polymer

Free radical polymerization of cyclohexyl acrylate involving interconversion between propagating and mid-chain radicals

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Abstract

The ESR spectrum of the propagating radical of cyclohexyl acrylate (CHA) overlapping with a three-line spectrum of a mid-chain radical was recorded in benzene as a non-polar solvent. The hyperfine coupling constants for the α- and β-hydrogens of the propagating radical of CHA were assigned based on the spectrum of the polymer radical of CHA-α-d. The polymerization of CHA was found to proceed in the presence of two types of radical species with different reactivities, the propagating radical and the mid-chain radical. The content of the mid-chain radical produced by abstraction of the α-hydrogen of the monomeric unit of the polymer was found to increase up to 25% with increasing conversion. The content of branching in the polymers arising from the hydrogen abstraction, 1.2–3.5%, determined by ^{13}C NMR spectroscopy was also found to increase with progress of the polymerization. The rate of the intramolecular formation of the mid-chain radical relative to propagation was estimated from the branching content at an infinitely low conversion, which was obtained by extrapolation, to be 0.65% at 1 mol/l of CHA. The absolute rate coefficients for the propagation (k_p) and termination (k_t) of CHA were determined using kinetic data obtained by FT-near infrared spectroscopy and the concentration of the propagating radical extrapolated to 0% conversion to minimize the influence of the mid-chain radicals: $k_p = 1224$ l/mol s and $k_t = 5.7 \times 10^5$ l/mol s at 60°C. These seemed to be apparent values because the propagating radical is repeatedly converted to the less reactive mid-chain radical by the intramolecular hydrogen abstraction during the lifetime of each radical. Slow initiation by the mid chain radical would result in the propagating radical which propagates further and accompanies the conversion to the mid-chain radical. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

ESR spectroscopy is one of the most promising techniques to obtain invaluable and quantitative information about free radical polymerization [1]. Recently, we have detected the propagating radical of phenyl acrylate (PhA) in a benzene solution at different conversions for the first time [2]. Simulation of the observed ESR spectra revealed that the polymerization involves two types of radicals, the propagating radical and a mid-chain radical, throughout the polymerization. Complication arising from the participation of these radicals with different reactivities has been discussed in a preceding paper [2], and FT-near infrared spectroscopy (FT-NIR) was conveniently used to measure the polymerization rate (R_p) of the acrylic ester. Propagation in the presence of two interconverting radical species is quite unique for acrylate polymerization, and the rate

coefficient of propagation (k_p) and termination (k_t), which are expected to be underestimated, have been obtained as apparent values.

To obtain consistent values of k_p for various monomers, GPC analysis of the polymer prepared by pulsed laser polymerization has been employed (PLP(GPC) method) [3]. In the case of an acrylic ester, a lower temperature and adjusted pulse interval have been required as the special requirements to avoid the influence of the chain transfer to monomer as the chain-stopping event [4–7]. However, the intramolecular formation of the mid-chain radical could not be excluded by the recommended conditions, as discussed in our previous paper [2], and the rate constants determined by the PLP method could be overestimated [2]. Gilbert et al. [8] have revealed by a flow technique using ESR spectroscopy that the radical addition to acrylic acid accompanies the mid-chain radical resulting from the 1,5-hydrogen shift. The determination of the k_p value for the acrylic ester in the absence of the mid-chain radical seems to be impractical because the polymerization of acrylic ester

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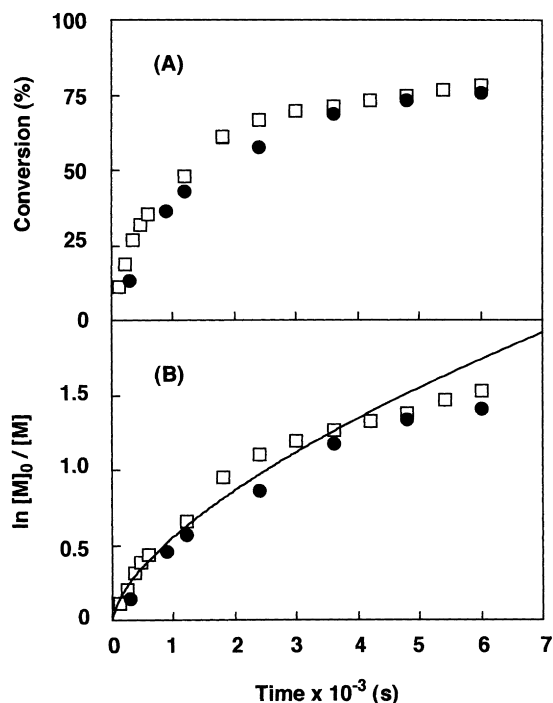*E-mail address:* yamada@a-chem.eng.osaka-cu.ac.jp (B. Yamada).

