2. Acetone and nitrosomethane were found to be initial products of the decomposition. The latter new compound was identified as the hitherto unknown crystalline dimer.

3 Some of the properties of nitrosomethane and its dimer have been determined.

WILMINGTON, CALIFORNIA
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Copolymerization. IV. Effects of Temperature and Solvents on Monomer Reactivity Ratios

BY FREDERICK M. LEWIS, CHEVES WALLING, WILLIAM CUMMINGS,[1] EMORENE R. BRIGGS[2] AND FRANK R. MAYO

Previous papers from this Laboratory and elsewhere[3] have shown that the behavior of monomers in free radical type copolymerizations may be described accurately by the copolymerization equation[3a,4,5]

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \qquad (1)$$

where $[M_1]$ and $[M_2]$ are concentrations of unreacted monomers, r_1 is the ratio of the rate constants for the reaction of an M_1-type radical with M_1 and M_2, respectively, and r_2 is the ratio for reaction of an M_2-type radical with M_2 and M_1, respectively. The quantities r_1 and r_2 have been designated *monomer reactivity ratios*, and it should be noted[3b] that a comparison of the *reciprocals* of a series of monomer reactivity ratios for a particular radical with a number of monomers yields the *relative reactivities* of the monomers toward that radical. If such series for all radicals were the same, *i. e.*, if, in general, $r_1r_2 = 1$, Equation (1) would reduce to the simpler form earlier proposed by Wall.[6] However, a striking feature of free radical copolymerizations is that, in many pairs, each monomer prefers to react with the opposite type radical. This "alternating effect," which can be discussed qualitatively in terms of r_1r_2 products (r_1r_2 being zero for complete alternation), appears to be an additional effect superimposed upon a fundamental order of monomer reactivity,[3b] and Price[7] has suggested, on the basis of the data available at the time, that it arises from polar interaction between radical and monomer. The present series of nine papers increases five-fold the number of monomer pairs for which monomer reactivity ratios are available. The results give partial support to Price's suggestion and permit a much more detailed discussion of copolymerization phenomena than has hitherto been possible.

The present paper discusses refinements in techniques and in the treatment of data which have been developed in this Laboratory during the past three years and presents measurements of the temperature coefficients of monomer reactivity ratios for five monomer pairs. It also reports more precise measurements of the effects of solvents on the monomer reactivity ratios for styrene and methyl methacrylate.

The next three papers, V–VII, describe new experiments on twenty-nine monomer pairs. In VIII, all of these data are reviewed and the theoretical implications discussed in terms of monomer activity and polarity series. Copolymerization IX presents and discusses experiments on the relative reactivities in copolymerization of *cis* and *trans* isomers. The last three papers, X–XII, are a study of the effect of nuclear substitution on the reactivity of styrene in copolymerization. Here, measurements on thirty-six systems throw further light on the nature of the "alternating effect" in copolymerization.

Experimental

Materials.—Diethyl maleate and diethyl fumarate were Eastman Kodak Co. materials, melting points −12 to −11 and 0 to 1°, respectively. They were used without further purification. Styrene, methyl methacrylate and methyl acrylate were commercial materials, fractionally distilled and stored in the ice-box until used. *p*-Chlorostyrene was prepared by the decarboxylation of *p*-chlorocinnamic acid. Its preparation and physical properties are described elsewhere.[8]

Polymerization Technique.—Polymerizations were carried out in duplicate or triplicate on 1:4 and 4:1 molar ratios of monomers in sealed tubes in absence of air, essentially as described in previous papers in this series.[3a] At 60°, 0.1 mole % benzoyl peroxide was used as catalyst, at 131°, no catalyst except for the styrene–methyl methacrylate system where 0.1% acetone peroxide was added. All polymers were soluble in benzene and were isolated by the frozen benzene technique.[9] Results of all experiments reported here are listed in Tables I and II.

Experimental Errors.—Extensive experience in this laboratory has shown that, although any set of experiments may give a very small intersection in the graphical

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[4] (a) Alfrey and Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944); (b) Wall, THIS JOURNAL, **66**, 2050 (1944).

