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Estimation of Reactivity Ratios from Multicomponent Copolymerizations

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ABSTRACT

The composition of the copolymer formed from n monomers in addition polymerization can be expressed in terms of the monomer feed composition and $n(n - 1)$ binary reactivity ratios, according to the familiar simple copolymer model. Reactivity ratios are determined experimentally from corresponding feed and monomer compositions in binary copolymerizations. This article reports methods for deriving such reactivity ratios directly from multicomponent polymerization data. Analytical solution of the multicomponent copolymer equations is not feasible because of the limited number of experimental points and experimental uncertainty in the copolymer composition. Computer-assisted procedures have been developed to estimate reactivity ratios by optimizing the fit of predicted and experimental copolymer compositions, given the monomer feed composition and preliminary values of the reactivity ratios. All $n(n - 1)$ reactivity ratios are adjustable. The

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methods are demonstrated for styrene/methacrylonitrile/ α -methylstyrene, butadiene/styrene/2-methyl-5-vinylpyridine and acrylonitrile/methyl methacrylate/ α -methylstyrene systems. Binary reactivity ratios predict ternary copolymer compositions generally well in these cases. Reasons are suggested why reactivity ratios from multicomponent experiments may not match the corresponding parameters from binary copolymerizations.

INTRODUCTION

The composition of the copolymer formed from given concentrations of three monomers is determined by the values of six binary reactivity ratios, according to the familiar simple copolymerization model for addition polymerizations [1, 2]. Reactivity ratios are determined experimentally from corresponding monomer feed and polymer compositions in binary copolymerizations. Estimation of reactivity ratios directly from feed and copolymer compositions in multicomponent systems has not been practical to date. The reactivity ratios measured in two-component experimental studies seem to be generally applicable in multicomponent copolymerizations [1-5], although exceptions to this conclusion have been recorded [6, 7].

The reports cited have involved comparisons of experimental copolymer compositions with those predicted by use of selected reactivity ratios. The adequacy of the reactivity ratio values and of the copolymerization model used is judged subjectively by the agreement between experimental and predicted polymer compositions.

The general difficulties in determining polymer composition make it impractical to derive reliable reactivity ratios from analytical solutions of the multicomponent copolymer equation, in parallel with standard methods in binary systems. The techniques reported here estimate multicomponent reactivity ratios by minimizing the deviations between predicted and observed polymer compositions. Analytical solutions of the copolymer equations are not attempted.

This article describes three somewhat different methods for optimizing reactivity ratios from multicomponent copolymerization data. All six terpolymerization reactivity ratios are considered to be adjustable. A differential form of the simple copolymer equation [1, 2] is used, and the procedures outlined are readily extended to systems containing more than three monomers.

The methods reported are intended to produce the best-fit reactivity ratios, given copolymer and corresponding monomer feed compositions and preliminary values of the reactivity ratios.

The accuracy of such preliminary values is not critical. Q-e calculations could be used, for example, if experimental binary system values are lacking.

At present, the preferred methods for deriving reactivity ratios from differential forms of the binary copolymer equation rely on nonlinear fits of calculated and experimental copolymer compositions [8-10]. Nonlinear optimization is applied also to terpolymerization data in this work.

The optimization procedures used avoid the difficulties of a direct solution of the differential terpolymer equation. The number of experimental feed compositions is usually quite small and the analytical uncertainty in copolymer composition may be appreciable. Reactivity ratios which could be derived by direct solution of the terpolymer equations would therefore probably have fairly large uncertainties, and it is likely that best-fit reactivity ratios estimated as described here would be within such confidence intervals.

ESTIMATION OF REACTIVITY RATIOS

The data used for development of the mathematical procedures reported are from free radical copolymerizations of methacrylonitrile (MAN), styrene (S), and α -methylstyrene (AMS) at 60°C [5]. Table 1 compares experimental terpolymer compositions with those calculated from reactivity ratios measured in binary copolymerizations [10-12]. We feel that the present accuracy of analytical data in copolymer systems is such that only gross discriminations between copolymerization models can usually be attempted. The principle of minimum hypothesis suggests a preference for the model with the fewest parameters. The simple copolymerization model [1, 2] is seen to be consistent with the experimental data in Table 1 [5], and more complicated mechanisms such as those in penultimate effect, charge transfer, or reversible polymerization models are therefore not considered in this report.

The instantaneous copolymer composition is given in terms of decrements in monomer feed concentration, dM_1 , by the differential equation of Alfrey and Goldfinger [1]:

$$\frac{dM_1}{dM_3} = \frac{M_1(M_1r_{23}r_{32} + M_2r_{31}r_{23} + M_3r_{32}r_{21})(M_2r_{12}r_{13} + M_2r_{13} + M_3r_{12})}{M_3(M_1r_{12}r_{23} + M_2r_{13}r_{21} + M_3r_{12}r_{21})(M_3r_{31}r_{32} + M_1r_{32} + M_2r_{31})} \quad (1)$$

$$\frac{dM_2}{dM_3} = \frac{M_2(M_1r_{32}r_{13} + M_2r_{13}r_{31} + M_3r_{12}r_{31})(M_2r_{21}r_{23} + M_1r_{23} + M_3r_{21})}{M_3(M_1r_{12}r_{23} + M_2r_{13}r_{21} + M_3r_{12}r_{21})(M_3r_{31}r_{32} + M_1r_{32} + M_2r_{31})} \quad (2)$$

TABLE 1. Experimental and Calculated Copolymer Compositions^{a,b}

Experiment No.	Feed composition MAN:S:AMS	Copolymer composition (mole fraction)					
		MAN		S		AMS	
		Calc	Exptl	Calc	Exptl	Calc	Exptl
1	0.420:0.307:0.273	0.436	0.485	0.303	0.284	0.261	0.231
2	0.555:0.290:0.155	0.525	0.544	0.306	0.332	0.169	0.123
3	0.264:0.450:0.286	0.334	0.330	0.410	0.412	0.247	0.259
4	0.414:0.424:0.162	0.443	0.452	0.403	0.389	0.154	0.162
5	0.180:0.527:0.293	0.264	0.265	0.491	0.464	0.245	0.271
6	0.184:0.337:0.480	0.256	0.287	0.339	0.309	0.405	0.405

^a Reactivity ratios: r_{12} 0.44, r_{21} 0.37, r_{13} 0.38, r_{31} 0.53, r_{23} 1.124, r_{32} 0.627 ($M_1 = \text{MAN}$, $M_2 = \text{S}$, $M_3 = \text{AMS}$).

