

## Copolymerization Characteristics of Ethyl Vinyl Ether and Its Beta-Bromo and Beta-Carbethoxy Derivatives

CHARLES C. PRICE,\* *Department of Chemistry, University of Notre Dame, Notre Dame, Indiana*, and THEODORE C. SCHWAN,† *Valparaiso University, Valparaiso, Indiana*

### INTRODUCTION

The importance of polar groups of opposite electrical influence in promoting copolymerization of monomer pairs prompted an investigation of the possible influence two such opposite groups might have at opposite ends of the same monomer molecule. The ether group was chosen as the electron-releasing group (negative  $e$ ) and bromine and carbethoxy as the electron-accepting groups (positive  $e$ ).

In addition data are reported on the copolymerization characteristics of ethyl vinyl ether, enabling an estimate of its copolymerization parameters,  $Q$  and  $e$ .

### EXPERIMENTAL

All microanalyses were performed by Micro Tech. Laboratories, Skokie, Illinois.

**$\beta$ -Bromovinyl Ethyl Ether.** To a solution of 54.2 g. (0.752 mole) of ethyl vinyl ether in 250 ml. of cyclohexane, cooled to  $-10$  to  $-15^\circ$  and containing two drops of triethanolamine and two pellets of potassium hydroxide, bromine was added dropwise with stirring until a permanent straw color was produced. This required 118 g. (0.739 mole) of bromine. After adding 114 g. (0.765 mole) of diethylaniline, the mixture was heated to boiling under reflux for two hours. The gray crystals of diethylaniline hydrobromide were separated, washed with additional cyclohexane, and the filtrate was distilled to give 78 g. of crude bromovinyl ethyl ether, b.p.  $35-45^\circ$  (15-20 mm.).

Redistillation through a 30-cm. tantalum-spiral packed column gave the results given in Table I. Fractions 25-4 to 25-7, inclusive, were assumed to be fairly pure  $\beta$ -bromovinyl ethyl ether; 35.7 g. (31.5%).

\* Present address: John Harrison Laboratory of Chemistry, University of Pennsylvania, Philadelphia 4, Pa.

† The authors are indebted to the Research Corporation for support of this investigation. Abstracted from the Ph.D. dissertation of T. C. S., submitted to the University of Notre Dame, June, 1953. A preliminary report of some of the data has appeared in *Proc. Indiana Acad. Sci.*, 63, 103 (1953).

TABLE I  
FRACTIONAL DISTILLATION OF CRUDE  $\beta$ -BROMOVINYL ETHYL ETHER

Fraction	Wt., g.	B.p., final, °C. (30 mm.)	$n_D^{20}$
25-1	0.5	43.5	1.4238
25-2	5.9	46.5	1.4685
25-3	8.0	48.0	1.4702
25-4	10.5	48.5	1.4723
25-5	10.4	52.0	1.4728
25-6	9.8	52.5	1.4728
25-7	5.0	55.0	1.4715
25-8	2.1	58.5	1.4691
25-9	3.6	64.0	1.4561

The products of several such preparations were combined and dried over a mixture of calcium chloride and potassium carbonate. The combined products were filtered and distilled through the 60-cm. glass helix-packed column at 25 mm. pressure with partial take-off, total condensation head. Initially, the reflux ratio was ten to one, later reduced to five to one. Purity of the distillate was followed by refractive index. The distillation proceeded as in Table II.

TABLE II  
REFRACTIONAL DISTILLATION OF  $\beta$ -BROMOVINYL ETHYL ETHER

Fraction	Wt., g.	Boiling range, final, °C. (25 mm.)	$n_D^{20}$
48-1	6.4	42.0	1.4646
48-2	6.2	39.6	1.4645
48-3	7.5	39.6	1.4650
48-4	7.2	43.0	1.4662
48-5	6.6	45.1	1.4679
48-6	9.3	47.0	1.4701
48-7	8.7	48.0	1.4709
48-8	10.4	48.5	1.4722
48-9	8.3	49.3	1.4730
48-10	8.7	49.7	1.4735
48-11	8.4	49.6	1.4738
48-12	9.0	49.4	1.4737
48-13	8.3	49.4	1.4738
48-14	7.0	49.3	1.4739
48-15	41.7	49.8	1.4741
48-16	8.9	49.1	1.4739
48-17	8.1	49.3	1.4739
48-18	8.7	49.4	1.4740
48-19	9.1	49.3	1.4739
48-20	9.3	49.4	1.4739
48-21	9.2	49.3	1.4739
48-22	8.6	49.3	1.4739
48-23	9.0	49.3	1.4732
48-24	1.1	p	1.4733

Densities of several fractions were determined:

Fraction.....	48-10	48-11	48-14	48-15	48-17
$d_4^{20}$ .....	1.4242	1.4237	1.4242	1.4245	1.4243

ANALYSIS: *Calcd. for*  $C_4H_7OBr$ : C, 31.81; H, 4.67; Br, 52.92;  $MR_D$ , 29.61. *Found*: C, 32.06; H, 4.79; Br, 53.09,  $MR_D$ , 29.80.

