

Pulsed Laser Polymerization of Cyclohexyl Acrylate Involving Fragmentation of Mid-Chain Radical

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ABSTRACT: Pulsed laser polymerization (PLP) of cyclohexyl acrylate (CHA) was carried out to optimize the PLP conditions for determination of consistent propagation rate coefficients (k_p s). Concurrence of mid-chain radicals (MCRs) formed primarily by backbiting and propagating radicals as an unavoidable feature of acrylate polymerization for kinetic study was confirmed by ESR spectroscopy. The molecular weight distributions (MWDs) of the resultant polymers measured by GPC were carefully inspected to exclude the influence of the low reactivity and β -fragmentation of MCR in order to obtain consistent values of k_p . The PLPs at the low initiator concentrations where the influence of MCR could be minimized were found to give MWDs suitable for k_p determination. The k_p values obtained for CHA were comparable with reported values for other acrylic esters.

KEY WORDS Radical Polymerization / Propagation Rate Constant / Mid-Chain Radical / Pulsed Laser Polymerization / Molecular Weight Distribution / Fragmentation /

Radical polymerization is a typical chain reaction consisting of elementary reactions where short lived propagating radicals (PRR) are involved as chain carriers. The value of the rate constant for propagation (k_p) is one of the most important numerical values relating to polymer formation. GPC analysis of the polymer formed by pulsed laser polymerization (PLP) is known as one of the modern techniques to obtain the value of k_p according to the following equation.^{1–4}

$$L_n = nk_p[M]t_d \quad (1)$$

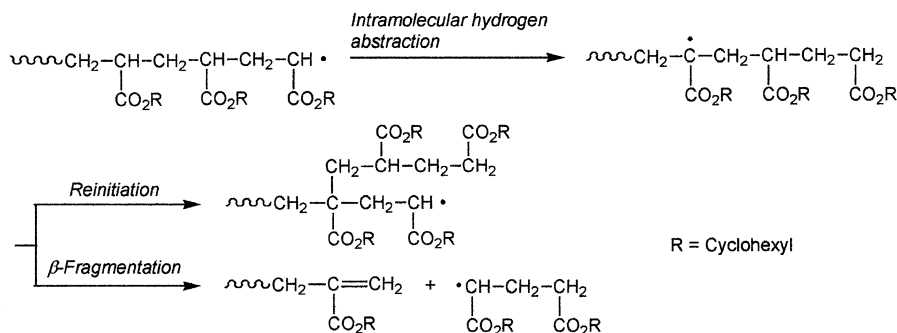
where $[M]$ and t_d denote the monomer concentration and the dark time between pulses, respectively. L_n , the chain length of polymer formed between consecutive laser pulses, is obtained from the inflection point of the GPC elution curve corresponding to the polymerization for the n th pulse. The polymerizations of alkyl methacrylates,^{5,6} styrene,^{7,8} and some other monomers^{9–13} followed eq 1 and consistent values of k_p for these monomers have been determined by the PLP method.^{3,4} However, the k_p values of acrylic esters have been known to depend on the PLP conditions because of chain transfer affecting the chain length of the polymer.^{12,13} In order to avoid the influence of chain transfer, sufficiently short pulse intervals and low temperature have been recommended.^{12–14}

Determination of k_p based on ESR quantification of PRR is also one of the modern techniques for kinetic analysis of radical polymerization as well as the PLP

method. The ESR method has conveniently been employed for polymerizations of a variety of monomers including mono-substituted, 1,1-disubstituted, and 1,2-disubstituted ethylenic monomers under optimized conditions.^{15,16} However, the ESR detection of PRR during acrylate polymerization was not successful until our recent studies^{17,18} because of too fast polymerization to high molecular weight accompanying rapid increase in viscosity of polymerization mixture and a continuous increase in the sensitivity of the cavity with conversion arising from a considerable dielectric loss due to monomer. These difficulties were overcome by dilution of monomer with benzene as a non-polar solvent, and the mid-chain radical (MCR) in acrylate polymerization was succeeded detecting by ESR spectroscopy together with PRR.^{17,18}

