

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

The Reactivities of α -Substituted Acrylonitriles and Acrylic Esters in Radical Copolymerizations

Bunichiro Yamada^a; Takayuki Otsu^a

^a Department of Applied Chemistry Faculty of Engineering Osaka City, University Sugimotocho, Sumiyoshi-ku, Osaka, Japan

To cite this Article Yamada, Bunichiro and Otsu, Takayuki(1969) 'The Reactivities of α -Substituted Acrylonitriles and Acrylic Esters in Radical Copolymerizations', Journal of Macromolecular Science, Part A, 3: 8, 1551 – 1569

To link to this Article: DOI: 10.1080/10601326908051952

URL: <http://dx.doi.org/10.1080/10601326908051952>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

The Reactivities of α -Substituted Acrylonitriles and Acrylic Esters in Radical Copolymerizations

BUNICHIRO YAMADA and TAKAYUKI OTSU

Department of Applied Chemistry

Faculty of Engineering

Osaka City University

Sugimotocho, Sumiyoshi-ku, Osaka, Japan

SUMMARY

In order to clarify the effect of the substituents in α -substituted acrylonitriles and acrylic esters on their relative reactivities toward a polystyryl radical, the radical copolymerizations of diethyl methylene-malonate, ethyl α -chloroacrylate, ethyl α -bromoacrylate, α -chloroacrylonitrile, methyl α -methoxyacrylate, and α -methoxyacrylonitrile with styrene (M_2) were investigated at 60°C. From the copolymerization parameters obtained in this study and those reported in the literature, it was confirmed that the α substituents additively contributed to the values of $\log Q$ and e of the monomers. Hence, the reactivities of α -substituted acrylonitriles and acrylic esters relative to unsubstituted acrylonitrile and methyl acrylate toward polystyryl radical, respectively, were expressed by the following equation:

$$\log (\text{rel. react.}) = \Delta \log Q_X + 0.83 \sigma_p$$

where $\Delta \log Q_X$ and σ_p are the resonance and polar substituent constants of α substituents, respectively. The values of $\Delta \log Q_X$ were determined for CH_3O , CH_3 , C_6H_5 , Cl , Br , OCOCH_3 , COOCH_3 , and CN substituents, and these values were closely related to the other resonance substituent constants such as E_R and R of corresponding substituents, except for OCH_3

substituent. This relationship could also be applied to monosubstituted ethylenic monomers by using the same parameters. However, the reactivities of α -substituted styrenes deviated from this relationship because of the low ceiling temperatures of these monomers.

INTRODUCTION

Many attempts to clarify the correlation between the structure and the reactivity of a series of vinyl monomers in their radical copolymerizations have been made on the basis of the effect of their substituents. In 1948, Walling and co-workers [1] reported that the reactivities of nuclear-substituted styrenes toward a polymer radical were correlated with the polar substituent constants in the Hammett equation. Similar correlations were recently observed on phenyl vinyl sulfides [2] and vinyl benzoates [3].

However, the importance of the resonance effect of the substituents on the copolymerization reactivities of *p*-substituted styrenes [4] and phenyl methacrylates [5] and on the chain-transfer reactivities of such compounds as substituted cumenes [6] was pointed out recently. Yamamoto and Otsu [7] have proposed a generalized Hammett equation which includes the resonance term of the substituents, and this equation has been found to be satisfactorily applicable in many radical reactions.

On the other hand, we have found that the effect of the ester groups on the reactivities of alkyl acrylates [8], alkyl methacrylates [9, 10], alkyl thiolacrylates [11], alkyl cinnamates [12], and vinyl esters [13] toward a polymer radical was fitted with the polar substituent constants in the Taft equation. However, Chikanishi and Tsuruta [14] have suggested that the effect of α -alkyl groups in methyl α -alkylacrylates on their copolymerization reactivities was determined only with the steric substituent constants of their α -alkyl groups. Recently, Cameron [15] also stated the importance of both polar and steric effects of α substituent in these α -substituted acrylate monomers.

In an original discussion of the Alfrey-Price Q-e scheme [16], it was suggested that the log Q and e values of 1,1-disubstituted ethylenic monomers could be predicted from the additivity with respect to both substituents. But since accurate copolymerization data of 1,1-disubstituted ethylenic monomers were not known extensively, the validity of such an expectation was unproved.

Therefore, we attempted to investigate systematically the substituent effects of 1,1-disubstituted ethylenic monomers on their copolymerization reactivities. The present paper describes these substituent effects on the radical

copolymerization reactivities of some *α*-substituted acrylonitriles and acrylic esters with styrene as a reference monomer.

EXPERIMENTAL

Monomers

α-Methoxyacrylonitrile and methyl *α*-methoxyacrylate were prepared according to Baker's method [17]. Ethyl *α*-chloroacrylate and ethyl *α*-bromoacrylate were synthesized by dehydrohalogenation of corresponding ethyl *α,β*-dihalopropionate. Diethyl methylenemalonate was prepared from diethyl malonate and p-formaldehyde in acetic acid [18]. Ethyl *α*-acetoxyacrylate was prepared by dehydrochlorination of ethyl *α*-acetoxy-*β*-chloropropionate [19]. These synthesized monomers were confirmed to be pure by elementary analyses, refractive indices, and infrared spectra. Commercially available methyl *α*-cyanoacrylate, *α*-chloroacrylonitrile, and styrene were purified by fractional distillation under reduced pressure.

