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On Numerical Problems When Reactivity Ratios Are Computed Using the Integrated Copolymer Equation

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The copolymer equation introduced in 1944^{1,2}

$$\frac{dM_1}{dM_2} = \frac{r_1 q + 1}{r_2/q + 1} \quad (1)$$

describes, at any time during the course of a reaction, the exact relationship between the composition of the momentary monomer feed mixture ($q = M_1/M_2$) and the instantaneous copolymer composition (dM_1/dM_2) formed. A number of methods to determine the reactivity ratios r_1 and r_2 are based on eq. (1) using observed feed and copolymer compositions. However, as the degree of conversion increases most copolymerization systems will show a drift in both the monomer feed ratio and the copolymer composition, due to the different reactivities of the radical toward each of the monomers. So model (1) is not exactly valid for nonzero conversion. In some methods this problem is approximately solved by using average feed ratio and copolymer composition or some other approximation.³⁻⁶ Nevertheless, all methods result in biased values for the reactivity ratios. This bias is not always insignificant.⁷

Integration of eq. (1) gives an exact relationship between conversion (based, for example, on monomer 2) and the monomer feed ratio:

$$G_2 = \left(\frac{q}{q_0}\right)^{-1-x_2} \left(\frac{q - x_1/x_2}{q_0 - x_1/x_2}\right)^{1+x_1+x_2} \quad (2)$$

where ($G_2 = 1 -$ conversion monomer 2, $q_0 =$ initial q , $x_1 = 1/(r_1 - 1)$, and $x_2 = 1/(r_2 - 1)$). Equation (2) is valid also for high conversion. From a computational point of view eq. (2) is far more difficult than eq. (1). This may be the reason that methods based on eq. (2) have not been considered in literature until quite recently.^{8,9} An additional problem is that G_2 and q both are measured with error. This means that the nonlinear regression approach, where q is treated as if it were measured without error, is inadequate and may result in strongly biased values for the reactivity ratios.^{8,10}

A method for the determination of r values, which takes into account measurement errors in both G_2 and q and uses the integrated copolymer equation, has been described in literature⁸ and is reported to result in reliable r values.^{7,11} Although the results are not very sensitive to the error structure of the observations,¹¹ some information on it is necessary for the method to be applicable. In this article we

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will describe and solve two numerical problems that may occur when applying the above method: the problem of the *dangerous region* and the problem of the *forbidden region*.

THE DANGEROUS REGION

As can easily be seen, eq. (2) is numerically unstable in the neighborhood of $r_1 = 1$ or $r_2 = 1$. On a computer, intermediate values of r_1 that are too close to 1 will give rise to abortion of the execution of a program that uses eq. (2) because of exponential overflow. To avoid unnecessary abortion, eq. (2) is replaced by an approximation. By taking the limit $r_1 \rightarrow 1$, it can be seen that eq. (2) transforms to:

$$G_2 = (q/q_0)^{-1-x_2} \exp[x_2(q_0 - q)] \quad (3)$$

Likewise, the derivative of G_2 with respect to r_1 converges to:

$$\frac{\partial G_2}{\partial r_1} = G_2 x_2 (q_0 - q) [1 + x_2 + x_2(q_0 + q)/2] \quad (4)$$

where G_2 is given by eq. (3) of course, instead of by eq. (2). As soon as r_1 gets too close to 1 one should use eqs. (3) and (4) instead of eq. (2) and its derivative. To determine what is meant by "too close" we first rewrite eq. (2):

$$G_2 = \left(\frac{q_0(q - x_1/x_2)}{q(q_0 - x_1/x_2)} \right)^{1+x_2} \left(\frac{1 - qx_2/x_1}{1 - q_0x_2/x_1} \right)^{x_1} \quad (5)$$

The first factor converges to $(q_0/q)^{1+x_2}$ for $r_1 \rightarrow 1$. With respect to the second factor we have that (ref. 12, eq. 4.2.36)

$$\exp(-qx_2) > (1 - qx_2/x_1)^{x_1} > \exp[(-qx_1x_2/(x_1 - qx_2))]$$

where for simplicity it is assumed that x_1 and $x_2 > 0$ (if one or both of the x 's are smaller than zero, the results remain essentially the same).

