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Determination of Reactivity Ratios in Radical Copolymerization: A Comparison of Methods for a Methacrylate/*N*-Vinylpyrrolidone System

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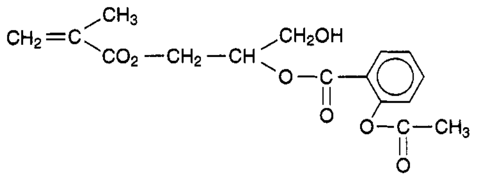
ABSTRACT: To determine the reactivity ratios in the radical copolymerization of the reaction product of acetylsalicylic acid with 2,3-epoxypropyl methacrylate and *N*-vinylpyrrolidone, all available methods are used and compared. Using as criteria the accuracy of the confidence interval and the impossibility of obtaining in any case negative values for a reactivity ratio, the Tidwell−Mortimer method is recommended.

Introduction

To prepare water-soluble polymeric derivatives of acetylsalicyclic acid (ASA), we copolymerize a methacrylate containing an ASA moiety with *N*-vinylpyrrolidone (NVP). The synthesis and the characterization of the methacrylate **1** obtained by reacting 2,3-epoxypropyl methacrylate with ASA will be described elsewhere. To control the copolymer composition, it is first necessary, to know the reactivity ratios r_1 of monomer **1** (methacrylate) and r_2 of monomer **2** (NVP).



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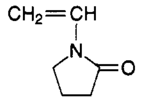

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The determination of r_1 and r_2 gives us the opportunity to compare the different evaluation methods, which are based on the analysis of reactants or copolymer at the beginning of the reaction.

Experimental Section

NVP is distilled under nitrogen before use, and concentrations of methacrylate **1** are (2−3) × 10^{-3} mol·L^{-1}. Initiator concentration is 1% of the total concentration of both monomers.

The copolymerization reactions are carried out in acetonitrile at 80 °C in the presence of azobis(isobutyronitrile) (AIBN) as initiator. Each solution is prepared with a given molar fraction f_1 of monomer **1**, and equal volumes are placed in several (10−15) sealed tubes. The tubes are put in an oil bath at 80 °C and stirred magnetically. Every 2 or 3 min, a tube is taken out of the bath and rapidly cooled. A given quantity of chlorobenzene is then added as an internal standard, and the solution is analyzed using high−pressure liquid chromatography (standard C_{18} column; eluant: acetonitrile). The consumption curves of each monomer are plotted, and the molar fraction F_1 of monomer **1** in the copolymer at the beginning of the reaction is calculated from the slopes of the curves at the origin of time.

Table 1. Experimental Results: Molar Fractions of Monomer 1 in the Feed f_1 and in the Copolymer F_1

f_1	F_1
0.10	0.219
0.30	0.452
0.50	0.514
0.70	0.762
0.90	0.901

Five different compositions of the feed solution are studied, regularly chosen over the whole range of variation of f_1.

Results and Calculation

The experimental results are given in Table 1. Despite the extent of the experimental error in F_1, three significant digits (as written in Table 1) are taken into account for the calculations.

The methods to determine the reactivity ratios from experimental results can be separated into four groups.[1]

(i) The approximate methods constitute the first group. They will not be used here because, as they are based on approximate kinetic equations or approximate calculations, they are expected to give biased values of r_1 and r_2.

(ii) The second group includes the straight-line intersection methods. The Mayo−Lewis method is the oldest one.[2] However, it difficult to apply, because the values of r_1 and r_2 can be given by each of the $n(n - 1)/2$ intersections (10 in our case) of the n (5 in our case) straight lines plotted from the n experimental couples of values. Lewis and Mayo do not indicate any particular means to choose between these numerous possibilities. Fortunately, Joshi and Kapur[3] and subsequently Joshi and Joshi[4] proposed two different ways to find the most representative intersection point. The Joshi−Kapur (JK) method takes into account all the interaction points between any couple of straight lines. Each point is weighted by multiplying r_1 and r_2 values by the tangent value of the angles of both lines (the lines are more clear-cut when the angle is near a right angle than when it is close to zero). Then the most probable values of r_1 and r_2 are the average values of all the weighted intersections. The calculation of the confidence interval in the Joshi−Kapur method will be discussed in a forthcoming paper. The Joshi−Joshi (JJ) method chooses

