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ON THE DETERMINATION OF MONOMER REACTIVITIES IN COPOLYMERIZATION

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Abstract—Existing methods to determine reactivity ratios in copolymerizations are critically discussed; particular emphasis is placed on the difference between exact and approximate procedures. Among the latter, the "intersection" method (Mayo and Lewis) and the "linearization" method (Fineman and Ross) are still preferred. They are compared from the point of view of projective geometry, and a "duality" is shown to exist between them.

A new procedure, based on the so-called "method of grouping", is then suggested: it allows ready evaluation of reactivity ratios with a minimum of computational difficulties. The results obtained by this procedure are, as such, good estimates for systems reported in the literature without the information necessary for a careful statistical treatment, and may best be used as the starting data for subsequent and more sophisticated elaborations.

INTRODUCTION

THE PROBLEM of computing copolymerization reactivity ratios has been tackled by several authors.[1–13] However, not all the proposed methods handle the subject with the same mathematical exactitude; most of them share the drawback of relying on a rather subjective evaluation of the results of copolymerization experiments (it is possible that a particular set of data, handled by different observers even by the same method, lead to appreciably different values of the reactivity ratios; moreover, no objective rules for quantitative estimation of the confidence limits for the calculated values are provided).

There exist only two mathematically rigorous treatments, due to Behnken[7] and Tidwell and Mortimer.[8] Both treatments use a nonlinear least-squares procedure and show how to select experimental conditions that will produce the most efficient use of the data and the obtainment of a unique pair of values of the reactivity ratios, which is independent of the personal judgement of the investigator, is the best obtainable from the data at hand, and is affected by errors quantitatively defined in meaningful terms. Despite these advantages the "intersection" method of Mayo and Lewis (ML)[2,3] and the "linearization" method of Fineman and Ross (FR)[4] are more commonly used in subsequent literature. This is partly explained by the requirement of an electronic computer to apply the exact procedures.

The present paper has a twofold objective. First, it shows the essential identity of the approximate ML and FR approaches, and second it presents another approximate procedure of evaluating reactivity ratios, based on the method of grouping. This approach is usually employed to fit a linear functional relationship when both variables are subject to error and have unknown variances. It permits rapid calculation of reasonably accurate values, which are suitable as initial data for more sophisticated calculations.

THE CORE OF THE PROBLEM OF REACTIVITY RATIOS' EVALUATION

Most methods used to determine the reactivity ratios take as a starting point the differential form of the copolymerization equation:

$$\frac{m_1}{m_2} = f = F\frac{r_1F + 1}{r_2 + F}, \tag{1}$$

where F is the initial molar ratio of the concentrations M_1 and M_2 of the two monomers (or the average value between the ratios at the start and the end of the copolymerization run) and m_1, m_2 are the molar fractions in the copolymer. In some cases the hypothesis of low conversion underlying the differential copolymerization equation is a poor approximation, and the integrated form due to Skeist[14] better fits the experimental data.

The difficulty of Eqn. (1) is its nonlinearity in the parameters r_1 and r_2, which are the quantities to be determined on the basis of a number of copolymerization runs and are connected to the experimentally measured quantities M_1 and m_1 in a nonlinear fashion. When computing reactivity ratios, it is then imperative to make a preliminary choice between two possible options: either to solve the problem exactly, noting the computational difficulties, or to solve the problem approximately. In the latter case one seeks transformations which will "linearize" the original function: the FR method is the best known example of such linearization. It is possible to apply least-squares procedures to the transformed function and to obtain useful estimates of the reactivity ratios and approximate confidence limits for them. But it is essential to note that transformation of the original function entails transformation also of the original error structure: the transformed error no longer has an expected value of zero, and its magnitude becomes a function of the variables. Application of least-squares in the usual form is no more a reliable estimation procedure, and the same disadvantages are encountered in graphical methods, e.g. ML. To put it another way, approximate methods do not give good estimates of the reactivity ratios since they fail to guarantee the randomness of variation which is an essential property of all experimentally obtained observations. Consequently, these methods result, in principle, in wasting a significant amount of the information contained in the experimental data.[15] Were the number of observations large, this waste would not be too harmful; but if only a limited number of observations are available, as is always the case when determining the reactivity ratios, the rejection of any information is unjustified. However, the loss of accuracy inherent in all approximate procedures can be acceptable if the results are obtained in a much simpler and more straightforward way: that is the reason why most polymer chemists continue to use the latter of the two aforementioned procedures for evaluation of reactivity ratios.

