_n of the resultant polymers. \bar{M}_n increased with an increase in the monomer concentration and a decrease in the initiator concentration. The kinetic chain length (ν) at the steady state is given by³⁸:

$$\nu = R_p/R_t = R_p/R_i = R_p/(2k_d f [I]) \quad (1)$$

where R_t and R_i are the rate of termination and initiation, respectively, and k_d , f and $[I]$ are the decomposition rate constants of the initiator, initiating efficiency and the initiator concentration, respectively. ν can be estimated by substitution of the numerical values, $k_d = 8.9 \times 10^{-6}$ s⁻¹ (ref. 39), $f = 0.5$, and the respective values of R_p and $[I]$. Although the degree of polymerization calculated from \bar{M}_n is always less than ν , changes in the \bar{M}_n of the resultant polymers by the polymerization conditions correspond to the changes in ν .

The kinetic orders with respect to the monomer and initiator for the MAcMA polymerization were determined to be 1.21 and 0.48, respectively, from the slopes of the linear relationships obtained from log-log plots of R_p versus the concentrations of MAcMA and MAIB as shown in Figure 2. R_p is expressed as follows:

$$R_p = k [\text{MAcMA}]^{1.21} [\text{MAIB}]^{0.48} \quad (2)$$

The monomer kinetic order is higher than the ideal value. This fact may arise from the increasing viscosity of the polymerization mixture because the viscosity of the monomer is higher than that of benzene. The k_t value is proportional to the reciprocal of the viscosity; therefore, the order of the monomer concentration on $R_p/\eta^{0.5}$ was estimated to be 1.07 as shown in Figure 2. It was theorized that the radical polymerization of MAcMA under these conditions proceeded through a mechanism close to the usual elementary reactions, which are initiation, propagation and bimolecular termination, and primary radical termination was almost negligible.

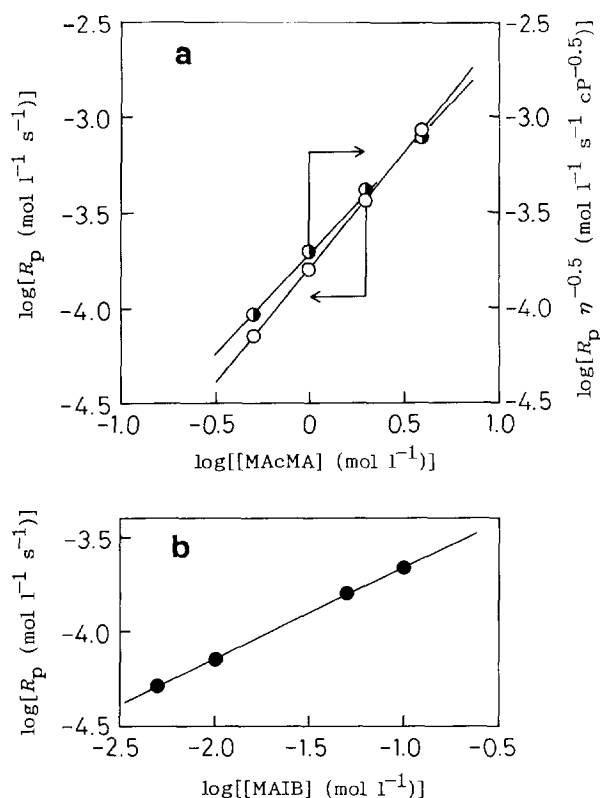


Figure 2 Dependence of R_p on the concentrations of MAcMA (a) and MAIB (b) in benzene at 60°C: (a) $[MAIB] = 5.0 \times 10^{-2} \text{ mol l}^{-1}$, (b) $[MAcMA] = 1.0 \text{ mol l}^{-1}$

Table 2 Radical polymerization of methyl 2-(acyloxymethyl)acrylate in benzene at 60°C^a

Monomer	$R_p \times 10^4$ (mol l ⁻¹ s ⁻¹)	$\bar{M}_n \times 10^{-4}$ (g.p.c.)	\bar{M}_w/\bar{M}_n (g.p.c.)	η^b (cP)
MMA	0.68	1.5	1.8	0.55
MAcMA	1.6	3.7	2.0	0.65
MnBMA	2.1	5.2	2.1	0.68
MIBMA	1.9	5.1	1.9	0.68
MPiMA	2.0	5.0	1.9	0.70

^a $[Monomer] = 1.0 \text{ mol l}^{-1}$, $[MAIB] = 5.0 \times 10^{-2} \text{ mol l}^{-1}$

