

A Revised Q - e Diagram

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INTRODUCTION

In 1947 Alfrey and Price¹ proposed the Q - e scheme for correlating the mass of data which had then accumulated on free radical copolymerizations. The Q - e scheme defines the copolymerization behavior of a monomer in terms of two parameters, Q and e , which are related to the resonance stabilization and polarity, respectively, of a copolymerizing monomer. In effect, the scheme defines a monomer map on which the positions of two monomers relative to each other define their behavior in copolymerization. Styrene was chosen as the reference monomer and arbitrarily assigned a Q value of 1.0 and an e value of -1.0 . Shortly after publication of the original paper, Price² proposed a revision in which styrene was assigned a Q value of 1.0 and an e value of -0.8 . These revised values for styrene have remained the accepted standard.

Although the theoretical basis of the Q - e scheme has been criticized,³⁻⁵ it is worthy of note that no other device has been proposed which satisfies the data as well. The Q - e scheme has generally been regarded as yielding, at best, only approximate values of monomer reactivity ratios. However, it should be pointed out that, since the revision proposed by Price in 1948, no attempt has been made to improve upon the accuracy of the scheme by securing better data. Some of the data used to formulate the original Q - e diagram are of doubtful value because the polymerizations were carried to high conversions where the experimental errors in calculating the reactivity ratios become large. Some of the original data were obtained over wide ranges of polymerization temperature, which condition produces small but significant changes in the values of the reactivity ratios. In only a few systems was there an effort to secure data distributed over a wide range of monomer compositions. Errors in the original formulation have affected subsequent tests of the Q - e scheme.

In the course of many years our laboratories have studied the copolymerization of nearly 600 monomers. Some such device as the Q - e scheme is almost imperative to reduce this mass of data to reasonable proportions. It is the purpose of this paper to offer data which should begin to place the Q - e scheme on a better experimental basis. Three monomers were chosen so as to obtain, with styrene, a good system of reference for the Q - e dia-

gram. The three monomers were: vinylidene chloride, acrylonitrile, and vinyl chloride. With styrene, these monomers formed six copolymerization systems.

EXPERIMENTAL

The materials used for this work were of commercial polymerization grades used without further purification. All the data were secured from

TABLE I
Copolymerization of Vinylidene Chloride (M_1) and Styrene (M_2)

Styrene in initial monomer mixture M_2 , mole-%	Styrene in copolymer, m_2 , mole-%	Conversion, %
8.6	32.7	5.6
8.9	34.2	4.0
17.7	47.4	7.6
18.0	45.7	6.5
27.6	54.1	7.2
27.9	56.2	5.4
37.0	63.9	9.0
45.2	74.2	19.0
46.3	72.0	14.0
46.6	70.5	13.0
47.1	68.1	10.1
47.4	70.4	7.0
47.5	76.0	4.5
56.9	76.7	12.5
67.9	81.6	8.5
68.2	83.1	4.2
77.6	92.5	16.4
87.2	87.0	18.5
89.2	92.8	11.5
89.3	93.7	5.7

TABLE II
Copolymerization of Acrylonitrile (M_1) and Styrene (M_2)

Styrene in initial monomer mixture, M_2 , mole-%	Styrene in copolymer, m_2 , mole-%	Conversion, %
4.1	29.5	11.0
4.3	28.6	9.7
7.0	35.0	11.0
9.9	40.1	11.0
10.3	39.4	8.0
17.2	43.3	7.3
24.0	48.7	11.0
24.7	47.4	6.0
33.3	51.3	4.7
67.4	63.4	12.0
74.8	67.3	10.0
81.7	73.0	11.0
91.2	81.9	14.0

TABLE III
Copolymerization of Vinyl Chloride (M_1) and Acrylonitrile (M_2)

Acrylonitrile in initial monomer mixture, M_2 , mole-%	Acrylonitrile in copolymer, m_2 , mole-%	Conversion, %
1.0	11.6	3.0
1.1	11.6	2.3
2.1	21.6	2.3
2.1	21.6	2.0
4.3	36.7	2.0
4.3	34.6	2.3
7.6	46.1	3.0
7.8	44.0	2.3
10.2	52.5	6.0
10.7	52.1	4.0
10.8	49.6	3.7
16.3	58.1	4.0
20.6	64.0	9.0
22.1	63.0	3.3
32.8	72.5	4.0
33.1	69.6	2.3
43.2	78.3	5.0
53.7	83.7	3.0
63.8	83.4	1.0
63.8	86.7	1.0
73.0	91.3	3.0
82.3	94.7	4.0
91.3	97.3	6.0

TABLE IV
Copolymerization of Vinylidene Chloride (M_1) and Acrylonitrile (M_2)

