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Analysis of the Linear Methods for Determining Copolymerization Reactivity Ratios.

I. A New Improved Linear Graphic Method

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ABSTRACT

A new graphically-evaluable linear method is suggested for the determination of the reactivity ratios of copolymerization. The proposed new equation is very well adaptable for visual determination of the applicability of the copolymer composition equation. If the experimental data are adequate to the composition equation, the procedure offers a simple and reliable method for the graphical determination of copolymerization constants.

INTRODUCTION

The methods currently applied for the determination of reactivity ratios are not entirely satisfactory. Since the copolymer composition equation was derived approximately 30 years ago [1], there have been several attempts to elaborate a simple but reliable method for the computation of these ratios.

The linear equation published by Fineman and Ross in 1950 [2], which allows the determination of constants by a simple graphic method, has been a considerable step forward and is still widely applied today (henceforth: the FR method).

Another linear, although only numerically evaluable relationship, has been suggested by Yezrielev, Brokhina, and Roskin [3] (the YBR method).

The first approach to determine the reactivity ratios by a nonlinear method was made by Behnken [4]. In detailed critical treatises [5, 6], Tidwell and Mortimer pointed out the defects of the different methods, including those of the Fineman-Ross equations, and suggested their replacement by a standard computerized procedure, the method of nonlinear least squares (the TM method). A recent survey of the various methods by Joshi [7] gives preference to the two numerical methods (YBR and TM).

MAIN SOURCES OF ERROR

There have been thousands of reactivity ratio values recorded in the literature of copolymerization (see, e.g., Ham [8]). It often occurs that various authors give different or contradictory data of the same copolymerization system. Based on a study of a great number of copolymerization systems, the deviations or contradictions may be attributed to the following factors:

1. The data on the composition of copolymers are generally evaluated on the basis of Eq. (1), suitable for the description of only the simplest copolymerization mechanism. The question of whether the experimental data can be approximately treated on the basis of Eq. (1) is generally not examined.

In fact, Eq. (1) cannot be as widely applied as implicitly assumed in the literature. In a most simple case, in a binery system, two radicals and two monomers are to be considered from a kinetic point of view; accordingly, the composition of the copolymer is determined by the relative rate of four chain propagation reactions. All further intramolecular action or intermolecular interaction will lead to considering kinetically more than two radicals and/or two monomers, i.e., more than four chain propagation elementary reactions in the system. Consequently, the equation describing the composition of the copolymer will be a more complex relationship with more than two parameters and, accordingly, the experimental data will have to be evaluated adequately in a more complex way. Mechanical evaluation of the data of these complex systems by Eq. (1) gives apparent reactivity ratios that are actually not constant composition- and concentration-dependent amounts.

The most important cases where Eq. (1) is not valid in a binery system are:

a) The case of the penultimate effect where four (or more) radicals are to be kinetically considered [9].

b) The case where one or both monomers are capable of association, owing to secondary valency forces (by way of homo- or hetero-association, e.g., donor-acceptor or hydrogen bridge interaction, formation of salt, acid-base interaction), or where more than two "monomers" are to be considered in the system, owing to the different reactivity of the associates. Similar interaction is assumed between growing radicals and monomer and/or solvent molecules.

c) If one of the monomers is a diene, it may participate in chain propagation in various ways (1,2-, or 3,4-, or 1,4-addition or cycloaddition).

d) In the case of semivinyl copolymerization, i.e., if one of the monomers shows a tendency for depolymerization (e.g., α-methylstyrene), certain chain propagation reactions may be absent from the mechanism. On the other hand, a unimolecular depolymerization process contributes to the formation of the composition of the copolymer.

e) If the reactivity of the two monomers and/or the two radicals is markedly different, then the equality $k_{12}R_1M_2 = k_{21}R_2M_1$ does not hold; in such cases the reaction is not a copolymerization but an inhibition process [10].

f) According to the theory of hot radicals [11], the individual radicals may react in two different energetical states. Accordingly, at least eight chain propagation reactions must be considered. The theory—the application of which in copolymerization will be treated elsewhere—leads to the conclusion that the rate constants of chain propagation reactions, and consequently also the reactivity ratios, may depend on the composition of the monomer mixture or the dilution.

Presumably, such complications may occur in a considerable proportion of copolymerization systems. Therefore, the primary task is to clarify whether the experimental data can be adequately treated with Eq. (1). There is no simple and reliable method described in the literature to facilitate this task.

2. In general, analytical errors and reproducibility of the data are not given due attention in copolymerization investigations. Apparently irrelevant factors, such as the presence of a (1 to 2%) solvent or precipitating agent in the polymer, can be a rather annoying systematic sources of error. Systematic errors, mainly occurring in physicochemical analytical procedures, are especially deceiving as they are generally latent mistakes and are revealed only in the change of the r_1 and r_2 values.

3. Finally, application of an inadequate evaluation method may lead to further—occasionally rather serious—errors. The studies of Behnken [4] and Tidwell and Mortimer [5, 6] point out several essential aspects of this many-fold problem.

The strongly criticizable practice of determining the r_1 and r_2 values from merely a few measurement data makes things even worse. It not only renders the application of correct statistical methods illusory, but also excludes the possibility of determining the adequacy of the method.

For the time being, the majority of data published in the literature do not satisfy any of the triple requirement complexes. At the very best, these results can be considered merely as informatory data. It is all the more so regrettable as some reactivity theories are founded on the basis of copolymerization data.

As the application of the nonlinear least squares method is rather complicated, the search for a simple, readily applicable and reliable method of evaluation seemed justified. A method of this type is presented in the first part of our paper. A number of further, practically all acceptable, linear methods of evaluation and the most important comparative examinations are summarized in the Appendix.

A NEW IMPROVED LINEAR GRAPHIC METHOD

In the following we present a simple graphically evaluable linear equation. The method allows quick and reliable determination of the reactivity ratios and can also be applied for the estimation of the adequacy of the composition equation, i.e., the assumed mechanism of copolymerization.

