

TABLE II  
MONOMER REACTIVITY RATIOS

Monomer	$r_1$	Monomer	$r_2$	$r_1 r_2$
Vinyl acetate	6.8 $\pm$ 0.5	Tetrachloroethylene	(0)	
Acrylonitrile	470 $\pm$ ?	Tetrachloroethylene	(0)	
Styrene	185 $\pm$ 20	Tetrachloroethylene	(0)	
Vinyl acetate <sup>a</sup>	0.66 $\pm$ 0.04	Trichloroethylene	0.01 $\pm$ 0.01	0.007
Styrene	16 $\pm$ 2	Trichloroethylene	0.0 $\pm$ ?	
Styrene <sup>b</sup>	1.85 $\pm$ 0.05	Vinylidene chloride	0.085 $\pm$ 0.010	0.16
Acrylonitrile <sup>c</sup>	0.91 $\pm$ 0.1	Vinylidene chloride	0.37 $\pm$ 0.1	0.34
Vinyl acetate	0.0 $\pm$ 0.03	Vinylidene chloride	3.6 $\pm$ 0.5	< .1
Diethyl fumarate	0.046 $\pm$ 0.015	Vinylidene chloride	12.2 $\pm$ 2.0	.56
Styrene	17 $\pm$ 3	Vinyl chloride	0.02 $\pm$ ?	.34
Vinyl acetate <sup>a</sup>	0.23 $\pm$ 0.02	Vinyl chloride	1.68 $\pm$ 0.08	.38
Acrylonitrile <sup>d</sup>	3.28 $\pm$ 0.06	Vinyl chloride	0.02 $\pm$ 0.02	.07
Diethyl fumarate <sup>e</sup>	0.47 $\pm$ 0.05	Vinyl chloride	0.12 $\pm$ 0.01	.056
Vinyl acetate <sup>f</sup>	6.3 $\pm$ 0.2	<i>cis</i> -Dichloroethylene	0.018 $\pm$ 0.003	.11
Vinyl acetate <sup>g</sup>	0.99 $\pm$ 0.02	<i>trans</i> -Dichloroethylene	0.086 $\pm$ 0.010	.085

<sup>a</sup> Ref. 1. <sup>b</sup> Lewis, Mayo and Hulse<sup>ab</sup> reported 2.0  $\pm$  0.1 and 0.14  $\pm$  0.05. <sup>c</sup> Ref. 3b. <sup>d</sup> Lewis, Walling, Cummings, Briggs and Wenisch, *THIS JOURNAL*, **70**, 1527 (1948). <sup>e</sup> Ref. 6.

helpful discussions during the course of this work.

TABLE III

RELATIVE REACTIVITIES OF CHLOROETHYLENES WITH DIFFERENT RADICALS

Monomer radical type	Vinyl acetate	Styrene	Acrylonitrile	Diethyl fumarate
Vinylidene chloride	>7.5	9.2	3.6	10.5
Vinyl chloride	1.00	1.00	1.00	1.00
Trichloroethylene	0.34	1.06		
<i>trans</i> -Dichloroethylene <sup>a</sup>	.12	0.27 <sup>b</sup>		
<i>cis</i> -Dichloroethylene <sup>a</sup>	.018	.039 <sup>b</sup>		
Tetrachloroethylene <sup>a</sup>	.017	.046	0.0035	

<sup>a</sup> The values for the symmetrical monomers have been divided by two, since there are two equivalent ways in which they can add to a radical. <sup>b</sup> Ref. 6.

## Summary

Monomer reactivity ratios have been determined for several new systems of chloroethylenes with other monomers. The data are correlated with other available data to give the following reactivity series: vinylidene chloride > vinyl chloride > trichloroethylene > *trans*-dichloroethylene > *cis*-dichloroethylene and tetrachloroethylene. This series can be accounted for qualitatively by a consideration of steric effects and of the ease of formation of di- and trisubstituted radicals. Differences in alternating tendencies in various systems are consistent with existing theories of alternation.