Copolymerization Procedure

The bulk copolymerizations were carried out in a sealed ampoule at 60°C. The ampoule containing the comonomers and *α,α'*-azobis-isobutyronitrile (AIBN) was degassed by a freezing and thawing method and then sealed off under vacuum, after which polymerization was begun. After a given polymerization time, the contents of the ampoule were poured into a large amount of methanol or diethyl ether to isolate the copolymer. The copolymer thus obtained was purified by reprecipitating from benzene or dimethylformamide solution into methanol. The compositions of the copolymers were calculated from the results of their carbon, nitrogen, or halogen analyses. The monomer reactivity ratios were determined from the copolymer composition curve by the curve-fitting method.

Ultraviolet Spectra

Ultraviolet spectra of *α*-substituted acrylonitriles and acrylates were measured by a Hitachi EPS-IIU spectrophotometer, using *n*-heptane as a solvent over the wavelength range of 195-300 μ .

Table 1. Copolymerization of Diethyl Methylenemalonate (M_1) with Styrene (M_2) in the Presence or Absence of Acetic Acid at 60°C : $[\text{AIBN}] = 1.7 \times 10^{-3}$ Mole/Liter

[M_1] in co- monomer, mole %	[AcOH]/[M_1], molar ratio	Time, min	Conversion %	Copolymer	
				Carbon, %	[M_1], mole %
14.9	0	20	3.4	70.62	46.6
23.1	0	20	4.2	70.00	48.7
30.2a	0.19	30	3.9	69.97	48.8
31.8	0	20	5.8	69.62	49.8
41.2	0	20	7.2	69.42	50.4
51.2	0	20	8.5	69.12	51.2
62.0	0	20	8.4	68.98	51.7
72.1a	0.19	15	5.6	68.07	54.4
73.7	0	20	7.7	68.08	54.4
88.7b	0.19	15	8.9	67.90	54.7

a[AIBN] = 2.0×10^{-3} mole/liter.

b[AIBN] = 2.4×10^{-3} mole/liter.

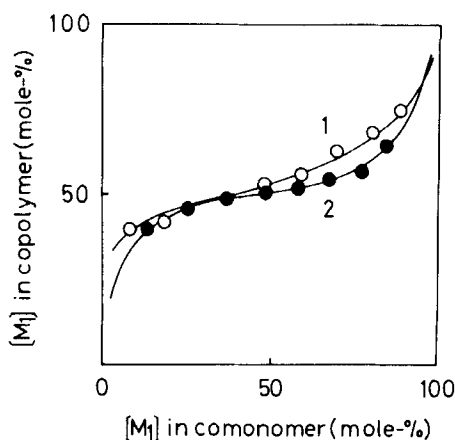


Fig. 1. Copolymer composition relation for the copolymerization of diethyl methylenemalonate (M_1) with styrene (M_2) at 60°C in the presence (\circ) and absence (\bullet) of acetic acid.

RESULTS AND DISCUSSION

The results of the bulk copolymerization of diethyl methylenemalonate (M_1) with styrene (M_2) at 60°C are shown in Table 1; the composition curve is illustrated in Fig. 1. Although diethyl methylenemalonate, as well as methyl α -cyanoacrylate, is expected to be readily polymerized anionically, the results of the copolymerization in the presence or absence of acetic acid, which was an inhibitor for anionic polymerization, were unchanged, as shown in Table 1 and Fig. 1. Accordingly, it was concluded that the copolymer was obtained solely via radical mechanism.

Table 2 and Fig. 2 show the results of the radical copolymerization of ethyl α -bromoacrylate (M_1) with styrene (M_2) at 60°C.

Table 2. Copolymerization of Ethyl α -Bromoacrylate (M_1) with Styrene (M_2) at 60°C: [AIBN] = 1.8×10^{-3} Mole/Liter

[M_1] in comonomer, mole %	Time, min	Conversion %	Copolymer	
			Bromine, %	[M_1], mole %
9.5	85	4.7	24.04	40.4
18.9	65	5.9	26.84	46.6
28.5	50	5.6	27.38	52.7
38.3	40	5.9	29.37	56.6
48.3	40	5.8	31.85	59.0
58.3	40	5.6	33.08	63.4
68.5	40	6.0	34.28	65.3
78.8	40	5.9	36.62	72.5
89.6	40	5.9	39.31	80.9

Although the copolymerizations of α -chloroacrylonitrile [20] and methyl α -chloroacrylate [21] were made previously, the reported monomer reactivity ratios were doubtful as compared with the results of the present study. The copolymerizations of these monomers with styrene were re-examined at 60°C. The results are shown in Tables 3 and 4 and Fig. 3.