Acrylate polymerization involving two types of radical species in comparable concentrations has drawn attention because MCR is denoted to be considerably less reactive than PRR.¹⁹ Furthermore, MCR which would slowly add to acrylate monomer undergoes β -fragmentation (main chain scission) to form an unsaturated end group and a small radical that smoothly initiates a new chain as shown in Scheme 1.²⁰ Extrapolation of the MCR concentration to 0% conversion revealed that MCRs are formed intramolecularly almost exclusively at low conversions.^{17,18} Alternatively, we monitored M_n s of poly(CHA) formed at narrow conversion ranges up to high conversion and found a significant decrease in M_n at the conversion range higher than 90%.²¹ This finding can be explained by fragmen-

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Scheme 1.

tation of MCR formed by intermolecular hydrogen abstraction with PRR from the polymer.

The PLP method requires the chain length of polymer formed, and the fragmentation of MCR would seriously bias the PLP data for the k_p calculation.²² The PLP of the methyl acrylate dimer (methyl α -(2-carbomethoxyethyl)acrylate, MAD), which forms a PRR structurally similar to the MCR in acrylate polymerization, suggested that the fragmentation of MCR and the reaction of the unsaturated end group arising from the fragmentation affects the molecular weight distribution (MWD).²³

In the present article, PLP of cyclohexyl acrylate (CHA) in bulk was carried out using high frequency of the laser pulse at different laser intensities and initiator concentrations over a wide temperature range. The PLP conditions were optimized to exclude the effects of the MCR.

EXPERIMENTAL

Materials

Commercially available CHA (Tokyo Kasei Kogyo) was distilled under reduced pressure in a nitrogen stream to remove the inhibitor and subsequently stored in a refrigerator. The concentration of bulk CHA was 6.57 mol L^{-1} at room temperature. Benzoin (Fluka) was used as photoinitiator as supplied. Methyl 2,2'-azobisisobutyrate (MAIB; Wako) was used after recrystallization from *n*-hexane.

PLP Procedure

All PLP experiments were performed at Eindhoven University of Technology. The reaction mixture was bubbled with dry nitrogen for 30 s to remove the oxygen before polymerization. About 1 mL of the reaction mixture was placed in a temperature controlled reaction cell made of quartz. The constant temperature during the polymerization was checked by a platinum resistance element (Netsushin, type PT100 MG-1505) connected to a recorder (Philips, PM8100) inserted in the

thermostated water or isopropanol circulating outside the polymerization cell. The polymerization mixture was irradiated by an excimer laser (Lambda Physik, LPX110iMC). The laser pulse frequency was fixed at 100 Hz, and the constant power was internally monitored by the laser producing instrument. After the polymerization, a small amount of solid hydroquinone was added to the mixture to prevent further polymerization. The conversion was calculated from difference in the weight of the polymerization mixture after evaporation of the remaining monomer under vacuum.

ESR Measurement

The ESR spectrum was acquired using a Bruker ESP-300 spectrometer at X-band (*ca.* 9.6 GHz) with 100 kHz field modulation at a microwave power of 10 mW and a modulation amplitude 10 G. The spectrum recorded over a magnetic field of 150 G centered at 3380 G was divided into 1024 points, and the conversion time and time constant were 40.96 ms and 655.36 ms, respectively. A 5 mm o.d. quartz tube sealed under vacuum containing the polymerization mixture was irradiated by a 1.5 kW xenon lamp (Ushio) from a distance of *ca.* 20 cm.

GPC Analysis

MWDs were obtained by GPC analysis carried out with a Waters system equipped with two Polymer Laboratory's PL2mixC columns and a RI detector. Tetrahydrofuran was used as the eluent at 40°C. Polystyrene (PSt) standards (Polymer Laboratories, $M_n = 580$ to $M_n = 7.1 \times 10^6$) were used for calibration. In order to use the universal calibration method, Mark-Howink-Sakurada's (MHS) parameters for PSt standard and sample polymer are required. In this study, $K = 1.14 \times 10^{-4} \text{ dL g}^{-1}$ and $\alpha = 0.716$ ²⁴ for standard PSt, and the values for PCHA were approximated by $K = 1.22 \times 10^{-4} \text{ dL g}^{-1}$ and $\alpha = 0.700$ ²⁴ for poly(*n*-butyl acrylate) (poly(BA)) because the values for PCHA were not available.

