

## Penultimate Unit Effect in the Radical Copolymerization of $\alpha$ -, $\beta$ -Alkylstyrenes and Cycloalkenes with Acrylonitrile

Yoshiaki INAKI, Sumio HIROSE, Katsutoshi YASUFUKU,  
Shun-ichi NOZAKURA, and Shunsuke MURAHASHI

*Department of Polymer Science, Faculty of Science, Osaka University,  
Toyonaka, Osaka, Japan.*

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**ABSTRACT:** In order to investigate the effect of alkyl substituents of  $\alpha$ - and  $\beta$ -alkylstyrenes on their reactivities in the radical copolymerization, these monomers were copolymerized with acrylonitrile. Copolymerization data show that the penultimate unit effects are operative in the copolymerization. Monomer reactivity ratios were calculated using the copolymer composition equation which takes into account the penultimate unit effect. Since the magnitude of the penultimate effect is parallel to the Hancock's constants  $E_s^c$ , the origin of the penultimate effect operating here seems to be of steric nature.

In the case of the copolymerization of cycloalkenes with acrylonitrile, an effect which might be attributable to a further remote unit than the penultimate unit was observed.

**KEY WORDS** Penultimate Unit Effect / Penultimate Unit Effect /  
Radical Copolymerization /  $\alpha$ -Alkylstyrene /  $\beta$ -Alkylstyrene / Cyclo-  
alkene / Acrylonitrile / Steric Effect /

The relationship between the monomer structure and its relative reactivities is one of the main problems in polymer synthesis. In our previous paper, the relative reactivity of 1,2-disubstituted ethylenes in radical copolymerization has been reported.<sup>1-4</sup> In these works, relative reactivities of monomer were obtained from the Mayo—Lewis equation, and the effect of the remote unit was neglected. This equation rests on the assumptions of long chains, no penultimate unit effect, and no reversibility of the propagation reactions.<sup>5</sup> With these assumptions the results may be analyzed in terms of four propagation rate constants. For monomers with large substituents there is a possibility of the penultimate unit effect and/or reversibility of the propagation reaction in the copolymerization.

It is necessary to estimate quantitatively the penultimate unit effect of 1,2- and 1,1-disubstituted ethylenes with bulky substituents in order to make a detailed discussion on the relative reactivities of these monomers. In the present paper, the data of radical copolymerization of  $\alpha$ - and  $\beta$ -alkylstyrenes and cycloalkenes with acrylonitrile were analyzed considering the

penultimate unit effect. The penultimate unit effects have been observed in the copolymerization of, for example, acrylonitrile,<sup>6</sup> fumalonitrile,<sup>7,8</sup> methyl acrylate, methyl methacrylate, or diethyl fumarate<sup>9</sup> with hydrocarbon monomers. The former comonomers contain polar substituents and the observed penultimate unit effect is generally explained in terms of an electrostatic interaction.<sup>10</sup> It was reported recently that a penultimate unit effect, which is due to a steric repulsion, was found in the copolymerization of halogenated cyclopropenes and other cycloalkenes with acrylonitrile.<sup>11,12</sup> In the case of 1,2- and 1,1-disubstituted ethylenes with bulky groups, there seems to be a possibility of the steric hindrance effect of the monomer substituent with the substituent of the propagating penultimate unit.

### EXPERIMENTAL

#### *Materials*

$\alpha$ -Methylstyrene was obtained commercially. The other  $\alpha$ -alkylstyrenes were synthesized by the Wittig reaction of alkylphenylketones.<sup>13</sup>  $\alpha$ -Alkylstyrenes were purified by rectification under