COMPARISON OF THE INTERSECTION AND THE LINEARIZATION METHODS

As remarked above, the approximate ML and FR methods are still widely applied for determining reactivity ratios. It therefore is worth considering their essential features in detail. For this purpose we shall deal with the subject from a view point

quite different from the usual ones, and one which—as far as we are cognizant—has never previously been considered.

In the ML method, Eqn. (1) is written in the form

$$r_2 = \frac{F^2}{f} r_1 + F\left(\frac{1}{f} - 1\right): \tag{2}$$

it is seen that for any copolymerization a linear relationship exists between r_1 and r_2; by selecting, at first by trial and error, arbitrary values of r_1, corresponding values for r_2 are obtained, and the points for a single experiment lie on a straight line. For a set of copolymerizations, various lines are obtained, which ideally should cross each other at a unique point, defining the reactivity ratios r_1 and r_2: because of experimental errors the intersections are actually spread over an area, and the basic problem is to locate the "best" point in this area to represent the solution of Eqn. (1).

In the FR method, Eqn. (1) is put in one of the equivalent forms

$$F\left(1 - \frac{1}{f}\right) = -r_2 + \frac{F^2}{f} r_1 \tag{3'}$$

$$\frac{1-f}{F} = -r_1 + \frac{f}{F^2} r_2, \tag{3''}$$

and each experiment determines one point on the straight line of Eqn. (3') or (3''): if it were not for the experimental errors, all these points would be exactly aligned; in practice they are scattered, and the procedure suggested for evaluating the reactivity ratios consists of applying the method of least-squares to find the slope and the intercept of Eqn. (3') or (3'').

Now, Eqn. (1) and its equivalent forms (2) and (3')* can be written in general terms as

$$y - ax - b = 0, \tag{4}$$

where $x = r_1$, $y = r_2$, $a = F^2/f$ and $b = F\,[(1/f) - 1]$.

Equation (4) lends itself to a twofold consideration, depending on the coordinate system in which it is represented.

In the ML plot, x and y are the variables, of which a particular value must be selected, and a and b are the parameters; conversely, in the FR plot, a and b become the two variables, whereas x and y are two adjustable parameters.

That means that there exists a projective correspondence, or "duality", between the two coordinate systems (x,y) and (a,b). Due to such duality, points in the former system correspond to straight lines in the latter and vice versa, and collinear points in the former system correspond to concurrent lines in the latter (i.e. lines having a common point of intersection), as shown in the following scheme (see next page).

On account of this correspondence, it may be said that the ML and FR methods are two formally different but substantially identical expressions of a unique reality: therefore, any way to carry out calculations in either representation has its counterpart in the other which leads to the same results. Thus, e.g. to evaluate the reactivity ratios with the ML method by averaging the coordinates of the $\frac{1}{2} N (N - 1)$ points of

* Quite analogous considerations could be made for Eqn. (3'').

FR plot	ML plot
point (x_i, y_i)	straight line $b = -x_i a + y_i$
straight line $y = a_i x + b_i$	point (a_i, b_i)
collinear points	concurrent lines
$(x_1, a_0 x_1 + b_0)$,	$b = -x_1 a + (a_0 x_1 + b_0)$,
$(x_2, a_0 x_2 + b_0)$,	$b = -x_2 a + (a_0 x_2 + b_0)$,
.....	.....
$(x_N, a_0 x_N + b_0)$	$b = -x_N a + (a_0 x_N + b_0)$
lying on the common line	crossing each other in the
$y = a_0 x + b_0$	common point (a_0, b_0)

intersection of the straight lines corresponding to N copolymerization experiments* is tantamount to evaluating r_1 and r_2 with the FR method by plotting the $\frac{1}{2} N(N-1)$ lines joining all possible pairs of points, and then averaging both the slopes and the intercepts of the resulting lines.†