**$\beta$ -Chlorovinyl Methyl Ether.** Although the preparation of  $\beta$ -chlorovinyl ethyl and butyl ethers through addition of chlorine to the corresponding vinyl ethers, followed by diethylaniline dehydrochlorination, has been reported<sup>1</sup> since our work was completed, attempted preparation of  $\beta$ -chlorovinyl methyl ether by this type of procedure in our hands, starting with methyl vinyl ether and using a variety of dehydrochlorinating agents, including diethylaniline, sodium tertiary butoxide, tri-*n*-butylamine, calcium oxide, and numerous others, gave liquid products boiling over a wide range from which no pure fractions were isolated. In a few experiments, fractions boiling at about 125–130°,  $n_D^{21}$  *ca.* 1.43,  $d_{21}^{21}$  *ca.* 1.15 were obtained, which may have been impure samples of  $\beta$ -chlorovinyl methyl ether. At least, the fractions boiling higher and lower had lower densities and refractive indices, as was the case for  $\beta$ -bromovinyl ethyl ether described above.

Further attempts to prepare  $\beta$ -chlorovinyl ether by reaction of acetylene with *tert*-butyl hypochlorite in methanol and by reaction of  $\beta$ -chlorovinyl iodide with sodium methoxide each produced a spontaneously inflammable gas, presumably chloroacetylene.

**Purification of Monomers.** Maleic anhydride (Matheson) was recrystallized from chloroform, m.p. 56–56.5°. Vinylidene chloride (Dow) was distilled at room temperature from a common distilling flask into a receiver immersed in an ice bath; the middle fraction was taken. Ethyl fumarate (Eastman) was dried over calcium chloride and potassium carbonate and distilled from a Claisen flask at atmospheric pressure (741.8 mm.), b.p. 215.2–215.6°. The rest of the monomers were distilled with exclusion of air through a 60-cm. glass helix-packed column equipped with a total condensation, partial take-off head. Only the middle fractions were used. Boiling points were as given in Table III.

TABLE III  
PROPERTIES OF MONOMERS

Monomer	Source	Boiling range, °C.	Pressure, mm.	$n_D^{20}$
Styrene.....	Matheson	27.5–28.0	9	1.5468
Methyl acrylate.....	Matheson	79.0–79.5	743.6	1.4026
Vinyl acetate.....	Matheson	71.8–72.1	742.9	1.3944
Acrylonitrile.....	Matheson	76.0–76.1	740.6	1.3912
Ethyl vinyl ether.....	Matheson	35.3–35.4	744.2	1.3771
Methyl methacrylate.....	Rohm & Haas	45.3–45.8	100	—
Ethyl $\beta$ -ethoxyacrylate.....	“ “ “	71.7–72.2	4	1.4475
$\beta$ -Bromovinyl ethyl ether....	—	49.1–49.6	25	1.4739

**Preliminary Experiments on the Copolymerization of Various Monomers with  $\beta$ -Bromovinyl Ethyl Ether.** Soft glass test tubes approximately 150 mm. by 18 mm. were drawn out to a diameter of 3 mm. about 40 mm. from the mouth of the test tubes. Using a balance sensitive to 5 mg., 0.1 g. (0.004 mole) of benzoyl peroxide, 6.04 g. (0.04 mole) of  $\beta$ -bromovinyl ethyl ether, and 0.04 mole of the second monomer were weighed into the test tubes. The test tubes were then placed in an ice bath, sealed off at the constriction, and placed in a constant temperature water bath maintained at  $60 \pm 1^\circ\text{C}$ . An attempt was made to remove the test tubes from the bath when approximately 10% conversion had taken place as indicated by a slight increase in viscosity of the solution. In some instances, conversion was determined by pouring the solution into methyl alcohol, drying and weighing the resulting precipitated copolymer. Monomers used and results were as in Table IV. Solid copolymer separated

TABLE IV

COPOLYMERIZATIONS WITH  $\beta$ -BROMOVINYL ETHYL ETHER (1:1)

Comonomer	Time, hours	Conversion, %
Styrene.....	20.2	20
Methyl acrylate.....	20.4	10
Methyl methacrylate.....	2.7	24
Maleic anhydride.....	97	10
Acrylonitrile.....	26.5	1.8
Vinylidene chloride.....	4	4
Vinyl acetate.....	97	None
Ethyl fumarate.....	189	None
Ethyl vinyl ether.....	70	None

during copolymerization with maleic anhydride, acrylonitrile, and vinylidene chloride. Elemental analyses were obtained for the styrene, methyl acrylate, methyl methacrylate, acrylonitrile, and vinylidene chloride copolymers (Table V).

