

Estimation of the Reactivity Ratios in the Copolymerization of Acrylic Acid and Acrylamide from Composition–Conversion Measurements by an Improved Nonlinear Least-Squares Method

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Synopsis

A new method is developed to estimate the reactivity ratios from composition–conversion data based on nonlinear regression. Previously published experimental data for the copolymerization of acrylic acid and acrylamide are analyzed by the new method and the results compared to those reported by the original investigators. Composition–conversion data were collected for this copolymerization system at intermediate conversion levels and over a limited range of compositions. Values for the reactivity ratios at 40°C were obtained from these data by the new algorithm and compared to the literature values.

INTRODUCTION

The Copolymer Composition from the Chain Copolymerization Model¹

Under the assumption that the reactivity of a propagating chain is dependent only on the monomer unit at its end, the model for the copolymerization of two monomer species, M_1 and M_2 , leads to the following equation:

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

This is the differential copolymer composition equation relating the instantaneous molar concentrations of monomers M_1 and M_2 to $d[M_1]/d[M_2]$, the composition of the copolymer formed at that instant. Parameters r_1 and r_2 are termed the reactivity ratios.

The differential copolymer composition equation may be expressed in terms of mole fractions as follows:

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \quad (2)$$

where these mole fractions are defined by the following equations:

$$f_1 = 1 - f_2 \equiv \frac{[M_1]}{[M_1] + [M_2]} \quad (3)$$

$$F_1 = 1 - F_2 \equiv \frac{d[M_1]}{d[M_1] + d[M_2]} \quad (4)$$

In a batch reactor, the monomer mixture changes in composition toward the

less reactive monomer as the degree of conversion increases. This results in a similar drift in the copolymer composition as a function of conversion. The appropriate integral material balance equation expressing this composition drift with conversion is

$$\ln(1 - X) = \int_{f_{10}}^{f_1} \frac{df_1}{F_1 - f_1} \quad (5)$$

where X is the fractional monomer conversion and where subscript 0 refers to conditions at zero conversion.

Equation (5) was first integrated by Mayo and Lewis² to yield

$$r_2 = \frac{\log \frac{[M_{20}]}{[M_2]} - \frac{1}{p} \log \left(\frac{1 - p[M_1]/[M_2]}{1 - p[M_{10}]/[M_{20}]} \right)}{\log \frac{[M_{10}]}{[M_1]} + \log \left(\frac{1 - p[M_1]/[M_2]}{1 - p[M_{10}]/[M_{20}]} \right)} \quad (6)$$

where p is an integration constant defined by

$$p = \frac{1 - r_1}{1 - r_2} \quad (7)$$

Meyer and Lowry³ integrated eq. (5) into the following closed-form expression:

$$X = 1 - \left(\frac{f_1}{f_{10}} \right)^\alpha \left(\frac{f_2}{f_{20}} \right)^\beta \left(\frac{f_{10} - \delta}{f_1 - \delta} \right)^\gamma \quad (8)$$

where

$$\alpha = \frac{r_2}{1 - r_2} \quad \beta = \frac{r_1}{1 - r_1}$$

$$\gamma = \frac{1 - r_1 r_2}{(1 - r_1)(1 - r_2)} \quad \delta = \frac{1 - r_1}{2 - r_1 - r_2}$$

In eq. (8), f_1 is the mole fraction of M_1 in the residual monomer mixture at conversion X . It may be related to \bar{F}_1 , the cumulative average mole fraction of M_1 in the copolymer formed up to that conversion, by the following material balance relationship:

$$f_1 = \frac{f_{10} - \bar{F}_1 X}{1 - X} \quad (9)$$

Experimental Evaluation of the Reactivity Ratios

Data Obtained at Low Conversions

The traditional method for estimating r_1 and r_2 involves the experimental determination of the compositions of the copolymers formed from several comonomer feed compositions at low degrees of conversion. The monomer and copolymer compositions are assumed not to change significantly during the course of the reaction. Therefore, the differential copolymer composition equations, eqs. (1) and (2), are used to fit the data.

