

Steric Effects in the Radical Copolymerization of α - and β -Alkylstyrenes

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ABSTRACT: The effect of alkyl substituents in the radical copolymerizations of α - and β -alkylstyrenes with acrylonitrile was investigated. For α - and β -methylstyrenes, the radical copolymerizations with methyl acrylate and methacrylonitrile were also carried out. It was shown that when Q and e values are tentatively assigned to these methylstyrenes, the steric effect of the methyl substituent is mainly included in Q values.

The relative reactivities within each series of α -alkyl-, *cis*- β -alkyl-, and *trans*- β -alkylstyrenes toward the acrylonitrile radical are related to the steric repulsion effect and the hyperconjugation effect of alkyl substituents. Differences in reactivities among these isomer series are attributed to the resonance factor.

KEY WORDS Steric Effect / Radical Copolymerization / α -Alkylstyrene / β -Alkylstyrene / Acrylonitrile / Methyl Acrylate / Methacrylonitrile / Hyperconjugation / Reactivity /

1,2-Disubstituted ethylenes are in general reluctant to undergo homopolymerization by the radical mechanism. This low reactivity of internal olefins has been explained by Alfrey, *et al.*,¹ to be due to the steric interaction in the transition state between substituents of the reacting monomer and of the propagating polymer end. The present authors have investigated some aspects of the low reactivity.² However, few detailed papers on the steric effect have been reported probably because of the difficulty of separating the steric effect from other factors.

It is reported in the study of the radical copolymerization of methyl α -alkylacrylate with styrene that monomer reactivities toward the styryl radical have a linear correlation with Taft's steric substituent constant E_s .³ It is also reported that in the case of alkyl methacrylates relative reactivities of the monomers toward the styryl radical are controlled only by the polar effect of substituents of the monomers and have no relation to the steric effects of the substituents.⁴ On the other hand, relative reactivities of β -alkylstyrenes toward the acrylonitrile radical were shown to have a linear relation-

ship to E_s .⁵

The steric effect may involve not only the steric interference between the substituent of the monomer and that of the propagating polymer end (ultimate unit), but also interactions between the substituent of the monomer and that of the penultimate unit. It seems necessary to separate the ultimate and the penultimate unit effects in the process of analyzing the copolymerization data in order to discuss the steric effect in detail. The presence of the penultimate unit effect in the radical copolymerization of α - and β -alkylstyrenes with acrylonitrile has been shown in the preceding paper.⁶ In the present paper, the steric interaction of the substituent of the reacting monomer with that of the ultimate unit in the transition state of the radical copolymerization will be dealt with.

In one of our papers, the steric effect in the silver ion complex formation of styrene derivatives was investigated.⁷ It was concluded that the equilibrium constant K is determined by the steric effect as well as by the hyperconjugation effect of alkyl substituents. In another paper dealing with the steric effect in the radical copolymerization of β -alkylstyrenes, the hyper-

conjugation effect of alkyl groups was not taken into consideration.⁵ It now seems necessary to reinvestigate the hyperconjugation effect along with the steric effect. Szwarc referred to the hyperconjugation effect in the reaction of olefins to the methyl radical.⁸

EXPERIMENTAL

Synthesis of *cis*- and *trans*- β -methylstyrenes were reported previously.⁶ Acrylonitrile and methyl acrylate were obtained commercially. These monomers were purified by distillation.

Table I. Copolymerization of methyl acrylate (M_1) and β -methylstyrenes (M_2)^a

M_1 , mol% in monomer	Time, hr	Conversion, %	Rate, %/hr	Copolymer		
				C%	m_1 , mol%	η_{sp}/c^b
<i>trans</i> - β -methylstyrene						
91.45	0.79	6.65	8.42	57.70	96.70	0.64
77.40	1.50	2.05	1.37	60.98	89.85	0.33
59.71	4.90	3.55	0.72	64.22	82.99	0.20
58.45	6.60	2.88	0.43	65.49	80.38	0.21
50.31	13.03	6.35	0.48	65.96	75.82	0.15
32.93	16.00	0.74	0.46	69.27	66.58	0.09
<i>cis</i> - β -methylstyrene						
77.74	0.85	6.63	7.80	57.85	95.79	0.53
70.58	1.33	6.87	5.16	58.62	93.28	0.39
61.11	2.50	6.40	2.56	60.16	91.22	0.38
52.31	10.20	11.73	1.15	61.54	87.64	0.22
40.19	12.10	5.56	0.460	63.09	84.53	0.18
30.80	25.00	3.65	0.146	65.92	75.19	0.13
20.01	42.60	0.198	0.0047	68.86	70.97	—

^a Monomer mixture 2 g, bulk at 60°C, AIBN 1% by weight.

