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ORIGINAL CONTRIBUTION

H. Nakamura
M. Seno
H. Tanaka
T. Sato

Kinetic and EPR studies on radical polymerization. Radical polymerization of di-2[2-(2-methoxyethoxy)ethoxy]ethyl itaconate

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Prof. Dr. T. Sato (✉)
H. Nakamura · M. Seno ·
H. Tanaka
Department of Chemical Science and Technology
Faculty of Engineering
Tokushima University
Minamijousanijima 2–1
Tokushima 770, Japan

Abstract The polymerization of di-2[2-(2-methoxyethoxy)ethoxy]ethyl itaconate (1) with dimethyl 2,2′-azobisisobutyrate (2) was studied, in benzene, kinetically and spectroscopically with the electron paramagnetic resonance (EPR) method. The polymerization rate (R_p) at 50 °C is given by the equation: $R_p = k[2]^{0.48}\,[1]^{2.4}$. The overall activation energy of polymerization was calculated to be 34 kJ·mol^{-1}. From an EPR study, the polymerization system was found to involve EPR-observable propagating polymer radicals of 1 under the actual polymerization conditions. Using the polymer radical concentration, the rate constants of propagation (k_p) and termination (k_t) were determined. With increasing monomer concentration, k_p(1.5 ~ 4.3 L·mol^{-1}·s^{-1} at 50 °C) increases and k_t(1.0·10^4 ~ 4.2·10^4 L·mol^{-1}·s^{-1} at 50 °C) decreases, which seems responsible for the high dependence of R_p on the monomer concentration. The activation energies of propagation and termination were calculated to be 11 kJ·mol^{-1} and 84 kJ·mol^{-1}, respectively. For the copolymerization of 1(M_1) and styrene (M_2) at 50 °C in benzene the following copolymerization parameters were found: $r_1 = 0.2$, $r_2 = 0.53$, $Q_1 = 0.57$, and $e_1 = +0.7$.

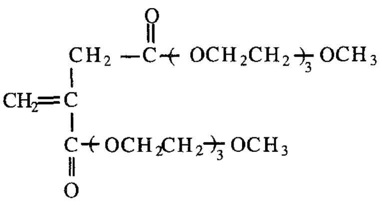
Key words: Radical polymerization – propagating polymer radical – EPR spectrum – poly(ethylene glycol)

Introduction

Recently, itaconic acid esters have attracted considerable attention because they are radically polymerized at moderate rates to yield polymers of high molecular weights in spite of their two bulky α-substituents, and the practical polymerization systems involve stable propagating polymer radicals enough to be detectable by means of electron paramagnetic resonance (EPR) spectroscopy [1–3].

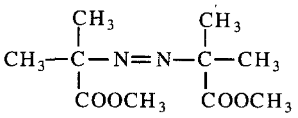
On the other hand, interest has been shown in vinyl monomers carrying poly(ethylene glycol) because of the valuable properties of poly(ethylene glycol) such as high crystallinity, hydrophilicity and strong coordination capacity for metal ions [4–10]. Coordination complexes of poly(itaconic acid)s bearing oligo(ethylene glycol) side chains with $LiClO_4$ or $NaClO_4$ are noted as the solid polymer electrolytes [7]. Therefore, we have synthesized di-(2[2-(2-methoxyethoxy)ethoxy]ethyl itaconate (**1**) possessing three ethylene glycol units and studied its radical polymerization behavior. This article describes the results of the kinetic and EPR studies on the radical polymerization of **1** in benzene, where dimethyl 2,2′-azobisisobutyrate (**2**) was used as initiator because the use of azonitrile initiators causes formation of persistent primary propagating radicals in the polymerization of itaconates

[1].



$CH_2{=}C(CH_2-C(=O)-(OCH_2CH_2)_3-OCH_3)-C(=O)-(OCH_2CH_2)_3-OCH_3$

(1)



$CH_3-C(CH_3)(COOCH_3)-N{=}N-C(CH_3)(COOCH_3)-CH_3$

(2)

Experimental part

Materials

Di-2-[2-(2-methoxyethoxy)ethoxy]ethyl itaconate (**1**) was prepared in the following manner [11]. Acid-catalyzed esterification of itaconic acid with 2-[2-(2-methoxyethoxy)ethoxy]ethanol using *p*-toluene sulfonic acid as catalyst and toluene as solvent was used to prepare **1**, where the resulting water was removed by azeotropic distillation. The reaction mixture was evaporated and, subsequently, the residue was dissolved in chloroform. Unreacted alcohol was removed by washing the chloroform solution several times with water. Column choromatographic separation using silica gel(70 ~ 230 mesh) as packing and ethyl acetate as developing solvent gave pure **1**. ^{1}H-NMR($CDCl_3$):$\delta =$ 3.32(8H, $=CCH_2$–, –OCH_3), 3.45 – 3.80(m, 20H, –CH_2O–), 4.12 – 4.39(m, 4H, –CO_2CH_2–), 6.29(s, 1H, $CH_2 =$), 5.70(s, 1H, $CH_2 =$).