^b Data from Ref. 5.

where the M_i are the molar concentrations of monomer i ($i = 1, 2, 3$) and r_{ij} ($i \neq j$) are the appropriate binary reactivity ratios. In the present example the monomer subscripts 1, 2, 3 refer to MAN, S, and AMS, respectively, and the definitions of r_{ij} are the ones in standard use.

Computer search programs were written to vary the r_{ij} to minimize the variations between the estimated and experimental copolymer compositions (dM_i) of Eqs. (1) and (2).

Three computer search techniques were used in this study. They had in common a linear search which could be conducted along any direction with an accelerating stepsize and a quadratic smoothing feature to obtain more accuracy. The search proceeds along the chosen direction with stepsize at the i -th trial being $2^{i-1}h$ (for suitably chosen h) until the minimum in that direction has been bracketted. The bracketting interval is then searched with stepsize $2^{k-2}h$ (where the minimum was bracketted on the k -th trial). This is continued until the minimum is known to lie in an interval of length $2h$. A quadratic fit is then performed on these three points and the minimum of this quadratic is chosen as the new minimum. If the quadratic fit has resulted in a significant improvement, it is repeated once more using the three best points.

Three methods for searching were developed:

Method 1

This is the least elegant of the three procedures and needed many more function evaluations than the other two methods to obtain the same coincidence between calculated and experimental polymer compositions. One cycle with Method 1 involved searching along each of the six dimensions sequentially. This cycle was then repeated as many times as were necessary to find the minimum. That is,

$(x_1, x_2, x_3, x_4, x_5, x_6)$ - (search along dimension 1) - $(x_1^*, x_2, x_3, x_4, x_5, x_6)$ - . . . - (search along dimension 6) - $(x_1^*, x_2^*, x_3^*, x_4^*, x_5^*, x_6^*)$ - (repeat above searches if necessary)

Method 2

In this procedure one cycle consists of approximating the gradient and searching in the direction of the gradient until the minimum is found. If necessary, the gradient at this minimum is approximated and the search is repeated. The direction of the gradient is given by the vector $\underline{G} = (G_1 \dots G_6)$ where

$$G_i = \frac{\Delta f(x_i)}{\left(\sum_1^s (\Delta f(x_i))^2\right)^{1/2}} \quad (3)$$

with

$$\Delta f(x_i) = \frac{f(x_1 \dots x_i \dots x_s) - f(x_1 \dots x_{i+h} \dots x_s)}{h} \quad (4)$$

The computer program for one cycle is flow-charted in Fig. 1.

Method 3

Each cycle of this search first involves a search along the first coordinate axis. If a point is found which is significantly different from the starting point, a search along the second axis is begun from this new point. If no such point is found, the search along the second axis starts at the original point. A successive search of each axis in turn is thus carried out either until all six have been found to give no improvement or until a significant improvement has been found along two of them. In the former case the search is terminated, and in the latter a new search is conducted along the direction defined by a line through the original starting point and the new minimum point. The point resulting from this search is then treated as a new starting value, and beginning there, the remaining coordinate axes are searched as above.

The new direction to be searched is defined by

$$\underline{H} = (H_1 \dots H_n) = \frac{(x_i^* - x_i^0)}{\left(\sum_{i=1}^n (x_i^* - x_i^0)^2\right)^{1/2}}$$

where x_i^0 is the i -th component of the original point and x_i^* is the i -th component of the minimum point obtained. Because a new direction is searched every time a significant move is detected along any two axes, only two of the x_i^0 will differ from the corresponding x_i^* .

Figure 2 shows the flow chart for one cycle of this procedure.

As shown in Table 1, the binary reactivity ratios and Eqs. (1) and (2) produced an apparent satisfactory coincidence of experimental and calculated copolymer compositions. The sum of squared deviations between experimental and calculated mole ratios in the copolymers for the six experimental compositions are listed in Table 2 along with the

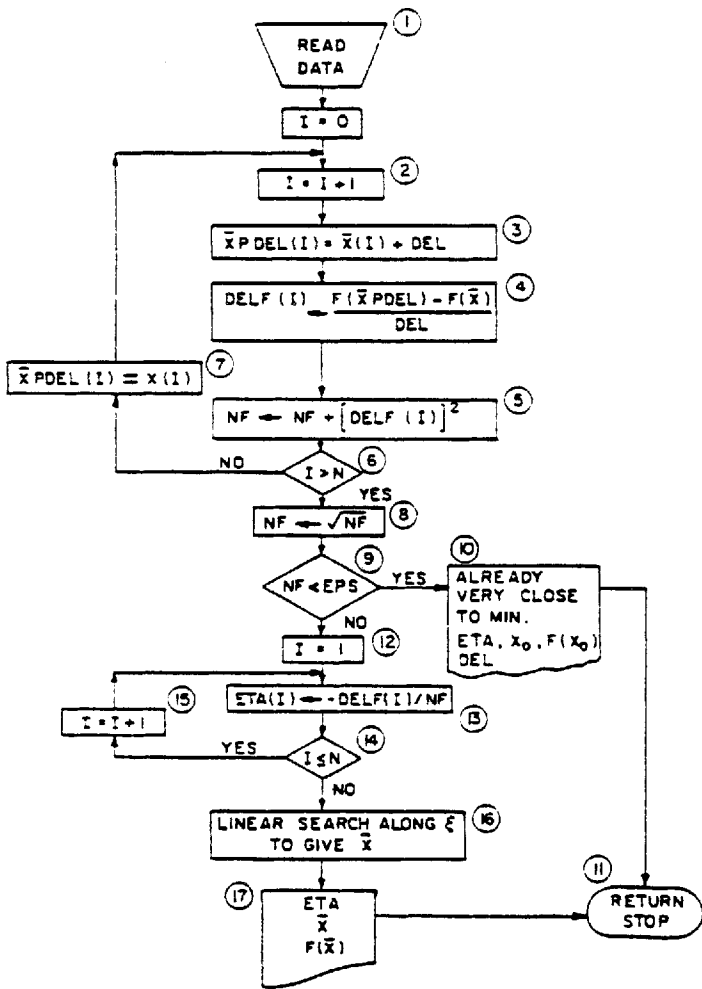


FIG. 1. Flow chart (Method 2).

