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How Powerful Are Composition Data in Discriminating between the Terminal and Penultimate Models for Binary Copolymerization?

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ABSTRACT: The terminal model for binary copolymerization is often accepted simply on the grounds that it provides a satisfactory fit to a set of experimental data. The penultimate (and other) models are often not considered or are rejected as making no significant improvement. It is argued that such inferences are invalid unless reference is made to the power of the experiments in estimating penultimate unit effects. A method for assessing the possible magnitude of penultimate unit effects in binary copolymerization is offered. This involves using a nonlinear least-squares method to fit the penultimate model and constructing an approximate 95% joint confidence interval for r_1/r_1' and r_2/r_2'. The method is illustrated with reference to literature data for methyl methacrylate/styrene copolymerization. An analysis of the composition data of Fukuda et al. for this system shows that while the terminal model is a possible solution, the size of the 95% joint confidence interval shows that penultimate unit effects could be substantial and the model may still give an adequate fit to the experimental composition data ($0.4 \leq r_1/r_1' \leq 2.7$ and $0.3 \leq r_2/r_2' \leq 2.2$). Design criteria for evaluation of reactivity ratios which take into account the need for model discrimination are discussed.

An understanding of the factors which influence the composition of copolymers is of significance both for industrial application and for the advancement of polymer science. Of particular importance is a need to have reliable reactivity ratios with which to predict the course of copolymerization and the composition and microstructure of the copolymers produced. At present this need is not satisfied. A variety of factors contribute to this situation and discussions on this can be found in the polymer literature.[1]

In this paper[2] we are concerned specifically with discriminating between the terminal and penultimate models used to describe binary copolymerization and with assessing the power of copolymer composition data in this context. In much of the literature on copolymerization, it is presumed that the terminal model [so called because the propagation rate constants are dependent solely upon the nature of the monomer and the last added (ultimate) unit in the polymer chain] is applicable unless proven otherwise. While this might be consistent with the application of Ockham's razor,[3] it is our view that the influence of remote unit effects on the propagation (and other steps) should *never* be ignored.[4]

It is well recognized that copolymer composition data are often not sufficiently sensitive to enable unambiguous discrimination between polymerization mechanisms.[5] In some cases, the answer may be to turn to other methods of measuring reactivity ratios (e.g., from sequence distribution information).[1] However, often such methods are not applicable and composition measurements are all that is available.

For *any* data set, the four-parameter (penultimate) model will give an improved fit over the two-parameter (terminal) model. Cases have been reported where the improvement in fit is substantial and it is clear that the penultimate model is more appropriate. An example is the copolymerization of styrene and acrylonitrile.[6,7] However, for most cases, the improvement in fit is not statistically significant and estimates of penultimate model reactivity ratios are of low precision. In this circumstance it is common practice to use terminal model reactivity ratios. However, we believe that before using terminal model reactivity ratios for predicting monomer sequence distributions or certain aspects of polymerization kinetics, it is essential that we first assess the power of the experimental data used to derive the reactivity ratios. *It is not sufficient simply to establish that the terminal model fits the data; it is necessary to establish that remote unit effects are negligible.*

One way to demonstrate whether a given set of experimental data are able to discriminate between the terminal and penultimate models and gain some knowledge on the error that may be introduced by choosing the simpler model is to establish what magnitude the penultimate unit effects might assume while remaining consistent with the experimental data. We suggest that a reasonable approach to this end is to obtain estimates of penultimate unit effects, r_1/r_1' and r_2/r_2' (where r_1, r_1', r_2, and r_2' are the penultimate model reactivity ratios) and to use the joint confidence regions for these ratios as a measure of the *possible* deviation from the terminal model. Note that the terminal model corresponds to a special case of the penultimate model where $r_1 = r_1'$ and $r_2 = r_2'$.

We illustrate this method by reexamining recent literature data for the copolymerization of methyl methacrylate (MMA) with styrene. We have chosen to examine this system because of the large body of reliable experimental data available from the literature.

Estimation of Reactivity Ratios. There have been many studies on the copolymerization of MMA and styrene.[8,9] Most have agreed that the dependence of the instantaneous copolymer composition on monomer feed composition is adequately described by the terminal model.

