Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

A New Analytical Solution of the Binary Copolymer Composition Equation and Suggested Procedure for Deriving the Monomer Reactivity Ratios

R. M. Joshi[a]; S. G. Joshi[a]
[a] National Chemical Laboratory, Poona, India

To cite this Article Joshi, R. M. and Joshi, S. G.(1971) 'A New Analytical Solution of the Binary Copolymer Composition Equation and Suggested Procedure for Deriving the Monomer Reactivity Ratios', Journal of Macromolecular Science, Part A, 5: 8, 1329 — 1338

To link to this Article: DOI: 10.1080/00222337108061112

URL: http://dx.doi.org/10.1080/00222337108061112

J. MACROMOL. SCI.–CHEM., A5(8), pp. 1329-1338, December, 1971

A New Analytical Solution of the Binary Copolymer Composition Equation and Suggested Procedure for Deriving the Monomer Reactivity Ratios*

R. M. JOSHI and S. G. JOSHI

National Chemical Laboratory
Poona, India

SUMMARY

An absolute analytical procedure is found for obtaining the parameters of the differential, binary, copolymer composition equation, setting up a least-squares condition that places equal weight on all experimental lines of the Mayo-Lewis plot. The values of monomer reactivity ratios for the system ethyl methacrylate (M_1)-vinylidene chloride (M_2), studied by Agron et al., are $r_1 = 2.052 \pm 0.043$ and $r_2 = 0.346 \pm 0.052$. These values, especially r_1, differ from the estimates by Agron et al. The new solution, however, appears to yield the estimate of maximum likelihood for the reactivity ratios based on the given experimental data.

INTRODUCTION

Several methods [1-6] have been evolved since 1944 for working out the monomer reactivity ratios r_1 and r_2 from the well-known copolymer composition equation in the differential form:

---

*NCL Communication No. 1567.

$$\frac{d\,M_1}{d\,M_2} = \frac{M_1}{M_2}\,\frac{r_1 M_1 + M_2}{r_2 M_2 + M_1} \approx \frac{m_1}{m_2} \tag{1}$$

A recent paper by Tidwell and Mortimer [6] reports that the existing methods fall into three main categories: 1) curve fitting, 2) intersection, and 3) linearization, none of which are entirely satisfactory, and recommends a nonlinear least-square method which is a modification of the curve-fitting method. This method employs initial approximate estimates of r_1 and r_2 to define the initial copolymer composition relation in the form due to Skeist, which is then progressively refined by a number of iterations so as to minimize the sum of squares of the differences between the observed and computed copolymer compositions. The method thus suffers from the awkwardness of having to know the answer in order to estimate it efficiently. In this paper we propose a least-squares solution of r_1 and r_2 which is derived analytically (and not by numerical iterations) from the intersecting multiple lines of the copolymer composition equation in the format due to Mayo and Lewis [1].

PROCEDURE

In the Mayo-Lewis plot a set of intersecting lines, each representing one copolymerization experiment, is produced on an r_2 vs. r_1 plot. The basic problem is to locate the best point in the intersection area to represent the solution of the copolymer equation. This point of intersection has hitherto been located either graphically through personal judgment [3] or by use of arbitrary empirical weighting factors [4] such as tan θ, sin θ, where θ is the angle between any two intersecting lines. An exact analytical solution of this problem seems possible.

We define the best point of intersection as the point (r_1^0, r_2^0) which is (statistically) closest to all the experimental lines, and which, if it were not for the experimental errors, would lie on every line of the Mayo-Lewis plot, resulting ideally in a unique intersection point. In the practical case, a condition is set up where the coordinates of the intersection point would be such that the sum of squares of its perpendicular distances from all the experimental lines would be a minimum. Thus if an experimental line is represented by $r_2 = mr_1 + c$, where $m = F^2/f$, $c = F(1/f - 1)$, $F = M_1/M_2$, and $f = m_1/m_2$. The perpendicular distance δ of the point (r_1^0, r_2^0) from the line is given by

$$\delta^2 = \frac{(r_2^0 - mr_1^0 - c)^2}{1 + m^2}$$

For the set of lines $r_2 = m_i r_1 + c_i$, where i is the number of experiment, 1,2,3, . . . , N

$$\sum_{i=1}^{N} (\delta_i)^2 = \sum_{i=1}^{N} \frac{(r_2^0 - m_i r_1^0 - c_i)^2}{1 + m_i^2}$$