Fig. 1. (A) Conversion-time plot; and (B) first-order kinetic plot for CHA polymerization in benzene at 60°C based on conversion measured by gravimetric (●) and NIR (□) methods: [CHA] = 1.0 mol/l and [AIBN] = 0.025 mol/l. Curvature in (B) was calculated from Eq. (3).

always involves the intramolecularly formed mid-chain radical.

As a result of the formation of the mid-chain radical, the branching during the polymerization of acrylic ester has been determined by ^{13}C NMR structural analysis based on the assignments of the resonances of the carbons related to the branching of the poly(butyl acrylate) as reported by Ahmad et al. [9]. However, the reactivity of the mid-chain radical has never been discussed. A radical given by the following generalized structure has been known to exhibit low reactivities or long life times because of steric crowding around radical center
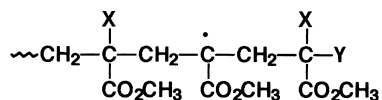
The propagating radical of a methyl acrylate dimer (X = Y = H) [10] and the radical produced by addition to a MMA dimer (X = Y = CH$_3$) [11] exemplify the steric effect on the life time of radical. Further, the extraordinarily small k_p and k_t values of a trimer of the acrylic ester, which yields a propagating radical (X = H, Y = CH$_2$CH$_2$CO$_2$CH$_3$) structurally similar to the mid-chain radical, suggests a considerably lower reactivity and a longer lifetime in comparison with the propagating radical of the acrylic ester [12].

This paper deals with the ESR detection and quantification of the propagating and mid-chain radicals involved in the polymerization of cyclohexyl acrylate (CHA) for the

determination of k_p and k_t using R_p measured by FT-NIR. CHA, whose polymer shows a T_g higher than room temperature was chosen to provide more convenient isolation of the polymer using methanol as a precipitant, and no significant effect of the type of the ester group on the rate constants could be anticipated.

2. Experimental

CHA was commercially available and distilled under reduced pressure. CHA-α-d was synthesized by the reaction of acryloyl-α-d chloride which was prepared from acrylic acid-α-d and benzoyl chloride. Acrylic-α-d acid was obtained by the alkaline hydrolysis of methyl acrylate-α-d [13]. The extent of deuteration of CHA-α-d was determined by ^{1}H NMR spectroscopy: 92.7%, 2.2′-azobisisobutyronitrile (AIBN; Wako) was recrystallized from methanol. The polymerization of CHA was carried out in a sealed tube at 60°C and AIBN was used as the initiator. Conversion was determined by weighing the polymer precipitated with methanol and by monitoring the carbon–carbon double bond of the monomer by FT-NIR.

The NIR spectra were measured using a Perkin–Elmer 1600 spectrometer equipped with an external bench MCT detector during the polymerizations in a custom-made aluminum furnace that set the light path [14,15]. To monitor the polymerization of CHA, the absorption due to the first overtone stretching vibration of the C–H bond of the C=C–H group at 6150 cm^{-1} was used as the reference. The baseline of the spectrum was measured using an empty 5 mm o.d. Pyrex tube for polymerization. The spectrum measured, after polymerization for 24 h at the polymerization temperature, was adopted as the background from the polymerization mixture to determine the signal intensity arising from the C–H bond, and the spectra observed during the polymerization were then calibrated.

