

Kinetic study on free radical polymerization of alkyl acylamidoacrylates by pulsed laser polymerization using nitrogen laser

Hitoshi Tanaka*, Takahiko Gohda, Akihisa Ohta

Department of Optical Science and Technology, Faculty of Engineering, Tokushima University, 2-1 Minamijosanjima-cho, Tokushima 770-8506, Japan

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Abstract

Radical polymerization of captodatively substituted alkyl acylamidoacrylates was studied by pulsed laser polymerization using a N₂ laser. Propagation rate coefficient of the acrylates was varied with solvents used in spite of a radical mechanism, but little varied with methyl, *n*-propyl, and isopropyl substituents on the acrylates. Arrhenius parameters for the propagation indicated that a solvent affected mostly on a frequency factor rather than a activation energy. In addition, it was suggested that these captodatively substituted propagating radicals were thermodynamically persistent but kinetically active in propagation, which resulted in rather smooth propagation in spite of bulky 1,1-disubstituted olefins. The mechanism of the polymerizations was discussed in detail on the basis of the kinetic studies and ESR spectroscopy.

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Keywords: Radical polymerization; Pulsed laser polymerization; Captodative

1. Introduction

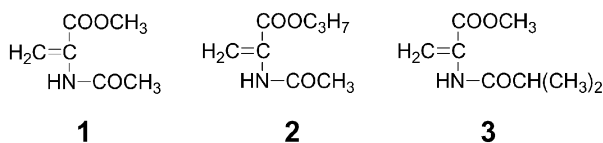
Radical polymerization has received considerable attention because of high reproducibility, application to wide variety of monomers, and simple reaction procedure with convenient apparatus [1]. In contrast to an ionic polymerization, however, steric effect becomes important, and sterically hindered olefins including bulky 1,1- or 1,2-disubstituted olefins represent poor polymerizability, and control of polymerization rate and stereostructure of polymer with additives including solvent is much more difficult in radical polymerization. However, captodatively (cd) [2] substituted olefins, so-called cd olefins, i.e. olefins substituted by both electron-withdrawing (captive) and -donating (dative) groups on the same atom, have often displayed special reactivity to give a polymer in high or moderate yield through a radical mechanism in spite of the sterically hindered 1,1-disubstitution and synergistic cd resonance stabilization of the resulting propagating radical [3]. In addition, the rate of

polymerization of the cd olefins and molecular weight of the polymer have been influenced by the solvent used in spite of a radical polymerization [4], and the polymers obtained showed advanced solvent affinity, thermal behavior, optical and electronic properties, and metal adsorption due to their high polar, asymmetric, and bifunctional cd geminal substitution [5].

2-Acylamidoacrylic acid, i.e. *N*-acyldehydroalanine, belongs to the cd olefin [6], and has been reported to polymerize very easily by a radical initiator or spontaneous thermal polymerization [6] to give a polymer with super high molecular weight, e.g. number-average molecular weight $M_n = 7\text{--}15 \times 10^6$, in high yield [7] in spite of the resulting propagating radical to be persistent as demonstrated by the large resonance stabilization (Alfrey-Price *Q* value: 2.42) [8] and high synergistic stabilization enthalpy (-28.5 to -45.2 kJ mol⁻¹) [9] of analogous aminocarbonylmethyl radicals. In addition, polymerization of dehydroalanine (DHA) has also been interested in connection with a synthesis of new functional materials including thermoresponsive hydrogel, amphoteric coagulant, and biodegradable polymers [7,10]. Polymerization kinetics and mode including electronic and steric effects on the polymerization of the DHA, however, has not yet been clarified in detail.

* Corresponding author. Tel./fax: +81 88 656 9420.

E-mail address: tanaka@opt.tokushima-u.ac.jp (H. Tanaka).



The present report deals with the kinetics of the radical polymerization of methyl 2-acetamidoacrylate (**1**), *n*-propyl 2-acetamidoacrylate (**2**), and methyl 2-isobutyramidoacrylate (**3**), and discusses on why such α -olefins can easily homopolymerize in spite of giving a thermodynamically persistent propagating radical. In such a kinetic study, propagation rate coefficient of **1–3** was examined by means of pulsed laser polymerization (PLP) [11] according to the following equation:

$$L_i = ik_p[M]t_p$$

where t_p stands for the time between two pulses, $[M]$ is a monomer concentration, $i=1, 2, 3, \dots$, k_p is the propagation rate coefficient, and L_i denotes a chain length of the polymer formed in the time between two pulses, which can be determined by size exclusion chromatography (SEC). In the present study, N_2 gas laser was first used for PLP as a convenient light source since Nd:YAG [12,13] and excimer [14] lasers and UV flash-lamp [15] commonly used for PLP experiment were expensive and sometimes induced light ablation.