From these results, the copolymerization parameters for α -substituted acrylonitriles and acrylic methyl or ethyl esters are summarized in Tables 5 and 6 respectively, in which the reported values are also indicated. As can be seen from these tables, all the α -substituted acrylonitriles and acrylates, except for methyl α -methoxyacrylate and α -methoxyacrylonitrile, were

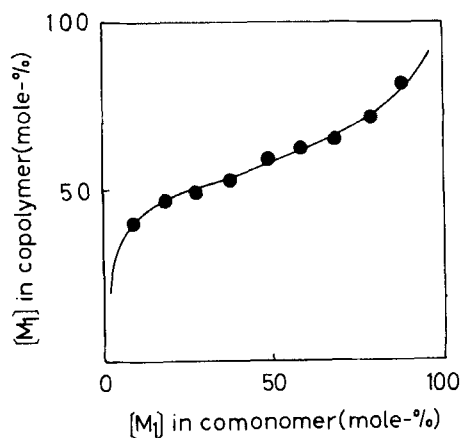


Fig. 2. Copolymer composition relation for the copolymerization of ethyl α -bromoacrylate (M_1) with styrene (M_2) at 60°C .

Table 3. Copolymerization of α -Chloroacrylonitrile (M_1) with Styrene (M_2) at 60°C : $[\text{AIBN}] = 5.9 \times 10^{-3}$ Mole/Liter

$[\text{M}_1]$ in comonomer, mole %	Time, min	Conversion, %	Copolymer	
			Chlorine, %	$[\text{M}_1]$, mole %
15.5	10	0.7	15.20	39.3
29.2	60	4.5	17.00	43.5
41.2	60	4.9	17.55	44.7
52.4	60	4.9	18.93	47.7
62.3	60	4.0	19.67	49.3
71.3	90	5.7	20.65	51.4
79.4	90	4.6	21.11	52.4
86.9	360	7.5	24.29	58.9

Table 4. Copolymerization of Ethyl α -Chloroacrylate (M_1) with Styrene (M_2) at 60°C: $[AIBN] = 1.8 \times 10^{-3}$ Mole/Liter

$[M_1]$ in comonomer, mole %	Time, min	Conversion, %	Copolymer	
			Chlorine, %	$[M_1]$, mole %
9.3	90	3.1	12.70	41.8
18.8	45	1.6	13.10	43.3
37.5	30	2.3	14.86	46.9
48.0	30	2.6	15.96	54.2
58.1	15	1.6	16.72	57.2
68.3	15	1.8	18.63	65.0
78.1	15	1.9	19.64	69.2
89.3	15	1.7	21.25	76.2

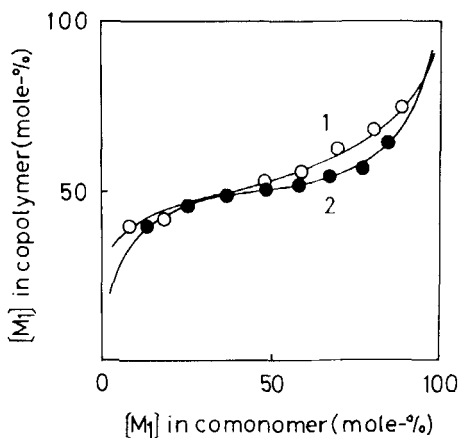
**Fig. 3.** Copolymer composition relations for the copolymerizations of (1) ethyl α -chloroacrylate (M_1) with styrene (M_2) and (2) α -chloroacrylonitrile (M_1) with styrene (M_2) at 60°C.

Table 5. Copolymerization Parameters of α -Substituted Acrylonitrile (M_1 : $\text{CH}_2=\text{C}(\text{X})\text{CN}$) in Their Radical Copolymerizations with Styrene (M_2) at 60°C

X	r_1	r_2	$\log 1/r_2$	Q_1	e_1	Ref.
OCH_3	0.35	0.53	0.276	0.72	0.40	[22]
CH_3	0.16	0.30	0.522	1.12	0.81	[24]
C_6H_5	0.7	0.02	1.699	9.60	1.26	[23]
H	0.04	0.40	0.398	0.60	1.20	[24]
Cl	0.13	0.06	1.223	2.83	1.40	This work
OCOCH_3	0.20	0.16	0.796	1.17	1.06	[25]
COOCH_3	0.03	0.01	2.00	12.6	2.1	[26]
CN^a	0.001	0.005	2.301	20.1	2.85	[27]

^aAt 45°C .