Differentiating with respect to r_1 and r_2 and equating the two differentials to zero as the condition for the minimum of $\Sigma(\delta)^2$, the following equations result:

$$\frac{\partial \Sigma(\delta_i)^2}{\partial r_1} = \Sigma \frac{-2(r_2 - m_i r_1 - c_i)m_i}{1 + m_i^2} = 0$$

$$\frac{\partial \Sigma(\delta_i)^2}{\partial r_2} = \Sigma \frac{-2(r_2 - m_i r_1 - c_i)}{1 + m_i^2} = 0$$

Therefore

$$r_2 \Sigma \frac{m_i}{1 + m_i^2} - r_1 \Sigma \frac{m_i^2}{1 + m_i^2} - \Sigma \frac{m_i c_i}{1 + m_i^2} = 0$$

and

$$r_2 \Sigma \frac{1}{1 + m_i^2} - r_1 \Sigma \frac{m_i}{1 + m_i^2} - \Sigma \frac{c_i}{1 + m_i^2} = 0$$

These equations are solved to give the solution of r_1^0 and r_2^0 in terms of the various functions of m_i and c_i (slopes and intercepts):

$$r_1^0 = \frac{\Sigma \frac{1}{1 + m_i^2} \Sigma \frac{m_i c_i}{1 + m_i^2} - \Sigma \frac{m_i}{1 + m_i^2} \Sigma \frac{c_i}{1 + m_i^2}}{(\Sigma \frac{m_i}{1 + m_i^2})^2 - \Sigma \frac{1}{1 + m_i^2} \Sigma \frac{m_i^2}{1 + m_i^2}} \qquad (2)$$

$$r_2^0 = \frac{\Sigma \frac{m_i}{1 + m_i^2} \, \Sigma \frac{m_i c_i}{1 + m_i^2} - \Sigma \frac{m_i^2}{1 + m_i^2} \, \Sigma \frac{c_i}{1 + m_i^2}}{(\Sigma \frac{m_i}{1 + m_i^2})^2 - \Sigma \frac{1}{1 + m_i^2} \, \Sigma \frac{m_i^2}{1 + m_i^2}} \qquad (3)$$

Inspection of Eqs. (2) and (3) reveals that the new solution (r_1^0,r_2^0) is almost identical to the one obtainable from the usual linearization procedure of Fineman and Ross [2]:

$$r_1 = \frac{N \, \Sigma \, m_i c_i - \Sigma \, m_i \, \Sigma \, c_i}{(\Sigma \, m_i)^2 - N \, \Sigma \, m_i^2} \qquad (4)$$

$$r_2 = \frac{\Sigma \, m_i \, \Sigma \, m_i c_i - \Sigma \, m_i^2 \, \Sigma \, c_i}{(\Sigma \, m_i)^2 - N \, \Sigma \, m_i^2} \qquad (5)$$

In the new procedure only the weighting factor $1/(1 + m_i^2)$ occurs with every summation term in m_i and c_i, $\Sigma \, 1/(1 + m_i^2)$ corresponding to N in Eqs. (4) and (5). This factor seems to normalize the numerical extremities of the summation terms, imparting a uniform weight to every experimental line in the new procedure, and eliminating some of the well-known deficiencies of the simple least-square procedure. For instance, the simple least-squares procedure due to Fineman and Ross [2] fails to yield the same solution when the datum is merely inverted, i.e., the monomer formerly taken as M_1 is taken as M_2 and the former M_2 as M_1. In the present method a unique solution is obtained from one and the same datum, whichever of the two monomers is taken first as M_1. It can be easily seen that for any experimental line $r_2 = mr_1 + c$ on r_2 vs. r_1 plot, the slope $m = \tan \theta$ is changed on inversion of data to $1/m = \tan (90 - \theta)$, where θ is the angle made by the line with the r_1-axis. The inverted line subtends the same angle θ but now with the r_2-axis and makes the same intercept of magnitude c, but on the r_1-axis. Each inverted line is thus a mirror image in the 45°-bisection line with the equation $r_2 = r_1$, so that the best point of intersection is also a mirror image in the 45°-line, with the coordinates interchanged but unaltered in magnitude.

