

Polymerization and Copolymerization of Methyl 2-(Chloromethyl)acrylate in Competition with Addition–Fragmentation

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ABSTRACT: Polymerization and copolymerization of methyl 2-(chloromethyl)acrylate (MCMA) to low molecular weight with accompanying β -fragmentation of the MCMA radical leading to the 2-carbomethoxyallyl end group were investigated. The ^1H NMR spectrum of poly(MCMA) revealed that the fragmentation is predominant as the chain-stopping process when $\bar{M}_n = 4400$. In this case, the fragmentation occurred every 33 propagation steps on average, and the ratio of the rate constants for propagation to fragmentation was estimated to be 11 L/mol at 60 °C. The copolymerization of MCMA with methyl methacrylate (MMA) gave copolymer with unsaturated end groups adjacent to MCMA and MMA units as observed by ^1H NMR spectroscopy. The contents of MCMA and MMA units bound to the unsaturated end group depend on the comonomer composition and the monomer reactivity ratio. The relative reactivities of poly(MCMA) and poly(MMA) radicals toward MCMA were determined from the comonomer–copolymer composition relation and the amount of the different monomer units linked to the unsaturated end group. The effect of the adjacent units on fragmentation was considered in relation to the content of the unsaturated end group relative to the MCMA units comprising the main chain. Fragmentation was facilitated more than propagation by raising the temperature.

Introduction

The versatile behavior of 2-(substituted methyl)acrylates in radical polymerization^{1,2} has drawn much attention, because 2-(hydroxymethyl)acrylic esters, which are common precursors of a number of 2-(substituted methyl)acrylates, can be conveniently synthesized by the base-catalyzed reaction of acrylic esters with formaldehyde.³ Among the substituted acrylates derived from (hydroxymethyl)acrylates, the 2-alkoxymethyl,⁴ (fluoroalkoxy)methyl,^{5–7} (acetoacetoxy)methyl,⁸ (benzoyloxy)methyl,⁹ and fluoromethyl^{2,10,11} derivatives have recently been reported as highly polymerizable monomers.

Although 2-(alkylthio)methyl,^{12,13} bromomethyl,^{14,15} and other 2-substituted acrylic esters,^{16,17} styrenes, and acrylonitriles bearing substituents undergo radical addition, fast β -fragmentation of the resultant radicals brings about unsaturated end groups and small radicals. When a conventional monomer such as methyl methacrylate (MMA) or styrene (St) is polymerized in the presence of an acrylate ($\text{CH}_2=\text{C}(\text{CH}_2\text{X})\text{COOR}$) which can undergo the addition–fragmentation reaction, the radical produced from the acrylate by addition of the polymer radical rapidly fragments into the 2-substituted allyl end group ($\text{CH}_2=\text{C}(\text{COOR})\text{CH}_2$) and a small radical (X^\bullet). While extension of the polymer chain is interrupted by the fragmentation, propagation may proceed, since the small radical expelled by the fragmentation can initiate a new polymer chain. When the cleavage and reinitiation are sufficiently fast, the molecular weight of the resultant polymer can be reduced efficiently with no change in the polymerization rate by the addition of a transfer agent. A detailed ^1H NMR spectroscopic study of the low molecular weight polymers from MMA and ethyl methacrylate that were prepared by polymerization in the presence of methyl 2-(bromomethyl)acrylate permitted the assignment of the resonances due to the olefinic and methoxy protons of the unsaturated end group and the bromomethyl group of the MMA unit bound to bromine at the α -end.¹⁵

Methyl 2-(phenoxyethyl)acrylate (MPMA)^{18,19} polymerizes slowly to low molecular weight during which

propagation and addition–fragmentation take place simultaneously. The ^1H NMR spectra of poly(MPMA) exhibited weak resonances from the unsaturated end group. Recently, Mathias et al.²⁰ and Yamada and Otsu¹¹ have independently reported the polymerization of ethyl 2-(chloromethyl)acrylate (ECMA). We have pointed out the quite different behaviors of the 2-(halomethyl)acrylates; i.e., 2-(fluoromethyl)acrylate exclusively undergoes the addition–fragmentation reaction.¹¹ After careful inspection of the ^1H NMR spectrum of poly(ECMA), the carboethoxyallyl group arising from the addition–fragmentation was shown to be bound to the polymer. The polymerization of methyl 2-(chloromethyl)acrylate (MCMA) is also expected to involve addition–fragmentation.

In this article, the polymerization and copolymerization of MCMA in competition with addition–fragmentation are described. In addition, the temperature dependence of the addition–fragmentation process relative to polymerization and copolymerization of MCMA is also discussed.