^b The viscosity of the polymerization mixture before polymerization at 30°C

The polymerizations of MMA, MnBMA, MIBMA and MPiMA at 60°C were compared with that of MAcMA at $[Monomer] = 1.0 \text{ mol l}^{-1}$ and $[MAIB] = 5.0 \times 10^{-2} \text{ mol l}^{-1}$. The results of polymerization are shown in Table 2. MAcMA polymerized faster than MMA by a factor of two or above despite the presence of a 2-substituent group larger than the methyl group. Furthermore, the polymerizations of MnBMA, MIBMA and MPiMA were faster than that of MAcMA. It was noted that the \bar{M}_n of the poly[methyl 2-(acyloxymethyl)acrylates] is higher than that of the poly(MMA). The considerable change in the R_p cannot be accounted for by a change in η . Because the R_p and the \bar{M}_n of the resulting polymer are governed by the balance of the propagation and termination rates, the absolute values of k_p and k_t must be estimated for further discussion of the steric hindrance in elementary reactions.

Absolute rate constants

The e.s.r. spectra of the poly[methyl 2-(acyloxymethyl)acrylate] radicals were observed during the polymerizations under the conditions shown in Table 2. Figure 3 depicts the e.s.r. spectra recorded after a single scan or an accumulation of four scans. The recorded five-line spectra were interpreted by splitting with two sets of β -hydrogens whose line spacing was estimated to be $\sim 16 \text{ G}$. These spectra were similar to those of polymer radicals of 2-(substituted methyl)acrylates such as dialkyl itaconates^{19–24}, methyl 2-(butoxymethyl)acrylate⁷, methyl 2-(2,2,3,3-tetrafluoropropoxymethyl)acrylate¹¹, methyl 2-(phenoxymethyl)acrylate³², ethyl 2-(acetoacetoxymethyl)acrylate¹⁴ and ethyl 2-(benzoyloxymethyl)acrylate¹⁵.

Although the signal intensity of the spectrum is proportional to the square root of the microwave power, saturation of the spectrum occurs only at a high microwave power⁴⁰. To avoid saturation during the polymerization of MAcMA at 60°C under the conditions of $[MAcMA] = 1.0 \text{ mol l}^{-1}$ and $[MAIB] = 5.0 \times 10^{-2} \text{ mol l}^{-1}$, the peak intensity of the e.s.r. spectrum of the poly(MAcMA) radical was recorded at the microwave power up to $\sim 20 \text{ mW}$.

Because a considerable change in the e.s.r. sensitivity was brought about by the polymerization of a polar monomer such as MMA^{41,42}, the peak heights of the Mn^{2+}/MnO signals were recorded at different conversions of MAcMA to monitor the change in the sensitivity of the cavity. However, the peak intensity was confirmed not to change during the conversion as shown in Figure 4 because of a relatively low monomer concentration in the benzene.

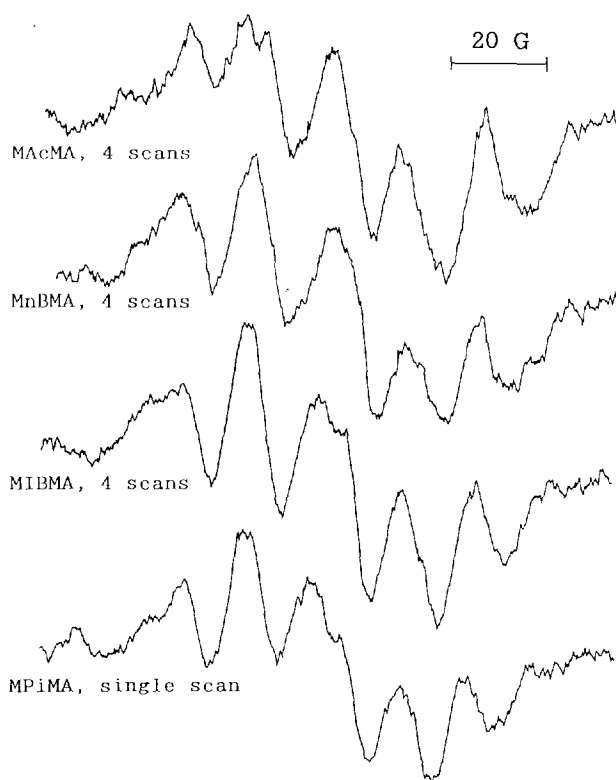
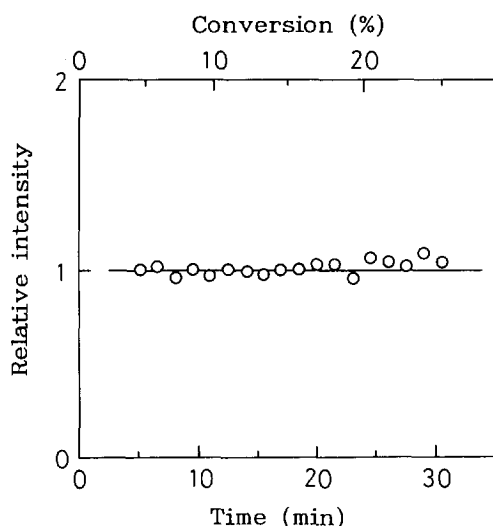


