

Graphical Presentation of the Copolymerization Equation and of Conversion in Batch Copolymerization

The Copolymerization Equation

The copolymerization equation (ref. 1-3), which relates instantaneous copolymer composition to instantaneous reactor composition and reactivity ratios for a free-radical copolymerization, may be given in the form:

$$Z_{12} = (r_1 z_{12} + 1) / [(r_2 / z_{12}) + 1] \quad (1)$$

where r_1 and r_2 are the two reactivity ratios, and Z_{12} and z_{12} are polymer and reactor compositions expressed as mole ratios of monomer 1 to monomer 2. It is the purpose of this paper to point out a particularly useful and simple method of plotting this relation. Further, it will be shown how this plot may be used to follow reactor and copolymer composition changes with conversion in a batch reaction.

The two variables y and x are defined as

$$y = \ln Z_{12} \quad (2A)$$

$$x = \ln z_{12} \quad (2B)$$

where y and x may be thought of as relative polymer and reactor compositions. In terms of these variables the copolymerization equation (1) becomes:

$$y = \ln [(r_1 e^x + 1) / (r_2 e^{-x} + 1)] \quad (3)$$

A plot of this function for a given r_1 and r_2 has a number of interesting and useful characteristics.

(a) The function has an upper and a lower asymptote, both of which have unit slope. If y^U designates the upper and y^L the lower asymptote, their equations are:

$$y^U = \ln r_1 + x \quad (4A)$$

$$y^L = -\ln r_2 + x \quad (4B)$$

(b) The y and x intercepts of the upper asymptote occur at $\ln r_1$ and $\ln (1/r_1)$ and for the lower asymptote at $\ln (1/r_2)$ and $\ln r_2$.

(c) The distance from the x intercept of the lower asymptote to the x intercept of the upper asymptote is $-\ln p$, where p is the product of reactivity ratios, $r_1 r_2$.

(d) The function itself has an x intercept of $1/2 \ln (r_2/r_1)$, which is midway between the x intercepts of the two asymptotes. Further, this point is at the inflection of the curve and is a center of symmetry, i.e., $y(U) = -y(-U)$, where $U = x - x_i$ and $x_i = 1/2 \ln (r_2/r_1)$.

(e) The slope of the function at the inflection (which corresponds to 1:1 copolymer composition) is:

$$(dy/dx)_i = 2/[1 + (1/\sqrt{p})] \quad (5)$$

The above characteristics are shown in Figure 1. It may be noted that the shape of the curve is completely determined by the product of reactivity ratios, p , whereas the placement of the curve along the x axis is determined by the quotient of reactivity ratios, $q = r_2/r_1$, or more precisely, \sqrt{q} .

The shape of the curve falls into one of three forms, depending on whether p is less than, equal to, or greater than one. p less than one corresponds to a point below the

downward sloping diagonal line in Figure 2, which displays the $\ln r_1, \ln r_2$ plane. This form might be called the "chair" form and is the form shown in Figure 1. It is characterized by a slope at the inflection between 0 and 1 and by the upper asymptote intercepting the x axis to the right of the lower asymptote x intercept. The case of $p = 1$ is a de-

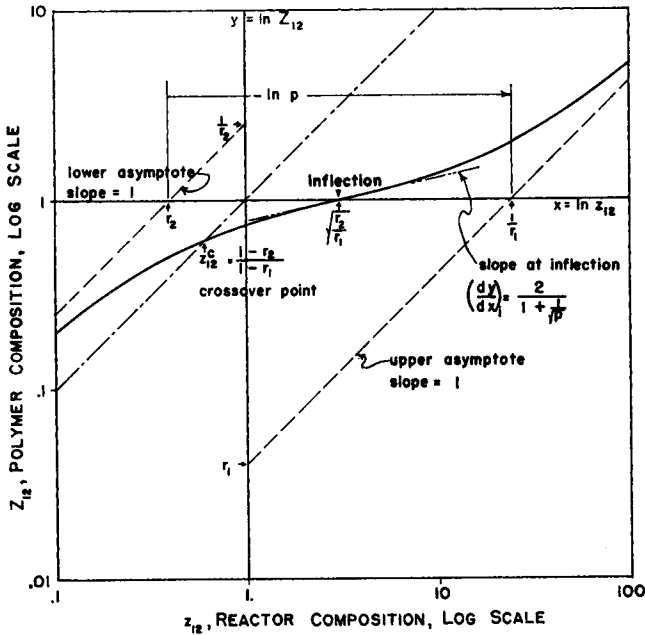


Fig. 1. Geometry of the copolymerization equation.