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Copolymerization. VII.<sup>1</sup> Copolymerizations of Some Further Monomer Pairs

By FREDERICK M. LEWIS, CHEVES WALLING, WILLIAM CUMMINGS,<sup>2</sup> EMORENE R. BRIGGS<sup>3</sup> and W. J. WENISCH<sup>4</sup>

This paper presents experimental data on the copolymerization of eight monomer pairs needed to supplement our series of relative reactivities of monomers with radicals. The monomer reactivity ratios calculated from these data are summarized in Table I. Since the data were gathered over an interval of four years, the standard deviations of the separate experiments rather than any established analytical error<sup>5</sup> have usually been used

to determine the stated experimental errors. Also included in this paper are some less reliable mono-

TABLE I  
MONOMER REACTIVITY RATIOS AT 60°<sup>6</sup>

M <sub>1</sub>	$r_1$	M <sub>2</sub>	$r_2$
Styrene	0.78 $\pm$ 0.01	Butadiene	1.39 $\pm$ 0.03
Styrene	.54 $\pm$ .01	$\beta$ -Chloroethyl acrylate	0.10 $\pm$ .01
Styrene	.30 $\pm$ .10	Methacrylonitrile	0.16 $\pm$ .06
Styrene <sup>b</sup>	.29 $\pm$ .04	Methyl vinyl ketone	0.35 $\pm$ .02
Acrylonitrile <sup>c</sup>	.61 $\pm$ .04	Methyl vinyl ketone	1.78 $\pm$ .22
Acrylonitrile	3.28 $\pm$ .06	Vinyl chloride	0.02 $\pm$ .02
Methyl methacrylate	0.67 $\pm$ .10	Methacrylonitrile	0.65 $\pm$ .06
Isobutylene	0.08 $\pm$ .10	Vinyl chloride	2.05 $\pm$ .3

<sup>a</sup> M's and  $r$ 's in each line correspond to the particular monomer pair indicated. <sup>b</sup> Experimental error from 0.2% error in carbon analysis. <sup>c</sup> Experimental error from 0.1% error in nitrogen analysis.

(1) For the preceding paper in this series see Doak, *THIS JOURNAL*, **70**, 1525 (1948).

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(5) Lewis, Walling, Cummings, Briggs and Mayo, *THIS JOURNAL*, **70**, 1519 (1948).

mer reactivity ratios for six additional pairs (Table II). Most of the experiments were carried out in the course of preliminary studies using three experiments at 4:1, 1:1, and 1:4 mole ratios of the two monomers, but the lower accuracy obtained (*cf.* experimental errors in Table II) does not appear to justify detailed presentation.

TABLE II

## ADDITIONAL MONOMER REACTIVITY RATIOS AT 60°

M <sub>1</sub>	r <sub>1</sub>	M <sub>2</sub>	r <sub>2</sub>
Vinyl acetate <sup>a</sup>	0.60 ± 0.15	Allyl acetate	0.45 ± 0.15
Styrene	90 ± 20	Vinyl ethyl ether	0
Methyl methacrylate <sup>a,b</sup>	0.25 ± 0.03	Butadiene	0.75 ± 0.05
β-Chloroethyl acrylate	5.5 ± 1	Allyl acetate	0
β-Chloroethyl acrylate	4 ± 1	Methallyl acetate	0
β-Chloroethyl acrylate <sup>c</sup>	0.9 ± 0.1	Methyl acrylate	0.9 ± .1

<sup>a</sup> Experiment by Mr. R. H. Snyder. <sup>b</sup> At 90°. <sup>c</sup> Experiment by Dr. K. W. Doak.

