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Steric Effects in the Copolymerization of β-Alkylstyrenes with Acrylonitrile*[1]

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To investigate the steric effect of β-substituents of styrene derivatives on their reactivities in radical copolymerization, fourteen *cis*- and *trans*-β-alkylstyrenes were synthesized and copolymerized with acrylonitrile. The reactivities of β-alkylstyrenes toward the acrylonitrile radical decreased in the order: $CH_3 > C_2H_5 \gtrsim n\text{-}C_3H_7 \gtrsim n\text{-}C_4H_9 > iso\text{-}C_3H_7 > s\text{-}C_4H_9 > t\text{-}C_4H_9$ in both the *cis*- and *trans*-series. Linear relationships were found between the relative reactivities and Taft's or Hancock's steric parameter. These relationships and the study of the monomer structures led to the following conclusions: 1) The low reactivity of β-alkylstyrenes in radical polymerization is to be attributed to the steric hindrance of β-alkyl substituents. 2) The effect of the hyperconjugation of the β-alkyl groups is not important. 3) The difference in the reactivities among intramolecularly-hindered *cis*-β-alkylstyrenes is due not to the difference in resonance of the monomer, but to the difference in the steric hindrance of the β-alkyl groups toward the attacking radicals.

The resistance of 1, 2-disubstituted ethylenes (internal olefins) to radical homopolymerizations has been considered to be due to steric hindrance between the β-substituents on the radical end and that on the monomer. In copolymerization with vinyl monomers, however, the moderate reactivity of internal olefins may be explained by assuming that steric hindrance between the internal olefins and the radical end of vinyl monomers is small because of the lack of a β-substituent on the radical end.[1)]

It was considered necessary to estimate quantitatively the effect of β-substituents in order to make a detailed discussion of the reactivities of the internal olefins.

Even towards the methyl radical, the internal olefins are much less reactive than terminal olefins.[2)] Szwarc suggested that this low reactivity is due to the blocking effect of a β-substituent. Hayashi proposed, in terms of a quantum chemical treatment, that it can be explained by a decrease in the stabilization energy of the transition state with β-substitution.[3)]

The purpose of this paper is to determine the effects of β-substituents, in particular steric effects, on the reactivities of β-substituted styrenes in radical copolymerization. *cis*- and *trans*-Isomers of seven β-alkylstyrenes were copolymerized with acrylonitrile, and the copolymerization parameters were determined. The data revealed that the low reactivity of β-alkylstyrenes toward an acrylonitrile radical is mainly due to the steric hindrance of the β-alkyl substituents.

In the cationic copolymerization of β-methylstyrenes with styrenes, the use of the steric effect of the β-methyl group was reported not to be essential in explaining the reactivities of β-methylstyrenes toward the styrene-active end.[4)] In this

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*[1] Paper XI in a series on "The Polymerization of Internal Olefins." For the preceding paper, see S. Murahashi, S. Nozakura and M. Furue, *Kobunshi Kagaku (Chem. High Polymers)*, **23**, 543 (1966).

1) T. Alfrey, J. J. Bohrer and H. Mark, "Copolymerization," Interscience Publishers, N. Y. (1951), p. 51.

2) F. Carrock and M. Szwarc, *J. Am. Chem. Soc.*, **81**, 4138 (1959).

3) K. Hayashi, T. Yonezawa, C. Nagata and S. Okamura, *J. Polymer Sci.*, **20**, 537 (1965).

4) A. Mizote, T. Tanaka, T. Higashimura and S. Okamura, *ibid.*, **A3**, 2567 (1965).

TABLE 1. PHYSICAL CONSTANTS OF β-ALKYLSTYRENES

Monomer	*cis*			*trans*		
	bp, °C/mmHg	n_D^{30}	d_4^{30}	bp, °C/mmHg	n_D^{30}	d_4^{30}
CH_3	47—48/10.5	1.5342	0.8992	68.5—69/18.0	1.5422	0.8979
C_2H_5	75—76/17.5	1.5245	0.8883	85—85.5/17.5	1.5335	0.8909
n-C_3H_7	79—80.6/11.5	1.5198	0.8854	86—86.6/10.0	1.5262	0.8844
iso-C_3H_7	73—74/13.5	1.5134	0.8761	85/12.5	1.5232	0.8802
n-C_4H_9	76—76.5/7.0	1.5143	0.8791	84/6.5	1.5220	0.8808
s-C_4H_9	81—82/9.0	1.5090	0.8774	84—84.5/6.0	1.5202	0.8768
t-C_4H_9	80.5—81/16.0	1.4955	0.8631	90—91/13.0	1.5149	0.8672

connection, the effect of α-alkyl groups on the reactivities of methyl-α-alkyl-acrylates toward a styrene radical was investigated by Tsuruta.5)