According to the description considering the effect of only the last term of the chain, the change in the composition of the copolymer in the copolymerization of two monomers can be expressed by the following equation:

$$\frac{dM_1}{dM_2} = \frac{M_1}{M_2}\,\frac{r_1M_1 + M_2}{r_2M_2 + M_1} \tag{1}$$

where M_1 and M_2 are the concentration of monomers, $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ are the monomer reactivity ratios. At low conversions dM_1/dM_2 corresponds to the concentration ratio of the copolymer components. After introduction of

$$M_1/M_2 = x \quad \text{and} \quad dM_1/dM_2 = y \tag{2}$$

the composition equation may be written as:

$$y = x\,\frac{1 + r_1x}{r_2 + x} \tag{3}$$

Equation (3) was linearized by Fineman and Ross [2] as:

$$G = r_1 F - r_2 \tag{4}$$

and/or

$$\frac{G}{F} = -r_2 \frac{1}{F} + r_1 \tag{5}$$

where the transformed variables are:

$$G = x(y - 1)/y \quad \text{and} \quad F = x^2/y \tag{6}$$

Graphical plotting of Eq. (4) gives r_1 as the slope and r_2 as the intercept, while the plot of Eq. (5) presents r_2 as the slope and r_1 as the intercept.

As pointed out by Tidwell and Mortimer, the experimental data are unequally weighted by the Fineman-Ross equations, the data obtained under extreme experimental conditions (in Eq. 4 at rather low M_2 and in Eq. 5 at very low M_1 comonomer concentrations) have the greatest influence on the slope of a line calculated by the usual linear least-squares procedure, and accordingly, the calculated r_1 and r_2 values depend on arbitrary factors, such as which monomer is selected as M_1. This holds true even when both equations are involved in the calculation of the reactivity ratios: there is often considerable deviation between the corresponding values derived from Eqs. (4) and (5).

The situation is similar in the case of graphically evaluable linear equations. As shown in the Appendix, it is characteristic of all graphically evaluable linear equations of (A-1)-(A-6) obtained by linearization of Eq. (3) that on inversion of the data (re-indexing of the monomers and reactivity ratios) the equations are not invariant but transform into each other.

Further disadvantage of the FR method and other graphic procedures is that in case the copolymerization experiments are carried out by steadily changing the mole fraction $x/(1 + x)$ of the comonomer mixture or, occasionally, by a steady change of the mole fraction $y/(1 + y)$ of the copolymer, the values calculated from the experimental data will appear along the ordinate at growing intervals (e.g., in the case of Eq. 4, F may take all positive values).

The above disadvantages may, however, be abolished by the following graphically evaluable linear equation:

$$\frac{G}{\alpha + F} = \left(r_1 + \frac{r_2}{\alpha}\right) \frac{F}{\alpha + F} - \frac{r_2}{\alpha} \tag{7}$$

where α denotes an arbitrary constant ($\alpha > 0$). The most feasible choice of the α value will be dealt with later on.

By introducing

$$\eta = \frac{G}{\alpha + F} \quad \text{and} \quad \xi = \frac{F}{\alpha + F} \tag{8}$$

for Eq. (7) we may write

$$\eta = \left(r_1 + \frac{r_2}{\alpha}\right) \xi - \frac{r_2}{\alpha} \tag{9}$$

and/or

$$\eta = r_1 \xi - \frac{r_2}{\alpha} (1 - \xi) \tag{10}$$

The variable ξ cannot take any positive value, only those in interval (0,1). Thus plotting the η values calculated from the experimental data in the function of ξ, we obtain a straight line, which extrapolated to $\xi = 0$ and $\xi = 1$ gives $-r_2/\alpha$ and r_1 (both as intercepts).

The suggested relationship is invariant to the inversion of data: re-indexing of the monomers and reactivity ratios does not change the calculated results. Uniform distribution of the experimental data in the interval (0,1) may be attained by proper choice of the α value. If the reactivity ratios are nearly identical ($r_1 \approx r_2$), the choice of $\alpha = 1$ is generally satisfactory: in the case of markedly different reactivity ratios or if the choice of $\alpha = 1$ involves rather asymmetric data distribution along the interval (0,1), in our experience it is most feasible to choose the α value with regard to the entire experimental range of composition for both the polymer and comonomers. Of the F values calculated from the series of measurements, if F_m stands for the lowest and F_M for the highest value, then the choice of

$$\alpha = \sqrt{F_m F_M} \tag{11}$$

will afford optimum distribution of the data, which ensures validity of the relationship between ξ_m related to the lowest F value and ξ_M related to the highest F value, i.e.,

$$\xi_m = 1 - \xi_M \tag{12}$$

Accordingly, the experimental data will be located symmetrically along the interval (0,1).

By means of Eq. (7) and the equivalent Eqs. (9) and (10), the experimental data can be evaluated both by the graphic method and the method of least squares. In the latter case, the r_1 and r_2 values may be derived from the relations

$$r_1 = \frac{\Sigma\eta\xi(n - \Sigma\xi) - \Sigma\eta(\Sigma\xi - \Sigma\xi^2)}{n\Sigma\xi^2 - (\Sigma\xi)^2}$$

$$r_2 = \alpha\frac{\Sigma\eta\xi\Sigma\xi - \Sigma\eta\Sigma\xi^2}{n\Sigma\xi^2 - (\Sigma\xi)^2} \tag{13}$$

where n denotes the number of experimental data. The summation limits of the individual sums have not been specified; in all cases the summation refers to all data, e.g.,

$$\Sigma\xi = \sum_{i=1}^{n} \xi_i$$

The r_1 and r_2 values calculated by this procedure correspond to the best straight line obtained by the graphic method of evaluation.

In order to show the application of Eq. (7), we present the evaluation of experimental data of Mayo and Lewis [12] and Ito and Yamashita [13] for the system styrene/methyl methacrylate/benzoyl peroxide/60°C (Fig. 1.). The reactivity ratios obtained are depicted in Table 1.

In order to show that application of the Fineman-Ross equation may lead to erroneous results, Tidwell and Mortimer [6] applied their own copolymerization data obtained under extreme concentration conditions (data of Table III of Ref. 5). They have shown that application of the two variations of the Fineman-Ross equation in this system gives different, physically impossible (negative) reactivity ratios (Table 1 in Ref. 6). Their data evaluated by our equation are presented in Fig. 2; the reactivity ratios ($r_1 = 0.185$ and $r_2 = 0.476$) are in good agreement with those obtained by the authors by application of the nonlinear least-squares method ($r_1 = 0.182$ and $r_2 = 0.488$).