Experimental data of Agron et al. [7] on copolymerization of ethyl methacrylate (M_1) and vinylidene chloride (M_2) are taken to illustrate the new procedure. This is given in Table 1. Table 2 shows various numerical operations on the data and the summations of various $m_i - c_i$ functions.

Table 1. Experimental Data of Copolymerization of Ethyl Methacrylate (M_1) and Vinylidene Chloride (M_2) Taken from the Work of Agron et al. [7]

Expt. No.	M_2	m_2	$F = M_1/M_2$	$f = m_1/m_2$	$F^2/f = m_i$	$F(1/f - 1) = c_i$
1	0.115	0.061	7.695652	15.393442	3.847280	-7.195719
2	0.273	0.144	2.663004	5.944444	1.192974	-2.215023
3	0.422	0.241	1.369668	3.149378	0.595671	-0.934767
4	0.621	0.400	0.610306	1.500000	0.248315	-0.203435
5	0.798	0.610	0.253133	0.639344	0.100221	0.142793
6	0.926	0.805	0.079914	0.176471	0.036187	0.372932
					Σ 6.020648	-10.033219

Table 2. The Operational Treatment of the Copolymerization Data

Line No.	$m_i c_i$	m_i^2	$\frac{1}{1 + m_i^2}$	$\frac{m_i}{1 + m_i^2}$	$\frac{c_i}{1 + m_i^2}$	$\frac{m_i c_i}{1 + m_i^2}$	$\frac{m_i^2}{1 + m_i^2}$
1	-27.683946	14.801563	0.063284	0.243471	-0.455374	-1.751951	0.936702
2	-2.642465	1.423187	0.412679	0.492315	-0.914093	-1.090490	0.587319
3	-0.556814	0.354824	0.738103	0.439666	-0.689954	-0.410986	0.261897
4	-0.050519	0.061660	0.941921	0.233893	-0.191620	-0.047585	0.058079
5	0.014311	0.010044	0.990055	0.099224	0.141373	0.014169	0.009944
6	0.013495	0.001309	0.998690	0.036140	0.372443	0.013477	0.001308
Σ	-30.905935	16.654373	4.144732	1.544709	-1.737225	-3.273366	1.855249