Table I. PLP conditions and the results of k_p calculation

No.	Temp. °C	[I] mmol L ⁻¹	Laser power mJ	Polymn. time s	Convn. %	MWD ^a	Inflection point ×10 ⁻³ (g mol ⁻¹)		$k_p \times 10^{-2}$ L mol ⁻¹ s ⁻¹	$m(I_3) \times 10^{-3}$ (g mol ⁻¹), $m(I_2)/$ $m(I_1)$, and k_p (L mol ⁻¹ s ⁻¹) from $m(I_2)$		
							$m(I_1)$	$m(I_2)$				
1	-20.2	0.25	30	10	2.7	A	316	—	—	—	—	—
2	-10.1	0.25	24	20	0.8	A	661	—	—	—	—	—
3	20.0	10.0	24	2	11.4	A	89	—	—	—	—	—
4	39.8	1.0	50	3	5.8	A	209	—	—	—	—	—
5	49.9	1.0	50	5	10.0	A	257	—	—	—	—	—
6	-15.0	0.25	29	10	0.4	B	44	89	43 ^b	—	2.02,	4400
7	0.0	0.25	30	10	0.7	B	71	151	70 ^b	—	2.13,	7500
8	20.2	1.0	50	3	6.4	C	123	234	121 ^b	—	1.90,	11500
9	30.0	1.0	50	3	10.7	C	155	257	153 ^c	—	1.66,	12500
10	30.0	1.0	20	3	3.5	C	162	295	160 ^b	—	1.82,	14600
11	39.8	1.0	20	3	2.2	C	214	324	211 ^c	—	1.51,	16000
12	10.0	10.0	50	2	13.1	D	28	58	27 ^d	89,	2.07,	2900
13	10.0	10.0	79	2	16.1	D	28	53	27 ^d	89,	1.89,	2600
14	19.7	42.4	29	5	20.3	D	27	54	27 ^d	—	2.00,	2700
15	20.0	10.0	77	2	21.9	D	25	58	25 ^d	—	2.32,	2500
16	39.9	10.0	70	2	19.1	D	24	54	25 ^d	—	2.08,	2700

^aSee Figure 2. ^b Calculated from $m(I_1)$ within $1.80 < m(I_2)/m(I_1) < 2.20$. ^cCalculated from $m(I_1)$ out side of $1.80 < m(I_2)/m(I_1) < 2.20$. ^dCalculated from $m(I_1)$ and underestimated, see Figure 3.

RESULTS AND DISCUSSION

ESR Spectrum

The ESR spectrum consisting of PRR and MCR has already been observed during the polymerization of CHA at 60°C.¹⁸ In order to confirm the presence of MCR under experimental conditions comparable to those of the present PLP carried out at temperature lower than 60°C, and ESR spectrum was recorded during CHA polymerization at 0°C (Figure 1). Hyperfine coupling with only two of the four β -protons of MCR could be distinguished to show the three-line spectrum.²⁷ PRR of CHA appears as a seven-line spectrum arising from the coupling of α - and β -protons to which three types of the coupling constants were assigned.^{17, 18} The observed spectrum can be accounted for by overlapping of the spectra of PRR (30%) and MCR (70%) based on simulation using the hyperfine coupling constants 12.0, 22.0, and 33.0 G for PRR and 27.5 G for MCR in agreement with those already reported.^{17, 18, 25–28} The reactions of MCR, β -fragmentation giving polymer bearing the unsaturated end group and a small radical and slower addition to monomer than propagation as shown in Scheme 1, would affect the MWD of the polymer of CHA formed by PLP.^{22, 23} Although MCR might be formed by intermolecular hydrogen abstraction, intramolecular hydrogen abstraction (backbiting) would be the main reaction at low conversion.^{17, 18}

