

Computer Calculation of Reactivity Ratios from the Integrated Form of the Copolymer Equation

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A computer programme has been devised to solve the copolymer composition equation in its integrated form (necessary when large differences in monomer reactivity cause considerable 'drift' in monomer composition). It uses the well-known 'method of intersections' and the averaging calculation of Joshi and Kapur. It accepts the experimental data in their most direct form and yields weighted average values of the reactivity ratios (i.e. values which are weighted against the undue influence of extreme solutions). It can give the computed intersection plot directly on the line printer.

THE calculation of monomer reactivity ratios from the copolymer composition is simple when the differential form of the equation can be used. This, however, is not possible when the monomers differ very considerably in reactivity, since appreciable drifts 'occur' in the relative concentrations even when the reactions are restricted to low conversions. Examples can be seen in the systems studied in the previous paper¹.

The best known procedure for solution of the integrated equation is Mayo and Lewis's 'Method of intersections'². It is, however, laborious, as the values of the parameter p (see later) must be chosen by trial and error. It also needs an objective method of averaging the 'solutions'. This last point can be very important, since by the nature of the method some of the solutions are necessarily of low reliability (intersections of lines crossing at small angles). Because the method is essentially the solution of simultaneous equations from pairs of experiments, the number of solutions is $n(n-1)/2$ for each n experiments and it soon becomes impracticable by 'hand calculation' to extract the full potential information from the results. Repetition of the full calculation to study the effects of possible systematic errors in the experimental methods becomes virtually impossible.

While the present computer calculation was under development another method was described by Montgomery and co-workers³. Its procedure is different in a number of respects and it does not include an averaging stage.

COMPUTER PROGRAMME

The programme is written in Fortran IV (and has been run on an IBM 1130 computer). It contains about 400 statements and can be obtained by application to the first named author, together with a commentary that also indicates a number of ways in which it may be modified and developed. Its procedures are indicated in outline in the following summary.

STAGES IN THE CALCULATION

The Mayo-Lewis equation to be solved relates the reactivity ratios (r_1, r_2) to the initial and final monomer concentrations via the parameter $p = (1 - r_1)/(1 - r_2)$ as follows

$$r_2 = \frac{\log [M_1^0]/[M_1] - 1/p \log A}{\log [M_2^0]/[M_2] + \log A}$$

where

$$A = \frac{1 - p [M_1]/[M_2]}{1 - p [M_1^0]/[M_2^0]}$$

The principal stages in the calculation are as follows.

(1) Approximate values of r_1 and r_2 are calculated by the 'slope and intercept' method of Fineman and Ross⁴, using an empirical correction for monomer drift.

(2) The p values are ranged to obtain a suitable set of conjugate r_1 and r_2 values for each set of experimental data, i.e. which give a straight line in the positive quadrant. Two special parameters and appropriate limits are needed; these are calculated from the result of (1) or can be separately inserted.

(3) The best r.m.s. straight lines are calculated, together with their intersections which are printed out. Far outlying intersections are rejected by imposing limits on acceptable values of r_1 and r_2 .

(4) The weighted average values \bar{r}_1 and \bar{r}_2 are calculated by the method of Joshi and Kapur⁵, i.e.

$$\bar{r}_1 = \Sigma r_1 \tan \theta / \Sigma \tan \theta$$

where θ is the angle between lines.

(5) The deviation is calculated for each value of \bar{r} . This is defined as

$$D = ([(r - \bar{r}) \times FAC]^2 / TL)^{\frac{1}{2}}$$

where

$$FAC = (\tan \theta / \Sigma \tan \theta)$$

and

$$TL = \text{No. of intersections.}$$

(6) Mean values and deviations are printed out.

(7) The familiar intersection plot is printed out (on the line printer).

TESTS OF THE PROGRAMME

Experience has been gained mainly with the results of cationic copolymerizations where large differences in reactivity ratios of different monomers are encountered (see previous paper¹). It is found that the calculation copes well with the particular difficulties of the method in such circumstances, e.g. avoiding the choice of unsuitable p values which make the calculation impossible. It provides well spaced and usually linearly related conjugate values of r_1 and r_2 and enables the reliability of any given line to be estimated by its deviation from the best r.m.s. line. The number of points on the line may be conveniently made as high as 15, which would be extremely laborious by hand. The facility for recalculation to allow for possible

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experimental error provides a reminder of how sensitive to such errors the derived results can be.

In addition the programme has been used with some of Mayo and Lewis's original data for the free radical copolymerization of styrene and methyl methacrylate². Here the reactivity ratios are both less than unity and different problems arise in the choice of suitable p values and limits. The set of results chosen for recalculation are those designated 2a-2f in the original paper. They are given as 1-6 here.

PARAMETERS USED IN CALCULATION

$TP=0.1$	Initial value of p —the only value required.
$TPH=0.05$	Increment on p . Neither value is critical—the magnitude of the expected result is a sufficient guide for choice.
$N=8$	Number of points per line. The maximum possible is 15.
$TRIM=TR2M=0$ $TRIA=TR2A=0.95$	Minimum and maximum acceptable conjugate values of r .
$TOL=0.1$ $TMAX=0.15$	The spacing of points on all lines is set in terms of these parameters which are the minimum and maximum values of Δr_1 considered suitable for a hypothetical line parallel to the r_1 axis.
$RIL=R2L=0$ $REX1=REX2=5$	Minimum and maximum acceptable values of r for solutions to equations.