TABLE V

COMPOSITION OF  $\beta$ -BROMOVINYL ETHYL ETHER COPOLYMERS (1:1)

Monomer	$M_1^a$	% C	% H	% Br	% N	$m_1^b$ (C)	$m_1^c$ (Br)
Styrene.....	0.501	90.57	7.69	0.90	—	0.027	0.017
Methyl acrylate.....	0.499	55.13	7.13	1.71	—	0.0036	0.032
Methyl methacrylate...	0.501	59.63	8.30	0.20	—	0.0083	0.0038
Acrylonitrile.....	0.501	62.38	5.58	7.50	15.61	0.153	0.142
Vinylidene chloride.....	0.454	25.81	2.71	<sup>d</sup>	—	0.146	0.153 <sup>d</sup>

<sup>a</sup> Mole fraction of  $\beta$ -bromovinyl ethyl ether in monomer mixture.

<sup>b</sup> Mole fraction of  $\beta$ -bromovinyl ethyl ether in copolymer, calculated from carbon analysis.

<sup>c</sup> Mole fraction of  $\beta$ -bromovinyl ethyl ether in copolymer, calculated from bromine analysis.

<sup>d</sup> 10.91 mg. sample of copolymer gave 29.42 mg. silver halide.

Attempts to copolymerize  $\beta$ -bromovinyl ethyl ether with acrylonitrile at 60° in dimethylformamide, chlorobenzene, dioxane, acetonitrile, and cyclohexanone solutions failed to give detectable polymer.

**Copolymerization Procedure.** The following procedure was used in all subsequent copolymerizations except as noted. Mixtures of monomer pairs containing a total of 0.08 mole of monomers and 0.00016 mole (0.2 mole per cent) of benzoyl peroxide were made up over a wide range of composition. The monomers were weighed to the nearest 0.5 mg. on an analytical balance in soft glass test tubes approximately 150 mm. by 18 mm. drawn out to a diameter of about 3 mm. about 40 mm. from the mouth of the test tube. Immediately after the final weighing, the tubes were placed in an ice bath, flushed with nitrogen for one minute, and sealed. The tubes were then placed in a constant temperature water bath maintained at  $80 \pm 0.2^\circ$ . When approximately 10% conversion had taken place, as indicated by an increase in viscosity, the tubes were removed from the bath, cooled in an ice bath, opened, and poured into 250 ml. of filtered methyl alcohol, filtered, and dried. Yield was computed on the basis of this dry, crude weight. Samples were prepared for analysis by redissolving the copolymer in 35 ml. of benzene, filtering and reprecipitating the copolymer in 250 ml. of filtered methyl alcohol. All copolymers containing acrylonitrile separated from the monomer solution during copolymerization. These copolymers also were insoluble in benzene. They were purified by dissolving in dimethylformamide, filtering and reprecipitating at least twice, and were dried for at least 48 hours in a vacuum oven at 65° and 30 mm. pressure. Results were as summarized in Tables VI to XII.

Both the "intersection" method of Mayo and Lewis<sup>2</sup> and the "curve-fitting" method of Alfrey<sup>3</sup> were used to determine  $r_1$  and  $r_2$  for the co-

TABLE VI  
COPOLYMERIZATION OF  $\beta$ -BROMOVINYL ETHYL ETHER ( $M_1$ )  
WITH STYRENE ( $M_2$ )

$M_1^a$	Time, hours	Conver- sion, %	% C	% H	% Br	$m_1^b$ (C)	$m_1^c$ (Br)
0.249	4.0	2.2	89.91	7.52	0.73	0.0389	0.0138
0.259 <sup>d</sup>	0.6	1.0	90.40	8.18	1.70	0.0308	0.0322
0.499	24.7	11.6	90.83	7.90	1.36	0.0237	0.0257
0.624	26.2	6.0	89.75	7.57	1.93	0.0416	0.0365
0.748	41.9	2.8	87.94	7.53	3.47 <sup>e</sup>	0.0716	0.0656 <sup>e</sup>
0.872	47.0	1.0	87.37	7.11	4.93	0.0810	0.0932
0.878 <sup>f</sup>	122.0	3.5	89.47	8.09	2.63	0.0462	0.0498

<sup>a</sup> Mole fraction of  $\beta$ -bromovinyl ethyl ether in monomer mixture.