Correlation and discussion of the results of Table I and II will be given in a subsequent paper in this series.<sup>6</sup>

## Experimental

**Materials.**—Isobutylene and butadiene were obtained from the Matheson Company and used without purification other than drying. Methacrylonitrile, from the Shell Chemical Company, was fractionated just prior to use;  $n_D^{20}$  1.4003. β-Chloroethyl acrylate was prepared by acid-catalyzed ester interchange from methyl acrylate and ethylene chlorohydrin in the presence of an inhibitor. The crude product was fractionated *in vacuo* under nitrogen; b. p. 94.1–95 at 18.5 mm.;  $n_D^{20}$  1.4490. Methyl vinyl ketone was obtained from E. I. du Pont de Nemours and Co. as an azeotrope with water containing 85% ketone. Upon saturating with potassium carbonate and distilling through a packed column the pure ketone was collected as a fraction boiling at 80.5–81.0° at one atmosphere. Since it was unstable and polymerized readily, it was stored in the ice-box and used as soon as possible. Other monomers, usually fractionated commercial materials, were those described in previous papers in this series.

**Polymerizations.**—Except as noted, experiments were carried out and polymers isolated as described in previous papers. Results are tabulated in Table III.

In styrene-butadiene experiments, styrene charges were first weighed accurately into tubes, then butadiene was added in approximate amounts to the chilled tube. The exact weights of butadiene used were then determined from the weights of the charged and sealed, and empty reaction tube.

Since both isobutylene and vinyl chloride are low boiling monomers, a manifold was constructed with stopcocks leading to a vacuum line, to a standard taper joint and to two graduated tubes for measuring the monomers. Tubes containing pure monomer were attached by the standard taper joint and the monomers were degassed and distilled into the respective graduated tubes. By suitable manipulation of the stopcocks the monomers could then be separately distilled *in vacuo* into the reaction tube attached to the ground joint. The graduated tubes were adjusted to approximately –50° for volume readings, the exact temperature noted, and the corresponding density read from graphs. Weights of single monomers measured from this apparatus showed that their densities were a linear function of temperature, varying from 0.949 g./ml. at 0° to 1.018 at –48° for vinyl chloride; and from 0.619 at 0° to 0.664 at –40° for isobutylene.

(6) Mayo, Lewis and Walling, *THIS JOURNAL*, **70**, 1529 (1948).

TABLE III

## EXPERIMENTAL DATA ON COPOLYMERIZATIONS AT 60°

[M <sub>1</sub> ] <sup>a</sup>	[M <sub>2</sub> ] <sup>a</sup>	[M <sub>1</sub> ] <sup>a</sup>	[M <sub>2</sub> ] <sup>a</sup>	Time, hr.	Polymer analysis
Styrene (M <sub>1</sub> )–Butadiene (M <sub>2</sub> )					$n_D^{20}$
69.45	12.40	40.60	6.24	72	1.5860
39.80	23.40	15.33	6.64	117	1.5730
16.00	36.80	13.43	29.03	239	1.5461
Styrene (M <sub>1</sub> )–β-Chloroethyl Acrylate (M <sub>2</sub> )					% Cl
57.70	17.32	49.15	14.19	5.3	8.5
41.00	42.70	33.32	37.25	3.5	12.8
16.31	68.60	9.85	59.60	2.5	17.0
Styrene (M <sub>1</sub> )–Methacrylonitrile (M <sub>2</sub> )					% N
63.58	18.88	42.65	8.21	62	4.63 4.67
39.68	39.20	24.30	25.56	62	7.56 7.52
15.87	63.05	8.00	47.84	62	11.58 11.57
Styrene (M <sub>1</sub> )–Methyl Vinyl Ketone (M <sub>2</sub> )					% C
64.28	16.11	50.71	9.45	11.3	86.28 86.44
63.80	16.39	49.63	10.02	11.3	86.85 86.64
16.62	64.34	10.74	50.72	2.7	77.92 77.65
16.66	64.34	11.86	53.34	2.7	77.79 77.71
Acrylonitrile (M <sub>1</sub> )–Methyl Vinyl Ketone (M <sub>2</sub> )					% N
15.61	64.25	14.10	53.53	0.84	2.53
15.63	64.10	14.40	54.92	0.84	2.42
16.47	63.30	14.66	52.75	1.00	3.03 3.01
64.90	16.14	55.34	12.44	0.67	17.46 17.49
64.78	16.07	52.50	11.07	0.67	17.16 17.20
64.08	16.17	58.12	13.64	4.25	16.94
Acrylonitrile (M <sub>1</sub> )–Vinyl Chloride (M <sub>2</sub> )					% N
23.72	39.49	4.87	30.87	9.5	16.94 17.37
64.55	24.34	36.98	21.02	1.1	23.02 23.29
62.80	17.60	31.11	14.42	1.1	23.48 23.71
24.21	38.44	5.13	29.31	9.5	16.77 16.98
Methyl Methacrylate (M <sub>1</sub> )–Methacrylonitrile (M <sub>2</sub> )					% N
79.06	19.88	61.58	14.35	15.5	3.65
79.61	19.93	63.02	14.78	15.5	3.61
19.95	87.24	14.79	68.78	49.5	14.38
20.12	87.77	14.55	69.39	49.5	14.29
Isobutylene (M <sub>1</sub> )–Vinyl Chloride (M <sub>2</sub> )					% Cl
64.5	21.0	61.4	16.5	56	35.65 35.57
43.0	43.3	36.4	27.6	56	41.70 41.91
17.0	59.0	13.17	31.5	56	50.53 50.79

