Some Comments on the *Q-e* Copolymerization Scheme[1]

T. C. SCHWAN, Valparaiso University
C. C. PRICE, University of Notre Dame

Introduction

The *Q-e* copolymerization scheme was developed by Alfrey and Price (1), to treat quantitatively the resonance and polarity factors which along with steric factors, of course, have been shown to be largely responsible for observed monomer behavior (2, 3). By relating the relative reactivity ratios to the Arrhenius equation for reaction rate, Alfrey and Price were able to calculate a series of relative values for the above resonance and polarity factors according to the following equations:

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

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

$$r_1 \; r_2 = e^{-(e_1-e_2)^2}$$

where r_1 and r_2 are the relative reactivity ratios, Q_1 and Q_2 are activation factors related to the resonance stabilization of the respective monomers, and e_1 and e_2 are electrical factors pertaining to the electron concentration at the double bond in the respective reacting monomers or monomer free radicals.

Since the above equations have only a quasitheoretical derivation, differences of opinion concerning the utility, accuracy, and validity of the *Q-e* scheme have arisen (4, 5, 6). Alfrey, Bohrer and Mark (4) have concluded that the values obtained for *Q* and *e* are only semiquantitative and that the real problem is the extent to which this scheme can be considered a quantitative method of correlation.

Q and *e* Values for Ethyl Vinyl Ether from Recorded Data

One facet of this problem was encountered in a recent investigation of the copolymerization properties of certain 1,2-disubstituted ethylenes (7). An attempt was made to calculate from data in the literature *Q* and *e* values for ethyl vinyl ether. There were found paired with ethyl vinyl ether five different monomers for which reactivity ratios had been recorded (8, 9, 10). However, each pair represented the extreme case in which one of the monomers, in this case ethyl vinyl ether, showed extreme reluctance to copolymerize. This reluctance to copolymerize results in a vanishingly small reactivity ratio for the reluctant monomer, and the ratio is usually and meaninglessly reported as zero. This was the case for ethyl vinyl ether. However, by using data from two different monomer

1. This paper was made possible largely by a grant-in-aid by Research Corporation, and is hereby gratefully acknowledged.

pairs in simultaneous equations, close agreement for the Q and e values was obtained from three of the five sets of data, but the other two gave widely divergent Q and e values. Since most of this recorded data was the result of single experiments, the divergent data was ignored. By this discriminatory use of data, Q and e for ethyl vinyl ether were found to be 0.01 and —0.7 respectively.

Q and e Values for Ethyl Vinyl Ether from Experimentally Obtained Data

An attempt was made to check this data experimentally by copolymerizing ethyl vinyl ether with styrene, acrylonitrile and ethyl fumarate. Reactivity ratios were calculated by the "intersection" method (11) which involves a graphic solution based on the following equation:

$$r_2 = \frac{M_1}{M_2}\left[\frac{m_2}{m_1}\left(1 + \frac{M_1}{M_2} r_1\right) - 1\right]$$

where M_1 and M_2 are the concentration of monomers in the original monomer mixture and m_1 and m_2 are the concentration of the respective monomers in the resulting copolymer. Since one monomer composition gives a single line on the plot, it does not afford a solution of the reactivity ratios. Several different concentrations of monomers are needed to give an area of intersection from which can be obtained values of r_1 and r_2 and a general idea of the size of the errors involved. The plots for the above copolymerizations are given in figures 1, 2 and 3.

Acrylonitrile was the only monomer to give a solution: $r_1 = 0.03 \pm .02$ and $r_2 = 0.7 \pm .02$. Using $r_1 = 0.03$ and $r_2 = 0.70$, for ethyl vinyl ether, $Q = 0.061$ and $e = -0.77$ which results are in excellent agreement with the above results calculated from the recorded data.

Styrene and ethyl fumarate gave no solution nor a single indication of an r_2 value. In fact, the plots indicate a negative r_1 value. The significance of this phenomenon has not been explained satisfactorily as yet. The widely divergent lines on the styrene-ethyl vinyl ether plot indicate a very low accuracy as might be expected from the very low concentration of ethyl vinyl ether found in the copolymer.