<sup>b</sup> Mole fraction of  $\beta$ -bromovinyl ethyl ether in copolymer, calculated from carbon analysis.

<sup>c</sup> Mole fraction of  $\beta$ -bromovinyl ethyl ether in copolymer, calculated from bromine analysis.

<sup>d</sup> Contained only 0.00008 mole of benzoyl peroxide.

<sup>e</sup> Recheck of bromine analysis gave 3.80% bromine. Using this value, mole fraction of  $\beta$ -bromovinyl ethyl ether in copolymer becomes 0.0719.

<sup>f</sup> Contained 0.0002 mole of benzoyl peroxide.

polymers of Table VI. The "intersection" method, using the carbon analysis, gave the following values:  $r_1 = 0.02 \pm 0.02$ ;  $r_2 = 37.5 \pm 2.0$ . These results are in agreement with the values found by "curve-fitting." The bromine analysis did not give a solution by the "intersection" method. Using the "best probable" values,  $r_1 = 0.02$  and  $r_2 = 38$ , and  $Q = 1$  and  $c = -0.8$  for styrene, gave  $Q = 0.017$  and  $e = 0.28$  for  $\beta$ -bromovinyl ethyl ether.

TABLE VII  
COPOLYMERIZATION OF  $\beta$ -BROMOVINYL ETHYL ETHER ( $M_1$ ) WITH METHYL ACRYLATE ( $M_2$ )

$M_1$	Time, hours	Conversion, %	% C	% H	% Br	$m_1$ (C)	$m_1$ (Br)
0.109 <sup>a</sup>	0.4	25.9	55.17	7.01	0.45	0.0262	0.0085
0.250	2.2	23.0	55.48	7.14	0.70	0.0133	0.0132
0.350	1.2	17.8	55.51	7.09	0.74	0.0121	0.0140
0.500	24.5	5.7	55.01	7.14	0.98	0.0330	0.0185
0.606	118.8	2 <sup>b</sup>					
0.750	239.9	<sup>c</sup>					

<sup>a</sup> Contained only 0.00008 mole of benzoyl peroxide.

<sup>b</sup> The copolymer was found to be soluble in methyl alcohol but was precipitated from methyl alcohol solution by addition of water. The sample was lost in attempted purification.

<sup>c</sup> No detectable conversion.

The "intersection" method gave no satisfactory solution for  $r_1$ , but indicated  $r_2$  was  $31.5 \pm 2.5$ . No direct solution for  $Q$  and  $e$  for  $\beta$ -bromovinyl ethyl ether could be obtained from these data. However, solution for  $Q$  and  $e$  was obtained by simultaneous solution of the following two equations using data obtained from Table VI in the first equation (styrene) and data from Table VII in the second equation:

$$r_2 = Q_2/Q_1 \cdot \exp \{ -e_2(e_2 - e_1) \}$$

$$r_{2'} = Q_2'/Q_1 \cdot \exp \{ -e_{2'}(e_{2'} - e_1) \}$$

TABLE VIII  
COPOLYMERIZATION OF ETHYL VINYL ETHER ( $M_1$ ) WITH STYRENE ( $M_2$ )

$M_1$	Time, hours	Conversion, %	% C	% H	% O <sup>a</sup>	$m_1$ (C)	$m_1$ (O)
0.200	3.4	5.4	92.30	7.86	—	<sup>b</sup>	—
0.201	2.8	4.2	92.09	7.94	—	0.0066	—
0.500	9.9	9.7	92.05	7.79	0.16	0.0082	0.0072
0.500	19.5	14.3	91.83	7.96	0.21	0.0168	0.0095
0.799	50.6	9.7	92.04	7.98	—	0.0086	—
0.799	141.5	12.3	91.50	8.03	0.47	0.0297	0.0212

<sup>a</sup> Obtained by difference.

<sup>b</sup> The reported carbon percentage was higher than the theoretical value for either component.

Solution using  $r_2 = 38$ ,  $r_2' = 31.5$ ,  $Q_2 = 1$ ,  $Q_2' = 0.42$ ,  $e_2 = -0.8$ , and  $e_2' = 0.6$  gave  $Q = 0.010$  and  $e = 0.42$  for  $\beta$ -bromovinyl ethyl ether.

