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Determination of Absolute Rate Constants for Radical Polymerization and Copolymerization of Ethyl α-Cyanoacrylate in the Presence of Effective Inhibitors against Anionic Polymerization

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SUMMARY:

The absolute rate constants of propagation k_p and of termination k_t of ethyl α-cyanoacrylate (ECNA) were determined in bulk at 30°C by means of the rotating sector method under conditions to suppress anionic polymerization; $k_p = 1\,622\ \mathrm{l\cdot mol^{-1}\cdot s^{-1}}$ and $k_t = 4{,}11\cdot10^8\ \mathrm{l\cdot mol^{-1}\cdot s^{-1}}$ for the polymerization in the presence of acetic acid, and $k_p = 1\,610\ \mathrm{l\cdot mol^{-1}\cdot s^{-1}}$ and $k_t = 4{,}04\cdot10^8\ \mathrm{l\cdot mol^{-1}\cdot s^{-1}}$ for the polymerization in the presence of 1,3-propanesultone. The magnitude of k_p^2/k_t determined was $6{,}39\cdot10^{-3}\ \mathrm{l\cdot mol^{-1}\cdot s^{-1}}$. The absolute rate constants for cross-propagation in ECNA copolymerizations were also evaluated. Quantitative comparison of the rate constants with those of common monomers and polymer radicals shows that the strong electron-withdrawing power of the ethoxycarbonyl and cyano groups enable the poly(ECNA) radical to add to monomers as fast as the other polymer radicals. The relatively high reactivity of ECNA, regardless of the type of attacking polymer radical, is interpreted by a transition state greatly stabilized by both the ethoxycarbonyl and the cyano groups.

Introduction

It is known that α-cyanoacrylic esters are highly susceptible to anionic polymerization even in the presence of a trace of a weak base[1,2], as well as vinylidene cyanide[3] and diethyl methylenemalonate[4]. The α-cyanoacrylates are, however, able to form homopolymers and copolymers exclusively by a radical chain mechanism[5-11], if the anionic polymerization is suppressed by an effective inhibitor. As the result of the radical copolymerization with a variety of monomers, the α-cyanoacrylates are known to be the most powerful electron-accepting monomers with homopolymerization ability. The e and Q values of methyl α-cyanoacrylate (MCNA) were evaluated to be 2,18 and 17, respectively[10], and these values have been explained in terms of the polar and resonance effect of the methoxycarbonyl and cyano group bound directly to the carbon-carbon double bond[11].

Recently, the reactivity of MCNA toward the benzoyloxyl radical generated from benzoyl peroxide has been estimated to be much lower than that of styrene (St) in conformity with the highly electronegative character of the reacting carbon-carbon double bond[12]. Furthermore, the heat of polymerization evaluated for the radical polymerization of MCNA was as low as 42 kJ · mol^{-1}, owing to destabilization of the polymer chain by the substituents and stabilization of the monomer due to conjugation[13].

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These observations suggest that the radical polymerization of α-cyanoacrylates proceeds without any anomalous behaviour under suitable conditions and hence is easier to control, as compared with their anionic polymerization. It is noted that in contrast to ordinary conjugated monomers, the α-cyanoacrylates having a cross-conjugated system form polymer radicals stabilized by linear conjugation during propagation. Radical copolymerizations of the α-cyanoacrylates have been studied[5,11], but a comprehensive determination of the rate constants for radical homopolymerization has not been reported.

In this paper, the absolute rate constants for propagation (k_p) and for termination (k_t) of ECNA are determined by means of the rotating sector method in the presence of acetic acid (AcOH) or 1,3-propanesultone (PS) as effective anionic inhibitors at 30 °C. By combining the absolute value of k_p obtained and those of common monomers with the monomer reactivity ratios of copolymerization, the absolute rate constants for the addition of ECNA and of the poly(ECNA) radical toward reference polymer radicals and monomers, respectively, are evaluated, and the effects of the ethoxycarbonyl and cyano groups on the reactivity are estimated on the basis of the rate data.