^b Concentration 0.2 g/dl in benzene at 30°C.

Table II. Copolymerization of methacrylonitrile (M_1) and β -methylstyrenes (M_2)^a

M_1 , mol% in monomer	Time, hr	Conversion, %	Rate, %/hr	Copolymer		
				N%	m_1 , mol%	η_{sp}/c^b
<i>trans</i> - β -methylstyrene						
89.77	8.2	5.73	0.69	20.01	97.00	0.12
80.36	13.40	6.71	0.50	20.00	97.00	0.09
79.18	9.00	3.77	0.41	19.64	96.29	0.10
70.12	15.90	6.62	0.41	18.37	92.81	0.08
60.34	17.90	4.98	0.27	16.92	88.35	0.06
51.03	23.40	2.87	0.12	16.43	86.69	0.06
38.27	38.50	2.87	0.07	14.85	81.27	—
<i>cis</i> - β -methylstyrene						
79.61	17.30	9.74	0.56	20.86	99.95	0.11
70.27	17.40	7.20	0.41	20.31	98.43	0.09
60.37	17.70	5.74	0.32	20.11	97.88	0.07
49.65	25.10	3.66	0.14	19.35	95.71	0.07
35.01	38.60	2.71	0.07	18.40	92.90	—
25.04	42.70	1.17	0.02	17.94	91.50	—

^a Monomer mixture 2 g, bulk at 60°C, AIBN 1% by weight.

^b Concentration 0.2 g/dl in dimethylformamide at 30°C.

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Bulk copolymerization was carried out in a sealed ampoule at $60 \pm 0.5^\circ\text{C}$ in the presence of AIBN. Resulted copolymers were purified by reprecipitation from acetone with petroleum ether in case of acrylonitrile copolymer, from acetone with ether for methyl acrylate copolymer, and from dimethylformamide with methanol for methacrylonitrile copolymer. Copolymer compositions were determined by C analysis for the copolymers of methyl acrylate and N analysis by Kjeldahl method for the copolymers of acrylonitrile and methacrylonitrile.

RESULTS

The data for the radical copolymerization of *cis*- and *trans*- β -methylstyrene (M_2) with methacrylonitrile and methyl acrylate (M_1) are summarized in Tables I and II. The monomer reactivity ratios for the copolymerization of methyl acrylate and methacrylonitrile are calculated by the Fineman—Ross method and those for the copolymerization of acrylonitrile are taken from the previous data with the consideration of the penultimate unit effect⁶ and are listed together in Table III.

Table III. Monomer reactivity ratios

M_1	r_1^b	
	M_2 : <i>trans</i> - β -Methylstyrene	<i>cis</i> - β -Methylstyrene
Acrylonitrile ^a	0.45	1.6
Methyl acrylate	2.7	6.0
Methacrylonitrile	4.4	27

^a Ref 6. ^b $r_2=0$.

DISCUSSION

Deviation from Q—e Scheme

In the case of 1,2-disubstituted and 1,1-disubstituted ethylenes with bulky substituents, the applicability of the Q — e scheme is limited. Because of the pronounced steric factor in the rate constant for the self-propagation of these monomers, it is clear that the Q — e scheme cannot be applied in the usual fashion to the copolymerizations involving internal olefins (M_2). It may be possible to apply the Q — e scheme to the r_1 values only, but even in this

Table IV. Q , e values and UV spectra of styrene perivatives

Monomer	Q	e	λ_{max} , m μ
Styrene	1.00	-0.80	244
α -Methylstyrene ^a	0.98	-1.27	244
<i>trans</i> - β -Methylstyrene	0.052	-1.30	250
<i>cis</i> - β -Methylstyrene	0.029	-0.92	241

^a Ref 9.

case the resulting Q and e values are less reliable than for vinyl monomers, and the steric effect may be involved both in the Q and e values.

Table IV shows the Q and e values of styrene derivatives. The table shows reasonable e values for β -methylstyrenes in comparison with those for styrene and α -methylstyrene.⁹ The Q values of β -methylstyrenes are abnormally small probably because of the steric effect of the β -substituent. The UV spectra of these monomers in Table IV indicates that the differences in conjugation between monomers are not so large. These facts suggest that the steric effect of substituents are included mainly in the Q values.

