Polymer Bulletin 2, 71–76 (1980)

Polymer Bulletin

Confidence Intervals for Copolymerization Reactivity Ratios Determined by the Kelen-Tüdös Method

Tibor Kelen, Ferenc Tüdös and Béla Turcsányi

Central Research Institute for Chemistry of the Hungarian Academy of Sciences, Budapest, Hungary

Summary

Calculation method of confidence intervals for copolymerization reactivity ratios determined by the linear Kelen-Tüdős method is described, both for low and high conversions. The intervals as well as the confidence regions were compared with those obtained using non-linear estimation. No considerable deviations were found either in the parameter values or in their errors.

Introduction

In our earlier work (KELEN and TÜDŐS, 1975) we proposed a simple, graphically evaluable linear method for determining reactivity ratios $\underline{r_1}$ and $\underline{r_2}$ of the copolymerization composition equation

$$\frac{dp_1}{dp_2} = \frac{m_1}{m_2}\,\frac{r_1 m_1 + m_2}{r_2 m_2 + m_1} \tag{1}$$

where molar quantities of the components are $\underline{m_1}$ and $\underline{m_2}$ in the monomer mixture, $\underline{p_1}$ and $\underline{p_2}$ in the polymer. According to the method proposed, the following linear equation can be used:

$$\eta = (r_1 + \frac{r_2}{\alpha})\,\xi - \frac{r_2}{\alpha} \equiv r_1 \xi - \frac{r_2}{\alpha}\,(1-\xi) \tag{2}$$

where

$$\eta = \frac{G}{\alpha + F} \qquad \text{and} \qquad \xi = \frac{F}{\alpha + F} \tag{3}$$

which contain $\underline{F}$ and $\underline{G}$ transformed variables:

0170-0839/80/0002/0071/$01.20

$$F = \frac{p_2}{p_1}\left(\frac{m_1^o}{m_2^o}\right)^2 \quad \text{and} \quad G = \frac{p_1-p_2}{p_1}\,\frac{m_1^o}{m_2^o} \tag{4}$$

at low conversions, i.e., when

$$\frac{dp_1}{dp_2} \approx \frac{p_1}{p_2} \quad \text{and} \quad \frac{m_1}{m_2} \approx \frac{m_1^o}{m_2^o} \tag{5}$$

In a later publication (TÜDŐS et al., 1976) we showed that the method, principially applicable only to infinitesimally low conversions, can be extended with very good approximation also for high conversions. In these cases the definitions of F and G are according to Eqs. (6):

$$F = \frac{p_1}{p_2}\left(\log \frac{m_2^o-p_2}{m_2^o} \Big/ \log \frac{m_1^o-p_1}{m_1^o}\right)^2$$

and (6)

$$G = \frac{p_1-p_2}{p_2}\left(\log \frac{m_2^o-p_2}{m_2^o} \Big/ \log \frac{m_1^o-p_1}{m_1^o}\right)$$

It can be shown, that the limiting cases of Eq. (2) for $\alpha \to 0$ and $\alpha \to \infty$ are equivalent to the two forms of the Finemann-Ross equation. Thus, α is a parameter of symmetrization, the optimal value of which for a given series of measurements being

$$\alpha = \sqrt{F_{min} \cdot F_{max}} \tag{7}$$

i.e., the geometric mean of the lowest and highest F values.

The copolymerization reactivity ratios may be determined by using Eq. (2) graphically or by applying a linear least-squares evaluation, i.e., by searching the minimum of the residual sum of squares:

$$S^2 = \sum \left[\eta_i - r_1\xi_i + \frac{r_2}{\alpha}(1-\xi_i)\right]^2 \tag{8}$$

The solution of this linear problem is

$$\begin{aligned} r_1 &= \frac{1}{D}\left[\Sigma\xi_i\eta_i\cdot\Sigma(1-\xi_i)^2 - \Sigma\xi_i(1-\xi_i)\cdot\Sigma(1-\xi_i)\eta_i\right] \\ r_2 &= \frac{\alpha}{D}\left[\Sigma\xi_i\eta_i\cdot\Sigma\xi_i(1-\xi_i) - \Sigma\xi_i^2\cdot\Sigma(1-\xi_i)\eta_i\right] \end{aligned} \tag{9}$$

where D stands for

$$D = \Sigma\xi_i^2\cdot\Sigma(1-\xi_i)^2 - [\Sigma\xi_i(1-\xi_i)]^2 \tag{10}$$

The method described here has found many applications in the literature. We would refer to our work with Kennedy where we made use of the discriminating power of the method: the linearity of the plot made with Eq. (2) rigorously proves the validity of the assumptions implicit in the copolymer composition equation (1). Based on this method cationic reactivity ratios have been critically reexamined (KENNEDY et al., 1975; KELEN et al., 1977). Since this time no method has been published on the determination of the confidence of the parameters; the aim of our present work is to give a short description of the method applied.

Confidence of the Estimated Parameters.

It is well known that the use of least squares estimation is legitimate only in case the errors of the dependent variable are normally distributed and their magnitude is constant. We may assume that in the estimation of copolymerization parameters these demands are satisfactorily fulfilled by choosing the copolymer composition expressed in mole fractions as the dependent variable (BEHNKEN, 1964; TIDWELL and MORTIMER, 1965, 1970). The estimation procedure is then non-linear involving typical difficulties of the method.

According to this, considering the error structure, the application of the least-squares treatment in the Eq. (2) is not strictly correct. On the other hand, linearity is from other aspects so advantageous that its use is justified if the value and accuracy of the parameters satisfactorily agree with those obtained by the non-linear treatment.