Experimental Part

Materials: Ethyl α-cyanoacrylate (ECNA) supplied from Taoka Chemical Co., Ltd., was distilled under reduced pressure before use. AcOH was distilled over phosphorus pentoxide and reagent grade PS was used without further purification. 2,2',4,4'-Tetramethyl-2,2'-azodivaleronitrile (AVN) and 1,1'-azodicyclohexane-1-carbonitrile (ACN), commercially available initiators, were recrystallized from ethanol. 9-(9-Fluorenylidenebenzyl)-9-fluorenyl (Koelsch's radical, BPA) was prepared by a sequence of reactions reported[14,15].

Polymerization: Polymerizations were carried out by using AVN and ACN as thermal- and photo-initiators in the presence of 7 wt.-% of AcOH or 0,5 wt.-% of PS relative to ECNA. Overall rates of polymerization, R_p, were determined by observing the contraction in a dilatometer using a cathetometer reading to 0,01 cm at 30 ± 0,005 °C. After degassing by the ordinary freezing and thawing, ECNA containing the desired amount of the anionic inhibitor was allowed to dissolve the initiator. The dilatometer filled with the polymerization mixture was sealed off under vacuum. The densities of ECNA and poly(ECNA) reported[16] were used to convert rates of contraction to R_p; the hypothetical contraction in volume at 100% conversion was 15,3%. It was postulated that the volume contraction in solution was proportional to the monomer concentration. All the measurements of R_p were carried out at conversions lower than 0,5%. Experimental details of the rotating sector method were described elsewhere[17].

Results and Discussion

Absolute values of k_p and k_t

In order to confirm the polymerization to proceed by a radical chain mechanism under the present conditions, kinetic orders with respect to 2,2',4,4'-tetramethyl-2,2'-azodivaleronitrile (AVN) and ECNA were determined at 30 °C. Although Canale et al.[5] have reported that R_p of MCNA increases in the low conversion range in bulk at 60 °C, a linear relationship between conversion and time was obtained in the initial stage of the ECNA polymerization.

The plot of R_p against the square root of the AVN concentration gives a straight line starting in the origin (Fig. 1) and between R_p measured in AcOH and the monomer concentration a linear relationship is observed. These findings definitely imply that R_p is expressed by the kinetic equation for ordinary radical polymerization:

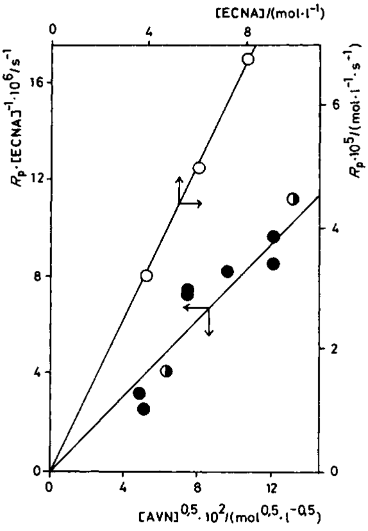


Fig. 1. Dependencies of the overall rate of polymerization R_p on ethyl α-cyanoacrylate concentration [ECNA] in acetic acid solution (○) and on $[\mathrm{AVN}]^{0,5}$ in the presence of acetic acid (7 wt.-%) (●) or 1,3-propanesultone (0,5 wt.-%) (◑); AVN: 2,2',4,4'-tetramethyl-2,2'-azodivaleronitrile

$$R_p = (2fk_d[\mathrm{AVN}]/k_t)^{0,5}\,k_p[\mathrm{ECNA}] = (R_i/k_t)^{0,5}\,k_p[\mathrm{ECNA}]$$

where k_d and f denote the rate constant for AVN decomposition and the initiation efficiency, respectively.

Therefore, the value of k_p^2/k_t may be calculated using the following equation:

$$k_p^2/k_t = R_p^2/([\mathrm{ECNA}]^2\,R_i)$$

Since in this equation R_p was measurable, R_i was determined by an inhibition method. Taking into account the susceptibility of ECNA to anionic polymerization possibly initiated by basic functional groups, the hydrocarbon BPA was employed as the radical inhibitor. Polymerizations in the presence of different amounts of BPA were undertaken at fixed concentration of AVN, and the results of the polymerization are shown in Fig. 2. Because after the induction period R_p is fairly steady and not seriously dependent on the initial concentration of BPA, BPA is satisfactory as an inhibitor for the ECNA polymerization.

