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RADICAL POLYMERIZATION BEHAVIOR OF ETHYL α-NAPHTHOYLOXYMETHYLACRYLATE

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ABSTRACT

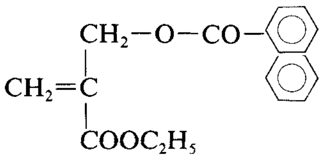
The polymerization of ethyl α-naphthoyloxymethylacrylate (ENMA) with dimethyl 2,2′-azobisisobutyrate (MAIB) in benzene was investigated kinetically and by means of ESR. Polymerization rate (R_p) was given by $R_p = k[\text{MAIB}]^{0.5}[\text{ENMA}]^{1.7}$ (50°C). The overall activation energy of polymerization was estimated to be 58.4 kJ/mol. The actual polymerization system was found to involve ESR-observable propagating polymer radicals of ENMA. ESR determination of the polymer radical concentration allowed rate constants of propagation (k_p) and termination (k_t) to be estimated at 60°C: $k_p = 320\ \text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$, $k_t = 3.7 \times 10^5\ \text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$. Dynamic thermogravimetry showed that the thermal degradation of poly(ENMA) begins at 340°C, and the residue at 500°C was only 4% of the initial polymer. Application of the Kelen–Tüdös method to the copolymerization results of ENMA (M_1) and styrene (M_2) at 50°C gave the following parameters: $r_1 = 0.24 \pm 0.01$ and $r_2 = 0.22 \pm 0.01$ giving $Q_1 = 1.14$ and $e_1 = +0.78$.

INTRODUCTION

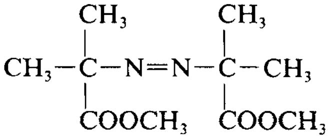
It is well known that α-methylstyrene and ethyl α-*n*-butylacrylate yield no polymers in the usual radical polymerization due to steric hindrance of their substituents [1]. Recently some α-(substituted methyl)acrylic acid esters have, however, been found to be easily polymerized by radical initiators to give high polymers in spite of their bulky substituents [2–12]. Dialkyl itaconates (DRIs) and alkyl α-acyloxymethylacrylates (RAAs) are representatives of such homopolymerizable monomers. It is of great interest that the polymerization systems of these monomers involve ESR-detectable propagating polymer radicals under practical polymerization conditions [2–6, 8, 9]. It is also noteworthy that RAAs show much higher radical polymerizability than DRIs although they have similar structures.

In order to elucidate the high polymerizability of RAAs, we have prepared ethyl α-naphthoyloxymethylacrylate (ENMA) and investigated its radical polymerization behavior.

The present paper deals with kinetic and ESR results of the polymerization of ENMA with dimethyl 2,2′-azobisisobutyrate (MAIB) in benzene and characterization of poly(ENMA).



(ENMA)



$CH_3-\overset{CH_3}{\underset{COOCH_3}{C}}-N=N-\overset{CH_3}{\underset{COOCH_3}{C}}-CH_3$

(MAIB)

EXPERIMENTAL

Materials

ENMA was prepared by the reaction of ethyl α-hydroxymethylacrylate (EHMA) with naphthoyl chloride in the following manner. EHMA was obtained by the reaction of triethylphosphonoacetate with formaldehyde in the presence of potassium carbonate according to the method of Villeras et al. [13]. An ethereal solution of α-naphthoylchloride (75 g, 0.39 mol) was added dropwise to an equimolar mixture of EHMA (46 g, 0.39 mol) and pyridine (30.8 g, 0.39 mol) in ether below 0°C with stirring. The mixture was allowed to stand for 1 day at room temperature to complete the reaction and then washed with water to remove the resulting pyridine hydrochloride. The solvent was evaporated, and to the residue was added a large excess of methanol to remove a by-product which seems to be an acid anhydride based on an IR spectrum. The methanolic solution was stirred at room temperature for a day. After evaporating the methanol, the residue was dissolved in ether. The solution was washed successively with 3% HCl, 3% NaOH aqueous solution, and finally water, and then it was dried over sodium sulfate. After evaporating the solvent, the remaining oil was passed through a silica gel column using benzene as eluent. The solution was evaporated and the residue was distilled three times to yield pure ENMA; yield: 31 g, 28%, bp 166°C/2 mmHg, mp 33°C.