Fukuda et al. have recently conducted comprehensive studies of the kinetics of styrene/MMA copolymerization in bulk[8] and in toluene[9] solution. As part of their investigations, they determined low-conversion polymer compositions by combustion analysis and used these data to evaluate terminal model reactivity ratios. They showed that the terminal model was able to explain the dependence of F_1 (the mole fraction of monomer 1 in the polymer) on f_1 (the mole fraction of monomer 1 in the feed) within experimental error. The estimated values of r_1 and r_2 were in accord with previous studies of this system.

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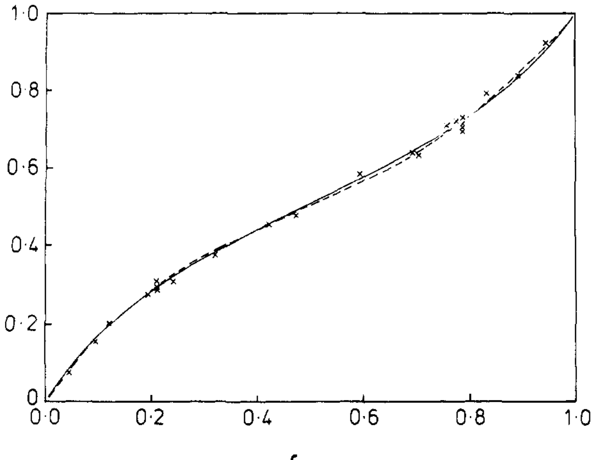

Figure 1. Dependence of the instantaneous copolymer composition (F_1) on the monomer feed composition (f_1) for bulk MMA/styrene copolymerization.[8] The curves were calculated by using the best estimates of the terminal (dotted line) and penultimate (solid line) model reactivity ratios (see text); (×) experimental points.

We have applied a nonlinear least-squares method[10] to fit the terminal model to Fukuda's data. The best estimates of r_1 and r_2 (bulk, 0.52, 0.46; toluene, 0.53, 0.39) agree closely with those reported by Fukuda and the 95% confidence regions are small. Analysis of the plot of residuals for the bulk data gives some indication that the variance declines toward $f_1 = 0.0$ and 1.0 but not sufficiently to justify a weighted analysis. No systematic deviation from the terminal model is evident.

The four-parameter penultimate model was then fitted to Fukuda's data by using nonlinear least squares. The estimates of r_1, r_1', r_2, and r_2' are consistent with substantial penultimate unit effects (bulk, 0.65, 0.33, 0.50, 0.33; toluene, 0.53, 0.66, 0.35, 0.54). However, the difference between the two predicted curves is extremely small (refer to Figures 1 and 2) and application of the familiar F test showed the drop in the residual sum of squares was not at all significant (bulk, "$F_{2,22}$" = 1.36; toluene, "$F_{2,6}$" = 1.0). Furthermore, it was found that other substantially different sets of r_1, r_1', r_2, and r_2' also gave an adequate fit to the experimental data.

In order to better ascertain the magnitude of the penultimate unit effects which are consistent with experimental data, we applied a nonlinear least-squares method[11] to obtain estimates of log (r_1), log (r_2), log (r_1/r_1'), and log (r_2/r_2') and constructed the joint confidence regions for r_1/r_1' and r_2/r_2'. The results of our analysis of Fukuda's data[8,9] are shown in Figure 3. The 95% confidence regions include the values $r_1/r_1' = r_2/r_2' = 1.0$ (the terminal model). However, it is clear that the experimental data do not prove the terminal model. The low power of the experimental data with respect to model discrimination is clearly demonstrated by the large size of the confidence intervals.