The propagating and mid-chain radicals were detected and quantified by a Bruker ESP 300, and the polymerization in the cavity was carried out using a 5 mm o.d. quartz tube sealed under vacuum. The ^{1}H and ^{13}C NMR spectra were recorded using a JEOL a-400. The number and weight average-molecular weights (M_n and M_w) and polydispersity (M_w/M_n) were determined by a Tosoh 8020 series HPLC equipped with TSK-gel columns G5000HHR, GMulti-poreHXL-M, and GMHHR-L connected in this order. The molecular weight was calibrated by poly(styrene) standards.

3. Results and discussion

3.1. Polymerization rate

Fig. 1A shows a plot of conversion versus time for the CHA homopolymerization obtained by weighing the formed polymer and the FT-NIR method. Both methods gave almost the same relationship up to a high conversions
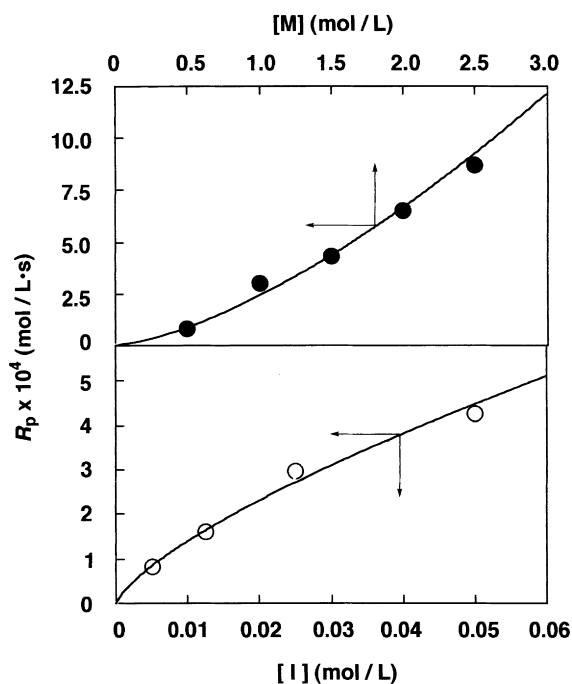
Fig. 2. Dependence of R_p on [CHA] and [AIBN] in benzene at 60°C: (a) [AIBN] = 0.025 mol/l; and (b) [CHA] = 1.00 mol/l.

showing that the precipitation of the polymer by methanol can be used for the determination of R_p as well as the quantification of the double bond by FT-NIR. However, a first-order kinetic plot according to Eq. (1) gave a curvature indicating a decrease in R_p with increasing conversion, as shown in Fig. 1B

$$\ln[CHA]_0/[CHA] = k_t \tag{1}$$

where $[CHA]_0$ and [CHA] denote the CHA concentrations before and after the polymerization for t s, respectively. k is a constant. A decrease in R_p with proceeding of polymerization could be explained primarily by a decrease in the concentration of the propagation radical ([CHA·]) because of a decrease in the initiation rate at a monomer concentration lower than 1 mol/l [16]. As already shown for the PhA

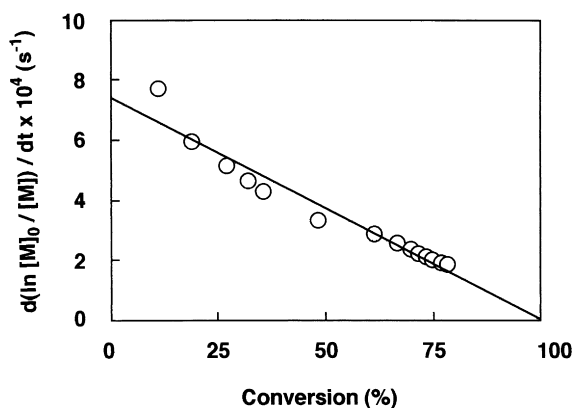

Fig. 3. A plot of $d(\ln[M]_0/[M])/dt$ versus conversion to extrapolate to 0% conversion. The intercept on the ordinate is 7.43×10^{-4} s^{-1}.

polymerization, an increase in the concentration of the less reactive mid-chain radical would suppress polymerization [2] similar to degradative transfer during the polymerization of an allylic compound. It should be noted that the formation of the mid-chain radical is not a chain transfer because the unpaired electron still remains in the same molecule.

