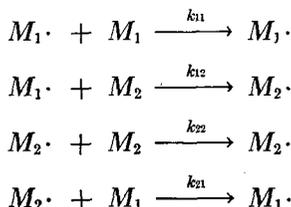


LETTERS TO THE EDITORS

Linear Method for Determining Monomer Reactivity Ratios in Copolymerization

The copolymerization of two monomers M_1 and M_2 may be described schematically as follows:



The monomer reactivity ratios are given by $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$, and the copolymer composition equation which relates the polymer composition to the monomer composition is given by:

$$\frac{dM_1}{dM_2} = \frac{M_1 r_1 M_1 + M_2}{M_2 r_2 M_2 + M_1} \left(= \frac{m_1}{m_2} \text{ for low conversions} \right) \quad (1)$$

where M_1 and M_2 refer to the monomer composition and m_1 and m_2 to the polymer composition.^{1a-c}

The values of the monomer reactivity ratios, r_1 and r_2 in equation (1), have been determined by the elegant but laborious graphical method of Mayo and Lewis,^{1b} using the integrated form of equation (1). A simpler method involves carrying out the copolymerizations to low conversions and using the approximate form of equation (1). The ratios r_1 and r_2 may then be obtained graphically from the initial and final slopes of the usual copolymerization curve in which the polymer composition is plotted against the monomer composition. This method may involve large uncertainties in the slopes and, consequently, in the r_1 and r_2 values, particularly in those cases where the slopes are steep or where experimental data at very low and very high concentration ratios are unavailable. The reliability of the determined values can be increased by the tedious method of calculating theoretical curves for pairs of values of r_1 and r_2 and fitting them to the experimental curves.

However, a simpler technique, which permits the use of data in the intermediate concentration regions and reduces the uncertainties in the r values, is possible. If $f = (m_1/m_2)$ and $F = (M_1/M_2)$, then equation (1) can be rewritten as:

$$f = F \frac{r_1 F + 1}{r_2 + F} \quad (2)$$

By rearranging terms one obtains:

$$\frac{F}{f} (f - 1) = r_1 \frac{F^2}{f} - r_2 \quad (3)$$

A plot of $(F/f)(f - 1)$ as ordinate and (F^2/f) as abscissa is a straight line whose slope is r_1 and whose intercept is minus r_2 . Equation (2) can also be rearranged to:

$$\frac{f - 1}{F} = -r_2 \frac{f}{F^2} + r_1 \quad (4)$$

In this case the slope is minus r_2 and the intercept r_1 . In addition to simplifying the calculations, the use of equations (3) and (4) offers the considerable advantage that they permit the facile use of the method of least squares to get the best fit to the experimental data.

It is of interest to note that in the special case where $r_2 = 0$, equations (3) and (4) reduce to:

$$(f - 1) = r_1 F \quad (5)$$

which is identical in form to one derived by Alfrey, Merz, and Mark.² Similarly, when $r_1 = 0$, the equations simplify to:

$$(1 - f) = r_2 (f/F) \quad (6)$$

In Table I the values of r_1 and r_2 determined by using equations (3) and (4) are compared with those reported in the literature. The examples were chosen to include systems in which:

- | | | |
|-----|------------|-----------|
| (a) | $r_1 > 1;$ | $r_2 < 1$ |
| (b) | $r_1 > 0;$ | $r_2 = 0$ |
| (c) | $r_1 < 1;$ | $r_2 < 1$ |

Excellent agreement was obtained between the reported values and those obtained by the use of either equation (3) or (4). The vinyl acetate-tetrachloroethylene* example gave a slightly negative value for r_2 when the best straight line was first drawn through the experimental points. Since neither r can be negative, the line was redrawn to make $r_2 = 0$ and this resulted in the second pair of values for r_1 and r_2 for this system reported in Table I.

As was to be expected, the values of r_1 and r_2 determined by plotting the terms of equations (3) and (4) agree very well. Having the two equations is, however, an advantage, since sometimes one of the two plots gives a better straight line through the points.

* The data for this system are relatively unsatisfactory. Only four experimental points were obtained, and, of these, two were for relatively high conversions, 30% and 22%.