Experimental Section

Materials. MCMA was prepared by reaction of methyl 2-(hydroxymethyl)acrylate⁸ with thionyl chloride as described in the literature for the synthesis of ethyl 2-(chloromethyl)acrylate from ethyl 2-(hydroxymethyl)acrylate²¹ and was distilled under reduced pressure. The structure of MCMA was verified by ^1H and ^{13}C NMR spectroscopy. MCMA: bp 40 °C/6 Torr; ^1H NMR (CDCl_3) δ = 3.81 (s, 3H, COOCH_3), 4.29 (s, 2H, CH_2Cl), 5.99 (s, 1H, $\text{CH}=\text{C}$), 6.39 (s, 1H, $\text{CH}=\text{C}$); ^{13}C NMR (CDCl_3) δ = 42.5 (CH_2Cl), 52.2 (OCH_3), 128.6 ($\text{CH}_2=\text{C}$), 136.9 ($=\text{C}$), 165.4 ($\text{C}=\text{O}$).

Commercially available MMA was distilled under reduced pressure before use. Commercial 2,2'-azobis(isobutyronitrile) (AIBN), 2,2'-azobis(2,4-dimethylvaleronitrile) (AVN), and 1,1'-azobis(cyclohexane-1-carbonitrile) (ACN) were recrystallized from methanol. 2,2'-Azobis(2,4,4-trimethylpentane) (ATMP) was purified by recrystallization from *n*-hexane. Solvents and all other reagents were purified by conventional methods.

Polymerization Procedure. Polymerizations and copolymerizations were run in glass tubes sealed under vacuum. After a selected period, the contents of the ampule were poured into a large amount of *n*-hexane for the copolymer with MMA or into

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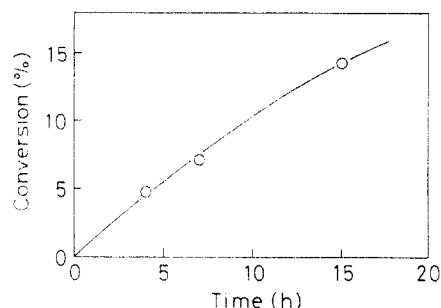


Figure 1. Time-conversion relation for the polymerization of MCMA in benzene at 60 °C: [MCMA] = 3.0 mol/L, [AIBN] = 5.0×10^{-3} mol/L.

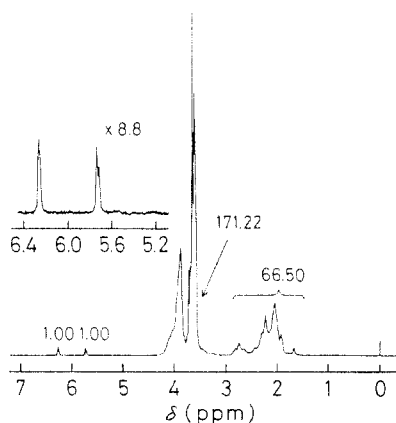


Figure 2. ^1H NMR spectrum of poly(MCMA) prepared as in Figure 1. The numbers in the spectrum indicate intensities of the resonances relative to those of the olefinic protons.

aqueous methanol for poly(MCMA). The overall rate (R_p) of homopolymerization was calculated from the weight of the polymeric product. R_p of the copolymerization was determined from the weight of the copolymer and copolymer composition. Compositions of the copolymers with MMA were calculated from the intensity ratio of the resonances of the methoxy protons of the MMA units and the chloromethyl protons of the MCMA units to the remaining resonances in the ^1H NMR spectra of the copolymers. Monomer reactivity ratios (r_1 and r_2) were evaluated by a nonlinear least-squares procedure.²²

Measurements. Number- and weight-average molecular weights (\bar{M}_n and \bar{M}_w , respectively) and polydispersities (\bar{M}_w/\bar{M}_n) of the resultant polymers were determined with a Tosoh 8000 series high-performance liquid chromatograph equipped with columns for gel permeation chromatography (GPC) packed with TSK Gel G2000HXL, G4000HXL, G4000HXL, and G6000HXL connected in this order at 38 °C with tetrahydrofuran used as eluent. A calibration curve for the determination of \bar{M}_n from 500 to 2 890 000 was obtained by plotting \bar{M}_n of standard poly(St) versus elution time. \bar{M}_n was also obtained with a Knauer vapor pressure osmometer (VPO) at 40 °C.

^1H and ^{13}C NMR spectra were recorded on a JEOL GX-400 spectrometer at 400 and 100 MHz, respectively, at 27 °C. Deuteriochloroform and tetramethylsilane were used as solvent and internal standard, respectively.