2. Experimental

2.1. Materials

Compound **1** was prepared by refluxing the mixture of methyl iodide and 2-acetamidoacrylic acid which was independently synthesized in the same manner as previous paper [6] in acetone containing anhydrous potassium carbonate for 9 h according to the procedure of Bueno and co-workers [16]. After removing a potassium carbonate by filtration and evaporating a solvent from the mixture under reduced pressure, resulting solid was recrystallized from *n*-hexane to give white needles in 50.0% yield, mp 50–52 °C (50–52 °C) [17]. ^1H NMR (DMSO- d_6 , TMS, ppm): 2.03 (s, 3H, COCH_3), 3.77 (s, 3H, OCH_3), 5.72 (s, 1H, =CH), 6.18 (s, 1H, =CH), 9.29 (br s, 1H, NH). Anal. Calcd for $\text{C}_6\text{H}_9\text{NO}_3$: C, 50.35; H, 6.29; N, 9.79. Found: C, 50.14; H, 6.20; N, 9.62.

Compound **2** was synthesized according to the procedure similar to that of **1**, in which *n*-propyl iodide was used instead of methyl iodide, and purified by a column chromatography using a chloroform as a developing solvent. Compound **2** was obtained as a colorless oil in 7.2% yield. ^1H NMR (CDCl_3 , TMS, ppm): 1.02 (t, $J=7.2$ Hz, 3H, CH_3), 1.75 (q, $J=7.2$ Hz, 2H, CH_2), 2.18 (s, 3H, COCH_3), 4.25 (t, $J=7.2$ Hz, 2H, CH_2), 5.89 (s, 1H, =CH), 6.69 (s, 1H, =CH), 8.02 (br s, 1H, NH). Anal. Calcd for

$\text{C}_8\text{H}_{13}\text{NO}_3$: C, 56.13; H, 7.65; N, 8.18. Found: C, 56.25; H, 7.42; N, 7.98.

Preparation of **3** was also followed to the procedure of **1**, other than 2-isobutyramidoacrylic acid used instead of 2-acetamidoacrylic acid, where 2-isobutyramidoacrylic acid was synthesized by refluxing pyruvic acid 88.0 g (1 mol) and isobutylamide 43.5 g (0.5 mol) in benzene 400 ml for 10 h in a 500 ml three-necked flask equipped with a condenser and a Dean–Starks apparatus. The precipitated white solid in the flask was filtered, washed with benzene, and recrystallization of the solid from acetone gave 2-isobutyramidoacrylic acid as white needles 7.0 g in 9.0% yield, mp 160–162 °C. Then, an esterification of the acid was carried out with methyl iodide to give **3** as a colorless oil in 68.3% yield. ^1H NMR for 2-isobutyramidoacrylic acid (DMSO- d_6 , TMS, ppm): 1.02 (d, $J=6.3$ Hz, 6H, CH_3), 2.73 (heptet, $J=6.3$ Hz, 1H, CH), 5.72 (s, 1H, =CH), 6.29 (s, 1H, =CH), 8.94 (br s, 1H, NH). Anal. Calcd for $\text{C}_7\text{H}_{11}\text{NO}_3$: C, 53.49; H, 7.05; N, 8.91. Found: C, 53.23; H, 6.93; N, 8.90. ^1H NMR for **3** (DMSO- d_6 , TMS, ppm): 1.04 (d, $J=6.3$ Hz, 6H, CH_3), 2.74 (heptet, $J=6.3$ Hz, 1H, CH), 3.83 (s, 3H, OCH_3), 5.69 (s, 1H, =CH), 6.19 (s, 1H, =CH), 9.21 (br s, 1H, NH). Anal. Calcd for $\text{C}_8\text{H}_{13}\text{NO}_3$: C, 56.13; H, 7.65; N, 8.18. Found: C, 56.08; H, 7.37; N, 8.39.

Commercially available (Wako Chemicals) 2,2'-azobisisobutyronitrile (AIBN) and benzoin were used after recrystallization from ethanol and toluene respectively. Commercial grade 2,2'-azobis(2,4,4-trimethylpentane) (ATMP) was used without further purification. Methyl methacrylate (MMA) was purified by ordinary method, and distilled just before use.

2.2. Polymerization

PLP was performed in a UV-quartz cell (10 mm thickness) attached thermostat using a N_2 gas laser (Laser Science VSL-337ND-S: $\lambda=337$ nm, 0.6 mJ per pulse) with monitoring the light frequency on oscilloscope. N_2 gas was passed through the sample in the cell containing the required amounts of reagents including monomer, solvent, and benzoin as a photoinitiator to remove the oxygen before polymerization. Then, the cell was capped after filling out with N_2 gas.

Co-polymerization of **3** and preparation of standard polymer **1** were carried out in toluene and acetonitrile at 50 and 60 °C, respectively, in a sealed ampoule with shaking at given temperature. The ampoule that contained the required amounts of reagents including AIBN, solvent, and so forth was degassed several times by a freeze–thaw method and then sealed under reduced pressure and placed in a constant temperature bath. The resulting polymer was isolated by pouring the contents of the ampoule into a large amount of diethyl ether. Co-polymer composition was determined from the carbon content found by elemental analysis of the co-polymer which was purified by reprecipitation.