- ① The input data includes the values necessary for function evaluations, the initial estimate for the search, and a series of search parameters to determine stepsizes, acceleration factors, and stopping criteria.
- ②-⑦ The gradient in each coordinate direction is approximated.
- ⑧-⑨ The length of the gradient is calculated and checked. If it is very small, we are sufficiently close to the minimum and the search prints results and terminates ⑩-⑪. If not, the direction ξ of the gradient is calculated ⑫-⑮.
- ⑯ The linear search is conducted along ξ until a minimum is found. This value is then printed ⑰ and the cycle terminates ⑪.

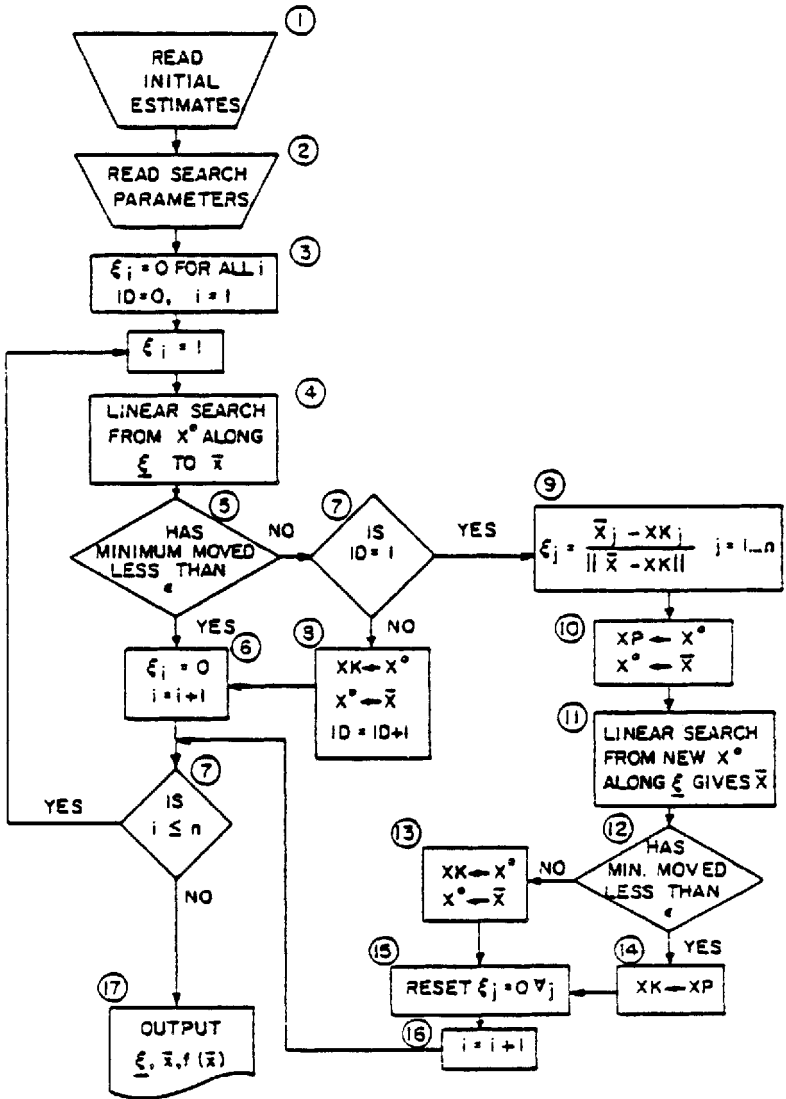


FIG. 2. Flow chart (Method 3).

- ① The data, initial estimates, and search parameters are read in.
- ②-③ The vector ξ , giving the direction of the search, is set to zero, then i is set to 1 to begin the search along the first axis.

(continued on opposite page)

corresponding binary reactivity ratios. Also included in this table are the reactivity ratios fitted by the three optimization methods described above and the matching minimum values of residual squared deviations. It is worth repeating here that these minima are obtained by adjusting the six binary reactivity ratios. The form of the simple copolymer equation in Eqs. (1) and (2) is not altered.

The entries in Table 2 show that the three search methods have reduced the sum of squared deviations between experimental and predicted copolymer compositions by an order of magnitude. The reactivity ratios listed should be considered to be approximate solutions of the ternary copolymerization equations with the given experimental data. The best estimates of reactivity ratios by the two preferred methods are fairly close but not coincident. This probably reflects uncertainties in the limited number of data points, and differences in the numbers and efficiencies of the iterative steps in the optimization methods.

Binary reactivity ratios are best cited as numbers with associated confidence limits. Since these reactivity ratios are determined experimentally in pairs, their experimental uncertainties are coupled. Thus the preferred procedure for estimating reliability involves calculation of joint confidence limits within which the correct values of the pair are believed to coexist with stated probability [9]. Approximate joint 95% confidence limits for the three reactivity ratio pairs involved in the present study have been reported in earlier articles [5, 10]. These calculations have been found to have been in error and the joint confidence limits are herewith recalculated using the computer program of

Fig. 2 continued.

- ④ The linear search is conducted along ξ from x^0 to yield \bar{x} .
- ⑤ A check is made to determine if the minimum point has moved significantly. If it has not, one proceeds to set up the search along the next coordinate axis ⑥.
- ⑦ This check is made only if the minimum did move significantly. Its purpose is to determine if this is the first or second time such a move has occurred. If it is the first, one proceeds to ⑧, otherwise to ⑨.
- ⑧ The original minimum x^0 is stored in XK and x^0 is then updated to contain the minimum from the first search. The dimension counter ID is incremented and one proceeds to set up the search along the next axis ⑥.
- ⑨-⑪ The new direction is defined ⑨ and the starting point is updated ⑩ before the search is conducted ⑪.
- ⑫-⑭ The new minimum is checked: if it has moved significantly, we store the new value ⑬. If not, we retain the old one ⑭.
- ⑮-⑯ The direction vector is reset to search the next coordinate axis.
- ⑰ If all axes have been searched once, the cycle terminates and prints results ⑰.

TABLE 2. Reactivity Ratios and Corresponding Residual Squared Deviations^a

Calculation method	Sum of squared deviations						
	r_{12}	r_{21}	r_{13}	r_{31}	r_{23}	r_{32}	
Unadjusted binary reactivity ratios with Eqs. (1) and (2)	2.9088	0.44	0.37	0.38	0.53	1.12	0.63
Optimization Method 1	0.3544	0.46	0.18	1.15	0.24	0.17	0.34
Optimization Method 2	0.3021	0.53	0.52	1.13	0.23	0.40	0.85
Optimization Method 3	0.2645	0.55	0.45	1.49	0.23	0.33	0.57

^aUsing data from Ref. 5.