Table I. Physical constants and analytical data of  $\alpha$ -alkylstyrenes

Monomer	Bp, °C (mm)	$d_4^{25}$	$n_D^{25}$	Analysis			
				Obsd, %		Calcd, %	
				C	H	C	H
Me		0.9078	1.5343	91.14	8.51	91.47	8.52
Et	65.0~66.0/14.5	0.9015	1.5218	90.74	9.18	90.85	9.15
<i>n</i> -Pr	75.5/ 9.5	0.8957	1.5161	89.75	9.63	90.35	9.65
<i>i</i> -Pr	78.0~79.0/16.0	0.8868	1.5090	90.35	9.65	90.35	9.65
<i>n</i> -Bu	83.0~84.0/ 8.5	0.8879	1.5123	89.56	10.02	89.94	10.06
<i>s</i> -Bu	67.0~67.8/ 7.0	0.8892	1.5100	89.51	10.04	89.94	10.06
<i>t</i> -Bu	77.5~78.5/15.0	0.8721	1.4973	89.66	10.01	89.94	10.06

reduced pressure, using a stainless steel helipack column of about 30 theoretical plates. The physical constants of these styrenes and analytical data are given in Table I. Purity of the monomers was confirmed by gas chromatography (Silicone DC 550 on celite 1.5 m, 160°) to be more than 99%.

#### Polymerization

The bulk polymerization was carried out in a sealed glass ampoule in the presence of 1 wt% of AIBN using about 2 g of a monomer mixture. The degassed and sealed ampoule was kept in a thermostat at  $60 \pm 0.1^\circ\text{C}$ . The copolymer was retained in solution after the polymerization except for the case of  $\alpha$ -*t*-butylstyrene. The copolymer was purified by reprecipitation into petroleum ether from an acetone solution, and dried overnight under a vacuum at room temperature. In the case of  $\alpha$ -*t*-butylstyrene di-

methylformamide and methanol were used as a solvent and nonsolvent and the reprecipitated polymer was dried under vacuum at  $80^\circ\text{C}$ . The composition of the copolymer was calculated from the results of nitrogen analysis determined by duplicate runs of the Kjeldahl method.

#### Viscosity

Viscosity of the copolymer was measured at  $30^\circ\text{C}$  in dimethylformamide at  $c=0.2$  g/dl using an Ostwald viscometer.

## RESULTS

The data for the radical copolymerization of acrylonitrile( $M_1$ ) with  $\alpha$ -alkylstyrenes( $M_2$ ) are summarized in Table II. Figure 1 shows the copolymer composition curves indicating that the monomers with normal alkyls and branched alkyls have different reactivities. Except for  $\alpha$ -

Table II. Copolymerization of acrylonitrile( $M_1$ ) and  $\alpha$ -alkylstyrenes

R	$M_1$ , mol% in monomer	Time, hr	Conversion, %	Rate, %/hr	Copolymer		
					N%	$m_1$ , mol%	$\eta_{sp}/c$
Me	89.19	1.07	5.88	5.50	9.77	56.69	0.478
	79.51	1.13	5.50	4.87	8.85	52.91	
	70.54	1.17	5.57	4.76	8.30	50.53	
	60.60	1.32	4.73	3.58	8.00	49.19	
	51.56	1.35	4.02	2.98	7.53	47.06	
	41.78	1.78	4.13	2.32	7.04	44.76	
	32.88	2.30	4.19	1.82	6.65	42.86	
	25.75	2.55	3.41	1.34	6.64	42.81	0.151
Et	90.09	1.50	2.57	1.71	12.13	67.93	0.144
	80.34	2.08	3.43	1.65	9.99	60.24	

(continued)

## Penultimate Unit Effect in Copolymerization

Table II. (continued)

