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Determination of Absolute Rate Constants for Radical Polymerization and Copolymerization of Ethyl α -Chloroacrylate: Effects of Substituents on Reaction Rates of Monomer and Polymer Radical

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ABSTRACT

The propagation and termination rate constants (k_p and k_t) for the radical polymerization of ethyl α -chloroacrylate (ECA) were determined by the rotating sector method; $k_p = 1660$ and $k_t = 3.33 \times 10^8$ L/mol·s at 30°C. The absolute rate constants for cross-propagations in copolymerization were evaluated from the k_p determined for ECA or those for common monomers and the monomer reactivity ratios. The reactivities of ECA and poly-(ECA) radicals estimated as the rate constants of cross-propagations were accounted for by using equations relating these rate constants to the polar and resonance effects of the substituents. ECA was highly reactive toward various polymer radicals as expected from the resonance effects of the carbethoxy and chloro substituents. The poly(ECA) radical was found to be more reactive than common polymer radicals. The reactivity of a polymer radical in cross-propagation seemed to increase with increasing electron-accepting power by facilitating electron transfer from a monomer required for the new C-C bond formation.

INTRODUCTION

Although absolute rate constants of the elementary reactions in radical polymerization of a number of monomers have been determined mainly by a rotating sector method [1], none of the 1,1-disubstituted ethylenes except for methacrylic monomers has been utilized for detailed kinetic studies. In the course of study on the radical polymerization of α -substituted acrylic esters [2], ethyl α -chloroacrylate (ECA) was chosen as one of the monomers of which rate constants of propagation (k_p) and termination (k_t) could be determined.

Since among the elementary reactions involved in radical polymerization, propagation directly relates to the polymerization ability of a monomer, determination of the k_p value enables us to discuss the reactivities of the monomer and the polymer radical quantitatively. From this point of view, the absolute values of k_p and k_t for ethyl α -cyanoacrylate (ECNA) were determined in a previous paper [3].

In this paper the determination of k_p and k_t for bulk polymerization of ECA by a rotating sector method at 30°C and evaluation of the rate constants for cross-propagations in copolymerization are described. On the basis of these rate data, the effects of carbethoxy and chloro substitutions on the reaction centers of the monomer and the polymer radical are discussed. Furthermore, equations relating these rate constants to the polar and resonance effects of the substituents are developed, and the corresponding rate constants of common monomers and polymer radicals are accounted for by use of the equation derived.

EXPERIMENTAL

Materials

ECA was prepared by continuous distillation from an equimolar mixture of ethyl α, β -dichloropropionate and quinoline under reduced pressure. Methyl α -methoxyacrylate, ethyl α -bromoacrylate, α -methoxyacrylonitrile, and ethyl α -fluoroacrylate (EFA) were synthesized as described elsewhere [2, 4]. Commercially available styrene (St), methyl methacrylate (MMA), methyl acrylate (MA), acrylonitrile, methacrylonitrile, vinyl acetate (VAc), and the synthesized monomers were distilled in a nitrogen stream under atmospheric or reduced pressure before use.

2,2'-Azobisisobutyronitrile (AIBN) and 1,1'-azobiscyclohexane-1-carbonitrile (ACN) were purified by recrystallization from ethanol. Diphenylpicrylhydrazyl (DPPH) was recrystallized from benzene and used as the benzene complex. *p*-Benzoquinone was purified by sub-

limation after recrystallization from ligroine. 1,3,5-Triphenylverdazyl was prepared by the reported reactions and recrystallized from methanol [5].

Polymerization

Polymerizations were carried out with AIBN and ACN as the thermal- and photoinitiators. Overall rates of polymerization (R_p) were measured by dilatometry at $30 \pm 0.005^\circ\text{C}$. Details of the rotating sector method have been described elsewhere [6]. In order to suppress photopolymerization of ECA, a concentrated sulfuric acid solution of picric acid [7] was used as the filter for cutting off wavelengths shorter than 380 nm.

Copolymerization

Copolymerizations of ECA were run in sealed tubes at 60°C . Copolymer compositions were calculated from chlorine analysis, and the monomer reactivity ratios were determined by a nonlinear least squares procedure [8].