Monomer reactivity ratio (r) was calculated from the Kelen-Tudos plot [18].

2.3. Measurement

^1H NMR spectra were measured on a JEOL JNM-MY60 (60 MHz) spectrometer in CDCl_3 or $\text{DMSO}-d_6$ (dimethylsulfoxide- d_6) at 23°C . ESR spectra were recorded on a JEOL JES-RE1X spectrometer with a TE mode cavity. Polymerization in ESR measurement was carried out in the conditions of $[\text{ATMP}] = 10 \text{ mmol l}^{-1}$ at 20°C under irradiation of a 500 W high pressure mercury lamp in $[\mathbf{1}] = 2.0 \text{ mol l}^{-1}$ in homopolymerization and $[\mathbf{1}] = 0.5 \text{ mol l}^{-1}$ and $[\text{styrene}] = 2.5 \text{ mol l}^{-1}$ in co-polymerization. Hyperfine splitting constant (a) in ESR was estimated by comparison with that of MnO . Molecular weight distribution (MWD) of a polymer was determined by SEC using a Tosoh HLC 8020 with columns: TSKgel α -M + α -3000 in methanol containing LiBr (10 mmol l^{-1}) for polymers **1–3** and with columns: TSKgel G7000HHR + G5000HHR + G3000HHR in tetrahydrofuran for poly(MMA) at 35°C . Chain length of polymer **1** produced by PLP was estimated on the basis of the SEC calibration curve obtained from standard polymer **1** in which weight-average molecular weight (M_w) was determined by a static light scattering spectrophotometry (Photal DLS-7000) to be 1.77×10^4 , 2.52×10^4 , 4.20×10^4 , 6.20×10^4 ($M_w M_n^{-1} = 1.62$ – 1.75 by SEC). Universal calibration curves for polymers **2** and **3** were depicted according to the Q -factor method [19] for convenience on the basis of the calibration curve for polymer **1**, where the molecular weight of the monomer unit in polymers **2** and **3** (171.2) is calculated to be higher than that of **1** (143.1) by 1.196 times, e.g. $M_n = 1.71 \times 10^4$ of polymers **2** or **3** corresponds to $M_n = 1.43 \times 10^4$ of polymer **1**. Reliability in such a calibration was confirmed by checking some of the polymers **2** and **3** using light scattering spectrophotometry. Polystyrene standards (Tosoh, $M_n = 495$ – $98,900$) and poly(MMA) standards (Polymer Laboratories, $M_n = 1020$ – $790,000$) were employed for the calibrations of MWD.

3. Results and discussion

3.1. PLP using N_2 laser

PLP using a N_2 laser as a light source was applied to MMA polymerization to verify an accuracy of the system. Fig. 1 represents the MWD and its derivative obtained from the PLP of MMA in bulk in the conditions of $[\text{benzoin}] = 5.0 \text{ mmol l}^{-1}$ and a laser frequency of 10 Hz ($t_p = 0.1 \text{ s}$) at 40°C . As seen in Fig. 1, inflection points are clearly observed and the molecular weights of the secondary and third inflection points are twice and triple that of the primary inflection point in MWD, exhibiting overtones corresponding to L_2 and L_3 . In addition, k_p values were little varied with

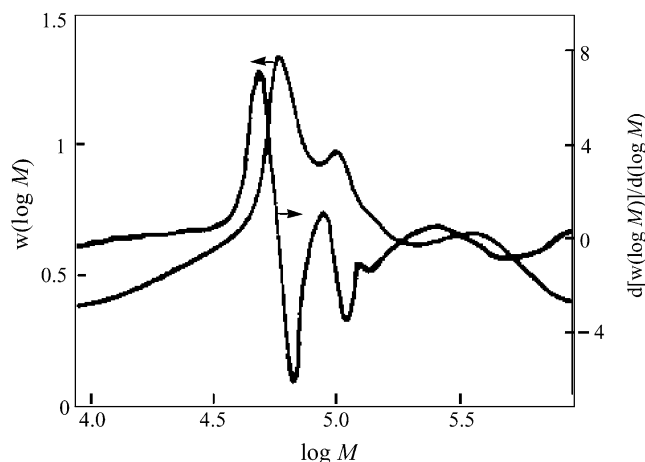


Fig. 1. Molecular weight distribution and its derivative for poly(MMA) produced by pulsed laser polymerization of $t_p = 0.1 \text{ s}$ in bulk and $[\text{benzoin}] = 5.0 \text{ mmol l}^{-1}$ at 40°C .

conditions including the concentration of benzoin in 5.0 – 10 mmol l^{-1} to be 471 – $484 \text{ l mol}^{-1} \text{ s}^{-1}$ in $t_p = 0.1 \text{ s}$ at 40°C , which are in the range of the IUPAC benchmark values of $497 \text{ l mol}^{-1} \text{ s}^{-1}$ obtained by PLP of MMA using Nd:YAG laser [12]. The present PLP-SEC system thereby was confirmed to be adequately suitable for practical use. Essentially, PLP using N_2 laser has rather some advantages in experiments, e.g. lower power of a N_2 laser can make it easy to control a temperature of polymerization system in contrast to the PLP employing Nd:YAG laser where the temperature sometimes goes up owing to the high power of the laser, i.e. laser ablation.

