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## **Analysis of Linear Methods for Determining Copolymerization Reactivity Ratios. III. Linear Graphic Method for Evaluating Data Obtained at High Conversion Levels\***

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### **ABSTRACT**

If copolymerizations are carried to high conversions, the determination of copolymerization parameters involves significant computational difficulties because the exact integrated form of the copolymerization equation has to be applied. A simple method has been developed to transform experimental data, even at high conversions, to be used in the differential form of copolymerization equation. In this method an average monomer composition is assigned to the corresponding experimental average copolymer composition. The proposed approximation extends the use of our linearization technique previously developed for low conversions. It was established that this method yields highly reliable results for practically all

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\*For Parts I and II see Tüdós et al. [1, 2].

copolymerization systems. The error of this approximation is generally insignificant, and it can simply be estimated for any conversion, composition, and copolymerization parameter with the aid of diagrams published in this paper.

## INTRODUCTION

A reliable knowledge of copolymerization parameters is both theoretically and practically of great significance. From the theoretical aspect, the copolymerization parameters of a given monomer pair provide valuable information on the correlation between chemical structure and reactivity and allow quantitative kinetic analysis of the system, the immediate practical value of which is also evident.

Although copolymerization parameters have been published in the literature for over three decades, no uniform method for their determination has been developed. As the various procedures are not equally reliable, the reliability of the vast number of published data is just as varied.

A reliable method of parameter determination is supposed to (1) provide optimal parameter values and (2) allow immediate evaluation of whether or not the system is in agreement with the copolymerization mechanism assumed.

In our previous publications [1, 3], we described a new linear method which does not have the deficiencies of computation techniques of other known linear methods and yields nearly identical values by use of the nonlinear method of least squares [4]. On the other hand, as it is a graphical method, correctness of the assumed mechanism can be immediately ascertained by the linearity of the data points.

The only deficiency of the procedure described in our previous papers [1, 3] is—although this is characteristic of all differential methods—that it is applicable only at "sufficiently" low conversions. Since, in addition, other errors may also occur at low conversion levels, a generally applicable parameter determination procedure is required to be extendable to higher ranges of conversion as well. The methods applied so far, satisfying these criteria, however, require cumbersome computer techniques and do not have the indisputable advantages of the linear graphical procedures. The fact that they can be applied in principle, up to arbitrary conversions, does not serve as compensation for the disadvantages. Our purpose was, therefore, to extend the application of the linear parameter determination method to higher conversion levels with preservation of the favorable aspects of the procedure.

## DISCUSSION

Extension of the Applicability of the Differential Method

The simplest binary copolymerization (with two different active centers and monomers) involves four elementary chain propagation steps. For such systems, the relation (1) holds [ 5, 6 ]:

$$\frac{dm_1}{dm_2} = \frac{m_1}{m_2} \frac{1 + \rho_1 m_1/m_2}{\rho_2 + m_1/m_2} \quad (1)$$

where  $m_1$  and  $m_2$  denote concentrations of the two monomers and  $\rho_1$  and  $\rho_2$  are copolymerization parameters. They are rate constant ratios of two different elementary chain propagation steps:

$$\rho_1 \equiv k_{11}/k_{22}$$

and

$$\rho_2 \equiv k_{22}/k_{21} \quad (2)$$

As pointed out in an earlier paper [ 1 ], Eq. (1) can be transformed into linear relations by various methods. By defining the variables:

$$F \equiv \frac{(m_1/m_2)^2}{dm_1/dm_2}$$

and

$$G \equiv \frac{(dm_1/dm_2 - 1)m_1/m_2}{dm_1/dm_2} \quad (3)$$

for example, the widely known Fineman-Ross [ 7 ] equations may be expressed as:

$$G = \rho_1 F - \rho_2 \quad (4)$$

$$G/F = \rho_1 - (\rho_2/F) \quad (5)$$

The linear form Eq. (6), found to be optimal by us

$$\eta = [\rho_1 + (\rho_2/\alpha)]\xi - (\rho_2/\alpha) \quad (6)$$

has the variables in terms of Eq. (3) as follows:

$$\eta \equiv G/(\alpha + F)$$

and

$$\xi \equiv F/(\alpha + F) \quad (7)$$

By our experience, the best value for the auxiliary parameter  $\alpha$  is:

$$\alpha = \sqrt{F_{\min} F_{\max}} \quad (8)$$

Naturally, the linear relationships derived from Eq. (1) are applicable only provided several (at least 5-8) corresponding value pairs ( $m_1/m_2$ ;  $dm_1/dm_2$ ) are known for the system examined. The molar ratio  $m_1/m_2$  characterizing the monomer phase can be calculated, at least at the beginning ( $x_0$ ) and termination ( $x$ ) of a given copolymerization experiment, from measureable parameters or direct measurement data. The value of the differential amount  $dm_1/dm_2$  (instantaneous monomer ratio in the copolymer formed), can, however, not be measured and/or calculated from direct measurement results.

The average composition of the copolymer up to the conversion  $\zeta$ , expressed in terms of mole ratios is

$$\begin{aligned} y &= \Delta m_1 / \Delta m_2 \\ &= (m_1^0 - m_1) / (m_2^0 - m_2) \end{aligned} \quad (9)$$

where the superscript zero stands for the initial value of monomer concentration.

It follows from the above that the molar conversion  $\zeta$  is

$$\begin{aligned} \zeta &= (\Delta m_1 + \Delta m_2) / (m_1^0 + m_2^0) \\ &= 1 - [(m_1 + m_2) / (m_1^0 + m_2^0)] \end{aligned} \quad (10)$$

TABLE 1. Variables of Equation (1) with Different Methods of Evaluation

Method	$m_1/m_2$	$dm_1/dm_2$	Note
1	$x_0$	$y_0$	Application of the exact differential method (experimentally impracticable)
2	$x_0$	$y$	Usual erroneous application of the differential method
3	$x$	$y$	A more cumbersome variation of Method 2 (not applied in practice)
4	$x_0$	$zx_0$	Approximations by Walling and Briggs [8] as well as Yezrielev, Brokhina, and Roskin [9]
5	$x$	$zx$	A more cumbersome variation of Method 4 (not applied in practice)
6	$y/z$	$y$	Approximation proposed by us

Method 1

Correctness of the relationship (11):

$$\lim_{\xi \rightarrow 0} y \equiv y_0 = (dm_1/dm_2)_0 \quad (11)$$

is evident.

It follows then that, in principle, the procedure by which the  $y_0$  value is determined by polymerization of monomer mixtures of identical composition to various conversions and extrapolation of the  $y$  values obtained, is correct. In this case (Method 1, see Table 1), the  $y_0$  value obtained and the initial mole ratio  $x_0$  of the monomer mixture are true corresponding values, and they can be correctly used for the determination of  $\rho_1$  and  $\rho_2$  in Eq. (1). In practice, however, this method can hardly be applied, due to the uncertainty of nonlinear extrapolation and especially to the enormous increase of experimental work involved.