Several graphic methods have been proposed to estimate r_1 and r_2 from these

equations. These methods have been critically reviewed by Tidwell and Mortimer.^{4,5} The most serious disadvantage associated with these methods is that considerable subjective judgement is exercised by the investigator in estimating r_1 and r_2 . To overcome this difficulty, several investigators applied the linear least-squares method to eq. (3) as rearranged by Fineman and Ross⁶:

$$\frac{f_1(1 - 2F_1)}{F_1(1 - f_1)} = r_2 + \left[\frac{f_1^2 + (F_1 - 1)}{F_1(1 - f_1)^2} \right] r_1 \quad (10)$$

However, Tidwell and Mortimer^{4,5} pointed out that the assumptions made about the independent and the dependent variables in a linear equation, to justify the use of least-squares methods, are not satisfied in eq. (10). Hence, no quantitative measure of the precision of the estimates of r_1 and r_2 can be inferred by this method.

To circumvent this difficulty, both Behnken⁷ and Tidwell and Mortimer³ suggested the use of a nonlinear least-squares method based on the Gauss linearization technique to estimate the reactivity ratios from eq. (2). In this case the error structure conforms to that required by the least-squares method. Therefore, the estimates of r_1 and r_2 thus obtained are unique and unbiased, and their precision may be quantitatively evaluated by calculating their individual confidence intervals as well as their joint confidence region.

Data Obtained at High Conversions

Montgomery and Fry⁸ pointed out that the requirement of stopping the reactions at very low conversions results in serious experimental difficulties. Furthermore, the assumption that no change in the monomer composition occurs during the reaction may be a significant source of error in some cases. Therefore, numerous advantages will result from using an integrated form of the copolymer composition equation to estimate r_1 and r_2 from data collected at higher conversion levels.

A graphic procedure to estimate the reactivity ratios from eqs. (6) and (7) has been suggested by Mayo and Lewis,² whereas Meyer⁹ proposed a similar procedure to be used with eq. (8). However, these methods suffer from the same disadvantages connected with the graphic methods used in conjunction with the differential copolymer composition equation.

To circumvent these disadvantages, Behnken⁷ suggested the use of a nonlinear least-squares technique, based on the Gauss linearization method, on eqs. (6) and (7). As these equations are implicit in the dependent variable, the final comonomer composition, Behnken used Newton's method to solve for it, given the measured values of the independent variables and the current estimates of the values of the parameters. The method yields unique and unbiased estimates of the values of r_1 and r_2 as well as their confidence intervals. However, it suffers from the fact that Newton's method used to search for the dependent variable may not converge if the original guesses are not close to the actual root of the equation. This problem becomes particularly serious in the calculation of the joint confidence region which entails the estimation of the sum of the squares of the residuals at a network of values for the parameters^{4,5,7} some of which being fairly removed from their best estimates.

It may be noted that fitting the composition-conversion data to eq. (8) would

also require Newton's method, or some similar search routine, to solve for f_1 at known values of f_{10} , x , r_1 , and r_2 . In our attempts to use eq. (8), convergence problems invariably occurred in the calculation of the confidence regions. An additional difficulty associated with eq. (8) is the presence of singularities at $r_1 = 1.0$, $r_2 = 1.0$, $r_1 + r_2 = 2.0$, and $f_1 = \delta$. If the best estimates of the reactivity ratios lie close to any of these singularities, convergence problems are to be expected. As will be seen later, the values for r_1 and r_2 for the acrylic acid-acrylamide copolymerization system nearly satisfy the relationship $r_1 + r_2 = 2.0$.

A New Procedure for Estimating the Reactivity Ratios from Composition-Conversion Measurements

This procedure overcomes the difficulties associated with previous methods. It entails the use of the copolymerization equation in its integral form, eq. (5), together with eq. (2) relating the instantaneous monomer mixture and copolymer compositions. The procedure is as follows:

1. Given the measured value of the conversion X , the left side of eq. (5), viz., $\ln(1 - X)$, is calculated.

2. A stepwise numerical integration algorithm (e.g., Simpson's rule) is successively applied to the right side of eq. (5), while incrementing the upper limit of integration "in the right direction," i.e., starting from f_{10} , f_1 is progressively decreased if monomer M_1 is the more reactive component and increased otherwise. At each point, the value of the integrand, $1/(F_1 - f_1)$, is computed using eq. (2).