Acrylonitrile in initial monomer mixture, M_2 , mole-%	Acrylonitrile in copolymer, m_2 , mole-%	Conversion, %
2.5	39.5	5.0
7.2	10.7	3.0
8.4	18.9	9.0
9.2	46.8	12.0
16.5	28.2	7.0
23.5	41.1	9.0
30.2	49.0	11.0
31.2	43.9	2.0
37.8	50.1	2.0
42.9	62.5	9.0
43.9	48.7	2.0
49.0	62.7	7.0
55.4	64.8	8.0
59.7	68.0	5.0
64.0	74.6	9.0
64.2	74.4	6.0
81.0	82.1	5.0
94.3	94.3	19.0

free-radical-initiated bulk or solution polymerizations conducted in sealed, glass ampules or in capped bottles. Emulsion polymerizations were not employed to avoid the partition effects sometimes encountered. Although

TABLE V
Copolymerization of Vinyl Chloride (M_1) and Vinylidene Chloride (M_2)

Vinylidene chloride in initial monomer mixture, M_2 , mole-%	Vinylidene chloride in copolymer, m_2 , mole-%	Conversion, %
9.6	39.3	9.0
9.7	38.4	9.0
28.3	63.6	6.0
28.6	59.0	5.0
44.2	79.9	6.0
44.4	79.9	5.0
65.4	79.9	8.0
65.8	72.1	8.0
84.6	92.4	17.0
84.6	92.4	17.0

TABLE VI
Copolymerization of Vinyl Chloride (M_1) and Styrene (M_2)

Styrene in initial monomer mixture, M_2 , mole-%	Styrene in copolymer, m_2 , mole-%	Conversion, %
0.5	5.6	8.0
0.7	8.8	1.3
2.2	25.3	3.0
2.4	27.8	0.7
3.1	36.7	5.0
3.5	36.7	1.3
9.6	66.6	0.5
10.4	68.3	0.8
11.0	68.7	0.8
21.3	82.9	2.8
35.6	90.1	5.7
35.8	90.0	5.6
36.2	90.4	3.1
36.5	89.7	1.8
36.6	91.6	2.4
44.9	93.0	5.0
48.3	91.1	4.0

some of the data were obtained from polymerizations conducted at temperatures as low as 40°C., the majority of the data were obtained at 50°C. Most of the data cited from the literature were obtained at 60°C. but no data obtained at a higher polymerization temperature were included. All

polymerizations were terminated at low conversions, generally less than 10% and never more than 20%. Copolymer compositions were determined from chlorine and nitrogen analyses. Table I-VI give the data obtained with the six copolymerization systems.

Several authors^{6,7} have pointed out that the drift in copolymer composition due to conversion can be compensated for by plotting the average rather than the initial monomer composition against the copolymer composition. A careful study showed this to be a very good approximation under the conditions reported in this paper. At least five methods have been published for estimating the best values of the reactivity ratios from the experimental data. The method introduced by Mayo and Lewis⁸ was used. This method still leaves some uncertainty as to the choice of the best value. A point was chosen on the Mayo and Lewis plot in such a way that the algebraic sum of the distances to the various intersecting lines was equal to zero. In effect, this procedure yields a weighted mean value.

Since the data from the vinylidene chloride-styrene, acrylonitrile-styrene, and vinyl chloride-acrylonitrile systems were so much better than those from the other three systems, only the data from the former three systems were used in computing the Q and e values of vinylidene chloride, acrylonitrile, and vinyl chloride. The data from the last three copolymerization systems were used only to demonstrate the consistency of the values selected.

RESULTS AND DISCUSSION

Figures 1-3 show plots of the initial copolymer compositions versus the composition of the initial monomer mixtures for the first three systems. The reactivity ratios calculated from these data are given in Table VII. Table VIII shows the Q and e values computed for the three reference

TABLE VII
Tabulation of Reactivity Ratios

System	M_1	M_2	r_1	r_2
I	Vinylidene chloride	Styrene	2.1 ± 0.2	0.145 ± 0.009
II	Acrylonitrile	Styrene	0.070 ± 0.006	0.37 ± 0.03
III	Vinyl chloride	Acrylonitrile	0.052 ± 0.009	3.6 ± 0.2

TABLE VIII
Calculated Values for Q and e

Monomer	Q	e
Vinylidene chloride	0.20	+0.29
Acrylonitrile	0.58	+1.11
Vinyl chloride	0.039	-0.17
Styrene (reference)	1.00	-0.80

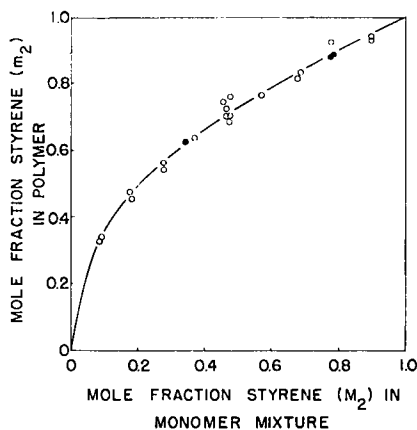


Fig. 1. Copolymer composition curve for vinylidene chloride (M_1) and styrene (M_2).
(●) Doak, *J. Am. Chem. Soc.*, **70**, 1525 (1948).

