Armstrong that a study of copolymerization would be one of the best approaches to a fundamental understanding of polymerization as a whole, a decision which we feel has been amply justified. We are also indebted to Dr. Oscar W. Lundstedt who was in charge of analytical work while most of the work in this series of papers was in progress. The consistency of analytical results discussed in this paper is largely the result of his efforts. Finally, we wish to acknowledge the considerable contributions of Mrs. Charles J. Pennino and Miss Lucille Librizzi, who have carried out much of the actual experimental work described in this series.

Summary

1. By carrying out copolymerizations at 60 and 131°, heat and entropy of activation differences for the reaction of each radical with the two monomers have been determined for the systems styrene–methyl methacrylate, styrene–methyl acrylate, styrene–diethyl maleate, styrene–diethyl fumarate and styrene–*p*-chlorostyrene.

2. In every case the difference in reactivity of the two monomers is found to be due, primarily, to differences in heat of activation. Only in the reaction of the diethyl fumarate radical with styrene does the difference in entropies of activation clearly differ from zero by more than experimental error.

3. Further data are presented showing that solvents (benzene, acetonitrile or methanol) are without effect on the monomer reactivity ratios of the system styrene–methyl methacrylate.

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Copolymerization. V.[1] Some Copolymerizations of Vinyl Acetate

BY FRANK R. MAYO, CHEVES WALLING, FREDERICK M. LEWIS AND W. F. HULSE[2]

This paper presents experiments on the copolymerization of vinyl acetate with eight representative monomers. The double bond of vinyl acetate proves to be one of the least reactive of any common monomers toward free radical attack.

Experimental

Materials.—Vinyl bromide was prepared from ethylene bromide by the action of alcoholic sodium hydroxide. After washing with water and drying with potassium carbonate, the fraction used boiled at 15.5–16.0° at 761 mm. Vinyl chloride, obtained from the Dow Chemical Co., was used without purification. The other monomers were commercial materials fractionally distilled before use and stored in a refrigerator.

Procedure.—With the exceptions noted below, reaction mixtures were prepared as described previously[1] and products were isolated by the frozen benzene technique.[3] In the trichloroethylene experiments (5.00 g. of total monomers and 6.1 mg. of benzoyl peroxide) air was displaced from the reaction tubes by flushing with nitrogen and the polymers obtained by distilling off the monomers and heating the residue for sixteen hours at 90–100° and 2 mm. pressure. The acrylonitrile runs were carried out in the presence of 5 cc. of acetonitrile. The low nitrile runs remained homogeneous. These polymers were precipitated twice from acetone solution with petroleum ether and were then pressed out into thin sheets and dried for twenty hours at 60° and 1 mm. pressure. The high acrylonitrile runs gave a very fine suspension of polymer which at first gave no indications of coagulating or settling. As soon as these indications appeared, heating was stopped. The mixtures were diluted with benzene and petroleum ether; the polymer was collected on a filter as a white powder, washed with the latter solvent and dried for twenty hours at 60° and 1 mm. pressure.

The vinyl halides were measured out approximately by volume; their exact weights were determined by difference from the weights of the total contents of the reaction tubes. Copolymers containing large proportions of vinyl halide were insoluble in the reaction mixture (except when chlorobenzene was used as solvent) and in benzene. The excess vinyl halide was allowed to escape and the polymers were precipitated twice from chloroform (bromide) or a chloroform–acetone mixture (chloride) and petroleum ether. The chloride polymers were broken up and heated for about twenty-four hours at 60° and 1 mm. pressure. Solvent was removed from the bromide polymers by twenty-four hours of evacuation at 0° and 1 mm. pressure. They were finally warmed cautiously for a few minutes in warm water. Longer or stronger heating led to very rapid discoloration.

Analyses for acetic acid[4] were carried out by determining hydrolyzable acetoxy groups as acetic acid. The polymer sample (0.3–0.8 g.) was weighed into a flask, dissolved in 30 ml. of benzene, and treated for forty-eight hours at room temperature with 50 ml. of 0.5 *N* alcoholic sodium hydroxide. Benzene and alcohol were then removed by steam distillation, adjusting heat and steam input to maintain about the same volume of solution. The mixture was next acidified with 15 ml. of phosphoric acid and 500 ml. of steam distillate collected. The steam distillate was gently aerated for twelve minutes to remove carbon dioxide and titrated to phenolphthalein end-point using decinormal sodium hydroxide. A blank correction (~0.3 ml.) was applied and the results calculated as per cent. acetic acid in the original polymer sample.

Data on experiments are summarized in Table I. In the copolymerization with vinyl ethyl ether, the monomer reactivity ratio for the ether was assumed to be zero and the vinyl acetate monomer reactivity ratio calculated from two duplicate experiments.

Discussion

Monomer reactivity ratios obtained from the data of Table I are summarized in Table II. Since data on the eight systems were gathered at scattered times over four years, during which analytical precision has varied, the standard deviation

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[1] For the preceding paper in this series, see Lewis, Walling, Cummings, Briggs and Mayo, THIS JOURNAL, **70**, 1519 (1948).