Table 6. Copolymerization Parameters of α -Substituted Acrylic Esters (M_1 : $\text{CH}_2=\text{C}(\text{X})\text{COOR}$) in Their Radical Copolymerizations with Styrene (M_2) at 60°C

X	R	r_1	r_2	$\log 1/r_2$	Q_1	e_1	Ref.
OCH_3	CH_3	0.51	1.10	-0.041	0.47	0.04	[22]
CH_3	CH_3	0.50	0.50	0.310	0.74	0.40	[24]
C_6H_5	C_2H_5	0.19	0.04	1.398	4.28	1.41	[11]
H	CH_3	0.18	0.75	0.124	0.42	0.60	[24]
Cl	C_2H_5	0.30	0.08	1.097	2.65	1.13	This work
Br	C_2H_5	0.50	0.06	1.301	3.70	1.07	This work
OCOCH_3	C_2H_5	0.20	0.57	0.243	0.54	0.67	[19]
COOC_2H_5	C_2H_5	0.08	0.03	1.522	4.78	1.66	This work
CN	CH_3	0.03	0.01	2.000	12.6	2.1	[26]

more reactive than the respective unsubstituted monomers. It was interesting to note that the reactivities of these *α*-methoxy derivatives were low, as was the case for vinyl ethers. It was also noted that *α*-cyano, carboethoxy, carbomethoxy, and phenyl derivatives showed an excellent alternating tendency with styrene.

As shown in Tables 5 and 6, it was highly improbable that the relative reactivities of these acrylonitrile and acrylate monomers were determined solely by the polar factor of their substituents. Since the reactivities for methyl and ethyl esters of some *α*-substituted acrylates were almost identical [12], the logarithms of relative reactivities ($1/r_2$) of these acrylonitriles and acrylates were plotted against the polar substituent constant (σ_p) of their *α* substituents, as shown in Fig. 4. From this figure, no definite correlation between the relative reactivities and the σ_p constants were found.

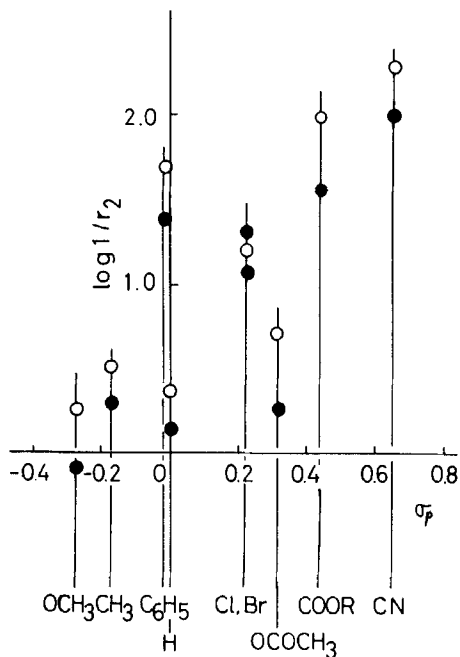


Fig. 4. Plots of $\log 1/r_2$ versus Hammett σ_p constants of *α*-substituents in the copolymerizations of *α*-substituted acrylonitriles (\circ) and acrylates (\bullet) with styrene (M_2).

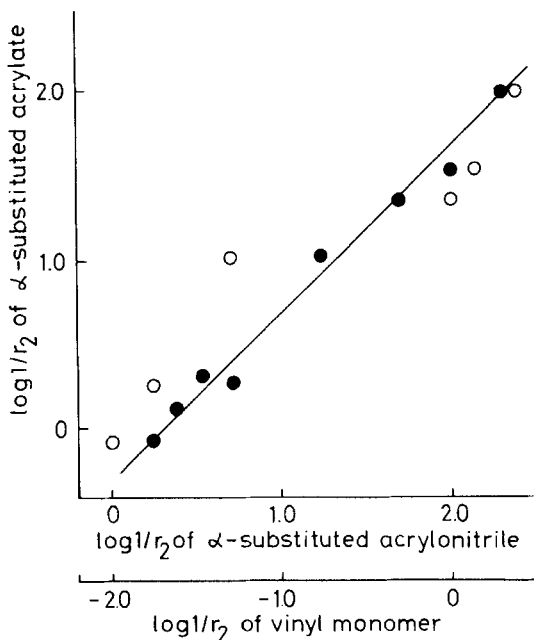


Fig. 5. Plots of relative reactivities of α -substituted acrylates toward polystyryl radical versus those of α -substituted acrylonitriles (\bullet) and of monosubstituted ethylenic monomers (\circ).

When the relative reactivities of α -substituted acrylates were plotted with those of α -substituted acrylonitriles and monosubstituted ethylenic monomers published in the literature [24], however, a fairly good straight-line relationship with unit slope was obtained, as shown in Fig. 5. From this figure, it was suggested that the α substituents in acrylates had as much effect on their relative reactivities as those in α -substituted acrylonitriles and monosubstituted ethylenes.

We next attempted to separate the relative reactivities of α -substituted acrylonitriles and acrylates toward polystyryl radical into the polar and resonance factors of α substituents according to the Q-e scheme. The values of Q and e for these acrylonitriles and acrylates are also summarized in Tables 5 and 6.