Another example given by the authors (Table 2, Ref. 6) concerns a system (data of Chapin, Ham, and Fordyce [14]) where the reactivity ratios are markedly different ($r_2 \approx 100r_1$) and the two variations of the

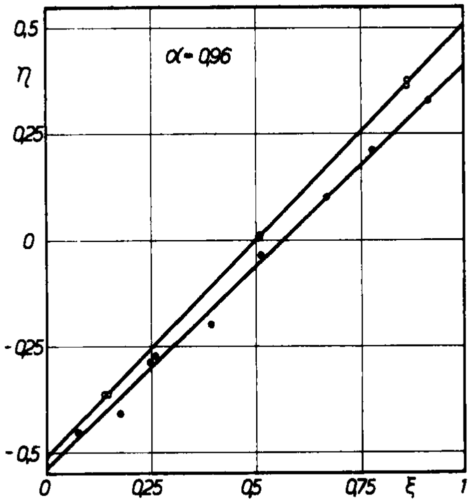

FIG. 1. Data of the system styrene/methyl methacrylate/benzoyl peroxide/60°C, plotted according to Eq. (7). (○) Data of Mayo and Lewis [12]; (●) data of Ito and Yamashita [13].

TABLE 1. Results Obtained for the System Styrene/Methyl Methacrylate/Benzoyl Peroxide/60°C

Value of copolymerization constants	Data of Ref. 12		Data of Ref. 13	
	r_1	r_2	r_1	r_2
By original authors	0.50	0.50	0.45	0.50
By Eq. (7)	0.511	0.488	0.414	0.518

Fineman-Ross equation give strongly contrasting results. Evaluation of the results of this system (vinyl chloride/methyl acrylate/benzoyl peroxide/50°C) by our equation (Fig. 3.) involves no difficulties at all (r_1 = 0.075 and r_2 = 9.071). Evaluation of the data of the latter two systems was carried out by other methods as well, and the results are listed in the Appendix.

Figure 4 presents data obtained by Wiley and Sale [15] for the system styrene/methyl methacrylate/60°C, evaluated by our equation. In these experiments the authors applied labeled styrene (styrene-β-^{14}C); according to their data, the weight percentage determined by activity

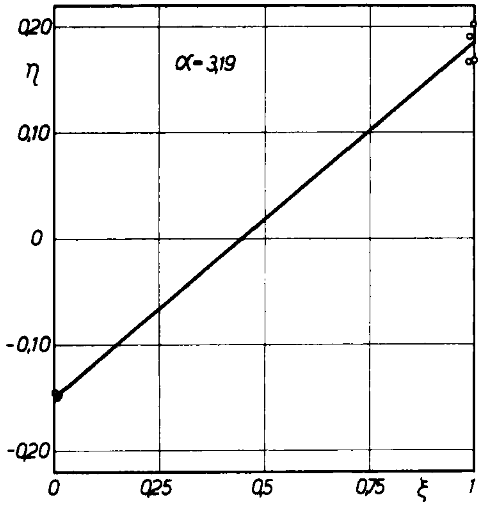

FIG. 2. Data of Table 3 of Ref. 5 (Tidwell and Mortimer) plotted by Eq. (7).

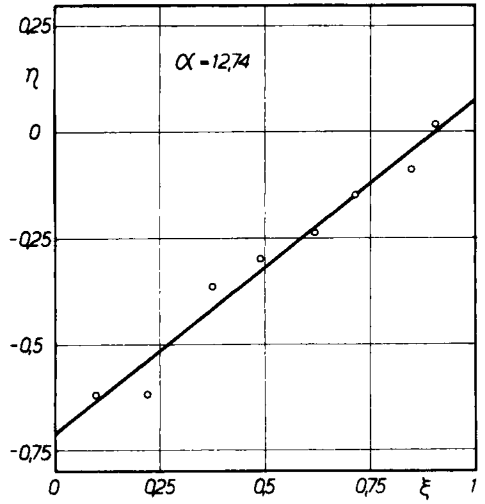

FIG. 3. Data of the system vinyl chloride/methyl acrylate/benzoyl peroxide/50° C, plotted according to Eq. (7) (data of Chapin, Ham, and Fordyce [14]).

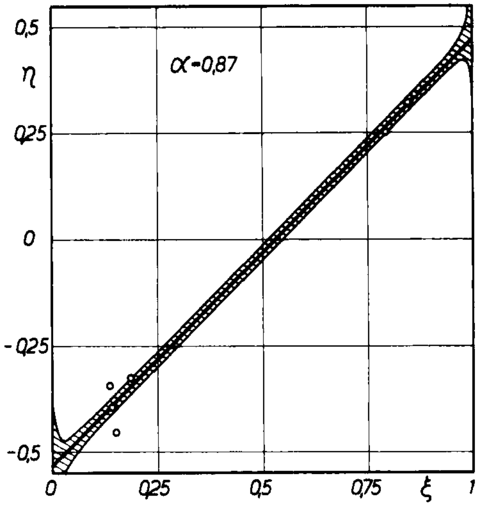

FIG. 4. Data of the system styrene/methyl methacrylate/benzoyl peroxide/60°C, plotted according to Eq. (7) (data of Wiley and Sale [15]). The band corresponds to the value Δ = ±0.47% of absolute error of the analysis (weight percent). The values determined are $r_1 = 0.471$ and $r_2 = 0.464$.

measurements carry an average absolute error of Δ = ±0.47%. In order to illustrate how such a large analytical error may affect the reactivity ratio determinations, we have also indicated the band representing the error in the figure. As may be seen, the error is appreciable only at extreme concentration ratios. Detailed analysis of the errors will be dealt with in a later publication.

The main advantage of Eq. (7) introduced by the authors is that it allows visual estimation of the fact of whether the copolymer composition Eq. (1) is adequate for the experimental data in a given system. In Fig. 5 we present the evaluation of experimental data by Gilbert et al. [16] for the system vinylidene cyanide/maleic anhydride/50°C, plotted by our equation. The limit of errors corresponding to the relative error σ = ±0.5%, given by the authors for nitrogen determination, is also presented. In spite of this particular error structure, it may be unambiguously established from the figure that the composition Eq. (1) does not correctly describe the system and that the experimental data show a systematic and significant deviation from the straight line (the straight line corresponding to the $r_1 = 45$ and $r_2 = 0$ values given by the authors is depicted in the figure by a dotted line).

