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The Relative Reactivities of Alkyl Acrylates in Their Radical Copolymerizations*

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In order to clarify the effect of the alkyl groups in alkyl acrylates (RA) on their reactivities to the attack of a radical, the copolymerization of RA (M_2) with styrene (M_1) has been carried out at 60°C. From the results obtained, the monomer reactivity ratios and the Q_2 and e_2 values were determined. It was found that the relative reactivities ($1/r_1$) of RA to a polystyryl radical were correlated only by the polar substituent constant (σ^*) of the alkyl group in RA, not by their steric substituent constant (E_s) in Taft's equation:

$$\log(1/r_1)=\rho^*\sigma^*+\delta E_s$$

According to the above equation, the ρ^* and δ values were obtained as 0.56 and 0, respectively. It was also observed that the Q_2 and e_2 values for RA were correlated by Taft's σ^* substituent constant.

In a previous paper,[1,2] it has been reported that the relative reactivities of alkyl methacrylates to attack by polymer radicals are correlated only by the polar substituent constants (σ^*) of their alkyl groups in Taft's equation (1)[3]:

$$\log(\text{rel. reactivity}) = \rho^*\sigma^* + \delta E_s \tag{1}$$

where E_s indicates the steric substituent constants of alkyl groups, and where ρ^* and δ are reaction constants. This result strongly indicated that the relative reactivities of alkyl methacrylates depended on the polar character of their alkyl groups, not on their steric characters.

Recently, we have obtained the same linear correlations between the reactivities of alkyl acrylates (RA) or nuclear-substituted phenyl methacrylates to attack by a polystyryl radical and the σ^* constants of alkyl groups or σ constants of para and meta substituents on the benzene ring, respectively. Some of these results have been reported in a previous short communication.[4] The present paper will present detailed results of the copolymerization of some RA with styrene. The RA used in this study were as follows: ethyl acrylate (EA), isopropyl acrylate (IPA), benzyl acrylate (BzA), 2-chloroethyl acrylate (CEA), and 2-cyanoethyl acrylate (CNEA).

Experimental

Materials.—The commercial EA was used after purification by the ordinary method. The other RA were prepared by the esterification of acrylic acid, methyl acrylate or acroyl chloride with the corresponding alcohols. The products thus obtained were distilled under reduced pressure until the absorption of unreacted alcohols disappeared in the infrared spectra. These RA were then used after redistillation in a nitrogen atmosphere. The physical constants of the RA used are shown in Table I.

TABLE I. PHYSICAL PROPERTIES OF RA MONOMERS

RA	b. p. °C/mmHg	n_D^{20}	d_4^{20}
EA	99/760	1.4020	0.913[a]
IPA	52/100	1.4070	0.893[a]
BzA	65/1	1.5180	1.057[a]
CEA	60/19	1.4487	1.121
CNEA	64/2	1.4417	1.062[b]

a) From data summarized by Clarke.[5]
b) Data of Rehberg et al.[6]

The styrene used as a reference monomer in the copolymerization was purified by the ordinary method and was distilled before used.

2, 2′-Azobisisobutyronitrile (AIBN), a radical initiator, was recrystallized twice from ethanol.

Benzene, methanol, petroleum ether, and the other solvents were purified by the usual technique.

Copolymerization Procedure.—The copolymerizations of RA (M_2) with styrene (M_1) were carried out in an ordinary sealed-glass tube in the presence of 6.1

[*1] Vinyl Polymerization. 153.

1) T. Otsu, T. Ito, and M. Imoto, *J. Polymer Sci.*, **B3**, 113 (1965).

2) T. Otsu, T. Ito and M. Imoto, Preprints of International Symposium on Macromolecular Chemistry, Prague (August, 1965), p. 254.

3) R. W. Taft, Jr., in "Steric Effect in Organic Chemistry," Ed. by M. S. Newman, Wiley, New York (1956), p. 556.

4) T. Otsu, T. Ito and M. Imoto, *J. Polymer Sci.*, **A4**, 733 (1965).