Method 2

It is a generally applied method, however, to approximate the

instantaneous composition of the copolymer at the time  $t = 0$  by the average copolymer composition:

$$(dm_1/dm_2)_0 \approx y \quad (12)$$

and to substitute the  $(x_0; y)$  value pairs into Eq. (1). This procedure (Method 2, see Table 1) can be used with adequate accuracy only at "sufficiently" low conversion data. With this approach, from Eq. (3) we have

$$F = x_0^2 / y$$

and

$$G = (y - 1)x_0 / y \quad (13)$$

by substitution of which we may obtain the usual forms of the Fineman-Ross equation [Eq. (4) and/or (5)]. According to Eq. (7) the values of the variables  $\eta$  and  $\xi$  by this method are

$$\eta = (y - 1)x_0 / (\alpha y + x_0^2)$$

and

$$\xi = x_0^2 / (\alpha y + x_0^2) \quad (14)$$

In applying the approximation of Eq. (12), we commit a systematic error, which can be lowered only by keeping the conversion levels as low as possible. Since, however, the minimum conversion is limited by the experimental method used, it is important to know the extent of the error made and its dependence on the parameters.

The relative error of approximation  $\delta$  in percent may be defined as:

$$\delta = |\eta - \eta(\xi)| / [\rho_1 + (\rho_2/\alpha)] \times 100 \quad (15)$$

where  $\eta(\xi)$  denotes the  $\eta$  value derived from Eq. (6) by substitution of  $\xi$  by Eq. (14). Its value depends on the conversion, but also on the values of  $\rho_1$ ,  $\rho_2$ , and  $x_0$ . This is well illustrated in Fig. 1, where the calculated values of error  $\delta$  are plotted against  $\rho_1$  at given conversions ( $\rho_2$  and  $x_0$  are constant,  $\alpha = 1$ ).

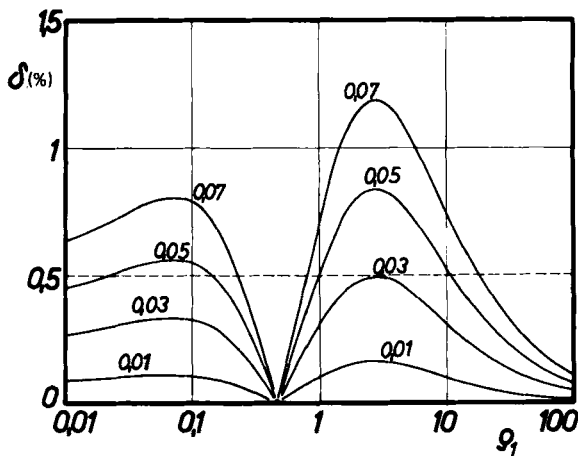


FIG. 1.  $\delta$  error (%) of the  $\eta$  variable in linear Eq. (6) for the conventional erroneous application of the differential copolymerization equation ( $m_1/m_2 = x_0$ ,  $dm_1/dm_2 = y$ ), as a function of  $\rho_1$ . The curves correspond to given conversion values (Method 2 at fixed  $\rho_2 = 0.1$  and  $x_0 = 1.667$  values.)

The error of approximation is zero at any conversion level in case  $\rho_1 = 1 - (1 - \rho_2)/x_0$  (azeotropic copolymerization).

Another presentation of this error is given in Fig. 2. where, up to conversions depicted on the bordering curves, the ranges with  $\delta < 0.5\%$  have been plotted in the plane ( $\rho_1; \rho_2$ ).

It is evident from the above that no maximum conversion value can be given as a criterion of the applicability of approximation by Eq. (12) (Method 2) and that already at so-called "low" conversions (usually 5-10%), the probability of systematic errors well exceeding the accuracy of measurements is rather high.

### Method 3

It is also evident that no significant decrease in error can be obtained by Method 3, which is analogous to approximation by Eq. (12) (see Table 1), where for the previously used value pair  $x_0, y$ , the value pair assigned to identical conversions,  $x, y$  is substituted in Eq. (1). Thus, the fundamental condition of the applicability of the linear parameter determination procedure is to find an approximation considerably better than those above.



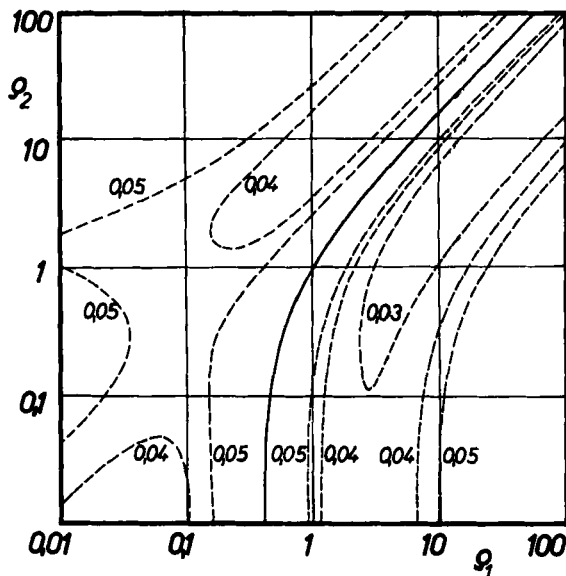


FIG. 2. Copolymerization parameters ( $\rho_1; \rho_2$ ) at given conversion levels resulting in  $\delta = 0.5\%$  relative error, by application of Method 2 ( $x_0 = 1.667$ ).

#### Method 4: The Approximation of Walling and Briggs

Differential equation (1) may also be written as:

$$dm_1/dm_2 = z^*(m_1/m_2) \quad (16)$$

As pointed out by Walling and Briggs [8], if  $z^*$  is constant, with the initial conditions  $t = 0$ ,  $m_1 = m_1^0$ , and  $m_2 = m_2^0$ , we obtain the following simple solution:

$$\log (m_1/m_1^0) = z^* \log (m_2/m_2^0) \quad (17)$$

The assumption of  $z^* = \text{constant}$  and Eq. (17) derived therefrom is strictly valid for any conversion only if  $\rho_1\rho_2 = 1$ . However, a conversion-dependent  $z$  value definable by (17) and calculable from measured data can be introduced:

$$z = \frac{\log (m_1/m_1^0) \quad \log (1 - \zeta_1)}{\log (m_2/m_2^0) \quad \log (1 - \zeta_2)} \quad (18)$$

where  $\zeta_1$  and  $\zeta_2$  are partial conversions of the individual monomers

$$\zeta_2 = w (\mu + x_0)/(\mu + y)$$

and

$$\zeta_1 = (y/x_0)\zeta_2 \quad (19)$$

In these relations,  $w$  denotes weight conversion;  $\mu \equiv \mu_2/\mu_1$  is the relationship between the molecular weights of the two monomers. If the conversion is given on the molar basis ( $\zeta$ ), the above relations substituting  $w = \zeta$  and  $\mu = 1$  have to be applied.