From the dependence of the length of the induction period on the concentration of BPA, R_i was obtained as $1{,}04\cdot10^{-8}\ \mathrm{mol\cdot l^{-1}\cdot s^{-1}}$ at $[\mathrm{AVN}] = 1{,}00\cdot10^{-2}\ \mathrm{mol\cdot l^{-1}}$. Hence

$$k_p^2/k_t = 6{,}39\cdot10^{-3}\ \mathrm{l\cdot mol^{-1}\cdot s^{-1}}$$

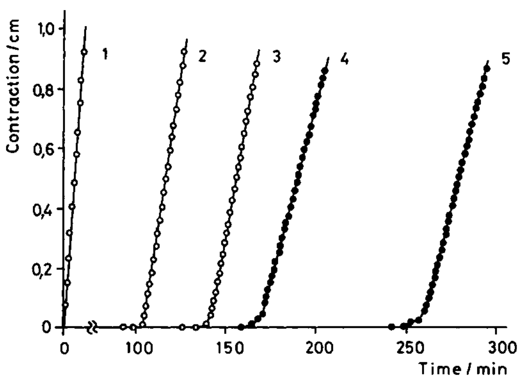


Fig. 2. Polymerization of ethyl α-cyanoacrylate in the presence of 9-(9-fluorenylidenebenzyl)-9-fluorenyl (BPA) and acetic acid (7 wt.-%) (○) or 1,3-propanesultone (0,5 wt.-%) (●) at 30 °C; 2,2',4,4'-tetramethyl-2,2'-azodivaleronitrile concentration [AVN] = $1{,}02 \cdot 10^{-3}$ mol · l^{-1}. [BPA] = 0 (curve 1), $8{,}14 \cdot 10^{-5}$ (curve 2), $9{,}77 \cdot 10^{-5}$ (curve 3), $11{,}24 \cdot 10^{-5}$ (curve 4), $15{,}66 \cdot 10^{-5}$ mol · l^{-1} (curve 5)

Employing $k_d = 1{,}02 \cdot 10^{-6}\ s^{-1}$ at 30 °C[18] yields $f = 0{,}51$, which seems to be in reasonable agreement with literature values for azo initiators.

The rotating sector method was adopted for the determination of the average lifetime τ of the polymer radical, necessary for calculating the value k_p/k_t. The polymerization rate under intermittent irradiation with UV light, R_{sp}, is a function of the flash time and τ[19]. Figs. 3 and 4 show the plots of the ratio R_{sp}/R_p' as a function of the flash time, where R_p' is the polymerization rate under steady irradiation and y is the contribution of the polymerization in the dark.

Theoretical curves calculated with $\tau = 0{,}75$ s and $y = 0{,}03$, and $\tau = 0{,}81$ s and $y = 0{,}03$ fit the experimental points of the polymerization in the presence of AcOH and of

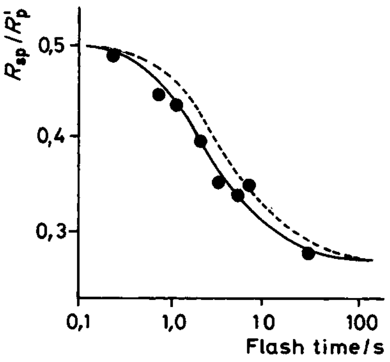


Fig. 3

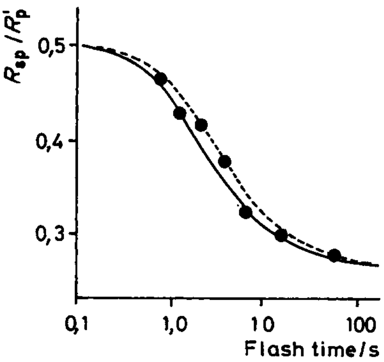


Fig. 4

Fig. 3. Photosensitized polymerization of ethyl α-cyanoacrylate under irradiation by UV light in the presence of acetic acid (7 wt.-%) at 30 °C; (– – –) theoretical curves for $\tau = 1{,}0$ s, $y = 0{,}03$; (———) $\tau = 0{,}75$ s, $y = 0{,}03$, see text

Fig. 4. Photosensitized polymerization of ethyl α-cyanoacrylate under irradiation by UV light in the presence of 1,3-propanesultone (0,5 wt.-%) at 30 °C; (– – –) theoretical curves for $\tau = 1{,}0$ s, $y = 0{,}03$; (———) $\tau = 0{,}81$ s, $y = 0{,}03$, see text