3. The midpoint of the interval of f_1 values that makes the right side of eq. (5) just exceed in absolute value the left side of the equation is taken as the solution of the equation. Hence, the corresponding value of the average cumulative copolymer composition, \bar{F}_1 , is obtained from eq. (9). The residual, or error, in each experimental run is taken as the difference between the value of \bar{F}_1 thus calculated and that measured experimentally.

4. The values of the reactivity ratios that minimize the sum of the squares of these residuals for all observations are then found by the nonlinear least-squares regression method developed by Marquardt.¹⁰ This method combines the Gauss linearization technique and the method of steepest descent.

Using this procedure to estimate the reactivity ratios of the acrylic acid-acrylamide copolymerization system, no convergence problems were encountered in the estimation of the values of the parameters or in the calculation of the confidence regions. The procedure has been implemented in computer programs that are general enough to be used for any copolymerization system that does not exhibit an azeotrope, where $F_1 = f_1$, and eq. (5) has a singularity.

Inherent in the above method is the assumption that all experimental errors are associated with the measured copolymer composition \bar{F}_1 , whereas conversion X is treated as an independent variable, hence is assumed to be exactly known. This assumption can be justified on the basis that the error inherent in measuring the conversion X is much smaller than that inherent in measuring the copolymer composition \bar{F}_1 . The alternative to making such an assumption is to treat the copolymerization problem as a multiresponse one and to use a weighted least-squares technique to estimate r_1 and r_2 which greatly complicates the procedure.

Analysis of Published Data of the Newly Developed Nonlinear Least-Squares Algorithm

The reactivity ratios of the acrylic acid-acrylamide copolymerization system have been reported at 25°C by Bourdais¹¹ and at 60°C by Cabaness et al.¹² In both investigations the reactions were stopped at low conversions, and graphic methods were used to estimate r_1 and r_2 from the differential copolymer composition equation. Table I lists the experimental results reported by these investigators, where subscript 1 refers to the acrylic acid monomer.

These data were presently analyzed by the nonlinear least-squares developed above. First, the composition data (f_1 versus F_1) were fitted to eq. (2), assuming that no appreciable change in compositions occurred during the reaction. The nonlinear least-squares technique due to Marquardt was also used to fit this equation. Secondly, the complete set of composition-conversion data listed in Table I was fitted to eq. (5) by the method detailed in the previous section.

Table II summarizes the results obtained from both of the above-mentioned methods as well as the values found by the original authors using graphic estimation techniques. The confidence intervals calculated by the least-squares method are at 95% confidence level. Figure 1 represents the estimates of r_1 and r_2 listed in Table II together with the joint confidence regions for the values of r_1 and r_2 calculated at an approximate confidence level of 95%, for both the differential and the integral equation. The expressions used for the estimation of the sum of squares of the residuals, the residual variance, and the correlation coefficient listed in Table II as well as the method used to estimate the joint confidence regions illustrated in Figure 1 have been detailed before.^{4,5,7}

The results shown in Table II and Figure 1 reveal the following:

1. The estimates of r_1 and r_2 obtained graphically by the previous investigators differ from those obtained from the same sets of data by the more accurate nonlinear least-squares method. These differences, however, are not significant at a 95% confidence level.

2. The individual confidence intervals on r_1 and r_2 reported by the original authors differed from those obtained at 95% confidence level by the nonlinear least-squares method. These differences were especially pronounced in the case

TABLE I
Experimental Results Reported by Previous Investigators

| Reference | f_1 | F_1 | X |
|-------------------------------|-------|--------|--------|
| Bourdais ¹¹ | 0.125 | 0.183 | 0.07 |
| | 0.250 | 0.327 | 0.10 |
| | 0.375 | 0.466 | 0.06 |
| | 0.500 | 0.607 | 0.06 |
| | 0.625 | 0.712 | 0.05 |
| | 0.750 | 0.817 | 0.02 |
| | 0.875 | 0.901 | 0.03 |
| | 0.800 | 0.8749 | 0.0392 |
| Cabaness et al. ¹² | 0.667 | 0.7688 | 0.0254 |
| | 0.500 | 0.6451 | 0.0430 |
| | 0.351 | 0.4997 | 0.1070 |
| | 0.200 | 0.3346 | 0.0446 |