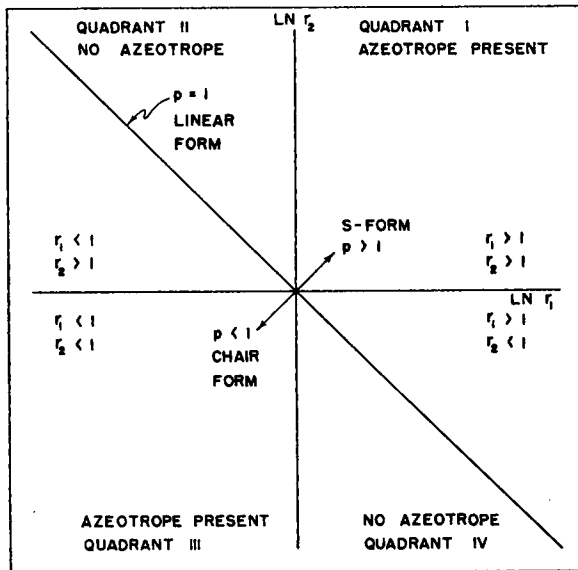


Fig. 2. The $\ln r_1, \ln r_2$ plane.

generate case for which the two asymptotes and the function itself coincide in a single straight line (linear form). The r_1, r_2 pairs which yield this case are points on the diagonal line in Figure 2. The third form ($p > 1$) might be called the "S" form and results from r_1, r_2 pairs above the diagonal in Figure 2. The slope at the inflection is between 1 and 2 and the x intercept of the upper asymptote is to the left of the lower asymptote x intercept.

If one places a line of unit slope through the origin of the x - y plot, the intersection with the composition function, if present, corresponds to the azeotrope. This point at which the reactor and polymer compositions are equal is sometimes called the crossover point and occurs at a composition of $Z_{12}^C = z_{12}^C = (1 - r_2)/(1 - r_1)$. The crossover is present when r_1 and r_2 are in quadrants I and III and absent when they are in II and IV of Figure 2. At any point on the composition function which is below the unit slope line through the origin, the direction of composition change in a batch reactor is to the right, and at points above the line, to the left.

A plot of experimental data from steady-state continuous or low-conversion batch reactions in the form y versus x provides simple visual estimates of the two reactivity ratios (the y and x intercepts of the upper and lower asymptotes) once the geometry of the curve in these coordinates is understood. These visual estimates may be used as initial estimates for a more precise determination of r_1 and r_2 using the nonlinear least-squares techniques described in ref. 4.

Conversion in Batch Copolymerization

In a batch copolymerization one may define the molar conversion, C , as the fraction of the initial moles of monomer 1 and 2 which have reacted, then

$$1 - C = (m_1 + m_2)/(m_1^\circ + m_2^\circ) = [(z_{12} + 1)/(z_{12}^\circ + 1)](m_2/m_2^\circ) \quad (6)$$

where the $^\circ$ superscript indicates initial conditions. Taking the \ln of both sides of (6) yields:

$$\ln(1 - C) = \ln[(z_{12} + 1)/(z_{12}^\circ + 1)] + \ln(m_2/m_2^\circ) \quad (7)$$

The integrated form of the copolymerization equation of Mayo and Lewis (Equation 11 of ref. 2) which is valid if both r_1 and r_2 are not one is:

$$\ln\left(\frac{m_2}{m_2^\circ}\right) = \frac{r_2}{1 - r_2} \ln\left(\frac{z_{12}}{z_{12}^\circ}\right) - \frac{1 - r_1 r_2}{(1 - r_1)(1 - r_2)} \ln\left(\frac{(1 - r_2) - (1 - r_1)z_{12}}{(1 - r_2) - (1 - r_1)z_{12}^\circ}\right) \quad (8)$$