$C_{19}H_{34}O_{10}$(422.5) Calc. C 54.02 H 8.11
Found C 53.89 H 7.94

Dimethyl 2,2′-azobisisobutyrate (**2**) was recrystallized from methanol. Commercial styrene was washed with a 5 wt.-% aqueous NaOH solution and a 20 wt.-% aqueous NaCl solution, dried over Na_2SO_4, and distilled under a reduced pressure before use. Benzene was purified by the usual method.

Measurements

Viscosity of benzene solution of **1** was measured with a Ubbelohde viscometer at 50 °C. Benzene was chosen as standard, and relative viscosities (η_{rel}) of the solutions containing different amounts of **1**(0.50–1.50 mol·L^{-1}) were calculated from the flow times. Gel-permeation chromatograms (GPC) were recorded on a TOSO HLC-802A apparatus at 38 °C using tetrahydrofuran as eluent. From the GPC results, the number-average ($\bar{M}n$) and weight-average ($\bar{M}w$) molecular weights of poly(**1**) were determined by standard procedures, using polystyrene standards. Electron paramagnetic resonance (EPR) measurements of the polymerization mixtures in a degassed and sealed EPR tube were carried out using a JEOL-JES-FG2XG spectrometer operating at X-band(9.5 GHz) with TE mode cavity.

Polymerization

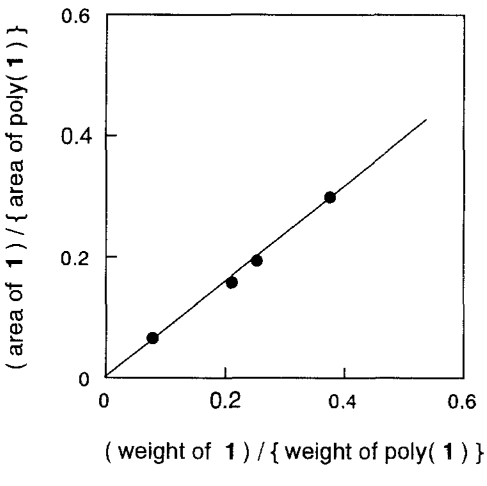
Polymerization of **1** initiated with **2** in benzene was carried out in a degassed and sealed glass tube with shaking at a given temperature. The resulting polymer which contained a small amount (ca.10%) of **1** was isolated by pouring the polymerization mixture into a large excess of diethyl ether-cyclohexane (5:3 (v/v)) mixture. Then, the conversion was corrected by GPC using a calibration curve for the relative weight between **1** and its polymer (Fig. 1).

Results and Discussion

Kinetic study on the polymerization of 1 with 2 in benzene

The polymerization of **1** with **2** was investigated kinetically in benzene, where the polymerization proceeds homogeneously. Figure 2 shows the time-conversion curves in the

Fig. 1. Calibration curve of relative area by GPC measurement for relative weight between **1** and poly(**1**)



temperature range from 40 ° to 70 °C, where the concentrations of **2** and **1** were $5.00 \cdot 10^{-2}$ and 1.00 $\mathrm{mol \cdot L^{-1}}$, respectively. The Arrhenius plot of the polymerization rate (R_p) determined from Fig. 2 is shown in Fig. 3. The slope of the plot allowed the overall activation energy of 34 $\mathrm{kJ \cdot mol^{-1}}$ to be calculated for the polymerization. This value is considerably lower than those (ca. 58 ~ 67 $\mathrm{kJ \cdot mol^{-1}}$) reported for the polymerizations of other itaconate esters [1, 2].

Figure 4 shows the relationship between R_p and the **2** concentration at 50 °C, where the concentration of **1** was 1.00 $\mathrm{mol^{-1}}$. The plot was linear with a slope of 0.48. Thus, R_p was nearly proportional to the square root of the initiator concentration, indicating usual bimolecular termination in the present polymerization.