From these tables, the e values obtained for α -substituted acrylonitrile and acrylate monomers were closely correlated with the σ_p values of their α substituents, as in Fig. 6, in which those for vinyl monomers carrying the

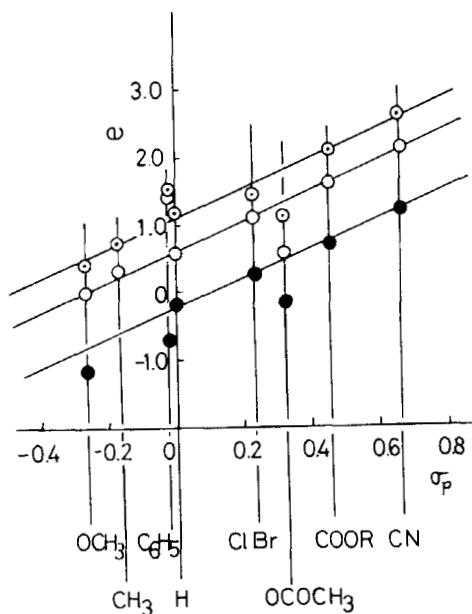


Fig. 6. Correlation between the e values of α -substituted acrylonitriles (\odot), α -substituted acrylic esters (\circ), and monosubstituted ethylenic monomers (\bullet), and the σ_p constants of their substituents.

corresponding substituents are also indicated. It was observed that the straight lines had almost the same slope, i.e., 2.4, which was very close to that for vinyl monomers reported by Furukawa and Tsuruta [28]. As seen in Fig. 6, the plots for the acetoxy group in vinyl acetate, ethyl α -acetoxyacrylate, and α -acetoxyacrylonitrile, and for the phenyl group in ethyl atropate and atropionitrile deviated from these straight lines. Since the negative e value was reported for vinyl acetate, the use of a positively large σ_p value (+0.31) [29] for the acetoxy group in radical polymerization might be doubtful. Alternatively, an appropriate σ_p value for the acetoxy group might be estimated, from Fig. 6, to be -0.05 . Similar deviations for the phenyl group in α -phenyl derivatives are discussed later.

The intercepts of three straight lines on the ordinate in Fig. 6 correspond to the differences in the e values for acrylonitrile, methyl acrylate, and ethylene. Hence the e values for α -substituted acrylonitriles, α -substituted acrylates, and monosubstituted ethylenes may be formulated as follows:

$$\begin{aligned}
 e_{\text{CH}_2=\text{C}_Y^X} &= e_{\text{CH}_2=\text{C}_Y^H} + (e_{\text{CH}_2=\text{C}_H^X} - e_{\text{CH}_2=\text{CH}_2}) \\
 &= e_{\text{CH}_2=\text{C}_Y^H} + 2.4 (\sigma_p)_X \\
 &= 2.4 \left\{ (\sigma_p)_X + (\sigma_p)_Y \right\} + e_{\text{CH}_2=\text{CH}_2} \quad (1)
 \end{aligned}$$

Since the polar factor of the α substituents of these monomers contributed additively to their e values, their resonance factors were expected to operate simultaneously with their $\log Q$ values. The increments in $\log Q$ values resulting from the introduction of cyano and carbomethoxy groups into the α position of monosubstituted ethylenic monomers are shown in Table 7. For example, since the $\log Q$ values of methyl α -cyanoacrylate and acrylonitrile were 1.10 and -0.22, respectively, the increment ($\Delta \log Q$) resulting from the introduction of the carbomethoxy group into the α position of acrylonitrile was 1.32.

Table 7. The Contributions of Cyano and Carbomethoxy Groups to the Values of $\log Q$ of α -Substituted Acrylonitrile and Acrylate

α Substitute	$\Delta \log Q_{\text{COOR}}$	$\Delta \log Q_{\text{CN}}$
OCH ₃	1.162	1.352
H	1.447	1.602
C ₆ H ₅	(0.681)	(0.982)
Cl	1.781	1.808
Br	1.892	—
OCOCH ₃	1.318	1.654
COOCH ₃	1.053	1.477
CN	1.320	1.525
Mean	1.43 ± 0.29	1.57 ± 0.10

From Table 7, it is obvious that the increments in a series of *α*-substituted acrylate and acrylonitrile monomers were almost constant regardless of their *α* substituents, except the phenyl group, and the mean values of the increments obtained for both *α*-substituted monomer series were determined as 1.57 ± 0.10 and 1.43 ± 0.29 for the cyano and carbomethoxy groups, respectively.

Table 8. The Increment of log Q by *α* Substitution on Acrylonitrile or Methyl Acrylate

<i>α</i> Substituent	$\Delta \log Q$	E_R^a	R^b
OCH ₃	0.06	0.11	0.11
CH ₃	0.26	0.03	0.03
H	0	0	0
C ₆ H ₅	(1.06)	—	—
Cl	0.74	0.10	0.07
Br	0.95	0.12	0.08
OCOCH ₃	0.20	—	—
COOCH ₃	1.43	—	—
CN	1.57	0.24	0.49

^a Reference [7].

^bReferences [4] and [30].

Similarly, the increments in log Q values resulting from the introduction of the other substituents into the *α* position of acrylonitrile and methyl acrylate monomers were determined. These values for various *α* substituents are shown in Table 8. Although the increment for phenyl substitution was also determined, the increment shown in Table 8 does not explain the increment of log Q value of ethylene by phenyl substitution to styrene.