<sup>a</sup> Millimoles of unreacted monomer; zero subscripts indicate initial quantities.

Isobutylene-vinyl chloride polymers were precipitated from acetone solution with methanol. Nitrile polymers were dissolved in dimethylformamide or acetonitrile, precipitated with petroleum ether or methanol, and dried for several days at 60° *in vacuo*.

Polymer compositions were determined by standard analytical methods except for styrene-butadiene systems. Several attempts to determine the monomer reactivity ratios for this pair by combustion analysis or by separation and analysis of the unreacted monomer mixture were unsatisfactory. The data given in Table I are based on polymer analysis by index of refraction. Since, for emulsion copolymers of styrene and butadiene, other

factors being constant, the index of refraction of the copolymers is a linear function of composition,<sup>7</sup> the same relation has been assumed here for oil-phase copolymers, using for the pure polymers of styrene and butadiene, made under the same conditions as the copolymers,  $n_D^{20}$  1.5935 and 1.5160, respectively. The high-styrene polymer was quite hard and an optical surface was generated by pressing the polymer against a hot glass plate and allowing it to cool in contact. Optical contact of the resulting surface with the prism of an Abbe refractometer was made with a saturated aqueous solution of cadmium borotungstate and the refractive index was measured by reflected light. The intermediate-styrene polymer

(7) "Analyses by Refractive Index," Lundstedt and Hampton, Akron Copolymer Research Group Meeting, June 12-13, 1944.

was soft enough to make optical contact with the prism directly under pressure, allowing measurement by reflected light. The low-styrene polymer was soft enough to squeeze between the two prisms of the refractometer for measurement by transmitted light. All readings were reproducible to  $\pm 0.0002$ .

### Summary

1. Copolymerization data and monomer reactivity ratios at 60° are given for eight new monomer pairs.

2. Monomer reactivity ratios of lower precision are given for six additional pairs.

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## Copolymerization. VIII. The Relation Between Structure and Reactivity of Monomers in Copolymerization<sup>1</sup>