EVALUATION OF r_1 AND r_2 BY THE METHOD OF GROUPING

The determination of reactivity ratios from the feed and the copolymer compositions presents, from the statistical point of view, two peculiarities: only a small number of observations are at hand, and in addition estimation is nonlinear. In this case the method of least squares is not a suitable estimation procedure and by analogy graphical subjective schemes tend to suffer.[7]

It is then tempting to seek some simplified procedure, capable of giving results as accurate as those obtained by the approximate methods, though involving a minimum of computational difficulties.

We believe that such an aim is reached by resorting to the so-called "method of grouping".[16–18] The essential features of this procedure will be described now. For the sake of evidence the experimental points corresponding to N copolymerization runs will be considered in the FR plot [Eqn. (3′)]: anyhow, it may be anticipated that, with this procedure, no graphical representations are necessary.

Let a_i be the abscissa F_i^2/f_i and b_i the ordinate $F_i[(1/f_i) - 1)]$ of the i-th point. Since it is a property of all linear functional relations of passing through the mean, one point on the sought-for straight line is readily determined:

$$\bar{a} = \frac{1}{N} \sum_{i=1}^{N} a_i, \quad \bar{b} = \frac{1}{N} \sum_{i=1}^{N} b_i.$$

It remains to estimate the slope. For this purpose, we divide the N plotted points into three groups, the two outer groups G_1 and G_3 containing the same number of points, chosen as near to $\frac{1}{3} N$ as possible. The (a_i, b_i)'s may be ordered by the magnitude of the a_i's, so that the three groups are nonoverlapping in the a-direction. It is assumed that this method of grouping is independent of the error. After discarding G_2, the

* This could be a criterion, though not commendable, to eliminate the subjectiveness in the location of the best point in the intersection area.

† By the way, these values do not coincide with those obtained through application of least-squares to the N points of the FR plot.

middle group of observations, we compute the means of each one of G_1 and G_3, $(\bar{a}_1,\bar{b}_1)$ and $(\bar{a}_3,\bar{b}_3)$: the slope of the line joining these two points gives the estimate of r_1:

$$r_1 = \frac{\bar{b}_3 - \bar{b}_1}{\bar{a}_3 - \bar{a}_1} = \frac{\sum_{G_3} b_i - \sum_{G_1} b_i}{\sum_{G_3} a_i - \sum_{G_1} a_i}.$$

The functional relation is then a line with this slope passing through the grand mean $(\bar{a},\bar{b})$:

$$b - \bar{b} = \frac{\bar{b}_3 - \bar{b}_1}{\bar{a}_3 - \bar{a}_1}(a - \bar{a}).$$

The intercept of this line is

$$-r_2 = \bar{b} - \bar{a}\frac{\bar{b}_3 - \bar{b}_1}{\bar{a}_3 - \bar{a}_1}.$$

It should be observed at this point that it would be desirable that both the slope and the intercept of the straight line through the experimental points should be calculated with the same precision; with the former procedure, instead, the uncertainty attached to the intercept could be much higher than that attached to the slope. We therefore believe that the best way of determination of the reactivity ratios by the method of grouping consists in applying Eqn. (3′) to obtain r_1 and Eqn. (3″) to obtain r_2. Calculation of the grand means thus becomes an unnecessary complication: only the means of G_1 and G_3 for each one of Eqns. (3′) and (3″) need to be computed.

The suggested number p of points to assign to G_1 and G_3 on varying N (over the range usually covered by copolymerization experiments) is reported below.

N	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
p	2	2,3	3	3	3,4	4	4	4,5	5	5	5,6	6	6	6·7	7

Two important goals are achieved by this procedure: on the one hand, the final results are less sensitive to different choices of the number of points assigned to the groups G_1, G_2 and G_3; on the other hand, the two FR plots are no more a source of ambiguity, but the best utilization of each of them is made.

The procedure may also be transferred to the ML plot, bearing in mind the duality of this representation and of the FR one pointed out in the foregoing section.

