The Copolymerization of β-Substituted Styrenes with Maleic Anhydride*

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It has been reported that 1,2-disubstituted ethylenes, such as *p*-dioxene,⁽¹⁾ dihydropyrane,⁽²⁾ butene-2,⁽³⁾ and stilbene,⁽⁴⁾ do not homopolymerize by a radical mechanism, but do copolymerize with maleic anhydride (MAn) to yield copolymers with a 1 : 1 alternating composition. The present paper will describe copolymerizations of some β-substituted styrenes with MAn by a radical mechanism and will compare their reactivities.

The copolymerizations were carried out in

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* Paper III in a series on "The Polymerization of Internal Olefins;" for the preceding paper, see This Bulletin, 38, 156 (1965). Presented at the Annual Meeting of Polymer Science, Kyoto, June, 1964.

1) S. Iwatsuki, Y. Tanaka and Y. Yamashita, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **67**, 1467 (1964).

2) R. D. Kimbough, Jr., Wm. P. Dickson and J. M. Wilkerson, *J. Polymer Sci.*, **B2**, 85 (1964).

3) T. Otsu, A. Shimizu and M. Imoto, ibid., **B2**, 973 (1964).

4) T. Wagner-Jauregg, *Chem. Ber.*, **63B**, 3213 (1930).

Table I. Copolymerization of β-substituted styrenes (M_2) with MAn (M_1) in benzene
$[M_1]=[M_2]=1.0$ mol./l. $[AIBN]=1.0\times10^{-2}$ mol./l.

β-Substituent of M_2		Time hr.	Yield %	%/hr.	Copolymer				
					C%	H%	m_1/m_2	Soft. P., °C	η_{sp}/c*
-Ph	t	1.0	15.7	15.7	76.48	5.06	1.06	>300	insol.
$-OCH_3$	t	5.0	25.0	5.0	66.17	5.16	1.08	230—250	0.209
$-CH_3$	t	1.12	2.13	1.9	71.15	5.78	0.96	260—270	0.127**
$-CO_2CH_3$	t	23.2	34.8	1.5	64.45	4.74	0.95	180—200	0.148
-Cl 67%	t	18.7	5.05	0.27	Cl%	14.31	1.12	240—250	0.039
$-COCH_3$	t	19.6	4.9	0.25	63.28	3.78	2.34	240—250	—
-Ph	cis	17.3	3.3	0.19	71.70	5.20	1.21	230—250	—
-H		0.24	32.6	(136)	70.07	5.34	0.88	—	—

t: trans 100%
*: η_{sp}/c was measured in acetone (1%) 30°C.
**: Mol. wt. determined by a vapor pressure osmometer was 2000—2100.

Table II. Copolymerization of *p*-substituted β-methylstyrenes (M_2) with MAn (M_1)
$[M_1]=[M_2]=1.0$ mol./l. $[AIBN]=1.0\times10^{-2}$ mol./l.

p-Substituent of M_2		Time hr.	Yield %	%/hr.	Copolymer				
					C%	H%	m_1/m_2	Soft. p., °C	η_{sp}/c
CH_3O-	t	0.61	6.1	10.0	66.83	5.87	0.99	260—270	insol.
CH_3-	t	3.45	8.6	2.49	71.56	6.26	0.97	270—290	0.390
H-	t	1.12	2.13	1.90	71.15	5.78	0.96	260—270	0.127
Cl-	t	13.65	10.8	0.79	Cl%	13.20	1.20	220—240	—

t: trans 100%.

Table III. Effect of the monomer feed ratios on the copolymerization of *p*-substituted β-methylstyrenes (M_2) with (MAn (M_1)
$[M_1+M_2]=2.0$ mol./l. $[AIBN]=1.0\times10^{-2}$ mol./l.