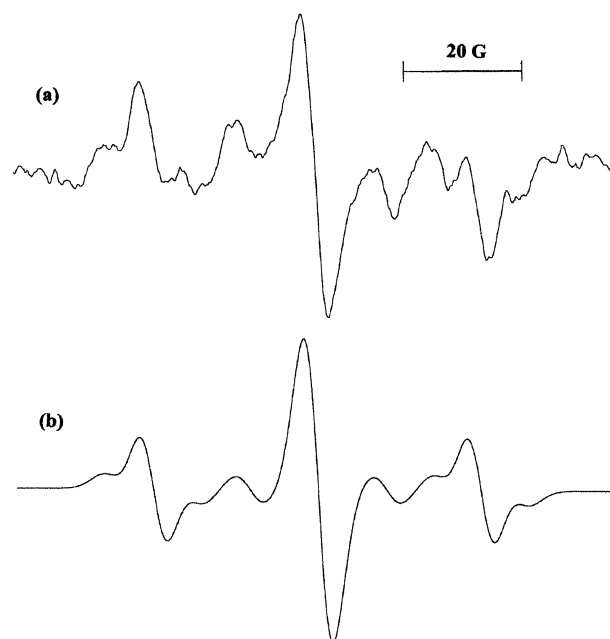


Figure 1. ESR spectrum recorded during the CHA polymerization in toluene at 0°C initiated by irradiation of a 1.5 kW xenon lamp ([CHA] = 1.0 mol L⁻¹, [MAIB] = 25 mmol L⁻¹) (a) and simulation of the observed spectrum (b).

Results of PLP

Table I summarizes the results of the PLP experiments of CHA under different conditions of temperature, initiator concentration and laser power. The polymerization time, which was varied to adjust the amount of polymer formed, is not expected to exert any decisive influence on the MWD. An increase in temperature