IR (neat) (cm^{-1}); 1720(—COO—), 1645(—C=C—), 780(—naphthyl). ^{1}H-NMR (CCl_4) (TMS, ppm): 1.29 (t: $-O-CH_2-C\underline{H}_3$, 3H), 4.20 (q: $-O-C\underline{H}_2-CH_3$, 2H), 5.03 (s: $-C=C-C\underline{H}_2-O-$, 2H), 5.88, 6.31 ($C\underline{H}_2=C-$, 2H), 7.22-9.00 ($-C_{10}\underline{H}_7$, 7H).

Elemental analysis, $C_{17}H_{16}O_4$ (284.3). Calculated: C 71.75, H 5.67%. Found: C 71.70, H 5.62%.

Styrene (St) and benzene were purified by the usual methods. MAIB was recrystallized from methanol.

Polymerization Procedure

Homo- and copolymerizations of ENMA were conducted in a degassed and sealed glass tube at a given temperature under shaking. The resulting polymer was isolated by pouring the polymerization mixture into a large excess of methanol, filtering, drying under vacuum, and weighing.

Elemental analysis of poly(ENMA), $C_{17}H_{16}O_4$ (284.3). Calculated: C 71.75, H 5.67%. Found: C 71.74, H 5.58%.

Measurements

^{1}H- and ^{13}C-NMR spectra were recorded on Hitachi R-24B (60 MHz) and JEOL GX-400 (100 MHz ^{13}C) spectrometers, respectively. Gel permeation chromatograms (GPC) were obtained by a TOSO HLC-802A chromatograph at 38°C using tetrahydrofuran (THF) as eluent. From the GPC results, the number-average ($\overline{M}_n$) and weight-average ($\overline{M}_w$) molecular weights of poly(ENMA) were determined on the basis of poly(St) calibration. Dynamic thermogravimetry (TG) was carried out in an N_2 stream (flow rate; 20 mL/min) with a Shimadzu TG-50 thermogravimeter at a heating rate of 10°C/min. A differential scanning calorimeter (DSC) (Shimadzu DSC-50) was used for examination of the thermal behavior of poly(ENMA) (heating rate; 10°C/min). ESR spectra of the polymerization mixture were recorded on a JES-FG2XG spectrometer operating at the X-band (9.5 GHz) with a TE mode cavity.

RESULTS AND DISCUSSION

Kinetic Study on the Homopolymerization of ENMA in Benzene

The polymerization of ENMA with MAIB was kinetically investigated in benzene. Linear time–conversion plots were observed without any induction period in the polymerization in the 50 to 70°C temperature range where the concentrations of ENMA and MAIB were 1.00 and 5.00×10^{-3} mol·L^{-1}, respectively. Figure 1 shows the Arrhenius plot of the polymerization rate (R_p) estimated from the time–conversion plot at each temperature. From the slope of straight line, the overall activation energy of polymerization was calculated to be 58.4 kJ·mol^{-1}. This value is similar to those for the polymerizations of ethyl α-benzoyloxymethylacrylate (EBMA) (53 kJ·mol^{-1}) [9] and DRIs (60 kJ·mol^{-1}) [2, 3, 6] initiated MAIB or azobisisobutyronitrile (AIBN) but much lower than those (84 kJ·mol^{-1}) for the

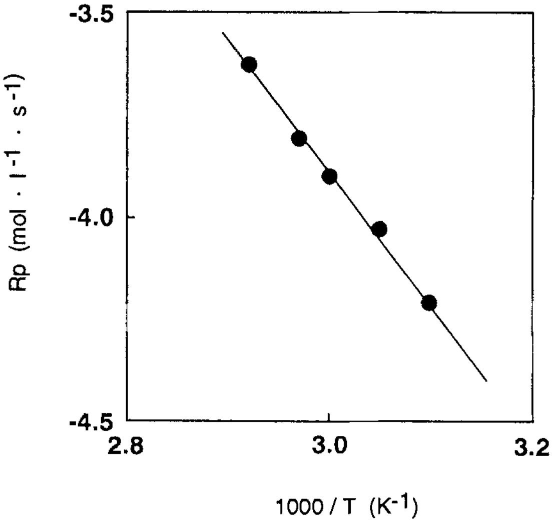


FIG. 1. Temperature effect on the polymerization rate (R_p): [ENMA] = 1.00 mol·L^{-1}; [MAIB] = 5.00 × 10^{-3} mol·L^{-1}.