5) J. T. Clarke, in "Monomers," Ester of Acrylic Acid, Ed. by E. R. Blout and H. Mark, Interscience, New York (1951), p. 22.

6) C. E. Rehberg, M. B. Dixon and W. A. Faucette, *J. Am. Chem. Soc.*, **72**, 5199 (1950).

$\times 10^{-3}$mol./l. of AIBN at 60°C. The resulting copolymer was precipitated by the addition of a large amount of methanol or petroleum ether, and then reprecipitated from the benzene - petroleum ether system for the copolymer of EA and IPA, or the benzene-methanol system for the other copolymers. Most of the copolymerizations were run to five percent conversion.

The composition of the copolymer was determined from chlorine analysis (CEA copolymer), nitrogen analysis (CNEA copolymer), and carbon analysis (other copolymers). The monomer reactivity ratios, r_1 and r_2 were calculated by the method of Fineman and Ross.7)

Results and Discussion

The results of the copolymerizations of RA with styrene are summarized in Table II. From this table, it may be observed that the rate of these copolymerizations increases with an increase in the concentration of RA in the monomer mixture. The monomer reactivity ratios, r_1 and r_2, and Alfrey-Price Q_2 and e_2 values of RA were found to be as is shown in Table III.

As can be seen from Table III, the relative reactivities, $1/r_1$, of RA toward the attack of a polystyryl radical increased with the increase in the electron-attracting nature of their alkyl substituents. When $\log(1/r_1)$ were plotted against the σ^* constant of the alkyl group according to Eq. 1, a straight line, with $\rho^*=0.56$ was obtained, as Fig. 1 shows.

However, the plot of $\log(1/r_1)-\rho^*\sigma^*$ (where $\rho^*=0.56$) against the E_s constant of the alkyl group also gave a straight line, with $\delta=0$, as is shown in Fig. 2. This result strongly indicated that the relative reactivities of RA toward a polystyryl radical were dependent on the polar character of their alkyl substituents, not on their steric characters. A similar correlation was also observed for the relative reactivities of alkyl methacrylates;1,2) in this case, the ρ^* and δ values were found to be 0.33 and 0 respectively. The increased ρ^* value in this case might be understood from the fact that the e_2 values for RA were larger than those for alkyl methacrylates.

Figure 3 shows the relationship between the Q_2

TABLE II. THE RESULTS OF COPOLYMERIZATIONS OF RA (M_2) WITH STYRENE (M_1) AT 60°C

RA (M_2)	[M_2] in comonomer, mol.-fraction	Time min.	Conversion %	C (%) in copolymer	[M_2] in copolymer mol.-fraction
EA	0.205	60	2.9	86.51	0.214
	0.325	60	2.6	82.37	0.319
	0.508	60	3.0	80.03	0.390
	0.657	60	3.1	77.15	0.480
	0.805	60	3.4	73.59	0.589
IPA	0.183	110	4.1	86.27	0.195
	0.278	100	3.9	84.24	0.260
	0.473	80	3.1	80.12	0.399
	0.574	60	1.9	78.82	0.443
	0.677	50	0.9	76.86	0.510
	0.890	40	1.8	71.33	0.705
BzA	0.158	100	5.8	86.84	0.229
	0.287	100	6.4	85.24	0.308
	0.428	80	5.4	83.17	0.418
	0.581	60	4.5	82.07	0.483
	0.749	60	4.3	80.48	0.582
CEA	0.160	60	3.6	6.50a)	0.200
	0.389	60	3.3	12.07a)	0.391
	0.555	60	4.6	14.48a)	0.480
	0.724	60	4.4	15.98a)	0.537
	0.899	60	2.3	19.20a)	0.667
CNEA	0.147	30	2.2	3.11b)	0.243
	0.289	30	2.8	4.26b)	0.340
	0.443	30	3.1	5.13b)	0.415
	0.592	30	4.0	5.85b)	0.479
	0.745	30	4.2	6.79b)	0.564
	0.898	30	4.3	7.89b)	0.843

a) Chlorine % in the copolymers.
b) Nitrogen % in the copolymers.