PS, respectively. $R_p' = 4{,}11 \cdot 10^{-5}\ \mathrm{mol \cdot l^{-1} \cdot s^{-1}}$ and $[\mathrm{ECNA}] = 7{,}85\ \mathrm{mol \cdot l^{-1}}$ for the polymerization in the presence of AcOH, and $R_p' = 4{,}12 \cdot 10^{-5}\ \mathrm{mol \cdot l^{-1} \cdot s^{-1}}$ and $[\mathrm{ECNA}] = 8{,}41\ \mathrm{mol \cdot l^{-1}}$ for the polymerization in the presence of PS. With

$$k_p/k_t = R_p' \tau/[\mathrm{ECNA}]$$

the values of k_p/k_t were obtained as $3{,}94 \cdot 10^{-6}$ and $3{,}98 \cdot 10^{-6}$ in the presence of AcOH and PS, respectively.

The absolute values of k_p and k_t were evaluated by combination of the numerical values of k_p^2/k_t and k_p/k_t:

$$k_p = 1622\ \mathrm{l \cdot mol^{-1} \cdot s^{-1}} \text{ and } k_t = 4{,}11 \cdot 10^8\ \mathrm{l \cdot mol^{-1} \cdot s^{-1}}$$
(AcOH, 7 wt.-%)

$$k_p = 1610\ \mathrm{l \cdot mol^{-1} \cdot s^{-1}} \text{ and } k_t = 4{,}04 \cdot 10^8\ \mathrm{l \cdot mol^{-1} \cdot s^{-1}}$$
(PS, 0,5 wt.-%)

The fairly good agreement of the k_p and k_t values determined for the polymerizations in the presence of the two types of anionic inhibitors indicates that these rate constants are ensured to be those of the respective elementary reactions of radical polymerization. In Tab. 1, the values of k_p and k_t for some α-substituted acrylic esters are summarized and compared with those of ECNA. It is noted that k_p of ECNA is greater than that for MA, MMA, and EFA and as large as that of ECA (for explanation of abbreviations see footnote Tab. 1).

Tab. 1. Absolute values of k_p and k_t for radical polymerizations at 30 °C

Monomer[a]	k_p / $\mathrm{l \cdot mol^{-1} \cdot s^{-1}}$	$k_t \cdot 10^{-7}$ / $\mathrm{l \cdot mol^{-1} \cdot s^{-1}}$	Ref.
MA	720	0,34	[19]
MMA	450	4,20	[20]
EFA	1 120	48	[21]
ECA	1 660	33,3	[22]
ECNA (AcOH, 7 wt.-%)	1 622	41,1	This work
ECNA (PS, 0,5 wt.-%)	1 610	40,4	This work

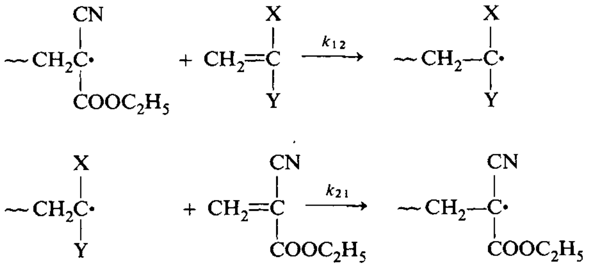
[a] MA, methyl acrylate; MMA, methyl methacrylate; EFA, ethyl α-fluoroacrylate; ECA, ethyl α-chloroacrylate; ECNA, ethyl α-cyanoacrylate; AcOH, acetic acid; PS, 1,3-propanesultone.

Being closely related to the polymerization ability of a monomer in a kinetic sense, the magnitude of k_p is dependent on the reactivity of both the polymer radical and the monomer. In a radical chain process, however, substituents which increase the reactivity of the double bond, greatly decrease the reactivity of the polymer radical. This compensating phenomenon has been taken into account for a discussion of the relationship between the magnitudes of k_p and the structure of the monomers; usually, the k_p value is expected to increase with increasing reactivity of the polymer radical. Because ECNA, which is a cross-conjugated system, forms a linear conjugated poly(ECNA) radical during propagation, the simple compensating phenomenon would not be observed in ECNA polymerization, in contrast to the polymerization of common conjugated monomers. Therefore, an estimation of the absolute reactivities of ECNA and the poly(ECNA) radical is required for the further discussion.