By the use of the conversion-dependent  $z$  value, based on Eq. (16), an approximate  $dm_1/dm_2$  value can be given for any  $x$  value. Thus, e.g., by use of the mole ratio  $x_0$  characterizing the initial composition of the monomer charge,

$$dm_1/dm_2 \approx zx_0 \quad (20)$$

Applicability of this approximation (Method 4, see Table 1) is referred to by Walling and Briggs [8] and Yezrielev et al. [9]. With the approximation of Eq. (20) based on Eq. (3), the  $F$  and  $G$  variables are

$$F = x_0/z$$

and

$$G = (zx_0 - 1)/z \quad (21)$$

and the variables of the linear equation, Eq. (6) are

$$\eta = (zx_0 - 1)/(az + x_0)$$

and

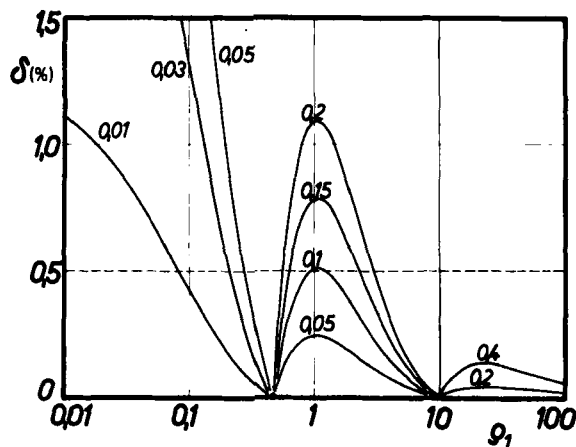


FIG. 3. Relative error  $\delta$  (%) as a function of  $\rho_1$  by application of Method 4 ( $m_1/m_2 = x_0$ ,  $dm_1/dm_2 = zx_0$ ;  $\rho_2 = 0.1$  and  $x_0 = 1.667$ , constants).

$$\xi = x_0/(az + x_0) \quad (22)$$

The error of approximation (20) has been examined in a similar manner as above. Figure 3 depicts the error  $\delta$ , calculated according to Eq. (15) but with application of the expressions (22), against  $\rho_1$ . The  $x_0$  and  $\rho_2$  values are the same as in Fig. 1.

It is apparent that at certain values of  $\rho_1$  the error is actually smaller than obtained by Method 2 illustrated in Fig. 1. With the use of Method 4, in addition to the  $\rho_1$  value corresponding to an azeotropic copolymerization, there is a further  $\rho_1 = 1/\rho_2$  value where  $\delta = 0$  at any conversion level (which corresponds to the case when  $z \equiv z^*$ , i. e., the value is constant irrespective of the conversion); in some ranges, however, the error considerably exceeds the error of the approximation given by Eq. (12). This fact is also supported by comparison of Figs. 2 and 4.

It may be stated that although approximation (20) (Method 4) extends the applicability of linear methods compared to approximation (12) (Method 2), it cannot be considered a generally applicable procedure, as in certain instances it may cause considerable systematic errors at low conversion levels already.

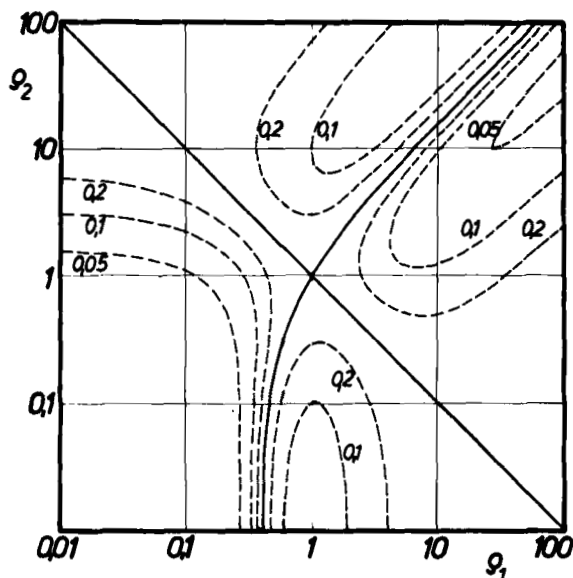


FIG. 4.  $(\rho_1; \rho_2)$  values corresponding to  $\delta = 0.5\%$  relative error (Method 4;  $x_0 = 1.667$ ).

#### Method 5

An analogous procedure is the approximation in which the approximate value

$$dm_1/dm_2 \approx zx \quad (23)$$

and the  $x$  value corresponding to conversion  $\zeta$  is employed to calculate the variables. It is easy to demonstrate that the error of parameter estimation cannot be reduced considerably by this method either.

#### Method 6: Proposed Approximation

In closer investigation of the problem we found that the use of the  $z$  value defined by Eq. (18) affords an approximation significantly better than those obtained by previous procedures. In the course of the

copolymerization the real value  $z^*$  given by Eq. (16) continuously changes, showing greatest deviation from the "average"  $z$  value by Eq. (18) at the terminal points of the  $x_0$ - $x$  range. With a well selected average  $\bar{x}$  value, this approximation must yield results by all means better than obtained with Method 4 by Eq. (20) or with the analogous Method 5 by Eq. (23). The approximate  $dm_1/dm_2$  value belonging to it also corresponds to an average value of the composition of the copolymer formed and can be identical to the experimentally measured  $y$  value (an average value by definition). Thus,

$$y \approx z\bar{x} \quad (24)$$

i. e., the average  $\bar{x}$  value may be defined by the  $y$  and  $z$  values reflecting actual conversion:

$$\bar{x} = y/z \quad (25)$$

Thus, by the approximation suggested by us (Method 6, Table 1), the values of  $F$  and  $G$  by (3) are:

$$F = y/z^2$$

and

$$G = (y - 1)/z \quad (26)$$

and the  $\eta$  and  $\xi$  variables are

$$\eta = z(y - 1)/(az^2 + y)$$

and

$$\xi = y/(az^2 + y) \quad (27)$$

Table 1 offers a comprehensive review of relationships between the different approximations.

Figure 5 clearly shows the relationships between the above systems,

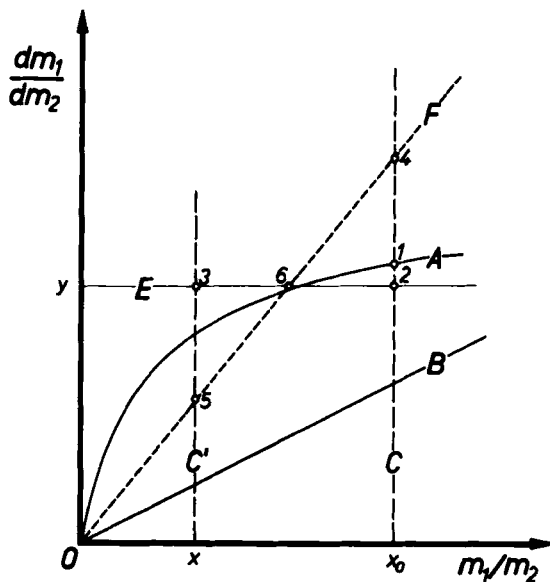


FIG. 5. Pairs of values (points 2-6, numbered corresponding to Table 1) satisfying approximately the differential form of the copolymerization equation (A). Point 1 corresponds to  $(x_0; y_0)$  exactly satisfying the equation. Straight line F corresponds to the relation  $dm_1/dm_2 = z m_1/m_2$  and B to  $dm_1/dm_2 = m_1/m_2$ .

of which, the superiority of the proposed Method 6 described by Eqs. (24)-(27) over the other treatments is immediately evident (see also Fig. 16).