[5] Hereafter in this series the new nomenclature for copolymerization constants, *cf.* Alfrey, Mayo and Wall, *J. Polymer Sci.*, **1**, 581 (1946), is used. Thus, M_1, M_2, r_1 and r_2 correspond to S, M σ and μ in previous papers.

[6] Wall, *ibid.*, **63**, 1862 (1941).

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

[8] Walling and Wolfstirn, THIS JOURNAL, **69**, 852 (1947).

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

Table I

Copolymerization Experiments at Two Temperatures

$[M_1]_0$[a]	$[M_2]_0$[a]	$[M_1]$[a]	$[M_2]$[a]	Time, hr.	% C in polymer		
Styrene (M_1)–Methyl Methacrylate (M_2) at 60°[b]							
63.21	16.03	58.80	14.43	5.0	83.66	83.77	83.94
39.77	39.67	36.24	36.27	5.0	76.52	76.61	
16.04	63.42	14.46	59.41	2.68	69.13	69.11	
63.24	15.81	58.76	14.24	89[e]	83.98	84.00	
39.62	39.37	35.88	35.78	89[e]	76.70	76.53	
15.75	63.97	12.83	56.39	68.5[e]	68.90	69.07	
Same at 131°							
63.0	16.19	46.3[d]	10.73[d]	1.0	84.45	84.34	
39.50	39.64	29.56	29.99	1.0	76.59	76.42	
15.95	6.45	12.38	54.4	0.83	68.39	68.41	
Styrene (M_1)–Methyl Acrylate (M_2) at 60°							
17.67	78.65	14.28	73.30	2.8	71.55	71.49	71.59
19.24	80.88	15.66	75.25	3.7	71.55	71.67	71.68
19.15	80.98	15.37	74.98	3.7	71.59	71.61	71.73
79.85	20.21	74.12	18.68	3.7	85.68	85.63	85.69
79.78	20.18	74.72	18.85	3.7	85.79	85.72	85.62
80.28	21.03	75.62	19.74	3.7	85.48	85.39	85.46
Same at 131°							
19.65	80.92	16.38	75.28	.67	70.69	70.77	70.84
19.64	80.85	16.13	74.86	.67	70.94	70.93	70.88
22.32	81.20	18.42	75.00	.67	71.67	71.68	71.65
79.80	20.17	68.10	17.24	.67	86.03	85.99	86.04
80.30	20.00	68.80	17.17	.67	86.09	86.18	86.11
78.80	20.81	67.60	17.94	.67	85.92	85.87	85.90
Styrene (M_1)–Diethyl Maleate (M_2) at 60°							
63.51	15.68	37.79[c]	14.54	36	89.81	89.71	
64.05	15.62	38.77	14.48	36	89.63	89.76	
16.13	62.77	7.985	59.12	100	76.75	76.74	
16.05	62.69	8.030	59.31	100	76.60	76.57	
Same at 131°							
63.88	15.87	6.056	10.59	66	87.50	87.42	
63.53	15.95	12.31	12.45	18	88.62	88.47	
65.68	15.85	11.94	11.89	18	88.22	88.35	
Styrene (M_1)–Diethyl Fumarate (M_2) at 60°							
15.93	63.48	2.979	49.90	62.6	69.27	69.03	
15.72	63.61	3.191	50.13	62.6	68.89	68.96	
15.88	63.28	3.096	49.45	62.6	69.00	68.82	
64.99	16.94	4.936	9.83	23	76.42	76.79	
63.83	16.03	4.790	9.34	23	77.22	77.39	
Same at 131°							
16.12	64.22	3.307	45.22	219.3	66.30	66.43	
16.61	63.81	3.574	44.81	219.3	66.50	66.59	
63.80	16.34	53.13	12.16	2.0	78.02	78.07	
63.85	16.10	52.33	11.76	2.0	78.20	78.30	
Styrene (M_1)–*p*-Chlorostyrene (M_2) at 60°							
9.615	32.27	6.825	22.10	14	21.18[f]	21.18	
40.09	10.06	31.33	7.32	14	7.48[f]	7.51	
39.57	10.96	29.97	7.77	12	7.87[f]	7.78	
10.14	41.61	7.555	30.47	12	21.70[f]	21.78	
Same at 131°							
39.70	10.34	24.73	5.86	1.75	7.21[f]	7.41	
10.07	39.90	5.78	21.80	1.25	21.66[f]	21.71	
10.09	39.55	6.34	23.90	1.25	21.63[f]	21.74	
40.00	10.15	19.29	4.30	1.50	6.90[f]	7.08	
10.21	39.90	3.80	13.37	1.0	21.56[f]	21.68	