Figure 5 shows the dependence of R_p on the **1** concentration at 50 °C, where the **2** concentration was kept constant at $5.00 \cdot 10^{-2}\ \mathrm{mol \cdot L^{-1}}$. The order of the polymerization rate with respect to the concentration of **1** was 2.4. The orders with respect to monomer being significantly greater than unity have also been reported for the radical polymerizations of itaconic acid esters [1, 2]

Thus, the polymerization of **1** with **2** in benzene was found to give kinetics as follows:

$$R_p = k[\mathbf{2}]^{0.48}[\mathbf{1}]^{2.4} . \qquad (1)$$

A kinetic order higher than unity with respect to the monomer is thought to be because of the effect of the increasing viscosity of the polymerization mixture with the

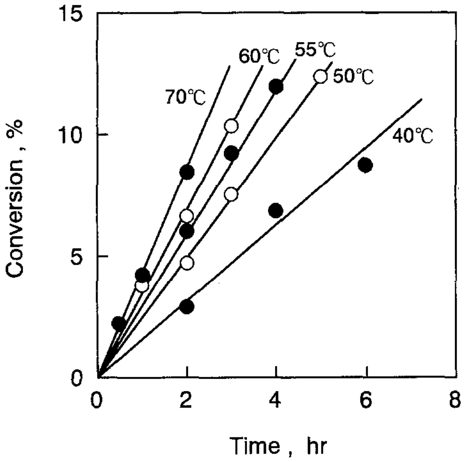
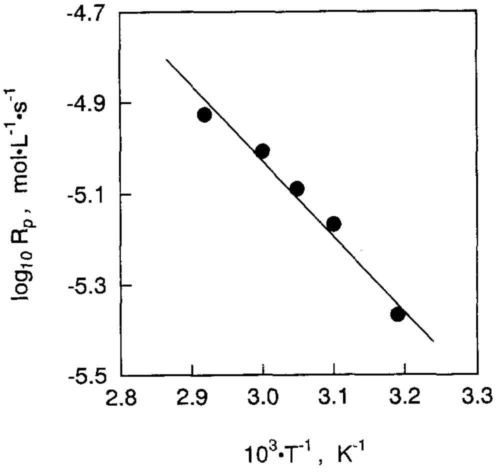


Fig. 2. Time-conversion curves for the polymerization of 1 with 2 in benzene at various temperatures. [1] = $1.00\ \mathrm{mol \cdot L^{-1}}$; [2] = $5.00 \cdot 10^{-2}\ \mathrm{mol \cdot L^{-1}}$

Fig. 3. Dependence of the polymerization rate (R_p) on temperature in benzene. [1] = $1.00\ \mathrm{mol \cdot L^{-1}}$; [2] = $5.00 \cdot 10^{-2}\ \mathrm{mol \cdot L^{-1}}$



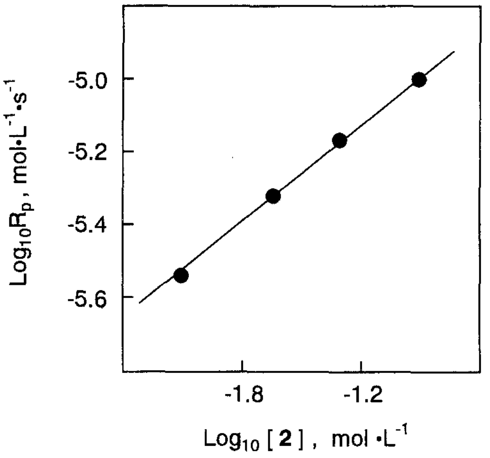
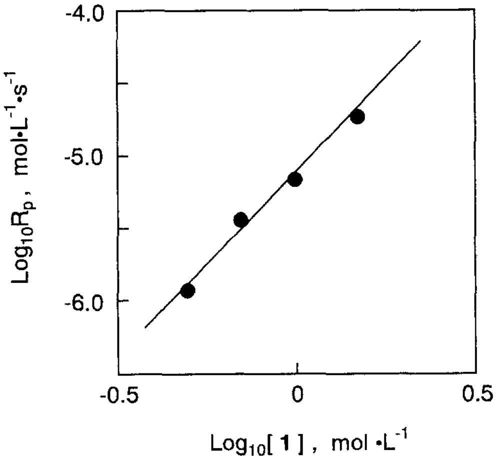


Fig. 4. Dependence of the polymerization rate (R_p) on [2] at 50 °C in benzene. [1] = $1.00\ \mathrm{mol \cdot L^{-1}}$

Fig. 5. Dependence of the polymerization rate (R_p) on [1] at 50 °C in benzene. [2] = $5.00 \cdot 10^{-2}\ \mathrm{mol \cdot L^{-1}}$



monomer concentration. So, we have measured the viscosity of the polymerization system at 50 °C and the obtained results are presented in Table 1.