TABLE II
 Reactivity Ratios for the Acrylic Acid-Acrylamide Copolymerization System from Previously Published Experimental Data

| Reference | Values reported by original authors | Values obtained by fitting differential copolymer equation eq. (12) | Values obtained by fitting integral copolymer equation eq. (5) | |
|------------------------------|---|---|--|------------------------------|
| Bourdais ¹¹ | r_1^a | 1.43 ± 0.03 | 1.46 ± 0.16 | 1.44 ± 0.17 |
| | r_2^a | 0.60 ± 0.02 | 0.66 ± 0.08 | 0.63 ± 0.07 |
| | residual sum of squares | — | 3.1×10^{-4} | 3.0×10^{-4} |
| | residual variance correlation coefficient | — | 6.2×10^{-5} 0.75 | 6.0×10^{-5} 0.75 |
| Cabanes et al. ¹² | r_1^a | 1.73 ± 0.21 | 1.60 ± 0.17 | 1.62 ± 0.13 |
| | r_2^a | 0.48 ± 0.06 | 0.45 ± 0.06 | 0.44 ± 0.05 |
| | residual sum of squares | — | 9.5×10^{-5} | 8.1×10^{-5} |
| | residual variance correlation coefficient | — | 3.2×10^{-5} 0.75 | 2.7×10^{-5} 0.61 |

^a Subscript 1 refers to acrylic acid monomer; subscript 2, to acrylamide.

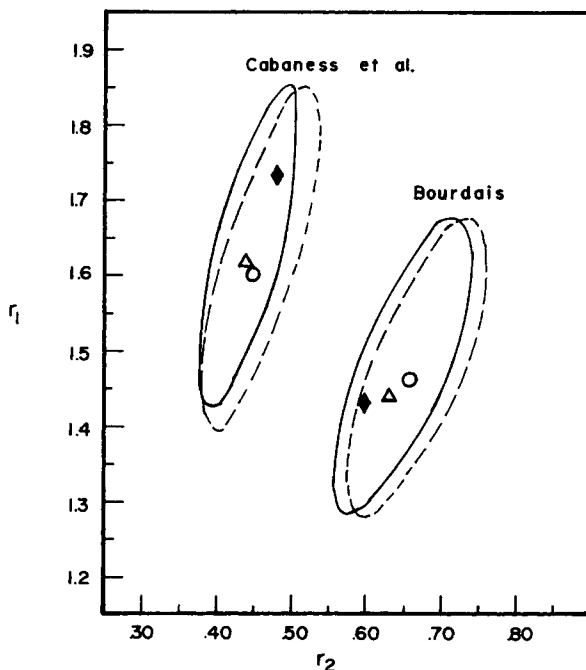


Fig. 1. Joint confidence regions for the reactivity ratios from previously published experimental data: (◆) best estimates of r_1 and r_2 reported by original author; (○) best estimates obtained by fitting differential eq. (2); (△) best estimates obtained by fitting integral eq. (5); (- - -) 95% confidence region from differential equation; (—) 95% confidence region from integral equation.

of Bourdais.¹¹ This was to be expected, as graphic methods do not provide quantitative estimates of the confidence intervals.

3. Figure 1 shows that the joint confidence regions for r_1 and r_2 obtained from the two sets of data in Table I do not overlap. Therefore, it may be stated that each set of data yields values for r_1 and r_2 that are significantly different from those yielded by the other set at a 95% confidence level. This has to be attributed to the difference in temperature between the two sets of experiments. It may be noted that it is only by using nonlinear regression techniques that such a comparison can be performed, because it is only such techniques that permit the calculation of confidence intervals and confidence regions.

