Copolymerization. V. Relative Monomer Addition Rates in Vinyl Copolymerization

BY REID G. FORDYCE, EARL C. CHAPIN AND GEORGE E. HAM

Until the recent publication by Alfrey and Price[1] it has been necessary to refer relative monomer reactivity ratios to the particular two-component system investigated. These authors, however, have indicated that it may be possible by means of two constants, Q and e, to characterize the relative rates of copolymerization of any vinyl monomer with any other vinyl monomer whose Q and e parameters are known. Utilizing the experimental study of Lewis, Mayo and Hulse,[2] Q and e values were assigned to styrene, methyl methacrylate, acrylonitrile and vinylidene chloride which appeared to account satisfactorily for their behavior in copolymerization. Because of the practical and theoretical usefulness of this general approach to the problem of copolymerization, it appeared desirable to test the validity of their relationships[1] for a number of additional systems. It is the purpose of this communication to present additional data on relative monomer addition rates and to examine these results, along with previously published values, in the light of the Alfrey and Price equations.

In this work, the four base monomers cited above were used as reference points to calculate the Q and e values for new monomers. The Q and e values reported for any monomer are based on copolymerization rate data of that monomer with at least two other monomers. To obtain cross checks of this kind, it was necessary to supplement published results with a study of the following systems: vinyl acetate–acrylonitrile, vinyl acetate–methacrylonitrile, α-methylstyrene–acrylonitrile, α-methylstyrene–methacrylonitrile and styrene–methacrylonitrile.

In determining monomer–polymer composition curves for the above systems, polymerizations were allowed to proceed to low conversions (mainly < 4%) and the initial copolymer formed was isolated, purified and analyzed in duplicate by the micro-Dumas method.

The relationships of Alfrey and Price[1] were used to derive simplified forms of the copolymer equations involving n components. Copolymer compositions were calculated by substituting the Q and e values reported in these equations, and a comparison of the predicted composition with the composition determined by analysis was made.

Results and Discussion

The shapes of the monomer–polymer composition curves for the systems vinyl acetate–acrylonitrile, vinyl acetate–methacrylonitrile, α-methylstyrene–acrylonitrile, α-methylstyrene–methacrylonitrile and styrene–methacrylonitrile are shown

(1) Alfrey and Price, *J. Polymer Science*, **2**, 101 (1947).
(2) Lewis, Mayo and Hulse, THIS JOURNAL, **67**, 1701 (1945).

in Fig. 1. These curves are based on data obtained from mass copolymerizations, interrupted at low conversions. Table I summarizes the polymerization conditions and the analytical results of the experiments.

TABLE I

Monomer, mole % acrylonitrile	Time at polymerization temp., hr.	Wt. % conversion	Nitrogen analyses, % I	II	Copolymer, mole % acrylonitrile[a]
Vinyl Acetate–Acrylonitrile copolymerizations Mass polymerization at 60°, 0.1% Bz₂O₂					
12.18	4.0	0.5	14.37	14.51	67.8
17.86	4.25	0.9	17.86	17.88	79.2
52.0	4.5	1.2	21.00	21.36	88.9
70.8	5.0	0.4	22.12	22.19	92.5
93.6	8.0	1.2	24.90	25.10	98.8
100.0	…	…	25.50	25.58	96.8[b]
Vinyl Acetate–Methacrylonitrile Copolymerizations Mass polymerization at 70°, 0.05% Bz₂O₂					
12.47	24	1.0	13.44	13.62	73.0
24.35	25.5	0.2	15.51	15.74	82.1
46.2	10.5	0.2	17.38	17.52	90.0
82.8	10.5	0.3	19.26	19.29	99
100.0	…	…	19.90	19.98	95.5[b]
α-Methylstyrene–Acrylonitrile Copolymerizations Mass polymerization at 75°, 0.05% Bz₂O₂					
9.1	23	3.0	5.34	5.22	36.7
22.8	23	2.4	6.35	6.41	42.5
36.0	23	1.6	7.14	6.77	45.4
42.4	15	4.0	7.90	7.83	49.8
53.0	15	3.5	8.63	8.54	53.0
84.0	15	2.3	9.82	9.52	57.4
94.0	15	2.6	11.74	11.98	65.9
α-Methylstyrene–Methacrylonitrile Copolymerizations Mass polymerization at 80°, 0.10% Bz₂O₂					
7.05	6	<1.0	4.34	4.27	32.6
25.5	6	<1.0	6.10	6.19	43.8
44.0	6	<1.0	7.68	7.76	52.6
63.0	6	2.4	9.54	9.46	61.5
85.0	6	4.6	12.09	12.29	73.4
Styrene–Methacrylonitrile Copolymerizations Mass polymerization at 80°, 0.1% Bz₂O₂					
6.5	9	1.0	2.59	2.75	19.2
25.2	9	2.0	5.66	5.89	38.7
54.3	3	1.6	8.21	8.16	52
84.6	11	1.8	11.98	11.84	69.7