Experimental

Monomers. *cis*-β-Methylstyrene and *trans*-β-methylstyrene were obtained by the half-reduction6) of methylphenylacetylene and by the dehydration of ethylphenylcarbinol on activated alumina at 350°C7) respectively. β-Ethyl, β-*n*-propyl, β-*n*-butyl, β-isopropyl, β-*s*-butyl, and β-*t*-butylstyrenes were synthesized by the Wittig reaction.8) All were obtained in yields of 60—70 percent from the reaction of corresponding aldehydes with benzylphosphonium chloride in ethanol, using lithium ethoxide as the base and under a nitrogen atmosphere. *cis*- and *trans*-Isomers of these styrenes were separated by rectification under reduced pressure, using a stainless helipack column of about 30 theoretical plates. No isomer impurities were detected by gas chromatography or by infrared or nuclear magnetic resonance measurements. The physical constants of these monomers are shown in Table 1. The other reagents were purified as usual.

Polymerization. About a 2 g portion of a monomer mixture of β-alkylstyrene and acrylonitrile was accurately weighed into a glass tube, and then about 20 mg of azobisisobutyronitrile were added as an initiator. The tube contents were degassed using three freeze-thaw-cycles, and sealed under a vacuum. The sealed tube was kept in a thermostat at 60±0.1°C. Polymerization was stopped at less than 10% conversion. The copolymer was purified by reprecipitation into methanol from a dimethylformamide solution and dried overnight under a vacuum at about 90°C. When the copolymer did not precipitate with methanol, the polymerization mixture was evaporated, using a high-vacuum system to remove any volatile matter. The copolymer was then dissolved in dimethylformamide and shaken with peteroleum ether, and the dimethylformamide was removed *in vacuo*. The composition of the copolymer was calculated from the results of nitrogen analysis determined by duplicate runs of the Kjeldahl method.9) The viscosity was measured in a dimethylformamide solution at 30°C, using an Ostwald viscometer.

Spectra. The ultraviolet spectra were measured in a hexane solution, using a Hitachi-Perkin-Elmer UV spectrometer.

Results

The data for the radical copolymerization of acrylonitrile (M_1) with *trans*- and *cis*-β-alkylstyrenes (M_2) are summarized in Tables 2 and 3. The

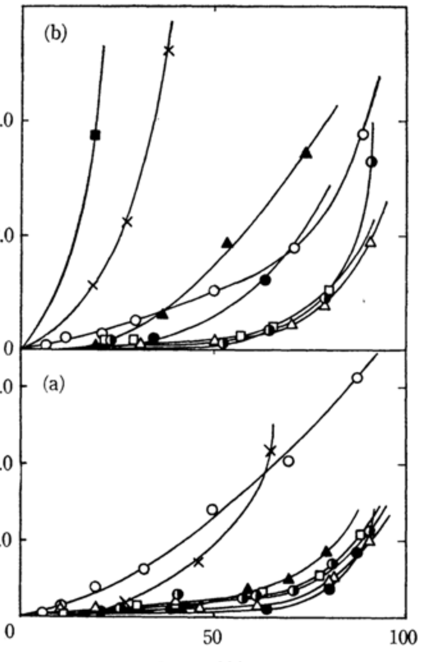

Fig. 1. Relation between copolymerization rate and monomer composition for the copolymerization systems of acrylonitrile (M_1)-β-R-substituted styrenes (M_2): (a) *trans*-monomers, (b) *cis*-monomers.
R: ○, Me; △, Et; □, *n*-Pr; ◑, *n*-Bu; ●, *iso*-Pr; ▲, *s*-Bu; ×, *t*-Bu (■, AN homopolymn. in C_6H_6)

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5) T. Tsuruta and K. Chikanishi, *Makromol. Chem.*, **81**, 211 (1965).

