

ultraviolet absorption spectra of some thirty hydroxynaphthalenes.

2. The correlation of spectra with molecular structure has been attempted.

3. It appears that the changes produced in the

naphthalene curve on substitution are due chiefly to the stabilization of polarized structures along two axes in the molecule, normal to one another.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

## Copolymerization of Butyl Vinylsulfonate. Comments on Sulfur Shell Expansion<sup>1</sup>

BY C. G. OVERBERGER, DAVID E. BALDWIN AND HARRY P. GREGOR

Since the development of the copolymer composition<sup>2</sup> equation, a large amount of copolymerization data has been obtained in the form of reactivity ratios. Such studies permit one to obtain, by a simple experimental procedure, useful information relating to the reactivity of double bonds toward radicals<sup>3a,3b,3c</sup> and polar factors<sup>3d,3e,3f</sup> in radical reactions. In particular, we were interested in information regarding the expansion of the sulfur shell in radical transition states.

This paper describes the copolymerization of butyl vinylsulfonate with vinyl acetate, vinyl chloride, styrene, methyl acrylate and vinylidene chloride.

Heuer<sup>4</sup> has described the copolymerization of small quantities of vinylsulfonic acid or one of its soluble salts with aqueous suspensions of vinyl acetate, vinyl chloride and other monomers, but no polymer analyses are reported. Since the polymers gave stable emulsions, it was concluded that vinylsulfonic acid entered the copolymer chain. Alderman and Hanford<sup>5</sup> reported a very slow bulk polymerization of vinylsulfonic acid and ethyl vinylsulfonate catalyzed by ultraviolet irradiation or benzoyl peroxide. They also reported copolymers prepared in bulk of ethyl vinylsulfonate and vinylsulfonic acid with vinyl acetate, methyl methacrylate and methyl- $\alpha$ -chloroacrylate and other monomers, but no polymer analyses were reported. The emulsion copolymerization of vinylsulfonic acid with chloroprene was likewise reported and it was shown by analyses that some vinylsulfonic acid had entered the chain.

### Experimental

**Materials.**—The styrene, vinyl acetate, vinylidene chloride, methyl acrylate and vinyl chloride were commer-

cial products, and except for the vinyl chloride, were fractionally distilled through a 12-inch "Vigreux" column immediately before use. The vinyl chloride was passed through two bubblers containing 10% sodium hydroxide solution, one containing solid flake sodium hydroxide, and one containing "Drierite" before being condensed in a receiver cooled in a Dry Ice-acetone-bath and protected from moisture with a drying tube. The *n*-butyl vinylsulfonate was prepared by the method of Whitmore and Landau.<sup>6</sup> From 187.5 g. (1.5 moles) of sodium sulfite and 427.5 ml. (937.5 g., 4.95 moles) of ethylene dibromide was obtained 413 g. of crude dry salts which, with 225 g. (1.1 moles) of phosphorus pentachloride, yielded 195.5 g. (65%) of 2-bromoethanesulfonyl chloride,  $n_D^{20}$  1.5230, b. p. 85° at 3 mm. (82° at 5 mm.,  $n_D^{20}$  1.5227).<sup>6</sup> From 327.5 g. (1.58 moles) of 2-bromoethanesulfonyl chloride and 107.3 g. (1.45 moles) of *n*-butyl alcohol there was obtained 90 g. (36%) of *n*-butyl vinylsulfonate, b. p. 89° at 5 mm.,  $n_D^{20}$  1.4410 (116° at 15 mm.,  $n_D^{20}$  1.4416)<sup>6</sup>. The *n*-butyl vinylsulfonate was redistilled immediately before use.

**Procedure.**—With the exception of the vinyl chloride samples the monomers (40 millimoles of total monomers) were weighed into small test-tubes on an analytical balance, cooled, mixed well, and transferred to ampoules containing 0.0484 g. ( $2 \times 10^{-4}$  mole, 0.5 mole %) of benzoyl peroxide which were then chilled thoroughly and sealed. The vinyl chloride samples were made up by adding the approximate desired amount of vinyl chloride to weighed ampoules containing known amounts of butyl vinylsulfonate and 0.05 g. (approximately 0.5 mole %) of benzoyl peroxide, after which the ampoules were sealed and reweighed on an analytical balance and the amount of vinyl chloride used obtained by difference. The above quantities were doubled in cases where a low yield of copolymer was anticipated. When the degree of conversion was judged to be near 10%, as evidenced by the change in viscosity, the ampoules were removed, chilled, and opened. In each case where the sample contained 90 mole % or more of butyl vinylsulfonate far less than 10% polymerization was achieved in several days of heating. The copolymers from the samples containing 95, 90 and 70 mole % of vinylidene chloride precipitated from the monomer mixtures during the reaction. Each polymerization mixture was diluted with 1–5 ml. of the solvent for the copolymer, poured dropwise with stirring into 150 ml. of the precipitant, and the tube rinsed with 1 ml. of solvent. The styrene copolymers were precipitated in methanol, redissolved in 5 ml. of methyl ethyl ketone and reprecipitated twice more. Several drops of 1:1 hydrochloric acid were added at the end of each precipitation to coagulate the copolymer. The vinylidene chloride copolymers from the monomer mixtures containing 50 mole % or more of vinylidene chloride were purified by the same technique except that 10–15 ml. of hot dioxane was used as a solvent in each case. Those from the mixtures containing 30 mole % of vinylidene chloride were too soft to handle if the methanol was at room temperature and reprecipitation and drying were carried out at 5–10°. The copolymer from the mixture containing 5 mole % of vinyl-