Accordingly, it is necessary to estimate quantitatively the steric effect of internal olefins and 1,1-disubstituted ethylenes with bulky substituents in order to discuss reactivity in any detail.

In Table V relative reactivity of *trans*- β -methylstyrenes is compared with that of styrene. Decreased reactivity of β -methylstyrenes by a factor of 15—17 may be due to a blocking effect of the β -methyl group. A similar blocking effect was reported by Szwarc¹⁰ in the case of relative reactivity of olefins towards the methyl radical.

Table V. Relative reactivity of styrene and β -methylstyrenes

Radical (M_1)	$1/r_1$		
	<i>trans</i> - β -Methylstyrene	Styrene ^a	$r_1(\beta\text{-MeSt})/r_1(\text{St})$
Acrylonitrile	1.75	25	14
Methyl acrylate	0.37	5.7	15
Methacrylonitrile	0.23	3.8	17
Methyl ^b	92.5	792	8.6

^a Ref 9. ^b Ref 10.

Effect of Alkyl Substituent on Styrene

The effect of substituents on relative reactivity of monomers may generally be divided into the independent contributions of the polar, resonance and steric effects of the substituents. Relative reactivity of monomers towards a radical copolymerization may be given by Taft's equation 1

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

where $\rho^* \sigma^*$, δE_s , γE_ϕ are terms of the polar, steric, and resonance effects, respectively. Relative reactivity of the series of alkylstyrenes toward the acrylonitrile radical are summarized in Table VI.⁶ The reactivity is affected remark-

Table VI. Monomer reactivity ratio for the copolymerization of α - and β -alkylstyrenes (M_2) and acrylonitrile (M_1)^a

R	1/r ₁		
	α -Alkylstyrene	<i>trans</i> - β -Alkylstyrene	<i>cis</i> - β -Alkylstyrene
Me	0.31	0.45	1.6
Et	0.07	0.95	2.5
<i>n</i> -Pr	0.07	1.05	3.0
<i>n</i> -Bu	0.08	1.1	3.0
<i>i</i> -Pr	0.17	3.5	15.0
<i>s</i> -Bu	0.24	6.1	22.0
<i>t</i> -Bu	1.5	18.8	—

^a Ref 6.

ably by the specific type of alkyl substituent in each series:



This order is opposite to the order of the favorable polarity of alkyl groups, since the acrylonitrile radical has an electrophilic character. Unfortunately, the polar effect of substituents of α - and β -substituted styrene toward the acrylonitrile radical has not been investigated in the Hammett relation. The reaction constant $\rho = -0.25$ was reported for ring-substituted styrenes toward the *p*-cyanostyrene radical in the Hammett $\rho-\sigma$ relation.¹¹ Relative reactivity of *p*-substituted β -methylstyrenes toward maleic anhydride radical were related to $\rho-\sigma^+$ relation and a reaction constant $\rho = -1.13$ was reported.¹² Since the maleic an-

Table VII. Ultraviolet spectra of styrene derivatives in hexane

R	α -Alkylstyrene		<i>cis</i> - β -Alkylstyrene		<i>trans</i> - β -Alkylstyrene	
	λ_{max} , m μ	$\log \epsilon_{\text{max}}$	λ_{max} , m μ	$\log \epsilon_{\text{max}}$	λ_{max} , m μ	$\log \epsilon_{\text{max}}$
H	244	4.08				
Me	243	4.04	241	4.11	249	4.16
Et	239	4.03	242	4.11	251	4.19
<i>n</i> -Pr	239	3.97	242	4.13	251	4.23
<i>n</i> -Bu	239	3.97	241	4.08	251	4.23
<i>i</i> -Pr	234	3.86	242	4.09	251	4.21
<i>s</i> -Bu	234	3.93	242	4.09	251	4.23
<i>t</i> -Bu	about 220	3.62	about 220	3.58	251	4.23

hydride radical probably has a more electrophilic character than the acrylonitrile radical, the polar effect of alkyl substituents may be much smaller than the actual difference in reactivity.