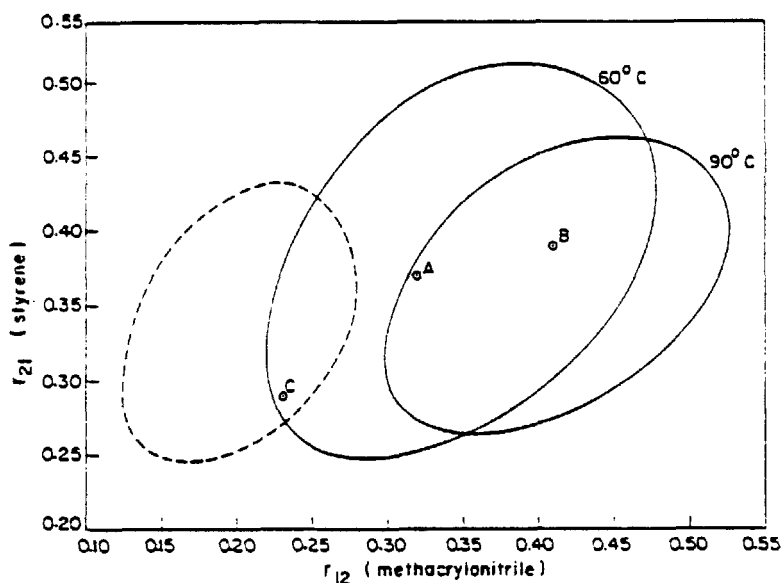


FIG. 3. Joint confidence limits for free-radical copolymerization of methacrylonitrile (r_{12}) and styrene (r_{21}) at 60 and 90°C. The solid line loops are from data of Rudin and Yule [12] for toluene solutions, for which the best-fit reactivity ratio pairs are given by Points A (60°C) and B (90°C). The dashed line loop is from Cameron and Esslemont [27] with corresponding reactivity ratio pair shown as Point C.

Tidwell and Mortimer. [9]. The corrected confidence limit loops are shown in Figs. 3 and 4.

Figure 3 in particular illustrates the utility of this method of reporting reactivity ratio data. Rudin and Yule [12] reported negligible effect of reaction temperature on the copolymerization of styrene and methacrylonitrile in toluene. The confidence limit loops for 60 and 90°C measurements overlap, as shown in Fig. 3. The corresponding loop for 120°C encompasses the other two and is omitted from this figure for clarity. Figure 3 also includes the confidence limit loop calculated from the data given by Cameron and Esslemont [27] for the same monomer pair in benzene solution at 60°C. The 60°C data are clearly not significantly different. Figure 4 depicts the confidence limit loops for styrene- α -methylstyrene [11] and α -methylstyrene-methacrylonitrile [10], all at 60°C. It is evident that the best-fit reactivity ratios (Table 2) estimated from terpolymerization data do not lie within the

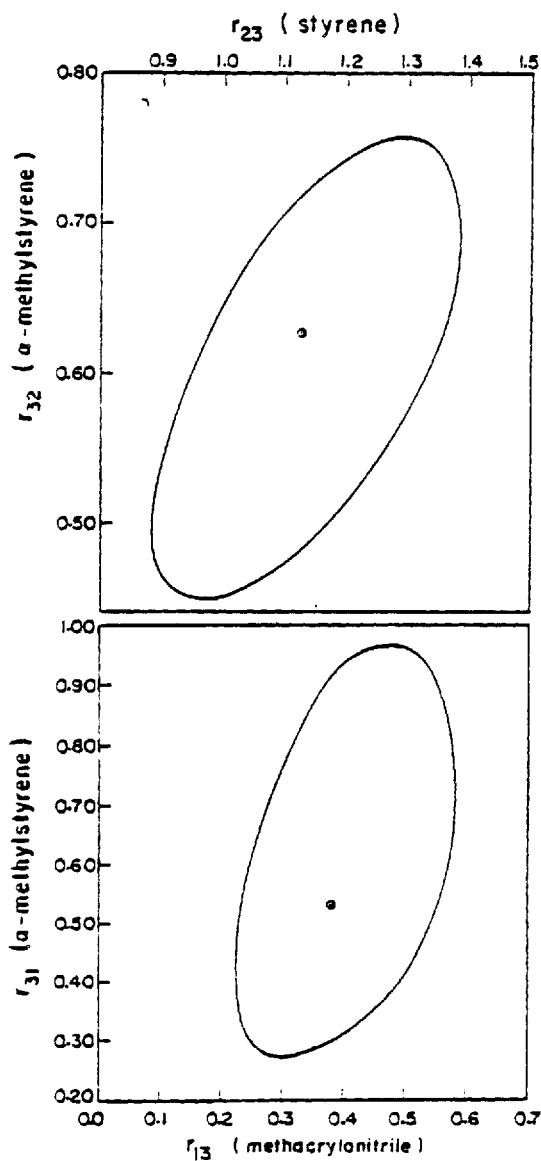


FIG. 4. Joint confidence limits for free-radical copolymerization at 60°C of: (a) α -methylstyrene (r_{12}) and styrene (r_{23}) [11], and (b) α -methylstyrene (r_{31}) and methacrylonitrile (r_{13}).

joint confidence limit loops calculated from binary copolymerization experiments and shown in Figs. 3 and 4. This is discussed in the following paragraphs and later in this article.

To analyze the data further, Method 3 optimizations were performed on groups of results of three experiments. The computed r_{ij} values are listed in Table 3 along with the results based on the entire six experiments (Table 2). The experiment numbers in Table 3 refer to the feed compositions listed under the corresponding numbers in Table 1.

The calculated reactivity ratios are seen to range quite broadly, depending on the accidental choice of a particular trio of experiments. This is particularly so for monomer pairs involving α -methylstyrene. The range of r_{12} and r_{21} (MAN-S) reactivity ratios is less sensitive to the particular feed compositions. The variations in reactivity ratios seem to be specially large for experiments which included feed compositions 1 and 2 (as listed in Table 1). The reasons for this are not clear. The data groupings which exclude these two experiments have the lowest sums of squared deviations and fit reactivity ratios which are closest to the binary values.