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

[4] The authors are indebted to Dr. Ellen Bevilacqua for the development of the analytical method described, and also for most of the analyses reported here.

TABLE I

PEROXIDE-CATALYZED POLYMERIZATIONS OF VINYL ACETATE (M_2) AT 60°

$[M_1]_0$[a]	$[M_2]_0$[a]	$[M_1]$[a]	$[M_2]$[a]	Reaction time, hr.	Polymer analysis			
		M_1 = styrene			% C			
16.20	66.45	5.35	65.60	120	89.69	89.80		
10.86	62.70	3.22	61.55	168	87.46	87.30		
39.50	35.99	6.13	34.95	168	91.24	91.13		
39.20	36.38	5.96	34.92	168	90.76	90.90		
		M_1 = methyl methacrylate			% AcOH			
41.98	158.43	29.77	157.5	5.3	7.80	7.89		
40.61	159.80	29.84	158.9		7.43	7.52		
41.33	158.70	28.23	157.7		8.02	7.59		
161.02	42.58	133.83	40.3	2.7	0.76	0.56		
159.20	40.56	131.97	38.28		0.69	0.81		
158.62	35.78	131.6	33.51		0.68	0.8		
		M_1 = methyl acrylate			% AcOH			
17.36	63.89	11.80	61.31	.25	22.06	22.08		
41.69	40.53	32.26	39.62	.11	6.21	6.11		
65.45	17.16	28.33	15.13	.07	3.64	3.60		
		M_1 = acrylonitrile; each run contained 5 cc. acetonitrile			% N (Dumas)[d]			
16.45	63.04	5.97	54.65	15.75	11.45	11.27	11.31	
16.42	62.88	5.95	54.93		11.73	11.62		
63.75	15.91	56.72	15.504	2	23.51	24.04		
63.93	16.03	56.70	15.556		23.69	23.40		
		Vinyl bromide = M_1			% Br[b]			
15.70	63.28	6.32	47.95	3	32.16	32.33		
17.64	64.65	7.86	51.59		35.96	35.97		
69.70	16.14	47.71	14.44		70.38			
63.54	16.08	40.69	14.79		71.22	71.69		
47.61	16.22	37.03	15.35		70.09			
		Vinyl chloride = M_1 (12 mg. Bz_2O_2)			% Cl			
23.39	78.70	12.76	64.17	4.5	19.66	19.71		
25.60	78.35	14.62	64.46		20.62	20.76		
65.08	19.88	53.81	18.25	3.5	47.23	47.41		
64.42	19.70	56.06	18.24		45.87	45.63		
		Following runs contained 5.00 cc. chlorobenzene, 10 mg. Bz_2O_2						
92.80	16.67	84.40	15.84	6	49.02	49.86	50.95[c]	
88.16	16.50	78.10	15.39		49.09	49.52	49.22	49.03[c]
		Vinyl ethyl ether = M_1			% AcOH			
16.06	62.85	12.43	25.26	19.76	63.75	63.65		
15.60	63.30	11.79	24.03		63.70	63.50		
		Trichloroethylene = M_1			% Cl			
7.61	46.46	3.42	25.27	24	18.80	18.81		
15.23	34.96	12.35	27.84		31.54	31.61		
19.04	29.04	14.96	21.12		35.64	35.65		
23.98	23.35	21.26	17.98		38.56	38.59		

[a] Millimoles of unreacted monomers; zero subscripts indicate initial quantities. [b] Analyzed by combustion in stream of oxygen, as described by Gregg and Mayo,[e] after unsuccessful attempts to obtain reasonable and reproducible results by other methods. [c] Heterogeneity of sample may be responsible for poor checks. All sample used in analyses and all results averaged. [d] Calculations based on experimental value of 26.06% *N* in polyacrylonitrile. In press.

of separate experiments is taken as the experimental error.[1] The outstanding feature of the results is the low reactivity toward free radicals of vinyl acetate as compared with other monomers: except for vinyl ethyl ether, the vinyl acetate radical prefers to react with the other monomer of the pair. A similar conclusion, based on α-values[5] derived from single experiments, has been reached by Nozaki.[6] Although the unconjugated monomers (unsaturated halides) have the same order of

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(5) Wall, THIS JOURNAL, **63**, 1862 (1941).

(6) Nozaki, *J. Polymer Sci.*, **1**, 455 (1946).

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 ± 10	0.01 ± 0.01
Methyl methacrylate	20 ± 3	.015 ± .015
Methyl acrylate	9 ± 2.5	.1 ± .1
Acrylonitrile	4.05 ± .3	.061 ± .013
Vinyl bromide	4.5 ± 1.2	.35 ± .09
Vinyl chloride	1.68 ± .08	.23 ± .02
Vinyl ethyl ether	0	3.0 ± .1
Trichloroethylene	.01 ± .01	0.66 ± .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 coworkers[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.

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[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).

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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)

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[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).