Figure 3 E.s.r. spectra of the propagating radicals observed during the polymerizations of MAcMA, MnBMA, MIBMA and MPiMA in benzene at 60°C: $[monomer] = 1.0 \text{ mol l}^{-1}$, $[MAIB] = 5.0 \times 10^{-2} \text{ mol l}^{-1}$

Table 3 k_p and k_t of 2-(substituted methyl)acrylic esters at 60°C

2-Substituent	[M] (mol l ⁻¹)	[I] (mol l ⁻¹)	[M·] × 10 ⁷ (mol l ⁻¹)	k_p (l mol ⁻¹ s ⁻¹)	$k_t \times 10^{-6}$ (l mol ⁻¹ s ⁻¹)	-E _s ^a
CH ₃ ^b	bulk	AIBN, 0.1	1.5	510	42	-
CH ₂ COOCH ₃ ^c	1.5	MAIB, 0.02	6.1	5.2	0.36	-
CH ₂ OCOCH ₃ ^d	1.0	MAIB, 0.050	4.6	350	2.1	1.24
CH ₂ OCOC ₃ H ₇ -n ^d	1.0	MAIB, 0.050	5.7	360	1.4	1.60
CH ₂ OCOCH(CH ₃) ₂ ^d	1.0	MAIB, 0.050	6.3	300	1.1	1.71
CH ₂ OCOCH ₂ COCH ₃ ^e	2.55	MAIB, 0.100	10	300	1.0	1.99
CH ₂ OCOC(CH ₃) ₃ ^d	1.0	MAIB, 0.050	8.7	230	0.59	2.78
CH ₂ OCOC ₆ H ₅ ^f	1.56	AIBN, 0.10	6.3	990	2.9	-
CH ₂ OCH ₂ C ₆ H ₅ ^g	2.0	AIBN, 0.050	5.4	182	1.6	-

^a The E_s values of R group in CH₂=C(CH₂OCOR)COOR' from ref. 43^b Methyl ester⁴⁴^c Methyl ester²³^d Methyl ester in this work^e Ethyl ester¹⁴^f Ethyl ester¹⁵^g Methyl ester⁹**Figure 4** A plot of the relative peak height of the integrated Mn²⁺/MnO signal versus polymerization time or conversion of MAcMA

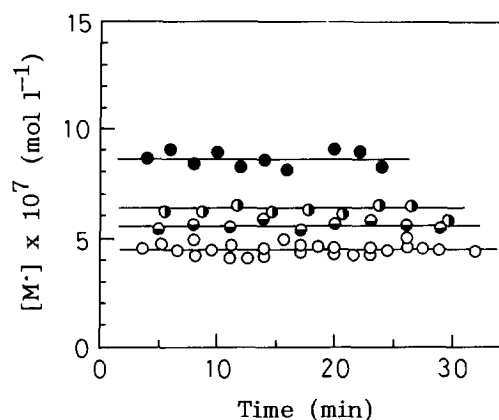
The monomer is consumed solely by propagation, and R_p is expressed as follows:

$$R_p = k_p [M\cdot] [M] \quad (3)$$

where $[M\cdot]$ and $[M]$ are the concentrations of the propagating polymer radical and monomer, respectively. The absolute value of k_p can be obtained from R_p if the radical concentration is provided.

The signal intensity of the e.s.r. spectra in Figure 3 was calibrated by known concentrations of TPV dissolved in the benzene solution of the monomers. Figure 5 shows the changes in the radical concentration with time for the polymerizations of MAcMA, MnBMA, MIBMA and MPiMA. Although the conversion of the monomers reached 25 to 30% after 30 min, the concentrations of the propagating radicals remained constant.