[a] Corrected for incomplete nitrogen evolution.   [b] Not corrected.

It was found that the micro-Dumas method of nitrogen analysis gave only 96.8 and 95.5% of the theoretical nitrogen content for polyacrylonitrile or polymethacrylonitrile, respectively. For this reason the nitrogen analyses obtained on the above
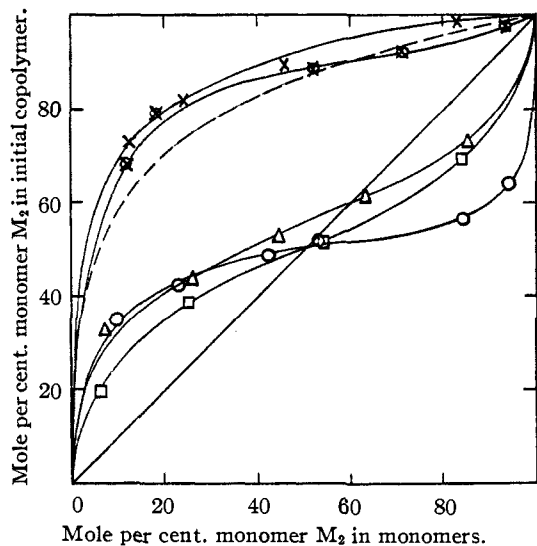
Fig. 1.—Monomer–polymer composition curves: $\otimes$, vinyl acetate–acrylonitrile (experimental); ---, vinyl acetate–acrylonitrile (theoretical $r_1 = 0.02$, $r_2 = 6$); $\times$, vinyl acetate–methacrylonitrile; O, α-methylstyrene–acrylonitrile; $\triangle$, α-methylstyrene–methacrylonitrile; $\square$, styrene–methacrylonitrile.

systems were corrected by assuming that any acrylonitrile or methacrylonitrile in a copolymer would evolve a proportionate amount of nitrogen.

Monomer reactivity ratios for these systems were determined by varying their values in the differential copolymer equation[3,4] until a good curve through the experimental points was obtained. This was possible in every case except the vinyl acetate–acrylonitrile system. Here some divergence between the experimental points and the theoretical curve exists as shown in Fig. 1. The relative reactivity ratios[5] for these systems were determined:

	r_1	r_2
Vinyl acetate–acrylonitrile	0.02 ± 0.02	6 ± 2
Vinyl acetate–methacrylonitrile	$.01 \pm .01$	12 ± 2
α-Methylstyrene–acrylonitrile	$.1 \pm .02$	0.06 ± 0.02
α-Methylstyrene–methacrylonitrile	$.12 \pm .02$	$.35 \pm .02$
Styrene–methacrylonitrile	$.25 \pm .02$	$.25 \pm .02$

In connection with the above data it is interesting to note that whereas α-methylstyrene readily forms copolymers containing more than 50 mole per cent. combined α-methylstyrene, we have been unable to polymerize it alone by a free radical mechanism.

The following relationships of Price and Alfrey[1] were employed for assigning Q and e values

(3) Mayo and Lewis, THIS JOURNAL, **66**, 1594 (1944).

(4) Alfrey and Goldfinger, J. Chem. Phys., **12**, 205 (1945).

(5) The values correspond to the r_1 and r_2 nomenclature of Alfrey, Mayo and Wall, J. Polymer Science, 1, 581 (1946).

$$r_1 = \frac{Q_1}{Q_2} e^{-e_1(e_1-e_2)} \qquad (1)$$

$$r_2 = \frac{Q_2}{Q_1} e^{e_2(e_1-e_2)} = \frac{Q_2}{Q_1} e^{-e_2(e_2-e_1)} \qquad (2)$$

Owing to the nature of the equations and to the inherent inaccuracies of the values of r_1 and r_2, the Q and e values for a given monomer varied somewhat depending on the system chosen for calculation. Consequently, the values reported represent only a fit to the data available. Undoubtedly, these values will have to be modified as more information becomes available.