Results and Discussion

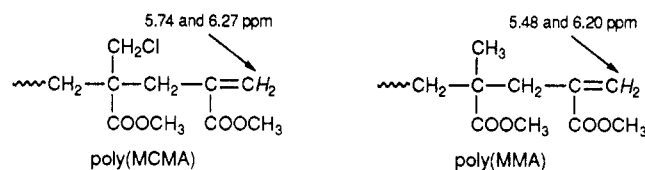
Homopolymerization. Polymerization of MCMA was initiated with AIBN in benzene at 60 °C using [MCMA] = 3.0 mol/L and [AIBN] = 5.0×10^{-3} mol/L. A conversion-time relationship for the MCMA polymerization is shown in Figure 1. The polymerization proceeded slowly and reached 14.3% conversion after 15 h.

Figure 2 shows the ^1H NMR spectrum of poly(MCMA) ($\bar{M}_n(\text{VPO}) = 4400$). The main peaks are assignable to the protons of CH_2Cl and OCH_3 at 3.2–4.2 ppm and of CH_2 at 1.5–3.0 ppm. Weak signals at 5.74 and 6.27 ppm are attributed to the olefinic protons of the end group produced

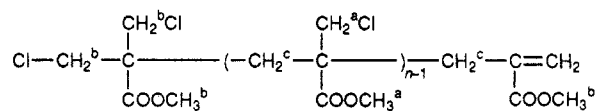
Table I. Relative Intensity of Resonances in the ^1H NMR Spectrum of Poly(MCMA)

chem shift range, ppm	type of proton	notation	rel intens
1.5–3.0	CH_2 (repeating unit)	c	$2(n-1)$
	CH_2 (ω -end group)	c	2
		total	$2n$
3.2–4.2	OCH_3 (repeating unit)	a	$3(n-1)$
	CH_2Cl (repeating unit)	a	$2(n-1)$
	OCH_3 (α -terminal unit)	b	3
	CH_2Cl (α -terminal unit)	b	4
	OCH_3 (ω -end group)	b	3
		total	$5(n+1)$

by β -fragmentation of the poly(MCMA) radical; those of monomeric MCMA appeared at 5.99 and 6.39 ppm. The intensity ratios of the peaks in the ^1H NMR spectrum are given in Figure 2. The chemical shifts of the olefinic protons of the end group bound to the poly(MCMA) chain are different from those of poly(MMA), which appear at 5.48 and 6.20 ppm.¹⁵



If the addition-fragmentation were much faster than bimolecular termination and initiation with an initiator fragment under the present conditions, the resultant poly(MMA) can be shown by the following structure:



Because the resonances of the protons bound to different carbons of the poly(MCMA) appear in either of two chemical shift ranges, 1.5–3.0 and 3.2–4.2 ppm, as shown in Figure 2 and Table I, the ratios of the intensity of the resonances in the lower magnetic field to that of the resonances in the higher magnetic field should be $(5n+5)/2n$. The average value of n was determined to be 33.2. The estimate of \bar{M}_n based on $n = 33.2$ is 4600, and \bar{M}_n determined by VPO was 4400. Fair agreement in \bar{M}_n indicates that the chlorine atom which reinitiates the polymerization of MCMA and the unsaturated end group arising from chain stopping by the fragmentation are introduced quantitatively. The ratios of the amounts of MCMA units to unsaturated end groups in the poly(MCMA) ($[\text{MCMA}]/[\text{CH}_2=\text{C}]$) were evaluated by eq 1 to give $k_p/k_t = 11.1$ L/mol from Figure 2.

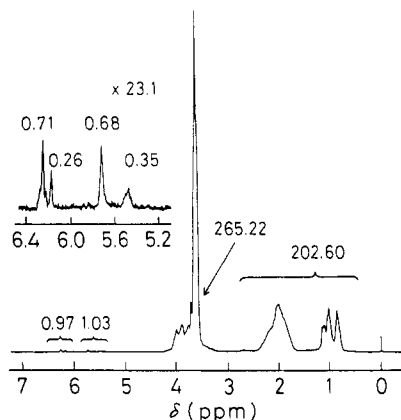
$$\frac{[\text{MCMA}]}{[\text{CH}_2=\text{C}]} = \frac{k_p[\text{MCMA}^*][\text{MCMA}]}{k_t[\text{MCMA}^*]} = \frac{k_p[\text{MCMA}]}{k_t} \quad (1)$$

where k_p and k_t refer to the rate constants of propagation and β -fragmentation, respectively.