Fig. 2 represents a typical example of MWD for the polymerization of **1** at 40°C , 5 Hz, and $[\text{benzoin}] = 10 \text{ mmol l}^{-1}$. Well-defined bimodal MWD is observed, and their inflection points occur at the similar molecular weight independently on initiator concentration, and the position of the second inflection point (L_2) is located at twice the molecular weight of the first inflection point (L_1).

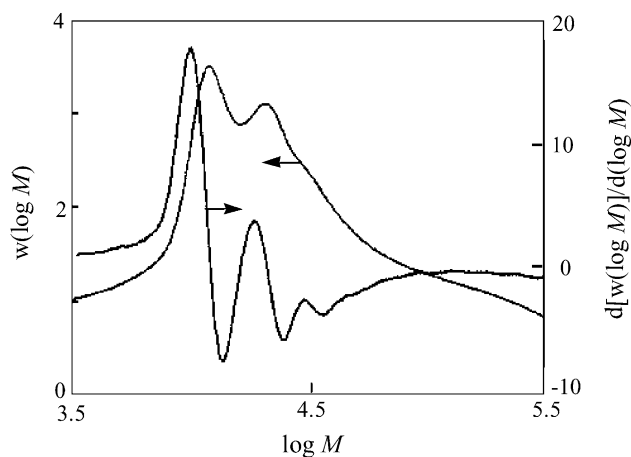


Fig. 2. Molecular weight distribution and its derivative for polymer **1** produced by pulsed laser polymerization of $t_p = 0.1 \text{ s}$ in ethanol and $[\text{benzoin}] = 10 \text{ mmol l}^{-1}$ at 40°C .

Table 1 shows the k_p values obtained for **1** in various laser frequencies and temperatures, in which k_p is estimated from L_1 since numerous simulations have suggested that the inflection point at the low-molecular side of the peak is the best measure of L_1 [20]. As clearly seen in this table, k_p is almost independent on laser frequency, and L_2 is always twice L_1 within an error of 10% [21]. The fulfillment of these two consistency criteria, i.e. invariant of k_p value with initiator concentration and pulse interval and also the overtones of MWD corresponding to $2L_1$, $3L_1$, serves as proof that appropriate reaction conditions have been settled in the present study.

3.2. Effect of solvent and temperature on propagation

Dependence of k_p value on solvent and temperature is shown in Tables 2–4 for the polymerizations of **1–3** respectively. It is noted that k_p varies with the solvents used in spite of a radical mechanism and has a tendency to become higher in protic solvent including ethanol ($E_T=51.9$) than in aprotic solvents including acetonitrile (46.0) acetone (42.2), dimethyl sulfoxide (45.0), and benzene (34.5) in every polymerization system, where E_T value [22] is a measure of a hydrogen bonding and a protonation power of solvent and is given from a UV absorption shift of diphenyl betain in an appropriate solvent. Kamachi [24] observed a drastic decrease (35–95% decrease) in k_p in the polymerization of vinyl esters and acrylates in aromatic solvents, and speculated a formation of charge-transfer (CT) complex between propagating radical and aromatic solvent k_p . Value of **3** in aromatic solvents including toluene, however, decreases only by 6–19% compared with that in ethanol and it is comparable to that in acetonitrile and acetone, which excludes a formation of the CT complex in the present system. Strong hydrogen bondings through an alkoxy carbonyl and an amide moieties in DHA and its polymer seem to play an important role in a higher k_p value observed in ethanol in the present system as is known in acrylates [25] and amide monomers [26].

Figs. 3–5 show the Arrhenius plots for the polymerizations of **1–3** in various solvents at 20–60 °C. In each case, slope corresponding to an activation energy (E_p) of propagation little varies with the solvents used within experimental uncertainty. Arrhenius parameters estimated from such a plot are summarized in Table 5.

Both E_p and a frequency factor (A_p) in Table 5 as well as k_p value in Tables 2–4 are little altered systematically by a change of the alkyl substituent on DHA. Such a tendency is analogous to that reported for methyl, ethyl, and butyl methacrylates, other than dodecyl methacrylate [27], but different from that observed in dialkyl itaconates [28] and dialkyl fumarates [29]. For dialkyl itaconates [28], k_p decreases as the alkyl chain becomes longer, e.g. k_p of dimethyl itaconate is 1.7 times higher than that of butyl itaconate at 50 °C, while k_p of dialkyl fumarates increases [29] with increasing size of the alkyl group, e.g. k_p of dimethyl fumarate is 11.7 times higher than that of diisopropyl fumarate at 60 °C. An electronic factor seems to dominate the propagation mode rather than a steric factor in the present polymerization system within a small limited size of alkyl substituents, which is supported from the copolymerization kinetics and so forth as mentioned later.