AIBN-initiated polymerization of St and methyl methacrylate (MMA) [14]. MAIB and AIBN have similar activation energies of decomposition [15].

Figure 2 shows the relations of R_p with the concentration of MAIB (a) and ENMA (b). R_p is proportional to the square root of the initiator concentration, indicating a usual bimolecular termination. On the other hand, R_p increases in proportion to the 1.7 power of monomer concentration. Dependences of R_p higher than first order on the monomer concentration were also observed in the polymerizations of EBMA and DRIs [2, 3, 6, 9], which can possibly be ascribed to the following reasons; (a) primary radical termination, (b) viscosity effect due to the monomer on initiator efficiency and termination, (c) effect of the monomer as solvent on propagation, (d) chain-length-dependent rate constant of termination [2, 7]. The observed square-root dependence of R_p on the initiator concentration excludes a significant contribution of primary radical termination.

R_p for the polymerization of ENMA with MAIB in benzene at 50°C is expressed by

$$R_p = k[\mathrm{MAIB}]^{0.5}[\mathrm{ENMA}]^{1.7} \qquad (1)$$

Determination of Rate Constants of Propagation (k_p) and Termination (k_t) by Means of ESR

Figure 3 shows the ESR spectrum of the polymerization mixture observed in the polymerization of ENMA with MAIB in benzene at 60°C where the concentrations of ENMA and MAIB were 1.0 and 1.00 × 10^{-1} mol·L^{-1}, respectively. The observed spectrum is ascribable to the propagating polymer radical (I) of ENMA:

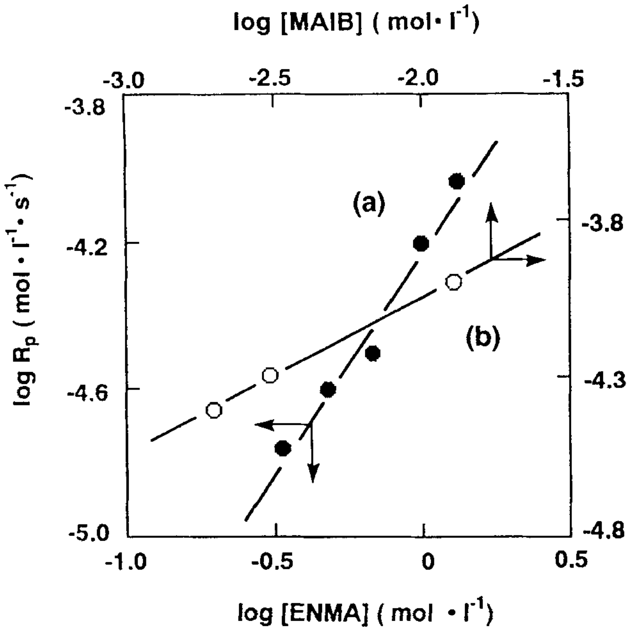
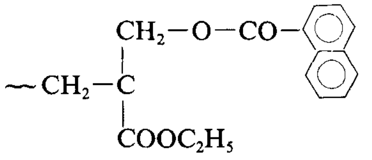


FIG. 2. Dependence of the polymerization rate (R_p) on the ENMA (a) and MAIB (b) concentrations at 50°C: (a) [MAIB] = 5.00×10^{-3} mol·L^{-1}; (b) [ENMA] = 1.00 mol·L^{-1}.



(I)

In order to estimate k_p and k_t, the concentration of propagating polymer radicals ([P•]) was determined by computer double integration of the ESR spectrum to be 1.74×10^{-6} mol·L^{-1}, where 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) in the same polymerization system without MAIB was used as standard. R_p was separately determined under the same polymerization conditions to be 5.59×10^{-4} mol·L^{-1}·s^{-1}. The value of k_p was estimated according to Eq. (2) for the polymerization rate.