The sequence of calculations used for determining Q and e values has a bearing on the results. From published data and data presented here, Q and e values were calculated from the systems indicated.

	Q	e	System
Methyl acrylate	0.34	0.38	Styrene–methyl acrylate[6]
Methacrylonitrile	.77	0.67	Styrene–methacrylonitrile
α-Methylstyrene	.59	-1.26	α-Methylstyrene–acrylonitrile
α-Methylstyrene	.67	-1.11	α-Methylstyrene–methacrylonitrile
Vinyl acetate	.013	-0.45	Vinyl acetate–acrylonitrile
Vinyl acetate	.024	-0.78	Vinyl acetate–methacrylonitrile
Vinyl chloride	.027	-0.22	Vinyl chloride–acrylonitrile[7]
Vinyl chloride	.03	-0.16	Vinyl chloride–methylacrylate[7]

The values of Q and e for methyl acrylate and for methacrylonitrile were not modified. The average of the two values obtained for α-methylstyrene, vinyl acetate and vinyl chloride was taken. The Q and e parameters determined in this manner are summarized, including those previously published[1]

	Q	e
Styrene	1.00	-1.0
Methyl methacrylate	0.64	0
Acrylonitrile	.34	1.0
Vinylidene chloride	.16	0
Vinyl chloride	.028	-0.19
Methyl acrylate	.34	$+0.38$
Vinyl acetate	.018	-0.61
α-Methylstyrene	.63	-1.18
Methacrylonitrile	.77	$+0.67$

The degree of agreement between calculated relative rates of polymerization and the values determined experimentally has been fully described by Price and Alfrey for the four reference monomers. A similar comparison for the monomers reported here is

	r_1		r_2	
	Calcd.	Obsd.	Calcd.	Obsd.
Vinyl chloride[a]–acrylonitrile	0.065	0.074[7]	3.7	3.7
Vinyl chloride[a]–methyl acrylate	0.074	0.083[7]	9.8	9.0
Vinyl chloride–styrene	0.046	0.067[7]	16	35
Vinyl chloride–vinyl acetate	1.7	1.8[8]	0.5	0.6

(6) Alfrey, Merz and Mark, J. Polymer Research, **1**, 37 (1946).

(7) Chapin, Ham and Fordyce, THIS JOURNAL, **69**, 538–542 (1948).

(8) From a paper by T. Alfrey, Jr., presented at the American Chemical Society Meeting, Atlantic City, N. J., April 8–12, 1946.

Styrene-methyl acrylate[a]	1.3	1.3[6]	0.20	0.20
Styrene-vinyl acetate	41.5	50	0.021	.02
Styrene-methacrylo-nitrile[a]	0.25	0.25	0.25	0.25
Vinyl acetate[a]-acrylonitrile	.02	.02 ± 0.02	3.4	6 ± 2
Vinyl acetate[a]-meth-acrylonitrile	.011	.01 ± .01	18	12 ± 2
α-Methylstyrene[a]-acrylonitrile	.14	.1 ± .02	0.06	0.06 ± 0.02
α-Methylstyrene[a]-methacrylonitrile	.09	.12 ± .02	0.35	0.35 ± .02

[a] The data which either were used directly or were used to calculate average Q and e values for the designated monomer. The results of greatest interest, however, are those systems which are not marked, since these data represent the cross checks on the validity of predictions based on the Price–Alfrey relationships.

An examination of the above reveals, first, that in no case has the predicted shape of the monomer-polymer composition curve, with respect to the azeotrope line, been in error. When the curve predicted from the above Q and e values lay above or below the azeotrope line, experimental data have been in agreement with the prediction. Unpublished results on a number of other vinyl copolymer systems studied at these laboratories have not as yet revealed a single exception to this.

Considering the assumptions and uncertainties involved in the derivation of the Alfrey–Price equations, as well as the experimental error involved in many of the rate function parameters, quantitative agreement is surprisingly good. Certain discrepancies shown above are not as significant as they appear. For example, in the system styrene–vinyl chloride the monomer–polymer composition curves drawn from the calculated and from the observed r_1, r_2 values actually lie quite close to each other in spite of the fact that superficial inspection of the figures indicates a serious divergence. It is concluded on the basis of available data that the Alfrey–Price relationship, when regarded as an empirical tool for predicting copolymerization behavior, is of the utmost utility qualitatively, and forecasts good values for the relative rates of copolymerization for comonomers whose Q and e values are known.