It is definite in Table 5 that A_p is higher in protic solvent than in other solvents in each polymerization of **1–3**, although E_p varies little with the solvents used. This may arise from an enhancement of the mobility of polymer chain and subsequently increase in k_p in protic solvent due to a reduction of inter and intramolecular hydrogen bondings between amide moieties in the polymer as well as an interaction between monomers and solvent [25]. Deformation in ESR spectrum of the propagating radical of **1** in aprotic solvents including *n*-hexane and aromatic solvents including benzene supports such a hydrogen bonding between the amide moieties as seen in Fig. 6. That is, a protic solvent prevents a hydrogen bonding and an aggregation between polymer amides due to a stronger amide–solvent interaction, which brings about a 1:2:1 triplet spectrum ($a_{\beta-H}=0.93$ mT) originated from two equivalent

Table 1
Propagation rate coefficient k_p for **1** as functions of laser frequency and temperature

Laser frequency (Hz)	Temperature (°C)	L_1	M_1	L_2	M_2	k_p ($1 \text{ mol}^{-1} \text{ s}^{-1}$)
5	30	39.7	5690	82.8	11,900	199
	40	57.0	8150	129	18,500	285
	50	65.8	9420	156	22,300	329
	60	94.3	13,500	262	37,500	471
10	30	21.3	3050	46.5	6660	213
	40	25.4	3630	51.1	7310	254
	50	35.3	5060	78.8	11,300	353
	60	45.5	6510	103	14,700	455
20	30	10.7	1530	20.3	2920	214
	40	13.8	1970	26.3	3860	276
	50	18.3	2610	38.1	5450	365
	60	23.0	3290	44.0	6290	460

[**1**]=1.0 mol l⁻¹, [benzoin]=10 mmol l⁻¹ in acetonitrile.

Table 2
Propagation rate coefficient k_p for **1** as functions of solvent and temperature

Solvent	Temperature (°C)	L_1	M_1	L_2	M_2	k_p (l mol ⁻¹ s ⁻¹)
Ethanol	30	23.6	3380	53.0	7580	236
	40	32.9	4710	68.2	9760	329
	50	41.7	5970	91.0	13,000	417
	60	50.7	7260	107	15,300	507
Acetonitrile	30	21.3	3050	46.5	6660	213
	40	25.4	3630	51.1	7310	254
	50	35.3	5060	78.8	11,300	353
	60	45.5	6510	103	14,700	455
Acetone	20	12.9	1850	24.2	3470	129
	30	21.6	3090	36.2	5180	216
	40	23.7	3390	49.0	7010	237
	50	31.1	4450	63.5	9080	311
Dimethyl sulfoxide	20	13.8	1970	27.7	3970	138
	30	16.6	2380	36.7	5260	166
	40	22.8	3270	50.4	7210	228
	50	29.4	4200	60.3	8640	294

[**1**] = 1.0 mol l⁻¹, [benzoin] = 10 mmol l⁻¹, laser frequency: 10 Hz.

β -hydrogens on the propagating terminal unit ($-C_\beta H_2-C_\alpha(COOCH_3)NHCOC(CH_3)_3$). However, an aprotic solvent stimulates such a formation of intra- and intermolecular hydrogen bondings, resulting in a deviation of the spectrum from the 1:2:1 triplet. Short spin–lattice relaxation time and a restriction of the free rotation of $C_\alpha-C_\beta$ bond (twisted structure) due to a hydrogen bonding may induce such an ESR deformation. For instance, dihedral angle between the β -hydrogen and the $2p_z$ orbital on C_α -carbon of the polymer terminal unit is calculated to be about 45 and 75° for each β -hydrogen atom, and the ESR spectrum observed in benzene is estimated to involve almost 40% of the twisted structure (Fig. 6) by computer simulation. However, the ESR spectrum (D) observed in the co-polymerization of **1** and styrene agrees well with the spectrum simulation (E) consist of 1:2:1 triplet, and resembles the spectrum (A) observed in ethanol very closely as seen in Fig. 6. This strongly suggests that the incorporation of styrene units in the polymer backbone can reduce a hydrogen bonding between polymer amides and enhance the mobility of the polymer terminal unit.

It has been believed that the larger the resonance stability is the lower the propagation rate is. However, k_p values (389–417 l mol⁻¹ s⁻¹) of **1–3** in ethanol at 50 °C, for