Number-Average Molecular Weight and Intrinsic Viscosity

The number-average molecular weight (\bar{M}_n) of poly(ECA) was measured by osmometry in 1,2-dichloroethane as the solvent using a Knauer membrane osmometer. The intrinsic viscosity ($[\eta]$) of the polymer in the same solvent was measured by an Ubbelohde viscometer at 30°C . The number-average degree of polymerization (\bar{P}_n) was calculated from \bar{M}_n .

RESULTS

Contraction-Conversion Factor

In order to monitor the polymerization by a dilatometer, the relationship between the conversion and the contraction in volume during polymerization should be known. The relationship for bulk polymerization was calculated from the difference in density between ECA monomer and the amount of poly(ECA) dissolved. According to the linear relationship shown in Fig. 1, the percentage volume contraction corresponding to 100% conversion is 20.3.

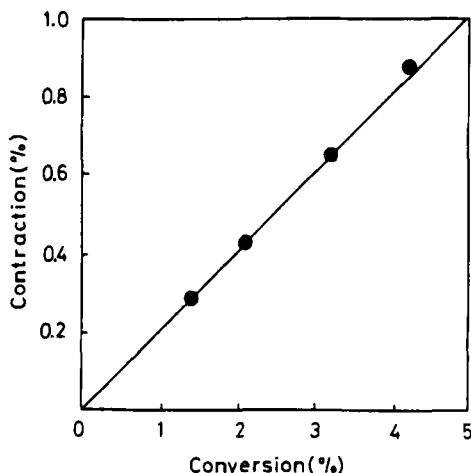


FIG. 1. Relationship between conversion and contraction during bulk polymerization of ECA at 30°C.

$[\eta] - \bar{M}_n$ Equation

By measuring $[\eta]$ (dL/g) of various \bar{M}_n samples of poly(ECA), the following equation was derived from the present study over the range of \bar{M}_n from 214,900 to 4,169,500 in 1,2-dichloroethane at 30°C:

$$[\eta] = 9.57 \times 10^{-5} \bar{M}_n^{0.74}$$

Values of R_p

Because the rotating sector method requires that chain polymerization be initiated photochemically and terminated with the bimolecular reaction of the polymer radicals, the kinetic order with respect to AIBN and ECA should be 0.5 and 1.0, respectively. As shown in Fig. 2, it was confirmed that R_p obeyed the following equation:

$$R_p = k[\text{AIBN}]^{0.5} [\text{ECA}]^{1.0}$$

The overall activation energy of the polymerization initiated with AIBN was 21.5 kcal/mol over the temperature range 25 to 50°C.

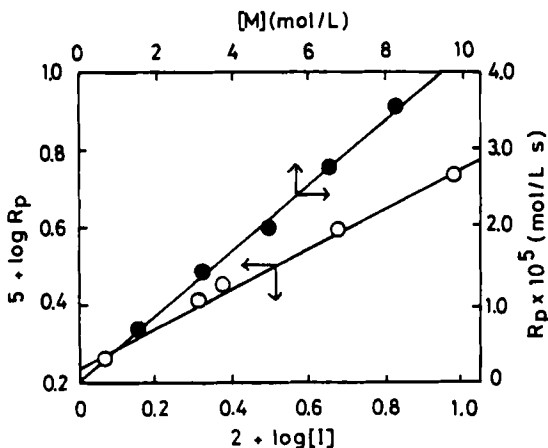


FIG. 2. Dependencies of polymerization rate on ECA concentration and on AIBN concentration.

Calculation of k_p^2/k_t from Initiation Rate

The value of k_p^2/k_t may be calculated from R_p and the initiation rate (R_i) according to

$$k_p^2/k_t = R_p^2/(R_i[M]^2)$$

Since R_p was measurable, R_i was determined by the length of the inhibition periods of an appropriate inhibitor. DPPH and verdazyl, the preferred inhibitors, were not used because ECA caused the characteristic colors of the solutions of these inhibitors to fade. p-Benzoquinone was found to function as a retarder because of its long period of retardation. Thus, determination of R_i by the inhibition method was unsuccessful, so it was estimated from the assumed efficiency of initiation (f) and the decomposition rate of the initiator.