Reactivities of ECNA and of the poly(ECNA) radical

It is known that the copolymerization of ECNA (e = 2,48) with electron donating monomers such as styrene (St), vinyl ethers, and vinyl sulfides is initiated spontaneously[5,11], analogous to vinylidene cyanide (e = 2,58)[3]. The main difference is that ECNA forms copolymers with vinyl ethers in contrast to the respective homopolymer formation of vinylidene cyanide and vinyl ethers[3]. The spontaneous copolymerization of ECNA has been confirmed to follow a radical chain mechanism and the copolymer composition is not affected by whether spontaneous or initiator induced copolymerization occurs[11].

The monomer reactivity ratios for MCNA or ECNA copolymerizations have been reported in our previous paper[11], and the results of the copolymerization with reference monomers, the k_p values of which have been determined at 30 °C, are quoted in Tab. 2. Since MCNA, designated by M_1 in this table, seems to be as reactive as ECNA, these monomer reactivity ratios were used for the calculation of the absolute rate constants of cross-propagations: $k_{12} = k_{11}/r_1$ and $k_{21} = k_{22}/r_2$. The values of k_{12} and k_{21} for the copolymerization of St and MMA were obtained by the same procedure from the k_p values and the monomer reactivity ratios given in lit.[1,19].



$$\sim CH_2\overset{CN}{\underset{COOC_2H_5}{C}}\cdot \;+\; CH_2{=}\overset{X}{\underset{Y}{C}} \xrightarrow{k_{12}} \sim CH_2{-}\overset{X}{\underset{Y}{C}}\cdot$$

$$\sim CH_2\overset{X}{\underset{Y}{C}}\cdot \;+\; CH_2{=}\overset{CN}{\underset{COOC_2H_5}{C}} \xrightarrow{k_{21}} \sim CH_2{-}\overset{CN}{\underset{COOC_2H_5}{C}}\cdot$$

Tab. 3 summarizes the rate constants for addition of poly(ECNA), poly(St), and poly(MMA) radicals to various monomers at 30 °C. It was found that the poly(ECNA) radical adds to the monomers as fast as the other polymer radicals; the k_{12} values vary from ca. 10^2 to $10^4\ l \cdot mol^{-1} \cdot s^{-1}$. The k_{12} values for poly(St) and poly(MMA) radicals are in the same range. Thus, poly(ECNA) radicals seem to be as reactive as the other polymer radicals in the cross-propagation reactions, while the ethoxycarbonyl and cyano groups may stabilize the polymer radical.

Tab. 2. Copolymerization reactivity ratios r_1 and r_2 for the copolymerization of methyl α-cyanoacrylate (MCNA = M_1) with some comonomers M_2

M_2 [a]	r_1	r_2
St	0,03 [b]	0,01 [b]
VAc [a]	8	0,1
MMA	0,16	0,08
MA	3,09	0,05
ECA	1,26	0,17

[a] VAc = vinyl acetate; other abbreviations see footnote Tab. 1; St = styrene.
[b] From ref. [5].

Tab. 3. Cross propagation rate constants k_{12} of poly(ECNA), poly(St), and poly(MMA) radicals toward various monomers at 30 °C

Monomer [a]	$k_{12}/(\mathrm{l \cdot mol^{-1} \cdot s^{-1}})$		
	poly(ECNA) radical	poly(St) radical [b]	poly(MMA) radical
VAc	201	1,9	22,7
MA	525	138	325
ECA	1 290	1 540	7 244
ECNA	1 622	10 600	5 616
MMA	10 100	204	450
St	54 100	106	970

[a] For explanation of abbreviations see footnotes Tabs. 1 and 2. St = styrene.
[b] $k_p = 106\ \mathrm{l \cdot mol^{-1} \cdot s^{-1}}$ at 30 °C, ref. [19].