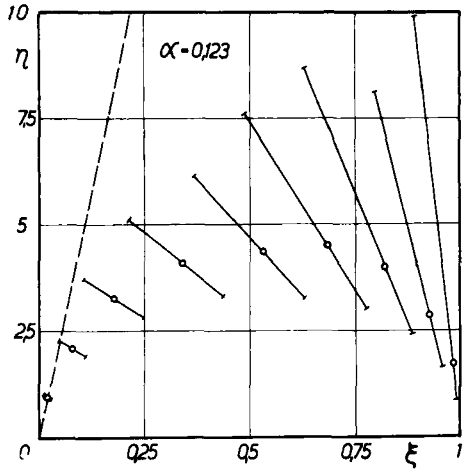

FIG. 5. Data of the system vinylidene cyanide/maleic anhydride/caproyl peroxide/benzene/50°C, plotted according to Eq. (7) (data of Gilbert et al. [16]). The limits depicted correspond to the relative error of the analysis $\delta = \pm 0.5\%$. The dotted line represents the $r_1 = 45$ and $r_2 = 0$ values given by the authors.

The TM method of nonlinear least squares, the application of which requires a tedious computerized procedure, and the YBR method as well as other numerical systems are not suitable for direct demonstration of the systematic deviation from the composition equation; even for systems as presented in Fig. 5 the numerical methods determine reactivity ratios whereas the copolymerization mechanism corresponding to Eq. (1) is not adequate.

The answer to the question of adequacy requires a special graphic investigation in the application of numerical (both linear and nonlinear) procedures. The correlation suggested by us allows direct determination of the adequacy and offers—if Eq. (1) holds true—a simple graphic method for the determination of copolymerization constants in a single step.

APPENDIX

Equation (1), which describes the composition of the copolymer, may be transformed into nonequivalent relationships of linear graphic experimental data processing (the markings correspond to those in Eqs. 2 and 6):

$$G = r_1F - r_2 \qquad \text{(A-1)}$$

$$\frac{G}{F} = -r_2\frac{1}{F} + r_1 \qquad \text{(A-2)}$$

$$F = \frac{1}{r_1}G + \frac{r_2}{r_1} \qquad \text{(A-3)}$$

$$\frac{1}{F} = -\frac{1}{r_2}\frac{G}{F} + \frac{r_1}{r_2} \qquad \text{(A-4)}$$

$$\frac{F}{G} = \frac{r_2}{r_1}\frac{1}{G} + \frac{1}{r_1} \qquad \text{(A-5)}$$

$$\frac{1}{G} = \frac{r_1}{r_2}\frac{F}{G} - \frac{1}{r_2} \qquad \text{(A-6)}$$

Of these linear equations, (A-1) and (A-2) correspond to the well-known Fineman-Ross equations. None of the equations is invariant to the inversion of the data. By re-indexing the monomers, for F we have 1/F, for G we obtain -G/F, and for r_1 we derive r_2 and vice versa; in other words, for (A-1) we obtain (A-2), for (A-3) we have (A-4), and for (A-5) we have (A-6) and vice versa.

Application of the method of least squares to the individual equations gives the following pairs of equations determining the value of r_1 and r_2:

$$r_1\Sigma F^2 - r_2\Sigma F = \Sigma FG \qquad \text{(A-1/1)}$$

$$r_1\Sigma F - r_2 n = \Sigma G \qquad \text{(A-1/2)}$$

$$r_1\Sigma\frac{1}{F} - r_2\Sigma\frac{1}{F^2} = \Sigma\frac{G}{F^2} \qquad \text{(A-2/1)}$$

$$r_1 n - r_2\Sigma\frac{1}{F} = \Sigma\frac{G}{F} \qquad \text{(A-2/2)}$$

$$r_1\Sigma FG - r_2\Sigma G = \Sigma G^2 \qquad \text{(A-3/1)}$$

$$r_1\Sigma F - r_2 n = \Sigma G \qquad \text{(A-3/2)}$$

$$r_1\Sigma\frac{G}{F} - r_2\Sigma\frac{G}{F^2} = \Sigma\frac{G^2}{F^2} \qquad \text{(A-4/1)}$$

$$r_1 n - r_2\Sigma\frac{1}{F} = \Sigma\frac{G}{F} \qquad \text{(A-4/2)}$$

$$r_1\Sigma\frac{F}{G^2} - r_2\Sigma\frac{1}{G^2} = \Sigma\frac{1}{G} \qquad \text{(A-5/1)}$$

$$r_1\Sigma\frac{F}{G} - r_2\Sigma\frac{1}{G} = n \qquad \text{(A-5/2)}$$

$$r_1\Sigma\frac{F^2}{G^2} - r_2\Sigma\frac{F}{G^2} = \Sigma\frac{F}{G} \qquad \text{(A-6/1)}$$

$$r_1\Sigma\frac{F}{G} - r_2\Sigma\frac{1}{G} = n \qquad \text{(A-6/2)}$$

In the above equations, n denotes the number of experimental data. The indices and summation limits have not been indicated in the individual sums: the summation refers to all data in each case, e.g.: $\Sigma G = \sum_{i=1}^{n} G_i$.

The r_1 and r_2 values derived from the equation pairs correspond to the best straight line obtained by plotting the experimental data according to the given equations. In order to illustrate the application of the equations, we present the various figures (A-1 to A-6) of the system vinyl chloride/methyl acrylate/benzoyl peroxide/50° C (data of Chapin, Ham, and Fordyce [14]); the corresponding copolymerization constants are depicted in Table A-1. The results derived by elaboration by the above equations of the copolymerization data of Tidwell and Mortimer (Table III, Ref. 5), gained under extreme concentration conditions, are presented in Table A-2.

On re-indexing the monomers, Eqs. (A-1/1) to (A-6/2) transform into each other: (A-1/1) into (A-2/1); (A-1/2) and the equivalent (A-3/2) into (A-2/2); as well as (A-3/1) into (A-4/1) and (A-5/1) into (A-6/1). Equation (A-5/2) or its equivalent (A-6/2) does not change.