In view of this observation, best-fit reactivity ratios were calculated by Method 3 optimizations on the data from Experiments 3-6 only. These reactivity ratios were then used to calculate the copolymer compositions of all six experiments. The reactivity ratios are listed in Table 4 along with the experimental and calculated copolymer compositions for each monomer feed ratio. The fit between the latter two quantities is good.

Table 5 compares the binary reactivity ratios measured in previous studies [10-12] to the present optimized "multicomponent" reactivity ratios from Experiments 1-6 and from Experiments 3-6. Although all three sets of parameters produce what seem subjectively to be adequate concordance of estimated and experimental copolymer compositions, the reactivity ratios from Method 3 optimizations are the most successful in this regard. The simple copolymer model analysis summarized in Table 3 suggests that results of Experiments 1 and 2 are not consistent with those of the other experiments. This is supported by the present estimates, in which reactivity ratios computed from Experiments 3-6 alone account nicely for the copolymer compositions in all six experiments (Table 4) and also agree fairly well with those from related binary copolymerization studies (Table 5). The inconsistency of the results of Experiments 1 and 2 are thus more likely due to analytical difficulties than to any change of reaction mechanism with monomer feed composition. If the latter were the case, the reactivity ratios estimated from the other four experiments should not have accounted for the copolymer compositions of Experiments 1 and 2.

The reactivity ratios estimated from Method 3 optimizations on Experiments 3-6 alone are much closer to the binary values. The

TABLE 3. Method 3 Optimizations Reactivity Ratios from Selected Groups of Experiments

Experiments	Minimum sum of squared deviations	Reactivity Ratios					
		r_{12}	r_{21}	r_{13}	r_{31}	r_{23}	r_{32}
1-6 ^a	0.2645	0.55	0.45	1.49	0.23	0.33	0.57
1-6 ^b	2.9088	0.44	0.37	0.38	0.53	1.12	0.63
123	0.0358	0.48	0.47	0.94	0.71	0.82	2.38
124	0.1328	0.54	0.67	1.77	0.71	0.54	∞ (?)
125	0.0432	0.37	0.26	0.71	0.87	0.73	1.88
126	0.0515	0.24	0.10	0.41	1.29	25.2	3.52
134	0.0356	0.56	0.35	0.74	0.10	0.36	0.17
135	0.0153	0.66	0.36	0.88	0.32	0.51	0.48
136	0.0521	0.36	0.33	0.57	0.32	0.52	0.85
145	0.0774	0.42	0.33	0.42	0.10	0.53	0.22
146	0.0919	0.42	0.40	0.42	0.12	0.63	0.37
156	0.0264	0.41	0.30	0.62	0.38	0.56	0.87
234	0.0718	0.62	0.86	4.15	0.23	0.74	1.44
235	0.0169	0.55	0.29	1.18	4.07	0.80	1.42
236	0.0328	0.39	0.37	0.88	0.56	0.55	1.30
245	0.0658	0.58	0.73	3.90	0.02	0.31	0.12
246	0.0367	0.55	0.67	0.41	0.35	0.33	3.42
256	0.0140	0.37	0.38	0.74	0.43	0.69	1.44
345	0.0123	0.45	0.37	0.38	0.56	0.99	0.85
346	0.0107	0.51	0.44	0.38	0.38	1.19	0.68
356	0.0119	0.50	0.43	0.38	0.26	0.81	0.45
456	0.0062	0.45	0.38	0.38	0.31	0.83	0.63

^aReactivity ratios from Method 3 optimizations.

^bBinary reactivity ratios (Table 2).

TABLE 4. Experimental and Calculated Copolymer Compositions^a

Experiment No.	Feed composition MAN:S:AMS	Copolymer composition (mole fraction)								
		MAN			S			AMS		
		Mole fractions	Calc	Exptl	Calc	Exptl	Calc	Exptl	Calc	Exptl
1	0.420:0.307:0.273	0.445	0.485	0.290	0.284	0.265	0.231			
2	0.555:0.290:0.155	0.531	0.544	0.297	0.332	0.173	0.123			
3	0.264:0.450:0.286	0.340	0.330	0.400	0.412	0.260	0.259			
4	0.414:0.424:0.162	0.449	0.452	0.389	0.389	0.162	0.162			
5	0.180:0.526:0.293	0.268	0.265	0.467	0.464	0.265	0.271			
6	0.184:0.337:0.480	0.266	0.287	0.320	0.309	0.415	0.405			

^a Reactivity ratios from Method 3 analysis of results of Experiments 3-6: r_{12} 0.45, r_{21} 0.35, r_{13} 0.39, r_{31} 0.40, r_{23} 0.81, r_{32} 0.61.

TABLE 5. Comparison of Reactivity Ratios

Source of estimate	r_{12}	r_{21}	r_{13}	r_{31}	r_{23}	r_{32}
Binary copolymerization studies [10-12]	0.44	0.37	0.38	0.53	1.12	0.63
Method 3, data from Experiments 3-6 (Table 1)	0.45	0.35	0.39	0.40	0.81	0.61
Method 3, data from Experiments 1-6 (Table 1)	0.55	0.45	1.49	0.23	0.33	0.57

r_{23} - r_{32} pair is close to (but not within) the approximate 95% confidence limits shown in Fig. 4. The other reactivity ratios are within the corresponding confidence limit loops from binary copolymerization data.

The binary reactivity ratios used in the initial calculations were obtained in this laboratory by gas-liquid chromatographic analysis of monomer losses from polymerizing mixtures. The results did not agree well with those of other laboratories which relied on analyses of polymer composition for estimation of the r_{ij} values. This

discrepancy has been particularly pronounced in the case of copolymerizations with α -methylstyrene (Monomer 3) [10, 11]. In view of this disagreement it was of interest to see whether the best-fit reactivity ratios from terpolymerization data might support binary reactivity ratio data from other laboratories. This comparison is made in Table 6. The ternary reactivity ratios calculated by Method 3 were used for this purpose since this method uses least computation time and produces the lowest sum of residuals.

The comparisons in Table 6 do not resolve the discrepancy between reactivity ratios calculated from terpolymerization and binary copolymerization data. The terpolymerization parameters are not obviously related to any set of values reported from binary copolymerization studies. The binary data from this laboratory [5, 11, 12] are generally the closest to the magnitudes of the terpolymerization data. A systematic study with a larger range of feed compositions is required to determine whether the differences noted above are reflections of real changes in copolymerization mechanisms or are simply artifacts of the rather small set of data points.