Since the literature data suggest that the f value closely relating to the cage effect of AIBN is about 0.5 [9-11], the choice of $f = 0.5$ for ECA polymerization seemed to be reasonable. The thermal decomposition rate constant of AIBN has been reported to be $8.9 \times 10^{-8} \text{ s}^{-1}$ at 30°C [12]. Hence, at $[\text{AIBN}] = 4.88 \times 10^{-2} \text{ mol/L}$,

$$R_i = 4.34 \times 10^{-9} \text{ mol/L}\cdot\text{s}$$

By using

$$R_p = 4.91 \times 10^{-5} \text{ mol/L}\cdot\text{s}$$

at the same concentration of AIBN in bulk, the value of k_p^2/k_t was obtained:

$$k_p^2/k_t = 8.27 \times 10^{-3} \text{ L/mol}\cdot\text{s}$$

Calculation of k_p^2/k_t from \bar{P}_n

In a typical radical polymerization the value of k_p^2/k_t may be calculated from \bar{P}_n by using

$$1/\bar{P}_n = k_t(1+x)R_p/(2k_p^2[M]^2) + C_m$$

where C_m is the chain transfer constant of the monomer and x is the contribution of disproportionation in termination.

Plots of $1/\bar{P}_n$ versus $R_p/[M]^2$ for ECA polymerization at 30°C, shown in Fig. 3, yield a straight line with a slope equal to $k_t(1+x)/2k_p^2$. However, the x value is not known and the prediction of x based on the structure of the polymer radical seems to be difficult [10, 11]. Consequently, the value of k_p^2/k_t was obtained as a range from 1.13×10^{-3} for complete combination ($x = 0$) to $2.26 \times 10^{-3} \text{ L/mol}\cdot\text{s}$ for complete disproportionation ($x = 1$). The value of k_p^2/k_t at $x = 0$ is close to that calculated from R_p , and similar values obtained by different methods suggest that k_p^2/k_t evaluated by assuming f is adequate.

From the intercept of the $1/\bar{P}_n - R_p/[M]^2$ plot, C_m of ECA was found to be 6.3×10^{-5} at 30°C.

Average Lifetime of Growing Radical

The polymerization rate under intermittent irradiation of UV light (R_{sp}) depends on the flash time and the average lifetime of the growing radical (τ) [13]. Figure 4 shows a plot of the ratio of the rates R_{sp}/R_p' against the flash time, where R_p' is the polymerization rate under steady irradiation of UV light and y denotes contribution of polymerization in the dark. The theoretical curve for $\tau = 0.97 \text{ s}$ and $y = 0.05$ was found to fit best for the experimental points. Since R_p'

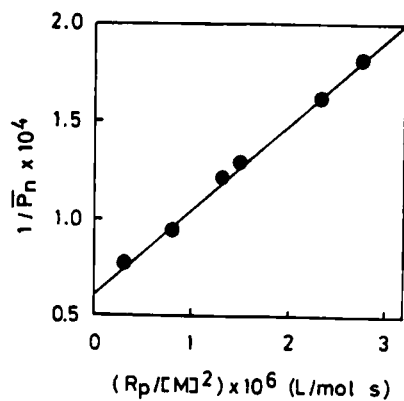


FIG. 3. Determination of k_p^2/k_t from polymerization rate and degree of polymerization.

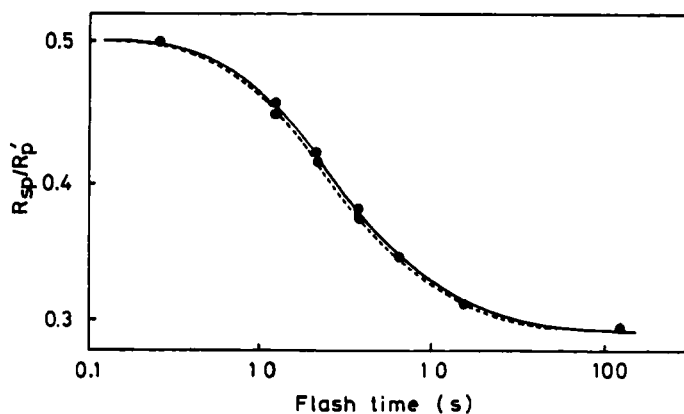


FIG. 4. Rate of photosensitized polymerization under intermittent irradiation of UV light as a function of flash time at 30°C: (—) $\tau = 1.0$ s and $y = 0$, (---) $\tau = 0.97$ s and $y = 0$.

was 4.24×10^{-5} mol/L's, the value of k_p/k_t obtained by using the following equation was 4.99×10^{-6} :

$$k_p/k_t = R_p' \tau / [\text{ECA}]$$

TABLE 1. Propagation and Termination Rate Constants at 30°C

Monomer	k_p (L/mol·s)	$k_t \times 10^{-7}$ (L/mol·s)	Q	Ref.
St	106	10.8	1.0	14
MMA	450	4.20	0.74	15
MA	720	0.43	0.42	16
EFA	1120	48	0.49	4
VAc	1228 ^a	6.72 ^a	0.026	17
ECNA	1622	41.1	17 ^b	3
ECA	1660	33.3	3.01	This work

^aCalculated from the activation parameters.