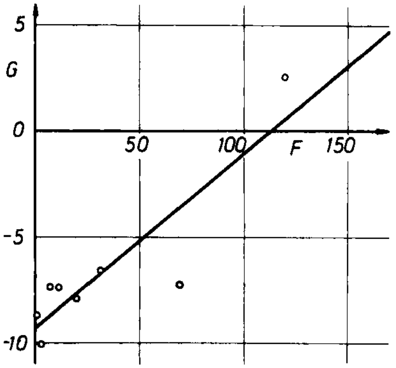

FIG. A-1. Data of the system vinyl chloride/methyl acrylate/ benzoyl peroxide/50°C, plotted according to Eq. (A-1) of Fineman and Ross (data of Chapin, Ham, and Fordyce [14]).

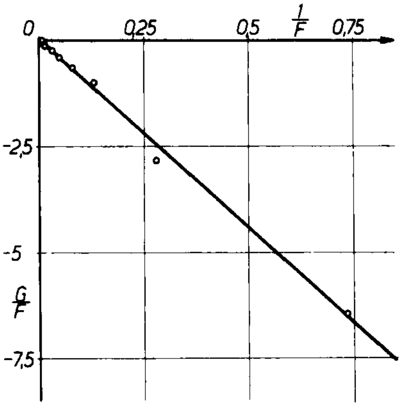

FIG. A-2. Data of the system vinyl chloride/methyl acrylate/ benzoyl peroxide/50°C, plotted according to Eq. (A-2) of Fineman and Ross (data of Chapin, Ham, and Fordyce [14]).

The equations transforming into each other are thus suitable to form pairs which, upon inversion of the data, afford invariant r_1 and r_2 values. The graphically linear relationships not evaluable are the following.

By applying (A-1/1) and (A-2/1) we obtain

$$r_1 = \frac{\Sigma FG \Sigma \frac{1}{F^2} - \Sigma \frac{G}{F^2} \Sigma F}{\Sigma F^2 \Sigma \frac{1}{F^2} - \Sigma \frac{1}{F} \Sigma F}$$

$$r_2 = \frac{\Sigma FG \Sigma \frac{1}{F} - \Sigma \frac{G}{F^2} \Sigma F^2}{\Sigma F^2 \Sigma \frac{1}{F^2} - \Sigma \frac{1}{F} \Sigma F} \qquad \text{(A-7)}$$

From (A-1/2) and (A-2/2) we have

$$r_1 = \frac{\Sigma G \Sigma \frac{1}{F} - \Sigma \frac{G}{F} n}{\Sigma F \Sigma \frac{1}{F} - n^2}$$

$$r_2 = \frac{\Sigma G n - \Sigma \frac{G}{F} \Sigma F}{\Sigma F \Sigma \frac{1}{F} - n^2} \qquad \text{(A-8)}$$

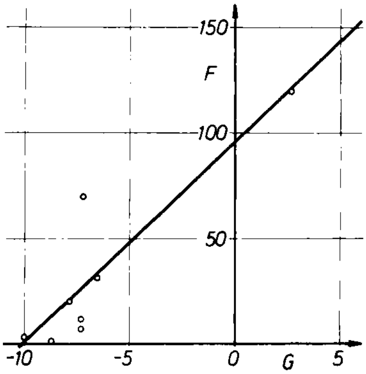

FIG. A-3. Data of the system vinyl chloride/methyl acrylate/benzoyl peroxide/50°C, plotted according to Eq. (A-3) (data of Chapin, Ham, and Fordyce [14]).

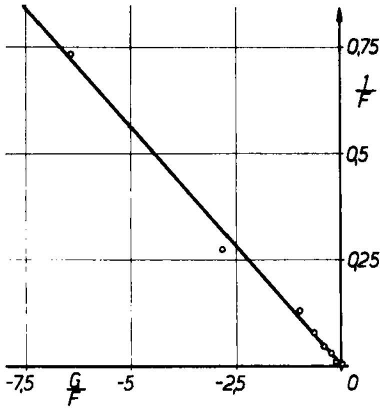

FIG. A-4. Data of the system vinyl chloride/methyl acrylate/benzoyl peroxide/50°C, plotted according to Eq. (A-4) (data of Chapin, Ham, and Fordyce [14]).

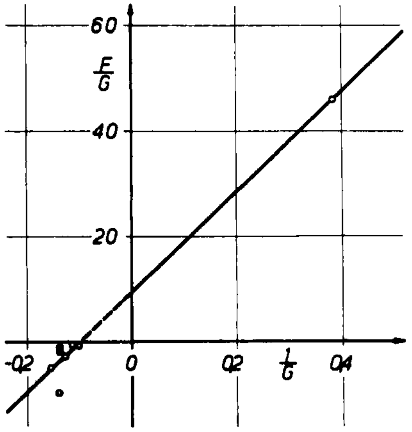

FIG. A-5. Data of the system vinyl chloride/methyl acrylate/benzoyl peroxide/50°C, plotted according to Eq. (A-5) (data of Chapin, Ham, and Fordyce [14]).

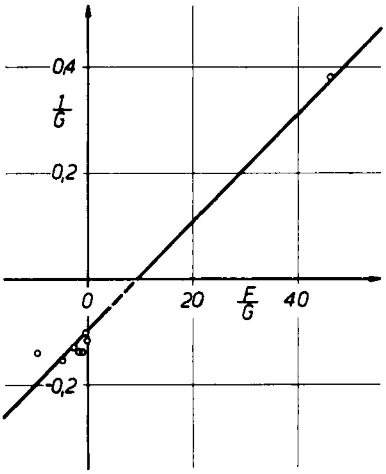

FIG. A-6. Data of the system vinyl chloride/methyl acrylate/benzoyl peroxide/50°C, plotted according to Eq. (A-6) (data of Chapin, Ham, and Fordyce [14]).