The "intersection" method gave no solution for  $r_1$  and  $r_2$ , but indicated the "best probable" value for  $r_2$  to be  $80 \pm 40$ , in reasonable agreement with previous reports of  $r_2 = 90 \pm 20$  and  $r_1 = 0$ .<sup>4</sup>

TABLE IX  
COPOLYMERIZATION OF ETHYL VINYL ETHER ( $M_1$ )  
WITH ACRYLONITRILE ( $M_2$ )

$M_1$	Time, hours	% C	% H	% N	% O <sup>a</sup>	$m_1$ (N) <sup>b</sup>	$m_1$ (O)
0.200	0.6	67.31	6.67	20.72	5.02	0.2046	0.2262
0.499	0.7	68.92	7.79	16.26	6.80	0.3763	0.3065
0.798	1.2	64.65	8.88	13.74	12.55	0.4728	0.5656

<sup>a</sup> Obtained by difference after adjusting the nitrogen value for the lower experimental value.<sup>4a</sup>

<sup>b</sup> Obtained by using 26.06% instead of 26.40% for the theoretical percentage of nitrogen.<sup>4a</sup>

The "intersection" method indicated that for these monomers  $r_1 = 0.03 \pm 0.02$  and  $r_2 = 0.7 \pm 0.2$ .<sup>5</sup> Using  $r_1 = 0.03$ ,  $r_2 = 0.70$ , and  $e = 1.2$  and  $Q = 0.44$  for acrylonitrile, for ethyl vinyl ether,  $Q = 0.06 \pm 0.025$  and  $e = -0.8 \pm 0.2$ . Because of the uncertainty in  $r_1$ , we believe the average value from Table XV,  $Q = 0.015 \pm 0.003$  and  $e = -1.6 \pm 0.4$ , is a more reliable estimate.

TABLE X  
COPOLYMERIZATION OF ETHYL VINYL ETHER ( $M_1$ ) WITH ETHYL  
FUMARATE ( $M_2$ )

$M_1$	Time, hours	Conversion, %	% C	% H	% O <sup>a</sup>	$m_1$ (C)	$m_1$ (O)
0.197	5.8	18.7	57.25	7.79	34.96	0.1340	0.1477
0.259 <sup>b</sup>	2.9	11.0	57.71	7.88	34.41	0.1767	0.1843
0.499	2.4	31.6	58.03	8.10	33.87	0.2063	0.2203
0.501 <sup>b</sup>	1.7	25.5	58.07	8.03	33.90	0.2098	0.2184
0.799	0.8	35	58.23	8.19	33.58	0.2247	0.2398
0.800 <sup>b</sup>	0.5	9.5	58.29	8.28	33.43	0.2303	0.2497

<sup>a</sup> Obtained by difference.

<sup>b</sup> Contained only 0.00008 mole of benzoyl peroxide.

The "intersection" method gave no solution for  $r_1$  and  $r_2$ , but did indicate a "probable" value for  $r_2$  of  $2.7 \pm 2$ .

The resulting copolymer was yielding to gradually applied pressures, but brittle to sudden or strong forces. The copolymer was a brilliant, transparent glass readily soluble in methyl alcohol. It was purified by solution in ethyl ether and precipitation, after filtration, in ligroin. It was dried for several days in a vacuum oven at 65° and 30 mm. pressure.

TABLE XI  
COPOLYMERIZATION OF ETHYL  $\beta$ -ETHOXYACRYLATE ( $M_1$ )  
WITH STYRENE ( $M_2$ )

$M_1$	Time, hours	Conversion, %	% C	% H	% O <sup>a</sup>	$m_1$ (C)	$m_1$ (O)
0.200 <sup>b</sup>	9.7	10.2	92.07	7.86	0.07	0.0056	0.0021
0.500	0.6	0.1	90.78	7.78	1.44	0.0438	0.0433
0.799	10.2	2.8	91.74	8.01	0.25	0.0153	0.0075

<sup>a</sup> Obtained by difference.

<sup>b</sup> Contained only 0.00008 mole benzoyl peroxide.

The "intersection" method failed to give a solution for  $r_1$  and  $r_2$ . Close agreement in carbon and oxygen analyses in the copolymer obtained from a 50-50 mixture of monomers as well as the plot of data indicate a "best probable" value of  $r_2 = 23.5 \pm 1$ .

TABLE XII  
COPOLYMERIZATION OF ETHYL  $\beta$ -ETHOXYACRYLATE ( $M_1$ ) WITH ACRYLO-  
NITRILE ( $M_2$ )

$M_1$	Time, hours	Conver- sion, %	% C	% H	% N	% O <sup>a</sup>	$m_1$ (C)	$m_1$ (N)
0.200 <sup>b</sup>	0.9	17.5	66.74	5.93	24.48	2.85	0.1353	0.0607
0.500	2.5	17.6	68.04	6.08	23.92	1.96	<sup>c</sup>	0.0823
0.800	21.0	5.8	65.85	6.21	20.44	7.50	0.2389	0.2157

<sup>a</sup> Obtained by difference.