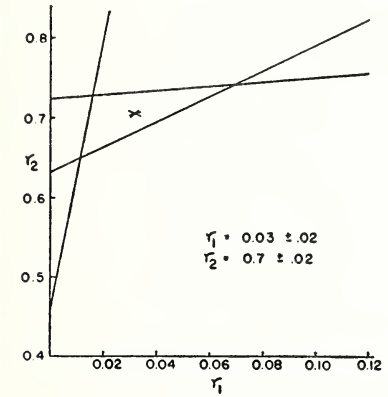
The ethyl fumarate-ethyl vinyl ether plot, however, indicates a certain degree of accuracy in that the two sets of lines are the results of two different series of copolymerization: one made near the beginning of the investigation and the other toward the end of the investigation. The same phenomenon of a possible negative r_1 value is exhibited here.

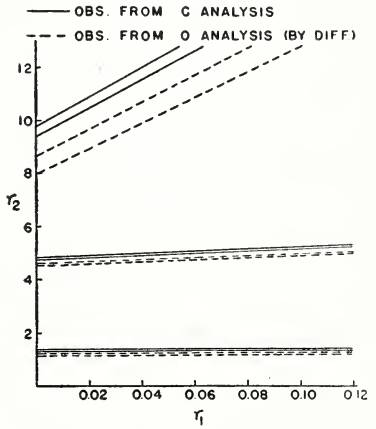
If in these last two copolymerizations, the r_2 values given by ethyl fumarate are used with the r_2 values obtained by the same monomer ratio of styrene with ethyl vinyl ether in simultaneous equations, the following values for Q and e for ethyl vinyl ether are obtained:

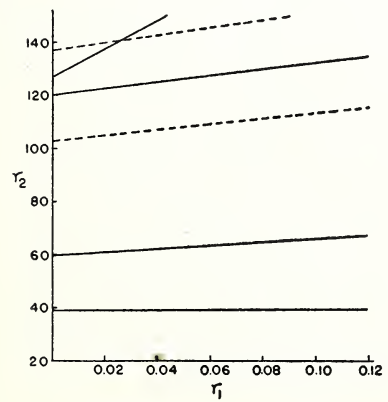
Mole Fraction Ethyl Vinyl Ether	r_2 Styrene	r'_2 Ethyl Fumarate	Q Ethyl Vinyl Ether	e Ethyl Vinyl Ether
0.2	40	1.2	0.02	–0.52
0.5	60	2.7	0.01	–0.33
0.8	130	9	0.005	–0.16

The most nearly horizontal lines on the plots give the least error in r_2. Therefore, the Q and e values obtained from these lines, which result from the lowest concentration of ethyl vinyl ether, should give the most accurate results. These results, $Q = 0.02$ and $e = -0.52$ are in good agreement with previously presented values (6).

While this last method is admittedly open to question, the agreement of results when the data in this rather extreme case is handled judiciously cannot help but add credibility to the accuracy and validity of the Q-e scheme.







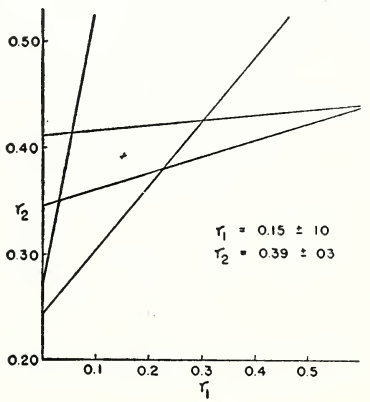


Fig. 1. (Upper left.) Copolymerization of ethyl vinyl ether (M_1) with acrylonitrile (M_2) indicating solution for the reactivity ratios.

Fig. 2. (Lower left.) Copolymerization of ethyl vinyl ether (M_1) with styrene (M_2) showing no solution for the reactivity ratios.

Fig. 3. (Upper right.) Copolymerization of ethyl vinyl ether (M_1) with ethyl fumarate (M_2) showing no solution for the reactivity ratios.

Fig. 4. (Lower right.) Copolymerization of crotonic acid (M_1) with vinyl acetate (M_2) (13) indicating solution for the reactivity ratios by the intersection method.

Recent Criticism of *Q-e* Scheme

A recent, damaging attack (12) on the basic validity of the scheme has resulted largely from the accumulation of certain contradictory data including Q and e values for crotonic acid. Reactivity ratios for the copolymerization of crotonic acid with vinyl acetate (13) were calculated by a curve-fitting method and were found to be $r_1 = 0.01$ and $r_2 = 0.3$ giving for crotonic acid $Q = 0.04$ and $e = 2.71$. Recalculation of the reactivity ratios by the intersection method gives the solution indicated in figure 4. Using $r_1 = 0.15$ and $r_2 = 0.39$, for crotonic acid, $Q = 0.053$ and $e = 1.43$ which results are in line with data for a large number of other monomers (6).