^bQ value for the methyl ester.

Absolute Values of k_p and k_t

Combining the numerical values of k_p^2/k_t and k_p/k_t yields the absolute values of k_p and k_t :

$$k_p = 1660 \text{ L/mol}\cdot\text{s}$$

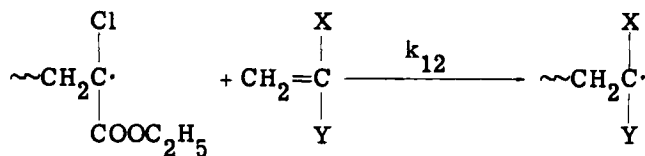
$$k_t = 3.33 \times 10^8 \text{ L/mol}\cdot\text{s}$$

In Table 1 the absolute values of the rate constants determined by the rotating sector method at 30°C are summarized.

Copolymerization

In Table 2 the monomer reactivity ratios for the copolymerizations of ECA (M_1) with a variety of monomers (M_2) are shown. The e and Q values calculated from the copolymerization with St were 1.14 and 3.01, respectively [14]. According to the definition of the monomer reactivity ratios, the absolute rate constants for the addition of poly(ECA) radical to the monomers are evaluated by

$$k_{12} = k_{11}/r_1 = 1660/r_1 \text{ L/mol}\cdot\text{s}$$



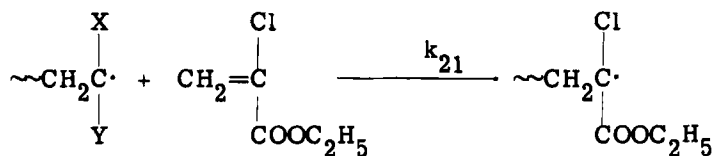
where k_{11} is equal to k_p of ECA. Because the monomer reactivity ratios have been known to be independent of polymerization temperature, the reactivity ratios at 30°C are approximated by those at 60°C.

The rate constants for the addition of M_2 radical to ECA were evaluated by using the k_p values of St, MMA, MA, VAc, EFA, and ECNA given in Table 1.

TABLE 2. Monomer Reactivity Ratios of Copolymerization of ECA (M_1) with Various Monomers (M_2) and k_{12} values at 30°C

No.	M_2	r_1	r_2	k_{12} (L/mol·s)	Ref.
1	St	0.33	0.07	5030	2
2	MMA	2.0	0.15	830	18
3	ECNA	0.17	1.3	9765	19
4	Vinylidene cyanide	0.41	0.09	4049	20
5	Acrylonitrile	2.0	0.15	830	21
6	EFA	2.90	0.21	572	This work
7	Methyl α -methoxyacrylate	0.58	0.11	2862	This work
8	Ethyl α -acetoxyacrylate	1.71	0.30	970	This work
9	α -Methoxyacrylonitrile	0.90	0.30	1844	This work
10	Methacrylonitrile	2.0	0.45	830	This work
11	MA	3.22	0.09	516	This work
12	VAc	30	0.03	55	This work
13	ECA	1.00	1.00	1660	This work

$$k_{21} = k_{22}/r_2$$



where k_{22} is identical to k_p of the M_2 monomer. The absolute values of k_{12} and k_{21} are tabulated in Tables 2 and 3, respectively. When $M_1 = M_2 = \text{ECA}$, both k_{12} and k_{21} become the k_p of ECA.