The trend of the error  $\delta$  versus  $\rho_1$  at different constant  $\rho_2$  values [calculated analogously to Eq. (15), but with the use of  $\eta$  and  $\xi$  by Eq. (27)], is presented in Figs. 6-10. Within this series, the value of  $x_0$  is identical and in agreement with that indicated in the case of Fig. 3, while the  $\rho_2$  value corresponds to those only given in Fig. 7. Therefore, only Fig. 7 can serve for direct comparison of the errors of Methods 2 and/or 4 with those given under identical conditions in Figs. 1 and/or 3.

Figure 11, plotting in the plane  $(\rho_1; \rho_2)$  the ranges where the error  $\delta$  does not exceed 0.5% up to conversions depicted on the bordering curves, can be compared with analogous Figs. 2 and/or 4, which have identical  $x_0$  values. The  $x_0$  values of Figs. 12-15 were so chosen that

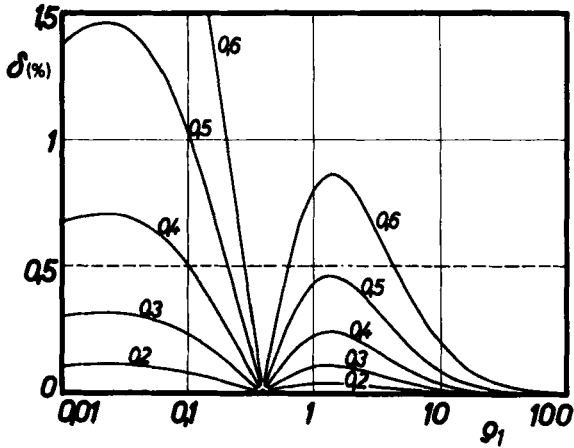


FIG. 6. Relative error  $\delta$  (%) of approximation proposed by us ( $m_1/m_2 = y/z$ ,  $dm_1/dm_2 = y$ ) as a function of  $\rho_1$  at given conversion values (Method 6, at fixed  $\rho_2 = 0.01$  and  $x_0 = 1.667$  values).

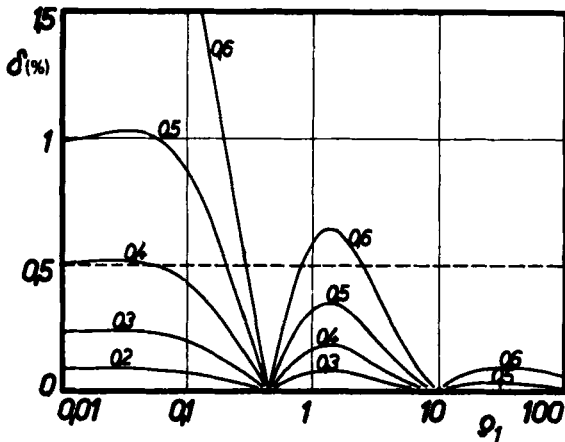


FIG. 7. Relative error  $\delta$  (%) of approximation proposed by us ( $m_1/m_2 = y/z$ ,  $dm_1/dm_2 = y$ ) as a function of  $\rho_1$  at given conversion values (Method 6, at fixed  $\rho_2 = 0.1$  and  $x_0 = 1.667$  values).

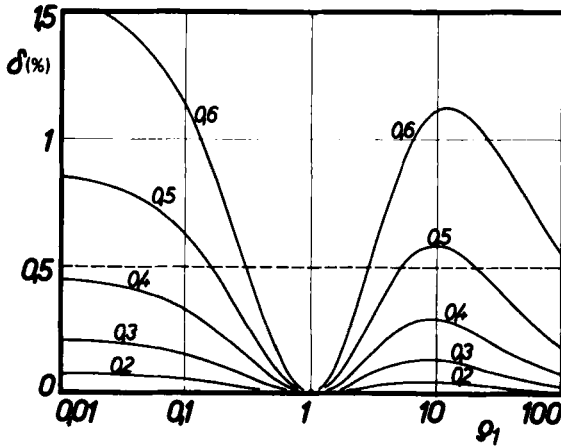


FIG. 8. Relative error  $\delta$  (%) of approximation proposed by us ( $m_1/m_2 = y/z$ ,  $dm_1/dm_2 = y$ ) as a function of  $\rho_1$  at given conversion values (Method 6, at fixed  $\rho_2 = 1$  and  $x_0 = 1.667$  values).

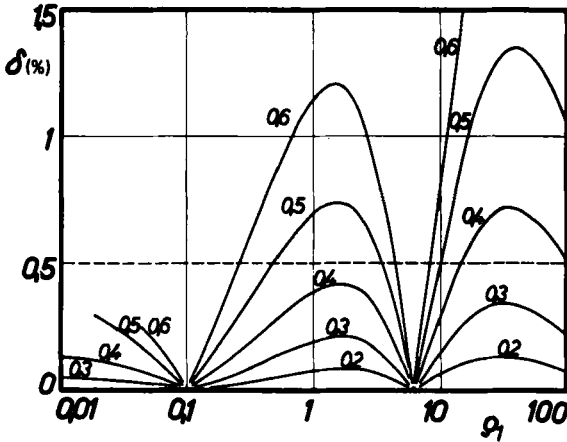


FIG. 9. Relative error  $\delta$  (%) of approximation proposed by us ( $m_1/m_2 = y/z$ ,  $dm_1/dm_2 = y$ ) as a function of  $\rho_1$  at given conversion values (Method 6, at fixed  $\rho_2 = 10$  and  $x_0 = 1.667$  values).



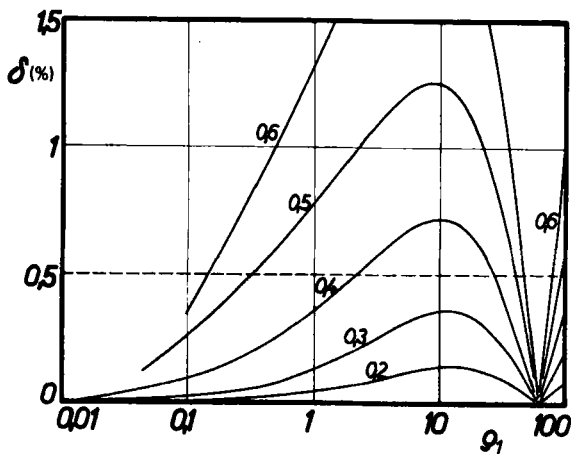


FIG. 10. Relative error  $\delta$  (%) of approximation proposed by us ( $m_1/m_2 = y/z$ ,  $dm_1/dm_2 = y$ ) as a function of  $\rho_1$  at given conversion values (Method 6, at fixed  $\rho_2 = 100$  and  $x_0 = 1.667$  values).