(1) This research was supported by a contract from the Office of Naval Research.

(2) (a) Alfrey and Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944); (b) Mayo and Lewis, *THIS JOURNAL*, **66**, 1594 (1944); (c) Wall, *ibid.*, **66**, 2050 (1944).

(3) (a) Lewis, Mayo and Hulse, *ibid.*, **67**, 1701 (1945); (b) Alfrey, Merz and Mark, *J. Polymer Sci.*, **1**, 37 (1946); (c) Lewis, Walling, Cummings, Briggs and Mayo, *THIS JOURNAL*, **70**, 1519 (1948); and succeeding papers, among which are Mayo, Lewis and Walling, *ibid.*, **70**, 1529 (1948); (d) Walling, Briggs, Wolfstirn and Mayo, *ibid.*, **70**, 1537 (1948); (e) Alfrey and Price, *J. Polymer Sci.*, **2**, 101 (1947); (f) Price, *ibid.*, **3**, 772 (1948).

(4) Heuer, German Patent 724,889 (1942); *C. A.*, **37**, 5808 (1943); Heuer, U. S. Patent 2,300,920 (1942).

(5) Alderman and Hanford, U. S. Patent 2,348,705 (1944).

(6) W. F. Whitmore and Landau, *THIS JOURNAL*, **68**, 1797 (1946).

idene chloride was soluble in methanol and was purified as described below. All other copolymers were purified and dried by the following procedure. The contents of the polymerization tubes, after diluting with toluene, were poured into hexane (b. p. 69°) and the tubes rinsed with 1 ml. of toluene which was also added to the hexane. The hexane was decanted, after centrifuging if necessary. The copolymer, usually a viscous liquid or soft solid at this point, was dissolved in sufficient toluene (benzene was unsatisfactory because of its high freezing point) to make approximately a 5% solution and added dropwise with

good stirring to 25 volumes of hexane cooled to below -20°. The copolymer precipitated as fine shreds which, when the hexane was allowed to warm to room temperature, became soft and sticky, allowing the hexane to be decanted without loss of copolymer. Each copolymer was subjected to three to five such precipitations. The hexane was allowed to warm only to a point where it could be decanted conveniently but at which the copolymer shreds were only lightly stuck to each other; the softer the copolymer the lower the temperature. A little practice with each copolymer in the previous precipitations enabled this point to be judged without difficulty. The beaker containing the copolymer was then chilled thoroughly in Dry Ice, whereupon the copolymer again became hard, and any lumps present were broken up. The chilled beaker and copolymer were placed in a vacuum desiccator (preferably which had been previously thoroughly chilled in Dry Ice) fitted with a still head, the receiver of which was kept cold by a Dry Ice-acetone-bath. The system was evacuated immediately to 1-2 mm. pressure and maintained there for two hours before opening. The copolymers were dried as shreds which could be powdered at room temperature; if slightly soft, they were powdered after cooling. If the evacuation was not thorough and rapid, if supernatant hexane was present when drying was commenced, or if the copolymer was allowed to warm or the system opened before all the hexane had been evaporated, the copolymer usually melted into a sticky lump which could not be dried completely and had to be reprecipitated. Final drying before analysis<sup>7</sup> of all copolymers was at 1-3 mm. at room temperature for 24 hours. The results are tabulated in Table I.

TABLE I

COPOLYMERIZATION OF REFERENCE MONOMERS ( $M_1$ ) WITH *n*-BUTYL VINYSULFONATE ( $M_2$ ) WITH 0.5 MOLE % BENZOYL PEROXIDE

Mole % $M_2$ in monomer mixture	Reaction time, hr.	Weight % polymerization	Polymer composition	
			% S	Mole % $M_2$
Vinyl Acetate ( $M_1$ )- <i>n</i> -Butyl Vinylsulfonate ( $M_2$ ) at 70°				
3.71	0.50	11.1	9.36	32.55
7.80	0.92	17.3	10.83	39.49
29.53	2.54	5.2	12.82	50.04
49.96	7.5	3.4	13.21	52.28
69.79 <sup>a</sup>			13.94	56.88
90.17	260	2.6	17.02	78.03

<sup>a</sup> Average of three determinations.