Obviously then, this attack on the basic validity of the *Q-e* scheme can be written off on the grounds of erroneous data or faulty computation.

Experimental

Monomers were purified by distillation through a 60 cm. glass helices packed column.

Mixtures of monomer pairs containing a total of 0.08 mole of monomer and 0.00016 mole of benzoyl peroxide were made up over a wide range of composition. The monomers were weighed to the nearest 0.5 mg. on an analytical balance in soft glass test tubes approximately 150 mm. by 18 mm. drawn out to a diameter of about 3 mm. about 40 mm. from the mouth of the test tube. Immediately after the final weighing, the tubes were placed in an ice bath, flushed with nitrogen for one minute and sealed. The tubes were placed in a constant temperature water bath maintained at 60° ± 0.2° C. When approximately ten per cent conversion had taken place as indicated by an increase in viscosity, the tubes were removed from the bath, cooled in an ice bath, opened and poured into 250 cc. of filtered methyl alcohol. Samples were prepared for analysis as follows. The acrylonitrile copolymer was dissolved in dimethyl formamide, filtered and slowly precipitated in methyl alcohol. The styrene copolymer was dissolved in benzene, filtered and reprecipitated in methyl alcohol. The ethyl fumarate copolymer, soluble in methyl alcohol, was precipitated in ligroin, redissolved in ether, filtered and reprecipitated in ligroin. All samples were reprecipitated at least twice and dried for at least 48 hours in a vacuum oven at 65°C and 30 mm. pressure. Analyses were performed by Microtech Laboratories, Skokie, Illinois.

Summary

Good agreement in judiciously treated recorded data and further experimental data for ethyl vinyl ether indicates even in this extreme case, the general accuracy of the *Q-e* scheme.

A recent attack on the basic validity of the *Q-e* scheme has been shown to be unsubstantiated.

Literature Cited

1. ALFREY, T., JR., and PRICE, C. C. 1947. Relative Reactivities in Vinyl Copolymerization. J. Polymer Sci. **2** :101.
2. LEWIS, F. M., MAYO, F. R., and HULSE, W. F. 1945. Copolymerization II. The Copolymerization of Acrylonitrile, Methyl Methacrylate, Styrene and Vinylidene Chloride. J. Am. Chem. Soc. **67** :1701.
3. PRICE, C. C. 1946. Mechanisms of Vinyl Polymerizations. IX. Some Factors Affecting Copolymerization. J. Polymer Sci. **1** :83.
4. ALFREY, T., JR., BOHRER, J. J., and MARK, H. 1952. "Copolymerization." Interscience Publishers, Inc., New York, N. Y., pp. 92-103.
5. LEWIS, F. M., and MAYO, F. R. 1948. Copolymerization. IX. A Comparison of Some *cis* and *trans* Isomers. J. Am. Chem. Soc. **70** :1533.
6. PRICE, C. C. 1948. Some Relative Monomer Reactivity Factors. J. Polymer Sci. **3** :772.
7. SCHWAN, T. C. 1953. "Some Copolymerization Properties of Certain 1,2-Disubstituted Ethylenes." Ph.D. Dissertation. University of Notre Dame. Notre Dame, Indiana.
8. LEWIS, F. M., WALLING, C., CUMMINGS, W., BRIGGS, E. R., and WENISCH, W. J. 1948. Copolymerization. VII. Copolymerization of Some Further Monomer Pairs. J. Am. Chem. Soc. **70** :1527.
9. MAYO, F. R., LEWIS, F. M., and WALLING, C. 1948. Copolymerization. VIII. The Relation Between Structure and Reactivity of Monomers in Copolymerization. J. Am. Chem. Soc. **70** :1529.
10. MAYO, F. R., WALLING, C., LEWIS, F. M., and HULSE, W. F. 1948. Copolymerization. V. Some Copolymerizations of Vinyl Acetate. J. Am. Chem. Soc. **70** :1523.
11. MAYO, F. R., and LEWIS, F. M. 1944. Copolymerization. I. A Basis for Comparing the Behavior of Monomers in Copolymerization, The Copolymerization of Styrene and Methyl Methacrylate. J. Am. Chem. Soc. **66** :1594.
12. CRAUWELS, K., and SMETS, G. 1950. Copolymerization of Methacrylate Derivatives. Bull. Soc. Chim. Belges **59** :443.
13. CHAPIN, E. C., HAM, G. E., and MILLS, C. L. 1949. Copolymerization. VII. Relative Rates of Addition of Various Monomers in Copolymerization. J. Polymer Sci. **4** :597.