6) C. M. Foltz and B. Witkop, *J. Am. Chem. Soc.*, **79**, 201 (1957).

7) D. T. Mowry, M. Renoll and W. F. Huber, *ibid.*, **68**, 1105 (1946).

8) M. Nakagawa and N. Kida, private communication.

9) J. O. Coleand and C. R. Parks, *Ind. & Eng. Chem.*, **18**, 61 (1946).

TABLE 2. COPOLYMERIZATION OF ACRYLONITRILE (M_1) AND *trans*-β-ALKYLSTYRENES (M_2), R-CH=CH-C_6H_5

R	M_1 mmol	M_2 mmol	M_1 mol%	Time hr	Yield %	Copolymer	
						N, %	m_1, mol%
CH_3	26.5	4.0	86.89	1.9	6.2	17.97	82.66
	19.4	8.5	69.47	2.5	5.1	13.53	69.97
	11.6	11.6	49.80	5.0	7.0	10.89	61.42
	6.6	14.4	31.58	13.7	8.8	9.55	55.83
	3.7	15.2	19.55	24.1	8.9	9.12	54.05
	1.8	16.2	10.20	27.2	3.2	8.62	51.94
	1.4	25.4	5.25	24.7	1.2	8.15	49.87
C_2H_5	30.2	3.2	90.42	3.9	4.0	21.21	91.10
	25.9	6.1	80.94	11.7	6.1	17.30	82.61
	22.5	5.7	79.99	7.1	3.0	17.37	82.78
	13.4	8.6	60.91	10.2	1.6	13.33	71.80
	9.0	10.6	45.92	22.9	1.8	9.84	59.71
	7.6	11.2	40.44	26.7	6.6	9.16	56.97
	3.3	13.3	19.87	49.2	5.3	9.11	56.80
	3.1	27.6	10.07	49.2	3.6	8.11	52.54
n-C_3H_7	28.1	3.9	87.81	3.5	3.8	19.97	89.58
	23.6	6.8	77.63	4.4	2.4	15.97	80.88
	13.7	8.1	62.88	14.9	5.2	13.55	74.43
	7.4	11.2	39.78	27.9	4.7	10.34	63.99
	5.1	11.8	30.18	47.5	4.7	9.43	60.51
	2.8	23.9	10.49	75.0	2.6	8.00	54.52
n-C_4H_9	29.1	3.2	90.09	1.7	1.9	20.64	91.58
	21.3	5.1	80.68	9.8	7.2	17.47	85.57
	16.5	6.9	70.51	9.8	3.5	15.77	81.79
	10.5	6.9	60.34	9.4	3.1	12.02	71.64
	11.6	8.5	57.72	10.0	2.5	11.63	70.41
	5.4	8.1	40.01	25.0	6.9	9.53	63.06
	3.2	9.5	25.21	45.1	5.4	8.48	58.86
iso-C_3H_7	30.1	4.5	86.99	4.8	4.2	23.64	95.97
	24.5	5.9	80.59	11.6	5.4	22.16	93.55
	23.2	5.9	79.73	3.7	1.4	22.65	94.38
	15.3	8.8	63.49	14.9	1.2	21.14	91.76
	7.3	11.3	39.25	12.3	1.1	14.10	76.00
	3.8	13.7	21.67	49.3	3.0	9.55	61.00
	2.7	23.4	10.31	49.3	2.9	8.48	56.62
s-C_4H_9	20.8	5.4	79.39	4.9	4.1	23.76	96.49
	15.6	6.9	69.34	5.6	2.8	23.15	95.60
	12.7	8.9	58.80	8.9	2.7	21.66	93.28
	6.7	9.4	41.61	20.4	2.4	20.65	91.60
t-C_4H_9	12.0	6.4	65.22	1.3	2.9	24.75	97.89
	7.7	9.1	45.83	2.3	1.7	25.17	98.45
	4.2	11.0	27.42	6.0	0.8	23.52	96.14