The combination of (A-3/1) and (A-4/1) gives

$$r_1 = \frac{\Sigma G^2 \Sigma \frac{G}{F^2} - \Sigma \frac{G^2}{F^2} \Sigma G}{\Sigma FG \Sigma \frac{G}{F^2} - \Sigma \frac{G}{F} \Sigma G}$$

$$r_2 = \frac{\Sigma G^2 \Sigma \frac{G}{F} - \Sigma \frac{G^2}{F^2} \Sigma FG}{\Sigma FG \Sigma \frac{G}{F^2} - \Sigma \frac{G}{F} \Sigma G} \tag{A-9}$$

Combination of (A-5/1) and (A-6/1) yields

$$r_1 = \frac{\Sigma \frac{1}{G} \Sigma \frac{F}{G^2} - \Sigma \frac{F}{G} \Sigma \frac{1}{G^2}}{\left(\Sigma \frac{F}{G^2}\right)^2 - \Sigma \frac{F^2}{G^2} \Sigma \frac{1}{G^2}}$$

$$r_2 = \frac{\Sigma \frac{1}{G} \Sigma \frac{F^2}{G^2} - \Sigma \frac{F}{G} \Sigma \frac{F}{G^2}}{\left(\Sigma \frac{F}{G^2}\right)^2 - \Sigma \frac{F^2}{G^2} \Sigma \frac{1}{G^2}} \tag{A-10}$$

TABLE A-1. Evaluation of Copolymerization Data [14] of the System Vinyl Chloride (1)/Methyl Acrylate (2) by the Methods Outlined

Equation	r_1	r_2	$\Delta_1 \times 10^2$ [a]	$\Delta_2 \times 10^2$ [b]
A-1 (FR method)	0.08266	9.337	1.318	0.665
A-2 (FR method)	0.05273	8.931	1.694	0.897
A-3	0.10484	10.077	1.181	0.600
A-4	0.06063	8.978	1.573	0.819
A-5	0.10614	10.147	1.190	0.608
A-6	0.10461	10.223	1.251	0.625
A-7	0.07815	8.983	1.345	0.681
A-8 (YBR method)	0.07439	9.061	1.382	0.698
A-9	0.02355	8.904	2.429	1.290
A-10	0.09864	9.568	1.210	0.597
A-11	0.08123	9.228	1.317	0.663
A-12	0.08432	9.470	1.320	0.673
A-13[c]	0.10595	10.121	1.182	0.605
A-14[d]	0.10206	9.796	1.165	0.586
7[e]	0.07488	9.071	1.376	0.695
TM method	0.09 ± 0.05	10.1 ± 3.0	1.460	0.729

[a] Δ_1 = difference (average absolute value of deviations) between calculated and measured values of mole fractions $y/(1 + y)$.

[b] Δ_2 = deviation between calculated and measured chlorine content (average absolute value of deviations).

[c] $\gamma = -22.969$.

[d] $\beta = -0.1424$.

[e] $\alpha = 12.780$.

It is easy to establish that the copolymerization constants of Eq. (A-8) are identical to those obtained by the YBR method [3]; namely, by the method of least squares, the equation suggested by Yezrielev, Brokhina, and Roskin

$$\frac{G}{\sqrt{F}} = r_1\sqrt{F} - r_2\frac{1}{\sqrt{F}} \qquad \text{(A-8/1)}$$

TABLE A-2. Evaluation of the Data of Table III of Ref. 5 by the Methods Described

Equation	r_1	r_2	$\Delta_1 \times 10^2$ [a]
A-1 (FR method)	0.1788	-2.2065	4.333
A-2 (FR method)	-0.0856	0.4612	17.152
A-3	0.1809	-0.9697	5.679
A-4	-0.0822	0.4613	18.451
A-5	0.1841	0.4757	0.226
A-6	0.1828	0.4791	0.213
A-7	0.1801	0.4626	0.275
A-8 (YBR method)	0.1833	0.4657	0.262
A-9	0.1816	0.4626	0.275
A-10	0.1828	0.4756	0.225
A-11	0.1801	0.4624	0.275
A-12	0.1801	0.4624	0.275
A-13[b]	0.1841	0.4769	0.221
A-14[c]	0.1872	0.4780	0.220
7[d]	0.1852	0.4762	0.225
TM method	0.182 ± 0.011	0.488 ± 0.027	0.201

[a] Δ_1 = difference (average absolute value of deviations) between calculated and measured values of mole fractions $y/(1 + y)$.

[b] $\beta = 1.0226$.

[c] $\gamma = -2.4475$.

[d] $\alpha = 3.1890$.

which is linear regarding r_1 and r_2 (though with two variables, thus graphically not evaluable) gives results corresponding to those obtained by Eq. (A-8).

The relationship (A-8/1) is the combination of Eqs. (A-1) and (A-2), graphically evaluable, not invariant equations in an invariant though only numerically evaluable form. The combination of Eqs. (A-3) and (A-4) gives an analogous invariant relationship:

$$\frac{1}{\sqrt{r_1 r_2}} \frac{G}{\sqrt{F}} = \sqrt{\frac{r_1}{r_2}} \sqrt{F} - \sqrt{\frac{r_2}{r_1}} \frac{1}{\sqrt{F}} \qquad \text{(A-8/2)}$$

which has two parameters but is not linear regarding r_1 and r_2.

The Eq. (A-10) constants are identical with the results obtained by the method of least squares from the linear (but graphically not evaluable) equation

$$r_1 \frac{F}{G} - r_2 \frac{1}{G} = 1 \tag{A-10/1}$$

With Eq. (A-10/1) an analogous invariant relationship can be derived from Eqs. (A-5) and (A-6):

$$\sqrt{\frac{r_1}{r_2}}\,\frac{F}{G} - \sqrt{\frac{r_2}{r_1}}\,\frac{1}{G} = \frac{1}{\sqrt{r_1 r_2}} \tag{A-10/2}$$

which has two parameters but is not linear for r_1 and r_2.

The results calculated on the basis of the invariant relationships (A-7) to (A-10) are shown in Tables A-1 and A-2.