Copolymerization. Copolymerization of MCMA (M_2) and MMA (M_1) was initiated with AIBN in benzene at 60 °C. The copolymerization data are shown in Table II together with those of the homopolymerization. Figure 3 and Table III show the comonomer-copolymer composition curve and the monomer reactivity ratios determined. The latter are in agreement with those for the MMA-ECMA copolymerization previously reported as in Table III.¹¹

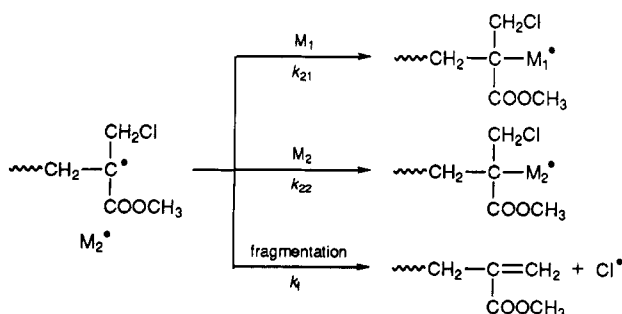
Table II. Copolymerization of MCMA (M_2) with MMA (M_1) in Benzene at 60 °C^a

[M_1] in comonomer (mol %)	$R_p \times 10^5$ (mol/L s)	copolymer			
		[M_1] (mol %)	[M_1]/[M_2] ^b	$\bar{M}_n \times 10^{-3}$ c (NMR)	$\bar{M}_n \times 10^{-3}$ (VPO)
0.0	0.89	0.0	0/33	4.6	4.4
10.0	1.3	15.8	7/34	5.3	5.0
30.0	2.3	40.9	26/36	7.6	7.4
50.0	3.4	63.9	65/36	11.5	10.9
70.0	4.6	76.9	124/36	17.4	16.9 ^d
90.0	6.2	93.6	570/39	62.3	46.5 ^d

^a [MCMA] + [MMA] = 3.0 mol/L, [AIBN] = 5.0×10^{-3} mol/L.^b Average numbers of the respective units per polymer chain calculated from the quantification of end groups by ¹H NMR spectroscopy. ^c Assuming that the end groups were quantitatively introduced. ^d Determined by GPC.**Figure 3.** ¹H NMR spectrum of MCMA-MMA copolymer (59.1:40.9 molar ratio) prepared by copolymerization in benzene at 60 °C: [MCMA] = 2.1 mol/L, [MMA] = 0.9 mol/L, [AIBN] = 5.0×10^{-3} mol/L.

\bar{M}_n of the copolymer was calculated from the molar ratios of the unsaturated end group to the monomeric units of the main chain, and the average numbers of monomeric units given by [M_1]/[M_2] were also estimated as in Table II. Figure 3 shows the ¹H NMR spectrum of the MCMA-MMA copolymer (\bar{M}_n (VPO) = 7400) obtained under the conditions of [MCMA] = 2.1 mol/L, [MMA] = 0.9 mol/L, and [AIBN] = 5.0×10^{-3} mol/L. The expanded spectrum with the four resonances observed in the chemical shift range 5.0–6.5 ppm is also shown in the same figure. One of the pairs of signals is assignable to the end group of poly(MMA).¹⁵ The resonances at 5.74 and 6.27 ppm are attributed to the end group adjacent to the MCMA unit, in conformity with the assignment of the MCMA homopolymer.

The MCMA radical participates in the following three reactions in the copolymerization with M_1 .



The carbomethoxyallyl group bound to the polymer chain, which can be regarded as an acrylic ester bearing a large 2-substituent, cannot homopolymerize.²³ However,

Table III. Monomer Reactivity Ratios for the Copolymerization of MCMA (M_2) with MMA (M_1) in Benzene at 60 °C^a

M_1	M_2	r_1	r_2	Q_2	e_2	ref
MMA	MCMA	1.53	0.56	0.56	0.78	this work
MMA ^b	ECMA	1.58	0.49	0.57	0.91	11

^a [Comonomer] = 3.0 mol/L, [AIBN] = 5.0×10^{-3} mol/L. ^b Copolymerization in bulk at 50 °C.**Table IV.** Copolymerization of MCMA (M_2) with MMA (M_1) with the Accompanying Addition-Fragmentation Affected by the Adjacent Monomeric Unit^a