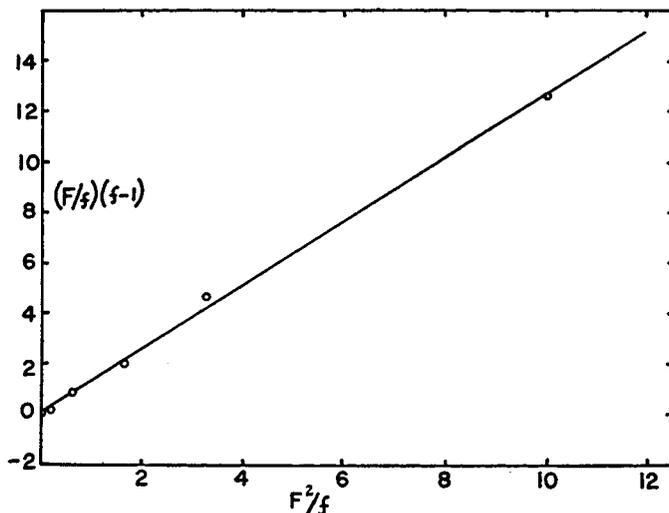


Fig. 1. Plot of $(F/f)(f-1)$ vs. F^2/f for styrene (M_1) pentachlorostyrene (M_2) copolymerization with least squares straight line.

The data for the styrene-pentachlorostyrene system have been treated by the method of least squares. This resulted in values of 1.26 and 0.064 for r_1 and r_2 , respectively. Figure 1 shows the least squares straight line and the values of $(F/f)(f-1)$ vs. F^2/f from the experimental data.

TABLE I

COMPARISON OF r VALUES DETERMINED BY NEW METHOD WITH THOSE REPORTED IN LITERATURE

System	From plot of equation (3)		From plot of equation (4)		Reported		Ref. No.
	r_1	r_2	r_1	r_2	r_1	r_2	
Styrene (M_1)-pentachlorostyrene (M_2)	1.28	0.05	1.31	0.09	1.31	0.10	3
Methyl methacrylate (M_1)-pentachlorostyrene (M_2)	4.25	0.35	4.17	0.33	4.0	0.35	3
Vinyl acetate (M_1)-vinyl chloride (M_2)	0.29	1.85	0.25	1.81	0.3	2.1	4
Vinyl acetate (M_1)-tetrachloroethylene (M_2)	3.5	-0.17	3.55	-0.22	5.0	0.0	4
			Assume $r_2 = 0.0$				
	5.15	0.0	5.29	0.0			
Vinyl acetate (M_1)- <i>trans</i> -dichloroethylene (M_2)	0.86	0.0	0.87	0.015	0.85	0.0	5
Allyl chloride (M_1)-vinyl acetate (M_2)	0.58	0.65	0.66	0.69	0.67	0.7	4

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MORTON FINEMAN
SIDNEY D. ROSS

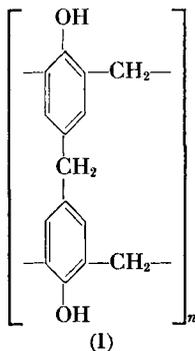
Research Laboratories
Sprague Electric Company
North Adams, Massachusetts

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"Bound" Water in Phenol-Formaldehyde Condensates

The paper by Bentz and Neville¹ in the December issue of this Journal is a valuable contribution to our understanding of the mechanism of the phenol formaldehyde reaction. The determination of free water by the Karl Fischer reagent is especially illuminatory. However, I feel that the authors' interpretation of "bound" water leaves something to be desired, since, in their discussion, they suggest it may be hydrogen bonded. It is hard to see why "free" water is not equally capable of forming hydrogen bonds.

We feel that the "bound" water is indeed chemically combined as methylol and dibenzyl ether groups, and that the authors' results can be interpreted in these terms.



The authors have suggested that the power of adsorption is lost as polymerization proceeds. We feel this loss of adsorption is dependent only on loss of hydrophilic groups. The adsorbent capacity of ion-exchange resins certainly indicates that high polymers are not inherently devoid of this property.