instance, are higher than that of styrene (236 at 50 °C) [13] and non-cd substituted 1,1- or 1,2-disubstituted olefins including dialkyl itaconates (5.9–20 at 50 °C) [28,30], α -methyl styrene (1.54 at 47.4 °C) [31], and dialkyl fumarate (0.058–0.68 at 60 °C) [28] in spite of a resonance-stabilized propagating radical of cd substituted **1–3**. Alfrey-Price Q -value of **1** is indeed high, e.g. $Q=6.03$ [23], and α -amino- α -carboalkoxy radicals analogous to the radicals derived from **1–3** has been known to be thermodynamically persistent due to a synergistic cd resonance stabilization [8]. To confirm why the propagation of **1–3** is so smooth in spite of a conjugated monomer, activity of the propagating radical of **3** was examined kinetically. Table 6 and Fig. 7 represent a dependence of a co-polymer composition on feed molar ratio in the co-polymerization of **3** (M_1) and styrene (M_2) in toluene at 50 °C. Monomer reactivity ratio was determined to be $r_1=6.78$ and $r_2=0.006$. Rate coefficient of the addition of propagating radical **3** (M_1) toward styrene (M_2), i.e. cross-propagation rate coefficient (k_{12}), is calculated to be 53.7 l mol⁻¹ s⁻¹ from $r_1 (=k_{11}/k_{12})=6.78$ and $k_p (=ca. k_{11})=364$ l mol⁻¹ s⁻¹ (Table 4) at 50 °C. Similarly, k_{12} for **1** is calculated to be 137 l mol⁻¹ s⁻¹ from $r_1=3.04$ [21] and $k_p=417$ l mol⁻¹ s⁻¹ (Table 2). Both k_{12} values for **1** and **3**, which are a measure of the kinetic activity of

Table 3
Propagation rate coefficient k_p for **2** as functions of solvent and temperature

Solvent	Temperature (°C)	L_1	M_1	L_2	M_2	k_p (l mol ⁻¹ s ⁻¹)
Ethanol	20	17.4	2980	32.9	5630	174
	30	25.5	4360	51.1	8740	255
	40	29.7	5080	59.9	10,300	297
	50	39.8	6810	89.0	15,200	398
Dimethyl sulfoxide	30	15.4	2630	27.8	4760	154
	40	20.9	3580	37.8	6470	209
	50	24.0	4110	37.0	6330	240
	60	32.9	5630	45.1	7720	329

[**2**] = 1.0 mol l⁻¹, [benzoin] = 10 mmol l⁻¹, laser frequency: 10 Hz.

Table 4
Propagation rate coefficient k_p for **3** as functions of solvent and temperature

Solvent	Temperature (°C)	L_1	M_1	L_2	M_2	k_p ($l\ mol^{-1}\ s^{-1}$)
Ethanol	30	24.7	4230	45.7	7820	247
	40	35.2	6030	66.5	11,400	352
	50	38.9	6670	77.4	13,300	389
	60	53.9	9230	114	19,400	539
Acetonitrile	30	22.2	3790	42.5	7270	222
	40	27.1	4650	57.6	9850	271
	50	35.7	6110	66.5	11,400	357
	60	43.7	7490	90.8	15,500	437
Acetone	20	13.8	2370	26.0	4450	138
	30	21.4	3660	38.9	6670	214
	40	22.8	3910	41.0	7020	228
	50	31.8	5450	62.3	10,700	318
Toluene	30	22.0	3770	40.1	6860	220
	40	28.6	4900	53.3	9130	286
	50	36.4	6240	70.9	12,100	364
	60	45.1	7720	85.2	14,600	451

[**3**] = $1.0\ mol\ l^{-1}$, [benzoin] = $10\ mmol\ l^{-1}$, laser frequency: 10 Hz.

propagating radicals **1** and **3** for the attack toward the monomers including styrene, are higher than those of diethyl itaconate ($k_{12}=19$) [32], diisopropyl itaconate ($k_{12}=25.5$) [33], and diisopropyl fumarate ($k_{12}=5.6$) [34]. This implies that the propagating cd radicals of **1** and **3** are thermodynamically persistent [8,23], but not kinetically persistent although details should be discussed by considering a penultimate effect and so forth [35].

Kinetic activity of the propagating cd radicals has also been demonstrated not only by such a cross-propagation, but also by a recombination reaction between cd radicals and an initiation or reinitiation of vinyl polymerization by cd substituted radicals. For a recombination, termination rate

coefficient (k_t) which mainly reflects a steric hindrance and diffusion of propagating radical is higher in DHA including 2-acetoamidoacrylic acid ($9.1 \times 10^6\ l\ mol^{-1}\ s^{-1}$ at $50\ ^\circ C$) [6] than in dialkyl itaconates (5.3×10^4 – 5.9×10^5 at $50\ ^\circ C$) [28] and dialkyl fumarates (30–560 at $60\ ^\circ C$) [29], demonstrating a relatively small steric hindrance and subsequently moderate activity of the cd radical. It has also been known that the carbon radicals substituted both by CN or COOCH₃ as a captive group and SC₂H₅, OCH₃, or amino groups as a dative group easily attack to vinyl monomers, even to the non-conjugated vinyl monomers including vinyl acetate [36], to initiate or reinitiate a homopolymerization [17] and block co-polymerization