It should be noted that the addition or subtraction of linear Eqs. (A-1) and (A-2) leads to further numerically evaluable invariant relationships. The equation obtained by addition:

$$\frac{G}{F} + G = r_1(1 + F) - r_2\left(1 + \frac{1}{F}\right) \tag{A-11}$$

and/or the relationship derived by subtraction

$$\frac{G}{F} - G = r_1(1 - F) + r_2\left(1 - \frac{1}{F}\right) \tag{A-12}$$

transform into each other on re-indexing the monomers. From this, by application of the least-squares method, we have:

$$r_1 = \frac{\Sigma \frac{G}{F}(1 + F)^2 \Sigma \frac{1}{F^2}(1 + F)^2 - \Sigma \frac{G}{F^2}(1 + F)^2 \Sigma \frac{1}{F}(1 + F)^2}{\Sigma(1 + F)^2 \Sigma \frac{1}{F^2}(1 + F)^2 - \left[\Sigma \frac{1}{F}(1 + F)^2\right]^2}$$

and (A-11/1)

$$r_2 = \frac{\Sigma \frac{G}{F}(1 + F)^2 \Sigma \frac{1}{F}(1 + F)^2 - \Sigma \frac{G}{F^2}(1 + F)^2 \Sigma(1 + F)^2}{\Sigma(1 + F)^2 \Sigma \frac{1}{F^2}(1 + F)^2 - \left[\Sigma \frac{1}{F}(1 + F)^2\right]^2}$$

i.e.,

$$r_1 = \frac{\Sigma\frac{G}{F}(1-F)^2\,\Sigma\frac{1}{F^2}(1-F)^2 - \Sigma\frac{G}{F^2}(1-F)^2\,\Sigma\frac{1}{F}(1-F)^2}{\Sigma(1-F)^2\,\Sigma\frac{1}{F^2}(1-F)^2 - [\Sigma\frac{1}{F}(1-F)^2]^2}$$

and (A-12/1)

$$r_2 = \frac{\Sigma\frac{G}{F}(1-F)^2\,\Sigma\frac{1}{F}(1-F)^2 - \Sigma\frac{G}{F^2}(1-F)^2\,\Sigma(1-F)^2}{\Sigma(1-F)^2\,\Sigma\frac{1}{F^2}(1-F)^2 - [\Sigma\frac{1}{F}(1-F)^2]^2}$$

The results derived by these equations are also collected in the tables.

Further, merely numerically evaluable invariant linear equations may be obtained by multiplying (weighting) the linear Eqs. (A-1) and (A-2) with such combinations of F and G, which transform into each other on re-indexing (e.g., G^2 and G^2/F^2, or F^2 and $1/F^2$, etc.).

It is noteworthy that the equation pair

$$r_1\Sigma F - r_2 n = \Sigma G \qquad \text{(A-8/3)}$$

$$r_1 n - r_2\Sigma\frac{1}{F} = \Sigma\frac{G}{F} \qquad \text{(A-8/4)}$$

corresponding to the YBR relation, can be derived in two ways: (a) by selecting 1/F for the weighting factor of Eq. (A-1) and F for the Eq. (A-2), (b) by multiplying both equations by 1; in other words, by not weighting at all.

Transformation of Eqs. (A-5) and/or (A-6) by the method applied for relation (7) gives a graphically evaluable, though, on reindexing noninvariant linear equation.

Plotting the equation

$$\frac{F/G}{2(\beta + 1/G)} = \left(\frac{r_2}{r_1} - \frac{1}{\beta r_1}\right)\frac{1/G}{2(\beta + 1/G)} + \frac{1}{2\beta r_1} \qquad \text{(A-13)}$$

obtained from Eq. (A-5) and the equation

$$\frac{1/G}{2(\gamma + F/G)} = \left(\frac{r_1}{r_2} + \frac{1}{\gamma r_2}\right)\frac{F/G}{2(\gamma + F/G)} - \frac{1}{2\gamma r_2} \qquad \text{(A-14)}$$

derived from Eq. (A-6) for graphical evaluation, similarly to the case where Eq. (7) is applied, by correct choice of the β and γ values, we have the interval (0,1) for the range of interpretation of the independent variable. The values (intercepts) extrapolated to 0 and 1 can be easily determined. This, as well as the fact that by correct choice of the β and γ values, the extreme values of experimental data can be symmetrically plotted in the diagram, greatly contribute to the accuracy and reliability of the evaluation. The transformation parameters can be most feasibly chosen as follows.

If $(1/G)_m$ and $(1/G)_M$ and/or $(F/G)_m$ and $(F/G)_M$ have different signs:

$$\beta = -\frac{(1/G)_m + (1/G)_M}{2} \qquad \text{(A-13/1)}$$

and/or

$$\gamma = -\frac{(F/G)_m + (F/G)_M}{2} \qquad \text{(A-14/1)}$$

and if the lowest and highest values have identical signs:

$$\beta = \sqrt{(1/G)_m (1/G)_M} \qquad \text{(A-13/2)}$$

and/or

$$\gamma = \sqrt{(F/G)_m (F/G)_M} \qquad \text{(A-14/2)}$$

Relations (A-3) and (A-5) are combined in Eq. (A-13), as well as Relations (A-4) and (A-6) in Eq. (A-14), therefore—although they are transformed into each other on re-indexing of the monomers—their application is far more reliable than separate application of the graphically evaluable (A-1) to (A-6) relations.

Equations (A-13) and (A-14) can be evaluated not only by the graphic procedure but also by the method of least squares. By introducing

$$\eta' = \frac{F/G}{2(\beta + 1/G)} \quad \text{and} \quad \xi' = \frac{1/G}{2(\beta + 1/G)} \qquad \text{(A-13/3)}$$

and

$$\eta'' = \frac{1/G}{2(\gamma + F/G)} \quad \text{and} \quad \xi'' = \frac{F/G}{2(\gamma + F/G)} \qquad \text{(A-14/3)}$$

we may calculate the r_1 and r_2 values by the relationships

$$r_1 = \frac{1}{2\beta} \; \frac{n\Sigma\xi'^2 - (\Sigma\xi')^2}{\Sigma\eta'\Sigma\xi'^2 - \Sigma\xi'\Sigma\eta'\xi'}$$

(A-13/4)

$$r_2 = \frac{1}{\beta}\left(1 - \frac{\Sigma\eta'\xi'n - \Sigma\eta'\Sigma\xi'}{2(\Sigma\eta'\xi'\Sigma\xi' - \Sigma\eta'\Sigma\xi'^2)}\right)$$

and

$$r_1 = \frac{1}{\gamma} \; \frac{\Sigma\eta''\xi''n - \Sigma\eta''\Sigma\xi''}{2(\Sigma\eta''\xi''\Sigma\xi'' - \Sigma\eta''\Sigma\xi''^2)}$$

(A-14/4)

$$r_2 = \frac{1}{2\gamma} \; \frac{n\Sigma\xi''^2 - (\Sigma\xi'')^2}{\Sigma\xi''\Sigma\eta'' - \Sigma\eta''\Sigma\xi''^2}$$

For the sake of comparison, the evaluation of the data of the system vinyl chloride/methyl acrylate/benzoyl peroxide/50°C (Chapin, Ham, and Fordyce [14]) by Eqs. (A-13) and (A-14) are presented in Figs. A-7 and A-8; the results are also listed in Table A-1. The results obtained by Eqs. (A-13) and (A-14) for the data of Table III of Ref. 5 are collected in Table A-2.