R	M <sub>1</sub> , mol% in monomer	Time, hr	Conversion, %	Rate, %/hr	Copolymer			
					N%	m <sub>1</sub> , mol%	$\eta_{sp}/c$	
	70.85	3.25	4.77	1.47	9.04	56.47	0.112	
	60.71	3.30	4.03	1.22	8.82	55.56		
	51.49	2.18	2.03	0.931	8.53	54.32		
	39.63	5.13	3.74	0.729	8.33	53.45		
	32.23	15.67	8.06	0.514	8.31	53.34		
	21.49	25.48	7.93	0.311	7.73	50.76		0.068
<i>n</i> -Pr	89.91	3.20	6.57	2.05	10.89	65.92	0.146	
	79.83	5.57	8.45	1.52	9.47	60.64		
	70.94	7.88	10.89	1.38	8.64	57.27		
	60.38	10.05	7.44	0.740	8.24	55.56	0.121	
	50.22	11.10	9.89	0.891	7.89	54.00		
	41.35	12.70	8.49	0.669	7.71	53.19	0.062	
	30.94	20.33	9.33	0.459	7.14	50.53		
	22.01	32.50	9.25	0.285	7.00	49.85		
<i>n</i> -Bu	90.38	3.47	6.24	1.80	9.85	64.23	0.154	
	80.25	3.55	6.99	1.97	8.81	60.20		
	71.59	5.48	6.45	1.18	8.25	57.87		
	60.07	7.98	8.78	1.10	7.60	54.98	0.084	
	50.16	9.84	8.18	0.863	7.30	53.59		
	39.90	13.78	7.76	0.563	7.07	52.49	0.075	
	32.62	16.35	7.80	0.477	6.96	51.95		
	22.07	32.27	8.16	0.253	6.91	51.71		
<i>i</i> -Pr	90.08	5.00	2.15	0.430	13.16	73.26	0.018	
	80.10	7.47	2.56	0.343	11.69	68.65		
	70.09	10.12	2.36	0.233	10.50	64.53		
	60.97	13.30	2.61	0.196	9.29	59.92		
	51.99	14.70	2.16	0.147	9.04	58.95		
	41.80	14.85	1.70	0.114	8.15	55.16		
	33.66	21.20	1.77	0.0835	8.03	54.64		
	27.32	41.38	2.74	0.0662	7.85	53.82		0.011
<i>s</i> -Bu	90.05	9.10	3.92	0.431	14.96	79.81	0.058	
	80.80	13.75	5.26	0.383	12.79	73.96		
	69.80	20.97	5.94	0.283	11.22	69.06		
	59.71	24.95	5.57	0.223	10.32	65.96	0.043	
	50.69	27.70	4.81	0.174	9.47	62.81		
	40.47	36.62	4.06	0.111	9.13	61.50	0.069	
	35.83	49.32	5.77	0.117	8.91	60.61		
	22.09	64.88	2.53	0.0390	8.41	58.55		
<i>t</i> -Bu	89.80	1.80	3.56	1.98	22.70	94.89	0.39	
	80.44	3.03	2.34	0.772	20.04	90.52		
	69.85	3.12	0.828	0.265	19.46	89.41		
	59.89	12.45	1.36	0.109	18.96	88.51		
	51.34	20.00	0.832	0.0416	19.04	88.65		
	40.08	94.12	0.990	0.0144	16.91	86.10		
	32.63	64.88	0.933	0.0218	14.61	78.90		0.034
	22.22	116.7	0.254	0.00218	13.52	76.07		

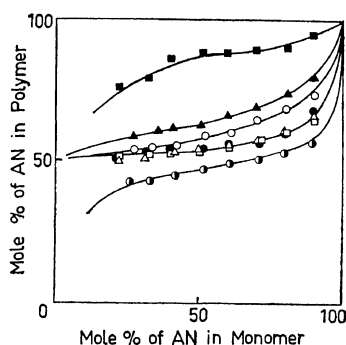


Figure 1. Copolymer composition curves for acrylonitrile and  $\alpha$ -alkylstyrenes at 60°C:  $\bullet$ , Me;  $\bullet$ , Et;  $\triangle$ , *n*-Pr;  $\square$ , *n*-Bu;  $\circ$ , *i*-Pr;  $\blacktriangle$ , *s*-Bu;  $\blacksquare$ , *t*-Bu.

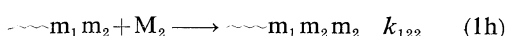
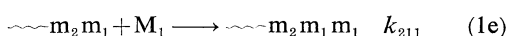
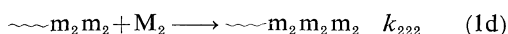
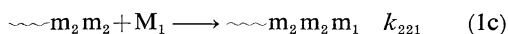
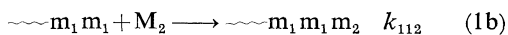
methylstyrene, these monomers did not undergo radical homopolymerization even after 72 hr under the present reaction conditions.

Results of the copolymerization of  $\beta$ -alkylstyrenes<sup>3</sup> and cycloalkenes<sup>4</sup> with acrylonitrile have been reported previously.