Plots of R_p versus [CHA] and [AIBN] shown in Fig. 2 indicate higher kinetic orders with respect to CHA and AIBN than those expected from the standard kinetics of radical polymerization. The higher kinetic order of CHA is ascribable to participation of the less reactive mid-chain radical of which the rate of formation relative to propagation could be decreased with increasing monomer concentration. The higher kinetic order with respect to AIBN suggests the contribution of "degradative chain transfer" to yield the mid-chain radical

$$R_p = k'[AIBN]^{0.73}[CHA]^{1.49} \tag{2}$$

To minimize the influence of the factors reducing R_p, the initial slope of the first order plot was required. The curvature given by Eq. (3) was found to fit the experimental points in Fig. 1B

$$\ln[CHA]_0/[CHA] = 0.007t^{0.634} \tag{3}$$

By differentiating Eq. (3), Eq. (4) is obtained

$$d(\ln[CHA]_0/[CHA])/dt = 4.44 \times 10^{-3}t^{-0.366} \tag{4}$$

A plot of $d(\ln[CHA]_0/[CHA])/dt$ versus conversion is shown in Fig. 3, and the value of $d(\ln[CHA]_0/[CHA])/dt$ at an infinitely low conversion was obtained by extrapolation of the plot to 0% conversion as 7.43×10^{-4} s^{-1}.

3.2. ESR spectra of propagating radical and mid-chain radical

The ESR spectrum recorded at ca. 15% conversion in the cavity at 60°C is shown in Fig. 4. The polymerization was initiated by 0.025 mol/l of AIBN at 1.0 mol/l of CHA using benzene as a non-polar solvent to avoid a significant change in the sensitivity of the cavity by proceeding of polymerization. Apparently, the spectrum consists of the propagating radical (a = 10.7, 17.7, and 29.5 G) and the mid-chain radical which would be a three-line spectrum (a_β = 27.5 G) [8] in conformity with the observation during the polymerization of PhA [2]. The content of the mid-chain radical was estimated to be 10% by simulation.