Table VII combines the UV spectra of α - and β -alkylstyrenes, indicating that for *cis*- and *trans*- β -alkylstyrenes the extent of conjugation does not change appreciably within each series except for *cis*- β -*t*-butylstyrene. This means that the resonance factor varies little within each series. Thus, the resonance effects of substituents in each series may be ignored from eq 1 except α -alkylstyrenes. In the case of α -alkylstyrenes, the wavelength of maximum absorption shifts lower with an increase in the bulkiness of the alkyl substituents. The shift was interpreted to be attributable to the twisting of the double bond from the plane of the benzene ring.¹³ This effect of resonance inhibition will be discussed later. These resonance factors may be taken into consideration implicitly by treating the hyperconjugation effect in the later section.

Another factor affecting the reactivity of alkylstylenes is the steric effect of alkyl substituents. Tsuruta and Chikanishi³ reported that relative reactivity of methyl α -alkylacrylates toward the styryl radical has a linear correlation with Taft's steric substituent constant E_s . One of the present authors also reported a linear relationship between the relative reactivity of β -alkylstyrene toward the acrylonitrile radical and Taft's E_s . In both investigations plots of reactivity against Taft's E_s values of RCH_2

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exhibited better linearities than those against E_s of R. Moreover, reactivity is significantly affected by the specific type of alkyl group as mentioned above. This order is that of the number of α -hydrogen atoms in the alkyl groups. These factors strongly suggest the importance of the hyperconjugation effect in radical copolymerization. The contribution of hyperconjugation to E_s values of RCH_2 may be the same magnitude and hence the use of the E_s values of RCH_2 instead of those of R would have eliminated the effect of hyperconjugation. In the study on the silver ion complex formation of α - and β -alkylstyrenes,⁷ it was concluded that the equilibrium constant K is mainly governed by the steric effect as well as the hyperconjugation effect of alkyl substituents. We tried to separate the effects of substituents into the independent contributions from the steric and the hyperconjugation effects of alkyl substituents, as represented by eq 2.

$$\log(1/r_1) = \delta E_s^c + h(n-3) + \text{constant} \quad (2)$$

where n is the number of α -hydrogen atoms in alkyl groups and h is an adjustable parameter representing a measure of the hyperconjugation effect.*

The correlation of $\log(1/r_1)$ with E_s^c by eq 2 is shown in Figure 1 for the copoly-

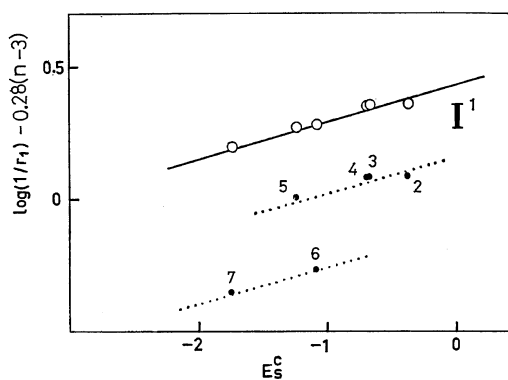


Figure 1. Relative reactivity of methyl α -alkylacrylates toward the styryl radical (Data are taken from Tsuruta and Chikanishi⁸): 1, Me; 2, Et; 3, *n*-Pr; 4, *n*-Bu; 5, *i*-Bu; 6, *i*-Pr; 7, *s*-Bu.

* We used Hancock's E_s^c values¹⁴ rather than Taft's E_s values, because the E_s^c values are based on the quantitative separation of the hyperconjugation effect from E_s .

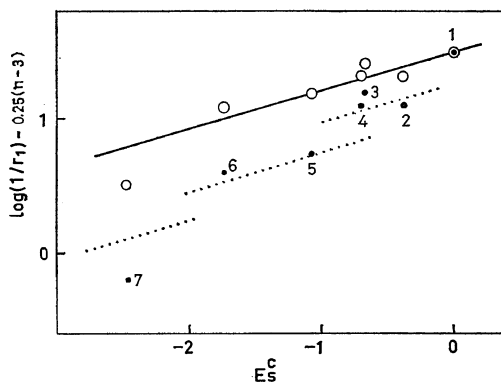


Figure 2. Relative reactivity of α -alkylstyrenes toward the acrylonitrile radical: 1, Me; 2, Et; 3, *n*-Pr; 4, *n*-Bu; 5, *i*-Pr; 6, *s*-Bu; 7, *t*-Bu.

