A Graphic Method for the Determination of Monomer Reactivity Ratios

The instantaneous copolymer composition equation for a binary components system

$$F_1 = 1 - F_2 = \frac{r_1f_1^2 + f_1f_2}{r_1f_1^2 + 2f_1f_2 + r_2f_2^2} \tag{1}$$

has been used for determining monomer reactivity ratios. Equation (1) has been rearranged in the form by Fineman and Ross[1] as follows:

$$\frac{f_1(1 - 2F_1)}{F_1(1 - f_1)} = r_2 + \frac{f_1^2(F_1 - 1)}{F_1(1 - f_1)^2} r_1 \tag{2}$$

The monomer reactivity ratios r_i are then determined graphically. The r_i values are estimated from the slope and intercept of the plot of $f_1(1 - 2F_1)/F_1(1 - f_1)$ against $f_1^2(F_1 - 1)/F_1(1 - f_1)^2$, respectively. The disadvantage of this method is that it is sometimes difficult to make a decision regarding the best straight line through a set of points since linear least-squares procedures are not appropriate.[2] In this work, using eq. (1), we propose a new graphic procedure for determining r_i. In this method, the r_i values are directly determined from both intercepts of the plot of f_1f_2/F_1F_1 vs. f_1 or F_1F_2/f_1f_2 vs. f_1. The procedure for making the plot is very simple and the linear least-squares procedure is unnecessary.

Equation (1) is rewritten as

$$\frac{f_1}{F_1} = \frac{r_1f_1^2 + 2f_1f_2 + r_2f_2^2}{r_1f_1 + f_2} \tag{3}$$

and then its limiting value at $f_1 = 0$ is found to be

$$\lim_{f_1 \to 0} (f_1/F_1) = r_2 \tag{4}$$

Equation (1) is further rearranged to be

$$F_2 = \frac{f_1f_2 + r_2f_2^2}{r_1f_1^2 + 2f_1f_2 + r_2f_2^2}$$

or

$$\frac{f_2}{F_2} = \frac{r_1f_1^2 + 2f_1f_2 + r_2f_2^2}{f_1 + r_2f_2} \tag{5}$$

The limiting value of f_2/F_2 at $f_1 = 0$ is also solved:

$$\lim_{f_1 \to 0} (f_2/F_2) = 1 \tag{6}$$

The combination of eqs. (4) and (5) yields

$$\lim_{f_1 \to 0} (f_1/f_2/F_1F_2) = r_2 \tag{7}$$

Similarily, we solve the limiting values of f_1/F_1 and f_2/F_2 at $f_2 = 0$ or $f_1 = 1$ for eqs. (3) and (5) and obtain

$$\lim_{f_1 \to 1} (f_1/F_1) = 1 \tag{8}$$

$$\lim_{f_1 \to 1} (f_2/F_2) = r_1 \tag{9}$$

$$\lim_{f_1 \to 1} (f_1f_2/F_1F_2) = r_1 \tag{10}$$

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TABLE I
Data for Determining the Monomer Reactivity Ratios

System	f_1	F_1
Styrene–methyl methacrylate[3,4]	0.048	0.093
	0.100	0.171
	0.111	0.168
	0.234	0.317
	0.300	0.371
	0.478	0.493
	0.500	0.510
	0.699	0.647
	0.700	0.648
	0.900	0.844
Methyl methacrylate–isoprene[5]	0.100	0.112
	0.300	0.261
	0.500	0.424
	0.700	0.547
	0.800	0.576
	0.850	0.676
	0.900	0.724
	0.950	0.843
	0.957	0.888
Acrylonitrile–ethyl acrylate[6]	0.380	0.439
	0.525	0.569
	0.647	0.697
	0.741	0.777
	0.823	0.850
	0.917	0.930
Vinyl acetate–methyl methacrylate[7]	0.19	0.01
	0.37	0.02
	0.54	0.05
	0.70	0.08
	0.86	0.17
	0.97	0.56

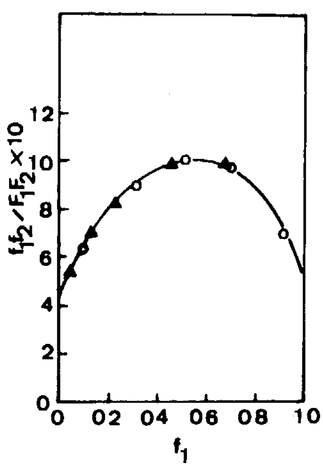

Fig. 1. Determination of reactivity ratios of monomers for styrene–methyl methacrylate system from intercepts of the plot of f_1f_2/F_1F_2 vs. f_1: (▲) Ref. 3; (O) Ref. 4.

