

NOTE

Comments on "A New Copolymerization Equation" (C. Zhou and S. Lin, *J. Appl. Polym. Sci.*, 55, 641–643, 1995)

Polymer composition drift during batch copolymerization is a well-known phenomenon. It is caused by distinct reactivities of different radical–monomer pairs. Based on the terminal model, the following equation was proposed by Mayo and Lewis¹ some fifty years ago. It relates the instantaneous copolymer composition (F_1 and F_2) to monomer fractions (f_1 and f_2):

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2}$$

$$F_2 = 1 - F_1 \quad (1)$$

where r_1 and r_2 are the reactivity ratios. In 1965, Meyer and Lowry² derived the relationship between the fractions (f_1 and f_2) and monomer conversion (c):

$$c = 1 - \left(\frac{f_1}{f_{1,0}}\right)^\alpha \left(\frac{f_2}{f_{2,0}}\right)^\beta \left(\frac{f_{1,0} - \delta}{f_1 - \delta}\right)^\gamma$$

$$\alpha = \frac{r_2}{1 - r_2} \quad \beta = \frac{r_1}{1 - r_1}$$

$$\gamma = \frac{1 - r_1 r_2}{(1 - r_1)(1 - r_2)} \quad \delta = \frac{1 - r_2}{2 - r_1 - r_2} \quad (2)$$

where the subscript 0 indicates an initial value. These two equations allow one to calculate the composition for copolymer chains produced instantaneously in a batch reactor as a function of monomer conversion, provided that the terminal model is valid.

The recent paper by Zhou and Lin³ suggests that a new instantaneous copolymerization equation for the calculation of copolymer composition as follows is valid:

$$F_1 = \frac{f_1 \ln[(1 - c)(f_1/f_{1,0})]}{f_1 \ln[(1 - c)(f_1/f_{1,0})] + f_2 \ln[(1 - c)(f_2/f_{2,0})]} \quad (3)$$

The feature of this equation is its independence of reactivity ratios; as it can be seen, these ratios are absent from their equation. The authors claim that the equation can be used to obtain the copolymer composition from experimental data when the reactivity ratios are unknown. They

also tried to verify this equation using the classical literature data of styrene/methyl methacrylate,⁴ methyl methacrylate/vinylidene chloride,⁵ and styrene/acrylonitrile⁵ and found that the comparisons with eq. (1) were satisfactory.

Unfortunately, a careful examination of eq. (3) reveals that it is not generally applicable. An assumption that does not have general validity was employed in its derivation. The authors integrated the following rate expressions:

$$-d[M_1]/dt = (k_{11}[M_1^*] + k_{21}[M_2^*])[M_1]$$

$$-d[M_2]/dt = (k_{12}[M_1^*] + k_{22}[M_2^*])[M_2] \quad (4)$$

to yield

$$-\ln([M_1]/[M_1]_0) = (k_{11}[M_1^*] + k_{21}[M_2^*])t$$

$$-\ln([M_2]/[M_2]_0) = (k_{12}[M_1^*] + k_{22}[M_2^*])t \quad (5)$$

where $[M]$, $[M^*]$, k , and t are monomer concentration, radical concentration, propagation rate constants, and polymerization time, respectively. The problem associated with this integration is that the right-hand terms

$$k_{11}[M_1^*] + k_{21}[M_2^*] \quad \text{and} \quad k_{12}[M_1^*] + k_{22}[M_2^*]$$

are assumed to be independent of time during copolymerization. This assumption is very specific and cannot be generally satisfied. Even under the conditions of constant total radical concentration ($[M_1^*] + [M_2^*]$) and propagation rate constants, the fractions of polymeric radicals of the two types are still subject to change. The use of the long chain assumption, $k_{12}[M_1^*][M_2] = k_{21}[M_2^*][M_1]$, results in

$$\phi_1^* = \frac{[M_1^*]}{[M_1^*] + [M_2^*]} = \frac{k_{21} f_1}{k_{21} f_1 + k_{12} f_2} \quad (6)$$

It is evident that the monomer fractions must be kept constant during a batch polymerization to have constant radical fractions. This requirement can only be satisfied at the azeotropic point. Indeed, substitution of $f_1 = f_{1,0}$ into their equation yields $F_1 = f_1$.