## DISCUSSION

### Penultimate Unit Effect

If the penultimate unit appreciably affects the reactivity of the radical end, the existence of four distinct types of the growing chain end must be considered in the copolymerization as in the following equations.



$$r_1 = \frac{k_{111}}{k_{112}}, \quad r_2 = \frac{k_{222}}{k_{221}}, \quad r_1' = \frac{k_{211}}{k_{212}}, \quad r_2' = \frac{k_{122}}{k_{121}}$$

where *m*, *M*, and *k* are the monomer unit in polymer, the monomer, and the propagation rate constant, respectively. From these equations, the copolymer composition equation 2 is obtained.<sup>14</sup>

$$\frac{dM_1}{dM_2} = \frac{1 + \frac{r_1' M_1}{M_2} \left( r_1 \frac{M_1}{M_2} + 1 \right)}{1 + \frac{r_2' \left( r_2 + \frac{M_1}{M_2} \right)}{1 + \frac{M_1}{M_2} \left( r_2' + \frac{M_1}{M_2} \right)}} \quad (2)$$

If the reactivities of the radicals are simply determined by the nature of the terminal group, *i.e.*,  $r_1 = r_1'$  and  $r_2 = r_2'$ , eq 2 is reduced to the simple form of the Mayo—Lewis equation, which is rearranged to the Fineman—Ross equation 3

$$\frac{F}{f}(f-1) = \left( \frac{F^2}{f} \right) r_1 - r_2 \quad (3)$$

where  $F = M_1/M_2$  and  $f = dM_1/dM_2$ . In a reverse definition eq 3 is transformed into eq 4.

$$\frac{F'}{f'}(f'-1) = \left( \frac{F'^2}{f'} \right) r_2 - r_1 \quad (4)$$

where  $F' = M_2/M_1$  and  $f' = dM_2/dM_1$ .

The assumption  $r_2 = r_2'$  simplifies eq 2 into eq 5 and 6.  $r_2 = r_2'$ :

$$\frac{F}{f}(f-1) = \left( \frac{F^2}{f} \right) r_1' \frac{\left( r_1 + \frac{1}{F} \right)}{\left( r_1' + \frac{1}{F} \right)} - r_2 \quad (5)$$

$$\frac{F'}{f'}(f'-1) = \left( \frac{F'^2}{f'} \right) r_2 - r_1' \frac{\left( r_1 + F' \right)}{\left( r_1' + F' \right)} \quad (6)$$

Combining eq 6 with an assumption  $r_2 = 0$  we obtain eq 7. This is the case where *M*<sub>2</sub> monomer does not self-propagate and the penultimate *m*<sub>2</sub> unit affects the reactivity of the terminal *m*<sub>1</sub> radical.  $r_2 = r_2' = 0$ :

$$\frac{F'}{f'}(f'-1) + F' = - \left[ \frac{F'^2}{f'}(f'-1) \right] \frac{1}{r_1'} - r_1 \quad (7)$$

If the above assumption is fulfilled, experimental results may give a straight line of eq 7,  $r_1$  and  $1/r_1'$  being given from the intercept and slope of the straight line.

If the penultimate effect is negligible, plots of eq 3 and 4 may give straight lines. Actual plots of eq 3 and 4 for the copolymerization of  $\alpha$ -alkylstyrenes with acrylonitrile did not give straight lines. This result suggests the existence of the penultimate unit effect. On the other

hand, the copolymerization of  $\beta$ -alkylstyrenes with acrylonitrile gave straight lines by eq 4, though the plots gave negative  $r_2$  value. This fact is also interpreted as the case where  $\beta$ -alkylstyrenes do not self-propagate and there is the penultimate effect. In this case  $r_1$  and  $r_1'$  values were obtained from the plots of eq 7.