TABLE 6. Comparison of Ternary and Binary Reactivity Ratios

Source	r_{12}	r_{21}	r_{13}	r_{31}	r_{23}	r_{32}
This work, Method 3 (using results of all experiments)	0.55	0.45	1.49	0.23	0.33	0.57
This work, Method 3 (Experiments 3-6 only)	0.45	0.35	0.39	0.40	0.81	0.61
Rudn and Yule [12, 5]	0.44	0.37				
Lewis et al. [13]	0.16	0.30				
Fordyce et al. [3] (80°C)	0.25	0.25	0.35	0.12		
Cameron et al. [14] (80°C)	0.26	0.38				
Rocke and Carey [15] (80°C)	0.28	0.43	0.15	0.21		
Johnston and Rudn [11]			0.38	0.54	1.124	0.627
Braun et al. [16] and Golubeva et al. [17]					1.20	0.35
Hanson and Zimmerman [18]					1.25	0.25
Morthland and Brown [19]					0.71	0.14

OTHER DATA

Crescentini, Gechele, and Zanella [20] have reported terpolymerization data for the butadiene (Monomer 1), styrene (Monomer 2), 2-methyl-5-vinyl pyridine (Monomer 3) system. Table 7 compares the experimental copolymer compositions to the values calculated from Eqs. (1) and (2) using the binary reactivity ratios reported by the original authors [20] and those estimated by our Method 3 optimization procedure. It is evident that the optimization procedure is applicable to these data and that the fit of experimental and calculated copolymer compositions is better with "ternary" reactivity ratios, as would be expected. The optimization procedure has changed the reactivity ratios rather less in this case than in the instance examined above. The major change in the present system is in r_{13} (butadiene-vinylpyridine).

Kang, O'Driscoll, and Howell [21] list experimental bulk terpolymerization data at four temperatures for reactions of acrylonitrile (Monomer 1), methyl methacrylate (Monomer 2), and α -methylstyrene (Monomer 3). The data were shown to coincide satisfactorily with estimates based on a model in which polymerization of the latter two monomers is reversible. The same results are seen here (Table 8) to be fitted well by calculations based on the present optimized simple terpolymerization model, with reactivity ratios estimated separately for each reaction temperature. The initial reactivity ratios used for the optimization procedure were the 60°C binary copolymer data given by Wittmer [22]. These are r_{12} 0.15, r_{21} 1.20, r_{23} 0.30, r_{32} 0.55, r_{13} 0.04, and r_{31} 0.13.

Table 8 compares the experimental copolymer compositions at 60°C for eleven feed compositions with those estimated by the reversible copolymerization model of Kang and co-workers [21] and the present simple copolymerization model. The optimum reactivity ratios at 60°C may not be significantly different from the 60°C binary reactivity ratios used as starting values, considering the experimental and computational uncertainties in the latter figures [23].

Table 8 also includes data for bulk polymerizations at 115, 130, and 140°C. The copolymer compositions can always be fitted well by varying reactivity ratios in the simple copolymerization model. There is no apparent uniform trend of computed reactivity ratios with temperature. We note, however, that the 60 and 130°C terpolymer values are reasonably consistent. These are computed from the experiments with the largest number of feed compositions. In view of the analysis summarized in Table 3, it may be more prudent to attribute the variations of the optimum reactivity ratios at 115 and 140°C to the influence of inadvertent bias in a relatively small number of experiments than to changes in polymerization mechanisms.

Since a differential form of the multicomponent copolymer equation is employed in this work, the calculations are applicable only to

TABLE 7. Experimental and Calculated Copolymer Compositions. ^a Butadiene (M_1):styrene (M_2):2-methyl-5-vinylpyridine (M_3)

Feed composition $M_1 \div M_2 \div M_3$ (mole)	Terpolymer composition										
	M_1			M_2			M_3				
	Calculated		Ternary r_{ij}^c	Calculated		Ternary r_{ij}^c	Calculated		Binary r_{ij}^b	Ternary r_{ij}^c	Found
0.0983 \div 0.7753 \div 0.1264	0.1245	0.1317	0.1502	0.7315	0.7293	0.7135	0.1440	0.1391	0.1362	0.1362	0.1362
0.0987 \div 0.7764 \div 0.1249	0.1250	0.1321	0.1139	0.7327	0.7305	0.7465	0.1423	0.1375	0.1396	0.1396	0.1396
0.1662 \div 0.6364 \div 0.1974	0.2143	0.2284	0.2216	0.5186	0.5330	0.5757	0.2070	0.1983	0.2027	0.2027	0.2027
0.2661 \div 0.5231 \div 0.2108	0.3323	0.3599	0.3622	0.4601	0.4475	0.4466	0.2076	0.1927	0.1912	0.1912	0.1912
0.3406 \div 0.1822 \div 0.4692	0.4604	0.4998	0.5101	0.1529	0.1443	0.1267	0.3867	0.3560	0.3632	0.3632	0.3632

^aData from Ref. 20.^bBinary reactivity ratios [20]: r_{12} 1.39, r_{21} 0.825, r_{13} 1.30, r_{31} 0.412, r_{23} 0.738, r_{32} 0.801.^cTernary^a reactivity ratios from Method 3 calculations: r_{12} 1.76, r_{21} 0.814, r_{13} 2.033, r_{31} 0.446, r_{23} 0.793, r_{32} 0.966.

TABLE 8. Experimental and Calculated Copolymer Compositions. ^a Acrylonitrile (M_1);methyl methacrylate (M_2); α -methylstyrene (M_3)

Feed composition (mole %)		Polymer composition (mole %)									
		Experimental			Reversible copolymer model ^a			Optimized simple copolymer model (Method 3)			
M_1	M_2	M_1	M_2	M_3	M_1	M_2	M_3	M_1	M_2	M_3	
8.7	48.0	43.3	21.4	36.6	41.9	16.7	40.2	43.2	18.2	37.8	44.0
16.6	41.3	41.9	28.3	27.9	43.9	26.7	29.1	44.2	27.9	27.5	44.6
31.3	29.2	39.6	35.5	19.0	45.5	28.1	16.4	45.5	38.3	15.8	45.8
44.2	18.4	37.4	43.0	10.4	46.6	44.7	8.9	46.4	44.1	8.9	47.0
16.2	59.5	24.3	22.6	43.8	33.7	21.1	43.7	35.3	21.5	45.0	33.5
30.2	46.8	23.0	31.2	32.8	36.0	22.6	29.8	37.6	32.2	31.6	36.0
42.7	35.6	21.8	39.0	22.5	38.6	20.1	20.7	39.3	39.0	22.8	38.2
54.1	26.3	20.6	43.5	15.6	31.0	45.6	13.8	40.7	43.7	16.3	40.0
9.06	27.7	63.3	27.4	23.5	49.1	23.4	26.6	50.1	24.3	22.2	53.5
17.5	21.4	61.1	36.2	14.6	49.3	34.2	15.8	50.0	34.5	13.3	52.2
32.4	10.2	57.4	44.5	6.2	49.3	44.5	5.5	50.0	43.7	4.76	51.56

60°C reactivity ratios: r_{12} 0.18, r_{21} 1.64, r_{23} 0.59, r_{32} 0.39, r_{13} 0.03, r_{31} 0.08. Minimum sum of squares = 0.052.