Thus, the relative viscosity (η_{rel}) of polymerization system appreciably increased with increasing monomer concentration. The rate of diffusion-controlled termination in radical polymerization should be proportional to the reciprocal of relative viscosity (η_{rel}) of the polymerization system [12]. Then, R_p is rewritten as follows:

$$R_p = k'(\eta_{rel})^{0.5}[2]^{0.48}[1]^n . \qquad (2)$$

Therefore, the logarithm of $R_p\cdot(\eta_{rel})^{-0.5}$ was plotted against [1] in Fig. 6. From the slope of the straight line in Fig. 6, R_p may be expressed as follow:

$$R_p\cdot(\eta_{rel})^{-0.5} = k'[2]^{0.48}[1]^{1.8} . \qquad (3)$$

In spite of considering the viscosity, kinetic order with respect to monomer is still higher than unity. To elucidate this, it is necessary to take into account other effects on the rate constants of propagation and termination. This will be discussed in the following section.

Table 1. The relative viscosity (η_{rel}) of the polymerization system at the various **1** concentrations at 50 °C.

[1] (mol·L^{-1})	η_{rel}[a])
0	1.00
0.50	1.53
0.70	1.87
1.00	2.51
1.50	4.45

[a]) The viscosity of benzene (0.439 cP at 50 °C, H. Kanbe, in Kagakubinran, 3rd, Kisohen II, edited by the Chem. Soc. Jpn., Maruzen, Tokyo, 1986, p.44) was taken as unity.
The difference in density was neglected.

Fig. 6. Dependence of $R_p\cdot(\eta_{rel})^{-0.5}$ on [**1**] at 50 °C in benzene. [**2**] = 5.00 · 10^{-2} mol·L^{-1}

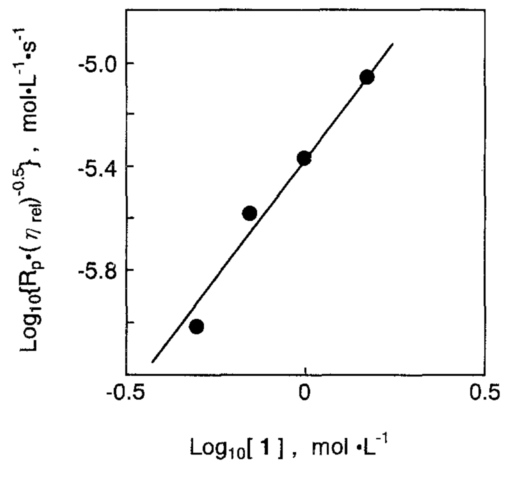


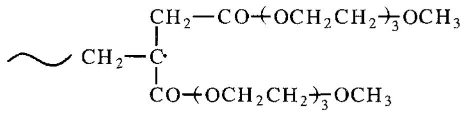
Table 2. Number- and weight-average molecular weights ($\bar{M}n$ and $\bar{M}w$) and molecular weight distribution ($\bar{M}w/\bar{M}n$) of poly(**1**) formed in the polymerization of **1** with **2** in benzene.

Temp. (°C)	[1] (mol·L^{-1})	[2]·10^2 (mol·L^{-1})	$\bar{M}n\cdot10^4$	$\bar{M}w\cdot10^4$	$\bar{M}w/\bar{M}n$
40	1.00	5.00	2.5	3.4	1.4
50	1.00	5.00	1.7	2.1	1.3
55	1.00	5.00	1.6	2.1	1.3
60	1.00	5.00	1.2	1.5	1.3
70	1.00	5.00	0.7	0.8	1.2
50	0.50	5.00	1.0	1.2	1.2
50	0.70	5.00	1.1	1.4	1.2
50	1.50	5.00	2.7	4.6	1.7
50	1.00	0.79	2.1	2.7	1.3
50	1.00	2.30	1.5	2.1	1.4
50	1.00	12.60	1.5	2.1	1.4

The molecular weights of the resulting poly(**1**) are summarized in Table 2. $\bar{M}n$ of poly(**1**) lies in the range from 7000 to 27000. The polydispersity($\bar{M}w/\bar{M}n$ = 1.3 ~ 1.7) is somewhat lower than those of the usual radical polymers, the reason for which is obscure at present. $\bar{M}n$ increases with increasing monomer concentration and decreases with rising temperture, and $\bar{M}n$ shows a small tendency to decrease with initiator concentration. These behaviors are also observed in the usual radical polymerization.