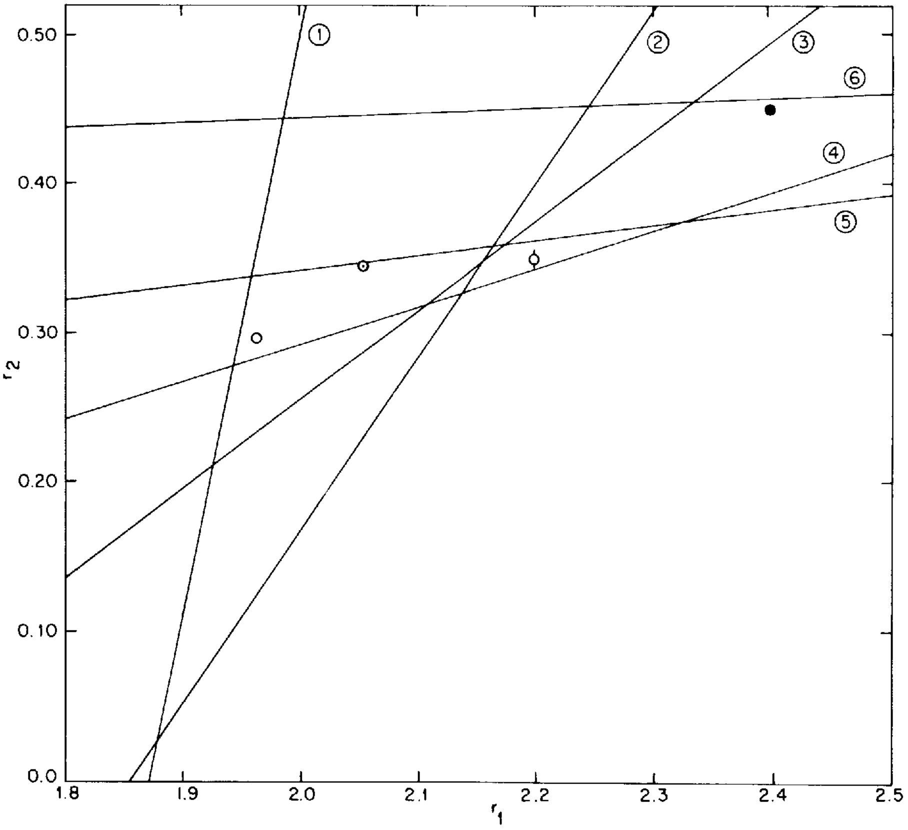

Fig. 1. Copolymerization data of Agron et al. [7] on the Mayo-Lewis plot. (ϕ) Authors' value (r_1 = 2.2, r_2 = 0.35). (○) Fineman and Ross [2] (r_1 = 1.962, r_2 = 0.296). (●) Fineman and Ross inverted data (r_1 = 2.396, r_2 = 0.450). (⊙) This work (r_1 = 2.052, r_2 = 0.346).

By the use of a 10-digit desk calculator, Eqs. (2) and (3) yielded the coordinates of the best point of intersection (being the closest point to all lines) as r_1^0 = 2.05222 and r_2^0 = 0.34570; the same data on inversion gave $r_1^{0\prime}$ = 2.05215 and $r_2^{0\prime}$ = 0.34568. The slight difference is due to the limitations of the desk calculations, but analytically the same solution must result. Figure 1 shows the Mayo-Lewis plot, the intersection area, and the location of our best solution of the monomer reactivity ratios for this system. The original authors have derived somewhat different values (r_1 = 2.2 and r_2 = 0.35) from the curve-fitting method, while the Fineman-Ross procedure applied to the data yields two very different solutions (with normal and inverted data) which are far apart, as seen from Fig. 1. The position of our intersection point on the Mayo-Lewis plot, being as close as possible to every experimental line by definition, suggests that it is the maximum likelihood estimator of the monomer reactivity ratios.

Estimation of Limits of Uncertainty

The statistical point of intersection (r_1^0, r_2^0) should ideally lie on every experimental line. Its distance from any line is therefore a measure of experimental deviation or error. The coordinates of the point of intersection of the i-th line and its perpendicular through (r_1^0, r_2^0) are analytically derived as:

$$r_1^i = \frac{r_1^0 + M_i r_2^0 - m_i c_i}{1 + m_i^2}$$

and

$$r_2^i = m_i r_1^i + c_i$$

The standard deviations $S_{r_1^0}$ and $S_{r_2^0}$ for the monomer reactivity ratios r_1^0 and r_2^0, respectively, are:

$$S_{r_1^0} = \pm\, [\Sigma\, (r_1^0 - r_1^i)^2/N]^{1/2} \tag{6}$$

$$S_{r_2^0} = \pm\, [\Sigma\, (r_2^0 - r_2^i)^2/N]^{1/2} \tag{7}$$

These work out to be ±0.0433 for r_1^0 and ±0.0520 for r_2^0. Our estimate of the monomer reactivity ratios for this system, therefore, are $r_1 = 2.052 \pm 0.043$ and $r_2 = 0.346 \pm 0.052$.