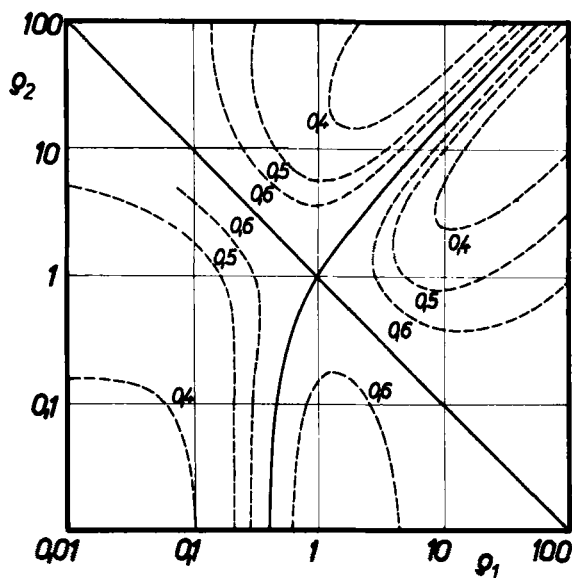


FIG. 11. ( $\rho_1; \rho_2$ ) values resulting in  $\delta = 0.5\%$  relative error by application of our approximation at 0.4-0.6 conversions (Method 6,  $x_0 = 1.667$ ).

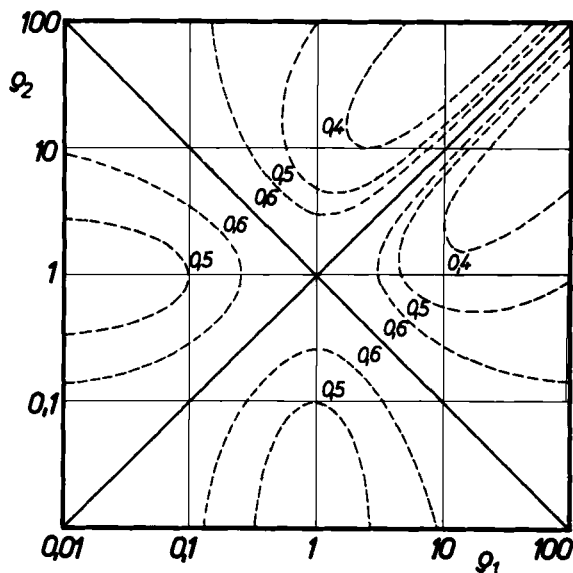


FIG. 12.  $(\rho_1; \rho_2)$  values resulting in  $\delta = 0.5\%$  relative error by application of our approximation at conversion values 0.4-0.6 (Method 6,  $x_0 = 1$ ).

the initial monomer composition should change linearly in terms of mole fraction  $\chi_0 = m_{1,0}/(m_{1,0} + m_{2,0}) = x_0/(1 + x_0)$ . The figures reflected on the diagonal  $\rho_1 = \rho_2$  give the figure corresponding to the initial mole fraction  $1 - \chi_0$  (see also Figs. 11 and 13).

By presentation of these figures, it has been our aim to allow, in case this method is applied, an estimation of the error of approximation for arbitrary  $x_0$ ,  $\zeta$ ,  $\rho_1$ , and  $\rho_2$  values. This is necessitated by the fact that the error, being a function of the above parameters, could be calculated only by complex computer techniques.

Based on Figs. 11-15 it may be established that at conversion levels below 40%, the relative error of approximation will be lower than 0.5% at any  $x_0$  value, in case (1)  $\rho_1\rho_2 < 30$  (which may be justly assumed for any real copolymerization system) and if (2)  $(\rho_1 + \rho_2) > 1$ . The latter condition may appear to be a rigorous limitation; in practice, however, at extreme monomer composition levels where the error might exceed 0.5% in case  $(\rho_1 + \rho_2) < 1$ , 40% conversion could not be easily attained anyhow. The approximation suggested by us (Method 6) is applicable for all real copolymerization systems up to high conversion levels: systematic error of the approximation

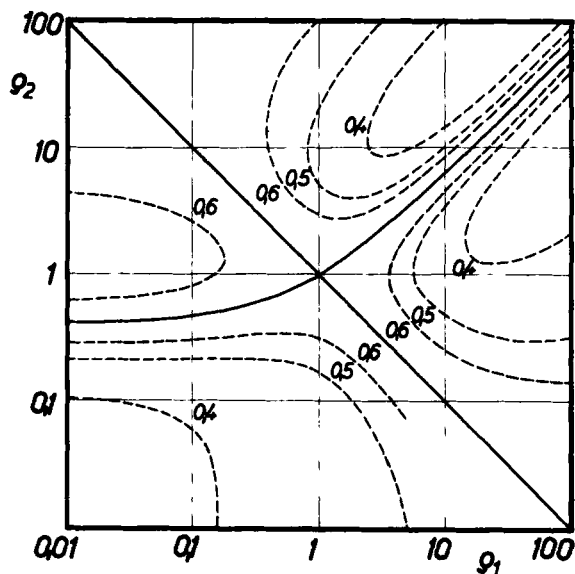


FIG. 13.  $(\rho_1; \rho_2)$  values resulting in  $\delta = 0.5\%$  relative error by application of our approximation at conversion values 0.4-0.6 (Method 6,  $x_0 = 0.6$ ).

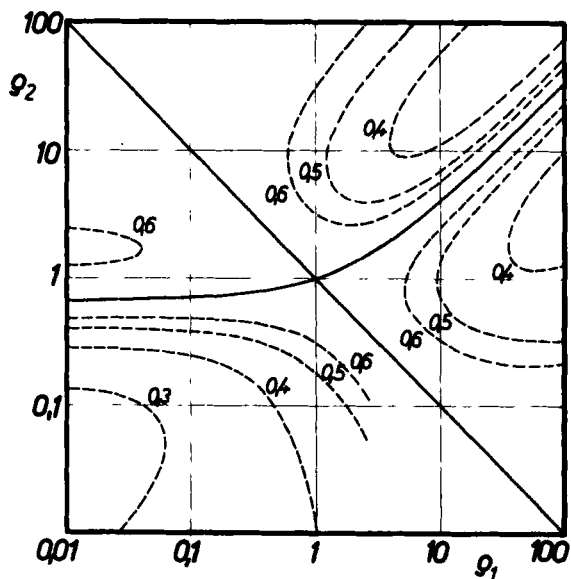


FIG. 14.  $(\rho_1; \rho_2)$  values resulting in  $\delta = 0.5\%$  relative error by application of our approximation at conversion values 0.4-0.6 (Method 6,  $x_0 = 0.333$ ).