4. The results obtained from fitting the composition data to the differential form of the copolymerization equation, eq. (2), agree closely with those obtained by fitting the composition-conversion data to the integral form of the equation, eq. (5), by the newly developed algorithm. This proves the soundness of this latter approach, which in turn implies that the conventional experimental technique of stopping the reactions at very low conversions is superfluous, and the experimental difficulties associated with it may be avoided.

EXPERIMENTAL

An experimental program was initiated with the following objectives:

1. To evaluate the reactivity ratios of the acrylic acid-acrylamide system from composition-conversion data collected at intermediate conversion levels (about

20–70% conversion). The data were to be fitted to eq. (5) by the nonlinear least-squares algorithm developed above. This was done to confirm our conclusion that in this method low conversion levels are not necessary.

2. The compositions of the resulting copolymers were deliberately limited to less than about 35% acrylic acid content in moles. The results thus obtained would help evaluate the possibilities and limitations of estimating reactivity ratios from a set of experimental data confined to a limited range of compositions. This also enabled us to avoid the experimental difficulties encountered by Bourdais.¹¹ He observed that copolymers with a high acrylic acid content became insoluble in water when dried.

3. The temperature chosen to conduct the experiments was 40°C. As we have proved that the values for r_1 and r_2 reported by the two previous investigators at 25° and 60°C, respectively, were significantly different from each other, it was hoped that by estimating these values at 40°C, an Arrhenius-type expression may be fitted to the set of three values for each reactivity ratio to describe its temperature dependence.

Reagents

Acrylamide monomer was recrystallized twice from chloroform. Acrylic acid monomer was purified by distillation under reduced pressure (10 mm Hg, bp 39°C). The water used as reaction medium was distilled twice, the second time out of alkaline permanganate solution. Potassium persulfate initiator was recrystallized from twice-distilled water at 60°C.

Experimental Conditions

Four different polymerization runs were carried out each at a different value of f_{10} , the mole fraction of acrylic acid in the monomer mixture at zero conversion. The values of f_{10} for these runs were 0.08, 0.15, 0.20, and 0.25, respectively. The total monomer concentration $[M]_0$ was always 1.0 g-mole/l. and the concentration of $K_2S_2O_8$ initiator was 10^{-3} g-mole/l. The reactions were carried out in a constant temperature bath kept at $40 \pm 0.1^\circ\text{C}$.

Experimental Procedures and Analytical Techniques

Reactions were carried out in screw-capped test tubes. The deaeration procedure consisted of bubbling nitrogen 15 min into the reaction mixture inside the tubes while these were immersed in an ice bath. Then the caps were secured to the tubes which were transferred to the constant-temperature bath. The reactions were quenched by thrusting the tubes into liquid nitrogen. Then the reaction mixture was transferred into a volume of water containing some hydroquinone inhibitor. This mixture was then stirred until dilution was complete.

Conversions were determined gravimetrically. The polymers were precipitated out by adding the above solutions to ten times their volumes of acetone acidified with a few drops of concentrated hydrochloric acid. The copolymers were then filtered, washed with benzene, and dried under vacuum to constant weight at 40°C.

The acrylic acid content in the copolymers was determined by potentiometric titration against sodium hydroxide in 0.1*N* aqueous solution of NaCl. Sharp inflection points in the titration curves were always observed.

RESULTS AND DISCUSSION

Table III lists the results obtained from the four copolymerization runs, with subscript 1 referring to acrylic acid. The newly developed nonlinear least-squares algorithm was used to fit these data to the integral copolymer composition equation, eq. (5). Table IV lists the results thus obtained with the individual confidence intervals calculated at 95% confidence level. In Figure 2, the least-squares estimators of r_1 and r_2 together with their 95% joint confidence region are shown. The dotted line in Figure 2 is part of the corresponding confidence region calculated from the experimental data reported by Bourdais¹¹ and shown in full in Figure 1. Figures 3 and 4 report the change of the average cumulative copolymer composition with conversion for the four values of f_{10}