DISCUSSION

k_p Value

Propagation in homopolymerization consists of the addition of a polymer radical to a monomer, leading to the formation of a polymer radical. A comparison of the k_p values of common monomers shows that the monomer with a larger Q value may have a smaller k_p value because of forming a less reactive polymer radical during propagation. According to this expectation, the k_p value of ECA should be the second smallest one among those in Table 1. Apparently this is

TABLE 3. Rate Constant for Cross-Propagation (k_{21}) at 30°C, $M_1 = \text{ECA}$

Polymer radical	k_{21} (L/mol·s)
St	1,514
VAc	40,933
MMA	3,000
MA	8,000
EFA	5,333
ECNA	1,248
ECA	1,660

not the case. Therefore, the magnitudes of k_p , especially those of the 1,1-disubstituted ethylenes, were considered on the basis of the reactivities of the monomers and the polymer radicals evaluated as the rate constants of cross-propagations.

Reactivity of Poly(ECA) Radical

As reported in a previous paper [2], the reactivities of the 1,1-disubstituted ethylenes (M_2) having substituents X and Y toward a certain polymer radical ($M_1 \cdot$) are correlated with the polar and resonance effects of the substituents:

$$\log k_{12} = \rho(\sigma_X + \sigma_Y) + A(\Delta \log Q_X + \Delta \log Q_Y) + (\log k_{12})_0 \quad (1)$$

where $\Delta \log Q$ is a parameter showing the resonance effect of the substituent and σ is Hammett's polar substituent constant. ρ and A are reaction constants, and the last term, $(\log k_{12})_0$, is also a constant corresponding to the logarithm of the rate constant for addition of the reference radical ($M_1 \cdot$) to ethylene, $X = Y = H$. Steric effects were ignored in developing this equation.

According to the additivity of $\log Q$ value, $\Delta \log Q$ values have been defined and evaluated by

$$\begin{aligned} \Delta \log Q_X &= \log Q_{\text{CH}_2=\text{CXY}} - \log Q_{\text{CH}_2=\text{CHY}} \\ &= \log Q_{\text{CH}_2=\text{CXH}} - \log Q_{\text{CH}_2=\text{CH}_2} \end{aligned}$$

where $Q_{\text{CH}_2=\text{CXY}}$, $Q_{\text{CH}_2=\text{CXH}}$, $Q_{\text{CH}_2=\text{CHY}}$, and $Q_{\text{CH}_2=\text{CH}_2}$ are the Q values of $\text{CH}_2=\text{CXY}$, $\text{CH}_2=\text{CXH}$, $\text{CH}_2=\text{CHY}$, and $\text{CH}_2=\text{CH}_2$, respectively. In Table 4, $\Delta \log Q$ and σ values are summarized, and as discussed before [2], the σ value for the acetoxy group is -0.05 instead of 0.31 [22] in radical polymerization.

As in Fig. 5, a plot of $[\log k_{12} - (\Delta \log Q_X + \Delta \log Q_Y)]$ against $(\sigma_X + \sigma_Y)$ for the addition of poly(ECA) radical to various monomers gives a straight line with a slope equal to -0.95. The experimental point for $M_2 = \text{ECA}$ also fits the straight line, revealing that the k_p value of ECA can be accounted for in terms of the effects of the carboxy and chloro substituents as well as the rate constants for addition of the poly(ECA) radical to the other monomers. The reaction

TABLE 4. $\Delta \log Q$ and ρ Values

Substituent	$\Delta \log Q^a$	σ^b
OCH ₃	0.06	-0.27
CH ₃	0.19	-0.17
OCOCH ₃	0.15	-0.05 ^a
C ₆ H ₅	2.01	-0.01
H	0.00	0
F	0.07 ^c	0.06
Cl	0.86	0.23
COOR	1.59	0.45
CN	1.64	0.66

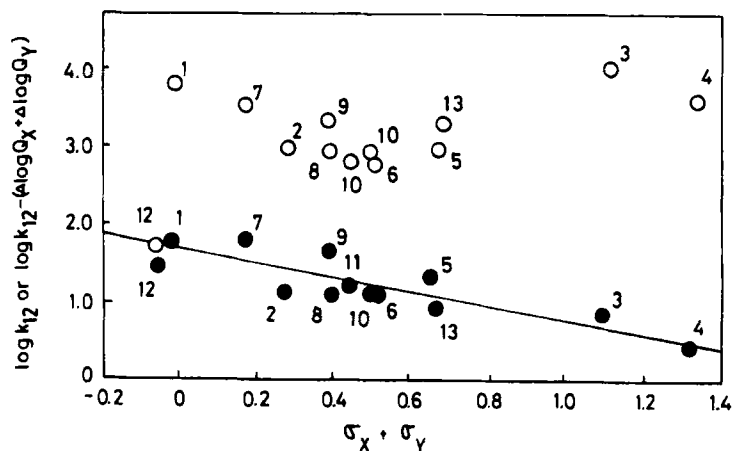
^aRef. 2.^bRef. 22.^cRef. 4.