A seven-line spectrum observed during the polymerization of CHA-α-d shown in Fig. 5 can be accounted for by an apparently four-line spectrum of the deuterated propagating radical ($a_{\alpha-D}$ = 2.7G, and a_β = 9.6 and 30.4 G) and the three-line spectrum due to the mid-chain radical. Considering that the hyperfine coupling for deuterium is ca. 1/6.5 of that of hydrogen, we can assign 17.7, 10.7 and 29.5 G for α-, β-, and β-hydrogens of the propagating radical of CHA, respectively. Two hydrogens among the four total β-hydrogens can couple with the unpaired electron of the mid-chain
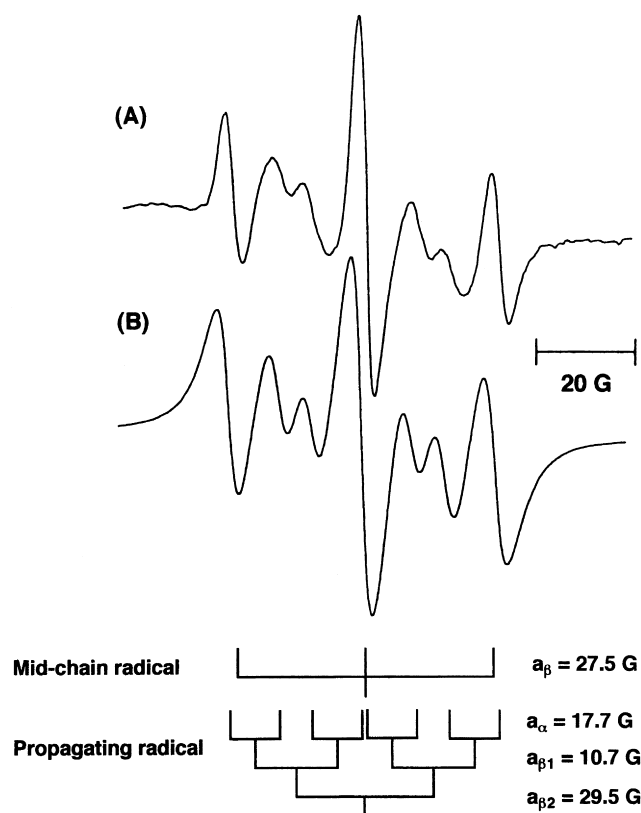
Fig. 4. (A) ESR spectrum observed during CHA polymerization in benzene at 60°C; and (B) simulation: [CHA] = 1.0 mol/l and [AIBN] = 0.025 mol/l.
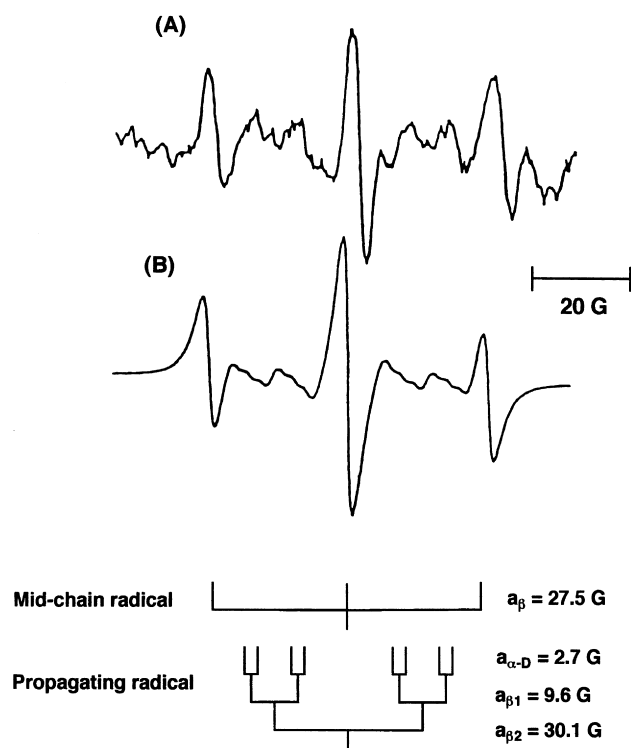

Fig. 5. (A) ESR spectrum of poly(CHA-α-d) radical; and (B) simulation: [CHA-α-d] = 1.0 mol/l and [AIBN] = 0.025 mol/l in benzene at 60°C.
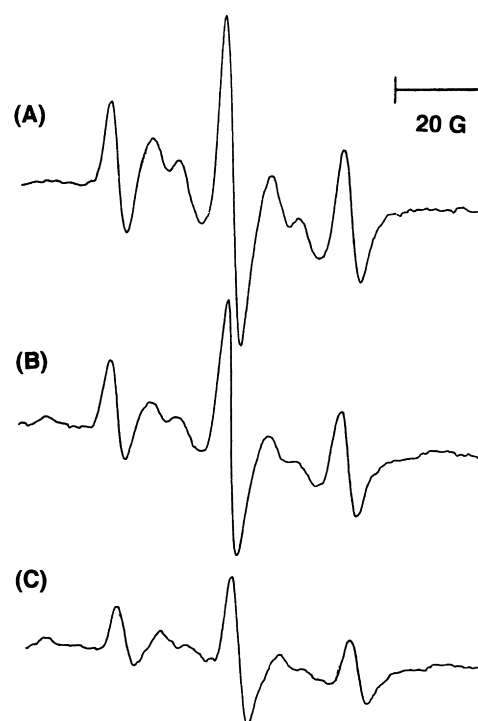
Fig. 6. ESR spectra observed during the homopolymerization of CHA at: (A) 15; (B) 60; and (C) 80% conversions.

radical irrespective of the chain length as expected from the similar three line spectra of the mid-chain radical detected by the flow technique [8] and by polymerization in a cross-linked system [17–19].