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7) M. Fineman and S. D. Ross, ibid., **5**, 269 (1950).

TABLE III. MONOMER REACTIVITY RATIOS FOR STYRENE (M_1) - RA (M_2) COPOLYMERIZATIONS AND Q_2, e_2 VALUES OF RA

RA	σ^* constant of R in RA	r_1	r_2	$1/r_1$	Q_2	e_2
MA[a]	0.1	0.75	0.18	1.34	0.42	0.60
EA	−0.100	0.77	0.17	1.30	0.42	0.62
n-BA[b]	−0.130	0.82	0.21	1.22	0.43	0.53
IPA	−0.190	0.76	0.26	1.32	0.48	0.45
s-BA[b]	−0.210	0.97	0.28	1.03	0.41	0.34
BzA	0.215	0.55	0.20	1.82	0.53	0.69
CEA	0.385	0.43	0.12	2.33	0.58	0.93
CNEA	0.46*	0.40	0.13	2.50	0.63	0.92

a) From Young's table for copolymerization.[8]
b) Data of Rohm & Haas Co.[9]
* Calculated from σ^* value for $CNCH_2$-group.

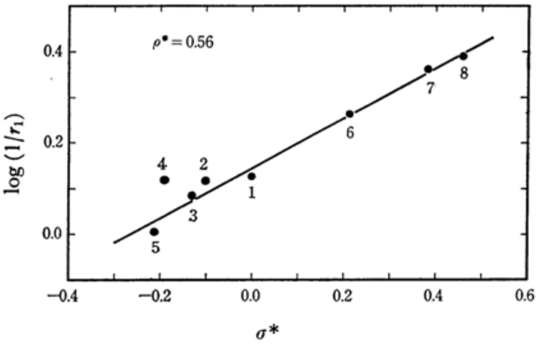

Fig. 1. The correlation between the relative reactivities of RA toward a polystyryl radical and σ^* constants of alkyl groups: 1, CH_3; 2, C_2H_5; 3, *n*-C_4H_9; 4, *i*-C_3H_7; 5, *s*-C_4H_9; 6, $C_6H_5CH_2$; 7, $ClCH_2CH_2$; 8, $CNCH_2CH_2$.

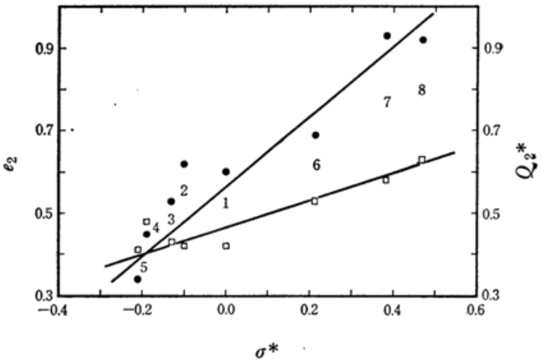

Fig. 3. The correlation between Q_2, e_2 values of RA and σ^* constants of alkyl groups: 1, CH_3; 2, C_2H_5; 3, *n*-C_4H_9; 4, *i*-C_3H_7; 5, *s*-C_4H_9; 6, $C_6H_5CH_2$; 7, $ClCH_2CH_2$; 8, $CNCH_2CH_2$.

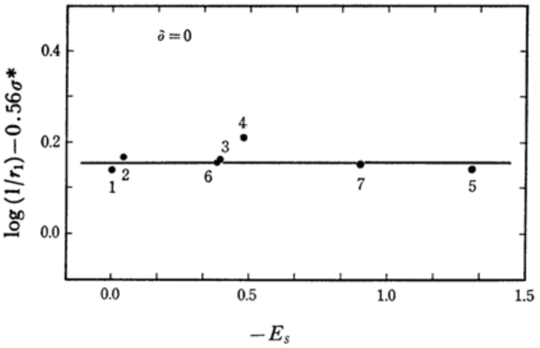

Fig. 2. The correlation between $\log(1/r_1) - \rho^*\sigma^*$ and E_s constants of alkyl groups: 1, CH_3; 2, C_2H_5; 3, *n*-C_4H_9; 4, *i*-C_3H_7; 5, *s*-C_4H_9; 6, $C_6H_5CH_2$; 7, $ClCH_2CH_2$.