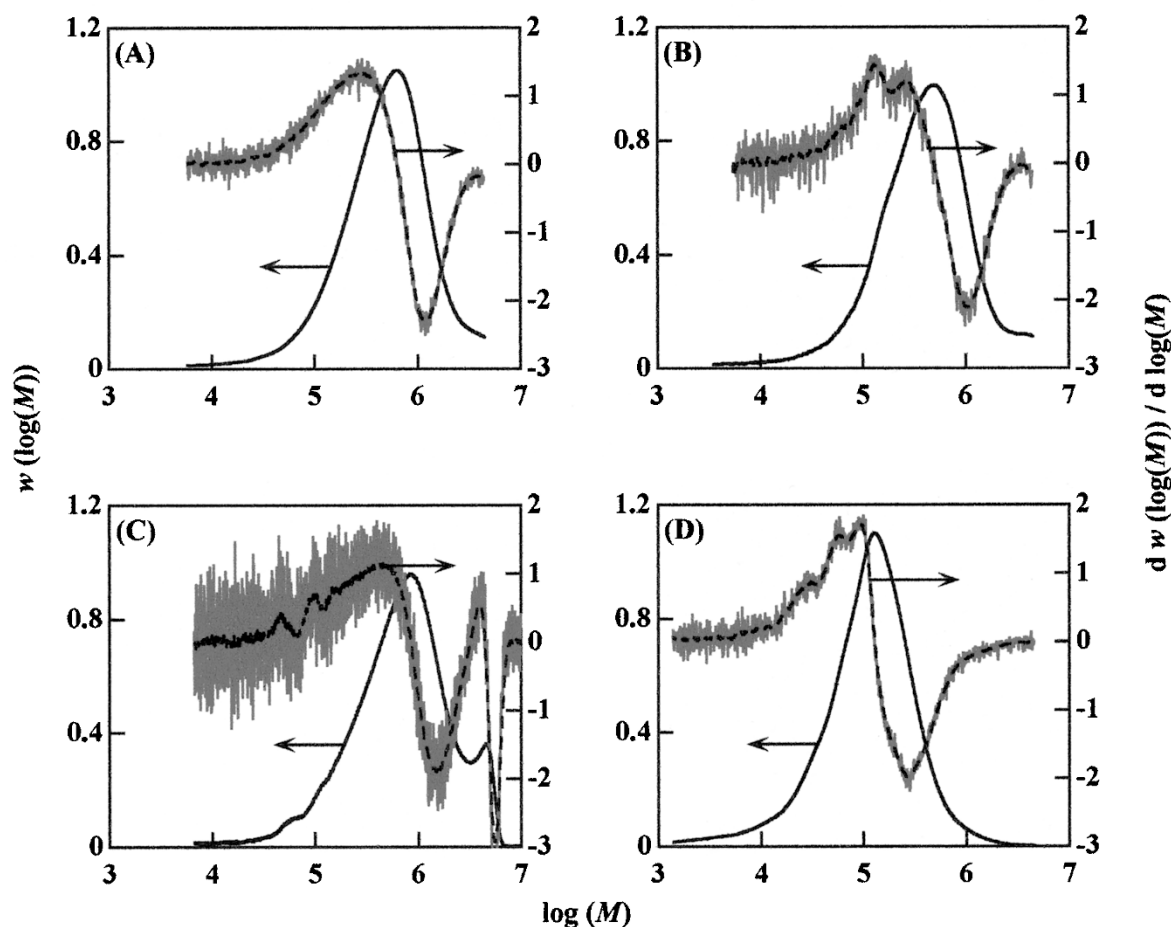


Figure 2. MWD (solid line), the derivative of MWD (gray line), and the noise reduced derivatives (broken line) for the polymer obtained under different conditions given in the order of initiator concentration, laser power, time, and temperature: (A) 1.0 mmol L⁻¹, 50 mJ, 5 s, and 49.9 °C (No. 5); (B) 0.25 mmol L⁻¹, 29 mJ, 10 s, and -15.0 °C (No. 6); (C) 1.0 mmol L⁻¹, 50 mJ, 3 s, and 20.2 °C (No. 8); (D) 10.0 mmol L⁻¹, 79 mJ, 2 s, and 10.0 °C (No. 13).

would bring about an increase in the fragmentation rate relative to the propagation rate leading to a decrease in the chain length used in eq 1. Increases in the initiator concentration and the laser power would result in an increase in the concentration of primary radicals from the initiator leading mainly to reduced molecular weight of the non “PLP” polymer according to the standard kinetics of radical polymerization. An increase in initiator concentration would cause the concentrations of PRR and MCR to increase to different extents as a result of different lifetimes.

It has been required as the most important consistency criterion that the molecular weight of the secondary inflection point ($m(I_2)$) should be twice that of the primary inflection point ($m(I_1)$) in MWD; *i.e.*, k_p calculated from $m(I_1)$ and $m(I_2)$ should be the same.^{7,29} This corresponds to a situation where the polymer radicals initiated by the primary radicals generated at the laser irradiation are instantaneously terminated by the primary radicals generated at the subsequent laser pulse after propagation during the dark period or exactly two dark periods. Some polymer rad-

icals would lose their activities through ordinary bimolecular termination to give molecular weight corresponding to the top peak of MWD, $m(T)$, different from the instantaneous primary radical termination yielding $m(I_1)$, $m(I_2)$, etc. Furthermore, the apparent k_p values obtained should be independent of the initiator concentration and the laser power.

PLP Conditions and MWD

The data in Table I were carefully inspected with reference to the MWD profiles obtained in the PLP of MAD.²² The PRR of MAD undergoing β -fragmentation is structurally similar to the MCR of CHA, and the effect of fragmentation on the MWD of the PLP polymer of CHA can be deduced on the basis of the results of the PLP of MAD.²² The MWDs of the CHA polymerization can fit into four categories, **A**, **B**, **C**, and **D**, which can be rationalized by taking into account the effects of bimolecular termination, fragmentation and the low reactivity of MCR. The representative MWDs and their derivatives are shown in Figure 2.

Based on the higher activation energy of β -frag-

Table II. Difference in PLP conditions and MWD

Group	No.	Difference in PLP conditions ^a	$m(I_1)$ or $m(T)$ $\times 10^{-3b}$ (g mol ⁻¹)	MWD
I	4 → 11	Laser power = 50 → 20 mJ [I] = 10.0 → 1.0 mmol L ⁻¹	209 → 214	A → C
II	3 → 8	Laser power = 24 → 50 mJ Temp. = 20.0 → 20.2°C [I] = 1.0 → 10.0 mmol L ⁻¹	89 → 123	A → C
III	8 → 15	Laser power = 50 → 77 mJ Temp. = 20.2 → 20.0°C [I] = 1.0 → 42.4 mmol L ⁻¹	123 → 25	C → D
IV	8 → 14	Laser power = 123 → 29 mJ Temp. = 19.7 → 20.2°C	123 → 27	C → D
V	5 → 9	Temp. = 49.9 → 30.0°C	257 → 155	A → C
VI	2 → 6 → 7	Laser power = 24 → 29 → 30 mJ Temp. = -10.1 → -15.0 → 0°C	551 → 44 → 71	A → B → B