Results. The numbers in parentheses refer to the stages described previously.

- (1) Approximate value of $r_1=0.56$
Approximate value of $r_2=0.47$

The close agreement between these values and the final averages is unusually good.

- (2) Sets of values of p , r_1 and r_2 are given for two lines by way of illustration.

Line (1)

p	0.499, 0.549, 0.599, 0.674, 0.774, 0.924, 1.174, 1.574
r_1	0.547, 0.568, 0.584, 0.602, 0.619, 0.636, 0.654, 0.668
r_2	0.095, 0.215, 0.307, 0.411, 0.509, 0.607, 0.705, 0.789

Line (5)

p	0.299, 0.499, 0.624, 0.699, 0.762, 0.812, 0.843, 0.868
r_1	0.938, 0.863, 0.782, 0.709, 0.622, 0.523, 0.441, 0.358
r_2	0.796, 0.726, 0.652, 0.584, 0.504, 0.413, 0.338, 0.261

The initial value of $p=0.1$ does not give a value of r within the set limits for either line. Had a limit been reached before the required number of points had been obtained, the sign of the increment would have been reversed. It may be seen that it is necessary to obtain points at unequal intervals of p in order to maintain a regular spacing.

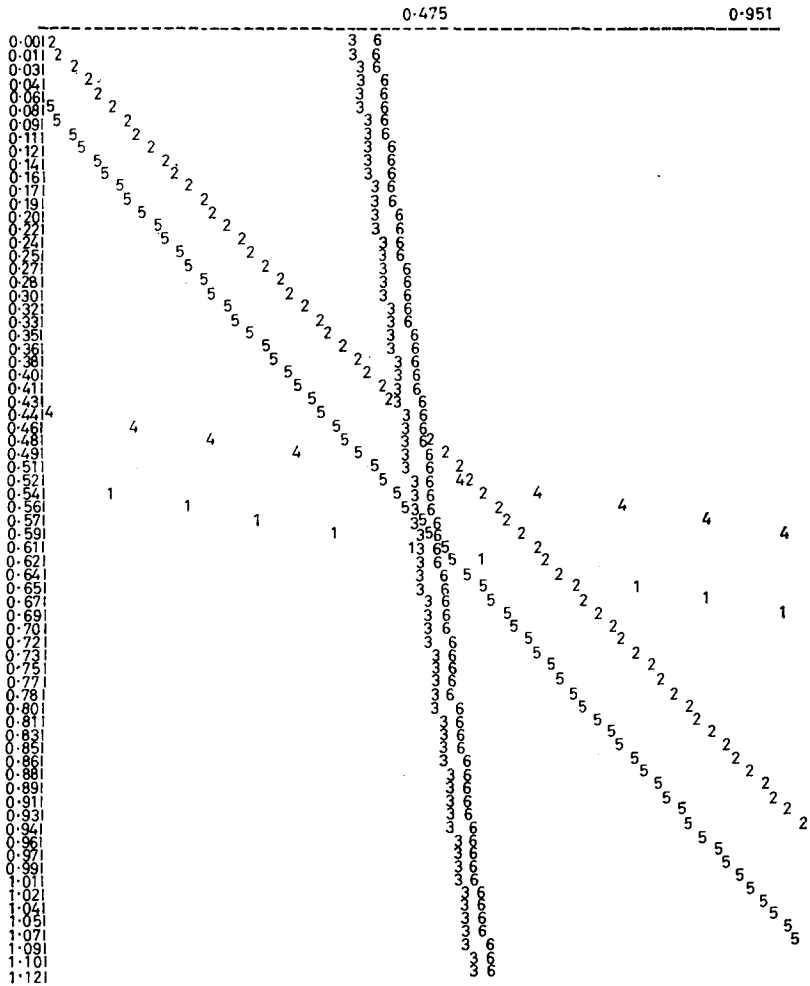


Figure 1—Typical intersection plot

(3) The printout of the individual solutions takes the form shown below. Most of the values have been omitted.

<i>L</i>	<i>I</i>	<i>J</i>	<i>r</i> ₁	<i>r</i> ₂	tan <i>θ</i>
1	1	2	0.642	0.638	0.715
2	1	3	0.611	0.464	3.18
†3	1	4			

 *12 3 6 4.990 1.046 0.005

†Denotes intersection below lower limit.

*Denotes 'bad' intersection.

(6) Mean values and deviations

$$\bar{r}_1 = 0.562 \pm 0.02 \quad \bar{r}_2 = 0.476 \pm 0.01$$

Mayo and Lewis give the extreme ranges $r_1=0.44$ to 0.65 , $r_2=0.41$ to 0.64 but do not settle on an average value.

(7) The intersection plot is shown in *Figure 1*. These lines are obtained from the calculated equations so that they are inherently straight. The zig-zag appearance is due to the minimum spacing on the line printer.

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