DISCUSSION

A vast amount of experimental data [8a] aimed at determining the monomer reactivity ratios exists on copolymerization systems. The pattern of errors in most of the previous experimental work is essentially unknown and unpredictable. It also differs from system to system depending upon the experimental conditions, especially the range of initial monomer feed ratios chosen in experimentation and the method of copolymer composition analysis employed. The recent work of Behnken [5] and of Tidwell and Mortimer [6] provide valuable suggestions for future copolymerization studies in regard to planning of optimum experimental designs to yield maximum reliable information on the reactivity parameters. A special study of some systems by Thompson and Raines [9] shows that much of the general copolymerization data needs careful repetition, especially in respect to the yield when a differential equation is employed. We feel the existing data also need a complete revision of calculations of the parameters with the help of some entirely objective, nongraphical, and uniform treatment, so that extensive correlation with structure and the task of predicting the parameters by the revised Q-e scheme [8b, 9] may be done with added confidence. In the absence of any knowledge of the error pattern in the previous data to be handled, the new procedure suggested here places equal emphasis or weight on all experimental lines covering any feed range studied, and should therefor form a preferred method for reanalysis of the previous nonspecific data. It should also serve as a valuable means of judging subtle differences in the copolymerization parameters caused by the change of pressure or temperature [10], the solvent influence [11], or the penultimate unit effect if it is experimentally discernible [12]. A few other systems treated by the new procedure have been found to yield very reasonable solutions which can be depicted convincingly on the Mayo-Lewis plot as in Fig. 1. A computer program for wider application of the method is being written and a report will follow.

ACKNOWLEDGMENT

One of us (S.G.J.) wishes to thank Prof. M. R. Railkar, S.P. College, for a helpful discussion.

REFERENCES

[1] F. R. Mayo and F. M. Lewis, *J. Amer. Chem. Soc.*, **66**, 1594 (1944).

[2] M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5**, 259 (1950).

[3] T. Alfrey, Jr., J. J. Bohrer, and H. Mark, *Copolymerization* (High Polymers VIII), Interscience, New York, 1952, pp. 8-23.

[4] R. M. Joshi and S. L. Kapur, *J. Polym. Sci.*, **14**, 508 (1954); **19**, 582 (1956).

[5] D. W. Behnken, *J. Polym. Sci.,* **A2**, 645 (1964).

[6] P. D. Tidwell and G. A. Mortimer, *J. Polym. Sci.,* **A3**, 369 (1965).

[7] P. Agron, T. Alfrey, Jr., J. Bohrer, H. Haas, and H. Wechsler, *J. Polym. Sci.,* **3**, 157 (1948).

[8] (a) H. Mark, B. Immergut, E. H. Immergut, L. J. Young, and K. I. Beynon, *Copolymerization* (G. E. Ham, ed.), Wiley (Interscience), New York, 1964, pp. 695-843.
(b) L. J. Young, *Ibid.,* pp. 845-863.

[9] B. R. Thompson and R. H. Raines, *J. Polym. Sci.,* **41**, 265 (1959); **54**, S31 (1961).

[10] R. D. Burkhart and N. L. Zutty, *J. Polym. Sci.,* **57**, 793 (1962).

[11] R. M. Joshi, *J. Sci. Ind. Res.,* **18B**, 279 (1959).

[12] R. M. Joshi, *J. Polym. Sci.,* **17**, 125 (1955).

Accepted by editor May 27, 1971
Received for publication July 12, 1971

Note Added in Proof: In his critical comments on the manuscript, Dr. F. R. Mayo pointed out that our Line 6 in Fig. 1 was incorrect. This was traced to a wrong m_1/m_2 value (now underlined) for Expt. No. 6 in Table 1, taken by us through an oversight in the preliminary calculations and thereafter. The line, when correctly drawn, shifts appreciably downward toward the area of intersection and somewhat lessens the exaggeration of scatter at present depicted by it, as does also the degree of imprecision ascribed to other methods. However, the essential part of the new analytical solution and arguments in its favor remain valid despite the illustrative example being in error. The exact solution for this system, as obtained from a computer program with the correct input data of Agron et al. [7] is: $r_1 = 2.014768 \pm 0.034266$ and $r_2 = 0.297357 \pm 0.029075$.