^aDetails of the PLP conditions are given in Table I. ^b $m(I_1)$ was chosen as the inflection point at the lowest M_n . In the case of a unimodal curve, only $m(T)$ was observed.

mentation than that of propagation in the case of MAD polymerization,³⁰ some polymerizations of CHA were carried out below 0°C to suppress the fragmentation of MCR. The profiles of the derivatives of MWD shown by No. 1 and 2 follow A which exhibits only $m(I_1)$ or $m(T)$ but no $m(I_2)$. The high values of $m(T)$ suggest polymerizations at higher temperatures than that prescribed, and the MWDs for No. 1 and 2 (A) are likely to be caused by polymerization after PLP prior to addition of hydroquinone at room temperature (see Experimental). No. 3, 4, and 5 gave MWDs of A by PLP at higher temperatures and high initiator concentrations. In these cases, the PLP and stopping the PLP by addition of hydroquinone were carried out at similar temperatures and undesirable polymerization can be ruled out. Therefore, A can be expected to arise from reduced M_n by an increase in the rate of “non-PLP” chain stopping event including bimolecular termination and fragmentation at the higher temperature or initiator concentration.

The MWDs resulting from No. 6 and 7 polymerized at -15 and 0°C using the lowest initiator concentration, 0.25 mmol L⁻¹, belong to B where $m(I_1)$ and $m(I_2)$ are clearly observed. However, $m(T)$ seems to be too high in comparison with those in A, C, and D as can be seen in Figure 2: $m(T) > 10 \times m(I_1)$. Again, the high $m(T)$ may be caused by polymerization after PLP prior to addition of hydroquinone, as explained in the case of A. C shows two inflection points corresponding to $m(I_1)$ and $m(I_2)$ such as No. 8–11 by PLPs at different temperatures depending on initiator concentration and laser power.

No. 12–16 gave D with two or three inflection points at 10.0 mmol L⁻¹ or higher initiator concentration. $m(I_1)$ and $m(I_2)$ of D are much lower than those of B and C under the comparable PLP conditions ex-

cept for the initiator concentration, suggesting that the inflections points are biased by the influence of MCR to lower molecular weight as D. Furthermore, $m(I_1)$ of D is much lower than $m(T)$ ($m(T) > 4 \times m(I_1)$) indicating the presence of a radical species surviving four pulse intervals. When the tertiary inflection point is obvious, $m(I_3) = 3.18 \times m(I_1)$ and $m(I_3) < m(T)$; $m(I_3)$ is corresponding to polymer produced during the four counts of the pulses. Although there is no direct evidence for such a long lifetime of the PRR or MCR of the acrylate under the PLP conditions, the PLP of dimethyl itaconate was found to involve PRR surviving for three or more dark periods.³¹

Effect of Experimental Parameter

Independence of k_p estimates of the initiator concentration and the laser power should be confirmed as the criteria for the PLP method.¹³ However, the k_p values calculated from D in Table I are smaller than those from B and C. In order to consider the effects of the changes in the individual experimental parameters of PLP on MWD, several combinations of the experiments were selected as I–VI in Table II.

An increase in laser power in I reduced $m(T)$ only slightly whereas C for No. 11 became A for No. 4 at 39.8°C. Comparison of the results in II revealed that ten times higher initiator concentration and higher laser power of No. 3 (A) resulted in lower $m(I_1)$ by a factor of 1.4 than for No. 8 (C). Although No. 8 in III fulfilled the consistent criterion as C, No. 15 (D) showing $m(I_1)$ and $m(I_2)$ obtained by the polymerization at higher initiator concentration and laser power gave a lower $m(I_1)$ by a factor of ca. 5. However, the $m(I_1)$ for No. 15 was considerably smaller than that of No. 8 at similar temperature and laser power but at lower initiator

concentration. In the cases of **II** and **III**, the low M_n of polymer terminated by bimolecular reaction and/or fragmentation might bias or hide $m(I_1)$ and $m(I_2)$, and those MWDs were not suitable for k_p calculation. A more significant effect of higher initiator concentration can be seen by comparison of *No. 8* (**C**) and *No. 14* (**D**) in **IV**. The higher initiator concentration for *No. 14* than that for *No. 8* by a factor of more than 40 and the $m(I_1)$ and $m(I_2)$ for *No. 8* were more than four times higher than those for *No. 14* as shown in Table I. In the ideal PLP, $m(I_1)$ and $m(I_2)$ should remain constant irrespective of the initiator concentration. The k_p values calculated from the biased $m(I_1)$ and $m(I_2)$ of *No. 14* would be underestimated.