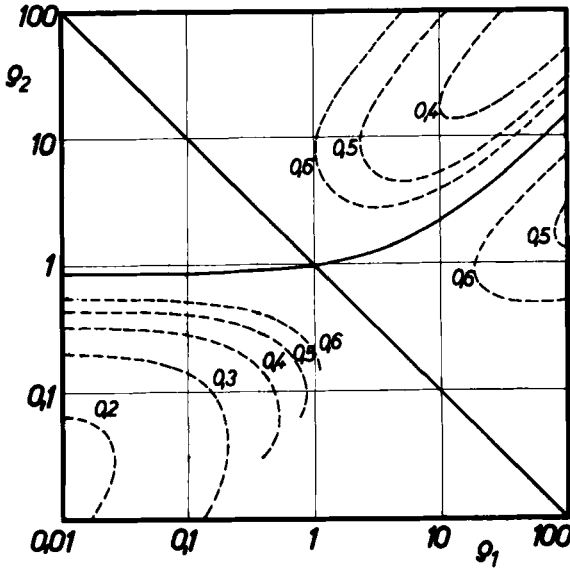


FIG. 15.  $(\rho_1; \rho_2)$  values resulting in  $\delta = 0.5\%$  relative error by application of our approximation at conversion values 0.4-0.6 (Method 6,  $x_0 = 0.1429$ ).

is negligible compared to the probable error of primary measurement data; thus, the reliability of the estimation of parameters  $\rho_1$  and  $\rho_2$  depends entirely on the latter.

It is instructive to examine the relationships of the various approximations on the Fig. 16. The points assigned to the approximations correspond to the numbering of the methods (see Table 1). The "faultless" point corresponding to  $x_0, y_0$  (designated 1) falls on the straight line A given in Eq. (6). Point 2 (corresponding to  $x_0, y$ ) as well as point 4 (derived from  $x_0, zx_0$ ) fall on the straight line C corresponding to identical  $x_0$  values; naturally, the line also crosses point 1. Analogously, by the use of  $x, y$  and  $x, zx$  we obtain points 3 and 5, respectively (the straight line C' indicates points corresponding to identical  $x$  values).

Points 2, 3 and 4, 5 correspond to identical  $y$  and  $z$  values, respectively. The intercept of the ellipse (E) crossing the former and the straight line (F) defined by latter points, yields point 6, corresponding to the proposed approximation, calculated from the value pair  $y/z, y$ . (It should be noted that Fig. 16 is only a  $\xi - \eta$  transformation of Fig. 5.)

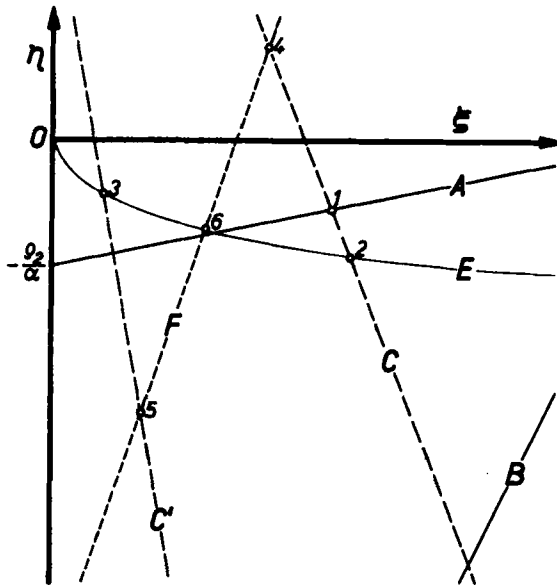


FIG. 16. Approximations of the copolymerization equation (differential form) in the  $\eta$ - $\xi$  coordinate system. Symbols as in Fig. 5.

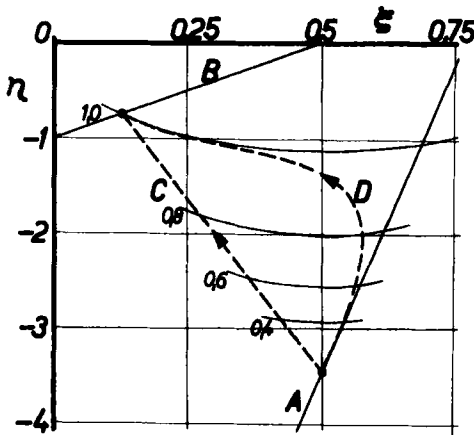


FIG. 17. Deviation of the  $(\eta; \xi)$  point from the line A corresponding to the linearized differential equation, as a function of conversion: (C) Method 2; (D) proposed Method 6,  $x_0 = 0.1429$ ,  $\rho_1 = 3$ ,  $\rho_2 = 10$ .

Figures 17 and 18 show how the point corresponding to the suggested Method 6 is shifted in the  $\xi - \eta$  system of coordinates with the increase of conversion  $\zeta$  (curves D). For reasons of comparison, the section of straight line C, describing the course of the point obtained by use of the generally applied differential equation has been presented (Method 2). (The common starting point of the two different courses is the intercept of A and C corresponding to  $\zeta = 0$  conversion.) The terminal of curve D can be in different positions, corresponding to the different limiting values of  $z$  at complete conversion ( $\zeta = 1, z = z_1$ ). In case  $\rho_1 > 1$  and  $\rho_2 > 1$ , this limiting value is  $z_1 = 1$ , and the terminal of curve D coincides with the end point of section C (Fig. 17), the coordinates of which are  $\xi = x_0/(\alpha + x_0)$  and  $\eta = (x_0 - 1)/(\alpha + x_0)$ . This point falls on the straight line B corresponding to parameters  $\rho_1 = 1$  and  $\rho_2 = 1$ .

In the case of  $\rho_1 < 1$  and  $\rho_2 > 1$  or  $(\rho_1$  and  $\rho_2) < 1$  and if in the latter case  $x_0 < (1 - \rho_2)/(1 - \rho_1)$ , then the limiting value  $z_1 = 1/\rho_2$  and the coordinates of the terminals of curve D are  $\xi = \rho_2^2 x_0/(\alpha + \rho_2^2 x_0)$  and  $\eta = \rho_2(x_0 - 1)/(\alpha + \rho_2^2 x_0)$ . A similar case is illustrated in Fig. 18. In other instances, the terminal is obtained corresponding to the limiting value  $z_1 = \rho_1$ .