The data also verify certain generalizations implicit in the Alfrey–Price relationships. Monomer–polymer curves which cross the azeotrope line occur principally when comonomers with similar Q values but with e values of opposite sign are copolymerized. The above data for the acrylonitriles with the styrenes exemplify this. The copolymerization of comonomers with widely different Q values gives curves which deviate widely from the azeotrope line. The systems styrene–vinyl chloride and vinyl acetate–acrylonitrile show this clearly.

The concepts of Price and Alfrey can be used to transform the equations for relative monomer addition rates into simpler forms requiring much less time for calculations. The simplification is particularly useful for systems containing three or more monomers. For the general case of n monomers substitution in the derivation of Walling and Briggs[9] gives $n - 1$ simultaneous equations.

It is of interest that these copolymer equations exist in a form which clearly shows the individual steps involved in the propagation reaction, i.e., the sum of all the terms in the numerator or denominator represent the sum of all possible propagation reactions resulting in addition of the given monomer to the growing chain.

The Q and e values given above have been substituted in these equations to predict interpolymer compositions for systems containing more than two monomers. These values were then compared with the results obtained. The following is typical of the agreement obtained between calculated and analytical values

	Initial[a] monomer composition	Predicted[a] polymer composition	Polymer[a] composition by analysis
Styrene	32.0	65.7	67.1[7]
Acrylonitrile	48.8	33.7	32.5
Vinyl chloride	19.2	0.6	0.4
Styrene	30.2	70.5	70.4[7]
Acrylonitrile	15.4	26.4	26.2
Vinyl chloride	54.4	3.1	3.4
Styrene	60	75.5	76.1[7]
Methyl acrylate	20	23.4	22.8
Vinyl chloride	20	1.1	1.1
Styrene	25.21	41.5	40.7[10]
Methyl methacrylate	25.48	27.4	25.5
Acrylonitrile	25.40	24.7	25.8
Vinylidene chloride	23.91	6.4	8.0

[a] Data for the three-component systems are expressed as weight per cent., those for the four-component system are expressed as mole per cent.

Agreement between calculated and observed values, as shown above, is further support for the general validity of the Alfrey–Price relationships. The agreement obtained also lends weight to the approximate correctness of the Q and e values reported.

Experimental

Vinyl Acetate Monomer.—Redistilled Niacet Chemical Co. material was taken for all experiments.

Styrene monomer was the redistilled product of Monsanto Chemical Co.

Acrylonitrile was the redistilled product of American Cyanamid Chemical Co.

Methacrylonitrile was redistilled Shell Development Co. product.

α-Methylstyrene.—Redistilled Dow Chemical Co. product was used.

Benzoyl Peroxide.—The product of the Lucidol Corp. was used as received.

(9) Walling and Briggs, THIS JOURNAL 67, 1774 (1945).

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]^2 Q_1^2 e^{-e_1^2} + [M_1][M_2]Q_1Q_2e^{-e_1e_2} + \cdots + [M_1][M_n]Q_1Q_ne^{-e_1e_n}}{[M_2]^2 Q_2^2 e^{-e_2^2} + [M_1][M_2]Q_1Q_2e^{-e_1e_2} + \cdots + [M_2][M]_nQ_2Q_ne^{-e_2e_n}}$$

$$\frac{d[M_1]}{d[M_n]} = \frac{[M_1]^2 Q_1^2 e^{-e_1^2} + [M_1][M_2]Q_1Q_2e^{-e_1e_2} \cdots + [M_1][M_n]Q_1Q_ne^{-e_1e_n}}{[M_n]^2 Q^2 ne^{-e_n^2} + [M_1][M_n]Q_1Q_ne^{-e_1e_2} \cdots + [M_n][M_{n-1}]Q_nQ_{n-1}e^{-e_ne_{n-1}}}$$