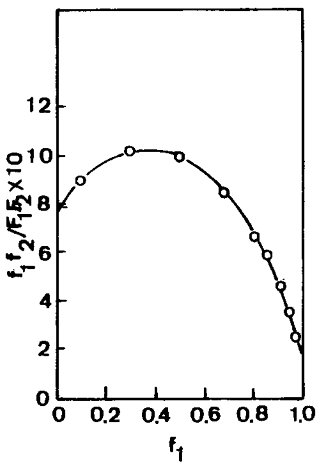

Fig. 2. Determination of reactivity ratios of monomers for methyl methacrylate–isoprene system from intercepts of the plot of f_1f_2/F_1F_2 vs. f_1.

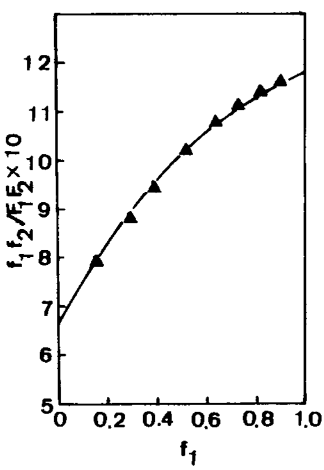

Fig. 3. Determination of reactivity ratios of acrylonitrile–ethyl acrylate system from intercepts of the plot of f_1f_2/F_1F_2 vs. f_1.

TABLE II
Monomer Reactivity Ratios Obtained by This Method and Literature Values

Systems	This method (r_1, r_2)	Literature values (r_1, r_2)	Remarks
Styrene–methyl methacrylate	(0.53, 0.45)	(0.52 ± 0.026, 0.46 ± 0.026)[8]	60°C
Methyl methacrylate–isoprene	(0.22, 0.71)	(0.22, 0.72)[5]	60°C
Acrylonitrile–ethyl acrylate	(1.18, 0.68)	(1.17 ± 0.1, 0.67 ± 0.02)[9]	50°C
Methyl methacrylate–vinyl acetate	(21.2, 0.016)	(20 ± 3, 0.015 ± 0.015)[10]	60°C

According to eqs. (7) and (10), we plot f_1f_2/F_1F_2 against f_1 or f_2. Then, the monomer reactivity ratios may be found from the intercepts of the curve at $f_1 = 0$ and $f_1 = 1$ simultaneously. We do not suggest that the r_i values be determined by use of eqs. (4) and (9). The main reason is that the plot of f_1f_2/F_1F_2 against f_1 gives a much more smooth curve than the plot of f_1/F_1 against f_1 or f_2/F_2 against

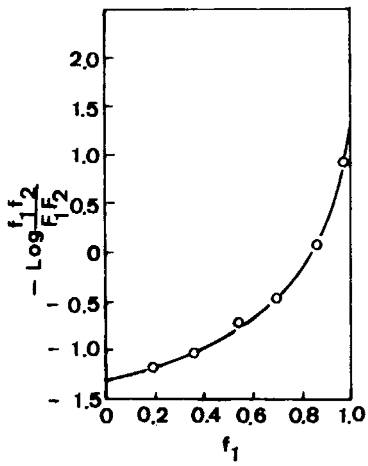

Fig. 4. Determination of reactivity ratios of monomers for vinyl acetate–methyl methacrylate system from intercepts of the plot of f_1f_2/F_1F_2 vs. f_1.

f_1 does. The other reason is that the former procedure needs only one plot for estimating r_i, but the latter technique requires two plots for finding r_i.

This method was verified by testing four copolymerization systems: styrene(1)–methyl methacrylate(2), methyl methacrylate(1)–isoprene(2), acrylonitrile(1)–ethylacrylate(2), and vinyl acetate(1)–methyl methacrylate(2). The data of Bevington et al.,[3] Kuo and Chen,[4] Haward,[5] Brandrup,[6] and Atherton and North[7] shown in Table I, were used to make the plots of Figures 1 to 4. The monomer reactivity ratios r_1 and r_2 for the illustrated four systems were obtained from the intercepts of the plots at $f_1 = 1$ and 0, respectively. The subindex 1 and 2 denote monomers 1 and 2, respectively. The results were given in Table II. For the MMA–VAc system the monomer reactivity ratios were determined from the logarithmic plot of f_1f_2/F_1F_2 vs. f_1 instead of using the ordinary plot, because the reactivity ratio for vinyl acetate is very small, i.e., $r_1 = 0.015$. If the ordinary plot is used, then the intercept for r_1 is too small for a precision determination. The literature values of these four copolymerizations are also listed in the same table. We find that the monomer reactivity ratios determined by this method are in very good agreement with the literature values.

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