Fig. 6 shows the ESR spectra observed at different conversions, and the intensities of these spectra decreased with increasing conversion. Moreover, relative intensities of the individual lines changed with conversion. These findings together with the spectra of the deuterated polymer radicals strongly support that the observed spectra in the polymerization of CHA are accounted for by overlapping of two components. Simulation of the spectra indicates a decrease and increase in the contents of the propagating radical and the mid-chain radicals, respectively, with conversion as can be seen in Fig. 7. This tendency is ascribable to an increase in the rate of the intramolecular hydrogen abstraction relative to propagation at higher conversions because of a decrease in the monomer concentration. To estimate [CHA ·] under the influence of a minimum amount of the mid-chain radical, a plot of [CHA ·] versus conversion was extrapolated to 0% conversion ([CHA ·]$_0$; [CHA·]$_0$ = 6.07×10^{-7} mol/l. Both the propagating radical and the mid-chain radical would participate in the propagation through interconversion between these radicals as shown in Scheme 1. The intermolecular hydrogen abstraction as shown by Scheme 2, which yields the same mid-chain radical, could also be involved in the conversion to the propagating radical.

Fig. 7. Dependence of radical concentration and composition on time: total concentration (■); propagating radical (⊕); and mid-chain radical (○). A straight line is drawn as a visual guide.

3.3. Absolute values of k_p and k_t

Combining the value of the $d(\ln[CHA]_0/[CHA])/dt$ and $[CHA\cdot]$ at the indefinitely low conversion, we can obtain the k_p value using Eq. (5); $k_p = 1224$ l/mol s at 60°C. However, the effect of the mid-chain radical could not be completely excluded as will be discussed later, and the k_p value would be underestimated

$$d(\ln[CHA]_0/[CHA]/dt = k_p[CHA\cdot] \tag{5}$$

The propagating radical of the dimer of methyl acrylate, structurally similar to the mid-chain radical, has been known to exhibit a lower reactivity than that of MMA toward poly(St) radical by a factor of 10 [10]. The mid-chain radical could be less reactive than the propagating radical of the dimer because of more significant steric congestion. Reinitiation by the mid-chain radical could be considerably slower than the reaction of the propagating radical with CHA, and the k_p value obtained is influenced by the low reinitiation reactivity of the mid-chain radical.

By substituting $[CHA\cdot]_0$ as $[CHA\cdot]$ into Eq. (6), the k_t value at 0% conversion was calculated from $R_i(= 2.11 \times 10^{-7}$ mol/ls $: k_d = 8.45 \times 10^{-6}s^{-1}$ [20] and $f = 0.5)$ at 60°C; $k_t = 5.7 \times 10^5$ l/mol s

$$k_t = R_i/[CHA\cdot]^2 \tag{6}$$

This k_t value, which is considerably smaller than those for conventional monomers [1] by two orders of magnitude, seems to be influenced by the less reactive mid-chain radical. The k_t value would also be underestimated.

The k_p for CHA is smaller than that for PhA, 3470 l/mol s [2], obtained by a similar procedure at the same monomer and initiator concentrations at 60°C. However, a larger amount of the mid-chain radical was observed during the polymerization of CHA, and $[CHA\cdot]_0$ was higher than $[PhA\cdot]_0$ by a factor of 3.9. So far, factors affecting the rate of formation and concentration of the mid-chain radical are not known.

The mid-chain radicals of acrylic esters and the propagating radical of the trimer of methyl acrylate, which are structurally similar, have been known to show different ESR spectra [2,12]. Best and Kasai [18] have suggested the presence of a labile α-hydrogen of poly(acrylate) towards propagating radical based on consideration of the conformation of the polymer. The reactivity of the α-hydrogen might depend on the main chain conformation resulting in a significant concentration of the mid-chain radical during the polymerizations of CHA and PhA whereas the propagating

Scheme 1.

Intermolecular hydrogen abstraction

X = $CO_2C_6H_{11}$-cyclo

Scheme 2.

radical of the trimer exhibits a five-line spectrum typical of those of α-(substituted methyl)acrylates.

The difference in the radical concentration was reflected in the value of k_p because the slope of the first order plot shown in Fig. 1a was almost the same for these monomers. Although the higher [CHA·] could be caused by several factors, the difference in the viscosity of the acrylate monomer can be ruled out in the benzene solution. As already mentioned, [CHA·]$_0$ is higher than [PhA·]$_0$. This tendency suggests that a larger amount of the mid-chain radical participates more frequently in the CHA polymerization than in the PhA polymerization. If the k_p for the propagating radical in the absence of the mid-chain radical is similar for these monomers, a faster conversion of the propagating radical to the mid-chain radical could be expected for the actual CHA polymerization.