EPR study on the polymerization of 1 with 2 in benzene

Figure 7 shows EPR spectra observed in the polymerization of **1** with **2** in benzene at 40°, 50°, and 60 °C, where concentrations of **1** and **2** were 1.00 and 5.00·10^{-2} mol·L^{-1}. This five-line spectrum is similar to those observed in the polymerizations of other itaconic acid esters [15] and is assignable to the propagating polymer radical of **1**(**3**), of which the unpaired electron interacts nearly equivalently with four β-hydrogens.


$$\sim\!\!\sim CH_2-\overset{\displaystyle CH_2-CO\!\left(OCH_2CH_2\right)_3OCH_3}{\underset{\displaystyle CO\!\left(OCH_2CH_2\right)_3OCH_3}{\overset{|}{\underset{|}{C\cdot}}}} \qquad (3)$$

All the spectra showed no change in shape and intensity during the EPR measurements, indicating that a stationary state with respect to the propagating radicals is reached in the present polymerization system. Using the EPR spectra, the concentration of the polymer radical (**3**) ([P·]) was determined by computer-double integration where 2,2,6,6-tetramethyl piperidin-1-oxyl radical (TEMPO), a stable radical, was used as reference in the same medium.

The results obtained are presented in Table 3 and they are expected to have an error of less than ± 15%. The polymer radical concentration was found to increase with increasing monomer concentration and rising temperature. Using R_p and $[P\cdot]$, the rate constant of propagation (k_p) value was estimated directly according to Eq. (4) for the stationary state polymerization.

$$R_p = k_p[P\cdot]\,[1] \tag{4}$$

Table 3 also summarizes the k_p values thus obtained which are expected to have an error of less than ± 20%. Thus, k_p was found to increase slightly with rising temperature and increase with increasing monomer concentration. The latter is considered as a reason for which the order with respect to monomer concentration becomes large (Eq. (1)). The dependence of k_p on the monomer concentration may be explained in terms of solvent effect observed in the polymerization of alkyl itaconates [3, 14], where the solvent affinity for the propagating polymer chain plays an important role. Since **1** carries polar oligo(ethylene oxide) side chains, it is also possible that monomer aggregations enhance propagation reaction leading to higher k_p value [15].

To estimate the rate constant of termination (k_t), the initiator efficiency (f) is required to be obtained under the actual polymerization conditions. The f value was obtained by conducting the decomposition of **2** in the polymerization system in the presence of TEMPO. **2** decomposes into the 1-methoxycarbonyl-1-methylethyl radical (**4**). Some of the primary radicals are deactivated by cage reactions. The others diffuse through the solvent cage to react with TEMPO, yielding the coupling product (**5**) according to Eq. (5).

If the primary radicals add to the monomer before they react with TEMPO, the resulting radicals can also be trapped by TEMPO. So, determination of the disappearance rate of TEMPO leads to an estimation of the f value.

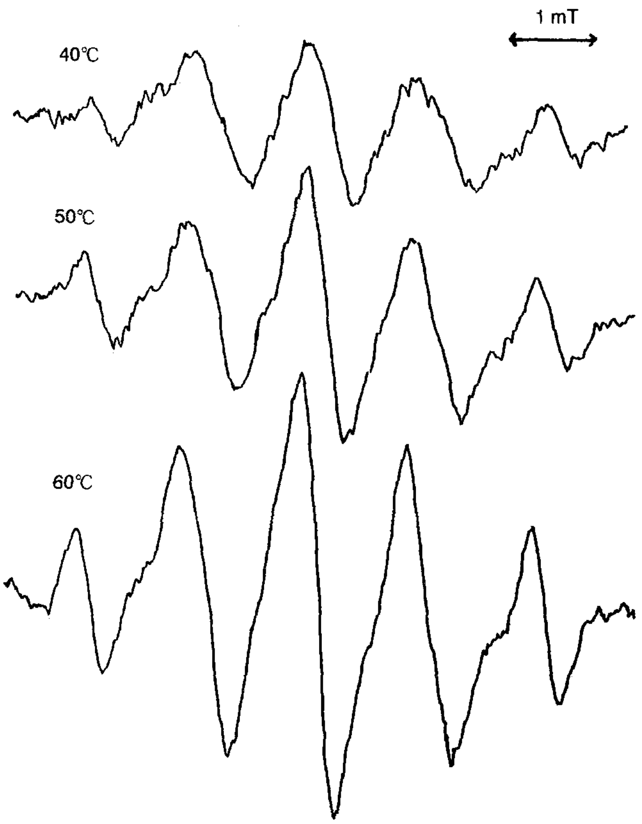
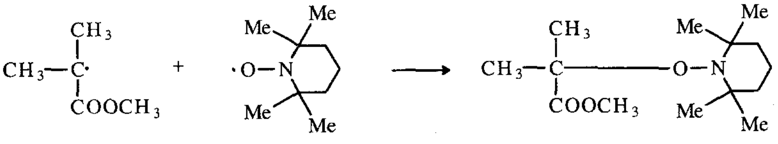