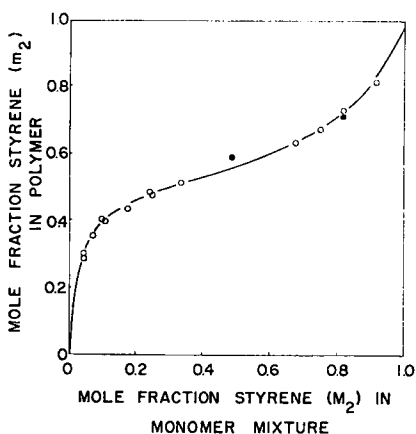


Fig. 2. Copolymer composition curve for acrylonitrile (M_1) and styrene (M_2).
(●) Lewis, Mayo, and Hulse, *J. Am. Chem. Soc.*, **67**, 1701 (1949).

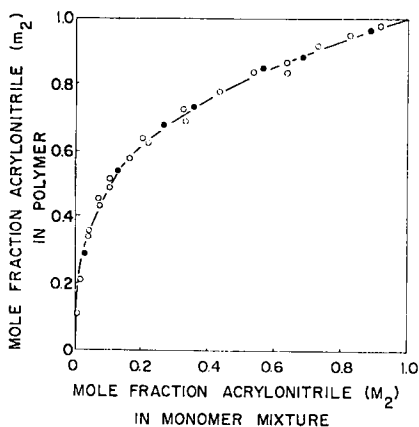


Fig. 3. Copolymer composition curve for vinyl chloride (M_1) and acrylonitrile (M_2).
(●) Chapin, Ham, and Fordyce, *J. Am. Chem. Soc.*, **70**, 538 (1948).

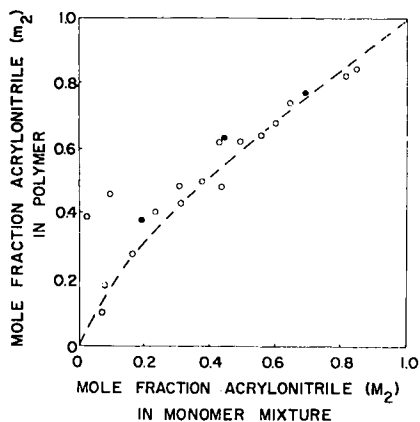


Fig. 4. Copolymer composition curve for vinylidene chloride (M_1) and acrylonitrile (M_2). (●) Lewis, Mayo, and Hulse, *J. Am. Chem. Soc.*, **67**, 1701 (1945).

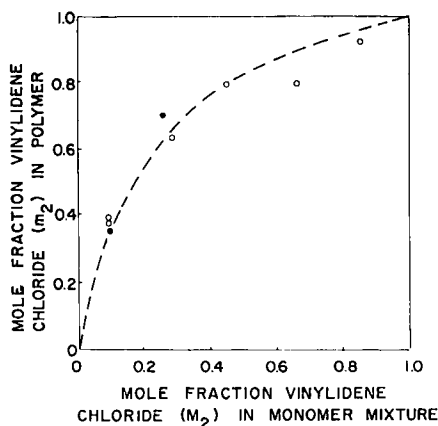


Fig. 5. Copolymer composition curve for vinyl chloride (M_1) and vinylidene chloride (M_2). (●) Agron, Alfrey, Bohrer, Haas, and Wechsler, *J. Polymer Sci.*, **3**, 157 (1948).

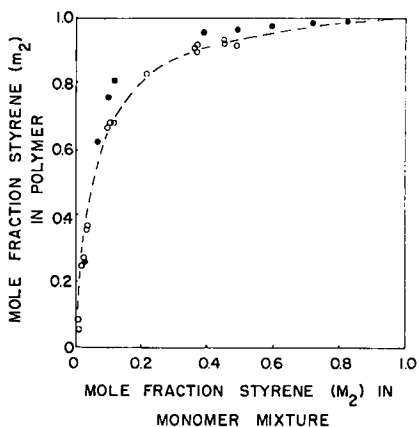


Fig. 6. Copolymer composition curve for vinyl chloride (M_1) and styrene (M_2). (●) Chapin, Ham and Fordyce, *J. Am. Chem. Soc.*, **70**, 538 (1948).

monomers. Finally Figures 4-6 show the agreement between the copolymer compositions calculated from the Q and e values given in Table VIII and the experimental data for the last three systems.