The question of whether it is impossible to derive a general $F - f - c$ relationship independent of reactivity ratios can be readily answered by analyzing eqs. (1) and (2). The two equations contain two reactivity ratios. An additional relationship is required to eliminate these parameters. For example, when $r_1 r_2 = 1$, eq. (1) becomes

$$F_1 = \frac{r_1 f_1}{r_1 f_1 + f_2} \quad (7)$$

and eq. (2),

$$\ln(1 - c) = \frac{1}{r_1 - 1} \ln(f_1/f_{1,0}) + \frac{r_1}{1 - r_1} \ln(f_2/f_{2,0}) \quad (8)$$

Elimination of r_1 from the above two equations yields eq. (3). However, this coincidence should not be considered as a justification for the Zhou-Lin equation.³ They suggested that their equation was general; it was not derived for $r_1 r_2 = 1$. This coincidence is due to the fact that when $r_1 r_2 = 1$, $(k_{11}[M_1] + k_{21}[M_2]) / (k_{12}[M_1] + k_{22}[M_2]) = r_1$. Another example is for $r_1 = r_2$,

$$F_1 = \frac{f_1 \ln(1 - c) + f_1(f_1 - f_2) \ln[(f_1 - \frac{1}{2}) / (f_{1,0} - \frac{1}{2})] + f_1 f_2 \ln[(f_1 f_2) / (f_{1,0} f_{2,0})]}{\ln(1 - c) + (f_1 - f_2)^2 \ln[(f_1 - \frac{1}{2}) / (f_{1,0} - \frac{1}{2})] + 2f_1 f_2 \ln[(f_1 f_2) / (f_{1,0} f_{2,0})]} \quad (9)$$

It should be emphasized that such equations are not general; they are applicable only for specific systems. A general $F - f - c$ relationship independent of reactivity ratios does not exist.

As to the comparison of calculations using eq. (3) with eq. (1) for the three copolymerization systems in the paper by Zhou and Lin,³ it is not a surprise that the results are "satisfactory." It is because most of the data have little compositional drift, i.e., the values of $f_1 - f_{1,0}$ are rather small.

In addition, four of the six kinds of copolymerization equations quoted in the paper by Zhou and Lin³ contained errors. In the denominator of the Mayo-Lewis differential equation,¹ r_1 is missing. The numerator of the last term on the right-hand side of the Mayo-Lewis integral equation¹ is $(r_1 - 1)[M_1]/[M_2] - r_2 + 1$, not $(r_1 - 1)[M_1]/[M_2]_0 - r_2 + 1$. The denominator of the right-hand term of the Walling-Briggs equation⁶ is $[M_1]_0 + r_2[M_2]_0$, not

$[M_1] + r_2[M_2]$. It should also be pointed out that this equation is not generally applicable; it is only an approximation valid when $\ln([M_1]/[M_1]_0) - \ln([M_2]/[M_2]_0)$ is small. The Skeist equation⁷ is $\ln(M/M_0) = \int_{f_{1,0}}^{f_1} df_1 / (F_1 - f_1)$.

In summary, the reactivity ratio independent $F - f - c$ relationship recently derived by Zhou and Lin³ is in general incorrect and misleading. The reason for this is that an unrealistic assumption was introduced in its derivation. The paper also contains other errors as have been pointed out. We hope this note can serve to clarify these misconceptions. Furthermore, on the basis of our analysis of the Mayo-Lewis¹ and Meyer-Lowry² equations, we conclude that a general $F - f - c$ relationship independent of reactivity ratios does not exist; such a relationship is inevitably system specific, as the ones derived in this note for $r_1 r_2 = 1$ and $r_1 = r_2$.

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