reactivity as vinyl acetate, the monomers with conjugated phenyl, ester, or nitrile groups are so much more reactive than vinyl acetate that the monomer reactivity ratios for the vinyl acetate radical are indistinguishable from zero and it is therefore impossible to compare the reactivities of these monomers.

TABLE II

SUMMARY OF MONOMER REACTIVITY RATIOS IN COPOLYMERIZATIONS OF VINYL ACETATE (M_2)

M_1	r_1		r_2	
Styrene	55	$\pm$ 10	0.01	$\pm$ 0.01
Methyl methacrylate	20	$\pm$ 3	.015	$\pm$ .015
Methyl acrylate	9	$\pm$ 2.5	.1	$\pm$ .1
Acrylonitrile	4.05	$\pm$ .3	.061	$\pm$ .013
Vinyl bromide	4.5	$\pm$ 1.2	.35	$\pm$ .09
Vinyl chloride	1.68	$\pm$ .08	.23	$\pm$ .02
Vinyl ethyl ether	0		3.0	$\pm$ .1
Trichloroethylene	.01	$\pm$ .01	0.66	$\pm$ .04

Vinyl ethyl ether not only is less reactive than vinyl acetate with both the latter and with styrene, it retards the polymerization of vinyl acetate. Thus a 4:1 ether–acetate feed gives <3% polymer in two-hundred fifty-eight hours. This retardation may be due to the formation of a less reactive α-vinyloxyethyl radical by chain transfer, the α-hydrogen of the ethyl group being easily susceptible to free radical attack, or to as rapid decomposition and inefficient utilization of the catalyst.[7]

Experiments on the vinyl chloride–vinyl acetate system indicate a possible effect of precipitation of the polymer on its composition. The polymers from the high vinyl chloride feeds precipitated as they formed, yielding a highly swollen but fairly stiff gel. Such experiments failed to give reproducible results, although the homogeneous runs gave good checks. The monomer reactivity ratios here obtained are consistent with the observation of Staudinger and Schneiders[8] that fractionation of a 1:1 copolymer gave fractions containing as much as three chlorine atoms per acetate group. The difficulty encountered by Marvel and co-workers[9] in obtaining consistent α-values with these monomers may have been partly due to precipitation of polymer.

The vinyl bromide results are subject to considerable uncertainty because of analytical difficulties. The lowest values of the monomer reactivity ratios are the most probable because otherwise the product of the ratios exceeds unity by an unexpected margin. Even so, the results indicate that, in comparison with a chlorine atom, a bromine atom gives much less tendency to alternate with vinyl acetate, but a considerably higher average activity.

A comparison of the reactivity of several chloroethylenes with vinyl acetate[10] and a discussion of rate phenomena in the styrene–vinyl acetate system[11] will be given in later papers in this series.

Summary

Copolymerizations of eight monomers with vinyl acetate have been examined. The data show that, in comparison with monomers with conjugated substituents, the double bond in vinyl acetate is unreactive.

(7) See, e. g., Cass, THIS JOURNAL, 69, 500 (1947).

(8) Staudinger and Schneiders, Ann., 541, 193 (1939).

(9) Marvel, Jones, Mastin and Schertz, THIS JOURNAL, 64, 2356 (1942). Plotting these data with the integrated copolymerization equation gives erratic results, the monomer reactivity ratios for the chloride and acetate radicals ranging from 1.0 to 2.8 and from 0.2 to 1.3, respectively.

(10) Doak, THIS JOURNAL, 70, 1525 (1948).

(11) Mayo, Lewis and Walling, ibid., 70, 1529 (1948).

Copolymerization. VI.[1] The Copolymerization of Chloroethylenes with other Monomers

BY KENNETH W. DOAK

This paper presents a comparison of the reactivities of all the chlorinated ethylenes with each of two or more other radicals. Some data have been taken from other papers in this series; the new data include the systems vinyl chloride and trichloroethylene with styrene, tetrachloroethylene with styrene, vinyl acetate and acrylonitrile, and vinylidene chloride with vinyl acetate and diethyl fumarate. More precise data for the system styrene and vinylidene chloride have been obtained.

The relative reactivities of 1,1- and 1,2-dichloroethylenes with some other monomers have been reported by Nozaki[2] on the basis of single experiments, but strong alternation tendencies[3] involved in some of the systems make the present method more reliable.

The monomers were commercial samples which had been carefully refractionated. Except as indicated, the experimental procedure was similar to that of Mayo and Lewis.[3a] The copolymers of acrylonitrile and tetrachloroethylene and of vinylidene chloride (80 mole % in reaction mixture)

(1) For the preceding paper in the series, see Mayo, Walling, Lewis and Hulse, THIS JOURNAL, 70, 1523 (1948).