The resulting $\Delta \log Q$ values are considered to be a measure of the resonance contribution made by the corresponding *α* substituents to the reactivities, if their steric effects are neglected. Accordingly, it is interesting to compare these values with the reported resonance substituent constants.

Yamamoto and Otsu [7] have presented the following generalized Hammett equation, which contains both polar and resonance contributions by the substituents:

$$\log (\text{rel. react.}) = \rho \sigma + \gamma E_R$$

where σ and E_R are polar and resonance substituent constants, respectively, and ρ and γ are reaction constants. Imoto et al. [4] have evaluated the resonance substituent constants (R) from the mutual copolymerization of *p*-substituted styrenes. The values of E_R and R are also shown in Table 8.

From Table 8 it is clear that the $\Delta \log Q$ values of the substituents follow a trend similar to the E_R or R values. Since the values of E_R or R are those determined for the para substituents across the benzene ring, this finding indicated that the steric factor of the *a* substituents in the present monomer series did not significantly affect their reactivities, i.e., their Q values. Accordingly, $\log Q$ values of 1,1-disubstituted ethylenic monomers might be formulated as in the following equation, in a manner similar to the formulation of their e values:

$$\begin{aligned} \log Q_{\text{CH}_2=\text{C}\begin{matrix} \text{X} \\ \text{Y} \end{matrix}} &= \log Q_{\text{CH}_2=\text{C}\begin{matrix} \text{H} \\ \text{Y} \end{matrix}} + (\log Q_{\text{CH}_2=\text{C}\begin{matrix} \text{X} \\ \text{H} \end{matrix}} - \log Q_{\text{CH}_2=\text{CH}_2}) \\ &= \log Q_{\text{CH}_2=\text{C}\begin{matrix} \text{H} \\ \text{Y} \end{matrix}} + \Delta \log Q_X \end{aligned} \quad (2)$$

A relationship similar to those of Eqs. (1) and (2) seems to be unable for evaluating the Q and e values of various 1,1-disubstituted ethylenic monomers.

It has been assumed by Alfrey et al. [16] that the copolymerization reactivities (k_{21}) of vinyl monomers are represented as the sum of both polar and resonance factors due to the substituents, i.e.,

$$k_{21} = P_2 Q_1 e^{-e_1 e_2}$$

By combining this equation with Eqs. (1) and (2), the relative reactivities of *a*-substituted acrylonitrile and acrylate monomers can be formulated as follows:

$$\begin{aligned} \log (k_{21})_X / (k_{21})_0 &= \log (Q_1)_X / (Q_1)_0 + \frac{(2.4 \sigma_p \times 0.8)}{2.303} \\ &= \Delta \log Q_X + 0.83 \sigma_p \end{aligned} \quad (3)$$

where $(k_{21})_0$ and $(Q_1)_0$ are the relative reactivities and the Q values of unsubstituted acrylonitrile and methyl acrylate, respectively, and $(k_{21})_X$ and $(Q_1)_X$ are those for α -substituted monomers. The plot of $\log (k_{21})_X / (k_{21})_0$ with σ_p values is shown in Fig. 7, in which the straight line with slope of 0.83 in Eq. (3) is indicated. Hence the deviations from this line must correspond to $\Delta \log Q_X$ values thus graphically obtained are compared with their mean values (Table 8), the mean values for the cyano and carbomethoxy groups are somewhat larger than those obtained from Figure 7.

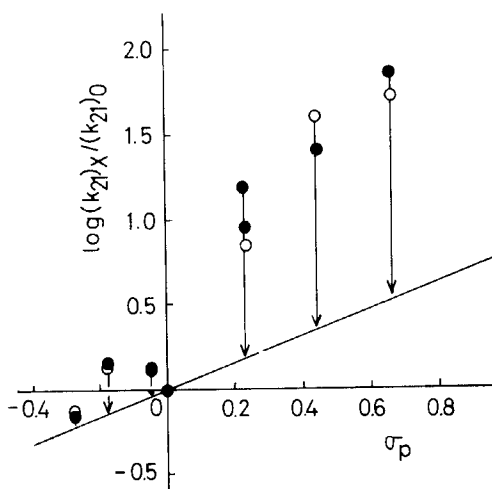


Fig. 7. Application of Eq. (3) to the relative reactivities of α -substituted acrylonitriles (\circ) and acrylic esters (\bullet). The deviations from the straight line with the slope of 0.83 correspond to $\Delta \log Q_X$.

These discrepancies might be due to the uncertainties in the copolymerization parameters for unconjugated ethylenic monomers which were used to calculate the mean values of $\Delta \log Q$ for the cyano and carbomethoxy groups.

It is known that vinyl monomers in which the double bond is conjugated with the substituent are more reactive than unconjugated vinyl monomers, and a linear correlation between their log Q values and absorption maxima is given in Ref. [31]. In Fig. 8, when absorption maxima of α -substituted acrylonitriles and acrylates in n-heptane were plotted against log Q values, no straight-line relationship was obtained. It is clear that the log Q values for 1,1-disubstituted ethylenic monomers cannot be predicted simply from their absorption maxima.

