NOTE

Monomer Reactivity Ratios in Styrene/2-Ethylhexylacrylate Copolymer

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In a recent article, Kavousian et al.[1] reported the determination of the monomer reactivity ratios for the styrene/2-ethylhexylacrylate monomer pair. They used a terminal model and applied various linear and nonlinear methods, including the errors-in-variable method. Recently, a penultimate model was intensely evaluated[2–6] for copolymerization, particularly for the styrene/methyl methacrylate system, because of the terminal model's ability to explain composition on the one hand and its inability to explain rate data on the other hand. Fukada et al.[7] proposed an implicit penultimate model that introduced radical reactivity ratios s_1 and s_2 and the effect of penultimate units on specific rates of propagation. One inherent limitation of the implicit model is that the introduction of s_1 and s_2, with the assumption of $r_1 = r_1'$ and $r_2 = r_2'$ (where r_1, r_1', r_2, and r_2' are the monomer reactivity ratios), implies an insensitivity of s_1 and s_2 to the monomer types, which is hard to comprehend. Recent studies[5,6] have also indicated that an explicit penultimate model ($r_1 \neq r_1'$, $r_2 \neq r_2'$, $s_1 \neq s_2$), rather than an implicit one ($r_1 = r_1'$, $r_2 = r_2'$, $s_1 \neq s_2$), seems to explain the styrene/methyl methacrylate system better. Attempts have, therefore, been made to determine consistent and reliable values of all four reactivity ratios through nonlinear regression methods.[8–11] However, the nonuniqueness of the reactivity ratios signifying the penultimate unit effect and their dependence on initial guess values have been indicated. We recently carried out an analysis[12] of nonlinear regression methods and identified the simple yet powerful capability of a nonlinear curve-fitting method (Curve Expert).[13] We observed that the use of approximate values of r_1 and r_2 and the assumption of $r_1 = r_1'$ and $r_2 = r_2'$ gave reasonably consistent values for all four reactivity ratios for the styrene/methyl methacrylate monomer pair. The four reactivity ratios explain compositional data better than the optimum terminal-model values.

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Because the styrene/2-ethylhexylacrylate monomer pair is somewhat similar to the styrene/methyl methacrylate system, we thought that it would be interesting to apply the penultimate model to this system and determine the values of the reactivity ratios. We applied the following compositional equation as implicit in the penultimate model. This was chosen as a power-law equation to subject the compositional data to the Curve Expert regression program:

$$F_1 = \frac{a_1x^4 + a_2x^3 + a_3x^2 + a_4x}{b_1x^4 + b_2x^3 + b_3x^2 + b_4x + b_5}$$

where F_1 is the molar fraction of monomer 1 in the copolymer, x is the molar ratio of monomer 1 in the feed, a_1 is equal to r_1r_1', a_2 is equal to $r_1r_1'r_2' + 2r_1'$, a_3 is equal to $2r_1'r_2' + 1$), a_4 is equal to r_2', b_1 is equal to r_1r_1', b_2 is equal to $r_1r_1'r_2' + 3r_1'$, b_3 is equal to $4r_1'r_2' + 2$, b_4 is equal to $3r_2' + r_1'r_2r_2'$, and b_5 is equal to r_2r_2'.

This equation was derived from the classical copolymer composition equation:

$$\frac{F_1}{F_2} = \left\{1 + \frac{r_1'x(r_1x + 1)}{r_1'x + 1}\right\} \Big/ \left\{1 + \frac{r_2'(r_2 + x)}{x(r_2' + x)}\right\}$$

where F_2 is equal to $1 - F_1$.

The square of the sum of residuals (SSR) and the standard deviation (SD) were also calculated for the styrene/2-ethylhexylacrylate monomer pair with the compositional data[1] and are shown in Table I:

$$\mathrm{SSR} = \sum^{n} (F_{1\,\mathrm{exp}} - F_{1\,\mathrm{cal}})^2$$

$$\mathrm{SD} = \sqrt{\frac{\mathrm{SSR}}{n-1}}$$

where n is the number of data points, $F_{1\ \mathrm{exp}}$ is the experimental F_1 value, and $F_{1\ \mathrm{cal}}$ is the calculated F_1 value. We have included in the table values of the reactivity ratios for

TABLE I
Monomer reactivity ratios, SSR, and SD values as Calculated with Curve Expert Nonlinear Least-square (CE-NLLS) Regression for the Styrene/2-Ethylhexylacrylate System

Model	Reactivity ratio	SSR $\times 10^4$	SD
Terminal	$r_1 = 0.9624$[a]		
	$r_2 = 0.2843$	12.7779	1.3511×10^{-2}
	$r_1 = 0.979$[1]		
	$r_2 = 0.292$	12.9615	1.3608×10^{-2}
Penultimate	$r_1 = 1.0111$[b]		
	$r'_1 = 0.6361$		
	$r_2 = 0.6348$	11.3314	1.2723×10^{-2}
	$r'_2 = 0.1084$		

[a] CE-NLLS guess values $r_1 = 0.979$ and $r_2 = 0.292$.[1]
[b] CE-NLLS guess values $r_1 = r'_1 = 0.979$, $r_2 = r'_2 = 0.292$.[1]

both the terminal and penultimate models along with the values of r_1 and r_2 by error in variable method (EVM), as reported by Kavousian et al.[1]

The values in Table I show that the penultimate-model reactivity ratios explain the compositional data better than the terminal-model reactivity ratios. They also indicate that the terminal-model reactivity ratios, as evaluated with Curve Expert, are at least as good as, if not better than, the values obtained through EVM.

Moreover, the product of the reactivity ratios ($r_1 r_2$), when calculated from the penultimate model, does not indicate alternation, whereas azeotropic behavior at high styrene feed compositions is understandable by both the terminal-model and penultimate-model reactivity ratios. Microstructural evaluation would help in identifying reliable compositions and verifying the theoretical predictions.

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