(2) Nozaki, J. Polymer Sci., 1, 455 (1946).

(3) (a) Mayo and Lewis, THIS JOURNAL, 66, 1594 (1944); (b) Lewis, Mayo and Hulse, ibid., 67, 1701 (1945); (c) Bartlett and Nozaki, ibid., 68, 1495 (1946).

with vinyl acetate and diethyl fumarate precipitated from the reaction mixtures as finely divided powders which were washed with ethanol and dried at 65° and 1 mm. All other copolymers were purified by the frozen benzene technique of Lewis and Mayo.

The monomer reactivity ratios were determined graphically from the data in Table I. For the

TABLE I

COPOLYMERIZATIONS WITH 0.1 MOLE PER CENT. BENZOYL
PEROXIDE AT 60°

$[M_1]_0{}^a$	$[M_1]^a$	$[M_2]_0{}^a$	$[M_2]^a$	Time, hr.	Polymer analysis (% Cl)	
Vinyl Acetate		Tetrachloroethylene				
160.3	63.7	40.6	35.9	9	7.20	7.45
80.84	25.52	19.73	16.80	18	7.96	7.87
80.50	25.86	19.92	17.00	18	8.00	7.96
Acrylonitrile		Tetrachloroethylene				
94.1	36.0	94.0	93.8	1 ?	0.79	0.90
Styrene		Tetrachloroethylene				
48.00	16.10	94.02	93.50	168	2.12	2.17
49.87	41.09	49.85	49.80	25	0.88	0.78
Vinylidene Chloride		Vinyl Acetate				
78.58	74.40	21.64	21.33	3	26.72	26.63[b]
79.09	73.31	22.62	22.17	3	26.69	26.91[b]
19.14	9.45	78.70	72.86	8	35.43	35.71[b]
19.16	9.05	78.28	72.36	8	35.50	35.37[b]
Vinylidene Chloride		Diethyl Fumarate				
77.31	59.11	21.06	20.62	6	26.04	26.09[b]
76.56	59.14	21.18	20.72	6	26.07	26.24[b]
18.40	6.62	83.60	77.86	24	39.17[b]	
19.34	7.15	83.83	78.34	24	38.57[b]	
Styrene		Vinyl Chloride				
80.82	51.64	53.59	52.32	39	1.43	1.45
20.75	5.60	101.53	95.50	130	10.93	10.95
79.91	56.61	29.82	29.08	29	0.85	0.89
Styrene		Vinylidene Chloride				
76.03	65.86	20.02	18.67	13	8.06	
75.45	66.36	20.88	19.63	13	8.28	
34.48	29.84	63.16	60.40	15	26.05	
34.42	29.79	62.71	59.95	15	26.08	
Styrene		Trichloroethylene				
68.83	55.20	29.97	29.59	20	2.76	
68.68	55.22	30.35	29.93	20	3.06	
20.20	16.62	79.16	78.41	68	16.95	

^{a} Millimoles of unreacted monomers; zero subscripts indicate initial quantities. ^{b} % C.

(4) Lewis and Mayo, *Ind. Eng. Chem., Anal. Ed.*, **17**, 134 (1945).

systems containing tetrachloroethylene, it was assumed that the reactivity ratio for the tetrachloroethylene radical is zero, since this monomer did not homopolymerize under the experimental conditions. The other reactivity ratio was considered to be the intersection of the calculated lines with the r_1 axis. Monomer reactivity ratios, together with literature data necessary for the discussion, are given in Table II.

Results and Discussion

Relative reactivities of the chloroethylenes with four radicals were determined from the reciprocals[3,5] of r_1, and are recorded in Table III. The values for vinyl chloride are taken as unity.

The relative reactivities of the chloroethylenes depend upon the reference radical, presumably because of the alternating tendency, although qualitatively the general order, with one possible exception, is the same for different radicals. As shown qualitatively by Nozaki,[2] unsymmetrical substitution of a second chlorine increases the reactivity, since extra resonance forms are possible. These data show the increase to vary from a factor of 3.6 to 10.5 or greater. Symmetrical substitution of the second chlorine decreases the reactivity, presumably because of steric interference with the approaching radical. The difference in the *cis*- and *trans*-dichloroethylenes is discussed by Lewis and Mayo in a later paper in this series.[6] Trichloroethylene, in which the effects are opposed, has a reactivity intermediate between that of the symmetrical and unsymmetrical dichloroethylenes. Tetrachloroethylene offers additional steric hindrance, and is much less reactive than trichloroethylene.