The condition that the straight line must pass, in the FR plot, through the mean $(\bar{a},\bar{b})$ of the points, becomes in the ML plot that the point $(\bar{x},\bar{y})$ must lie on the straight line of which the parameters are $-\bar{a}$ and $\bar{b}$. The condition that the slope of the straight line is the same as that of the line joining the means of G_1 and G_3 gives us the abscissa of the point $(\bar{x},\bar{y})$, i.e. r_1:

$$r_1 = (\bar{b}_3 - \bar{b}_1)/(\bar{a}_3 - \bar{a}_1).$$

r_2 is then obtained as the intersection of the straight lines $y = -\bar{a}x + \bar{b}$ and $x = (\bar{b}_3 - \bar{b}_1)/(\bar{a}_3 - \bar{a}_1)$, the latter of which is parallel to the ordinate axis. By exchanging

the coordinates of the ML plot we could also obtain a more accurate evaluation of r_2, as seen above.

The former procedure was applied to many copolymerizations reported in the literature; very good results were obtained in most cases, three of which are reported below.

We first consider the data from Table 3 of Ref. (8) (it is not specified to which pair of monomers they refer):

No.	M_1	m_1	$a' = F^2/f$	$b' = F[(1/f) - 1]$	$a'' = (f/F^2)$	$b'' = (1-f)/F$
1	0·9977	0·9867	2536·3	−427·9	0·00039	−0·169
2	0·9972	0·9866	1722·7	−351·3	0·00058	−0·204
3	0·9811	0·9169	244·2	−47·2	0·0041	−0·193
4	0·9763	0·8890	211·9	−36·0	0·0047	−0·170
5	0·0637	0·1110	0·037	0·477	27·0	12·9
6	0·0613	0·1055	0·036	0·488	27·7	13·5
7	0·0115	0·0238	0·0055	0·466	180·2	83·9
8	0·0085	0·0180	0·0040	0·459	249·4	114·5

Placing points 1, 2 and 3 in the G_1 group, points 4 and 5 in the G_2 group and points 6, 7 and 8 in the G_3 group, it is immediately obtained:

$$r_1 = -\frac{(b'_6 + b'_7 + b'_8) - (b'_1 + b'_2 + b'_3)}{(a'_6 + a'_7 + a'_8) - (a'_1 + a'_2 + a'_3)} = 0{\cdot}184$$

$$r_2 = \frac{(b''_6 + b''_7 + b''_8) - (b''_1 + b''_2 + b''_3)}{(a''_6 + a''_7 + a''_8) - (a''_1 + a''_2 + a''_3)} = 0{\cdot}465.$$

These data compare favourably with those obtained by the exact procedure, $r_1 = 0{\cdot}182$ and $r_2 = 0{\cdot}488$. Notice that application of the FR method gives $r_1 = 0{\cdot}179$, $r_2 = -2$ with Eqn. (3′) and $r_1 = -0{\cdot}09$, $r_2 = 0{\cdot}461$ with Eqn. (3″), showing the physical impossibility of the values obtained as intercepts.

The second example refers to the system isobutene (M_1)–chlorotrifluoroethylene described by Carcano *et al.*:[12]

No.	M_1	m_1	a'	b'	a''	b''
1	0·0148	0·4530	0·00027	+0·0031	3670·9	+11·441
2	0·0163	0·4406	0·00034	+0·0045	2868·6	+12·817
3	0·0198	0·4462	0·00050	+0·0049	1976·5	+9·624
4	0·0351	0·4631	0·0015	+0·0058	652·1	+3·780
5	0·0495	0·4722	0·0030	+0·0061	330·0	+2·023
6	0·0510	0·4830	0·0031	+0·0038	323·6	+1·224
7	0·0548	0·4813	0·0036	+0·0045	276·2	+1·244
8	0·0960	0·4955	0·0115	+0·0019	87·11	+0·168
9	0·2964	0·5129	0·1685	−0·0212	5·934	−0·126
10	0·5010	0·5095	0·9704	−0·0374	1·0305	−0·0386
11	0·7000	0·5249	4·928	−0·2214	0·2029	−0·0449
12	0·9000	0·5676	61·71	−2·144	0·0162	−0·0347
13	0·9026	0·5786	62·54	−2·505	0·0160	−0·0402
14	0·9100	0·5786	74·46	−2·747	0·0134	−0·0369