The concentration of propagating radical at the steady state is shown in Table 3. The absolute value of k_p can be estimated using equation (3). At the steady state, the

**Figure 5** Changes in the concentration of the propagating radical with time during the polymerizations of MAcMA (○), MnBMA (◐), MIBMA (◑) and MPiMA (●) at 60°C

initiation rate may be equal to the termination rate:

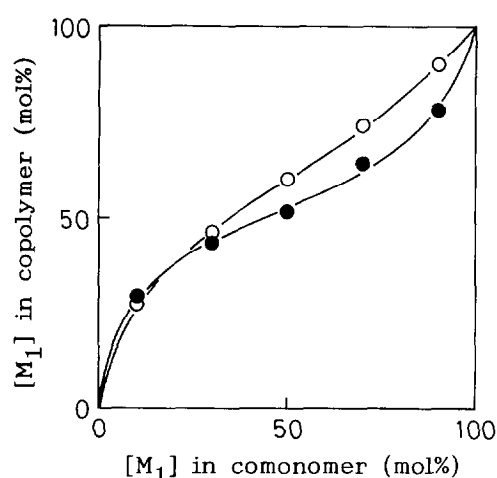
$$2k_d f [MAIB] = k_t [M\cdot]^2 \quad (4)$$

The absolute value of k_t can be obtained from equation (4) by substituting $k_d = 8.9 \times 10^{-6} \text{ s}^{-1}$ (ref. 39), $f = 0.5$, $[MAIB] = 5.0 \times 10^{-2} \text{ mol l}^{-1}$ and the experimental value of $[M\cdot]$. If the f value was less than 0.5, the k_t value would be less than that at $f = 0.5$. Although f values smaller than 0.5 have been suggested in the polymerization of fumaric esters and itaconic esters initiated with azonitriles, the polymerizations initiated with MAIB have been expected to proceed smoothly without decreases in the f value.

Table 3 also lists the k_p and k_t values of the 2-(acyloxymethyl)acrylates together with those of MMA, dimethyl itaconate and methyl 2-(benzyloxymethyl)acrylate. The k_p and k_t values of the methyl 2-(acyloxymethyl)acrylates were lower than those of MMA. Although R_p increased in the order of MAcMA < MIBMA < MPiMA < MnBMA, the absolute values of k_p and k_t decreased in the following order depending on the 2-substituent: MAcMA > MnBMA > MIBMA > MPiMA. The order of decreasing k_p or k_t is in agreement with the

Table 4 Copolymerization parameters for methyl 2-(substituted methyl)acrylate (M_2)/St or MMA (M_1) copolymerization

2-Substituent in M_2	M_1	r_1	r_2	Q_2	e_2	Ref.
$\text{CH}_2\text{OCOCH}_3$	St	0.34	0.19	0.78	0.86	This work
$\text{CH}_2\text{OCOCH}_2\text{COCH}_3^a$	St	0.22	0.28	1.2	0.87	14
$\text{CH}_2\text{OCOC}_6\text{H}_5^a$	St	0.30	0.27	0.93	0.78	15
CH_2OCH_3	St	0.42	0.29	0.75	0.65	8
$\text{CH}_2\text{OC}_2\text{H}_5$	St	0.37	0.24	0.78	0.75	7
$\text{CH}_2\text{OCH}_2\text{C}_6\text{H}_5$	St	0.27	0.36	1.10	0.73	9
CH_3	St	0.52	0.46	0.74	0.40	45
$\text{CH}_2\text{OCOCH}_3$	MMA	0.91	0.24	—	—	This work
CH_2OCH_3	MMA	1.20	0.52	—	—	8

^a Ethyl ester**Figure 6** Comonomer-copolymer composition curves for the copolymerizations of MAcMA (M_2) with St (●) and MMA (○) (M_1) in benzene at 60°C

order of increase in size of the acyloxy group. The k_p for MAcMA is less than that for MMA, and the k_p for the acyloxymethylacrylate decreases further with increasing size of the acyl group.