115°C reactivity ratios: r_{12} 0.01 ₂ , r_{21} 0.23 ₃ , r_{13} 0.003, r_{23} 1.667, r_{32} 0.65. Minimum sum of squares = 0.0021.											
8.7	48.0	43.3	20.8	42.1	37.1	16.9	45.3	32.8	20.67	41.99	37.34
16.8	41.3	41.9	28.9	31.7	39.4	27.3	32.0	40.7	28.88	31.47	39.65
31.3	29.2	39.6	35.8	20.3	43.9	30.9	17.4	43.7	41.02	12.32	46.66
44.2	18.4	37.4	41.7	12.4	45.9	45.3	9.3	45.4	36.72	19.97	43.30
130°C reactivity ratios: r_{12} 1.67, r_{21} 1.12, r_{23} 0.91, r_{32} 0.15, r_{13} 0.03, r_{31} 0.03. Minimum sum of squares = 0.031.											
16.2	59.5	24.3	22.4	49.7	28.0	21.4	50.7	27.9	21.5	50.6	27.9
30.2	46.8	23.0	31.2	37.4	31.5	33.5	33.6	32.9	32.8	35.6	31.6
42.7	35.6	21.8	39.0	25.3	35.7	41.1	22.8	36.1	39.9	25.4	34.6
54.1	26.3	20.6	45.7	17.3	37.0	46.7	14.9	38.4	44.7	18.2	37.1
9.06	27.7	63.3	26.8	29.7	44.5	25.5	30.9	43.6	25.1	27.6	47.2
17.5	21.4	61.1	37.9	15.9	46.2	26.2	17.3	46.5	35.7	16.4	47.9
32.4	10.2	57.4	44.9	6.6	48.5	45.8	5.7	48.5	45.2	5.8	49.0
140°C reactivity ratios: r_{12} 0.10, r_{21} 0.315, r_{13} 0.028, r_{31} 0.28, r_{23} 3.52, r_{32} 0.55. Minimum sum of squares = 0.0058.											
8.9	48.0	43.3	21.9	47.1	31.0	17.6	50.6	31.8	21.0	47.8	31.2
16.8	41.3	41.9	28.3	36.2	35.5	28.3	35.1	36.6	29.6	34.9	35.4
31.3	29.2	39.6	39.0	20.3	40.7	39.9	18.7	41.4	37.9	21.4	40.7
44.2	18.4	37.4	42.1	12.8	45.1	46.3	9.8	43.9	42.5	12.9	44.6

^aData and reversible copolymer model predictions from Ref. 21.

polymer compositions formed instantaneously from given monomer feed compositions. That is to say, reactivity ratios can be optimized on experimental data only when the polymer composition is invariant over the experimental range of conversions [5] or when the extent of polymerization is kept low. For this reason we have not attempted to apply our procedures to high conversion terpolymerization results such as those of Kahn and Horowitz [24].

DISCUSSION

Harwood and co-workers have reported a method for estimating one pair of reactivity ratios from terpolymerization data, given the other four reactivity ratios involved [25, 26]. The procedure involves a least squares fit to a linear form of the copolymer equation. These calculations were applied to our methacrylonitrile, styrene, α -methylstyrene data using Harwood's program. Reactivity ratios calculated in this instance were unfortunately negative and therefore physically meaningless. The reasons for these results are probably not very different from the difficulties found occasionally with application of linear fits to binary copolymerization data [8, 9]. They reflect inadvertent heavy weighting of extreme data values and can be minimized by nonlinear optimization in the ternary as well as in the binary cases.

We have noted above that the best-fit reactivity ratios from ternary copolymerizations of MAN, S, and AMS are not within the approximate joint 95% confidence limits calculated from binary experiments. Table 9 compares experimental ternary copolymer compositions with those calculated from Eqs. (1) and (2) using binary and the present best-fit ternary reactivity ratios. The sum of squared deviations between experimental and predicted polymer compositions is smaller by an order of magnitude when ternary reactivity ratios are used in Eqs. (1) and (2). The experimental polymer compositions are, however, not exact quantities. While the predictions based on the use of binary reactivity ratios are further from the experimental values, they are nevertheless probably still within experimental error of the experimental compositions. (This hypothesis can be maintained, of course, only if the deviations between the estimated and measured values are themselves randomly distributed.)

The comparison between the best-fit reactivity ratios found here and those computed earlier from binary copolymerization studies is carried further in Table 10. Here the compositions of binary copolymers are compared with estimates computed using both corresponding sets of reactivity ratios. The "ternary" reactivity ratios do not predict the binary copolymer compositions as well as the "binary" parameters. This is as expected, of course, since the binary data were chosen as best-fit adjustments to the corresponding

TABLE 9. Experimental and Calculated Copolymer Compositions

Feed composition (mole fraction)		Copolymer composition (mole fraction)									
MAN (M_1)	S (M_2)	AMS (M_3)	MAN			S			ANS		
			Exptl ^a r_{ij}^a	Calc binary r_{ij}^b	Calc ternary r_{ij}^c	Exptl ^a r_{ij}^a	Calc binary r_{ij}^b	Calc ternary r_{ij}^c	Exptl ^a r_{ij}^a	Calc binary r_{ij}^b	Calc ternary r_{ij}^c
0.420	0.307	0.273	0.485	0.436	0.463	0.284	0.303	0.315	0.231	0.261	0.222
0.555	0.290	0.155	0.544	0.525	0.557	0.332	0.306	0.347	0.123	0.169	0.128
0.204	0.450	0.286	0.330	0.334	0.330	0.412	0.419	0.404	0.259	0.247	0.266
0.414	0.424	0.162	0.452	0.443	0.446	0.389	0.403	0.402	0.162	0.154	0.152
0.180	0.527	0.293	0.265	0.264	0.250	0.464	0.491	0.451	0.271	0.245	0.299
0.184	0.337	0.480	0.287	0.256	0.275	0.309	0.339	0.328	0.405	0.405	0.397

^aData and binary r_{ij} from Ref. 5.^b r_{12} 0.44, r_{21} 0.37, r_{13} 0.38, r_{31} 0.53, r_{23} 1.124, r_{32} 0.627 (Table 1).
^c r_{12} 0.546, r_{21} 0.445, r_{13} 1.486, r_{31} 0.226, r_{23} 0.334, r_{32} 0.565 (Method 3 results, Table 2).