[M_1] in comonomer (mol %)	[MCMA]/[CH ₂ =C] ^b (molar ratio)	k_{22}/k_f (L/mol)	[M_1] _{ad} /[M_2] _{ad} (molar ratio)	
			calcd ^d	found ^e
0.0	33.2	11.1	0	0
10.0	33.9	10.5	0.20	0.13
30.0	36.5	9.8	0.77	0.44
50.0	35.9	8.6	1.79	1.04
70.0	36.1	7.8	4.17	2.41
90.0	38.7	7.6	16.1	large ^f

^a [M_1] + [M_2] = 3.0 mol/L, [AIBN] = 5.0×10^{-3} mol/L. ^b The ratio of MCMA units relative to CH₂=C groups in the copolymers evaluated from ¹H NMR spectra. ^c Determined by eq 1 or 2. ^d Calculated from eq 4. ^e Evaluated by ¹H NMR spectroscopy. ^f Not determined.

the substituted allyl group exhibits similar reactivity with St toward the poly(St) radical, and a considerable increase in \bar{M}_n with conversion was brought about by addition of the polymer radical to the unsaturated end group during the polymerization of St in the presence of MBMA.^{24,25} Actually, the poly(MMA) radical does not add to the 2-substituted allyl group, because of steric hindrance against addition of a quaternary carbon radical and because of the unfavorable combination of the electron-accepting radical and the electron-deficient carbon-carbon double bond.^{24,25} Poly(MCMA) radical bearing the larger and stronger electron-withdrawing chloromethyl group than the methyl group could not be more reactive than the poly(MMA) radical toward the allyl end group. Therefore, the carbomethoxyallyl group formed could remain intact during the homopolymerization and copolymerization.

The [MCMA]/[CH₂=C] ratio in the copolymer is determined by competition between the additions of poly-(MCMA) radical to M_1 (MMA) and M_2 (MCMA) with the fragmentation.

$$\frac{[\text{MCMA}]}{[\text{CH}_2=\text{C}]} = \frac{k_{21}[\text{M}_2^\bullet][\text{M}_1] + k_{22}[\text{M}_2^\bullet][\text{M}_2]}{k_f[\text{M}_2^\bullet]} = \frac{k_{22}}{k_f} \left(\frac{[\text{M}_1]}{r_2} + [\text{M}_2] \right) \quad (2)$$

Calculation using the experimentally determined values of [MCMA]/[CH₂=C] and r_2 gave the results in Table IV. The k_{22}/k_f value seems to decrease with [M_1], and such changes could be attributed to variation in k_{22} or k_f as considered below. The fragmentation is slower than the homopropagation of MCMA and the addition of poly-(MCMA) radical to MMA by factors of 11 and 20, respectively, according to eqs 1 and 3.

$$k_{22}/k_{21} = r_2$$

and

$$k_{21}/k_f = k_{22}/(k_f r_2) \quad (3)$$

Table IV also summarizes the estimates of the molar ratios of the unsaturated end groups bound to the MMA

and MCMA adjacent units given by $[M_1]_{ad}/[M_2]_{ad}$, which is calculated from eq 4 at the steady state.

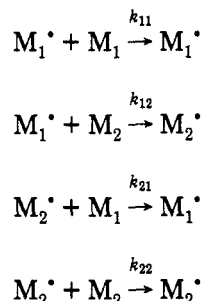
$$k_{12}[M_1^*][M_2] = k_{21}[M_2^*][M_1]$$

$$\frac{[M_1]_{ad}}{[M_2]_{ad}} = \frac{k_{12}[M_1^*][M_2]}{k_{22}[M_2^*][M_2]} = \frac{k_{21}[M_2^*][M_1]}{k_{22}[M_2^*][M_2]} = \frac{[M_1]}{r_2[M_2]} \quad (4)$$

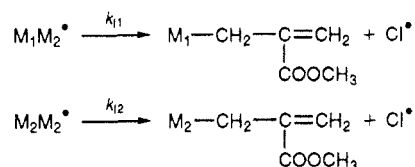
This equation was derived based on the assumption that the adjacent unit does not affect the fragmentation rate of the poly(MCMA) radical.

The values of k_{22}/k_f and $[M_1]_{ad}/[M_2]_{ad}$ in Table IV depend on the composition of the copolymer, and the experimental values of $[M_1]_{ad}/[M_2]_{ad}$ are always smaller than those calculated. Two models were therefore considered for interpretation of these findings. One considers the influence of an adjacent unit of the MCMA radical on the fragmentation rate (model I), and the other is based on the penultimate model of copolymerization (model II).

Model I. The copolymerization of the two monomers (M_1 and M_2) leads to four types of propagation reactions.