FIG. 3. ESR spectrum observed at 60°C in the ENMA/MAIB/benzene system: [ENMA] = 1.00 mol·L^{-1}; [MAIB] = 1.00×10^{-1} mol·L^{-1}.

$$R_p = k_p[\mathrm{P}\cdot][\mathrm{ENMA}] \tag{2}$$

The initiator efficiency (f) of MAIB in the present polymerization system was determined for estimating the k_t value in the same manner described previously [6]. In the polymerization system, MAIB decomposes into 1-methoxycarbonyl-1-methylethyl radicals and nitrogen. Some of the primary radicals are lost through cage reactions. The others diffuse through the solvent cage to initiate the polymerization. When the decomposition of MAIB is carried out in the presence of TEMPO, the solvent-cage-escaping primary radicals are trapped with TEMPO to yield a coupling product. So the f value of MAIB was obtained by following the decrease in the TEMPO concentration by means of ESR as shown in Fig. 4, which presents the relationship between time and the TEMPO concentration. The decomposition rate of MAIB was calculated from Eq. (3) of its decomposition rate constant (k_d) [15].

$$k_d\,(\mathrm{s}^{-1}) = 5.69 \times 10^{13} \exp(-120.5\ \mathrm{kJ/RT}) \tag{3}$$

The f value obtained thus was 0.68.

As mentioned above, the present polymerization involves the usual bimolecular termination. So the k_t value was estimated using Eq. (4).

$$2fk_d[\mathrm{MAIB}] = k_t[\mathrm{P}\cdot]^2 \tag{4}$$

The k_t value is possibly somewhat overestimated because the use of high MAIB concentration may cause primary radical termination.

The values of k_p and k_t obtained are listed in Table 1 along with those of some other vinyl monomers. The k_p and k_t values of ENMA are fairly smaller than those

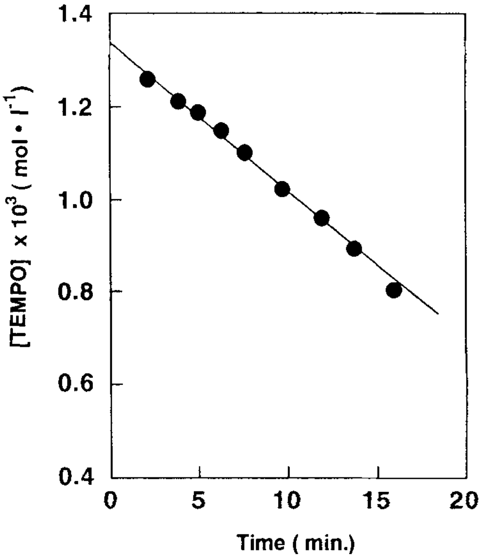


FIG. 4. Relationship between reaction time and [TEMPO] during the polymerization of ENMA with MAIB in benzene at 60°C: [ENMA] = 1.00 mol·L^{-1}; [MAIB] = 5.00 × 10^{-3} mol·L^{-1}; [TEMPO] = 1.33 × 10^{-4} mol·L^{-1}.

TABLE 1. Propagation (k_p) and Termination (k_t) Rate Constants of Some Vinyl Monomers in Benzene at 60°C

Monomer[a]	[Monomer], mol·L^{-1}	k_p, L·mol^{-1}·s^{-1}	$k_t \times 10^{-5}$, L·mol^{-1}·s^{-1}	Ref.
ENMA	1.00	320	3.7	This work
EBMA	1.56	990	29	9
DBI	1.99	11	1.2	2
MMA	Bulk	712	187	16, 18
St	Bulk	295	720	17, 19

[a] ENMA, ethyl α-naphthoyloxymethylacrylate; EBMA, ethyl α-benzoyloxymethylacrylate; DBI, di-*n*-butyl itaconate; MMA, methyl methacrylate; St, styrene.

of EBMA, another RAA monomer, indicating that the bulkier naphthyl group exerts more steric effects on the polymerizability than the phenyl group although their positions are remote from the active radical center. While k_p of ENMA is about 30 times that of dibutyl itaconate, k_t is only twice as large. This is the reason why RAAs show much higher radical homopolymerizability than DRIs. The k_t value of ENMA is much smaller (by two orders) than those of St and MMA, while their k_p values are comparable. This finding also supports the high reactivity of RAAs in radical polymerization.

Polymer Characterization

Poly(ENMA) is a white solid, soluble in benzene, toluene, ethyl acetate, and THF but insoluble in methanol, *n*-hexane, and acetone. As described above, poly(ENMA) gave a satisfactory elemental analysis.