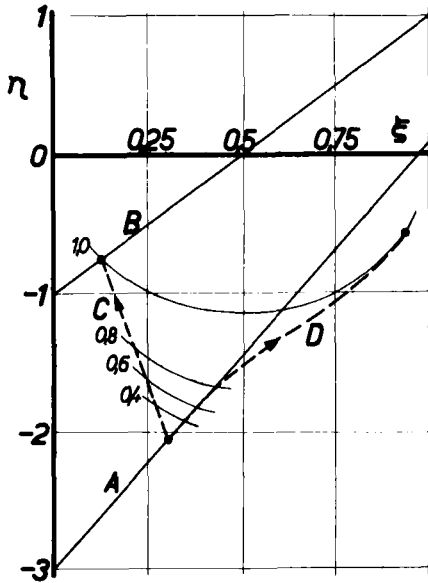


FIG. 18.  $(\eta; \xi)$  values plotted as a function of conversion: (C) Method 2; (D) proposed Method 6,  $x_0 = 0.1429, \rho_1 = 0.1, \rho_2 = 3$ .

TABLE 2. Experimental Data of the Styrene/Methyl Methacrylate/Benzoyl Peroxide (0.1 mole %)/60°C System and Data Calculated therefrom.

$x_0$	$y$	$w$	$z$	$F$	$G$	$\xi$	$\eta$	
1	4.1020	3.3132	0.3560	0.7604	5.7301	3.0421	0.8652	0.4593
2	0.9901	0.9935	0.3080	1.0039	0.9859	-0.0065	0.5245	-0.0034
3	0.2500	0.3673	0.3640	1.6579	0.1336	-0.3816	0.1302	-0.3717
4	3.9020	2.9000	0.3492	0.6832	6.2130	2.7810	0.8744	0.3913
5	1.0080	1.0752	0.3175	1.0819	0.9186	0.0695	0.5072	0.0383
6	0.2343	0.3397	0.3610	1.6267	0.1284	-0.4059	0.1256	-0.3974

<sup>a</sup>Data of Mayo and Lewis [5]; for  $\mu = 0.9613$ ,  $\alpha = 0.8930$ .

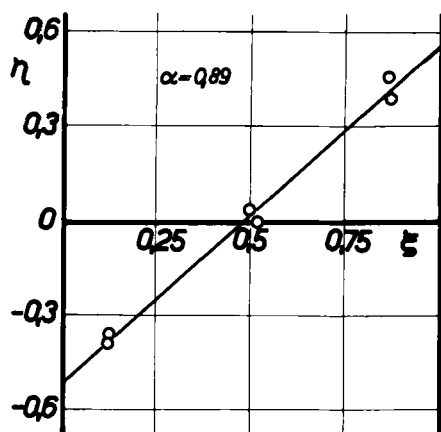


FIG. 19. Experimental data of the system styrene/methyl methacrylate/benzoyl peroxide/60° C [ 5 ], plotted as  $\xi$ - $\eta$  diagram (in terms of Method 6). Copolymerization parameters:  $\rho_1 = 0.559$ ;  $\rho_2 = 0.473$

Although the shapes of the curves D are, depending on the  $\rho_1$ ,  $\rho_2$ , and  $x_0$  values, rather variable, their characteristic feature is that up to high conversion levels, they practically coincide with straight line A, which corresponds to real  $\rho_1$  and  $\rho_2$  values; this section may be considered the range of applicability of the approximation.

In order to illustrate the practical application of the method proposed, we present in our evaluation the experimental data of Mayo and Lewis [ 5 ] for a styrene/methyl methacrylate/benzoyl peroxide (0.1 mole %)/60° C system. The data serving as a basis of calculation, the calculated  $z$  values, and obtained  $\xi$ ,  $\eta$  data ( $\alpha = 0.89$ ) are collected in Table 2.

Graphical evaluation of the data is presented in Fig. 19. The results obtained are  $\rho_1 = 0.559$ ;  $\rho_2 = 0.473$ ; the values determined by the original authors on the basis of the integrated composition equation by the method of intersections are  $\rho_1 = 0.44$ -0.65;  $\rho_2 = 0.41$ -0.64. (Data obtained by the method of intersections are depicted in Table 4).

### Application of the Integral Equation

It is feasible to compare the method of approximation proposed by us and the procedures of parameter determination by the integral



equation of copolymerization. The integral equation is nothing else but the exact solution of differential equation (1), not containing the differential amount  $dm_1/dm_2$  and giving relationships between directly measurable data.

Unfortunately, the solution of the differential equation, Eq. (1) [5] is in implicit expression with respect to parameters and measurable amounts,

$$\log \frac{m_2}{m_2^0} = \frac{\rho_2}{1 - \rho_2} \log \frac{x}{x_0} - \frac{1 - \rho_1 \rho_2}{(1 - \rho_1)(1 - \rho_2)} \log \frac{(\rho_1 - 1)x - (\rho_2 - 1)}{(\rho_1 - 1)x_0 - (\rho_2 - 1)} \quad (28)$$

which is difficult to handle and can be applied for the determination of parameters only by use of nonlinear estimation procedures.

A graphical parameter estimation method is possible if Eq. (28) is written as a system of parametric equations [5, 10]:

$$\rho_2 = \frac{\log \frac{m_2^0}{m_2} - \frac{1}{p} \log \frac{1 - px}{1 - px_0}}{\log \frac{m_1^0}{m_1} + \log \frac{1 - px}{1 - px_0}} \quad (29)$$

$$\rho_1 = 1 - \frac{1}{p} (1 - \rho_2) \quad (30)$$

In this case, for each experimental datum of a chosen set of copolymerization measurements with different  $p$  values the related  $\rho_1$  and  $\rho_2$  values can be calculated and, e. g., relation  $\rho_1 = f(\rho_2)$  can be plotted. The values of copolymerization parameters of the system studied can be estimated based on the intercepts of  $\rho_1 = f(\rho_2)$  curves corresponding to the individual experiments.

The procedure, which requires cumbersome computation, is somewhat simplified by the fact that in the range  $\rho_1 > 0$ ,  $\rho_2 > 0$ , the curves are, in good approximation, linear; therefore it is sufficient to calculate two points for each experimental result, suitably at two negative  $p$  values.

The graphical method can be replaced by a numerical procedure if the parameters of the linear equations (31), approximating the function  $\rho_2 = f(\rho_1)$ , are calculated by the expressions (32):

$$\rho_2 = A \rho_1 - B \quad (31)$$

$$A = \frac{\rho_{21} - \rho_{22}}{\rho_{11} - \rho_{12}}$$

and

$$B = \frac{\rho_{12}\rho_{21} - \rho_{11}\rho_{22}}{\rho_{11} - \rho_{12}} \quad (32)$$

where  $\rho_{11}$  and  $\rho_{21}$  are values calculated by one  $p$  value and  $\rho_{12}$  and  $\rho_{22}$  by the other, according to Eqs. (29) and (30).

Experimental data of the copolymerization system styrene/methyl methacrylate,  $\rho_1$  and  $\rho_2$  values calculated therefrom with parameters  $p = -0.5$  and  $p = -2$  by Eqs. (29) and (30) as well as coefficients  $A$  and  $B$  by Eq. (32) are indicated in Table 3. The last two columns ( $\xi$  and  $\eta$ ) of Table 3 will be referred to later.