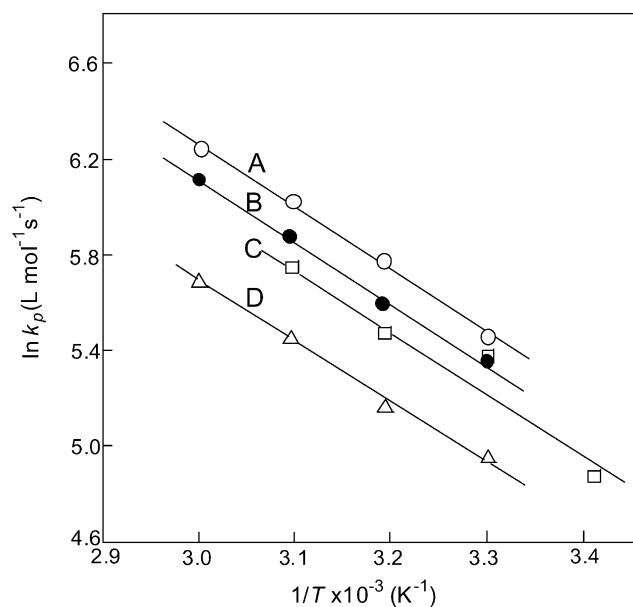


Fig. 3. Arrhenius plots of k_p determined by pulsed laser polymerization of **1** in various solvents under conditions given in Table 2. Polymerizations in (A) ethanol, (B) acetonitrile, (C) acetone, and (D) dimethyl sulfoxide.

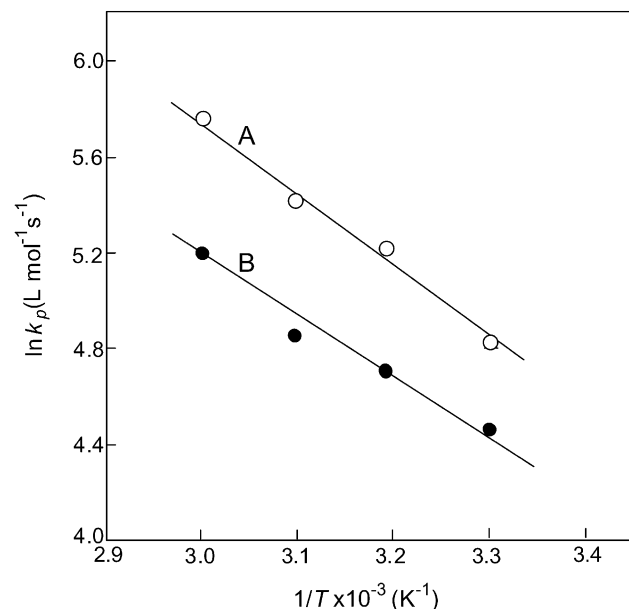


Fig. 4. Arrhenius plots of k_p determined by pulsed laser polymerization of **2** in various solvents under conditions given in Table 3. Polymerizations in (A) ethanol, (B) dimethyl sulfoxide.

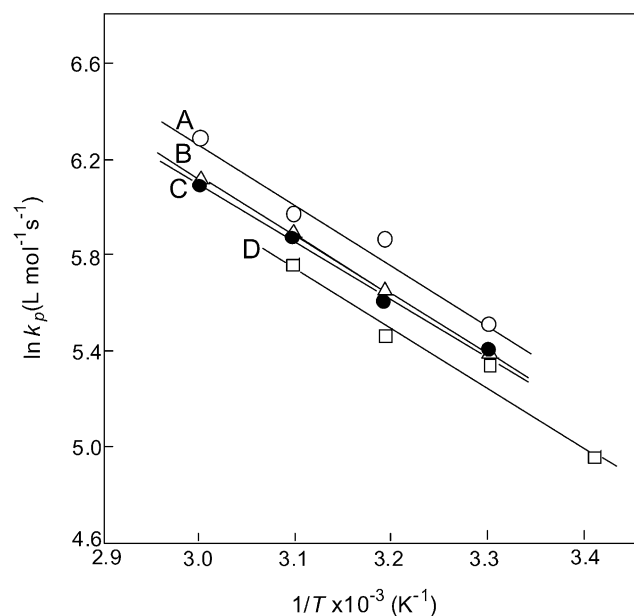


Fig. 5. Arrhenius plots of k_p determined by pulsed laser polymerization of **3** in various solvents under conditions given in Table 4. Polymerizations in (A) ethanol, (B) acetonitrile, (C) acetone, and (D) toluene.

[37]. Less activity of cd radicals for hydrogen abstraction also promotes a vinyl propagation without inducing side reactions including chain transfer [38]. These also support a kinetic activity of the cd radical, although a steric hindrance can not still completely ignore in the polymerization of the cd olefins bearing much more bulky substituent [39].