infrared spectra show the presence of a nitrile group and monosubstituted benzene in the copolymers, and no carbon-carbon double bonds. The rates of copolymerization and the viscosities of the copolymers are plotted against the monomer composition in Figs. 1 and 2. The rates of copolymerization decrease with an increase in the β-alkyl-styrene content of the monomer feed. The order of the rates for the *cis*-monomers was: t-$C_4H_9 > s$-$C_4H_9 > iso$-$C_3H_7 > CH_3 \sim n$-$C_4H_9 \sim n$-$C_3H_7 > C_2H_5$, and for the *trans*-monomers: t-$C_4H_9 > s$-$C_4H_9 > n$-$C_4H_9 \sim n$-$C_3H_7 \sim C_2H_5 \sim iso$-$C_3H_7$. The curves for the methylstyrenes differ a little from the others. The viscosities of the copolymers decrease with an increase in the β-alkylstyrene content, and the effect was more extensive in the

TABLE 3. COPOLYMERIZATION OF ACRYLONITRILE (M_1) AND *cis*-β-ALKYLSTYRENES (M_2)

R	M_1 mmol	M_2 mmol	M_1 mol%	Time hr	Yield %	Copolymer	
						N, %	m_1, mol%
CH_3	30.4	3.7	89.15	0.5	2.0	22.85	93.53
	18.2	7.6	70.54	2.1	3.8	18.27	83.39
	11.8	12.0	49.60	6.2	6.2	13.54	69.98
	6.0	14.2	29.62	11.2	5.7	11.63	63.61
	4.1	15.2	21.31	17.0	4.4	10.82	61.08
	2.1	16.1	11.75	18.0	4.0	9.57	55.89
	1.8	25.0	6.68	17.3	1.6	8.67	52.16
C_2H_5	31.9	3.6	89.86	1.9	3.7	23.87	95.96
	23.9	6.6	78.36	4.0	3.4	21.65	91.96
	16.0	6.9	69.87	4.2	1.9	18.94	86.40
	10.0	10.1	49.75	9.7	1.6	15.5	78.02
	6.1	12.2	33.33	18.6	1.8	12.68	69.77
n-C_3H_7	21.0	5.3	79.84	2.7	2.9	21.72	92.78
	15.3	8.3	64.83	8.4	8.1	19.82	89.28
	11.6	8.8	56.86	15.4	3.8	17.42	84.28
	4.6	11.2	29.13	23.8	4.3	10.52	64.63
	3.5	12.5	21.88	38.3	4.7	9.28	59.92
n-C_4H_9	27.7	2.7	91.12	2.0	6.6	25.03	98.26
	20.7	5.9	77.82	2.0	1.8	20.51	91.35
	14.7	8.2	64.20	7.9	3.0	18.75	88.13
	10.5	9.7	51.97	15.4	2.4	16.64	83.77
	3.4	11.2	23.31	18.7	2.8	8.65	59.56
i-C_3H_7	29.0	2.8	91.19	0.4	3.9	26.00	99.49
	22.4	5.4	80.58	0.7	5.2	25.51	98.79
	13.1	7.7	62.98	3.2	3.4	25.12	98.24
	5.0	9.6	34.25	15.4	3.6	23.68	96.04
	3.6	11.9	23.23	17.9	1.3	21.99	93.26
s-C_4H_9	27.0	2.7	90.91	0.2	4.4	26.03	99.57
	15.5	5.9	72.43	0.6	2.2	25.37	98.71
	9.5	8.3	53.38	1.6	3.0	25.22	98.16
	5.7	9.8	36.79	2.4	1.4	22.92	95.26
	2.6	10.8	19.40	4.8	0.4	21.73	86.40
t-C_4H_9	26.4	5.2	83.54	0.1	2.7	25.70	99.20
	14.6	7.2	66.97	0.2	5.1	26.33	99.96
	8.1	8.8	47.92	0.3	2.8	26.25	99.86
	6.4	10.4	38.08	0.5	2.8	26.09	99.65
	4.6	12.1	27.54	3.0	6.7	25.83	99.32
	2.7	11.7	18.77	1.0	1.2	25.14	98.41

TABLE 4. MONOMER REACTIVITY RATIOS (M_1: ACRYLONITRILE, M_2: β-ALKYLSTYRENES)