Fig. 7. ESR spectra of the polymerization mixture of 1 and 2 in benzene at different temperatures. $[1] = 1.00\ \mathrm{mol\cdot L^{-1}}$; $[2] = 5.00\cdot10^{-2}\ \mathrm{mol\cdot L^{-1}}$

Table 3 shows the f values obtained. Thus, the f value shows a reasonable increase with increasing temperature and decrease with increasing monomer concentration. These results indicate that higher viscosity leads to lower f value.

Using the f value and the polymer radical concentration, the k_t value was calculated according to Eq. (7),



(5)

(4) (TEMPO) (5)

Figure 8 shows a typical plot of the TEMPO concentration vs. the reaction time. Using the disappearance rate of TEMPO from the slope of the straight line in Fig. 8 and the reported rate constant (k_d, Eq. (6)) of the decomposition of **2** [16], the f value was estimated for each polymerization system.

$$k_d = 5.69\cdot10^{13}\exp(-118(\mathrm{kJ})\cdot R^{-1}\cdot T^{-1}) \tag{6}$$

where k_d is the decomposition rate constant of **2**.

$$2fk_d[2] = k_t[P\cdot]^2\ . \tag{7}$$

The results are also shown in Table 3 and they are expected to have an error of less than ± 40%. Thus, k_t was found to increase considerably with rising temperature and with decreasing monomer concentration. The

Table 3. Propagating polymer radical concentration ([P·][a]), initiator efficiency (f), propagation (k_p[b]), and termination (k_t[c]) rate constants in the radical polymerization of **1** with **2** in benzene.

Temp (°C)	[**1**] (mol·L^{-1})	[P·]·10^6 (mol·L^{-1})	k_p (L·mol^{-1}·s^{-1})	f	k_t·10^{-4} (L·mol^{-1}·s^{-1})
40	1.00	1.5	2.8	0.40	0.92
50	1.00	2.1	3.2	0.45	2.2
60	1.00	2.6	3.7	0.56	6.6
50	0.50	1.6	1.5	0.50	4.2
50	0.70	1.8	2.9	0.48	3.2
50	1.50	2.8	4.3	0.37	1.0

[a] [**2**] = 5.00·10^{-2} mol·L^{-1}.
[b] Determined according to Eq. (4).
[c] Determined according to Eq. (7).

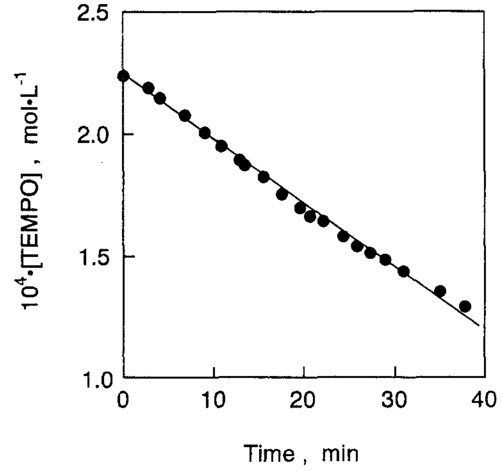


Fig. 8. Relationship between reaction time and concentration of 2,2,6,6-tetramethylpiperidin-1-oxyradical (TEMPO) during the polymerization of **1** with **2** at 50 °C in benzene. [**1**] = 1.00 mol·L^{-1}; [**2**] = 5.00·10^{-2} mol·L^{-1}; [TEMPO] = 2.23·10^{-4} mol·L^{-1}

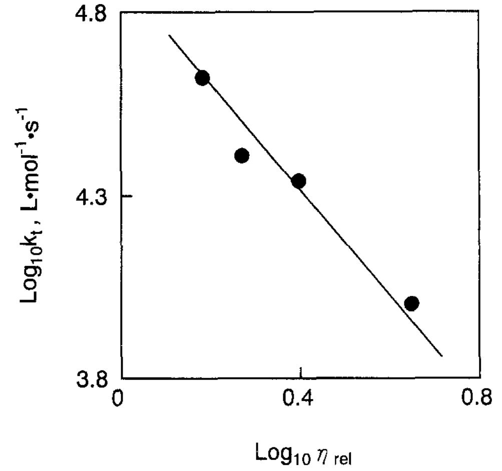


Fig. 9. Relationship between the termination rate constant (k_t) and relative viscosity (η_{rel}) of polymerization mixture

latter is considered as another reason for which the order with respect to monomer concentration becomes high (Eq. (1)).