BY FRANK R. MAYO, FREDERICK M. LEWIS AND CHEVES WALLING

The first papers in this series<sup>2</sup> showed that series of copolymerizations make possible the determination of the relative reactivities of monomers toward certain radicals, and that such relative reactivities are independent of the feed composition, conversion, solvents, regulators, sources of free radicals used and rates of polymerization. On the other hand, such relative reactivities do appear to depend upon the particular attacking radical, and the results indicate a general order of monomer reactivity toward radicals on which is superimposed a tendency of certain monomers to alternate in copolymerization. In some monomer pairs this alternating effect appears to be negligible; relative reactivities of the monomers are the same toward both types of radicals and the monomer reactivity ratio product,  $r_1 r_2$ ,  $\cong 1$ . Such systems, of which styrene-butadiene is an example ( $r_1 r_2 = 1.08$ ) have been termed "ideal" by Wall.<sup>3</sup> In other systems the "alternating effect" appears dominant,  $r_1 r_2 \cong 0$ , and the initial copolymer from any feed consists of regularly alternating units of the two monomers (e. g., styrene-maleic anhydride  $r_1 r_2 \leq 0.001$ ).<sup>4</sup> In the great majority of copolymerizations, however, both effects appear of importance and monomer reactivity ratios have intermediate values: styrene-methyl methacrylate,  $r_1 r_2 = 0.26$ ; acrylonitrile-methyl methacrylate,  $r_1 r_2 = 0.24$ .

The purpose of the present paper is to discuss

these phenomena in more detail using the extensive experimental data recently presented from this Laboratory,<sup>5</sup> and also making reference to additional material to appear in subsequent papers in this series.<sup>6</sup>

**The Alternation Tendency in Copolymerization.**—An earlier paper<sup>2b</sup> stated that the alternating effect "seems sometimes to be due to steric effects, at other times to dipole effects or specific interactions (compound formation) between monomers." This section will amplify this statement in the light of the work cited above.<sup>5,6</sup> Price<sup>7</sup> has proposed that substituents in a radical or monomer may withdraw or supply electrons from the site of reaction, resulting in effective charges on the trivalent or doubly bound carbon atoms. The alternating effect then arises from an attraction between a negative double bond and a positive radical, or *vice versa*. Alfrey and Price<sup>8</sup> have since attempted to place this suggestion on a general and quantitative basis, describing the reactivity of each monomer in terms of two parameters, referring to the "general monomer reactivity" ( $Q$ ) and "polarity factor" ( $e$ ). Bartlett and Nozaki<sup>9</sup> have mentioned the possibility that electron transfer from a donor radical to an acceptor monomer, or *vice versa*, in the activated complex may account for alternation tendencies, and we have developed and discussed this concept further in later papers in this series.<sup>10</sup>

(1) This paper is based on papers presented at the Atlantic City Meeting of the American Chemical Society, April 9, 1946 (Symposium on the Physical Chemistry of Copolymers and Copolymerization) and at the Gibson Island Conference on High Polymers, July 1, 1946.

(2) (a) Mayo and Lewis, *THIS JOURNAL*, **66**, 1594 (1944); (b) Lewis, Mayo and Hulse, *ibid.*, **67**, 1701 (1945).

(3) Wall, *ibid.*, **66**, 2050 (1944). This theoretical paper shows clearly how copolymer compositions depend on feed for representative monomer reactivity ratios. Some special cases were considered earlier by Jenckel, *Z. physik. Chem.*, **190A**, 24 (1942).

(4) Alfrey and Lavin, *ibid.*, **67**, 2044 (1945).

(5) (a) Lewis, Walling, Cummings, Briggs and Mayo, *ibid.*, **70**, 1519 (1947); (b) Mayo, Walling, Lewis and Hulse, *ibid.*, **70**, 1523 (1948); (c) Doak, *ibid.*, **70**, 1525 (1948); (d) Lewis, Walling, Cummings, Briggs and Wenisch, *ibid.*, **70**, 1527 (1948).

(6) (a) Lewis and Mayo, *ibid.*, **70**, 1533 (1948); (b) Walling, Briggs and Wolfstirn, *ibid.*, **70**, 1543 (1948).

(7) Price, *J. Polymer Sci.*, **1**, 83 (1946).

(8) Alfrey and Price, *ibid.*, **2**, 101 (1947); Alfrey, paper presented at Atlantic City Meeting, April, 1946.<sup>1</sup>

(9) Bartlett and Nozaki, *THIS JOURNAL*, **68**, 1495 (1946).

(10) (a) Walling, Briggs, Wolfstirn and Mayo, *ibid.*, **70**, 1537 (1948); (b) Walling, Seymour and Wolfstirn, *ibid.*, **70**, 1544 (1948).