According to the additivities of e and Q values[10], the reactivities of eleven monomers including those of Tab. 3 toward the poly(ECNA) radical are expressed using the monomer reactivity ratios of our previous paper[11]:

$$\log k_{12} = -2{,}1(\sigma_X + \sigma_Y) + (\Delta \log Q_X + \Delta \log Q_Y) + 2{,}30$$

where σ and $\Delta \log Q$ are Hammett's polar substituent constant and the increment of the $\log Q$ value for introducing a substituent X or Y, respectively. Fig. 5 shows a linear relationship between $[\log k_{12} - (\Delta \log Q_X + \Delta \log Q_Y)]$ and $(\sigma_X + \sigma_Y)$.

It is noted that this equation holds for electron-donating monomers as well as for electron-accepting monomers using the ordinary substituent constants. Therefore, participation of donor-acceptor complexes in the propagation step is ruled out. A negative coefficient of $(\sigma_X + \sigma_Y)$ shows that the poly(ECNA) radical is apparently electrophilic in character.

The large and small k_{12} values of the poly(ECNA) radical toward St and ECA or ECNA in Tab. 3 can be interpreted by the electron-donating and accepting character of the respective monomer. However, the k_{12} values toward MA and MMA, being

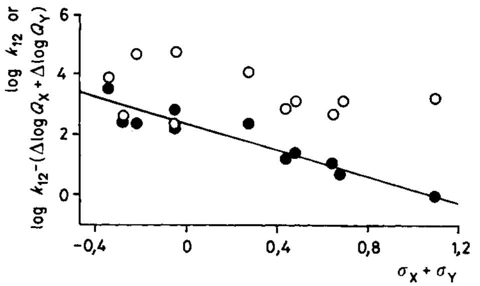


Fig. 5. Plots of $\log k_{12}$ versus (σ_X + σ_Y) (○) and [$\log k_{12}$ − ($\Delta \log Q_X$ + $\Delta \log Q_Y$)] versus (σ_X + σ_Y) (●); see text. M_1: ethyl α-cyanoacrylate; M_2: CH_2=CXY

rather electron-accepting monomers, are greater than those of poly(St) and poly(MMA) radicals, indicating that the poly(ECNA) radical is inherently reactive regardless of the polar character of the monomer. Similarly, reactivities of poly(*p*-substituted styrene) and poly(alkyl methacrylate) radicals toward certain monomers tend to increase with increasing electron-withdrawing power of the *p*-substituent and the ester group[23,24]. Generally, it is likely that the reactivity of a polymer radical increases with increasing electron-accepting power, because the polymer radical is required to accept one of the π-electrons being taken from a monomer for the formation of a new σ-bond.

Although the acetoxy groups of VAc shows a very weak electron-donating character in radical polymerization, $\sigma = -0{,}05$[10], the k_{12} value of the poly(ECNA) radical toward VAc is greater than those of the other polymer radicals. The reactivity of the poly(ECNA) radical may not be lowered significantly by resonance stabilization of the ethoxycarbonyl and cyano groups. Therefore, it is noted on the basis of the k_{12} values that the increase in the rate constant with increasing electron-accepting power of the radical is more pronounced than the decrease with increasing resonance stabilization.

The reactivity of ECNA toward different polymer radicals given by k_{21} is compared with that of St and MMA in Tab. 4. As can be seen, one of the most striking features of ECNA is that the rate constants of the most reactive poly(MA) radical and the least reactive poly(ECNA) radical are different by a factor of only 8,9, whereas the largest

Tab. 4. Cross propagation rate constants k_{12} of ECNA, St, and MMA[a] toward various polymer radicals at 30 °C

Polymer radical of[a]	$k_{21}/(\mathrm{l \cdot mol^{-1} \cdot s^{-1}})$		
	ECNA	St	MMA
ECNA	1 622	54 100	10 100
MMA	5 625	307	450
VAc[b]	12 280	81 400	54 300
ECA	9 760	5 090	83
St	10 600	106	204
MA	14 400	4 060	2 060

[a] For explanation of abbreviations see footnote Tab. 1. VAc = vinyl acetate; St = styrene.
[b] $k_p = 1\,228\ \mathrm{l \cdot mol^{-1} \cdot s^{-1}}$, ref.[19].

and smallest rate constants for St and MMA are different by factors of 770 and 650, respectively.

Another feature of the k_{21} value is that ECNA shows higher reactivity than St and MMA toward the polymer radicals. The insensitivity of the reactivity with the structure of the attacking polymer radical and the relatively high reactivity of ECNA may be interpreted as being due to a transition state greatly stabilized by both the ethoxycarbonyl and the cyano groups.