A similar expression with q_0 instead of q is valid for the denominator of the second factor in eq. (5). From these two inequalities it immediately follows that:

$$\exp\left(-qx_2 + \frac{q_0x_1x_2}{x_1 - q_0x_2}\right) > \left(\frac{1 - qx_2/x_1}{1 - q_0x_2/x_1}\right)^{x_1} > \exp\left(q_0x_2 - \frac{qx_1x_2}{x_1 - qx_2}\right)$$

Approximations (3) and (4) may be used if the lower and upper bounds of this inequality are almost equal, i.e.,

$$\exp\left[x_2\left(q + q_0 - \frac{qx_1}{x_1 - qx_2} - \frac{q_0x_1}{x_1 - q_0x_2}\right)\right] < 1 + \epsilon$$

with ϵ small. For large x_1 this is approximately equivalent to

$$x_1 > x_2^2(q_0^2 + q^2)/\epsilon \quad (6)$$

If $r_1 < 1$ then x_1 should be replaced by $|x_1|$. The case that $r_2 \rightarrow 1$ is very similar. Equation (2) transforms to

$$G_2 = \left(\frac{q}{q_0}\right)^{x_1} \exp\left[x_1\left(\frac{1}{q_0} - \frac{1}{q}\right)\right] \quad (7)$$

The derivative with respect to r_2 converges to

$$\frac{\partial G_2}{\partial r_2} = G_2 x_1 \left(\frac{1}{q_0} - \frac{1}{q}\right) \left[1 + x_1 + x_1 \left(\frac{1}{q_0} + \frac{1}{q}\right)/2\right] \quad (8)$$

Equations (7) and (8) may be used as a sufficiently accurate approximation to eq. (2) and its derivative when

$$x_2 > x_1^2(1/q_0^2 + 1/q^2)/\epsilon \quad (9)$$

If $r_2 < 1$ then x_2 should be replaced by $|x_2|$.

Note: If $r_1 \approx 1$ and $r_2 \approx 1$ neither eq. (3) nor eq. (7) is applicable. Rarely it may happen that an iterative process winds up with intermediate values of r_1 and r_2 that are almost equal to 1. One should then use some *ad hoc* method to escape from this doubly dangerous region.

THE FORBIDDEN REGION

Equation (2) is no longer of any use when

$$(q - x_1/x_2)/(q_0 - x_1/x_2) < 0 \quad (10)$$

The execution on a computer of an estimation program that uses eq. (2) will abort because of the invalid argument error. In the course of an iterative estimation process, however, intermediate values of q_0 , q , r_1 , and r_2 that satisfy eq. (10) may occur. These points will be called "forbidden" (see Fig. 1). In order to avoid abortion of the process in that case several *ad hoc* methods are feasible. The one the authors chose is based upon the fact that estimates result from the minimization of some criterion (least squares, for example). When forbidden points occur during this minimization the criterion is assigned a so-called "penalty value" with the effect that the minimization process turns away from those points.

When both r_1 and r_2 are smaller (or larger) than 1, "azeotropic" copolymerization may occur. This means that q remains equal q_0 regardless of the conversion. This only happens when starting at monomer feed ratio $q_0 = x_1/x_2 = q_A$ (see Fig. 1). Equation (10) and thus eq. (2) now become undefined. Azeotropic copolymerization, however, gives exact information about the linear combination of r_1 and r_2 , that is given by $q_A = x_1/x_2$ and no information about any other linear combination. So, if one happens to stumble upon azeotropic copolymerization, one may use this experiment to determine that particular linear combination, substitute it into the integrated equation, and determine the other linear combinations from the nonazeotropic experiments to estimate x_1 and x_2 .

For experiments with starting monomer feed ratios in the vicinity of q_A , the values of q_0 , q , and x_1/x_2 become almost equal and so a considerable number of forbidden points may occur, especially when the measurement error in q is not negligible compared with the drift in q . Routine penalty-value assignment may then have an unpredictable effect on the estimation process. A way to handle almost azeotropic copolymerizations is to screen the measurements and to remove outliers.

Fig. 1. Momentary monomer feed ratio versus conversion of monomer 2 ($1 - G_2$). Values of r_1 and r_2 , such that $(r_2 - 1)/(r_1 - 1)$ is contained in FR , are forbidden.

CONCLUSION

By solving the numerical problems discussed in this article the integrated copolymer equation considerably gains in usefulness and applicability. Using the integrated equation allows for higher conversions to be taken into account and consequently results in more precise and accurate estimates for the reactivity ratios.^{7,11}

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