The k_p values for CHA and PhA determined by the ESR method are smaller than those for the methyl, butyl and dodecyl acrylates obtained by the PLP(GPC) method by one order of magnitude [5,6,21]. The PLP experiments used for the k_p determination were conducted to allow propagation up to a degree of polymerization of 10^3–10^4 [6]. Taking into account the fact that Gilbert et al. have detected a mid-chain radical of acrylic acid together with a linear tetramer radical [8], we can deduce that the mid-

chain radical, which is expected to have a longer lifetime than the propagating radical itself, would react with the primary radical from the photosensitizer at a slower rate. If a certain amount of the mid-chain radical could survive after consecutive laser pulses, the polymer chain length of the first inflection point of the GPC elution curve might be longer than that attained purely by propagation without the influence of the mid-chain radical. Therefore, the obtained k_p value is expected to be overestimated by the PLP(GPC) method.

While the k_p value determined by the present study still involves the contribution of the mid-chain radical, the k_p value can be used for calculation of R_p, the chain length, etc., of the actual polymerization because the intramolecular hydrogen abstraction cannot be excluded from polymerization of the acrylic ester at any stage.

3.4. Formation of branching

The mid-chain radical was detected by ESR spectroscopy throughout the polymerization of CHA, and the branching content in the poly(CHA) produced by the hydrogen abstraction can be estimated by ^{13}C NMR spectroscopy. The polymer prepared under the conditions given in Fig. 4 exhibits a weak ^{13}C NMR resonance assigned to the quaternary carbon arising from the hydrogen abstraction followed by propagation at 47.5–49.0 ppm corresponding to the resonances at 47.2–48.4 ppm based on the assignment by Ahmad et al. [9]. The resonances due to the methylene and methine carbons adjacent to the quaternary carbon appeared at 37–40 ppm similar to the resonances at 37.4–38.6 and 38.6–39.9 ppm for the poly(butyl acrylate). The branching content of the poly(CHA) was calculated from the intensities of the resonances due to the quaternary carbon of the branching point, and the methylene and methine carbons adjacent to the branching point relative to the resonances of the methylene and methine carbons of the polymer main chain. The estimated contents of the branching of the poly(CHA) were 1.2, 2.4 and 3.5% at 15, 60 and 80% conversions, respectively.

A plot of the branching content versus conversion shown in Fig. 8 can be extrapolated to 0% conversion. The intercept on the ordinate indicates 0.65% of branching arising
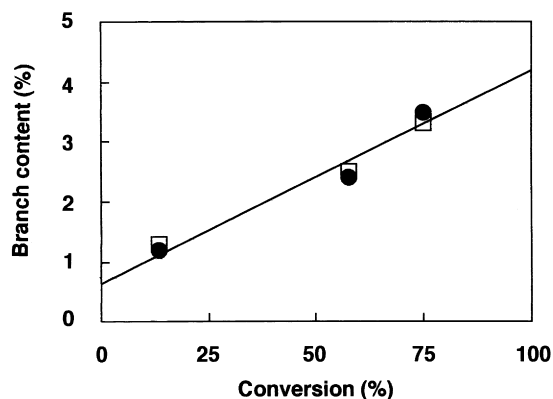