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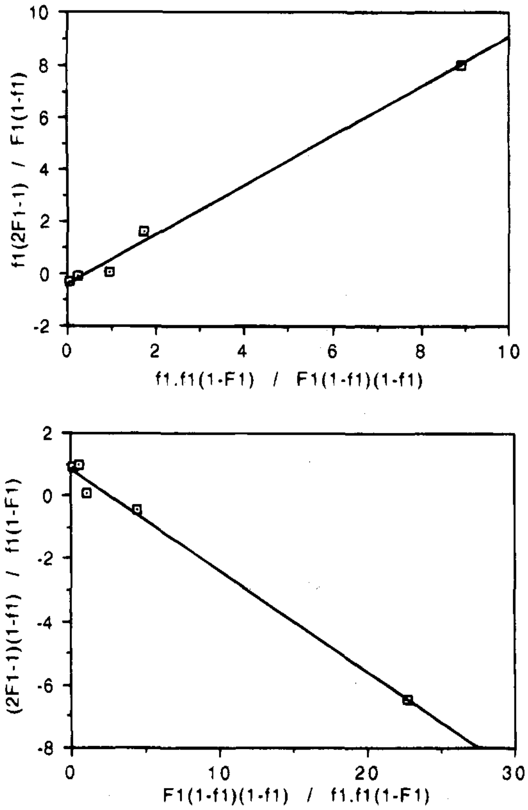

Figure 1. (a, Top) Fineman–Ross (FR1) plot. (b, Bottom) Fineman–Ross (FR2) plot.

as the best point that for which the sum of orthogonal distances to all lines is minimal. The confidence intervals are calculated according to the authors.

(iii) The third group is the linearization methods. The oldest and most famous one is due to Fineman and Ross.[5] In reality, it is a double method. On one hand, it is possible to plot $f_1(2F_1 - 1)/(1 - f_1)F_1$ versus $f_1{}^2(1 - F_1)/(1 - f_2)^2F_1$, and then r_1 is the slope of the straight line and $-r_2$ the intercept (FR1); on the other hand, if $(2F_1 - 1)(1 - f_1)/(1 - F_1)f_1$ is plotted versus $(1 - f_1)^2F_1/(1 - F_1)f_1{}^2$, the slope is $-r_2$ and the intercept r_1 (FR2). The obtained values of r_1 and r_2 using FR1 and FR2 are generally different. The confidence intervals are calculated according to the usual statistical least-squares method for linear regression.

The less known Tosi[6] method derives from the Fineman–Ross method. FR1 is used to determine r_1 and FR2 to determine r_2. The least-squares method is replaced by the method of grouping to plot the straight lines. The Tosi (T) method does not allow one to calculate any confidence interval. Another famous linearization method is due to Kelen and Tudos.[7] As shown in Figure 1, in the Fineman–Ross method, the experimental points are badly distributed over the range of variation of the abscissa: one point is generally isolated. Kelen and Tudos (KT) use a change of variables to obtain a better distribution of the points over the range of variation of the abscissa. Let G and F represent the ordinate and abscissa, respectively, in the FR1 method; the Kelen–Tudos variables are then defined as

$$\eta = \frac{G}{\alpha + F}$$

$$\xi = \frac{F}{\alpha + F}$$

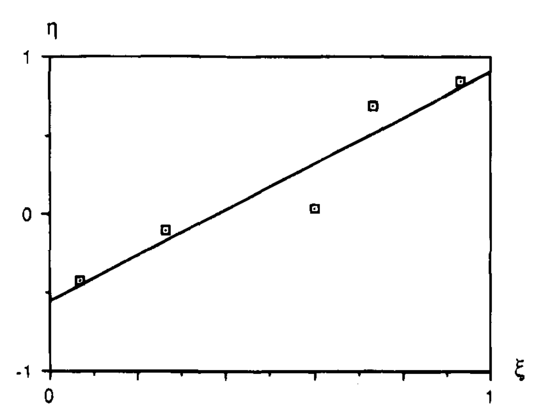

Figure 2. Kelen–Tudos plot.

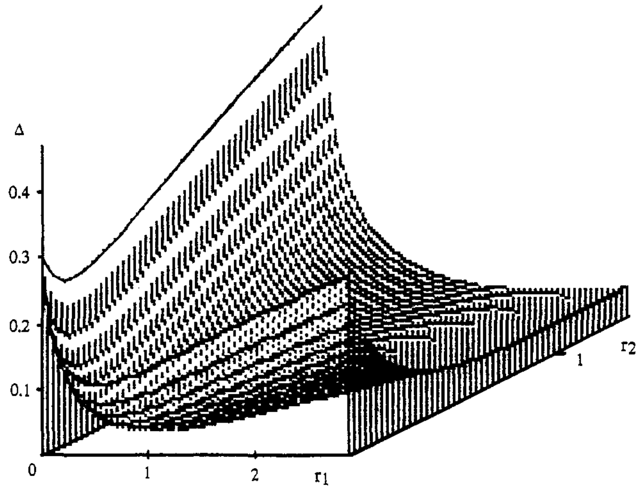

Figure 3. Sum of squared residuals Δ versus r_1 and r_2.