[a] Millimoles of unreacted monomers; zero subscripts indicate initial quantities. [b] Data taken from Mayo and Lewis, ref. 3, experiments 4B, 4C, 4D, 5A, 5B, 5C listed in that order but recalculated using empirical analyses on blanks (4A and 4E) for calculating polymer composition (see text). [c] Calculated using 92.24 as % C in styrene (see text). [d] Calculated using same blanks as 60° experiments. [e] Thermal polymerization, no catalyst added. [f] Per cent. Cl in polymer.

Table II

Effect of Solvents on Monomer Reactivity Ratios of Styrene (M_1) and Methyl Methacrylate (M_2) at 60°

$[M_1]_0$	$[M_2]_0$	$[M_1]$	$[M_2]$	Time, hr.	% C in polymer		
Benzene (9 vol.)[a]							
63.7	16.01	51.7	11.91	72	84.40	84.39	84.10
39.8	40.02	29.9	30.6	72	77.11	76.75	76.96
16.03	63.79	8.37	43.79	72	69.13	69.34	69.20
Acetonitrile (8 vol.)[a]							
63.06	17.07	55.74	14.27	72	83.74	83.43	
46.12	39.84	32.87	32.77	72	76.61	76.69	
16.13	71.70	9.55	52.47	72	68.49	68.45	
Methanol (2 vol.)[a]							
63.44	19.07	55.98	16.13	24	83.30	83.43	
40.60	39.54	32.33	32.12	24	77.31	77.29	
16.03	66.11	7.09	42.45	24	69.14	69.05	

[a] Per volume total monomers.

solution of the copolymerization equation, these intersections shift appreciably from set to set. In early work many of these shifts proved to be due to inadequate techniques of polymer isolation. With more refined methods, they now appear to be usually the result of small systematic errors in polymer analysis. The temperature coefficients of monomer reactivity ratios discussed in this paper represent, at best, small differences between experimentally measured quantities. Accordingly, the highest attainable accuracy in determination of monomer reactivity ratios is important. Further, since the desired quantities are *differences*, the presence of a small systematic error (so long as it is the same for the experiments at both temperatures) causes no trouble.

In order to "freeze" this error as nearly as possible, each set of experiments at two temperatures reported here was carried out and worked up by the same operator at the same time and using the same techniques. The relative experimental error at each temperature was then calculated as the standard deviation of duplicate experiments, and the errors in heats and entropies of activation were determined by the usual formulas for propagation of error. In the most fortunate cases, for example, styrene–methyl acrylate, the relative experimental error in monomer reactivity ratios determined in this way is considerably smaller than the probable *absolute* error. However, for the reasons outlined above, we consider it the proper one to use in the subsequent calculations. The styrene–methyl methacrylate system was studied before this procedure was adopted. The experimental error in this case was taken as that arising from a 0.1% error in carbon analysis (see below). An idea of the agreement obtained between experiments and the magnitude of the change in monomer reactivity ratios arising from a 70° change in temperature may be gotten from Fig. 1 in which the graphical solutions of the copolymerization equation for the styrene–methyl acrylate system are illustrated.

In the case of the styrene–diethyl maleate system, the monomer reactivity ratio for the maleate-type radical is indistinguishable from zero. Accordingly, only 4:1 styrene–maleate experiments were carried out at 131°, and the heats and entropies of activation differences for the reaction of the styrene type radical calculated from the shift of the intersection of the high styrene experiments with the zero axis.