If the transition state resembles the poly(ECNA) radical rather than ECNA, the properties of the radical should have the greatest influence on the k_{21} values; the resonance stabilization would be decisive while polar and resonance factors of the attacking polymer radical should be minor.

According to these interpretations of the values of k_{12} and k_{21} for poly(ECNA) radicals and the monomer ECNA, the large k_p value in the present study arises as a consequence of the high reactivity of the polymer radical and of the monomer, owing to mainly polar and resonance effects of the substituents, respectively.

1) H. W. Coover, Jr., T. H. Wicken, Jr., "Encyclopedia of Polymer Science and Technology", Vol. 1, edited by H. F. Mark, N. Gaylord, N. M. Bikales, Intersience Publ., New York 1964, pp. 337–342

2) D. S. Johnston, D. C. Pepper, Makromol. Chem. **182**, 393, 407, 421 (1981)

3) H. Gilbert, F. F. Miller, S. J. Averill, R. F. Schmidt, F. D. Stewart, H. L. Trumbull, J. Am. Chem. Soc. **76**, 1074 (1954)

4) H. Hopff, H. Lüssi, S. Allisson, Makromol. Chem. **44/46**, 95 (1961)

5) A. J. Canale, W. E. Goode, J. B. Kinsinger, J. R. Panchak, R. C. Kelso, R. K. Graham, J. Appl. Polym. Sci. **4**, 231 (1966)

6) J. B. Kinsinger, J. R. Panchak, R. L. Kelso, J. S. Bartlett, R. K. Graham, J. Appl. Polym. Sci. **9**, 429 (1965)

7) J. C. Bevington, J. A. L. Jemmett, P. F. Onyon, Eur. Polym. J. **12**, 255 (1976)

8) T. Otsu, B. Yamada, Makromol. Chem. **110**, 279 (1967)

9) M. Yonezawa, S. Suzuki, H. Ito, K. Ito, J. Synth. Org. Chem. Jpn. **27**, 280 (1969); Chem. Abstr. **70**, 106919s (1969)

10) B. Yamada, T. Otsu, J. Macromol. Sci., Chem. **3**, 1551 (1969)

11) T. Otsu, B. Yamada, S. Kusayama, S. Nagao, Kobunshi Ronbunshu **36**, 797 (1979); Chem. Abstr. **92**, 94753x (1980)

12) J. C. Bevington, J. A. L. Jemmett, J. Chem. Soc., Faraday Trans. 1, **69**, 1866 (1973)

13) J. C. Bevington, J. A. L. Jemmett, P. F. Onyon, Polymer **18**, 73 (1977)

14) J. L. Kice, J. Am. Chem. Soc. **80**, 348 (1958)

15) R. Kuhn, F. A. Neugebauer, Monatsh. Chem. **95**, 3 (1964)

16) M. Yonezawa, S. Suzuki, H. Ito, K. Ito, J. Synth. Org. Chem. Jpn. **24**, 1041 (1966); Chem. Abstr. **66**, 18918c (1966)

17) B. Yamada, H. Ohnishi, T. Otsu, Mem. Fac. Eng. Osaka City Univ. **19**, 189 (1978)

18) T. Otsu, B. Yamada, S. Sugiyama, Kobunshi Ronbunshu **35**, 705 (1978); Chem. Abstr. **90**, 72505z (1979)

19) R. Korus, K. F. O'Driscoll, in: "Polymer Handbook", edited by J. Brandrup, E. H. Immergut, John Wiley, New York 1975, 2nd edition, p. II-45

20) M. Kamachi, D. J. Liaw, S. Nozakura, Polym. J. **13**, 41 (1981)

21) B. Yamada, T. Kontani, M. Yoshioka, T. Otsu, J. Polym. Sci., Polym. Chem. Ed., in press

22) B. Yamada, T. Hayashi, T. Otsu, J. Macromol. Sci., Chem., in press

23) M. Imoto, M. Kinoshita, M. Nishigaki, Makromol. Chem. **86**, 217 (1965)

24) K. Yokota, M. Kani, Y. Ishii, J. Polym. Sci., Part A-1 **6**, 1325 (1968)