TABLE 2. The Molecular Weights of Poly(ENMA)[a] and Polydispersities

[ENMA], mol·L^{-1}	[MAIB] × 10^3, mol·L^{-1}	T, °C	$\overline{M}_n \times 10^{-5}$	$\overline{M}_w \times 10^{-5}$	$\overline{M}_n/\overline{M}_w$
1.00	5.00	70	2.41	4.85	2.0
1.00	5.00	65	3.25	6.55	2.0
1.00	5.00	60	3.52	7.50	2.1
1.00	5.00	55	4.15	9.94	2.4
1.00	5.00	50	5.55	12.1	2.2
1.00	13.0	50	2.99	6.83	2.3
1.00	3.12	50	5.92	12.0	2.0
0.686	5.00	50	3.05	6.14	2.0
0.486	5.00	50	2.85	5.72	2.0
0.336	5.00	50	1.74	3.87	2.2

[a] Poly(ENMA) of about 10% yield was used for GPC measurements.

Table 2 summarizes the molecular weights of poly(ENMA)s formed under various polymerization conditions. Thus ENMA was found to yield polymers of high molecular weights with ease. $\overline{M}_n$ increased with ENMA concentration and decreased with MAIB concentration and rising temperature, as expected in the usual radical polymerization.

IR, ^{1}H-NMR, and ^{13}C-NMR (Fig. 5) spectra of poly(ENMA) revealed the complete disappearance of the C=C bond of monomer, indicating that the polymerization proceeds through opening of the double bond. In contrast to poly(EBMA), analysis of the microstructure of poly(ENMA) from the ^{13}C-NMR spectrum was unsuccessful [9].

The thermal behavior of poly(ENMA) was examined by means of DSC and TG. Figure 6 shows the DSC curve of poly(ENMA). The glass transition point and the melting point of the polymer were observed at 70 and 140°C, respectively. Figure 7 shows TG and differential thermogravimetric (DTG) curves. Rapid decomposition began at 340°C. A maximum in the DTG curve was observed at 380°C. Thus poly(ENMA) is considerably thermally stable. The residue at 500°C was 4% of the initial polymer.

Copolymerization of ENMA with St

Table 3 presents the results of copolymerization of ENMA (M_1) and St (M_2) with MAIB in benzene at 50°C. The copolymer yields were less than 5%. The copolymer composition was determined from the carbon content by elemental analysis.

Figure 8 shows the Kelen-Tüdös plot for the copolymerization results, giving the following monomer reactivity ratios [20]:

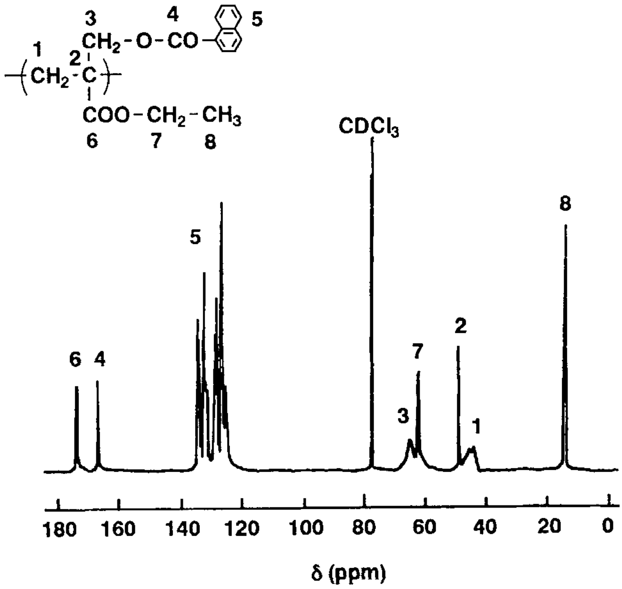


FIG. 5. ^{13}C-NMR spectrum of poly(ENMA) in $CDCl_3$.