In addition to these, two types of the fragmentation are considered.



where $M_1M_2^*$ and $M_2M_2^*$ are designated as an M_2 radical with M_1 and M_2 adjacent units, respectively. Consequently, $[MCMA]/[CH_2=C]$ can be expressed as

$$\frac{[MCMA]}{[CH_2=C]} = \frac{k_{21}[M_2^*][M_1] + k_{22}[M_2^*][M_2]}{k_{f1}[M_1M_2^*] + k_{f2}[M_2M_2^*]} \quad (5)$$

where $[M_1M_2^*] + [M_2M_2^*] = [M_2^*]$. Because the fragmentation is a unimolecular reaction, the value of $[M_1]_{ad}/[M_2]_{ad}$ can be expressed by eq 6.

$$\frac{[M_1]_{ad}}{[M_2]_{ad}} = \frac{k_{f1}[M_1M_2^*]}{k_{f2}[M_2M_2^*]} \quad (6)$$

Equation 5 can be reformulated as eq 7 by using eq 6:

$$\frac{[MCMA]}{[CH_2=C]} = \frac{k_{22}}{k_{f2}} \frac{[M_2^*](\frac{[M_1]}{r_2} + [M_2])}{[M_2M_2^*](\frac{[M_1]_{ad}}{[M_2]_{ad}} + 1)} \quad (7)$$

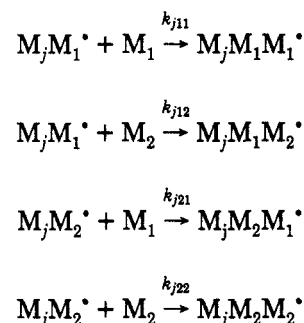
The k_{22}/k_{f2} value for the homopolymerization of MCMA is equal to 11.1 L/mol (Table IV). The values of $[M_1M_2^*]/[M_2^*]$ and $[M_2M_2^*]/[M_2^*]$ can be estimated from eq 7. The k_{f1}/k_{f2} value can also be calculated from eq 6 by using the values of $[M_1M_2^*]/[M_2^*]$ and $[M_2M_2^*]/[M_2^*]$ which have been evaluated. It can be seen that k_{f1}/k_{f2} remains constant irrespective of comonomer composition as shown in Table V. Because M_1 and M_2 are assigned to MMA and

Table V. Ratio of the Fragmentation Rate Constants of the MCMA Radical with Different Adjacent Units Based on Model I

[MMA] in comonomer (mol %)	$[M_1M_2^*]/[M_2^*]$ (molar ratio)	$[M_2M_2^*]/[M_2^*]$ (molar ratio)	k_{f1}/k_{f2}
10.0	0.065	0.935	1.87
30.0	0.219	0.781	1.57
50.0	0.368	0.632	1.78
70.0	0.582	0.418	1.73
		av	1.74 ± 0.13

MCMA, respectively, a value of k_{f1}/k_{f2} greater than unity means that $\sim\sim\sim$ MMA-MCMA \cdot undergoes faster fragmentation than $\sim\sim\sim$ MCMA-MCMA \cdot .

Model II. According to the penultimate model, the propagations in binary copolymerization are described as follows:²⁶



where j represents 1 or 2. It was assumed that the fragmentation takes place through the same elementary reactions as in model I with the single rate constant, k_f , for the MCMA radicals adjacent to MMA and MCMA units.

$$\frac{[M_1]_{ad}}{[M_2]_{ad}} = \frac{k_f[M_1M_2^*]}{k_f[M_2M_2^*]} = \frac{[M_1M_2^*]}{[M_2M_2^*]} \quad (8)$$

Consequently, $[MCMA]/[CH_2=C]$ can be given by

$$\begin{aligned} \frac{[MCMA]}{[CH_2=C]} &= \frac{k_{121}[M_1M_2^*][M_1] + k_{122}[M_1M_2^*][M_2]}{k_{f1}[M_1M_2^*] + k_{f2}[M_2M_2^*]} + \\ &\quad \frac{k_{221}[M_2M_2^*][M_1] + k_{222}[M_2M_2^*][M_2]}{k_{f1}[M_1M_2^*] + k_{f2}[M_2M_2^*]} = \\ &\quad \frac{k_{121}[M_1][M_1M_2^*]}{[M_2M_2^*]} + \frac{k_{122}[M_2][M_1M_2^*]}{[M_2M_2^*]} + \\ &\quad \frac{k_{221}[M_1] + k_{222}[M_2]}{k_{f1}[M_1M_2^*]/[M_2M_2^*] + k_{f2}} \quad (9) \end{aligned}$$

Because the copolymer composition is known to be insensitive to the penultimate effect,^{27,28} r_1 and r_2 defined by the terminal model were employed without modification. The penultimate effect is expressed by s_1 and s_2 .