Design Criteria for Model Discrimination. Two-point design criteria for the estimation of terminal model reactivity ratios have been reported. These schemes consider the sensitivity of the polymer composition to the feed composition[12-14] and the error structure of the variables[15] but do not take into account a need to distinguish the various models used to describe copolymerization. For the bulk MMA/styrene copolymerization data reported by Fukuda[8] the optimal design points correspond to $f_1 = 0.184$ and 0.796.[11] Fukuda chose similar compositions to carry out replicate experiments (same f_1).[8] However, at these feed compositions, both the terminal and penultimate

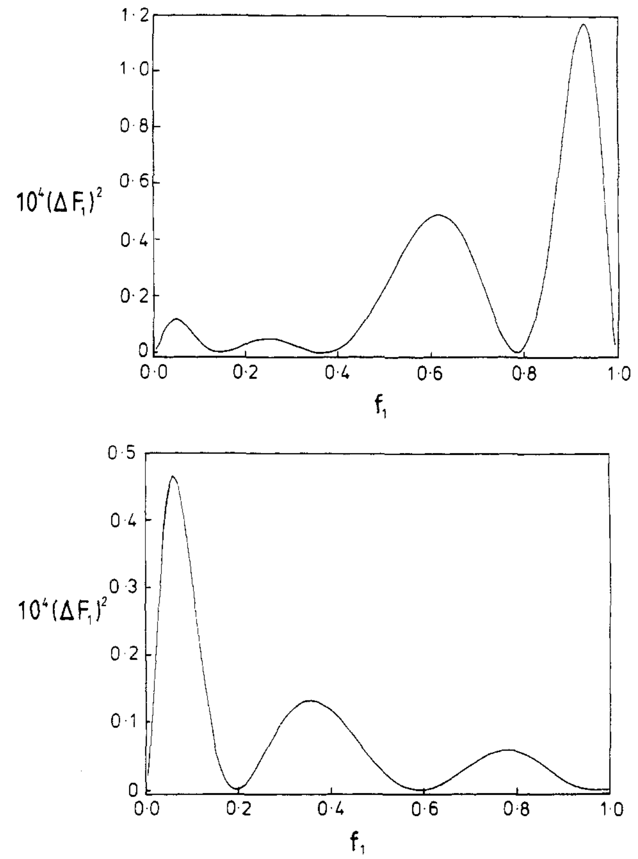

Figure 2. Plot of ΔF_1 [$=F_1$(penultimate model) − F_1(terminal model)]^2 versus f_1 for MMA/styrene copolymerization in (a, top) bulk[8] and (b, bottom) toluene solution.[9]

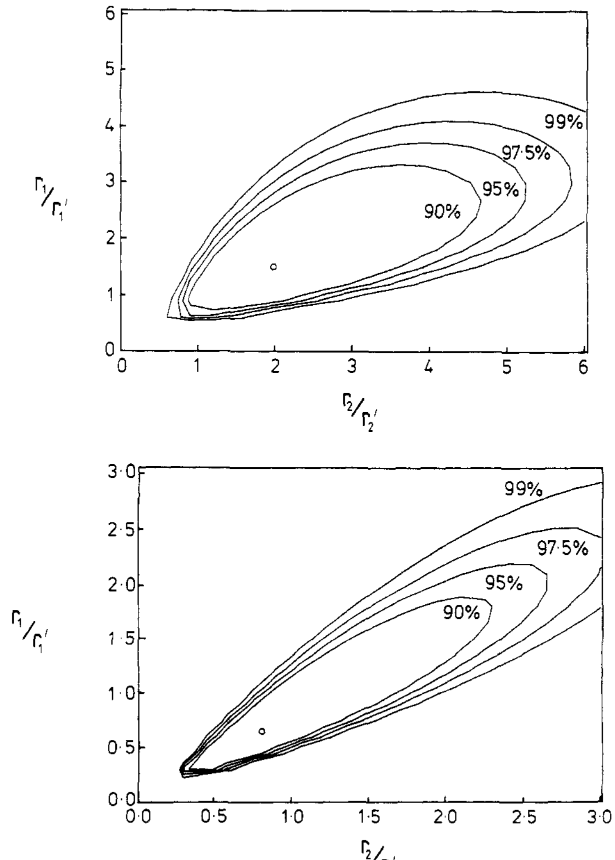

Figure 3. Approximate 95% joint confidence interval for r_1/r_1' and r_2/r_2' for MMA styrene copolymerization in (a, top) bulk[8] and (b, bottom) toluene solution.[9]

models (using the best estimates of the reactivity ratios) predict essentially the same polymer composition (see Figure 2). In order to discriminate between models, other design criteria must be applied.