TABLE III
Experimental Results

| f_{10} | X | \bar{F}_1 |
|----------|-------|-------------|
| 0.08 | 0.164 | 0.128 |
| | 0.241 | 0.115 |
| | 0.380 | 0.117 |
| | 0.509 | 0.111 |
| | 0.583 | 0.103 |
| | 0.689 | 0.096 |
| 0.15 | 0.234 | 0.217 |
| | 0.318 | 0.204 |
| | 0.472 | 0.210 |
| | 0.521 | 0.194 |
| | 0.602 | 0.186 |
| | 0.711 | 0.180 |
| 0.20 | 0.197 | 0.288 |
| | 0.276 | 0.273 |
| | 0.381 | 0.264 |
| | 0.490 | 0.266 |
| | 0.583 | 0.256 |
| | 0.621 | 0.239 |
| 0.25 | 0.228 | 0.335 |
| | 0.340 | 0.334 |
| | 0.449 | 0.323 |
| | 0.512 | 0.313 |
| | 0.638 | 0.309 |
| | 0.661 | 0.297 |

TABLE IV
Results Obtained from Fitting Experimental Data to Integral Copolymer Equation, Eq. (5)

| | |
|-------------------------|----------------------|
| r_1 | 1.45 ± 0.33 |
| r_2 | 0.57 ± 0.04 |
| Residual sum of squares | 5.4×10^{-4} |
| Residual variance | 2.5×10^{-5} |
| Correlation coefficient | 0.95 |

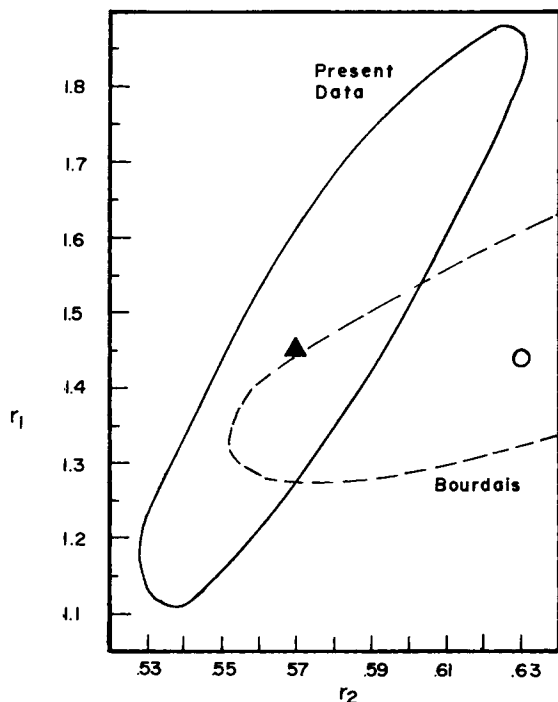


Fig. 2. Joint confidence regions for the reactivity ratios from the present data: (▲) best estimates of r_1 and r_2 from present data; (○) best estimates of r_1 and r_2 from data by Bourdais¹¹; (—) 95% confidence region from present data; (---) 95% confidence region from data by Bourdais.¹¹

examined in the present study. The solid lines are the results predicted by the copolymerization model, eq. (8), using the values of r_1 and r_2 listed in Table IV. The circles on these figures are the experimental results listed in Table III.

From these tables and figures the following observations can be made:

1. Figures 3 and 4 show satisfactory agreement between the measured and the predicted values of the copolymer composition drift with conversion. This validates the procedure of estimating the reactivity ratios from composition data at intermediate conversion levels with the presently developed nonlinear regression algorithm. It eliminates the necessity of obtaining the composition data at low conversion levels.

2. From Tables II and IV it is clear that although the variance of the present experimental results compares favorably with those of the previous investigators, the correlation between the values of r_1 and r_2 is more pronounced in the present case than in the previous ones. This is evidenced by the higher value of the correlation coefficient. This undesirable aspect of parameter estimation, viz., the high correlation between r_1 and r_2 , will always be characteristic of reactivity ratios estimated from data collected from a limited range of copolymer compositions. This is tantamount to bad experimental design and should be avoided whenever possible.