A comparison of the r_1r_2 products[5] in Table II shows that vinyl chloride alternates better than vinylidene chloride with the electron acceptors diethyl fumarate and acrylonitrile but less readily with the electron donors vinyl acetate and styrene. With vinyl acetate, all the dichloroethylenes alternate better than vinyl chloride. All these results are consistent with the idea that dichloroethylenes should be better electron acceptors[7] than vinyl chloride. Trichloroethylene, tetrachloroethylene, and the 1,2-dichloroethylenes, in comparison with vinyl chloride, are about three times as reactive toward the styrene radical as toward the vinyl acetate radical. If this result were wholly due to donor–acceptor effects, it would mean that styrene is a better donor than vinyl acetate, a conclusion which seems to be contradicted by the weight of other evidence.[7c]

Acknowledgment.—The author wishes to express his appreciation to Dr. Frank R. Mayo for

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

(6) Lewis and Mayo, THIS JOURNAL, **70**, 1533 (1948).

(7) (a) Price, *J. Polymer Sci.*, **1**, 83 (1946); (b) Alfrey and Price, *ibid.*, **2**, 101 (1947); (c) Mayo, Lewis, and Walling, THIS JOURNAL, **70**, 1529 (1948).

TABLE II
MONOMER REACTIVITY RATIOS

Monomer	r_1		Monomer	r_2	r_1r_2
Vinyl acetate	6.8	± 0.5	Tetrachloroethylene	(0)	
Acrylonitrile	470	± ?	Tetrachloroethylene	(0)	
Styrene	185	± 20	Tetrachloroethylene	(0)	
Vinyl acetate[a]	0.66	± 0.04	Trichloroethylene	0.01 ± 0.01	0.007
Styrene	16	± 2	Trichloroethylene	0.0 ± ?	
Styrene[b]	1.85	± 0.05	Vinylidene chloride	0.085 ± 0.010	0.16
Acrylonitrile[c]	0.91	± 0.1	Vinylidene chloride	0.37 ± 0.1	0.34
Vinyl acetate	0.0	± 0.03	Vinylidene chloride	3.6 ± 0.5	< .1
Diethyl fumarate	0.046	± 0.015	Vinylidene chloride	12.2 ± 2.0	.56
Styrene	17	± 3	Vinyl chloride	0.02 ± ?	.34
Vinyl acetate[a]	0.23	± 0.02	Vinyl chloride	1.68 ± 0.08	.38
Acrylonitrile[d]	3.28	± 0.06	Vinyl chloride	0.02 ± 0.02	.07
Diethyl fumarate[e]	0.47	± 0.05	Vinyl chloride	0.12 ± 0.01	.056
Vinyl acetate[e]	6.3	± 0.2	cis-Dichloroethylene	0.018 ± 0.003	.11
Vinyl acetate[e]	0.99	± 0.02	trans-Dichloroethylene	0.086 ± 0.010	.085

[a] Ref. 1. [b] Lewis, Mayo and Hulse[3b] reported 2.0 ± 0.1 and 0.14 ± 0.05. [c] Ref. 3b. [d] Lewis, Walling, Cummings, Briggs and Wenisch, THIS JOURNAL, **70**, 1527 (1948). [e] 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	Acrylo-nitrile	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		
trans-Dichloroethylene[a]	.12	0.27[b]		
cis-Dichloroethylene[a]	.018	.039[b]		
Tetrachloroethylene[a]	.017	.046	0.0035	

[a] 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. [b] 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.

Copolymerization. VII.[1] Copolymerizations of Some Further Monomer Pairs

BY FREDERICK M. LEWIS, CHEVES WALLING, WILLIAM CUMMINGS,[2] EMORENE R. BRIGGS[3] AND W. J. WENISCH[4]

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[5] 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°[a]

M₁	r_1	M₂	r_2
Styrene	0.78 ± 0.01	Butadiene	1.39 ± 0.03
Styrene	.54 ± .01	β-Chloroethyl acrylate	0.10 ± .01
Styrene	.30 ± .10	Methacrylonitrile	0.16 ± .06
Styrene[b]	.29 ± .04	Methyl vinyl ketone	0.35 ± .02
Acrylonitrile[c]	.61 ± .04	Methyl vinyl ketone	1.78 ± .22
Acrylonitrile	3.28 ± .06	Vinyl chloride	0.02 ± .02
Methyl methacrylate	0.67 ± .10	Methacrylonitrile	0.65 ± .06
Isobutylene	0.08 ± .10	Vinyl chloride	2.05 ± .3

[a] M's and r's in each line correspond to the particular monomer pair indicated. [b] Experimental error from 0.2% error in carbon analysis. [c] 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).