As shown in Fig. 9, a linear relationship was observed between the logarithm of k_t and the logarithm of η_{rel}, which were obtained on varying the monomer concentration. This finding reveals that k_t, which decreases with increasing monomer concentration, depends on the viscosity of the polymerization system. But the slope (1.3) of the straight line in Fig. 9 is larger than unity. This suggests that the decrement of k_t relates to not only the viscosity of the polymerization system but also to the dependence of k_t on chain length of propagating polymer radical [17]. Therefore, we have examined the relationship between $k_t \cdot \eta_{rel}$ and $\bar{M}n$ of the resulting polymer in Fig. 10. A linear relationship is observed with a slope of 0.34. This value is somewhat higher than those (0.1 – 0.3) reported for the polymer radicals of common vinyl monomers such as styrene (St) and methyl methacrylate (MMA) [18, 19].

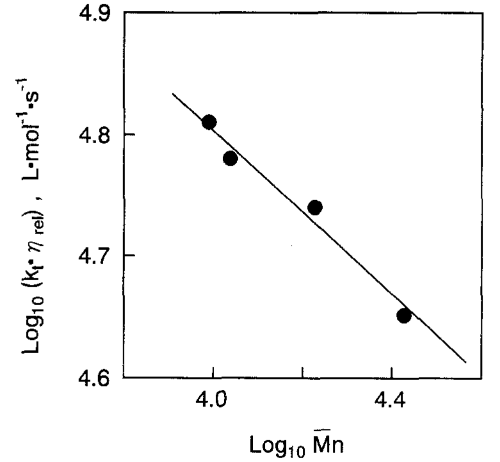


Fig. 10. Relationship between $k_t \cdot (\eta_{rel})$ and number-average molecular weight ($\bar{M}n$) of poly (**1**)

The Arrhenius plots of k_p and k_t above obtained are shown in Fig. 11, respectively. From the slope of the straight line in Fig. 11, the activation energy (E_p) of the propagation was calculated to be 11.1 kJ·mol^{-1}, which is fairly small compared to those of diethyl itaconate (DEI) (28.4 kJ·mol^{-1}) [20], MMA (28.0 kJ·mol^{-1}) [21], and St

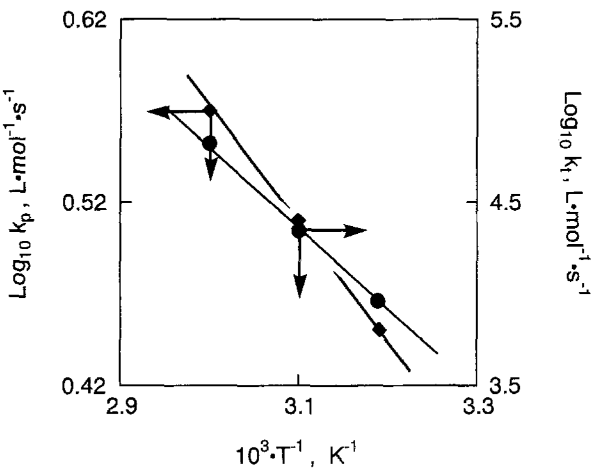


Fig. 11. Temperature effect on the propagation rate constant (k_p) (■) and termination rate constant (k_t) (●) in the polymerization of 1 with 2 in benzene

(17.7 kJ·mol^{-1}) [21]. From Fig. 11, the frequency factor was also calculated to be 2.34×10^2, which is much smaller than those of St (1.99×10^7) [22] and MMA (4.92×10^5) [22]. This is responsible for the extremely low k_p value of **1**.

The apparent activation energy (E_t) of termination was similarly estimated to be 82.8 kJ·mol^{-1}. The E_t value is much larger compared to those of DEI (28.5 kJ·mol^{-1}) [20]. MMA (9.5 kJ·mol^{-1}) [21], and St (2.9 kJ·mol^{-1}) [21]. Such an apparent high E_t of the present polymerization comes from lower viscosity of the polymerization system and shorter chain length of the propagating polymer radicals at higher temperatures.