FIG. 5. Application of Eq. (1) to reactivities of monomers toward poly(ECA) radical: plots of $\log k_{12}$ versus $(\sigma_X + \sigma_Y)$ (\circ) and $[\log k_{12} - (\Delta \log Q_X + \Delta \log Q_Y)]$ versus $(\sigma_X + \sigma_Y)$ (\bullet). Numbers are the same as in Table 2.

TABLE 5. ρ , A, and $(\log k_{12})_0$ Values in Eq. (1)

Polymer radical ($M_1 \cdot$)	ρ	A	$(\log k_{12})_0$
St ^a	0.83	1.0	1.78
MMA	-0.30	1.0	0.90
MA	-0.40	1.0	1.54
EFA	-0.69	1.0	1.85
ECNA ^b	-2.11	1.0	2.30
ECA	-0.95	1.0	1.66

^aRef. 2.^bRef. 19.

constants obtained for the poly(ECA) radical are shown in Table 5. In this table the reaction constants determined by the same procedure based on the k_p values in Table 1 and the monomer reactivity ratios in the literature [3, 4, 19, 23] are also summarized.

The reaction constant ρ , representing the polar character of the polymer radical, has a negative value for the poly(ECA) radical, consistent with the electron-withdrawing character of the carboxy and chloro-substituents. Another reaction constant, A, related to the resonance stabilization of the transition state, seems to be constant regardless of the structure of the polymer radical. Moreover, comparing the $(\log k_{12})_0$ values corresponding to the rate constants for addition of the respective polymer radicals to ethylene ($X = Y = H$) shows that the poly(ECA) and poly(ECNA) radical add faster than the other polymer radicals. As already mentioned for the inherent reactivity of the poly(ECNA) radical [3], the reactivity of a polymer radical tends to increase with increasing electron-accepting power because a growing polymer radical is required to accept one of the π electrons being taken from a monomer for the new σ bond formation.

Reactivity of ECA Monomer

As for Eq. (1), we tried to correlate k_{21} with the resonance and polar effects of the substituents. Contrary to the monomer reactivities given by k_{12} , the rate constants for the addition of polymer radicals to ECA, as expressed by k_{21} , should decrease with increasing resonance stabilization of the attacking radicals. The following equation was developed:

$$\log k_{21} = \rho'(\sigma_X + \sigma_Y) - A'(\Delta \log Q_X + \Delta \log Q_Y) + (\log k_{21})_0 \quad (2)$$

where ρ' and A' are the reaction constants corresponding to ρ and A in Eq. (1), respectively. The last term $(\log k_{21})_0$ denotes the logarithm of the rate constant for the addition of the polyethylene radical ($X = Y = H$) to ECA. The substituent constants σ and $\Delta \log Q$ refer to X and Y bound to the α -carbon of the attacking polymer radical.

The A' value was changed from 0 to 1 to give a linear relationship between $[\log k_{21} + A'(\Delta \log Q_X + \Delta \log Q_Y)]$ and $(\sigma_X + \sigma_Y)$. For the addition of polymer radicals to ECA, $\rho' = +0.21$ and $A' = 0.5$ were obtained as shown in Fig. 6. Equation (2) seemed to be appropriate to represent the reactivities toward various monomers. The k_{21} values for several monomers were calculated from the k_p values in Table 1 and the monomer reactivity ratios of copolymerization in the literature [3, 4, 19, 23]. The reaction constants ρ' , A' , and $(\log k_{21})_0$ for the monomers are summarized in Table 6.