It is of course important to have an idea, as well, of the magnitude of the *absolute* experimental error in the measurement of monomer reactivity ratios. Since, with suitable technique in polymer isolation, this error arises chiefly from errors in polymer analysis, we have adopted the following technique for its estimation, based upon the observation that blank carbon analyses run in our analytical laboratory on known samples deviate from calculated results by over 0.2% less than one time in five. For a given monomer pair two representative experiments, one at 1:4 and the other at 4:1 monomer ratios are chosen and $[M_1]$ and $[M_2]$ recalculated assuming +0.2% and −0.2% errors in analysis. The results are then replotted on a r_1 *vs.* r_2 plot, yielding a parallelogram about the former intersection. This parallelogram is now shifted so that its center coincides with the best value of r_1 and r_2 determined by the whole set of experiments carried out on the given monomer pair, and the absolute experimental error is taken as the range of values of r_1 and r_2 lying within the parallelogram. The best justification for the method, aside from the arguments just outlined, is that with sufficient care sets of experiments can generally be obtained in which all of the lines corresponding to the individual experiments pass through the parallelogram. In the case that they do not, and it does not appear feasible to run additional polymerizations, the standard deviation is taken as the absolute experimental error. However, this difficulty has not arisen with any of the monomer pairs reported here. In the cases where $[M_1]$ and $[M_2]$ are determined by nitrogen or chlorine analysis, calculations are based upon a 0.1% experimental error. In the case of the system styrene–methyl methacrylate, blanks of pure polymeric styrene and methyl methacrylate were analyzed simultaneously with the copolymers and the empirical carbon contents used in calculating copolymer compositions. Although the experiments are those described in the first paper of this series,[3a] this changes the values of the momomer reactivity ratios slightly from the values previously reported.[10] For styrene–diethyl maleate, polymer compositions lay very close to pure polystyrene. Accordingly, a sample of pure polystyrene to which diethyl maleate monomer had been added was worked up together with the copolymers and analyzed. The result (92.24% C) was used in calculations and served as a check both on the isolation procedure and the accuracy of carbon analysis (calcd. 92.26%). In view of the employment of these precautions, the use of 0.1% error in carbon seemed justified in calculating the experimental errors in this system.

Results and Discussion

Measurements at Two Temperatures.—Previous measurements of monomer reactivity ratios in copolymerizations have been limited to a single temperature. Measurement at two temperatures are of obvious practical interest. Further, since a monomer reactivity ratio represents the ratio of two rate constants which may be expressed in the form

$$r_1 = e^{\frac{\Delta S_{11}^{\ddagger} - \Delta S_{12}^{\ddagger}}{R} - \frac{\Delta H_{11}^{\ddagger} - \Delta H_{12}^{\ddagger}}{RT}} \qquad (2)$$

where $\Delta S_{11}^{\ddagger}$, $\Delta H_{11}^{\ddagger}$, $\Delta S_{12}^{\ddagger}$, and $\Delta H_{12}^{\ddagger}$ are, respectively, the entropies and heats of activation for the reaction of M_1 type radical with M_1 and M_2, measurement of r_1 at two temperatures permits the calculation of the differences in the heats and entropies of activation for the two reactions of the radical. These differences, for the monomer pairs of Table I, are listed in Table III. Since $(\Delta S_{11}^{\ddagger} - \Delta S_{12}^{\ddagger})/R = \ln (P_{11}Z_{11}/P_{12}Z_{12})$ in the Arrhenius treatment, and since this ratio perhaps provides a simpler way of visualizing the magnitude of a "steric" effect, it has been calculated as well, and is included in Table III.