*$\alpha$ -Alkylstyrene.* Fineman—Ross plots (eq 3) and reverse Fineman—Ross plots (eq 4) for the radical copolymerization of  $\alpha$ -alkylstyrene( $M_2$ ) with acrylonitrile( $M_1$ ) are given in Figures 2—5. These figures show that only  $\alpha$ -methylstyrene has a self-propagation ability and the other  $\alpha$ -alkylstyrenes do not react with their own radical, *i.e.*,  $r_2=0$ . Plots by eq 3 for  $\alpha$ -methylstyrene in Figure 2 show a straight line as if the penultimate effect were negligible. Plots by eq 4 in Figure 4, however, deviate remarkably from a straight line. This fact shows that the penultimate unit effect should be taken into

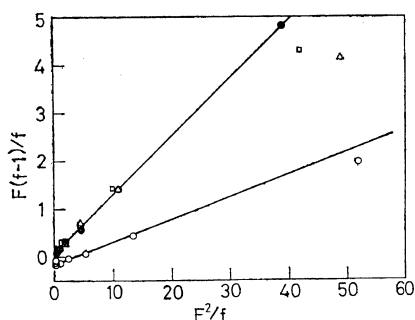


Figure 2. Fineman—Ross plots (eq 3) for the copolymerizations of acrylonitrile( $M_1$ ) and  $\alpha$ -alkylstyrenes ( $M_2$ ) at 60°C:  $\circ$ , Me;  $\bullet$ , Et;  $\square$ , *n*-Pr;  $\triangle$ , *n*-Bu.

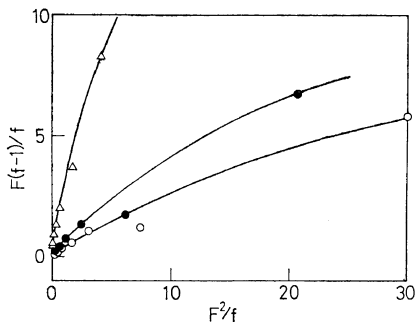


Figure 3. Fineman—Ross plots (eq 3) for the copolymerizations of acrylonitrile( $M_1$ ) and  $\alpha$ -alkylstyrenes( $M_2$ ) at 60°C:  $\circ$ , *i*-Pr;  $\bullet$ , *s*-Bu;  $\triangle$ , *t*-Bu.

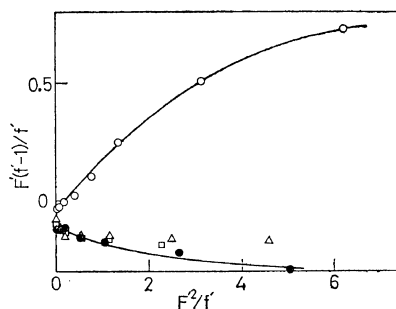


Figure 4. Reverse Fineman—Ross plots (eq 4) for the copolymerizations of acrylonitrile( $M_1$ ) and  $\alpha$ -alkylstyrenes( $M_2$ ) at 60°C:  $\circ$ , Me;  $\bullet$ , Et;  $\square$ , *n*-Pr;  $\triangle$ , *n*-Bu.

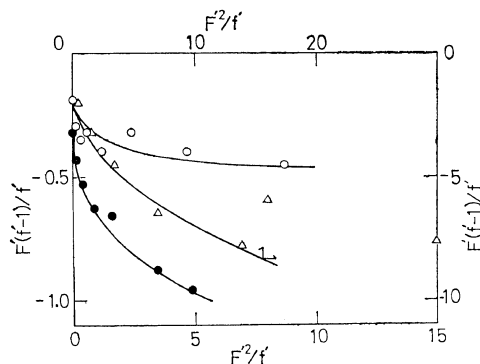


Figure 5. Reverse Fineman—Ross plots (eq 4) for the copolymerizations of acrylonitrile( $M_1$ ) and  $\alpha$ -alkylstyrenes( $M_2$ ) at 60°C:  $\circ$ , *i*-Pr;  $\bullet$ , *s*-Bu;  $\triangle$ , *t*-Bu.

consideration. The equation for the copolymerization of  $\alpha$ -methylstyrene including the penultimate unit effect is complicated as in eq 2 because of the self-propagation of  $\alpha$ -methylstyrene. Eq 2 is simplified to eq 6 by assuming no penultimate effect for  $r_2$ , *i.e.*,  $r_2=r_2'$ . In order to obtain  $r_1$  and  $r_1'$  values exactly, the curve fitting method must be applied to this curve.