Although there is considerable scatter in the data from the last three copolymerization systems, the agreement between the calculated curves and the data seems quite satisfactory. An earlier version of this paper⁹ included data for the vinyl chloride-styrene system obtained by emulsion polymerization. These data showed a small but significant deviation from the calculated curve which may be due to a partition effect or to contamination from residual emulsifier.

The revised Q - e diagram is shown in Figure 7. On this plot, the shift from the Q - e values suggested by Price is shown by an arrow for each of the

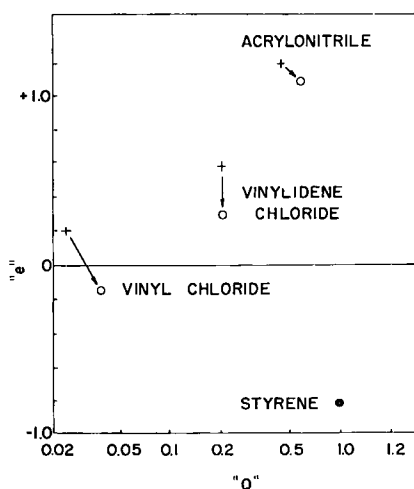


Fig. 7. The revised Q - e diagram. Arrows indicate the shifts from the positions assigned by Price, *J. Polymer Sci.*, **3**, 772 (1948).

reference monomers. It is obvious that these shifts could have been minimized by choosing different values of Q and e for styrene. However, this was not done since it was desirable to keep styrene the primary reference monomer to permit comparison of these data with data published in the literature. Only the values for vinyl chloride show appreciable deviation from those published by Price.

Experience with the vinyl chloride-styrene system and similar systems demonstrates that it is very difficult to obtain precise data on the copolymerization of two monomers with widely different Q values. Small errors in monomer composition or in copolymers analyses produce large errors in such systems. The effect of monomer conversion is too large to be neglected, even at low conversions. To minimize these errors it would have been preferable to choose as the reference a monomer like vinylidene chloride, which is more centrally located than styrene on the Q - e diagram.

Use of an appropriate one of the secondary reference monomers will now reduce the errors in estimating Q and e values for other monomers.

It seems entirely reasonable to conclude that, given accurate values of Q and e , the Q - e scheme is capable of making precise predictions of copolymer compositions. Except with unusual systems, it is likely that a much greater accuracy in copolymer analysis will be necessary to reveal any significant systematic deviations between the experimental data and the predicted values of copolymer compositions. This, then, represents the start of a more accurate formulation of the Q - e scheme. It is hoped that by placing this useful device on a better experimental basis others will be encouraged to seek a sound theoretical basis for it.

References

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Synopsis

New data are presented to establish the Q and e values of vinylidene chloride, acrylonitrile, and vinyl chloride relative to styrene as the reference monomer. Within the experimental error these values are shown to be entirely consistent with the observed copolymer compositions. Only the values for vinyl chloride are appreciably different from those published in the original paper of Alfrey and Price in 1947. With these better data it is hoped that renewed efforts will be made to place this empirical device on a sound theoretical basis.

Résumé

On présente des nouveaux résultats en vue d'établir les valeurs de Q et de e du chlorure de vinylidène, de l'acrylonitrile et du chlorure de vinyle par rapport au styrène comme monomère de référence. Mises à part les erreurs expérimentales ces résultats se montrent entièrement concordants avec les compositions observées des copolymères. Seules les valeurs obtenues pour le chlorure de vinyle révèlent une différence appréciable par rapport à celles indiquées antérieurement par Alfrey et Price, en 1947. À l'aide de ces résultats meilleurs on espère que des efforts renouvelés situeront des formules empiriques sur une base théorique.

Zusammenfassung

Es werden neue Ergebnisse zur Festlegung der Q - und e -Werte für Vinylidenchlorid-Acrylnitril und Vinylchlorid relativ zu Styrol als Bezugsmonomeres mitgeteilt. Inner,

halb der Versuchsfehlergrenzen stimmen diese Werte völlig mit der beobachteten Zusammensetzung der Copolymeren überein. Nur die Werte für Vinylchlorid zeigen eine beträchtliche Abweichung von den in der Arbeit von Alfrey und Price 1947 veröffentlichten. Mit Hilfe dieser verbesserten Daten kann man hoffen, neuerlich zu versuchen dieses, empirische System auf eine wirkliche, theoretische Basis zu stellen.

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