where α is an undetermined constant. The value $\alpha = (F_MF_m)^{1/2}$ (where F_M and F_m are the highest and the lowest values of F, respectively) leads to a better distribution of the experimental points in the range of variation of ξ, which is 0 ($F = 0$) to 1 ($F = \infty$) (Figure 2). Thus, r_1 is the value of η when $\xi = 1$, and the intercept of the straight line $\eta = f(\xi)$ gives $-r_2/\alpha$. The straight line is calculated according to the least-squares technique, as well as the confidence intervals.[8] One can notice that it is possible to calculate r_1 and r_2 in a similar manner from FR2 coordinates; $-r_2$ is then obtained for $\xi = 1$, and their intercept gives r_1/α. The values of r_1 and r_2 obtained are the same in both cases.

In the Fineman–Ross methods, the reactivity ratios are calculated from the slope and from a singular point (the intercept) in a straight line. In the Kelen–Tudos method, they are obtained from two singular points of a regression line.

In the linearization method of Yezreliev, Brokhina, and Roskin (YBR),[9] r_1 and r_2 appear to be the coefficients of the equation $y = r_1x_1 - r_2x_2$, where y is equal to $[F_1/(1 - F_1)]^{1/2} - [(1 - F_1)/F_1]^{1/2}$ and x_1 and x_2 are the square roots of the abscissas in the FR1 and FR2 methods, respectively. r_1 and r_2 as well as the confidence intervals are calculated according to the least-squares technique.

(iv) The fourth and last group of the methods for determining the reactivity ratios is curve fitting. These methods consist in fitting the copolymerization distribution curve with the experimental points. Alfrey, Bohrer, and Mark[10] originally presented this method. We have described the Alfrey–Bohrer–Mark (ABM) approach in a previous paper.[1] Figure 3 shows the surface of

Table 2. Calculated Values of r_1 (Methacrylate) and r_2 (NVP)

method	r_1	r_2
Joshi–Kapur (JK)	0.94 ± 1.01	0.364 ± 0.347
Joshi–Joshi (JJ)	0.92 ± 0.46	0.375 ± 0.432
Fineman–Ross		
FR1	0.945 ± 0.180	0.373 ± 0.743
FR2	0.87 ± 0.69	0.323 ± 0.067
Tosi (T)	0.97	0.329
Kelen–Tudos (KT)	0.90 ± 0.52	0.342 ± 0.345
Yezreliev–Brokhina–Roskin (YBR)	0.93 ± 0.33	0.332 ± 0.206
Alfrey–Bohrer–Mark (ABM)	0.85	0.340
Tidwell–Mortimer (TM)	0.85[a]	0.340[a]
Braun–Brendlein–Mott (BBM)	0.77	0.294

[a] The joint confidence interval for r_1 and r_2 is shown on Figure 4.

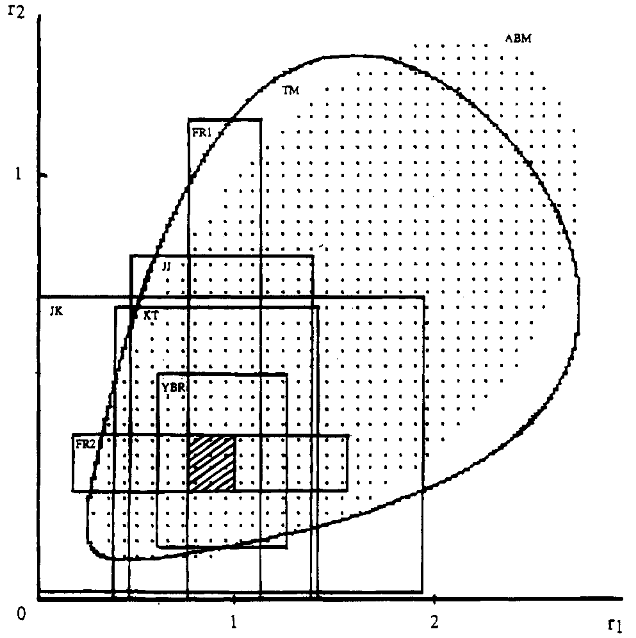

Figure 4. Confidence intervals given by each method (for abbreviations, see Table 2).

variation of the sum Δ of the squared residuals versus r_1 and r_2.