Mass Copolymerization.—The method for determining monomer–polymer composition curves for the five systems reported was essentially the same in each case. Solutions comprising 100 g. of total monomers were prepared by adding appropriate amounts of monomer, comonomer and benzoyl peroxide to 4-oz. French square bottles. The concentrations employed are given in Table I. Air above the monomers was swept out with nitrogen and a metal cap screwed tightly on the bottle mouth. Copolymerizations were carried out in an air oven regulated to ±1° within the polymerization temperature given in Table I. Polymerization at that temperature was continued until a slight increase in viscosity was observed or, in the case of copolymer samples high in combined nitrile, until a small amount of insoluble copolymer had precipitated from the comonomer solution. The reaction was then poured into 3000 ml. of stirred denatured ethanol (2B) at room temperature and the bottle rinsed with ethanol. In the case of vinyl acetate copolymers, hexane was used in place of ethanol throughout. The mixture was boiled to complete the coagulation and filtered. Final purification was effected by similar treatment with two fresh 1500-ml. portions of denatured ethanol. After drying in an evaporating dish for forty-eight hours in a circulating air oven at 60°, the copolymer was analyzed in duplicate for nitrogen by the micro-Dumas method. Analytical data and conversion values are summarized in Table I.

Summary

Monomer–polymer composition curves for the systems vinyl acetate–acrylonitrile, vinyl acetate–methacrylonitrile, α-methylstyrene–acrylonitrile, α-methylstyrene–methacrylonitrile and styrene–methacrylonitrile are reported. These data, along with previously published copolymerization rates, were used to check the validity of predictions based on the Price–Alfrey relationships. Excellent qualitative and good quantitative agreement was found for the systems studied.

Values for the Q and e parameters for five additional monomers are suggested, and simplified forms for copolymer equations involving any number of components are presented.

The Steric Inhibition of Resonance. III.[1] Acid Strengths of Some Nitro- and Cyanophenols

BY G. W. WHELAND, R. M. BROWNELL[2] AND E. C. MAYO

The acid strength of a phenol is greatly increased by the introduction of a nitro group para to the hydroxyl group. In most instances, in fact, the ionization constant of a p-nitrophenol is approximately a thousand times as large as is that of the corresponding unnitrated phenol; in other words, a para nitro group usually decreases the pK_a of a phenol by about 3 units. This greater acidity of the nitrophenol has been attributed[3,4] in part to an electrostatic interaction between the ionizable proton and the dipole moment of the nitro group; and in part also to resonance with a relatively unstable quinoid structure (such as I). Moreover, the effect produced by a para *cyano* group upon the acid strength of a phenol is qualitatively the same as (but usually rather smaller than) that produced by a para nitro group. Again, the observed increase in acid strength can be attributed[3] in part to an electrostatic interaction, since the dipole moment of the para cyano group (like that of the para nitro group) is directed so that its positive end points toward the aromatic ring, and hence toward the

(1) For the second paper of this series, see Spitzer and Wheland, THIS JOURNAL, **62**, 2995 (1940).

(2) A portion of this paper is an abstract of a thesis presented by R. M. Brownell to the faculty of the Division of the Physical Sciences of the University of Chicago in partial fulfillment of the requirements for the degree of Master of Science, March, 1943. Though here published for the first time, this portion of the work has already been briefly discussed in a book by one of us (Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York. N. Y., 1944, p. 185).

(3) Westheimer, THIS JOURNAL, **61**, 1977 (1939).

(4) Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940, p. 205.

ionizable proton; and in part also to resonance with an unstable quinoid structure (such as II).
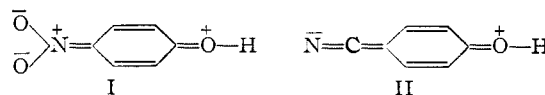
Although both the electrostatic and the resonance effects should therefore increase the acid strengths of the nitro- and cyanophenols, there is no *a priori* way for the estimation of either their absolute or their relative magnitudes. Data now in the literature suggest, however, that the two effects are fairly large and of comparable magnitude. Thus, calculations by Westheimer[3] have led to the conclusion that the electrostatic effect alone should decrease the pK_a of p-nitrophenol (with respect to that of phenol itself) by approximately 1.25 units; hence, it may be inferred that the resonance effect must be responsible for the observed further decrease of approximately 1.6 units (*cf.* Table I, below). Similarly, Westheimer's calculations show that, with p-cyanophenol, the electrostatic effect alone should decrease the pK_a by approximately 1.30 units; hence, it can likewise be inferred that the resonance effect must here be responsible for the observed further decrease of approximately 0.75 unit (*cf.* Table I, below).

The experiments reported in this paper were performed in order to obtain additional evidence either for or against the belief that the electrostatic and the resonance effects are about equally responsible for the relatively great acid strengths