The values of the estimated parameters can be directly calculated by Eqs. (9). Similarly, the 100β %

confidence intervals are obtainable by standard methods (see, e.g., BEHNKEN, 1964 or WILKS, 1963):

$$\Delta r_1 = \pm\ t_\beta(n-2)\ \sqrt{\frac{S^2_{min}}{n-2}\ \frac{\Sigma(1-\xi_i)^2}{D}}$$

$$\Delta r_2 = \pm\ \alpha t_\beta(n-2)\ \sqrt{\frac{S^2_{min}}{n-2}\ \frac{\Sigma\xi_i{}^2}{D}} \qquad (11)$$

where S^2_{min} is the minimum value of expression (7), i.e., its value calculated with the parameters estimated by (9), $t_\beta(n-2)$ is the tabulated value of the Student distribution for n data (i.e., n-2 degree of freedom) on the β probability level (see Table I).

TABLE I

Selected values of the Student distribution for β = 0.95 probability level

n	3	4	5	6	7	8	9	10
$t_\beta(n-2)$	12.71	4.30	3.18	2.78	2.57	2.45	2.37	2.31

Reactivity ratios and the corresponding 95 % confidence intervals were determined for a large number of real copolymerization systems by the linear method described above. For these systems we calculated also the 95 % joint confidence regions with the algorithm described in the literature (e.g., BEHNKEN, 1964), using Eq. (7) in the contour equation.

The results were compared with the respective values of non-linear calculations. It has been established that there is no significant deviation between the results obtained by these methods: both the joint confidence regions (error ellipses) and the rectangles corresponding to the confidence intervals are greatly overlapping. Typical examples are shown in Figs. 1. and 2.

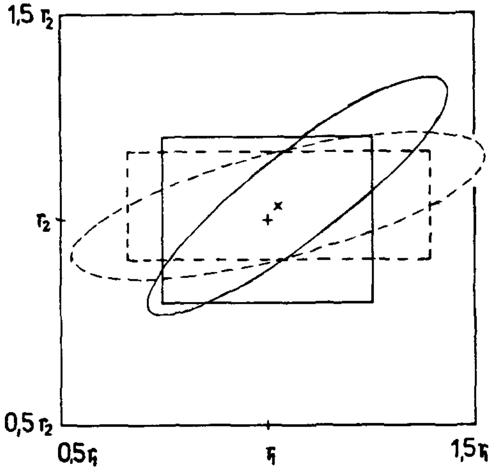

Figure 1. Confidence intervals (rectangles) and joint confidence regions (ellipses) corresponding to the non-linear least-squares (full line) and to the Kelen-Tüdős (dotted line) methods. System: styrene/indene/$TiCl_4/CH_2Cl_2$ (ANTON and MARÉCHAL, 1971). Scaling according to the non-linear estimation: $r_1 = 0.633 \pm 0.161$, $r_2 = 4.461 \pm 0.903$; the KT-values: $r_1 = 0.650 \pm 0.231$, $r_2 = 4.610 \pm 0.584$.

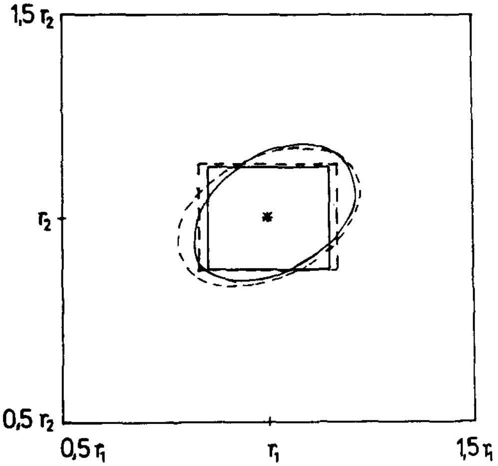

Figure 2. See Fig. 1. System: styrene/methyl methacrylate/benzoyl peroxide/60°C (WILEY and SALE, 1960). Scaling according to the non-linear estimation: $r_1 = 0.471 \pm 0.069$, $r_2 = 0.462 \pm 0.058$; the KT-values: $\dot{r}_1 = 0.471 \pm 0.079$, $r_2 = 0.464 \pm 0.059$.

We compared also the estimated parameters, confidence intervals and joint confidence regions obtained by the two methods for a number of "synthetic" data series i.e., when calculated copolymer composition values were modified by normally distributed random error. No marked deviation could be observed either in the parameters or their confidence interval.

References

ANTON, A. and MARÉCHAL, E.: Bull. Soc. Chim. Fr. 1971, 3753

BEHNKEN, D.W.: J. Polym. Sci. A2, 645 (1964)

KELEN, T. and TÜDŐS, F.: J. Macromol. Sci.-Chem. A9, 1 (1975)

KELEN, T., TÜDŐS, F., TURCSÁNYI, B. and KENNEDY, J.P.: J. Polym. Sci., Polym. Chem. Ed. 15, 3047 (1977)

KENNEDY, J.P., KELEN, T. and TÜDŐS, F.: J. Polym. Sci., Polym. Chem. Ed. 13, 2277 (1975)

TIDWELL, P.W. and MORTIMER, G.A.: J. Polym. Sci. A3, 369 (1965)

TIDWELL, P.W. and MORTIMER, G.A.: J. Macromol. Sci.-Revs. Macromol. Chem. C4, 281 (1970)

TÜDŐS, F., KELEN, T., FÖLDES-BEREZSNICH, T. and TURCSÁNYI, B.: J. Macromol. Sci.- Chem. A10, 1513 (1976)

WILEY, R.H. and SALE, E.E.: J. Polym. Sci. 42, 479 (1960)

WILKS, S.S.: Mathematical Statistics, Wiley, New York, London, 1963

Received November 15, 1979