R	*cis*		*trans*		$1/r_1$	
	r_1	r_2	r_1	r_2	*cis*	*trans*
Me	1.61 ± 0.13	-0.20 ± 0.06	0.57 ± 0.002	0.001 ± 0.021	0.62	1.75
Et	2.58 ± 0.09	-0.02 ± 0.34	0.98 ± 0.02	0.10 ± 0.06	0.39	1.02
n-Pr	3.04 ± 0.24	-0.05 ± 0.51	1.04 ± 0.03	0.002 ± 0.22	0.33	0.96
n-Bu	5.09 ± 0.96	-0.67 ± 2.17	1.09 ± 0.03	-0.09 ± 0.29	0.18	0.92
iso-Pr	18.0 ± 0.5	-0.38 ± 0.32	3.37 ± 0.20	-0.16 ± 0.50	0.06	0.30
s-Bu	22.6 ± 1.0	-0.34 ± 0.43	6.15 ± 0.54	-0.47 ± 0.33	0.04	0.16
t-Bu	—	—	18.8	—	—	0.05

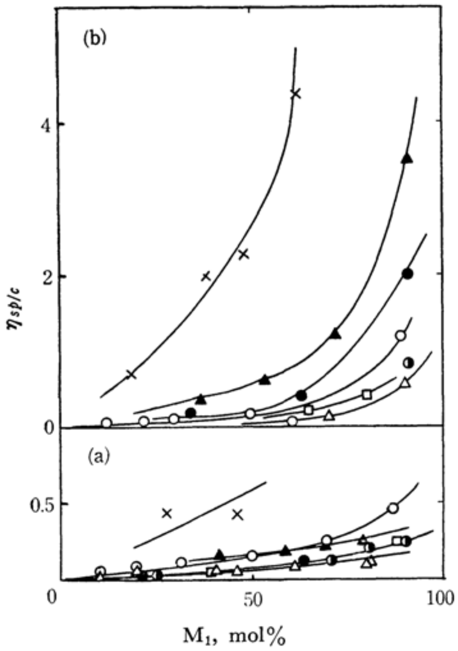

Fig. 2. Relation between copolymer viscosity ($\eta_{sp/c}$) and monomer composition for the copolymerization systems of acrylonitrile (M_1) - β-R-styrenes (M_2): (a) *trans*-monomer, (b) *cis*-monomers.

trans-monomers than in the *cis*-monomers. The order of viscosities in the *cis*-monomers was: t-$C_4H_9 >$ s-$C_4H_9 >$ *iso*-$C_3H_7 > CH_3 >$ n-$C_3H_7 \sim$ n-$C_4H_9 > C_2H_5$, and in the *trans*-monomers: t-$C_4H_9 > CH_3 \sim$ s-$C_4H_9 \sim$ *iso*-$C_3H_7 >$ n-$C_3H_7 \sim$ n-C_4H_9 $< C_2H_5$.

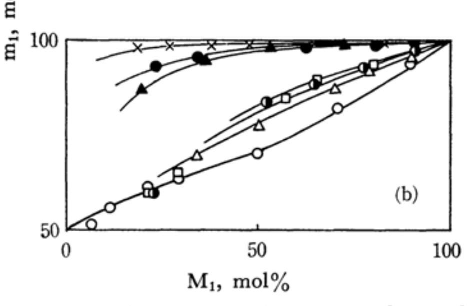

Fig. 3. Copolymer composition curves for acrylonitrile (M_1) - β-R-styrenes (M_2) systems: (a) *trans*-monomers, (b) *cis*-monomers.

Figure 3 shows the copolymer composition curves indicate that, in both the *trans*- and *cis*-series, monomers with normal alkyls and with branched alkyls have different reactivities. The reactivities of β-t-butylstyrenes were very low, but apparently the *trans*-monomer was more reactive than the *cis*-monomer. *cis*-β-t-Butylstyrene showed practically no copolymerization. An infrared spectrum of the polymer obtained from the monomer composition with the highest *cis*-β-t-butylstyrene content showed no mono-substituted benzene band. It was found, from a comparison of the copolymerization rate with of a benzene-acrylonitrile system (Fig. 1), that *cis*-β-t-butylstyrene was not merely a solvent, but has a retarding effect. The monomer reactivity ratios of these thirteen systems of β-alkylstyrenes (M_2) and acrylonitrile (M_1), as calculated by the Fineman-Ross method, are shown in Table 4. Some r_2 values with negative signs should be taken to be zero, considering the experimental errors.