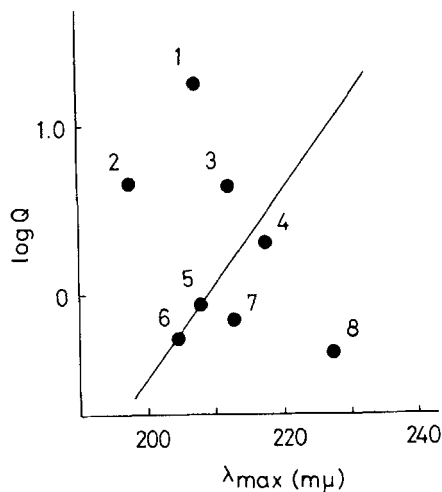


Fig. 8. Plot of the absorption maxima against the log Q values of α -substituted vinyl monomers: (1) methyl α -cyanoacrylate, (2) diethyl methylenemalonate, (3) ethyl atropate, (4) ethyl α -chloroacrylate, (5) α -chloroacrylonitrile, (6) ethyl α -acetoxyacrylate, (7) α -methoxyacrylonitrile, (8) methyl α -methoxyacrylate.

Since some 1,1-disubstituted ethylenic monomers, in which both substituents can conjugate with the reacting double bond, form a cross-conjugation system, a red shift in absorption maxima following the introduction of the α substituent into acrylonitrile and methyl acrylate monomers was not so large as compared with that following the introduction of the corresponding substituent into ethylene. Nor might the steric inhibition of the conjugation by the substituents be neglected. Absorption maxima of ethylene and methyl acrylate monomers were reported to be 170.3 $m\mu$ in vapor phase and 201.5 $m\mu$ in isoctane [31]. However, diethyl methylenemalonate showed an absorption maximum at 198 $m\mu$ in *n*-heptane.

Although the substituents in 1,1-disubstituted ethylenic monomer were conjugated with reacting double bond in a different manner from those in monosubstituted ethylenic monomer, the resonance contribution of the substituents to stabilize the incipient radical in the transition state was considered to be similar in 1,1-disubstituted ethylenes and monosubstituted ethylenes, as can be seen from the observed additivity in log Q value.

Table 9. Homopolymerizability of *α*-Substituted Vinyl Monomers by Radical Mechanism

<i>α</i> -Substituent	Parent monomer ^a		
	Acrylic ester	Acrylonitrile	Styrene
OCH ₃	○	×	× [32]
CH ₃	⊙	⊙	×
H	⊙	⊙	⊙
C ₆ H ₅	× [14]	× [23]	×
Cl	⊙	○	× [35]
Br	⊙	(○)	(×)
OCOCH ₃	⊙ [19]	⊙ [36]	× [37]
COOCH ₃	× [38]	⊙ [26]	× [14]
CN	⊙ [26]	× [27]	× [23]

^a⊙: Polymerized to high polymer. ○: Polymerized slowly to high polymer. ×: No polymerization.

As mentioned in the preceding section, the abnormal behavior of *α*-phenyl-substituted monomers must be considered. Although the introduction of *α*-methyl substituent into methyl acrylate or acrylonitrile leads to an increase in their Q values, as shown in Table 7, that into styrene decreases the Q value. The decrease in styrene Q value may be due to a low ceiling temperature of styrene derivatives. Recently, the ceiling temperatures in the polymerizations of methyl atropate [33] and *α*-methoxystyrene [34] at 1 mole/liter of solution were reported to be -40 and below -80°C, respectively.

Since no detailed data on the ceiling temperature of various monomers were available, the ceiling temperatures for *α*-substituted acrylonitriles, acrylates, and styrenes were qualitatively compared from their radical homopolymerizabilities at 60°C. These results are summarized in Table 9. It can be seen from this table that the homopolymers were obtained from most of the *α*-substituted acrylonitrile and acrylate monomers. However, among *α*-substituted styrenes, only the unsubstituted styrene was homopolymerized. Since the steric factor of *α* substituent was not considered to be the main factor for determining the homopolymerizability as expected from the copolymerization study, such an observation might suggest that the *α*-substituted styrenes except styrene had ceiling temperatures lower than 60°C.

We considered that the abnormal behavior of styrene derivatives was due to their low ceiling temperatures as compared with the present polymerization temperature. If copolymerization data obtained at a temperature sufficiently lower than the ceiling temperature were available, we could discuss the reactivity of α -substituted styrenes as we have discussed the reactivity of α -substituted acrylonitriles and acrylates.