The six linear equations corresponding to the number of experimental data afford fifteen "intersects" as presented in Table 4.

As pointed out by Yezrielev et al. [9], with knowledge of  $A$  and  $B$ , the method of intersections can be replaced by the procedure of linearization for the determination of  $\rho_1$  and  $\rho_2$ . The method developed by us [1, 3] can be favorably applied also in this instance. It is obvious from the equivalence of Eqs. (31) and (4), that  $A = F$  and  $B = G$ ; in this way the data can be transformed according to Eqs. (7) and (8) and plotted as  $\eta = f(\xi)$ . The last two columns of Table 3 indicate  $\xi$  and  $\eta$  values ( $\alpha = 0.89$ ) calculated as above. The parameters obtained by graphical evaluation of these data ( $\rho_1 = 0.560$ ,  $\rho_2 = 0.475$ ) are in perfect agreement with the results obtained by the method of approximation (Method 6) proposed by us.

It may be established that calculation of  $A$  and  $B$  and determination of the  $\rho$  values by the above described method is a considerably more laborious treatment than the application of approximation 6, which yields essentially equivalent results. The fact that the procedure is based on the exact integral equation [Eq. (28)] is not very favorable either, since Eq. (31) derived therefrom and applied in the evaluation is only approximately valid! Owing to this, the choice

TABLE 3. Evaluation of the Experimental Data in Table 2 by the Approximate Application of the Integrated Composition Equation<sup>a</sup>

	p = -0.5			p = -2			ξ	η
	ρ <sub>11</sub>	ρ <sub>21</sub>	ρ <sub>12</sub>	ρ <sub>22</sub>	A	B		
1	0.7815	1.4369	0.7292	1.1353	5.7582	3.0634	0.8659	0.4607
2	1.0028	0.9945	1.0055	0.9972	0.9856	-0.0062	0.5250	-0.0033
3	1.2270	0.5461	1.7653	0.6173	0.1323	-0.3837	0.1292	-0.3747
4	0.7036	1.5928	0.6378	1.1811	6.1562	2.8093	0.8752	0.3930
5	1.0516	0.8968	1.1062	0.9469	0.9180	0.0686	0.5072	0.0379
6	1.2187	0.5627	1.7416	0.6292	0.1272	-0.4077	0.1248	-0.4001

<sup>a</sup>For α = 0.8919.

TABLE 4. Copolymerization Constants Given by the Intersections of Linear Equations Determined by A and B Values of Table 3 (Method of Intersection)

		1	2	3	4	5
2	$\rho_1$	0.6432				
	$\rho_2$	0.6401				
3	$\rho_1$	0.6127	0.4425			
	$\rho_2$	0.4648	0.4423			
4	$\rho_1$	-0.5101	0.5342	0.5214		
	$\rho_2$	-6.0006	0.5327	0.4527		
5	$\rho_1$	0.6187	-1.1044	0.5757	0.5134	
	$\rho_2$	0.4994	-1.0823	0.4599	0.4027	
6	$\rho_1$	0.6164	0.4678	4.6402	0.5249	0.6023
	$\rho_2$	0.4861	0.4672	0.9978	0.4745	0.4843

of the value of the  $p$  auxiliary parameters slightly affects the results of the procedure.

As pointed out above, completely correct application of the integral equation is possible only by a nonlinear method. As is well known, nonlinear parameter estimation can be reasonably performed only by means of a computer and, as mentioned earlier, without a comprehensive view, formal application of the nonlinear method may lead to severe conceptual errors. In addition, parameter determination from Eq. (28) may involve other problems as well.

The nonlinear method requires, namely, explicit expression of some measured result (or amount derived therefrom) to construct a minimizable function of error. Such explicit expression can only be given for molar conversion with Eq. (33) obtained by integration of the Skeist equation [11, 12]. This expression may be derived also by transformation of Eq. (28):

$$\zeta = 1 - \left( \frac{\chi}{\chi_0} \right)^{S_1} \left( \frac{1 - \chi}{1 - \chi_0} \right)^{S_2} \left( \frac{\chi_0 - S_4}{\chi - S_4} \right)^{S_3} \quad (33)$$

where  $\chi_0$  and  $\chi$  is the mole fraction of monomer 1 in the monomer mixture at conversion 0 and  $\zeta$  conversion, respectively,  $S_1 = \rho_2/(1 - \rho_2)$ ,  $S_2 = \rho_1/(1 - \rho_1)$ ,  $S_3 = (1 - \rho_1\rho_2)/[(1 - \rho_1)(1 - \rho_2)]$ , and  $S_4 = (1 - \rho_2)/(2 - \rho_1 - \rho_2)$ .

Fitting to  $\zeta$  conversion, is, however, not very favorable in itself; the main difficulty arises, nevertheless, from the fact that at certain  $\rho_1$  and  $\rho_2$  values, Eq. (33) is not defined. Such values are, e. g.,  $\rho_1 = 1$  and  $\rho_2 = 1$ . In the immediate vicinity of these values, application of Eq. (33) is limited by the numerical accuracy of the computers. Similarly, Eq. (33) is not defined if in some experiment  $\chi_0 < S_4 < \chi$  or  $\chi_0 > S_4 > \chi$ . Due to above limitations, application of the gradient and the simplex method involves considerable difficulties.

On the grounds of the above, the treatment suggested by us (Method 6) seems, in spite of its approximative character, to be the most general and reliable method for the determination of copolymerization parameters.

#### REFERENCES

- [1] T. Kelen and F. Tüdös, J. Macromol. Sci.-Chem., **A9**, 1 (1975).
- [2] J. P. Kennedy, T. Kelen, and F. Tüdös, J. Polym. Sci., Polym. Chem. Ed., **13**, 2277 (1975).
- [3] T. Kelen and F. Tüdös, Reaction Kinetics Catalysis Letters, **1**, 487 (1974).
- [4] P. W. Tidwell and G. A. Mortimer, J. Polym. Sci. A, **3**, 369 (1965); J. Macromol. Sci.-Revs., **C4**, 281 (1970).
- [5] F. R. Mayo and F. M. Lewis, J. Amer. Chem. Soc., **66**, 1594 (1944).
- [6] T. Alfrey, Jr., and G. Goldfinger, J. Chem. Phys., **12**, 205 (1944).
- [7] M. Fineman and S. D. Ross, J. Polym. Sci., **5**, 259 (1950).
- [8] C. Walling and E. R. Briggs, J. Amer. Chem. Soc., **67**, 1774 (1945).
- [9] A. I. Yezrielev, E. L. Brokhina, and Ye. S. Roskin, Vysokomol. Soedin., **A11**, 1670 (1969).
- [10] F. R. Mayo and C. Walling, Chem. Revs., **46**, 191 (1950).
- [11] I. Skeist, J. Amer. Chem. Soc., **68**, 1781 (1946).
- [12] V. E. Meyer, J. Polym. Sci. A-1, **4**, 2819 (1966).

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