Elimination of $\ln(m_2/m_2^\circ)$ between (7) and (8) gives the following equation for molar conversion as a function of the initial and current reactor compositions and the reactivity ratios:

$$\begin{aligned} \ln(1 - C) = & \ln\left(\frac{z_{12} + 1}{z_{12}^\circ + 1}\right) + \frac{r_2}{1 - r_2} \ln\left(\frac{z_{12}}{z_{12}^\circ}\right) \\ & - \frac{1 - r_1 r_2}{(1 - r_1)(1 - r_2)} \ln\left(\frac{(1 - r_2) - (1 - r_1)z_{12}}{(1 - r_2) - (1 - r_1)z_{12}^\circ}\right) \quad r_1 \neq 1, r_2 \neq 1 \quad (9A) \end{aligned}$$

This is also equivalent to Meyer and Lowry's equation 1 (ref. 5). The special cases of $r_1 = 1, r_2 \neq 1$ and $r_1 \neq 1, r_2 = 1$ have been solved by Meyer and Lowry. In the symbolism of this paper their equations 2 of Appendix I and II become:

$$\ln(1 - C) = \ln\left(\frac{z_{12} + 1}{z_{12}^\circ + 1}\right) + \frac{r_2}{1 - r_2} \ln\left(\frac{z_{12}}{z_{12}^\circ}\right) + \frac{z_{12} - z_{12}^\circ}{1 - r_2} \quad r_1 = 1, r_2 \neq 1 \quad (9B)$$

and

$$\begin{aligned} \ln(1 - C) = & \ln\left(\frac{z_{12} + 1}{z_{12}^\circ + 1}\right) - \frac{1}{1 - r_1} \ln\left(\frac{z_{12}}{z_{12}^\circ}\right) + \frac{1}{1 - r_1} \left(\frac{1}{z_{12}} - \frac{1}{z_{12}^\circ}\right) \\ & \quad r_1 \neq 1, r_2 = 1 \quad (9C) \end{aligned}$$

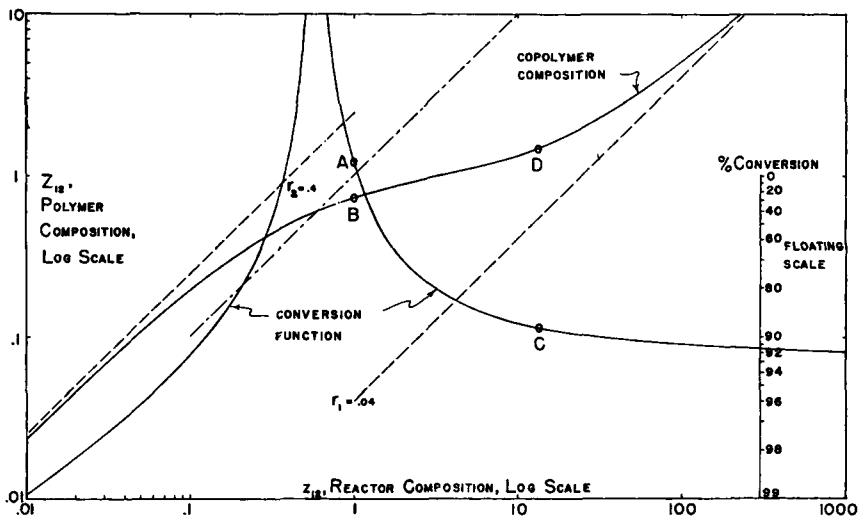


Fig. 3. Copolymer composition and conversion as a function of reactor composition.

The final case of $r_1 = r_2 = 1$ is trivial, since the reaction can proceed to 100% conversion from any starting composition with no change in reactor or polymer compositions, i.e., $Z_{12} = z_{12} = z_{12}^0 = Z_{12}^0$.