$$\begin{aligned} r_1 &= \frac{k_{111}}{k_{112}} = \frac{k_{211}}{k_{212}} & r_2 &= \frac{k_{122}}{k_{121}} = \frac{k_{222}}{k_{221}} \\ s_1 &= \frac{k_{211}}{k_{111}} & s_2 &= \frac{k_{122}}{k_{222}} \end{aligned}$$

Table VI. Estimation of Penultimate Effect of Model II in the Copolymerization Accompanying the Addition-Fragmentation

[M ₁] in comonomer (mol %)	<i>s</i> ₂
10.0	0.53
30.0	0.64
50.0	0.56
70.0	0.58
av	0.58 ± 0.05

Table VII. Homopolymerization of MCMA and MCMA-MMA Copolymerization in Benzene at Various Temperatures

temp (°C)	[I] ^a (mmol/L)	homopolymerization ^b		copolymerization ^c	
		time (h)	conv (%)	time (h)	conv (%)
40	AVN, ^d 10	8.0	5.3	4.6	12.1
60	AIBN, ^e 5.0	4.0	4.8	4.0	14.5
80	ACN/ ^f 7.2	5.5	10.3	3.5	20.3
100	ATMP, ^g 7.1	3.5	11.5	3.5	23.7

^a *k*_d[I] = 4.6 × 10⁻⁶ mol/L s. ^b [MCMA] = 3.0 mol/L. ^c [MCMA] = [MMA] = 1.5 mol/L. ^d *k*_d = 4.58 × 10⁻⁶ s⁻¹ at 40 °C. ^e *k*_d = 9.15 × 10⁻⁶ s⁻¹ at 60 °C. ^f *k*_d = 6.34 × 10⁻⁶ s⁻¹ at 80 °C. ^g *k*_d = 6.45 × 10⁻⁶ s⁻¹ at 100 °C.³¹

Equation 9 can be rewritten as eq 10 by using eq 8.

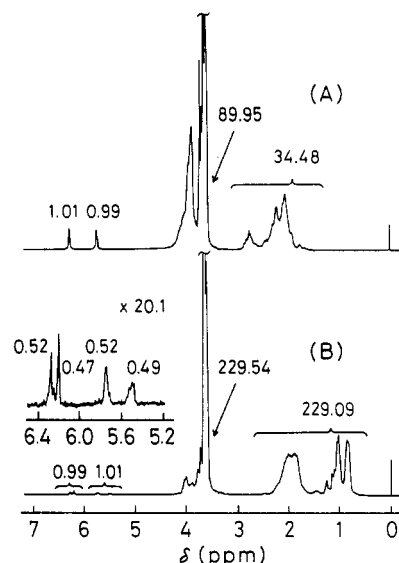
$$\frac{[\text{MCMA}]}{[\text{CH}_2=\text{C}]} = \frac{k_{222}}{k_f} \frac{([M_1]/r_2 + [M_2])(s_2[M_1]_{ad}/[M_2]_{ad} + 1)}{[M_1]_{ad}/[M_2]_{ad} + 1} \quad (10)$$

Because *k*₂₂₂/*k*_f was evaluated as given in Table IV, *k*₂₂₂/*k*_f = 11.1 L/mol, the value of *s*₂ can be estimated from eq 10 as shown in Table VI. Constant *s*₂ values less than unity were obtained for a wide range of copolymer compositions, indicating slower addition of ~~~MMA-MCMA* to MCMA than ~~~MCMA-MCMA*.

Thus, concurrent propagation and fragmentation were interpreted by model I and model II. The effects of the adjacent unit and the penultimate unit on the fragmentation and propagation, respectively, are likely to arise from differences in the polarities of MCMA and MMA. Greater ease of addition of ~~~MCMA-MCMA* to electron-accepting MCMA than ~~~MMA-MCMA* predicted by model II could not be expected, because the MCMA unit has a stronger electron-withdrawing character than the MMA unit and because the chloromethyl group is larger than the methyl group. Although factors affecting the fragmentation rate are not known, the fact that the fragmentation of the MCMA radical bound to the MCMA unit is slower than the fragmentation of the MCMA radical bound to the MMA unit in model I seems to reflect the polar effect of the chloromethyl group.²⁹

Homopolymerization and Copolymerization with Methyl Methacrylate at Various Temperatures. It was expected that the fragmentation of the poly(MCMA) radicals is accelerated by raising the temperature, similar to the behavior of poly(MPMA) radicals.¹⁹ The homopolymerization of MCMA and the copolymerization of MCMA with MMA were further carried out at higher temperatures using a selected initiator with an appropriate decomposition rate constant (*k*_d) at each temperature, and the results are summarized in Table VII.