Poly(ECA) radicals added faster to electron-donating monomers than to electron-accepting ones, as can be seen in Fig. 5, if the resonance effect due to the substituents of the monomer was excluded. Nevertheless, ECA is apparently nucleophilic in character ($\rho' = +0.21$)

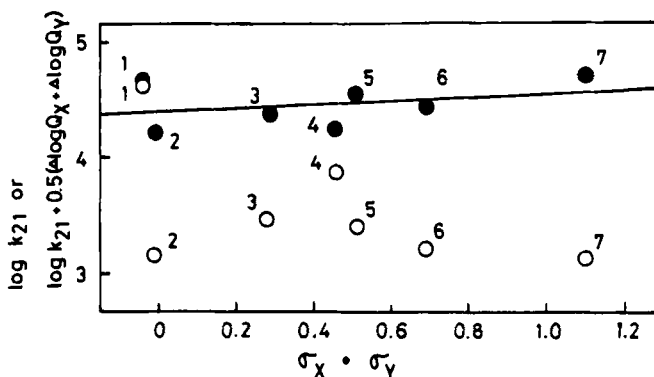
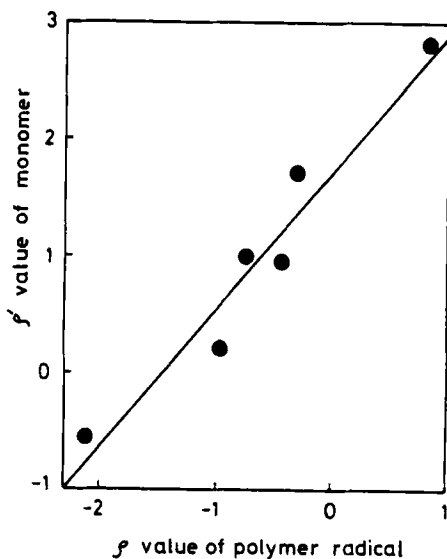


FIG. 6. Application of Eq. (2) to reactivities of polymer radicals toward ECA monomer: plots of $\log k_{21}$ versus $(\sigma_X + \sigma_Y)$ (\circ) and $[\log k_{21} + (\Delta \log Q_X + \Delta \log Q_Y)]$ versus $(\sigma_X + \sigma_Y)$ (\bullet). 1, Poly-(vinyl acetate) radical; 2, polystyrene radical; 3, poly(methyl methacrylate) radical; 4, poly(methyl acrylate) radical; 5, poly(ethyl α -fluoroacrylate) radical; 6, poly(ECA) radical; 7, poly(ethyl α -cyanoacrylate) radical.

TABLE 6. ρ' , A' , and $(\log k_{21})_0$ in Eq. (2)

Monomer (M_1)	ρ'	A'	$(\log k_{21})_0$
St	2.80	0.5	3.12
MMA	1.67	0.5	3.39
MA	0.95	0.5	3.40
EFA	1.00	0.5	3.25
ECNA	-0.59	0	4.11
ECA	0.21	0.5	4.35

FIG. 7. Plot of ρ' value for monomer against ρ value for polymer radical.

because the increasing electron-accepting power of the attacking polymer radical facilitates electron transfer from the monomer. The ρ' values for the monomers are consistently greater than the ρ values for the corresponding polymer radicals. This trend is obvious when the ρ' value for a monomer is plotted against the ρ value of the corresponding polymer radical as in Fig. 7, and the ρ' values may be correlated with the ρ values by

$$\rho' = 1.19\rho + 1.72$$

This ensures that the polar character of the monomer is not independent of that of the polymer radical.

The same tendency has been found by comparing the polar characters of *p*-substituted styrenes and alkyl methacrylates with poly(*p*-substituted styrene) and poly(alkyl methacrylate) radicals, respectively [14, 24].

Furthermore, the smaller contribution of ($\Delta \log Q_X + \Delta \log Q_Y$) for the $\log k_{21}$ value than that for the $\log k_{12}$ value ($A = 1.0$ and $A' = 0$ or 0.5) suggests that an increase in k_{21} value with increasing electron-accepting power of the polymer radical is more pronounced than the decrease with increasing resonance stabilization by the substituents of the radical. In agreement with this view, the reactivities of *p*-substituted styrenes toward certain poly(*p*-substituted styrene) radicals have been correlated with the polar effect of the substituents of the monomers and not to the resonance effect [14].

Although the accumulation of more data may be required before we have a better understanding of the influence of the structure of the polymer radical, Eq. (2) is considered to be valid for relating k_{21} values with the effects of the substituents *X* and *Y* in M_2^\cdot . Therefore, as a result of using carbethoxy and chloro-substituents to yield large k_{12} and k_{21} values, the k_p of ECA was observed to be as large as 1660 L/mol·s when $M_1 = M_2 = \text{ECA}$.

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