On the other hand, cd olefins would exhibit an extraordinarily high reactivity for the attack of the carbon radicals because of a resonance stabilization of the resulting cd radical [8,23,40]. Therefore, moderate and high activities of a propagating radical and a monomer respectively in the propagation of DHA might lead to a smooth polymerization. This is distinct from the mechanism proposed for other 1,1- or 1,2-disubstituted olefins including itaconates [28], fumarate [29],

Table 5
Arrhenius parameters A_p and E_p in the propagation of **1**, **2**, and **3** as a function of solvent

Monomer	Solvent	E_p (kJ mol ⁻¹)	A_p (10 ⁻⁵ l mol ⁻¹ s ⁻¹)
1	Ethanol	21.3	11.4
	Acetonitrile	21.8	11.8
	Acetone	21.6	9.97
	Dimethyl sulfoxide	21.6	7.19
2	Ethanol	20.8	9.05
	Dimethyl sulfoxide	20.3	4.90
3	Ethanol	20.5	8.66
	Acetonitrile	19.4	4.82
	Acetone	20.2	5.76
	Toluene	20.0	6.42

[DHA] = 1.0 mol l⁻¹, [benzoin] = 10 mmol l⁻¹, laser frequency: 10 Hz.

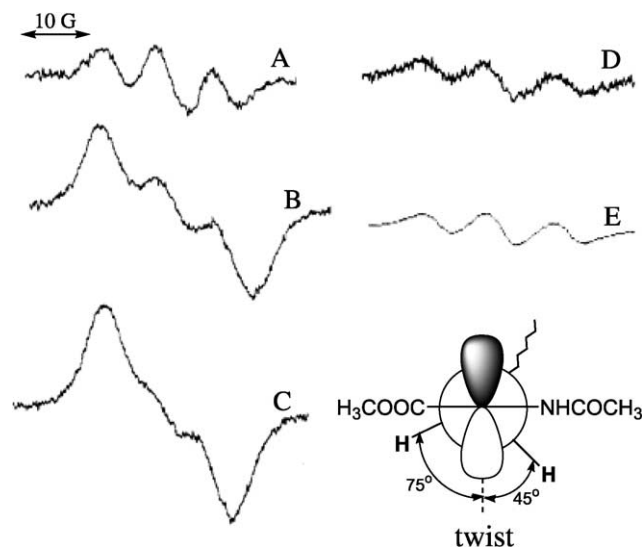


Fig. 6. Solvent effect on ESR spectra of the radicals observed in homopolymerization and co-polymerization of **1** with styrene at 50 °C and twisted structure of radical. Radicals observed in homopolymerizations in (A) ethanol, (B) benzene, (C) *n*-hexane, (D) co-polymerization in benzene, and (E) simulation of spectrum D.

and cinnamitriles [41]. In the polymerization of these non-cd disubstituted olefins, polymerizability is mainly controlled by a steric hindrance, in which k_t is reduced much higher than k_p , consequently a sequential propagation due to an increase in k_p/k_t ratio.

4. Conclusions

It was demonstrated that PLP using a N₂ laser was useful in determining a propagation rate coefficient. It was also found that the propagating radical derived from cd substituted DHA was thermodynamically persistent, but kinetically active, which resulted in rather smooth propagation in spite of 1,1-disubstituted olefins. In addition, propagation rate coefficient of DHA was varied with the solvents used in spite of a radical mechanism, and Arrhenius parameters for the propagation indicated that a solvent affected mostly on a frequency factor rather than an activation energy.

Table 6
Co-polymerization of **3** (M_1) and styrene (M_2) with AIBN at 50 °C

[M_1] in feed (mol%)	Time (min)	Yield (%)	C-content ^a (%)	[M_1] in co- polymer (mols%)
10	60	9.2	70.19	48.9
30	30	8.2	64.26	67.7
50	30	5.4	60.82	80.3
70	25	5.3	57.65	93.3
90	25	9.2	56.80	97.0

[M_1] + [M_2] = 1.0 mol l⁻¹ in toluene, [AIBN] = 5.0 mmol l⁻¹.

^a C-content: carbon content in co-polymer by elemental analysis.

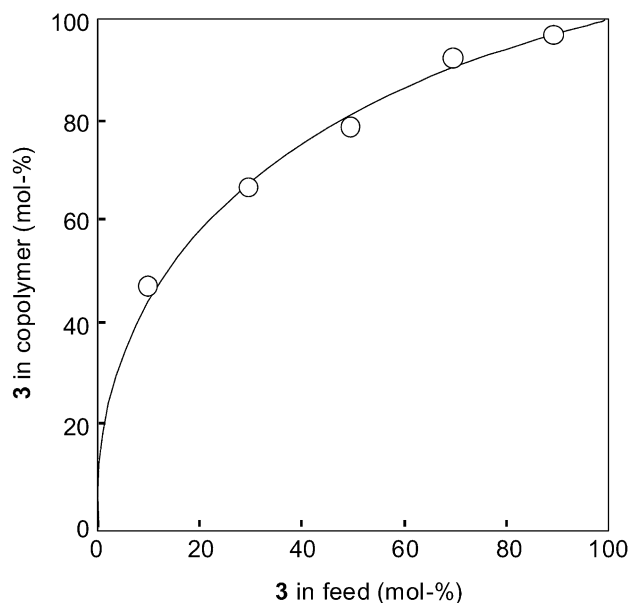


Fig. 7. Co-polymer composition curve for the co-polymerization of **3** with styrene in toluene at 50 °C.

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