The tables also contain results obtained by application of Eq. (7) as suggested by the authors as well as those gained by the TM method (nonlinear least squares [6]). Evaluation of the correctness of r_1 and r_2 values derived by various methods are depicted in the tables by average absolute values of the difference between calculated and measured mole fractions $y/(1 + y)$.

The average of absolute values of the difference between calculated and measured analytical data (chlorine content) are also figuring in Table A-1. This could not be shown in Table A-2 as the analytical data are not given in Ref. 5.

On evaluating the data, we may state that the Fineman-Ross relations (A-1) and (A-2) as well as the analogous graphically evaluable equations

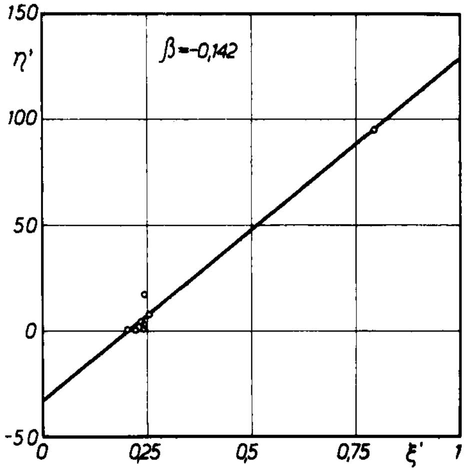

FIG. A-7. Data of the system vinyl chloride/methyl acrylate/ benzoyl peroxide/50°C, plotted according to Eq. (A-13) (data of Chapin, Ham, and Fordyce [14]).

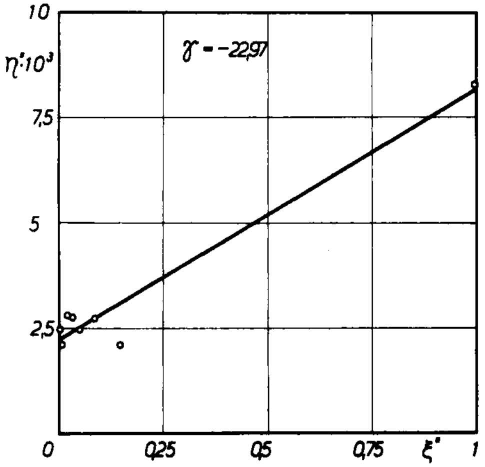

FIG. A-8. Data of the system vinyl chloride/methyl acrylate/ benzoyl peroxide/50°C, plotted according to Eq. (A-14) (data of Chapin, Ham, and Fordyce [14]).

(A-3) and (A-4) afford occasionally physically impossible (negative) copolymerization constants, therefore their further application for the determination of r_1 and r_2 cannot be suggested at present.

Application of Eqs. (A-5) and (A-6) gives, according to our experience, reliable evaluation of the data; this may be due to the fact that although these equations are not invariant, a member of each equation pair used for the calculation of r_1 and r_2 (Eq. A-5/2 and/or the equivalent Eq. A-6/2) is invariant.

The numerically evaluable invariant linear relations (A-7) to (A-12), including the YBR method, generally afford acceptable results; many of these are practically equivalent to the nonlinear TM method. Relation (7) suggested by us as well as the analogous but not invariant Eqs. (A-13) and (A-14) are all graphically evaluable linear relationships and also give reliable results for the systems presented here as well as for the approximately 100 further systems investigated so far.

The main properties of the linear equations studied are summarized in Table A-3.

SUMMARY

A new graphically evaluable linear method is suggested for the determination of the reactivity ratios of copolymerization. The main advantage of the proposed Eq. (7) is that it is very well adaptable for visual determination of the applicability of the copolymer composition equation. If the experimental data are adequate to the composition equation, the procedure offers a simple and reliable method for the graphical determination of copolymerization constants, owing to the following factors:

1. The relationship applied is invariant to the inversion of data (re-indexing of the monomers and reactivity ratios).
2. The range of interpretation for the independent variable is the interval (0,1) (e.g., in the Fineman-Ross equations, the independent variable may take up all positive values).
3. By appropriate choice of the parameter of the equation, the experimental data are located symmetrically along the interval (0,1).

The Appendix features a great number of further (in fact, all considerable) linear evaluation methods. Of the linear methods compared, only three are known in the literature. It has been stated that four of the six graphical procedures outlined here (including the Fineman-Ross equations) are not recommended for application. The six numerically applicable methods studied (including the YBR method) are rather reliable. Many of these give practically equivalent results to those obtained by the TM method. Finally, two graphically evaluable linear

TABLE A-3. Summary of Some Significant Properties of the Linear Equations Studied

Equations	Properties	Note
A-1 to A-4	Graphically evaluable. Not invariant on re-indexing.	Application not recommended.
A-5 and A-6	Graphically evaluable. Not invariant on re-indexing but shows symmetry properties.	Application recommended with reservations only.
A-7 to A-12	Only numerically evaluable. Invariant on re-indexing.	Applicable. Determination of adequacy requires further investigation.
A-13 and A-14	Graphically evaluable. Not invariant on re-indexing, but shows symmetry properties. Range of interpretation of independent variable: (0,1) interval. Has adjustable parameter.	Application recommended. Determination of adequacy requires no further investigation.
7	Graphically evaluable. Invariant on re-indexing, shows symmetry properties. Range of interpretation of independent variable: (0,1) interval. Has adjustable parameter.	Application recommended. Determination of adequacy requires no further investigation.

relations [(A-13) and (A-14)] analogous to Eq. (7) have been set up and studied. These relations, although not invariant upon re-indexing, afford reliable results in the course of evaluation of "critical" experimental data.

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