The values found by Carcano *et al.* by the exact procedure (slightly modified) are $r_1 = 0{\cdot}0378$ and $r_2 = 0{\cdot}0042$. If we place five points in both the G_1 and the G_3 group, we obtain from the above data $r_1 = 0{\cdot}0375$, $r_2 = 0{\cdot}0042$. Had we placed the former four points in G_1 and the latter four in G_3, we would have found $r_1 = 0{\cdot}0375$, $r_2 = 0{\cdot}0041$.

The next example is concerned with the system acrylonitrile (M_1)–styrene described by Thompson and Raines:[19]

No.	M_1	m_1	a'	b'	a''	b''
1	0·959	0·705	228·9	−13·60	0·0044	−0·0594
2	0·957	0·714	198·4	−13·34	0·0050	−0·0672
3	0·930	0·650	95·04	−6·13	0·0105	−0·0645
4	0·901	0·599	55·45	−3·01	0·0180	−0·0543
5	0·897	0·606	49·31	−3·05	0·0203	−0·0618
6	0·828	0·567	17·70	−1·138	0·0565	−0·0643
7	0·760	0·513	9·52	−0·160	0·105	−0·0169
8	0·753	0·526	8·38	−0·301	0·119	−0·0360
9	0·667	0·487	4·23	+0·107	0·234	+0·0253
10	0·326	0·366	0·405	+0·354	2·468	+0·874
11	0·252	0·327	0·234	+0·357	4·281	+1·526
12	0·183	0·270	0·136	+0·382	7·372	+2·813
13	0·088	0·181	0·042	+0·340	23·74	+8·07

The reactivity ratios for this system were calculated, together with their confidence limits, by the exact procedure of Tidwell and Mortimer [see Fig. 2 of Ref. (8)]: $r_1 = 0{\cdot}0667$, $r_2 = 0{\cdot}370$. Application of our procedure gives nearly the same values: $r_1 = 0{\cdot}065$, $r_2 = 0{\cdot}358$ (whether placing four or five points in each one of the G_1 and G_3 groups).

In some instances, the method of grouping failed to give quite satisfactory results, e.g. for the system vinyl chloride (M_1)–methyl acrylate described by Chapin *et al.*:[20]

No.	M_1	m_1	a'	b'	a''	b''
1	0·925	0·559	120·0	−2·603	0·0083	−0·0217
2	0·846	0·301	70·1	7·264	0·0143	0·1036
3	0·763	0·247	31·6	6·595	0·0316	0·2087
4	0·674	0·172	20·58	7·885	0·0486	0·383
5	0·579	0·136	12·02	7·362	0·083	0·613
6	0·479	0·100	7·608	7·355	0·131	0·967
7	0·256	0·032	3·582	10·065	0·279	2·810
8	0·133	0·017	1·361	8·717	0·735	6·406

As remarked by Tidwell and Mortimer,[8] these data are very scattered (in particular the b' values), "thus illustrating the obvious points that no calculation scheme can get good answers from bad data and that no amount of good planning can overcome the uncertainty generated in the answers by sloppy experimentation". It can then be predicted that an accurate evaluation of the reactivity ratios will be very difficult. This situation arises since the monomer reactivities (see below) are greatly different:

appreciable drifts occur in the relative concentrations, even if the copolymerizations are restricted to low conversions,[9] and however careful the experimentation may be. The values reported by Chapin *et al.*, obtained by the "curve fitting" method,[1] are $r_1 = 0{\cdot}083$, $r_2 = 9{\cdot}0$. The exact procedure by Tidwell and Mortimer gives $r_1 = 0{\cdot}0908$, $r_2 = 10{\cdot}066$. Our method, based on the three former and the three latter points, gives $r_1 = 0{\cdot}071$, $r_2 = 9{\cdot}06$; if only the two outer pairs of points (1, 2 and 7, 8) are taken into account, we find $r_1 = 0{\cdot}076$, $r_2 = 9{\cdot}20$.