In the case of the copolymerization of  $\alpha$ -alkylstyrene, it may be necessary to discuss the existence of the equilibrium polymerization with depropagation. The equilibrium monomer concentration of  $\alpha$ -methylstyrene at 60°C is reported to be 7.1 mol/l.<sup>15</sup> This concentration corresponds to that of the bulk homopolymerization. At the concentration below this, the homopolymer of  $\alpha$ -methylstyrene may not form. However,

the above-mentioned results show the existence of self-propagation of  $\alpha$ -methylstyrene. As shown in a following report,<sup>16</sup> short sequence lengths of  $\alpha$ -methylstyrene will be formed even if the monomer concentration is lower than the equilibrium monomer concentration. If  $\alpha$ -methylstyrene depropagates, the apparent value of  $r_2$  should decrease with a decrease of the  $\alpha$ -methylstyrene concentration (or high acrylonitrile concentration). The curve for  $\alpha$ -methylstyrene in Figure 5, however, shows that apparent values of  $r_2$  increase with the decrease of  $F'$  ( $\alpha$ -methylstyrene/acrylonitrile). This fact indicates that the penultimate unit effect is predominant over the depropagation of  $\alpha$ -methylstyrene.

As mentioned above, Figure 2 (plot by eq 3) shows a straight line for  $\alpha$ -methylstyrene but Figure 4 (plot by eq 4) shows a curved line for  $\alpha$ -methylstyrene. On the other hand, data of other  $\alpha$ -alkylstyrenes did not give straight lines by plotting either by eq 3 or 4. Apparent values of  $r_2$  in Figures 4 and 5 for  $\alpha$ -alkylstyrenes show negative signs. These negative values suggest the existence of the penultimate unit effect. In the case of  $\alpha$ -ethylstyrene Figure 2 shows an approximate linearity but Figure 4 shows negative  $r_2$  values as slopes. The reason may be as follows: data at small  $F$  values are relatively neglected in eq 3 (Figure 2) but those play a determinative role in eq 4 (Figure 4).

Figures 6 and 7 show the plot of  $\alpha$ -alkylstyrene by eq 7, intercepts and slopes giving  $r_1$  and  $1/r_1'$ , respectively. Since data at large  $-F'^2(f'-1)/f'$  values (small acrylonitrile content) were considered to have lower reliability because of difficulty of purification of low-

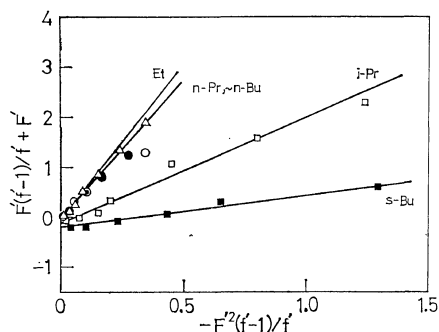


Figure 6. Evaluation of penultimate unit effects from eq 7:  $M_1$ , acrylonitrile;  $M_2$ ,  $\alpha$ -alkylstyrenes;  $\circ$ , Et;  $\bullet$ ,  $n$ -Pr;  $\triangle$ ,  $n$ -Bu;  $\square$ ,  $i$ -Pr;  $\blacksquare$ ,  $s$ -Bu.

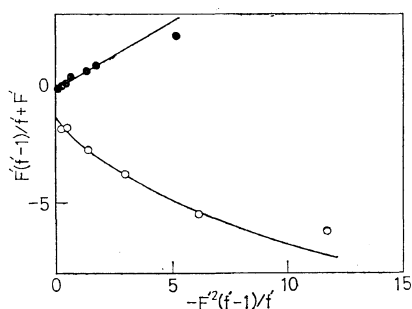


Figure 7. Evaluation of penultimate unit effects from eq 7:  $M_1$ , acrylonitrile;  $M_2$ ,  $\alpha$ -alkylstyrene;  $\bullet$ ,  $s$ -Bu;  $\circ$ ,  $t$ -Bu.

molecular-weight polymer, straight lines were drawn to fit best at low  $-F'^2(f'-1)/f'$  values. The results are given in Table III. Figure 7 shows that  $\alpha$ - $t$ -butylstyrene did not fit eq 7 and gave a negative  $1/r_1'$  value. Analogous to the former case where the negative  $r_2$  value was interpreted by the existence of the penultimate

Table III. Monomer reactivity ratio for the copolymerization of  $\alpha$ - and  $\beta$ -alkylstyrenes( $M_2$ ) and acrylonitrile( $M_1$ )