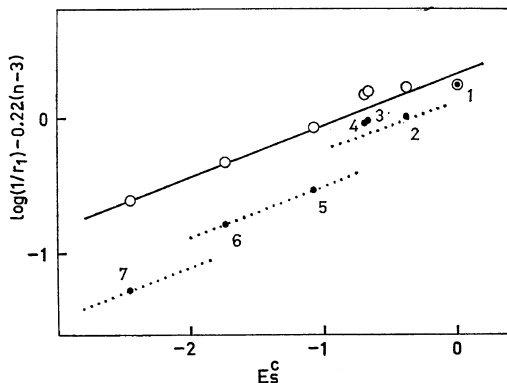


Figure 3. Relative reactivity of *trans*- β -alkylstyrenes toward the acrylonitrile radical: 1, Me; 2, Et; 3, *n*-Pr; 4, *n*-Bu; 5, *i*-Pr; 6, *s*-Bu; 7, *t*-Bu.

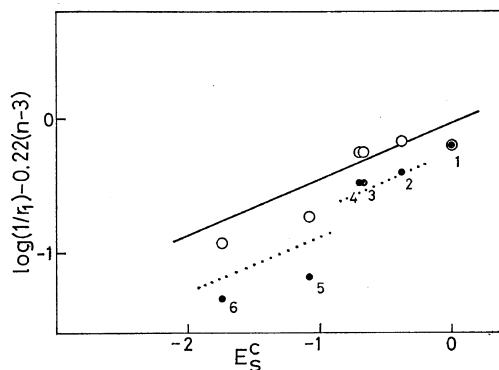


Figure 4. Relative reactivity of *cis*- β -alkylstyrenes toward the acrylonitrile radical: 1, Me; 2, Et; 3, *n*-Pr; 4, *n*-Bu; 5, *i*-Pr; 6, *s*-Bu.

merization of methyl α -alkylacrylates with styrene from the data of Tsuruta and Chikanishi,³ in Figure 2 for the copolymerization of α -alkylstyrenes with acrylonitrile and in Figures 3 and 4 for the copolymerization of β -alkylstyrenes with acrylonitrile. In these figures solid circles represent the relation between $\log(1/r_1)$ and E_s^c . All these data are represented by parallel dotted lines belonging to different n . Plots by eq 2 as shown in figures in full lines give linear correlations, where parameter h was determined by trial and error. Since the data for *cis*- β -alkylstyrene were rather scattered as shown in Figure 4, the h and δ values derived from the data for *trans*- β -alkylstyrene were used in this plot, showing poor linearity. Parameters h and δ thus obtained are given in Table VIII.

In this way, the reactivity of α - and β -alkylstyrenes in the radical copolymerization with acrylonitrile are represented by both the steric and the hyperconjugation effect. In the previous paper concerning the silver ion complex formation, the sign of parameter h is negative, while the parameter obtained above is positive. This is rationalized by the fact that the resonance effect in the formation of silver ion complex reduces the equilibrium constant, while the resonance effect in the radical copolymerization increases the monomer reactivity. α -Alkylstyrenes exhibit a steric inhibition of resonance, as has been shown above. UV spectra in Table VII, however, show that the resonance inhibition effect of alkyl substituents is nearly the same in each group having the same number of α -hydrogen atoms in alkyl groups. Thus the resonance inhibition effect may be included in the h parameter for α -alkyl series, and hence the resulting δ parameter may give the steric effect of alkyl substituents.

Difference among the Isomer Series

Now, we can compare the steric effects in the radical copolymerization of α - and β -alkylstyrenes in Table VIII, which indicates that the steric effect of α -alkyl groups are smaller than that of β -alkyl groups judging from the comparison of the δ parameter. In the formation of the silver ion complex with styrene derivatives, in which the complexes are known to be of the π -complex type, the steric effect of α -alkyl is nearly equal

Table VIII. Steric and hyperconjugation parameter for radical copolymerization

Monomer	δ	h
Methyl α -alkylacrylate	0.15	0.28
α -Alkylstyrene	0.30	0.25
<i>trans</i> - β -Alkylstyrene	0.42	0.22

to that of the β -alkyl series. Based on these observations, we may conclude that the transition state of the radical copolymerization with acrylonitrile is not the π -complex type but the σ -complex type, as was suggested by Szwarc.¹⁵ When we compare these three series using the same eq 2, however, the difference in the resonance factor should be considered and this may be the origin of the large differences in the constant term in eq 2—in other words, differences in intercepts on the ordinate in the figures.

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