3. From Figure 2 it is clear that some overlap exists between the 95% confidence region of the values of r_1 and r_2 obtained from the present data at 40°C and those obtained by Bourdais¹¹ at 25°C. Although this observation would indicate that the reactivity ratios are not significantly affected by temperature,

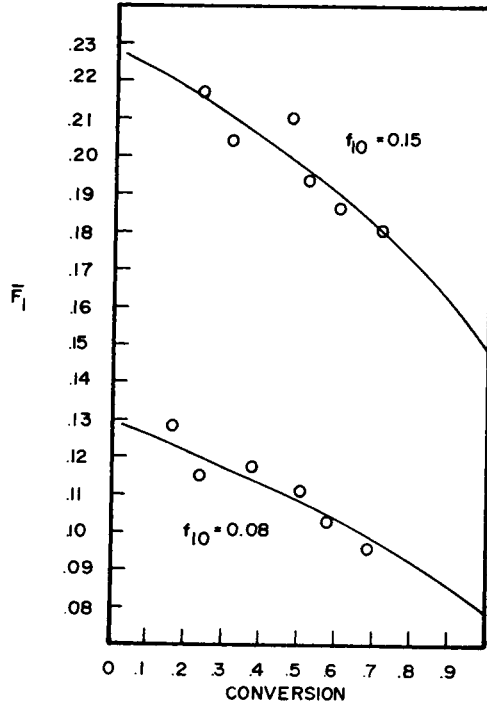


Fig. 3. Predicted and measured drift in the cumulative average copolymer composition with conversion; $r_1 = 1.45, r_2 = 0.57$.

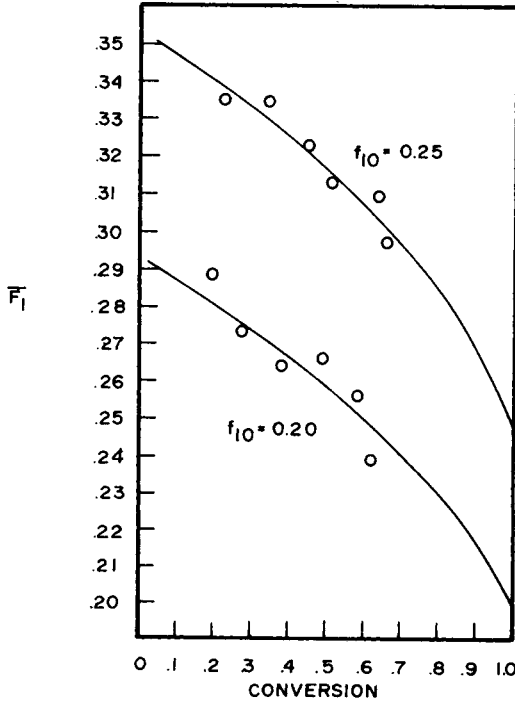


Fig. 4. Predicted and measured drift in the cumulative average copolymer composition with conversion; $r_1 = 1.45, r_2 = 0.57$.

this is contradicted by the fact that no overlap occurs with the confidence region obtained for data at 60°C.¹² Moreover, our attempt to fit the variation with temperature of each reactivity ratio to an Arrhenius-type expression, using its respective set of three values at 25°, 40°, and 60°C was not successful. It is likely that the accuracy of the experimental data, and hence that of the estimated parameters, do not warrant such a fit.

CONCLUSIONS

The new nonlinear regression algorithm has been proven successful in estimating the reactivity ratios from composition-conversion data collected at intermediate conversion levels. Thus, it eliminates the need to stop the reactions at very low conversions and makes it possible to avoid the experimental difficulties associated with this practice. The new method also does away with the assumption of constant compositions during the course of the reactions. The algorithm always converged and yielded unique and unbiased estimators for the reactivity ratios, together with quantitative measures of their accuracy.

It was found that the practice of estimating the reactivity ratios from a set of experimental data collected over a narrow range of copolymer compositions yields highly correlated estimators for the reactivity ratios.

Finally, the present attempt to describe the change with temperature of the reactivity ratio with an Arrhenius expression was not successful. It was concluded that more precise estimates of the reactivity ratios are needed to achieve this purpose.

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