Using the nonlinear least-squares technique of Behnken,[11] Tidwell and Mortimer[12] calculate more easily and more quickly the values of r_1 and r_2 which minimize Δ. Moreover, the Tidwell–Mortimer (TM) method allows one to determine the joint confidence interval for r_1 and r_2 for a given probability (generally 95%) from experimental data, on an accurate statistical basis.

According to remarks by Alfrey, Bohrer, and Mark, who noticed that the lowest values of f_1 are more representative of r_2 and the highest ones of r_1, Braun, Brendlein, and Mott[13] separate the experimental points into two groups (f_1 less than or more than 0.5) and use an iteration technique on r_1 and r_2 to minimize the mean residuals in both groups. The Braun–Brendlein–Mott (BBM) method is not fitted to give confidence interval.

The values of r_1 and r_2 determined by each method are tabulated in Table 2. The confidence intervals calculated by each method are shown in Figure 4. For the ABM method in this last figure, the points cover the surface for which Δ is less than 6.5 times the minimum value of Δ. The hatched part of Figure 4 is expanded in Figure 5 to show the mean values of r_1 and r_2 gathered in Table 2.

Comments and Discussion

From Figures 4 and 5 the general problems encountered in determining reactivity ratios are evidenced: the pairs of values of r_1 and r_2 are rather close, but the confidence intervals are very different. From a statistical point of view, the Behnken–Tidwell–Mortimer joint confidence interval is the only correct one. In least-squares methods, indeed, the usual calculation is valid only if the abscissa and ordinate are independent and if abscissas are not random variables. This is obviously not the case in any linearization method. The same is true also for the confidence intervals arising from intersection methods. As we already observed,[1] the level curves of the ABM surface (Figure 3) are similar to the joint confidence interval of Tidwell and Mortimer (Figure 4).

Some comments can be added about the Fineman–Ross method. As can be observed in Figure 1, in most cases, the Fineman–Ross straight line is plotted from several points gathered closely and an isolated point. This last point corresponds to the highest value of f_1 in the FR1 method and to the lowest one in the FR2 method. This point appears to be very important for the determination of the slope of the straight line (r_1 for FR1, $-r_2$ for FR2). Then, since high f_1 values are more representative of r_1 values and low ones of r_2

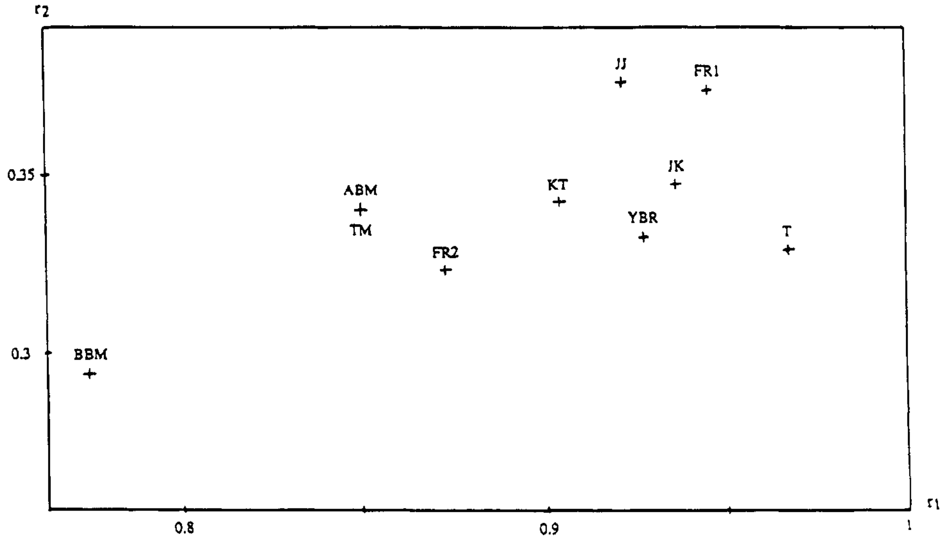

Figure 5. Expansion of the hatched part of Figure 4: mean values of r_1 and r_2 calculated from each method.