A final remark is concerned with the precision of the r_1 and r_2 measurement. It is common practice to give limits within which the true values are believed to exist with a certain probability, and these limits were mostly established by applying the linear least-squares procedure to the FR linear form. However, this procedure is incorrect: the simple plus–minus limits do not adequately define the precision when parameters are jointly estimated, as is the case for reactivity ratios, and only the *joint confidence interval* conveys the uncertainty associated with the estimation of r_1 and r_2.[8,21] Despite the existence of general formulae for assessment of precision in the method of grouping,[16–18] we, therefore, shall not deal with the establishment of the confidence limits for the particular application of the method described here.

CONCLUSIONS

The method of grouping described in this paper offers a simpler and more objective means of calculating values of reactivity ratios than the conventional Mayo–Lewis or Fineman–Ross methods. It should be stressed, however, that this method produces approximate values and for exact calculations the more involved procedures described by Tidwell and Mortimer[8,21] should be employed.

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Résumé—On discute les méthodes existantes de détermination des rapports de réactivités en copolymérisation. On insiste particulièrement sur les différences entre les procédés exacts et approximatifs. Parmi ces derniers, la méthode par "intersection" (Mayo et Lewis) et la méthode par "linéarisation" (Finemann et Ross) sont encore privilégiées. On les compare du point de vue de la géométrie projective et on montre qu'il existe entre elles une "dualité".

On propose ensuite un nouveau procédé basé sur "une méthode de groupement", il permet une évaluation rapide des rapports de réactivité avec un minimum de difficultés de calcul. Les résultats obtenus par ce procédé, sont, comme tel, bien évalués pour les systèmes mentionnés dans la littérature sans renseignement supplélentaire pour un traitement statistique soigné et peuvent être mieux utilisés comme données de départ pour des études postémieures et plus sophistiquées.

Sommario—Si discutono criticamente i metodi esistenti per la determinazione dei rapporti di reattivitá nella copolimerizzazione, ponendo in particolare l'accento sulle differenze fra i procedimenti rigorosi e quelli approssimati. Fra questi ultimi, il metodo delle "intersezioni" (Mayo e Lewis) e il metodo di "linearizzazione" (Fineman e Ross) sono tuttora i preferiti. Essi vengono confrontat dal punto di vista della geometria proiettiva, e si dimostra che fra di essi esiste una "dualitá".

Si suggerisce poi un nuovo procedimento, basato sul cosiddetto "metodo di raggruppamento": esso consente una rapida valutazione dei rapporti di reattivitá con minime difficoltá di calcolo. I risultati ottenuti con questo procedimento sono, di per sé, valide stime per sistemi riportati in letteratura senza l'informazione necessaria per una trattazione statistica accurata, e rappresentano un ottimo punto di partenza per successive e piú sofisticate elaborazioni.

Zusammenfassung—Die üblichen Methoden zur Bestimmung der Reaktivitätsverhältnisse bei Copolymerisationen werden kritisch diskutiert; besonders hervorgehoben wird die Unterscheidung zwischen exakten und näherungsweisen Verfahren. Bei den letzteren wird das Mayo–Lewis Diagramm und die Methode von Fineman und Ross immer noch bevorzugt. Sie werden unter dem Gesichtspunkt der projizierenden Geometrie verglichen und es wird gezeigt, daß zwischen beiden Methoden eine "Dualität" besteht.

Ein neues Verfahren, basierend auf der sogenannten "Gruppierungsmethode" wird vorgeschlagen: es erlaubt eine einfache Abschätzung der Reaktivitätsverhältnisse mit einem Minimum an rechnerischem Aufwand. Die nach dieser Methode erhalten Ergebnisse sind, als solche, gute Abschätzungen für in der Literatur angegebene Systeme, bei denen die für eine sorgfältige statistiche Behandlung erforderliche Information fehlt, sodaß sie als Ausgangswerte für eine nachfolgende detaillierte Ausarbeitung sehr gut verwendet werden können.