R	$\alpha$ -Alkylstyrene			<i>trans</i> - $\beta$ -Alkylstyrene			<i>cis</i> - $\beta$ -Alkylstyrene
	$r_1$	$r_1'$	$r_1'/r_1$	$r_1$	$r_1'$	$r_1'/r_1$	$r_1$
Me	0.31	0.045	1.45	0.45	0.75	1.7	1.6
Et	0.07	0.16	2.3	0.95	2.0	2.0	2.5
$n$ -Pr	0.07	0.17	2.4	1.05	2.0	2.0	3.0
$n$ -Bu	0.08	0.18	2.3	1.1	2.0	2.0	3.0
$i$ -Pr	0.17	0.50	2.9	3.5	—	—	15.0
$s$ -Bu	0.24	1.55	6.5	6.15	—	—	22.0
$t$ -Bu	1.5	—	—	18.8	—	—	—

effect and  $r_2=0$ , this negative  $1/r_1'$  value in Figure 7 for  $\alpha$ -*t*-butylstyrene might be explained by the penultimate unit effect or the effect of a further remote unit. In this case, however, only the penultimate unit effect is considered. In the case in which  $1/r_1'$  value is negative,  $r_1$  value is obtained by extrapolation to  $F^{1/2}(f'-1)/f'=0$  in Figure 7, since the data is more reliable at high acrylonitrile( $M_1$ ) monomer ratios.

**$\beta$ -Alkylstyrene.** Experimental error for *cis*- and *trans*- $\beta$ -alkylstyrenes is larger than that for  $\alpha$ -alkylstyrenes probably because of the lower reactivity of the former than the latter. Results of  $\beta$ -methylstyrene, experimental errors of which seem relatively small as compared to other  $\beta$ -alkylstyrene, were plotted in Figures 8 and 9. In the previous report on the copolymerization of  $\beta$ -alkylstyrene with acrylonitrile,<sup>3</sup> the penultimate unit effect was neglected. This is reasonable as far as the plot by eq 3 in Figure 8 is

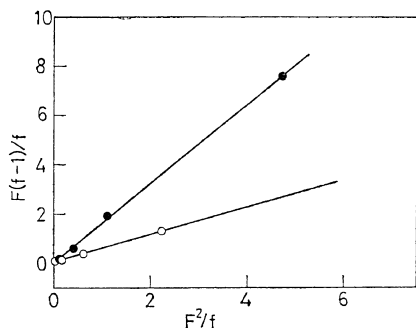


Figure 8. Fineman—Ross plots (eq 3) for the copolymerizations of acrylonitrile( $M_1$ ) and  $\beta$ -methylstyrenes( $M_2$ ) at 60°C: ●, *cis*-Me; ○, *trans*-Me.

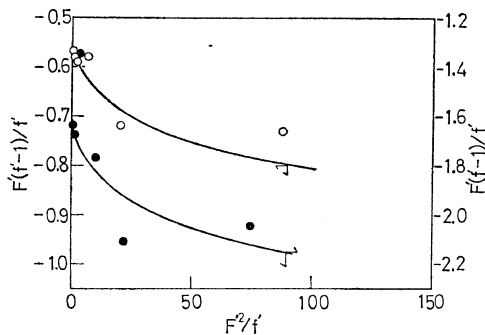


Figure 9. Reverse Fineman—Ross plots (eq 4) for the copolymerizations of acrylonitrile( $M_1$ ) and  $\beta$ -methylstyrenes( $M_2$ ) at 60°C: ●, *cis*-Me; ○, *trans*-Me.

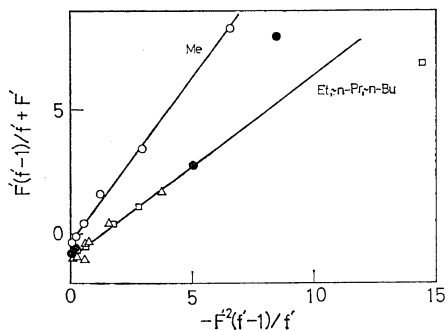


Figure 10. Evaluation of penultimate unit effects from eq 7:  $M_1$ , acrylonitrile;  $M_2$ , *trans*- $\beta$ -alkylstyrenes; ○, Me; ●, Et; □, *n*-Pr; △, *n*-Bu.