and e_2 values of RA and the σ^* constant of the alkyl groups. From this figure, it is obvious that both Q_2 and e_2 values for RA increase as a function of the electron-attracting nature of the alkyl substituents, as in the case of alkyl methacrylates.[1,2] As compared with both acrylate and methacrylate series, it was observed that the change in the Q_2 values of RA effected by the σ^* constant of the alkyl groups was smaller than that of alkyl methacrylates, while the change in e_2 values was larger. These differences are perhaps understandable from the consideration that the effects of hyperconjugation and the electron-releasing nature due to the α-methyl group in alkyl methacrylates were important factors.

Table IV shows the results of the measurement of the infrared spectra of RA monomers in liquid film. From this table, it was observed that the carbonyl-streching frequencies in RA were shifted

TABLE IV. INFRARED SPECTROSCOPIC DATA OF RA*

RA	σ^* of R	$\nu_{C=O}$	$\nu_{C=C}$	ν_{C-O}
IPA	−0.190	1723	1640, 1622	1204
EA	−0.100	1726	1638, 1622	1197
BzA	0.215	1726	1634, 1621	1186
CEA	0.385	1727	1636, 1621	1185
CNEA	0.46	1728	1631, 1619	1186

* Determined with a Hitachi EPI-2 infrared spectrophotometer.

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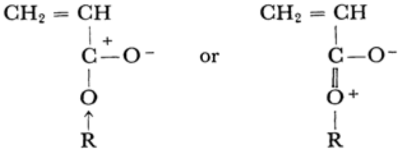
[8] L. J. Young, *J. Polymer Sci.*, **54**, 411 (1961).
[9] "Encyclopedia of Polymer Science and Technology," Vol. 1, Interscience, New York (1964), p. 246.

to longer wavelengths roughly as the electron-releasing character of the alkyl substituent increased. The same behavior has also been observed in a number of aliphatic or aromatic aldehydes, ketones, and acid esters.[10] Accordingly, the introduction of an electron-releasing substituent in RA makes their carbonyl groups more polar, and enhances the nature of the single-bonding of their carbonyl groups, as is shown in Eq. 2.



$$\begin{array}{c} CH_2=CH \\ | \\ \overset{+}{C}-O^- \\ | \\ O \\ \uparrow \\ R \end{array} \quad \text{or} \quad \begin{array}{c} CH_2=CH \\ | \\ C-O^- \\ \| \\ O^+ \\ | \\ R \end{array} \qquad (2)$$

This contribution leads to the isolation of the vinyl group from its conjugated structure with the carbonyl group, and results in a decrease in Q_2 values, as well as of the e_2 values of RA as a function of the electron-releasing nature of their alkyl substituents. Such a consideration was supported by the results of ultraviolet spectroscopic study of RA and other vinyl monomers.[11]

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10) M. St. Flett, *Trans. Faraday Soc.*, **44**, 767 (1948); N. Fuson, M.-L. Josien, and E. M. Shelton, *J. Am. Chem. Soc.*, **76**, 2526 (1954); H. H. Freedman, ibid., **82**, 2454 (1960); W. H. T. Davidson, *J. Chem. Soc.*, **1951**, 2456; E. J. Bourne, M. Stacey, J. C. Tatdow and R. Worrall, ibid., **1958**, 3268; M.-L. Josien, N. Fuson, J.-M. Lebas and T. M. Gregory, *J. Chem. Phys.*, **21**, 331 (1953); M. M. Morgoshes, F. Fillealk, V. A. Fassel and R. E. Randle, ibid., **22**, 281 (1954); G. Berthier, B. Pullman and J. Pontis, *J. Chim. Phys.*, **49**, 367 (1952); R. E. Kagarise, *J. Am. Chem. Soc.*, **77**, 1377 (1955).

11) T. Ito, T. Otsu and M. Imoto, *J. Polymer Sci.*, in press.