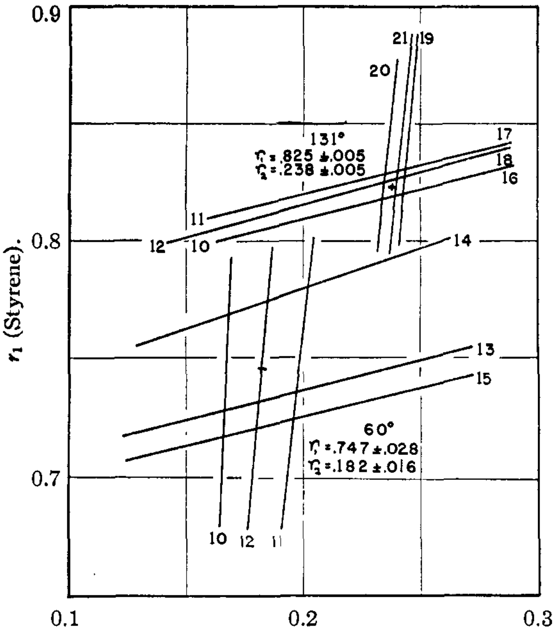

Fig. 1.—Copolymerization of styrene and methyl acrylate at 60° and 131°. Numbers of lines correspond to order of experiments in Table I.

Two conclusions may be safely drawn from the data of Table III. The first is that, despite the care with which the experiments were carried out, the resulting uncertainties in heat and entropy of activation differences are still quite large. The second is that, for most of the pairs, entropy of activation differences do not differ significantly from zero, and the major source of the differences in reactivity of monomers in polymerization lies in heats of activation. Accordingly, the practice of discussing these differences as due to resonance stabilization of complexes, polar interaction, etc., is in general justified. The only case where the entropy difference clearly differs from zero is that of the reaction of the fumarate type radical with styrene and diethyl fumarate. Although the reason for the difference, corresponding to a threefold difference in *PZ* factors, cannot be stated unequivocally, it lies in the direction which would be expected if the second carboethoxy group of diethyl fumarate offered steric hindrance toward the attack of the radical on the double bond. If this were the case, a similar difference should be anticipated for the styrene radical in the same copolymerization and in the system styrene–diethyl maleate. Although in both cases the entropy difference does lie in the right direction, it is smaller and, in the first, within experimental error of zero.

Another result of these measurements is that in general the temperature coefficients of the monomer reactivity ratios are rather small. This

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(10) Although blanks were run indicating slightly low (0.1–0.3%) carbon analyses, the original calculations were based on theoretical carbon analyses. We have since frequently based calculations on actual instead of theoretical analyses and this procedure is now extended to our earlier work; *cf.* Nozaki, ref. 11.

Table III

Heat and Entropy of Activation Differences in the Copolymerization of Some Monomer Pairs

Radical type[a]	r_1 60°	r_1 131°	$\Delta H_{11}^{\ddagger} - \Delta H_{12}^{\ddagger}$	$\Delta S_{11}^{\ddagger} - \Delta S_{12}^{\ddagger}$	$P_{11}Z_{11}/P_{12}Z_{12}$
Styrene	0.520 ± 0.026	0.590 ± 0.026	480 ± 250	0.12 ± 0.68	1.06 ± 0.30
Methyl methacrylate	.460 ± .026	.536 ± .026	580 ± 280	.19 ± .76	1.10 ± .34
Styrene	.747 ± .028	.825 ± .005	380 ± 140	.54 ± .36	1.31 ± .16
Methyl acrylate	.182 ± .016	.238 ± .005	1020 ± 340	.66 ± .86	1.39 ± .49
Styrene	6.52 ± .05	5.48 ± .56	−660 ± 480	1.87 ± 1.36	2.55 ± 1.26
Diethyl maleate	< .01	....	....	....	....
Styrene	.301 ± .024	.400 ± .014	1070 ± 320	.82 ± .82	1.50 ± .50
Diethyl fumarate	.0697 ± .0041	.0905 ± .0008	990 ± 290	−2.35 ± .73	0.31 ± .14
Styrene	.742 ± .030	.816 ± .015	360 ± 170	.48 ± .43	1.27 ± .24
p-Chlorostyrene	1.032 ± .030	1.042 ± .015	35 ± 120	.40 ± .32	1.22 ± .18

[a] Each monomer of the pair being considered as M_1 in turn.

is, indeed, a necessary consequence from the observed small differences in entropies of activation, and may be generalized to the statement that the composition of the copolymer obtained from systems in which neither monomer reactivity ratio differs greatly from unity will be quite insensitive to temperature. This conclusion is of some practical importance.