<sup>b</sup> Contained only 0.00008 mole benzoyl peroxide.

<sup>c</sup> The reported carbon percentage was higher than the theoretical value for either component.

The "intersection" method gave an indicated solution for  $r_1$  and  $r_2$ ,  $r_1 = 0.02 \pm 0.02$  and  $r_2 = 10.5 \pm 1.5$ . Calculation of  $Q$  and  $e$  values using  $r_1 = 0.03$ ,  $r_2 = 10.5$ , and  $Q_2 = 0.44$  and  $e_2 = 1.2$  for acrylonitrile gave  $Q = 0.012$  and  $e = 0.12$  for ethyl  $\beta$ -ethoxyacrylate. Solution of simultaneous equations for  $r_2$  (styrene) and  $r_2'$  (acrylonitrile) showed  $Q = 0.017$  and  $e = 0.41$  where  $r_2 = 23.5$ ;  $r_2' = 10.5$ ;  $Q_2 = 1.0$ ;  $Q_2' = 0.44$ ;  $e_2 = 0.8$ ; and  $e_2' = 1.2$ . Because of the uncertainty in  $r_1$  for the acrylonitrile copolymerization, we propose  $Q = 0.015$  and  $e = 0.3$  as most suitable values for the copolymerization parameters for ethyl  $\beta$ -ethoxyacrylate.

**Viscosities** of copolymer solution in benzene were measured with an Ostwald viscometer in a constant temperature water bath maintained at  $25.6 \pm 0.07^\circ\text{C}$ . The data are summarized in Table XIII. Estimation according to the formula<sup>6</sup>  $[\eta] = Km^\beta$ , in which the value for  $\beta$  was 0.7 and for  $K$  was  $1.28 \times 10^{-4}$  (styrene copolymers), or  $5 \times 10^{-4}$  (methyl acrylate or ethyl fumarate copolymers), indicated that the first three copolymers in Table XIII had molecular weights of 5000 to 10,000, while the last was somewhat over 25,000.



TABLE XIII  
VISCOSITIES OF SEVERAL COPOLYMERS

Monomers	$M_1^a$	$C^b$	$[\eta]$
$M_1$ $\beta$ -Bromovinyl ethyl ether	0.878	1.510	0.079
$M_2$ Styrene			
$M_1$ $\beta$ -Bromovinyl ethyl ether	0.350	1.719	0.192
$M_2$ Methyl acrylate			
$M_1$ Ethyl vinyl ether	0.499	1.653	0.167
$M_2$ Ethyl fumarate			
$M_1$ Ethyl $\beta$ -ethoxyacrylate	0.799	0.828	0.205
$M_2$ Styrene			

<sup>a</sup> Mole fraction of  $M_1$  in monomer mixture.

<sup>b</sup> Concentration is given in grams of copolymer per 100 g. of benzene.

**Infrared Absorption Measurements.** Infrared absorption measurements were made using a Baird double beam spectrophotometer with sodium chloride prism, except for that of the ethyl  $\beta$ -ethoxyacrylate, which was done on a Perkin-Elmer double beam instrument. The spectrum of a liquid film of  $\beta$ -bromovinyl ethyl ether was examined from 2 to 16  $\mu$ . That portion of the spectrum in the vicinity of 6  $\mu$  was of particular interest.  $\beta$ -Bromovinyl ethyl ether showed a strong, sharp absorption at 6.1  $\mu$ . The complete spectrum is reproduced in the Ph.D. dissertation of T. C. Schwan, Science Library, University of Notre Dame.

Strong sharp bands were observed for the following related compounds at the position indicated: vinyl bromide, 6.27  $\mu$ ; ethyl vinyl ether, 6.18  $\mu$  (courtesy of the Dow Chemical Co.); ethyl  $\beta$ -ethoxyacrylate 6.08 and 6.14  $\mu$ ; ethyl acrylate, 6.12 and 6.18  $\mu$  (courtesy of Rohm and Haas Co.). In spite of the excellent possibilities for extended resonance in the two disubstituted ethylenes, absorption in the 6  $\mu$  region shifts back toward the unconjugated wave length (6.1  $\mu$ ) compared to all the monosubstituted olefins cited above.

## DISCUSSION

A survey of the copolymerization data presented indicates that, far from being more reactive in polymer systems, the two  $\beta$ -substituted vinyl ethers were in fact quite unreactive. This is reflected in their low  $Q$  values (Table XVI), as well as the general sluggish polymerization rates and low molecular weights (Table XIII) observed.