The overall activation energy (E_a) of polymerization is given by Eq. (8).

$$E_a = E_i/2 + E_p - E_t/2 \qquad (8)$$

E_i: activation energy of initiation

From the plot of $\log_{10}(k_d \cdot f)$ vs. T^{-1}, E_i was estimated to be 134.0 kJ·mol^{-1}. Using the E_i, E_p, and E_t values obtained, E_a was calculated to be 36.7 kJ·mol^{-1} according to Eq. (8). This value is similar to Ea (34.0 kJ·mol^{-1}) observed in the practical polymerization system. Thus, small E_p and large E_t values are found to cause the small overall activation energy of the polymerization.

Table 4. Radical copolymerization of **1** (M_1) and styrene (M_2) with **2** in benzene at 50 °C for 2 h[a].

Content of M_1 in feed (mol-%)	Yield (%)	Carbon content[b] (%)	Content of M_1 unit in copolymer (mol-%)
0.125	2.4	74.96	17.0
0.25	1.9	68.19	30.0
0.375	2.1	65.21	37.4
0.50	2.2	63.21	43.6
0.625	2.4	61.42	50.7
0.75	2.0	60.12	56.6
0.875	2.0	57.84	69.0

a) $[M_1] + [M_2] = 1.00\ \mathrm{mol \cdot L^{-1}}$, $[\mathbf{2}] = 5.00 \cdot 10^{-2}\ \mathrm{mol \cdot L^{-1}}$.
b) Determined by elemental analysis.

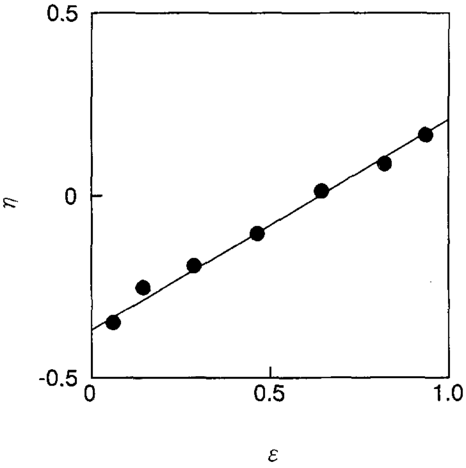


Fig. 12. Kelen-Tüdős plot for the polymerization of **1** (M_1) and styrene (M_2) with **2** in benzene at 50 °C. $[M_1] + [M_2] = 1.00\ \mathrm{mol \cdot L^{-1}}$; $[\mathbf{2}] = 5.00 \cdot 10^{-2}\ \mathrm{mol \cdot L^{-1}}$

Copolymerization of 1 (M_1) with styrene (M_2) in benzene

Copolymerization of **1** and St with **2** was carried out in benzene at 50 °C. Table 4 summarizes the copolymerization results. The copolymer composition was estimated on the basis of the carbon content by elemental analysis. Figure 12 shows the Kelen–Tüdős plot [23] for the copolymerization results. From the plot the monomer reactivity ratio was calculated to be $r_1 = 0.20 \pm 0.015$ and $r_2 = 0.53 \pm 0.022$. From these values, Q and e-values of **1** were estimated to be 0.57 and + 0.7, respectively, where Q = 1.0 and $e = -0.8$ were used for St. The Q value is somewhat smaller than those of itaconic acid esters (Q = 0.8 ~ 1.2) [24]. But these copolymerization parameters of **1** are similar to those of di-isopropyl itaconate; ($r_1 = 0.11$, $r_2 = 0.56$, Q = 0.47 and $e = +0.87$) [25]. The curve fitting method also gave similar results ($r_1 = 0.20$, $r_2 = 0.54$).

The rate constants of cross-propagations in the copolymerization which are based on the terminal model were calculated using the k_p values of comonomers [22] and the monomer reactivity ratios obtained above. The rate constants of four propagations in the copolymerization at 50 °C are as follows;

$$\sim M_1\cdot + M_1 \xrightarrow{k_{11} = 3.2\ \mathrm{L\cdot mol^{-1}\cdot s^{-1}}} \sim M_1\text{–}M_1\cdot \tag{9}$$

$$\sim M_1\cdot + M_2 \xrightarrow{k_{12} = 16\ \mathrm{L\cdot mol^{-1}\cdot s^{-1}}} \sim M_1\text{–}M_2\cdot \tag{10}$$

$$\sim M_2\cdot + M_1 \xrightarrow{k_{21} = 394\ \mathrm{L\cdot mol^{-1}\cdot s^{-1}}} \sim M_2\text{–}M_1\cdot \tag{11}$$

$$\sim M_2\cdot + M_2 \xrightarrow{k_{22} = 209\ \mathrm{L\cdot mol^{-1}\cdot s^{-1}}} \sim M_2\text{–}M_2\cdot \tag{12}$$

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