TABLE 10. Calculated and Experimental Binary Copolymer Compositions
(a) MAN (M_1) and S (M_2) at 60°C [12]

Mole ratio in copolymer $d[M_1]/d[M_2]$		Calculated		
Mole ratio in feed $[M_1]/[M_2]$	Exptl	"Binary" r_1 r_1 0.44, r_2 0.37 [12]	"Ternary" r_1 r_1 0.55, r_2 0.45 (Table 2)	"Ternary" r_1 r_1 0.45, r_2 0.35 (Table 4)
1.368	1.137	1.261	1.319	1.286
0.586	0.789	0.771	0.748	0.791
3.191	2.018	2.154	2.415	2.195
0.241	0.380	0.436	0.395	0.452
5.750	3.302	3.317	3.860	3.382
0.342	0.529	0.554	0.513	0.570

(b) MAN (M_1) and AMS (M_2) at 60°C

Mole ratio in copolymer $d[M_2]/d[M_1]$		Calculated		
Mole ratio in feed $[M_2]/[M_1]$	Exptl	"Binary" r_1 r_1 0.38, r_2 0.53 [10]	"Ternary" r_1 r_1 1.49, r_2 0.23 (Table 2)	"Ternary" r_1 r_1 0.39, r_2 0.40 (Table 4)
3.662	2.712	2.663	1.309	2.228
0.647	0.849	0.845	0.348	0.785
0.277	0.455	0.484	0.163	0.461
0.114	0.262	0.245	0.073	0.237

(c) S (M_1) and AMS (M_2) at 60°C [11]

Mole ratio in copolymer $d[M_2]/d[M_1]$		Calculated	
Mole ratio in feed $[M_2]/[M_1]$	Exptl	"Binary" r_i r_1 1.124, r_2 0.627 [11]	"Ternary" r_i r_1 0.33, r_2 0.57 (Table 2)
5.073	3.141	3.421	3.654
2.077	1.541	1.494	1.684
0.728	0.566	0.573	0.973
0.382	0.317	0.314	0.664
0.157	0.133	0.154	0.351
			"Ternary" r_i r_1 0.61, r_2 0.61 (Table 4)
			3.531
			1.632
			0.683
			0.395
			0.178

data [10-12]. The "ternary" reactivity ratios estimated from Experiments 3-6 only (Table 4) generally produce a much closer match to the binary copolymerization data than do the reactivity ratios from Experiments 1-6 (Table 2). This is further circumstantial support for the probable validity of the parameters given in Table 4. These reactivity ratios seem to provide acceptable predictions of binary and ternary copolymer compositions, although the estimated values are not the best that can be achieved in either case. Some of the best-fit ternary reactivity ratios are not within the 95% confidence intervals computed for the same parameters from binary copolymerization data. However, neither set of reactivity ratios produces results which are demonstrably wrong when used in the simple terpolymerization model. The ternary values must yield a closer fit between experimental and predicted compositions in the three-component systems, but the experimental compositions are themselves subject to uncertainty. The apparent paradox probably reflects the fact that the simple copolymer model requires six parameters (reactivity ratios) to predict the two (out of three) polymer compositions. (All other current copolymerization models use even more parameters.) There must be an infinite number of combinations of six reactivity ratios which will produce a match to within experimental uncertainty of the composition of a terpolymer from a given feed composition. The number of such possible combinations decreases as more corresponding feed and polymer compositions are measured, but it should not be surprising that the six monomer feeds used in the MAN-S-AMS study can apparently be matched adequately by two different sets of six reactivity ratios.

Similar observations apply to the comparisons of ternary and binary reactivity ratios in Table 7. The ternary values produce a better fit to the observed experimental polymer compositions, but this is almost by definition, since these values are derived for this purpose. The binary values, most of which do not differ greatly from the ternary reactivity ratios, yield polymer composition estimates which the original authors felt were an adequate fit to experimental values [20].

The "uncertainty principle" to which we have alluded above applies also to studies of various copolymerization models. Reactivity ratios are essentially kinetic parameters and an infinite number of mechanistic models can be postulated to fit observed kinetics. Reactivity ratio studies alone can show whether a given copolymerization model is consistent with experimental observations, but such studies cannot prove that the acceptable model does indeed reflect the mechanism of the actual polymerization. Other results (molecular weight measurements, independent demonstration of the existence of a complex, and so on) are also needed to support a particular reaction model.

The study of Kang and co-workers [21], summarized in Table 8,

is a case in point. These workers found a reversible copolymerization model to be consistent with their data. Our estimates which are based on a simple copolymer model match the experimental data quite well. It seems unlikely that the data cited would permit a conclusive decision in favor of either mechanism. Our inclination is to follow the principle of minimum hypothesis, which favors the simple copolymer model since this scheme uses the fewest adjustable parameters.

CONCLUSIONS

Methods have been described for estimation of reactivity ratios from multicomponent copolymerization data. The regression analysis has been developed for a simple (terminal-unit) copolymerization model. Extension of the technique to other copolymerization mechanisms would not appear to be complicated.

The techniques used optimize the coincidence between experimental copolymer compositions and estimated values by adjusting all the reactivity ratios in the copolymerization model. The efficiency of such statistical methods increases with the number of experimental observations. The new method has been demonstrated with data from three different terpolymer systems. The "ternary" reactivity ratios in these cases do seem not to differ greatly from those values established in the corresponding binary copolymerization studies.

Most practical copolymerizations involve reactions of three or more vinyl monomers. The present methods are directly applicable to such systems and should provide useful reactivity ratios with much less experimental effort than present procedures which require study of all the corresponding binary copolymers and an a priori assumption that binary reactivity ratios apply in multicomponent polymerizations.

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