Discussion

Steric Effect. Table 5 verifies that the reactivity of β-alkylstyrenes toward the acrylonitrile radical is affected remarkably by the specific type of β-alkyl. The reactivities decrease in both the *trans*- and *cis*-series in the order: $CH_3 > C_2H_5 \gtrsim$ n-$C_3H_7 \gtrsim$ n-$C_4H_9 >$ *iso*-$C_3H_7 >$ s-$C_4H_9 >$ t-C_4H_9. This order is opposite to the order of the polarities of the β-alkyls, since the acrylonitrile radical has a positive character. No correlation was observed between the relative reactivities of β-alkylstyrenes, $1/r_1$, and the polar substituent constant, σ^*,[10a] for β-alkyls.

When the relative reactivity is scarcely affected by the polar factor, Taft's equation can possibly be represented as follows[10b]:

$$\log k/k_0 = \delta \cdot E_s$$

in which E_s is Taft's steric substituent constant and δ is the steric reaction constant. In Fig. 4, the logarithms of $1/r_1$ are plotted against Taft's E_s values. Although all the plots of the *cis*-series were less reliable than those of the *trans*-series with respect to the reproducibility and sensitivity of the r_1 values, both plots showed a good linear relationship to the E_s values. The relative reactivity of styrene toward the acrylonitrile radical ($r_1 = 0.03 + 0.03$)[11] is also plotted, using a shaded circle, in Fig. 4. The introduction of alkyl groups into the β-position of styrene apparently resulted in a remarkable decrease in the reactivities. The linear relationships between the log $1/r_1$ and

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10) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," ed. by M. S. Newman, John Wiley & Sons, N. Y. (1956), a) p. 591; b) p. 643; c) p. 598.

11) H. Mark, "Copolymerization," ed. by G. E. Ham, Interscience Publishers, N. Y. (1964), p. 706.

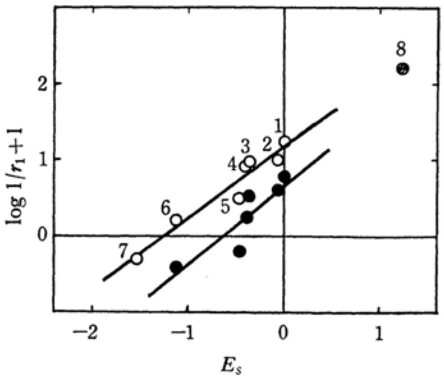

Fig. 4. Plot of $\log 1/r_1+1$ against E_s for β-R of β-R-styrenes; 1, Me; 2, Et; 3, *n*-Pr; 4, *n*-Bu; 5, *iso*-Pr; 6, *s*-Bu; 7, *t*-Bu; 8, H (styrene); ○, *trans*-monomers; ●, *cis*-monomers.

E_s values indicate that the difference in the reactivities of β-alkylstyrenes toward an acrylonitrile radical may mostly be attributed to the steric hindrance of the β-alkyl substituents.

Hancock[12] proposed $E_s{}^c$ values as corrected steric substituent constants. $E_s{}^c$ was obtained by the quantitative separation of the hyperconjugation effects from Taft's steric substituent constant, E_s. Plots of the $\log 1/r_1$ against Hancock's $E_s{}^c$ values gave an improved linearity, as is shown in Fig. 5. Table 5 shows the standard deviations of both the plots. The improvement seems to indicate that the hyperconjugation effect of alkyl groups does not contribute to the decrease in the reactivities in β-alkylstyrenes. This does not coincide with the previous suggestion[3] that the general low reactivities of internal olefins can be explained by the decrease in the π conjugation energy at the transition state due to β-substituents. The steric effects of β-substituents were not considered in making this suggestion, however.

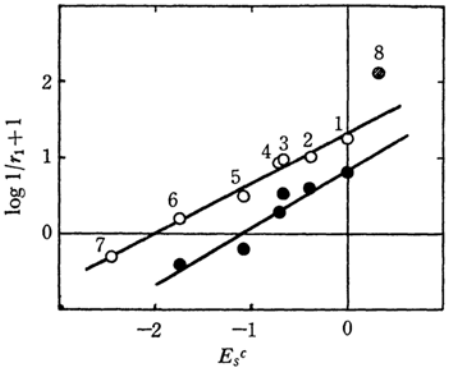

Fig. 5. Plot of $\log 1/r_1+1$ against $E_s{}^c$ for β-alkyl substituents.