Between *No. 5* and *No. 9* in **V** (**A** and **C**, respectively), difference in temperature can be the reason to change the profile of MWD. The polymerization at low temperature, *No. 9* (**C**), formed shorter polymers terminated by primary radicals to show $m(I_1)$ and $m(I_2)$. In the case of *No. 5* (**A**), $m(I_1)$ might be too close to $m(T)$ because of an increase in the rate of β -fragmentation of MCR relative to propagation at higher temperature. The molecular weight of the poly(CHA) formed by primary radical termination, $m(I_1)$ or $m(I_2)$, should be sufficiently lower than that of the polymer terminated by bimolecular reaction, chain transfer, or fragmentation. Among the polymerizations given by **VI**, *No. 2* (**A**) yielded much higher $m(T)$ in comparison with of *No. 6* and *7* (**B**). The higher molecular weight polymer of *No. 2* would be formed by polymerization before addition of hydroquinone as already mentioned.

In this study, the PLP yielding the MWDs of **B** and **C** seem to be preferable for the determination of k_p values of CHA. In order to accomplish such circumstances, the PLP of CHA should be carried out using sufficiently low initiator concentration under irradiation of low laser power at moderate temperatures.

Calculation of k_p and Arrhenius Plot for k_p

The k_p values were calculated from the selected MWD data using eq 2.

$$k_p = \frac{m(I_1)}{([CHA]=6.57 \text{ mol L}^{-1})(t_d=0.01 \text{ s})(m_{CHA}=154.2)} \quad (2)$$

where m_{CHA} is the molecular weight of monomeric CHA. The k_p value might have error arising from the MHS parameters for poly(BA) used for GPC universal calibration of poly(CHA). Furthermore, the CHA concentration was assumed to be independent of temperature. However, the errors relating to the MHS parameters and the temperature dependence of the monomer concentration would not affect the category assignment

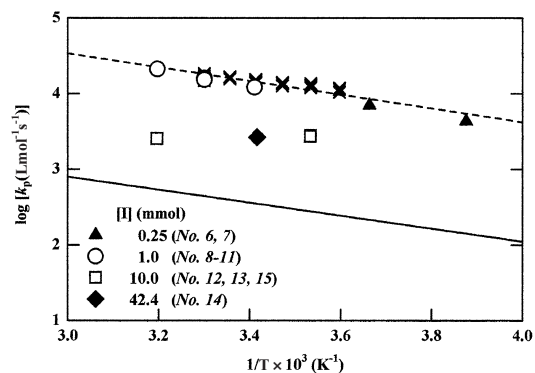


Figure 3. Arrhenius plots for k_p obtained by the present study under the conditions given in Table I, by the PLP study of BA at $-67 \sim -5^\circ\text{C}$ ¹² and at $5 \sim 30^\circ\text{C}$ ¹³ (\times and dotted line) and by the ESR study at $40 \sim 80^\circ\text{C}$ (solid line)²¹.

(**A**, **B**, **C**, and **D**) of the MWD profiles. The Arrhenius plot of the k_p values for CHA is shown in Figure 3. The k_p values determined by the PLP method are greater than the results of the ESR method; the lower reactivity of MCR than PRR reduces the polymerization rate which is used for k_p calculation by the ESR method.^{17, 18} In Figure 3, the k_p values for BA were already reported,^{12, 13} and the line for BA was drawn by Beuermann *et al.*¹³

Among the categories of **A–D**, **A** which shows only one inflection point was not used for k_p calculation. Furthermore, the data of **B**, **C**, and **D** which fulfilled $1.8 < m(I_2)/m(I_1) < 2.2$ were chosen with first priority for further analysis to minimize the effect of fragmentation on MWD. When the initiator concentration was 0.25 or 1.00 mmol L^{-1} , the experimental points are almost on the line for BA. Some of the MWDs belonging to **C** or **D** did not fulfill the consistency criterion of the PLP method because $m(I_2)/m(I_1)$ was too small or too large. The k_p values calculated from $m(I_1)$ of these experiments are shown in Table I. Most of the MWDs belonging to **B** and **C** were considered to fulfill the criterion as the MWD of PLP polymer, and the MWDs show $m(T) > m(I_2) > m(I_1)$. End forming events other than primary radical termination by pulse irradiation would decrease $m(T)$ to affect $m(I_2)$.