concerned. However, Figure 9 plotted by eq 4 gives a negative  $r_2$  value, showing a possibility of the existence of the penultimate unit effect. Plots by eq 7 are given in Figure 10 for  $\beta$ -alkylstyrene. Values of  $r_1$ ,  $r_1'$  and  $r_1'/r_1$  obtained in this way are listed in Table III. The term  $r_1'/r_1$  shows the magnitude of the penultimate unit effect. Table III shows a nearly equal tendency of the penultimate unit effect for  $\beta$ -alkylstyrene as for  $\alpha$ -alkylstyrene.

When the reactivity of  $M_2$  monomer is very low, the value of  $r_1$  becomes large and hence the variation of  $F$  does not affect the values of  $r_1'(r_1+1/F)/(r_1'+1/F)$  and  $r_1'(r_1+F)/(r_1'+F)$  in eq 5 and 6, respectively. Thus, eq 5 and 6 are nearly equal to eq 3 and 4 which do not contain the penultimate unit effect. This is the case of  $\beta$ -alkylstyrenes in which the penultimate unit effect is not recognized. To clarify the penultimate unit effect in the copolymerization of  $\beta$ -

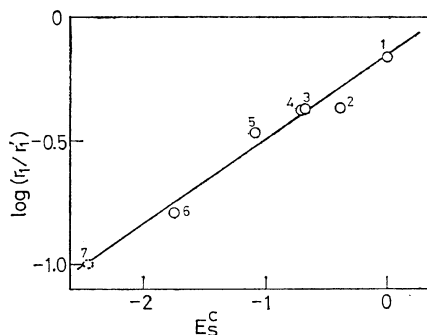


Figure 11. Relationship between penultimate unit effects and  $E_s^C$ : 1, Me; 2, Et; 3, *n*-Pr; 4, *n*-Bu; 5, *i*-Pr; 6, *s*-Bu; 7, *t*-Bu.

alkylstyrenes, more accuracy is needed for the analysis of the copolymer composition.

Plots of  $\log(r_1'/r_1)$  against Hancock's steric substituent constant  $E_s^c$  in Figure 11 show a considerable linearity. The penultimate unit effect is, therefore, of steric nature, presumably originating from a steric repulsion of a monomer and the penultimate unit both of which contain bulky alkyl substituents.

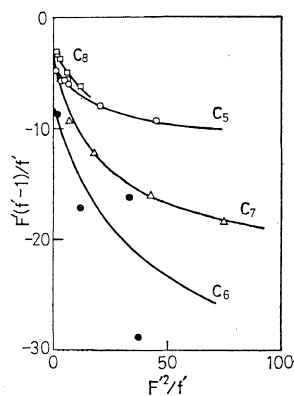


Figure 12. Reverse Fineman—Ross plots (eq 4) for the copolymerizations of acrylonitrile( $M_1$ ) and cycloalkenes( $M_2$ ) at 60°C.

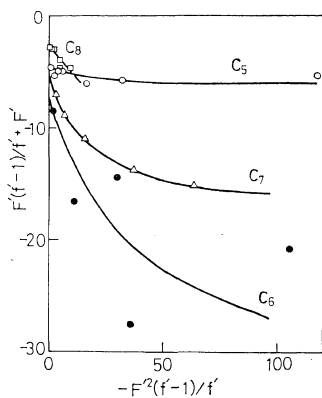


Figure 13. Evaluation of penultimate unit effects in the copolymerizations of acrylonitrile( $M_1$ ) and cycloalkenes( $M_2$ ) (eq 7).

*Cycloalkenes.* As in the case of the copolymerization of  $\alpha$ -alkylstyrenes with acrylonitrile, the reverse Fineman—Ross plots by eq 4 of the copolymerization of cyclic olefins with acrylonitrile give apparent negative values for  $r_2$  (Figure 12). This fact suggests the existence of the penultimate unit effect or the more remote unit effect. Plotting by eq 7, which is derived by considering the penultimate unit effect, still gives apparent negative signs for  $1/r_1'$  values (Figure 13). This fact indicates that there may be a more remote unit effect than the penultimate.

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