TABLE 5. STANDARD DEVIATION IN THE SLOPE OF THE LINEAR RELATIONSHIPS BETWEEN $1/r_1$ AND STERIC PARAMETERS

Steric substituent constant	*trans*-β-Alkyl styrene	*cis*-β-Alkyl styrene
E_s	0.94±0.116	1.06±0.273
$E_s{}^c$	0.64±0.048	0.75±0.123
$E_{s(\mathrm{RCH_2})}$	0.90±0.029	1.13±0.132

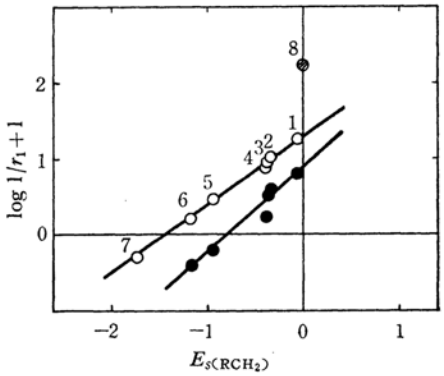

Fig. 6. Plot of $\log 1/r_1+1$ against $E_{s(\mathrm{RCH_2})}$ (E_s for R of $\mathrm{RCH_2CO_2R'}$). $E_{s(\mathrm{RCH_2})}$ values for *s*-Bu was estimated by Tsuruta[5] from Ref.[9c]

Interestingly, plots of $\log 1/r_1$ against Taft's E_s values of $\mathrm{RCH_2}$ instead of R[10c] (which is abbreviated as $E_{s(\mathrm{RCH_2})}$ hereafter) exhibited a better linearity than when plotted either against E_s or $E_s{}^c$, as is shown in Fig. 6 and in Table 5. The contribution of hyperconjugation to E_s values for $\mathrm{RCH_2}$ should be of same magnitude because of the constant number of α-C–H bonds; hence, the use of the E_s values of $\mathrm{RCH_2}$ instead of those of R would eliminate the effect of hyperconjugation, and so represent a measure of the pure steric effects. Thus, the better linearity of $\log 1/r_1$ against $E_{s(\mathrm{RCH_2})}$ may be another piece of evidence for the steric effect of a β-substituent.

Resonance Effect. It was verified on the basis of the above discussions that the reactivities are affected by the steric hindrance of β-alkyl groups toward the attacking radical within the *trans*-series as well as within the *cis*-series. The data also indicate that the reactivity of a β-alkylstyrene is lower in the *cis*-series than in the *trans*-series. In the case of conjugated monomers, the difference in the reactivities of the *cis* - and *trans*-monomers might originate from the difference in the resonance stabilization energies gained in the transition states.[13] As it is considered[14] that the transition state for radical polymerization is close to the monomer state, the observed difference in the reactivities of isomers seems to be due to the

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[12] C. K. Hancock, E. A. Meyers and B. J. Yager, *J. Am. Chem. Soc.*, **83**, 4211 (1961).

[13] F. M. Lewis and F. R. Mayo, *ibid.*, **70**, 1533 (1948).

[14] A. R. Bader, R. P. Buckley, F. Leavitt and M. Szwarc, *ibid.*, **79**, 5621 (1957).

TABLE 6. ULTRAVIOLET SPECTRA OF β-ALKYLSTYLENES IN HEXANE

R	*cis*		*trans*	
	λ_{max}, mμ	log ε_{max}	λ_{max}, mμ	log ε_{max}
CH_3*	241	4.11	249	4.16
			284	2.95
	290	2.06	293	2.80
C_2H_5*	242	4.11	251	4.19
			284	3.04
	291	2.19	293	2.88
n-C_3H_7*	242	4.13	251	4.23
			284	3.09
	291	2.16	293	2.93
n-C_4H_9	241	4.08	251	4.23
			284	3.12
	291	2.10	293	2.96
i-C_3H_7*	242	4.09	251	4.21
			284	3.06
	291	2.05	293	2.91
s-C_4H_9	242	4.09	251	4.23
			284	3.11
	291	2.10	293	2.96
t-C_4H_9	~220	3.58	251	4.23
			284	3.09
	292	1.05	293	2.94