If only $m(I_1)$ was obtained correctly, $m(I_2)/m(I_1)$ would be outside of the range from 1.8 to 2.2. The k_p values calculated from the $m(I_1)$ within the wider range of $m(I_2)/m(I_1)$ among **B** and **C** were also used for the Arrhenius plot in Figure 3. It was found that the k_p values calculated from $m(I_1)$ s of **B** and **C** for the polymers obtained by PLP at $[I] = 0.25$ and 1.00 mmol L^{-1} at $-15.0 \sim 39.8^\circ\text{C}$ fit the linear relationship for k_p of BA. Although the polymerizations at 10.0 and 42.4 mmol L^{-1} of the initiator (*No. 12–16*) gave **D** which exhibit $m(I_1)$ and $m(I_2)$ within $1.80 < m(I_2)/m(I_1) < 2.20$ except for *No. 15*, the Arrhenius

plot of the k_p values calculated from **D** deviated downward from the straight line for BA (Figure 3). The difference in the k_p value between BA and *n*-dodecyl acrylate (DA) is known to be small,¹³ and the k_p values for CHA and BA or DA are expected to be similar. Therefore, the k_p values obtained from **D** at the high initiator concentrations in this study are believed to be underestimated.

The inflection points of **D** were considered to be influenced by the high concentrations of MCR at the high initiator concentrations. The propagation involving the significant concentration of MCR would be slower than in its absence because of the expected lower reactivity of MCR resulting in a decrease in kinetic chain length. The small radical expelled by the fragmentation of MCR would smoothly initiate a new chain giving shorter polymer than that initiated and terminated by PLP. The high concentration of MCR might react with PRR as faster termination than the mutual reaction of PRR to decrease $m(T)$. If the reduced $m(T)$ biased $m(I_1)$ and $m(I_2)$, $m(I_2)$ is expected to be more subjected to the effect of $m(T)$ than $m(I_1)$ leading to $m(I_2) < 2m(I_1)$ because $m(I_2)$ is closer to $m(T)$ than $m(I_1)$. All the runs in **D** fitted to $m(I_2) \sim 2m(I_1)$ and the effects arising from participation of MCR in termination could be ruled out.

In the PLP of MAD, an increase in molecular weight was suggested by addition of the propagating radical of MAD to the unsaturated end group formed by β -fragmentation of the propagating radical.²³ However, any effects of further reactions of the end groups can be neglected in the present study of CHA because most of the polymerizations were stopped at low conversions. High initiator concentration seems to increase the influence of the β -fragmentation of MCR or the propagation rate on the MWD, and the initiator concentration should thus be minimized in order to obtain consistent k_p values.

CONCLUSIONS

PLP of CHA which involves PRR and MCR was performed to find optimum conditions for determination of consistent k_p values. MCR formed mainly by backbiting was detected by ESR. At too high concentration of initiator, the $m(I_1)$, $m(I_2)$, $m(I_3)$, and $m(T)$ seemed to be shifted to lower molecular weights as deduced from the underestimated k_p values. The fragmentation of MCR present in a high concentration would give a small radical to initiate a new chain propagating to shorter chain length than the PLP polymer. Slower propagation involving a significant concentration of MCR than propagation without MCR would also bias the inflection points. The PLP conditions must be selected so that the

laser pulses are the dominant chain-starting and chain-stopping events, and the propagation should not be affected by MCR. Consistent k_p values which fitted the linear Arrhenius plot for BA and LA were obtained by PLP of CHA under the conditions of low initiator concentrations ($\leq 1.0 \text{ mmol L}^{-1}$) and moderate temperature ($-15.0^\circ\text{C} \leq$ and $\geq 39.8^\circ\text{C}$) among the PLP conditions examined.

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