Because of the very low reactivity of ethyl vinyl ether in most free radical copolymerization systems, it has not been possible to evaluate the copolymerization parameters,  $Q$  and  $e$ , for this monomer from copolymerization with a single comonomer. However, since data are available now for one of the copolymerization ratios ( $r_2$ ) from experiments with several different comonomers (Table XIV), these data have been used to evaluate  $Q$  and  $e$  for ethyl vinyl ether (Table XV).

TABLE XIV

COPOLYMERIZATION RATIOS FOR ETHYL VINYL ETHER ( $M_1$ ) WITH SEVERAL OTHER MONOMERS ( $M_2$ )

$M_2$	$r_2$	$r_1$	Ref.	$Q_2$ (ref. 7)	$e_2$ (ref. 7)
Acrylonitrile.....	$0.7 \pm 0.2$	0	—	0.5	1.2
Styrene.....	$90 \pm 20$	0	4		
	$80 \pm 40$	0	—	1.0	-0.8
Vinyl acetate.....	$3.0 \pm 0.1$	0	8	0.03	-0.3
Vinyl chloride.....	$2.0 \pm 0.2$	0	9	0.05	0.3

From various combinations of the data in Table XIV, various values for  $Q$  and  $e$  for ethyl vinyl ether may be calculated. These are presented in Table XV.

TABLE XV

COPOLYMERIZATION PARAMETERS  $Q$  AND  $e$  FOR ETHYL VINYL ETHER

Comonomers	$Q$	$e$
Acrylonitrile		
and styrene.....	$0.022 \pm 0.003$	$-1.7 \pm 0.2$
and vinyl acetate.....	0.017	-2.0
and vinyl chloride.....	0.012	-2.2
Styrene		
and vinyl acetate.....	0.012	-0.9
and vinyl chloride.....	0.015	-1.2
Vinyl acetate		
and vinyl chloride.....	0.014	-1.5
Average.....	$0.015 \pm 0.003$	$-1.6 \pm 0.4$

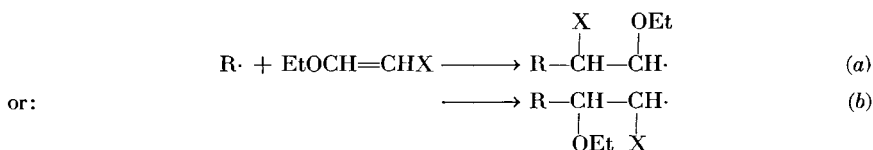
The data for all the vinyl ether derivatives are summarized in Table XVI.

TABLE XVI

COPOLYMERIZATION PARAMETERS  $Q$  AND  $e$  FOR VARIOUS VINYL ETHERS

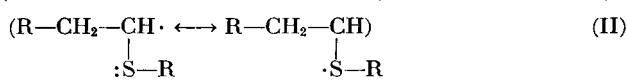
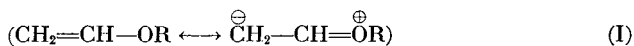
Monomer	$Q$	$e$
Ethyl vinyl.....	$0.015 \pm 0.003$	$-1.6 \pm 0.4$
Ethyl $\beta$ -bromovinyl.....	$0.014 \pm 0.003$	$0.35 \pm 0.1$
Ethyl $\beta$ -carbethoxyvinyl.....	$0.015 \pm 0.003$	$0.3 \pm 0.1$

There are two rather unexpected features of the values summarized in Table XVI. One is the very similar and very low values for the reactivity parameter  $Q$ , even for the  $\beta$ -ethoxyacrylate, with a conjugated carbonyl group. The other feature is the positive value for the electrical factor  $e$  for the two substituted vinyl ethers, in spite of the very negative  $e$ -value for ethyl vinyl ether itself. These results might be rationalized by assuming that the free radical added to the substituted vinyl ether at the positively substituted end of the double bond, by route (a) rather than route (b):



This mode of addition, however, would appear to be less likely than (b) on the basis of both steric hindrance and stability of the resulting radical.

It is of interest to compare the values of  $Q$  and  $e$  for ethyl vinyl ether with those previously determined for methyl vinyl sulfide,  $Q = 0.35$  and  $e = -1.45$ :<sup>10</sup>



The somewhat more negative value for  $e$  in ethyl vinyl ether would be expected on the grounds that resonance of type I, producing a negative charge at the double bond, would be more favorable when the heteroatom was oxygen (involving a  $2p$ - $2p$  double bond) rather than sulfur (involving a  $2p$ - $3p$  double bond).

The much greater resonance stabilization factor  $Q$  in methyl vinyl sulfide would be expected since resonance of type II would not be possible when the heteroatom is oxygen, since there are no stable orbitals for accommodating a ninth electron in the second valence shell involved in oxygen bonding.