* Private communication of Prof. M. Nakagawa (Fac. of Sci., Osaka Univ.)

difference in the magnitude of conjugation in the monomer. Table 6 collects the ultraviolet absorption spectra of fourteen β-alkylstyrenes. The absorptions in *cis*-β-methylstyrene are lower in wavelength and in intensity than in *trans*-β-methylstyrene. The shift of the absorption maximum from 249 mμ to 241 mμ was interpreted to be attributable to the twisting of the double bond of the *cis*-monomer about 60° from the plane of the benzene ring.[15] Table 6 also indicates that the change in β-alkyl groups results in little change in the spectra within either the *cis*- or *trans*-isomer series, except for the case of the *cis*-β-*t*-butylstyrene. In other words, the same situation as for β-methylstyrene seems to hold for the other monomers with the exception of *cis*-β-*t*-butylstyrene.

Stuart models show that the double bonds of all *trans*-β-alkylstyrenes can be co-planar to the benzene ring, while that of the *cis*-β-alkylstyrenes, except for *cis*-β-*t*-butylstyrene, can possess a structure similar to that of the above-mentioned *cis*-β-methylstyrene. The nodal plane of the double bond of *cis*-β-*t*-butylstyrene, which has no hydrogen at the γ-carbon, must be perpendicular to the benzene ring plane. This monomer has no reactivity, as has been shown before. Both the spectra and the models indicate that in both the *cis*- and the *trans*- series, the conjugation in the monomers does not change except for the case of *cis*-β-*t*-butylstyrene.

Taft's equation is, in full:

$$\log k/k_0 = \rho^*\sigma^* + \delta E_s + E_\phi$$

It may not be necessary to consider the first polar term in the present systems. E_ϕ indicates the difference in the resonance factor with the variation of substituents. An assumption of $E_\phi=0$, which could make discussions on steric effects possible, seems to be appropriate from the above facts. However, for a comparison of the reactivities of the *cis*-series and of the *trans*-series using the same equation, the difference in E_ϕ should be considered. The difference in E_ϕ might correspond to the difference between the experimental lines of the *trans*-series and the *cis*-series in Figs. 4, 5, and 6; it should be constant within a series, independent of the specific β-alkyl values. However, the small differences observed in the slopes of the *cis*- and the *trans*- series might not be attributable to the differences in the intramolecular inhibition of resonance in the *cis*-monomers, but, rather, to the difference in the extent of steric hindrance of the β-alkyls in the two series toward the attacking radical.

It is also interesting to note data which appear to show another effect of the monomer structure on the reactivity of allylic hydrogen. In both the *cis*- and the *trans*-series, the system of the more reactive styrene shows a lower copolymerization rate and viscosity (in Figs. 1 and 2). This may be due to the fact that the reactivity of β-alkylstyrene radicals toward acrylonitrile is lower than that of acrylonitrile.[16] Moreover, allylic hydrogens in the monomer may result in a decrease in rate and viscosity due to a chain transfer mechanism. However, when we compare the *cis*-series with the *trans*-series, it should be noted that the systems of *cis*-β-methyl, *cis*-β-ethyl, and *cis*-β-*n*-propylstyrene, which were found to be more reactive toward the acrylonitrile radical than *trans*-β-isopropyl and *trans*-β-*s*-butylstyrene, and which have more allylic hydrogens, showed much higher rates and higher viscosities than the latter systems. Since it is reasonable to consider that the radicals from *cis*- and *trans*-β-alkylstyrenes with the same alkyl group are not different in their reactivities toward acrylonitrile, the discrepancy may be due to a difference in the reactivity of the allylic hydrogen between *trans*-monomers and *cis*-monomers. An allylic radical which is derived from a *trans*-monomer may resonate with the benzene ring, but that from a *cis*-monomer will do so only to a smaller extent.

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[15] H. Suzuki, This Bulletin, **33**, 619 (1960).

[16] F. S. Bagdasariyan, "Theory of Vinyl Polymerization," translated by M. Imoto and S. Futami, Asakura Shoten, Tokyo (1960), Chapter 8.