REFERENCES

- [1] C. Walling, E. R. Briggs, K. B. Wolfstirn, and F. R. Mayo, *J. Am. Chem. Soc.*, **70**, 1537 (1948).
- [2] K. Tsuda, S. Kobayashi, and T. Otsu, *J. Polymer Sci.*, **A1(6)**, 41 (1968); *J. Macromol. Sci.*, **A1**, 1025 (1967).
- [3] M. Kinoshita, T. Irie, and M. Imoto, *Makromol. Chem.*, **110**, 47 (1967).
- [4] M. Imoto, M. Kinoshita, and M. Nishigaki, *Makromol. Chem.*, **94**, 238 (1966).
- [5] T. Otsu, T. Ito, and Y. Fujii, *Bull. Chem. Soc. Japan*, **41**, 204 (1968).
- [6] T. Yamamoto and T. Otsu, *J. Polymer Sci.* **B4**, 1039 (1966).
- [7] T. Yamamoto and T. Otsu, *Chem. and Ind.*, **1967**, 787.
- [8] T. Otsu, T. Ito, T. Fukumizu, and M. Imoto, *Bull. Chem. Soc. Japan*, **39**, 2257 (1966).
- [9] T. Otsu, T. Ito, and M. Imoto, *Kogyo Kagaku Zasshi*, **69**, 986 (1966).
- [10] K. Yokota, M. Kani, and Y. Ishi, *J. Polymer Sci.*, **A1(6)**, 1325 (1968).
- [11] T. Otsu, K. Tsuda, and Y. Fukumizu, *Makromol. Chem.*, **119**, 140 (1968).
- [12] T. Otsu, B. Yamada, and T. Nozaki, *Kogyo Kagaku Zasshi*, **70**, 1941 (1967).
- [13] T. Otsu and K. Hayashi, *Makromol. Chem.*, **127**, 54 (1969).
- [14] K. Chikanishi and T. Tsuruta, *Makromol. Chem.*, **73**, 231 (1964).
- [15] G. G. Cameron and G. P. Kerr, *European Polymer J.*, **3**, 1 (1967).
- [16] T. Alfrey, Jr., J. J. Bohrer, and H. Mark, *Copolymerization*, Wiley (Interscience), New York, 1952, p. 81; T. Alfrey, Jr., and L. J. Young, in *Copolymerization* (G. E. Ham, ed.), Wiley (Interscience), New York, 1964, p. 73.
- [17] J. W. Baker, *J. Chem. Soc.*, **1942**, 520.
- [18] G. B. Bachmann and H. A. Tanner, *J. Org. Chem.*, **4**, 493 (1939).
- [19] C. C. Unruh and J. M. Laakso, *J. Polymer Sci.*, **33**, 87 (1958); *Ind. Eng. Chem.*, **50**, 1119 (1958).

- [20] S. Bresadola and P. Canal, *J. Polymer Sci.*, **B1**, 523 (1963).
- [21] R. G. Fordyce and E. C. Chapin, *J. Am. Chem. Soc.*, **69**, 581 (1947).
- [22] T. Otsu, B. Yamada, and H. Yoneno, *Bull. Chem. Soc. Japan*, **42**, 3207 (1969).
- [23] M. Kreisel, U. Garbatski, and D. H. Kohn, *J. Polymer Sci.*, **A2**, 105 (1964).
- [24] H. Mark, B. Immergut, E. H. Immergut, L. J. Young, and K. I. Benynon, in *Polymer Handbook*, (J. Brandrup and E. H. Immergut, ed.), Wiley (Interscience), New York, 1966, p. II-141.
- [25] T. Oota, M. Kobayashi, and H. Ogawa, *Kogyo Kagaku Zasshi*, **71**, 1542 (1968).
- [26] J. B. Kinsinger, J. R. Panckak, R. L. Kelso, J. B. Bartlett, and R. K. Graham, *J. Appl. Polymer Sci.*, **9**, 429 (1967).
- [27] H. Gilbert, F. F. Miller, S. J. Averill, E. J. Carlson, V. L. Folt, H. J. Heller, F. D. Stewart, P. F. Schmidt, and H. L. Trumbull, *J. Am. Chem. Soc.*, **78**, 1669 (1956).
- [28] J. Furukawa and T. Tsuruta, *J. Polymer Sci.*, **36**, 275 (1959).
- [29] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).
- [30] M. Nishigaki, M. Kinoshita, and M. Imoto, *Kogyo Kagaku Zasshi*, **71**, 1938 (1968).
- [31] T. Ito, T. Otsu, and M. Imoto, *J. Polymer Sci.*, **B4**, 81 (1966).
- [32] L. C. Jones, Jr., and L. W. Taylor, *Anal. Chem.*, **27**, 228 (1955).
- [33] H. Lüssi, *Chimia*, **20**, 379 (1966).
- [34] H. Lüssi, *Makromol. Chem.*, **103**, 68 (1967).
- [35] C. S. Marvel and N. S. Moon, *J. Am. Chem. Soc.*, **62**, 45 (1940).
- [36] T. Oota, M. Kobayashi, and A. Okuda, *Kogyo Kagaku Zasshi*, **71**, 899 (1968).
- [37] E. C. Chapin, G. E. Ham, and C. L. Mills, *J. Polymer Sci.*, **4**, 597 (1949).
- [38] H. Hoppf, H. Lüssi, and S. Allison, *Makromol. Chem.*, **44/46**, 95 (1961).

Accepted by editor February 12, 1969

Received for publication July 3, 1969