M_1/M_2	*p*-Substituent							
	CH_3O-		CH_3-		H-		Cl-	
	m_1/m_2	%/hr.	m_1/m_2	%/hr.	m_1/m_2	%/hr.	m_1/m_2	%/hr.
0.43	—	—	—	—	0.92	0.8	—	—
0.67	—	—	—	—	0.93	1.2	—	—
1.00	0.99	10.0	0.97	2.5	0.96	2.1	1.20	0.97
1.50	1.07	12.6	0.97	2.9	1.04	2.9	1.33	1.11
2.33	1.02	14.7	0.97	5.3	0.98	3.5	1.09	1.29
4.00	1.05	29.7	1.02	5.8	1.08	4.2	1.05	1.83
9.00	1.06	22.3	1.02	5.9	1.00	4.6	1.06	1.33

a sealed glass tube at 60°C, using 2, 2'-azobisisobutyronitrile as the initiator and benzene as the solvent. β-Substituted styrenes of a known isomeric purity were used. The results are shown in Tables I, II and III.

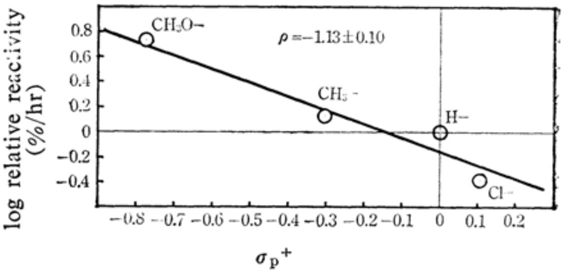

Fig. 1. Correlation of log relative reactivity and $\sigma_p{}^+$ for the copolymerization of *p*-substituted-β-methyl-Sts with MAn.

All the β-substituted styrenes were found to be markedly less reactive than styrene. The general low reactivity may be attributed to the steric factor of the β-substituent,[5] and the magnitude of the steric factor may be considered to differ from one substituent to another. In Table I, however, a tendency is observed for the rate of the copolymerization of the β-substituted styrenes with MAn to decrease approximately with the increase in the electron-attracting character of β-substituents, except for the case of stilbenes. Thus, the effect of β-substituents is rather complicated; they exert a predominant steric effect and a

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[5] T. Alfrey, Jr., J. Bohrer and H. Mark, "Copolymerization," Interscience Pub. Inc., N. Y. (1952), p. 51.

polar effect as well as, presumably, a resonance effect.

On the other hand, the effect of *p*-substituents of β-methylstyrenes is a little more clean-cut, as is shown in Table II. Since these systems gave 1:1 copolymers as Table III shows, the logarithms of the relative reactivities (%/hr. in Table II) of *p*-substituted β-methylstyrenes to that of β-methylstyrene are plotted against Brown-Okamoto $\sigma_p{}^+$ values for the substituents (in Fig. 1). When the Hammett σ_p was used instead of $\sigma_p{}^+$, the correlation was worse, the standard deviation of ρ being ± 0.9. A better linearity was observed for $\sigma_p{}^+$ with the ρ value of -1.13 ± 0.10, showing that the polar effect operates in this case. This result seems reasonable, since the steric factor around the double bond may not be altered by the *p*-substituent.

Table III demonstrates that these β-methylstyrenes formed 1:1 alternating copolymers with MAn independent of the monomer feed ratios, and that the rate of copolymerization increased with the increase in the fraction of MAn, sometimes showing maxima.

It should be noted that β-substituted styrenes of a comparatively high reactivity show thermal copolymerization with MAn, and that these copolymerization mixtures exhibit a deep yellow color. The phenomena of discoloring may be due to the formation of charge transfer complexes between the donor molecules (β-substituted-St-derivatives) and the accepter molecule (MAn), as reported by Walling⁶⁾ and Barb.⁷⁾ We are now studying whether the complex makes any contribution to the copolymerization reaction.

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6) C. Walling, D. Seymour and K. B. Wolfstirn, *J. Am. Chem. Soc.*, **70**, 1544 (1947).

7) W. G. Barb, *Trans. Faraday Soc.*, **49**, 143 (1953).