In order to display the conversion behavior graphically, the conversion function, $f(z_{12})$, is defined as follows:

$$\ln f(z_{12}) = \ln(z_{12} + 1) + \frac{r_2}{1 - r_2} \ln z_{12} - \frac{1 - r_1 r_2}{(1 - r_1)(1 - r_2)} \ln |(1 - r_2) - (1 - r_1)z_{12}| \quad r_1 \neq 1, r_2 \neq 1 \quad (10A)$$

$$\ln f(z_{12}) = \ln(z_{12} + 1) + \frac{r_2}{1 - r_2} \ln z_{12} + \frac{z_{12}}{1 - r_2} \quad r_1 = 1, r_2 \neq 1 \quad (10B)$$

$$\ln f(z_{12}) = \ln(z_{12} + 1) - \frac{1}{1 - r_1} \ln z_{12} + \left(\frac{1}{1 - r_1}\right) \left(\frac{1}{z_{12}}\right) \quad r_1 \neq 1, r_2 = 1 \quad (10C)$$

Comparison of equations 9 and 10 shows that:

$$\ln(1 - C) = \ln f(z_{12}) - \ln f(z_{12}^0) \quad (11)$$

This property provides a useful basis for displaying conversion as a function of reactor composition and of polymer composition when combined with the copolymer equation plot. One simply plots the conversion function on the same figure as the copolymer equation, using logarithmic scales for z_{12} and $f(z_{12})$. Both curves use the same abscissa, $x = \ln z_{12}$, but their ordinate scales differ. A "floating" ordinate scale is associated with the conversion function. Once the initial reactor composition, z_{12}^0 , is given, the zero of this scale is placed at the ordinate corresponding to the z_{12}^0 abscissa. By this means the same curve may be used for any initial reactor composition. The floating ordinate scale, which is logarithmic in $1 - C$ may be labeled with per cent conversion. One decade in $f(z_{12})$ corresponds to one decade in $1 - C$.

Figure 3 illustrates this procedure. The conversion function was plotted using the extreme right scale. In use, the floating per cent conversion scale is used, after vertical displacement of its zero to the ordinate on the conversion function corresponding to the

desired initial reactor composition. For example, with a 1:1 initial reactor composition, the per cent conversion scale is moved up to the level of point *A* on the conversion function. The initial polymer composition, 0.74, is found from point *B*. The reactor composition at any desired conversion may be determined from the conversion function. At 90% conversion, point *C*, the reactor composition is about 13. The polymer composition at this conversion is 1.5, from point *D*.

If neither r_1 nor r_2 is one, the conversion function on this logarithmic plot approaches linearity at sufficiently high and sufficiently low reactor compositions. For high z_{12} , the limiting slope, $d \ln(1 - C)/d \ln z_{12}$, is $-r_1/(1 - r_1)$, and for low z_{12} , the limiting slope is $r_2/(1 - r_2)$. The conversion function necessarily increases without limit as the azeotrope or crossover point is approached at a reactor composition of $(1 - r_2)/(1 - r_1)$.

If r_1 is 0.5 the limiting slope becomes -1 at high z_{12} , and if r_2 is 0.5 the limiting slope becomes 1 at low z_{12} . The limiting slope of unity implies that a decade change in $1 - C$ corresponds to a decade change in reactor or polymer composition. Values of the reactivity ratios less than or greater than 0.5 have limiting slopes, respectively, less than or greater than unity (in absolute value). The absolute value of the limiting slope increases without limit as the reactivity ratio approaches one from either side and it approaches one from above as the reactivity ratio increases without limit. With respect to "homopolymerization" during the final stages of polymerization, the value of 0.5 for a reactivity ratio does not seem to have quite such a critical nature as the limiting behavior of $(dm/m^\circ)/dF_1$ as F_1 approaches one, reported by Meyer and Lowry, ref. 5, might suggest.

A more practical approach to the question of "homopolymerization" at some stage of the reaction might be to arbitrarily specify some polymer mole ratio which one was willing to accept as essentially homopolymer, and to then determine the conversion which yielded this polymer composition for some specific initial reactor composition. When viewed in this manner, values of the reactivity ratio greater than 0.5 (but excluding 1) may produce "homopolymer," and conversely, for values less than 0.5 the conversion at which "homopolymer" occurs may be so far beyond the conversion to which the reaction will be taken that homopolymerization will be no problem.

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