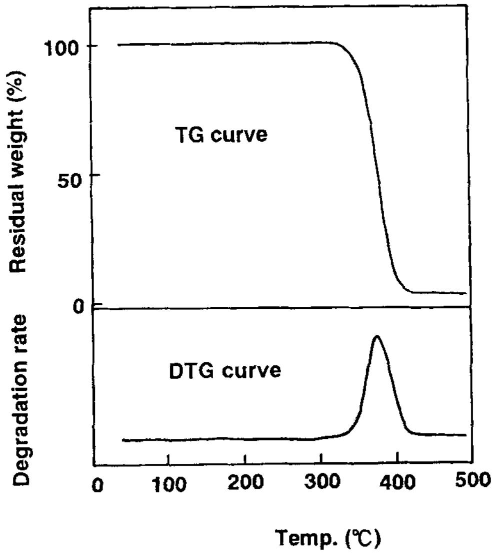


FIG. 6. TG and DTG curves of poly(ENMA).

$r_1 = 0.24 \pm 0.01, \quad r_2 = 0.22 \pm 0.01$

These values allowed Q- and e-values of ENMA to be estimated by setting $Q = 1.0$ and $e = -0.8$ for St; $Q_1 = 1.14$ and $e_1 = +0.91$. The curve-fitting method based on nonlinear least squares gave similar copolymerization parameters: $r_1 = 0.25$, $r_2 = 0.22$, $Q_1 = 1.17$, $e_1 = +0.91$.

As shown in Table 4, acrylate monomers with a wide variety of substituents were reported to show similar monomer reactivity ratios in the copolymerization

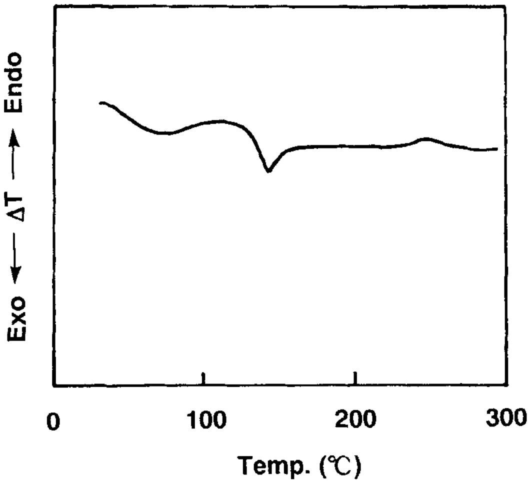


FIG. 7. DSC curve of poly(ENMA).

TABLE 3. Copolymerization of ENMA (M_1) and St (M_2) with MAIB in Benzene at 50°C

$[M_1]$ in the feed, mol%	Carbon content, %	$[M_1]$ in the copolymer, mol%
10	82.18	26.3
20	79.89	36.0
40	77.94	46.2
60	76.56	54.8
70	75.92	59.3
80	75.14	65.4
90	74.14	74.9

with St. This means that the propagating polymer radicals from acrylate monomers and the poly(St) radical show similar reaction selectivities in the copolymerizations.

The rate constants of cross-propagations in the copolymerization at 60°C were estimated by using the k_p values of comonomers and the monomer reactivity ratios, where the monomer reactivity ratios obtained at 50°C by the Kelen-Tüdös method were applied. In general, the monomer reactivity ratios are not very sensitive to temperature. The results are shown in Table 5 together with those of α-substituted acrylates, where M_1 = acrylate and M_2 = St.

k_{11} and k_{12} are highly dependent on the kind of α-substituent, whereas the effect of α-substituent on k_{21} is not so remarkable. This indicates that the α-

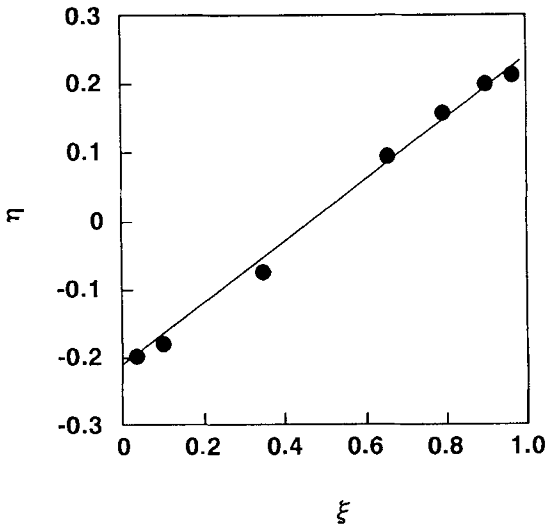
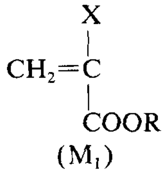


FIG. 8. Kelen-Tüdös plot for the copolymerization of ENMA (M_1) and St (M_2) at 50°C in benzene: [ENMA] + [St] = 1.00 mol·L^{-1}; [MAIB] = 5.00 × 10^{-3} mol·L^{-1}.