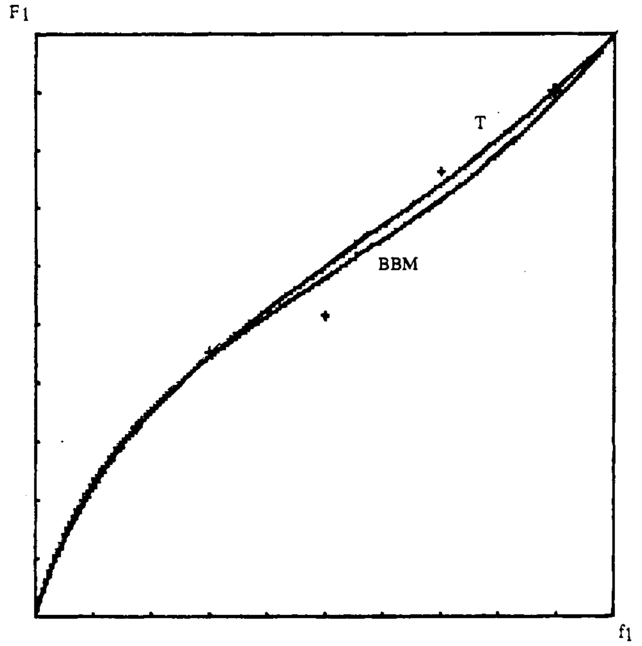

Figure 6. Distribution curves graphed for $r_1 = 0.77/r_2 = 0.294$ (Braun–Brendlein–Mott) and $r_1 = 0.97/r_2 = 0.329$ (Tosi).

values,[10,13] the FR1 method would be more accurate for determining r_1 and the FR2 method for calculating r_2. Moreover, in the least-squares regression method, the calculated confidence intervals are generally smaller for the slope than for the intercept. Thus, for the Fineman–Ross method, FR1 would be used to determine r_1 and FR2 to determine r_2. Tosi[6] and Chang, Miwa, and Tallent[14] did so without further explanation.

In this "brief survey of methods of calculating monomer reactivity ratios", Joshi[15] showed that in some cases the Yezreliev–Brokhina–Roskin method can be promoted because it leads to a best distribution of the experimental points around the determined distribution curve. However, all the linearization methods as well as all the intersection methods may give aberrant negative values of reactivity ratios. Then, despite many authors' habits, we agree with McFarlane, Reilly, and O'Driscoll[16] that the method best suited to calculate reactivity ratios with valid confidence intervals from the differential equation is that of Tidwell and Mortimer.

Finally, we would like to look at the actual differences between the proposed methods. Figure 6 shows the distribution curves graphed with the most different sets of values of r_1 and r_2 obtained, in our case, from the Braun–Brendlein–Mott and Tosi methods. It can be seen that both curves are very close, but one can imagine what would happen if one would compare between two extreme points of the Tidwell–Mortimer joint confidence interval, which is representative of the possible values of r_1, r_2 pairs with a 95% probability level.

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References and Notes

(1) Bauduin, G.; Boutevin, B.; Belbachir, M.; Meghabar, R. *Makromol. Chem.* **1990**, *191*, 2767.
(2) Mayo, F. R.; Lewis, F. M. *J. Am. Chem. Soc.* **1944**, *66*, 1594.
(3) Joshi, R. M.; Kapur, L. *J. Polym. Sci.* **1954**, *A1* (14), 508.
(4) Joshi, R. M.; Joshi, S. G. *J. Makromol. Sci., Chem.* **1971**, *A5* (8), 1329.
(5) Fineman, M.; Ross, S. D. *J. Polym. Sci.* **1950**, *5*(2), 259.
(6) Tosi, C. *Eur. Polym. J.* **1973**, *9*, 357.
(7) Tudos, F.; Kelen, T. *React. Kinet. Catal. Lett.* **1974**, *1* (4), 487.
(8) Kelen, T.; Tudos, F.; Turcsanyi, B. *Polym. Bull.* **1980**, *2*, 71.
(9) Yezreliev, A. I.; Brokhina, E. L.; Roskin, Ye. S. *Polym. Sci. USSR* (*Engl. Transl.*) **1969**, *11* (8), 1894.
(10) Alfrey, T.; Bohrer, J.-J.; Mark, H. *Copolymerization*; Interscience: New York, 1952; p 23.
(11) Behnken, D. W. *J. Polym. Sci.* **1964**, *A2*, 645.
(12) Tidwell, W. P.; Mortimer, G. A. *J. Polym. Sci.* **1965**, *A3*, 369.
(13) Braun, D.; Brendlein, W.; Mott, G. *Eur. Polym. J.* **1973**, *9*, 1007.
(14) Chang, S.-P.; Miwa, T. K.; Tallent, W. H. *J. Polym. Sci.* **1969**, *A1* (7), 471.
(15) Joshi, R. M. *J. Macromol. Sci., Chem.* **1973**, *A7* (6), 1231.
(16) McFarlane, R. C.; Reilly, M. P.; O'Driscoll, K. F. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 251.

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