However, R_p of the acyloxymethylacrylate was found to slightly increase with size of the acyl group as already shown in Table 2. It can be concluded that the balance of the propagation and termination rates governs the polymerization reactivity. The steric hindrance of the substituted methyl group probably suppresses termination more significantly than propagation. Faster polymerization of acyloxymethylacrylates than of MMA is primarily brought about by a smaller k_t . Therefore, polymerization of 2-(acyloxymethyl)acrylates is noted as a *steric hindrance-assisted polymerization*. Although the k_p for MIBMA is as large as that for methyl 2-(butoxymethyl)acrylate, 2981 mol⁻¹ s⁻¹, different values of k_t were observed for the respective monomers: $k_t = 1.1 \times 10^6$ mol⁻¹ s⁻¹ for MIBMA and 8.0×10^6 mol⁻¹ s⁻¹ for methyl 2-(butoxymethyl)acrylate. A similar tendency arises from the comparison of the k_p and k_t values of MPiMA and methyl 2-(benzyloxymethyl)acrylate. Among the 2-(substituted methyl)acrylates in Table 3, the 2-substituents of the acyloxymethylacrylates suppress termination more efficiently.

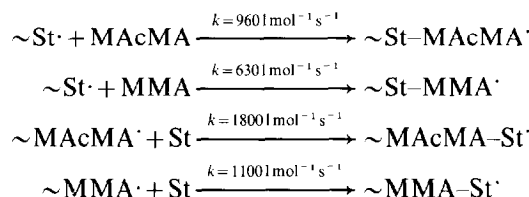
Copolymerization of MAcMA

Copolymerizations of MAcMA (M_2) with St and MMA (M_1) in benzene were initiated with AIBN at 60°C. Figure 6 shows the comonomer-copolymer composition curves for the respective copolymerizations. The experimental points fit quite well the theoretical curve calculated from the terminal model. The r_1 and r_2 values obtained are shown in Table 4 together with the parameters of the other 2-(substituted methyl)acrylates. These parameters for the copolymerization of MAcMA with St exhibited values similar to those of the other 2-(substituted methyl)acrylates. The Q and e values for these monomers were estimated from the values of r_1 and r_2 for the copolymerization with St. The Q value of MAcMA, which is the parameter of the resonance stabilization for the monomer, was similar to that of MMA because of the presence of a methylene spacer between the carbon-carbon double bond and the acetoxy group. The e value of MAcMA was larger than that of MMA. Consequently, the electron-withdrawing character of the acetoxy group through the methyl group exhibited an effect similar to that of the alkoxy group.⁷⁻⁹

The cross-propagation rate constants can be calculated from the k_p values of the respective monomers and the r_1 and r_2 values:

$$k_{12} = k_{11}/r_1, \quad k_{21} = k_{22}/r_2 \quad (5)$$

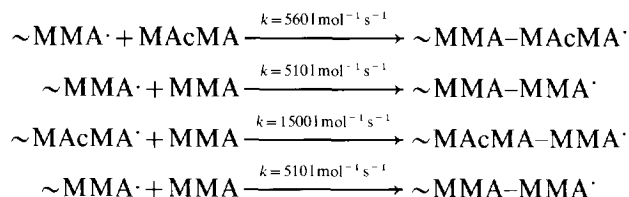
where the reported values for k_{11} and k_{22} were used in the calculation: $k_p = 3281$ mol⁻¹ s⁻¹ for St⁴⁶ and $k_p = 5101$ mol⁻¹ s⁻¹ for MMA⁴⁴.



The addition of the poly(St) radical to MAcMA is faster than that of the poly(St) radical to MMA because of the effect of the electronegative oxygen atom bound to the methylene in the 2-substituent. It has been found that the steric effect of a large 2-substituent causes a lower reactivity for the poly[methyl 2-(benzyloxymethyl)acrylate] radical than for the poly(MMA) radical towards the St monomer⁹, whereas the polar effect of the

benzyloxymethyl group might enhance addition to St. However, the MAcMA radical exhibits a higher reactivity than the MMA radical toward St despite consideration of the steric factor of the acetoxymethyl group in the k_p value. Considering the smaller k_p for the 2-(benzyloxymethyl)acrylate than that for the 2-(acetoxymethyl)acrylate, we can deduce less severe steric hindrance of the acetoxymethyl group than the benzyloxymethyl group in homo-propagation and cross-propagation.

MAcMA and MMA exhibit similar reactivities toward the poly(MMA) radical. However, the poly(MAcMA) radical adds to MMA faster than the poly(MMA) radical by a factor of three.



Kamachi *et al.*⁴⁷ pointed out that MMA, which is an electron-accepting monomer, can exhibit an electron-donating character depending on the electrophilicity of the attacking radical. The faster addition of the poly(MAcMA) radical to MMA could be attributed to the polar character of the poly(MAcMA) radical, indicating less severe steric hindrance of the acetoxymethyl group than the benzyloxymethyl group.

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