Fig. 8. Dependence of branch content on conversion. Content of branching was calculated from intensities of ^{13}C NMR resonance due to quaternary carbon (●) and methylene and methine carbons (□). A straight line is drawn as a visual guide and intercept on the ordinate is 0.65%.
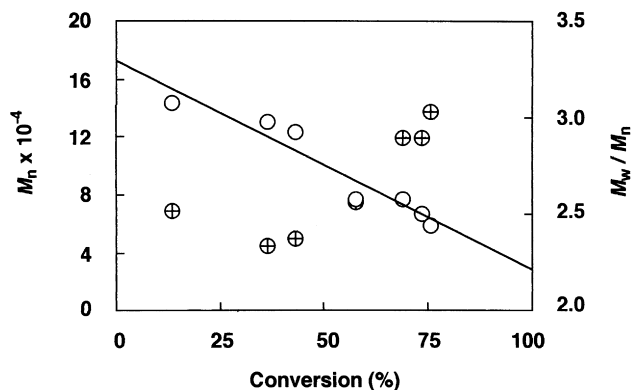
Fig. 9. Plots of M_n (□) and M_w/M_n (⊕) of poly(CHA) isolated at different conversions. A linear relationship between M_n and conversion is drawn as a visual guide and intercept on the ordinate is 1.73×10^5.

solely from the intramolecular hydrogen abstraction. Although the intramolecular hydrogen abstraction cannot be regarded as chain transfer as already mentioned, the rate of hydrogen abstraction relative to that of propagation can be compared with chain transfer constant. The ratio of the rate of the intramolecular hydrogen abstraction to the rate of propagation may be $0.65/99.35 = 6.5 \times 10^{-3}$ and 0.013 for CHA and PhA at 1 mol/l, respectively, which are considerably greater than the chain transfer constants of butyl acrylate, $(1.3 \pm 0.5) \times 10^{-4}$ [4] and 7×10^{-5} [22]. Apparently, the participation of the mid-chain radical in the elementary reactions has to be taken into account for kinetic consideration of the acrylate polymerization.

Fig. 9 shows M_n and M_w/M_n of the poly(CHA) at different conversions, and a decrease in M_n with increasing conversion is partly explained by a decrease in the monomer concentration. The poly(CHA) samples isolated at different conversions showed unimodal elution curves of which the peaks appeared at almost the same position. An increase in conversion brought about an increase in the peak width toward lower M_n side only. The fast reduction of M_n may also evidence the conversion of the reactive poly(CHA) radical to the less reactive mid-chain radical by Schemes 1 and 2 that suggests a decrease in the propagation rate.

The M_n of poly(CHA) at 0% conversion estimated by extrapolation is shown in Fig. 9; M_n of 1.73×10^5 corresponds to the degree of polymerization of more than 1120. Taking into account extrapolation of the branching percent to 0% conversion, 0.65%, we can predict that each polymer chain contains ca. 7.3 branches on the average. The mid-chain radical could not quantitatively reinitiate the polymerization of CHA, and the amount of the branching seems to be less than the frequency of the interconversion. Formation and reaction of the mid-chain radical were involved in the cycle shown in Scheme 1, and the ESR quantification as shown in Fig. 7 may allow to determine the steady state concentrations of the individual radicals.

Further the M_n of the polymer which was based on calibration by standard poly(styrene)s might not be the exact M_n

of the polymer. However, it is plausible that repetition of at least several interconversions between the poly(CHA) radical and the mid-chain radical are involved during the lifetime of each radical because sets of the conversions could proceed to form branchings. To exclude the effect of the mid-chain radical, the chain length should be less than $1120/73 = 153$ which is considerably shorter than that estimated for the PLP(GPC) experiments to exclude the chain transfer to the monomer during acrylate polymerization by a factor of about 60 or above [5].

4. Conclusion

The ESR spectrum of the propagating radical of CHA overlapping with that of the mid-chain radical was observed during the polymerization of CHA as well as that of PhA. Quantification of the propagating radical in combination with R_p measured by FT-NIR allowed determination of the k_p and k_t values for CHA in the presence of a minimum amount of the mid-chain radical; $k_p = 1224$ l/mol s and $k_t = 5.5 \times 10^5$ l/mol s at 60°C. A considerably lower reactivity of the mid-chain radical is expected to result in underestimation of the k_p and k_t values. Based on the M_n value of poly(CHA) and the branching content, the frequency of the conversion of the propagating radical to the mid-chain radical was estimated under the conditions of a solely intramolecular hydrogen abstraction taking place. Although the intermolecular reaction can yield the mid-chain radical, no quantitative consideration could be obtained because the route to the mid-chain radical cannot be distinguished between an intramolecular or intermolecular abstraction.

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