Vinyl Chloride ( $M_1$ )-*n*-Butyl Vinylsulfonate ( $M_2$ ) at 70°

4.54	0.75	18.9	4.55	10.36
8.06	0.75	16.9	6.69	16.55
21.87	4.08	10.8	10.90	32.52
47.62	10.11	3.3	13.68	47.09
69.98	46.5	1.0	15.18	57.04
70.83	20.5	1.7	15.64	60.46
89.56	94.0	1.2	17.59	77.51

Styrene ( $M_1$ )-*n*-Butyl Vinylsulfonate ( $M_2$ ) at 90°

5.05	0.20	8.4	1.20	3.99
10.20	0.25	10.9	1.98	6.68
31.02	0.42	12.6	4.53	16.08
30.36	0.17	4.9	4.66	16.59
52.17	0.58	12.8	6.16	22.61
71.56	1.16	7.2	8.86	34.50
71.44	0.84	6.1	8.31	31.96
90.17	5.0	1.3	14.66	65.63

Methyl Acrylate ( $M_1$ )-*n*-Butyl Vinylsulfonate ( $M_2$ ) at 70°

5.13	0.57	14.0	1.20	3.32
10.64	0.33	16.0	1.15	3.18
35.35	0.38	44.0	4.64	14.04
31.00	0.33	6.8	2.33	6.63
52.87	1.33	12.0	5.01	15.33
73.03	11.8	11.0	9.05	31.17
69.86	6.51	0.03	7.21	23.48
91.38	288	3.8	14.59	60.75

Vinylidene Chloride ( $M_1$ )-*n*-Butyl Vinylsulfonate ( $M_2$ ) at 80°

5.12	0.20	4.5	0.0	0.00
10.21	0.30	4.8	0.65	1.99
31.45	1.00	9.6	1.74	5.46
31.62	1.33	12.0	1.50	4.68
51.49	2.75	5.7	3.62	11.84
72.44	16.0	0.69	6.62	23.24
70.34	15.0	1.2	7.15	25.43
95.05	75.8	0.23	14.14	60.75

## Results and Discussion

The reactivity ratios are tabulated in Table II. The copolymer composition curves are recorded in Fig. 1. The compositions of the monomer mixtures are those obtained by averaging the initial and final compositions.

TABLE II

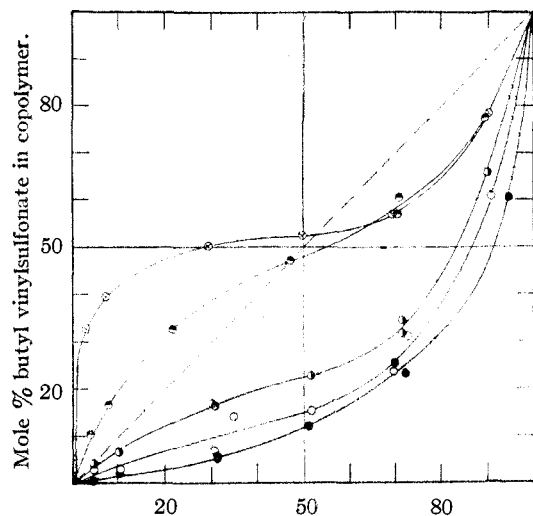
MONOMER REACTIVITY RATIOS IN COPOLYMERIZATIONS OF *n*-BUTYL VINYSULFONATE ( $M_2$ ) WITH REFERENCE MONOMERS

$M_1$	$r_1$	$r_2$	$r_1 r_2$
Vinyl acetate	0.04 ± 0.01	0.20 ± 0.05	0.005
Vinyl chloride	0.35 ± 0.05	.30 ± 0.05	.105
Styrene	2.5 ± 1.0	.13 ± 0.03	.325
Methyl acrylate	5.0 ± 1.5	.11 ± 0.03	.55
Vinylidene chloride	7.5 ± 0.6	.065 ± 0.007	.49

The reactivity ratios and their probable errors were obtained by the use of a previously described procedure.<sup>8</sup> In this method, the experimental points are fitted with two curves which represent the limits of reasonable values of  $r_1$  and  $r_2$ . The reactivity ratios are calculated for the curves and the averages of these limiting values are taken to be the most probable values of  $r_1$  and  $r_2$ . The variations of the latter from the limiting values are accepted as the probable errors. The evidence clearly shows that butyl vinylsulfonate is comparable in reactivity to vinyl acetate and vinyl chloride and much less reactive than

(7) Analyses were performed by Mr. Ralph E. Schachat of the Microanalytical Laboratory of the Polytechnic Institute of Brooklyn and by the Clark Microanalytical Laboratory, Urbana, Ill.