### References

1. M. M. Shostakovskii and F. P. Sidel'kovskaya, *Akad. Nauk. S. S. R., Inst. Org. Khim., Sintez. Org. Soedinenii Sbornik*, **2**, 81 (1952); *Chem. Abstracts*, **48**, 551g (1954).
2. F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1944).
3. T. Alfrey, J. Bohrer, and H. Mark, *Copolymerization*, Interscience, New York-London, 1952, p. 12.
4. F. M. Lewis, *J. Am. Chem. Soc.*, **70**, 1527 (1948).
- 4a. F. R. Mayo, C. Walling, F. M. Lewis, and W. F. Hulse, *J. Am. Chem. Soc.*, **70**, 1524 (1948).
5. F. R. Mayo, F. M. Lewis, and C. Walling, *J. Am. Chem. Soc.*, **70**, 1529 (1948), report  $r_2 = 5$  for this system from a single experiment.
6. C. E. H. Bawn, *The Chemistry of High Polymers*, Interscience, New York, Butterworth, London, 1948.
7. C. C. Price, *J. Polymer Sci.*, **3**, 772 (1948).
8. G. Dolgin and P. Gordon, M.S. Dissertation, Brooklyn Polytechnic Institute, 1948 (see ref. 3, p. 40).
9. E. C. Chapin, G. E. Ham, and C. L. Mills, *J. Polymer Sci.*, **4**, 597 (1949). These values are for vinyl isobutyl ether.
10. C. C. Price and J. Zomlefer, *J. Am. Chem. Soc.*, **72**, 14 (1950).

### Synopsis

The copolymerization of ethyl vinyl ether with acrylonitrile leads to values of the copolymerization parameters of  $Q = 0.06$  and  $e = -0.8$ . Calculations from other data in the literature suggested that  $Q = 0.015$  and  $e = -1.6$  are better values. Copoly-

merization of  $\beta$ -bromovinyl ethyl ether with styrene and methyl methacrylate indicates  $Q = 0.014$  and  $e = 0.35$ . For ethyl  $\beta$ -ethoxyacrylate, copolymerization with styrene and acrylonitrile indicates  $Q = 0.015$  and  $e = 0.3$ . Both substituted vinyl ethers showed a much lower reactivity ( $Q$  factor) than expected. The decreased resonance interaction in these molecules was further supported by infrared data. Attempts to prepare  $\beta$ -chlorovinyl methyl ether by three different methods were unsuccessful.

### Résumé

La copolymérisation de l'éther vinyléthylique avec l'acrylonitrile fournit des valeurs des paramètres de la copolymérisation égaux à  $Q = 0.08$  et  $e = -0.8$ . Au départ des données de la littérature, des valeurs meilleures sont calculées et égales à  $Q = 0.015$  et  $e = -1.6$ . La copolymérisation d'éther  $\beta$ -bromovinyléthylique avec le styrène et le méthacrylate de méthyle fournit des valeurs de  $Q = 0.014$  et  $e = 0.35$ . Dans le cas des  $\beta$ -éthoxyacrylates, on trouve par copolymérisation avec le styrène et l'acrylonitrile  $Q = 0.015$  et  $e = 0.3$ . Les deux éthers vinyliques substitués montrent une réactivité plus faible (facteur  $Q$ ) que prévue. Une diminution de résonance au sein de ces molécules a été mise en évidence par des données spectrométriques infrarouges. On a essayé vainement par trois méthodes différentes de préparer l'éther  $\beta$ -chlorovinylméthylique.

### Zusammenfassung

Die Copolymerisation von Äthylvinyläther mit Acrylonitril führt zu Werten der Copolymerisationsparameter von  $Q = 0,06$  und  $e = -0,8$ . Berechnungen aus anderen Daten in der Literatur lassen annehmen, dass  $Q = 0,015$  und  $e = -1,6$  bessere Werte sind. Copolymerisation von  $\beta$ -Bromovinyläthyläther mit Styrol und Methylmethacrylat geben  $Q = 0,014$  und  $e = 0,35$  an. Für Äthyl- $\beta$ -ethoxyacrylat gibt Copolymerisation mit Styrol und Acrylonitril  $Q = 0,015$  und  $e = 0,3$  an. Beide substituierten Vinyläther zeigten eine viel niedrigere Reaktivität ( $Q$ -Faktor) als erwartet wurde. Die verminderte Resonanz-Interaktion in diesen Molekülen wurde weiterhin durch infrarote Daten unterstützt. Versuche,  $\beta$ -Chlorovinylmethyläther durch drei verschiedene Methoden herzustellen, waren nicht erfolgreich.

Received December 3, 1954