The ¹H NMR spectra of poly(MCMA) and MCMA-MMA copolymer prepared at 80 °C are depicted in Figure 4. Apparently, both the polymer and copolymer prepared at 80 °C contain larger amounts of unsaturated end groups than do the polymer and copolymer polymerized at 60 °C. The intensities of the resonances from the olefinic protons

**Figure 4.** ¹H NMR spectra of poly(MCMA) (A) and MCMA-MMA copolymer (B) obtained at 80 °C.**Table VIII. Competition of the Fragmentation with the Polymerization and Copolymerization of MCMA at Various Temperatures^a**

temp (°C)	[MMA] in copolymer (mol %)	[MCMA]/[CH ₂ =C] (molar ratio)	<i>M</i> _n (NMR)	<i>M</i> _n (GPC)	<i>M</i> _w / <i>M</i> _n (GPC)
Homopolymerization					
40		65.7	9000	5700	1.50
60		33.2	4600	4400 ^b	
80		17.0	2400	1800	1.34
100		7.9	1200	800	1.41
Copolymerization					
40	58.9	96.8	27200	19027	1.76
60	63.9	35.9	11500	10900 ^b	
80	60.5	22.9	6900	5700	1.50
100	61.2	11.4	3600	3100	1.46

^a Polymerized under the conditions given in Table VII. ^b Determined by VPO.

of the polymer and copolymer obtained at 100 °C increased further. Changes in the ratios of the fragmentation to propagation rate constants and *M*_n are shown in Table VIII. The *M*_n estimated from ¹H NMR spectroscopy is almost consistent with that determined by GPC. As the temperature increased from 50 to 100 °C, the values of *M*_n and [MCMA]/[CH₂=C] decreased.

Differences in the frequency factor (*A*) and the activation energy (*E*) between propagation and fragmentation of MCMA polymerization were estimated by using eq 11 derived from eq 2.

$$\ln \frac{[\text{MCMA}]}{[\text{CH}_2=\text{C}]} = \ln \frac{A_p[\text{MCMA}]}{A_f} + \frac{E_f - E_p}{RT} \quad (11)$$

where the subscript f denotes the fragmentation of the MCMA radical. *E* and *A* for the competitive reactions were estimated from the plot shown in Figure 5.

$$E_f - E_p = 34.0 \text{ kJ/mol}$$

$$A_f/A_p = 2.0 \times 10^4 \text{ mol/L}$$

If the terminal model is used for the copolymerization of MCMA with MMA, differences in the *A* and *E* values between fragmentation and propagation at an equimolar mixture of MMA and MCMA can be determined

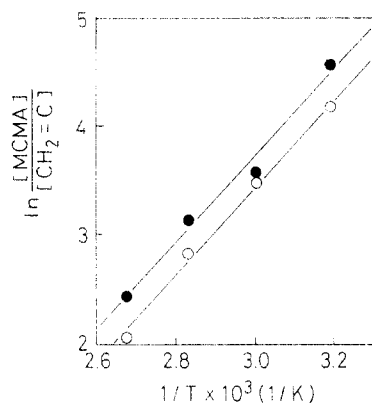


Figure 5. Arrhenius plots for competition between fragmentation and propagation in the polymerization of MCMA (O) and the copolymerization of MCMA with MMA (●) under the conditions given in Table VII.

from the following equation.

$$\ln \frac{[\text{MCMA}]}{[\text{CH}_2=\text{C}]} = \ln \frac{A_{22}}{A_f} \left(\frac{[\text{M}_1]}{r_2} + [\text{M}_2] \right) + \frac{E_f - E_p}{RT} \quad (12)$$

The Arrhenius plots based on eq 12 are depicted in Figure 5. E and A for the competitive reactions are evaluated as follows:

$$E_f - E_{22} = 33.5 \text{ kJ/mol}$$

$$A_f/A_{22} = 1.8 \times 10^4 \text{ mol/L}$$

The values of $(E_f - E_{22})$ and A_f/A_{22} for the copolymerization of MCMA (M_2) with MMA (M_1) are in fair agreement with $(E_f - E_p)$ and A_f/A_p for the homopolymerization of MCMA, respectively. Although k_f depends on the adjacent unit of the MCMA radical, no difference in activation energy between the fragmentation in the homopolymerization and copolymerization was observed. Thus, the fragmentation, which is a unimolecular reaction with larger E and A values than propagation, should become more important at higher temperatures.

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