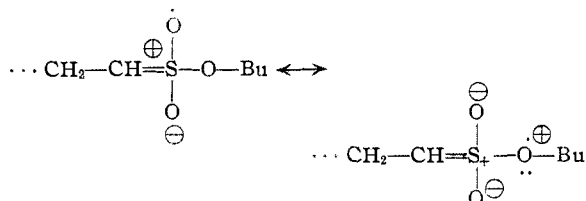
(8) Alfrey, Goldberg and Hohenstein, *THIS JOURNAL*, **68**, 2464 (1946).



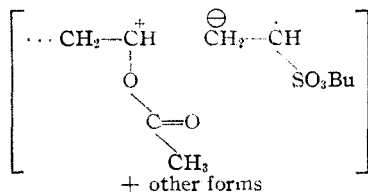
Mole % butyl vinylsulfonate in monomer mixture.

Fig. 1.—Copolymerization of butyl vinylsulfonate with reference monomers: ⊗, vinyl acetate; ⊙, vinyl chloride; ●, styrene; ○, methyl acrylate; ●, vinylidene chloride.

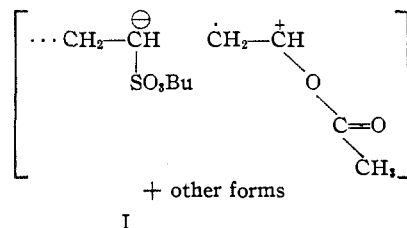
styrene, methyl acrylate and vinylidene chloride. Thus, it is reasonable to assume that the transition state involved in the formation of a growing chain ending in butyl vinylsulfonate  $\cdots\text{CH}_2\text{—CH—SO}_3\text{Bu}$  is not appreciably resonance stabilized by such forms as



which involve expansion of the sulfur shell beyond an octet.<sup>9</sup> Strong alternation occurs in the copolymer with vinyl acetate and vinyl chloride as noted by the crossover on the copolymer composition curves (Fig. 1). This is usual for two monomers, one of which can give rise to a radical of high electron density and one having a double bond of low electron density. On the basis of a one electron transfer,<sup>3d</sup> it is interesting that there is as much alternation as noted; thus, the possible transition state (I) is indicated below.



(9) A similar study has been reported by Price and Zomlefer, *THIS JOURNAL*, **72**, 14 (1950), by copolymerization studies of methyl vinylsulfone with other monomers. Professor Price kindly sent us a copy of his paper before the submitting of our work.



It is possible that there is some contribution to the transition state from forms other than those involving a one electron transfer, which also might account for alternation. The  $Q$ - $e$  values estimated from our data are  $Q = 0.021$ ,  $e = +0.84$  (this estimation was based on  $r_1$  and  $r_2$  values in the *n*-butyl vinylsulfonate–vinylidene chloride system using  $Q = 0.16$ ,  $e = 0.0$  as the values for vinylidene chloride).

Although the experimental details are not described here it was noted that vinylsulfonic acid<sup>10</sup> did not readily polymerize<sup>5</sup> under the conditions used with radical and cationic catalysis. However, when the sodium or barium salts were employed, polymers were obtained which could be converted to polyvinyl sulfonic acid by ion exchange. The fact that the anion of vinylsulfonic acid will readily polymerize by radical catalysis may indicate increased resonance

stabilization in the anion,<sup>11</sup>  $\cdots\text{CH}_2\text{—CH—}\overset{\oplus}{\text{S}}\text{—O}^{\ominus}$

The results of ion exchange experiments with polysulfonic acids will be reported separately.

**Acknowledgment.**—We gratefully acknowledge the advice of Professor Turner Alfrey, Jr., of the Polytechnic Institute of Brooklyn.

### Summary

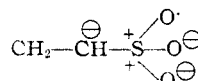
1. Butyl vinylsulfonate has been copolymerized with vinyl acetate, vinyl chloride, styrene, methyl acrylate and vinylidene chloride and the reactivity ratios obtained.

2. The results indicate that butyl vinylsulfonate is comparable in reactivity to vinyl acetate and vinyl chloride and indicates that the sulfur shell does not appreciably expand its octet in a radical of the type  $\cdots\text{CH}_2\text{—}\overset{\oplus}{\text{C}}\text{H—SO}_3\text{Bu}$ . Alternation of this monomer with vinyl acetate and vinyl chloride was also noted.

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(10) Kohler, *Am. Chem. J.*, **19**, 728 (1897); **20**, 680 (1898); **21**, 349 (1899); see also ref. 5.

(11) The referee has pointed out that such electronic distributions as



which do not involve expansion of the sulfur octet could contribute.