Absolute Values of Monomer Reactivity Ratios.—Using the procedure described in the Experimental Part, absolute experimental errors for monomer reactivity ratios for the monomer pairs studied here have been calculated, and results are summarized in Table IV, together with the results of other workers on the same systems. The agreement between work in this Laboratory and elsewhere will be seen to be quite satisfactory.

Table IV

Monomer Reactivity Ratios at 60° with Calculated Experimental Errors

Radical type	Error assumed, %	Monomer reactivity ratios This paper	Other workers
Styrene	0.2 C	0.520 ± 0.026	(60°) 0.65 ± 0.08[a]
Methyl methacrylate	.2 C	.460 ± .026	(60°) .51 ± .10[a]
Styrene	.2 C	.75 ± .07	(70°) .75 (±0.1)[b]
Methyl acrylate	.2 C	.18 ± .02	(70°) .2 (±0.05)[b]
Styrene	.1 C	6.52 ± .50	(70°) 5 (±1.5)[b]
Diethyl maleate	.1 C	.005 ± .01	(70°) 0 (±0.1)[b]
Styrene	.2 C	.30 ± .02	...
Diethyl fumarate	.2 C	.070 ± .007	...
Styrene	.1 Cl	.74 ± .03	[c]
p-Chlorostyrene	.1 Cl	1.025 ± .05	[c]

[a] Nozaki, *J. Polymer Sci.*, **1**, 455 (1946). Results of two sets of experiments have been averaged. [b] Alfrey, Merz and Mark, *ibid.*, p. 37. The experimental errors have been estimated by plotting their data on a r_1 *vs.* r_2 plot and by taking the axes of the smallest ellipses through which all the lines corresponding to their experiments would pass. [c] Marvel and Schertz, This Journal, **65**, 2054 (1943), prepared and analyzed samples of this copolymer but monomer compositions were not varied sufficiently for a calculation of monomer reactivity ratios.

Effect of Solvents.—Copolymerizations of styrene with methyl methacrylate in benzene and acetonitrile (solvents of low and high dielectric constant, respectively) and in methanol (a solvent from which the polymer precipitates) are listed in Table II and the graphical solutions illustrated in Fig. 2. Since experiments were carried out using better techniques than in the first paper, intersections are smaller and render more certain the conclusion[3a,11] that solvents have no detectable effect on monomer reactivity ratios. This conclusion is also in agreement with the results of other workers who have found identical monomer reactivity ratios for the systems styrene–methyl methacrylate[12] and styrene–acrylonitrile[3e] studied under homogeneous conditions and in emulsion.

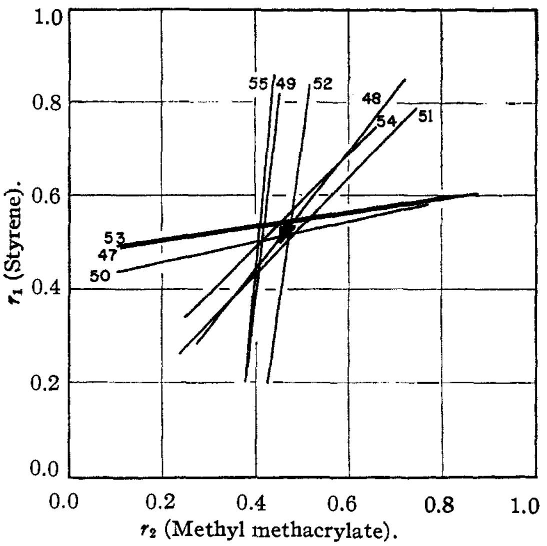

Fig. 2.—Constancy of monomer reactivity ratios for styrene–methyl methacrylate in various solvents at 60°: 47–49, benzene; 50–52 acetonitrile; 53–55, methanol. Numbers of line correspond to order of experiments in Table II. Black triangle represents intersection in absence of solvent.

Acknowledgment.—The inception of work on copolymerization in these laboratories is largely due to the early decision by Dr. Robert T.

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

(12) Smith, This Journal, **68**, 2069 (1946).

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.

PASSAIC, NEW JERSEY RECEIVED JULY 17, 1947

[CONTRIBUTION NO. 67 FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

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 ($\sim$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.