TABLE 4. Monomer Reactivity Ratios in the Copolymerization of Some Acrylate Monomers (M_1) and St (M_2)



$\mathrm{CH_2{=}C(X)COOR}$

(M_1)

Monomer[a]	X	R	r_1	r_2	Ref.
DEI	$CH_2COOC_2H_5$	C_2H_5	0.34	0.35	21
MPIA	$CH_2CONHC_6H_5$	CH_3	0.52	0.31	7
ENMA	$CH_2OCOC_{10}H_7$	C_2H_5	0.24	0.22	This work
EBMA	$CH_2OCOC_6H_5$	C_2H_5	0.27	0.30	9
MBOMA	$CH_2OC_4H_9$	CH_3	0.22	0.44	10
MMA	CH_3	CH_3	0.46	0.52	22
MA	H	CH_3	0.15	0.70	22

[a] DEI, diethyl itaconate; MPIA, methyl N-phenylitaconamate; ENMA, ethyl α-naphthoyloxymethylacrylate; EBMA, ethyl α-benzoyloxymethylacrylate; MBOMA, methyl α-butoxymethylacrylate; MMA, methyl methacrylate; MA, methyl acrylate.

substituent of acrylate influences the reactivity of the propagating radical much more than that of the monomer.

Thus the large difference in the k_p value of acrylate monomers originates from the difference in the reactivity of the propagating polymer radical.

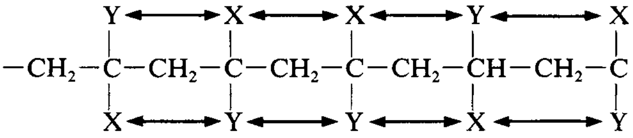
Recently Moad et al. found that the k_p values for the first few propagation steps are much higher (one order) than the k_p average values for the propagating

TABLE 5. The Rate Constants of Propagations Estimated for the Copolymerizations of Some Acrylate Monomers (M_1) and St (M_2)

	T,	k_{11}	k_{12}	k_{21}	k_{22} [17]	
Monomer[a]	°C	$L\cdot mol^{-1}\cdot s^{-1}$				Ref.
DEI	50	6.2	18	597	209	21
MPIA	55	12	23	803	249	7
ENMA	60	320	1,330	1,340	295	This work
EBMA	60	990	3,660	983	295	9
MBOMA	60	298	1,350	670	295	10
MMA	60	712	1,550	567	295	16
MA	60	2,090	13,930	421	295	23

[a] DEI, diethyl itaconate; MPIA, methyl N-phenylitaconamate; ENMA, ethyl α-naphthoyloxymethylacrylate; EBMA, ethyl α-benzoyloxymethylacrylate; MBOMA, methyl α-butoxymethylacrylate; MMA, methyl methacrylate; MA, methyl acrylate.

polymer radicals in the polymerizations of methyl acrylate and St [24, 25]. This means that the reactivity of the propagating polymer radical is governed by the steric effects based on interactions between the substituents on several monomer units near the terminal radical center (II). Such interactions may be referred to as a cumulative buttressing effect [26].



$$-CH_2-\overset{Y}{\underset{X}{C}}-CH_2-\overset{X}{\underset{Y}{C}}-CH_2-\overset{X}{\underset{Y}{C}}-CH_2-\overset{Y}{\underset{X}{C}}H-CH_2-\overset{X}{\underset{Y}{C}}$$

(II)

(cumulative buttressing effect)

Thus the widely different reactivities of the propagating polymer radicals of acrylate monomers are caused by the difference in the cumulative buttressing effect. The penultimate effect on the reactivity of the propagating polymer radical in the copolymerization [27, 28] can also be explained in terms of the cumulative buttressing effect. It is notable that acrylate propagating polymer radicals with such different reactivities show similar selectivities in reactions with acrylate monomer and St.

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