One approach is to proceed sequentially point by point,[16] reestimating penultimate and terminal model reactivity ratios and conducting new experiments at values of f_1 where the difference in fit between the terminal and penultimate models is greatest.

Alternatively, it is possible to devise a four-point design to give precise estimates of r_1/r_1' and r_2/r_2'. When applied to Fukuda's data for bulk styrene/MMA copolymerization[8] this approach yields design points at $f_1 = 0.063$, 0.336, 0.642, and 0.926, which lie close to maxima in the difference plot (Figure 2a). The values of these design points vary little over the range covered by the 95% confidence region (Figure 3a). Four-point design criteria to be applied in obtaining penultimate model reactivity ratios[17] have been reported and, for the styrene/MMA system, lead to similar design points. The designs may be applied sequentially for greater effectiveness.[12,17]

However, given the level of experimental error associated with the usual methods of copolymer composition measurement, it is unlikely that, for the particular case of styrene/MMA copolymerization, the two models can be unambiguously distinguished without either a significant advance in the techniques available for copolymer composition analysis or a substantially greater number of experiments.[18]

Discrimination between the terminal and penultimate models for the MMA/styrene system may not be an insurmountable problem. One solution may be to analyze the sequence distribution of the copolymer.[19] The best values of the terminal and penultimate model reactivity ratios predict substantially different triad distributions. For example, the triad distribution (MMM:MSM:SMM:SMS:SSM:SSS) for a copolymer of M (MMA) and S (styrene) prepared with a feed ratio of 1:1 will be 0.05:0.22:0.21:0.23:0.23:0.06 with terminal model reactivity ratios $r_1 = r_1' = 0.52$, $r_2 = r_2' = 0.46$ and with penultimate model reactivity ratios 0.05:0.27:0.18:0.27:0.18:0.06 for $r_1 = 0.65$, $r_1' = 0.33$, $r_2 = 0.50$, $r_1' = 0.33$. Unfortunately, although the available data appear to be more consistent with the terminal model,[20,21] determination of triad fractions for MMA/styrene copolymerization by either ^{13}C or ^{1}H NMR is far from straightforward. Another possibility is to examine the variation in composition with conversion.[22] While the terminal and penultimate model reactivity ratios predict essentially the same instantaneous copolymer composition (see Figure 1), depending on the particular f_1, they indicate a slightly different dependence of F_1 on conversion. The power of these methods with respect to model discrimination is a topic of current investigation.

Conclusion. The finding that a given set of experimental data are consistent with the terminal (or other) model does not necessarily prove the validity of that model in chemical terms. It is important to first consider how powerful the experiment is in detecting departures from the terminal model. *Extreme caution must be exercised before regarding an adequate fit to the terminal model as evidence for the absence of penultimate unit effects.*

Registry No. MMA, 80-62-6; S, 100-42-5.

References and Notes

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(2) An account of this work was presented at the joint RACI–ACS Copolymerization Symposium, Sydney, NSW, Australia, 1987.

(3) Ockham's Razor: "entities are not to be multiplied beyond necessity". William Ockham, 1300–1349.

(4) There is ample basis for believing that remote unit effects should be important. It is well-known that β- and γ-substituents can affect (sometimes substantially) the rates of radical reactions. Recently, several workers have attempted to quantify these effects for radical addition reactions (Giese, B.; Engelbrecht, R. *Polym. Bull.* **1984**, *12*, 55–58. Jones, S. A., Prementine, G. S.; Tirrell, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 5275–5276).

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(18) Consider, for example, the size of the study needed to simply reject the terminal model if the penultimate group effects are equal to the estimates from Fukuda's data. A significance test at the 5% level with 90% statistical power would require the design employed by Fukuda to be repeated seven times (180 experiments). The optimal four-point design would need to be repeated about 18 times (70 experiments). Even then the precision of the estimates would be low (Stone, R. A. CSIRO, Div. Maths. Stats. Report VT87/41, 1987).

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