

Discriminating between the Terminal and Penultimate Models Using Designed Experiments: An Overview

Annette L. Burke

NOVA Chemicals Research and Technology Corporation, 2928 16th Street N.E., Calgary, Alberta, Canada T2E 7K7

Thomas A. Duever and Alexander Penlidis*

Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

Statistical model discrimination methods have been applied to the modeling of copolymerization kinetics in order to improve our ability to correctly choose between competing models. The objectives were to quantify the benefits of using model discrimination methods, to examine available copolymer measurements, and to rigorously compare model discrimination techniques. Simulations were developed (for three representative free-radical systems) capable of generating data based on either the terminal or penultimate model. Using the simulations to generate data, three model discrimination methods were applied to the three copolymer systems alternatively using copolymer composition, triad fraction data, and the combination of copolymer composition and rate as the measured variable(s). The results showed that model discrimination methods can correctly discriminate often using fewer experiments than have been used in the past and that they should be able to detect smaller differences between models.

Introduction

The development of mechanistic process models facilitates many engineering activities including process design, optimization, and process control. Engineers and scientists spend a great deal of time estimating parameters, validating models, and developing process simulations. But before embarking on such work, how does one decide which model is the "best" model for a process? There are often several models which seem reasonable, and the first problem is to efficiently find the "best" model. This is one of the problems that exists in the area of copolymerization modeling. A number of models have been proposed for copolymerization kinetics (e.g., Tirrell (1986), Harwood (1987), Fukuda et al. (1992)), and at the beginning of a study there is often uncertainty with respect to which one of the models is "best". Despite the large number of papers that have appeared on the modeling of copolymerization kinetics, there is still active debate as to which model is "best" for specific systems of interest and which measurement(s) should be used to elucidate the kinetics (e.g., Maxwell et al. (1993), Moad et al. (1989), Schweer (1993), Hill et al. (1984), O'Driscoll (1992), Fukuda et al. (1992)).

Statistical model discrimination methods have been designed specifically for this type of problem. They describe how to design experiments which provide the maximum amount of information with respect to discrimination (Hill (1978), Reilly (1970)). They also explain how to analyze the resulting data to determine which of the models provides the "best" description of the system. Several methods have been proposed in the statistics and engineering literature. These were critically reviewed and three methods chosen for further study (Burke et al. (1994a)).

Statistical model discrimination methods have also been compared with past practice in the area of copolymerization (Burke et al. (1994a)). The comparison

shows that, although a rigorous statistical analysis has been used in many studies, most employ poorly designed experiments. Therefore, the use of model discrimination methods should improve our ability to discriminate between competing copolymerization models by improving the information obtained from experiments.

Although the application of model discrimination methods should improve our ability to discriminate, there are still many questions to be answered. How much will the application of model discrimination methods improve copolymerization modeling? Which model discrimination method is the most reliable and efficient? Which of the available copolymerization measurements (copolymer composition, triad fraction, or rate data) will provide the most information?

This tutorial paper provides an overview of the simulation work that was performed including the problem description, the approach taken, and a detailed discussion of the simulation results. The paper begins with a brief review of statistical model discrimination methods followed by a comparison to past practice in the area of copolymerization modeling. The approach taken for the development of the simulations is described next. Data are presented to show that the simulation can, in fact, duplicate the type of data that would be obtained in the laboratory. Results from the extensive simulation studies are then summarized based on the use of copolymer composition, triad fraction, and the combination of rate and copolymer composition data as the measured variable. Finally, our conclusions about the possible improvements to the modeling of copolymer systems and the comparison of model discrimination methods are presented.

Model Discrimination Methods

General Theory. The problem of model discrimination occurs when m rival models have been proposed to describe a system and it is not certain which of the m models is "best". The models are of the form:

$$y_{i,n} = f_i(\underline{x}_n, \underline{\theta}_i) + \epsilon_{i,n} \quad i = 1, 2, \dots, m \quad (1)$$

* To whom correspondence should be addressed. Phone: (519) 888-4567 Ext. 6634. FAX: (519) 746-4979. E-mail: penlidis@cape.uwaterloo.ca.

where $y_{i,n}$ is the measured variable for the n th observation, \underline{x}_n the $v \times 1$ vector of experimental conditions, $\underline{\theta}_i$ the $k_i \times 1$ vector of model parameters, and $\epsilon_{i,n}$ the experimental error. For example, for copolymerization composition experiments, the measured variable is copolymer composition, the experimental conditions include monomer feed composition and conversion, and the parameters are the reactivity ratios. The form of the model, f_i , is generally nonlinear (in the variables and the parameters), and the distribution of the error $\epsilon_{i,n}$ may not be known. When there are several measurements, the models are written in the multiresponse form

$$y_{i,n} = f_i(\underline{x}_n, \underline{\theta}_i) + \epsilon_{i,n} \quad i = 1, 2, \dots, m \quad (2)$$

where $\underline{y}_{i,n}$ is the $1 \times p$ vector of measured variables for the n th experiment and $\underline{\epsilon}_{i,n}$ the $1 \times p$ vector of experimental errors. The distribution of the error may not be known, but it is assumed that errors from different experiments are independent, while the p errors from a single experiment have mean zero and a $p \times p$ covariance matrix Σ .

For copolymer systems several measurements can be taken including copolymer composition, triad fraction measurements (a measure of the monomer distribution on the copolymer chain), and overall copolymerization rate. These measurements can be used individually or in combination. For this reason, both the single- and multiple-response situations need to be considered. However, the single-response case will be used to illustrate general theory.

To discriminate between m models, it is necessary to calculate the model predictions

$$\hat{y}_{i,n} = f_i(\underline{x}_n, \hat{\underline{\theta}}_i) \quad (3)$$

based on the parameter estimates $\hat{\underline{\theta}}_i$ for each of the m models. Parameter estimates can often be obtained from the literature or from a researcher's past work, but these parameter estimates may not be as precise as they could be, unless the experiments were designed specifically for the purpose of parameter estimation. For this reason, it is often beneficial to perform a few preliminary parameter estimation experiments in order to obtain precise parameter estimates or improve existing estimates.

To discriminate between models, it is also often necessary to calculate prediction variances. The variance of the average prediction $\hat{y}_i(\underline{x}_n)$ is given by

$$\sigma_i^2 = \underline{j}_n (\mathbf{J}^T \mathbf{J})^{-1} \underline{j}_n^T \sigma^2 \quad (4)$$

where σ^2 is the experimental error variance. If the model is linear, \mathbf{J} is the $(n-1) \times v$ matrix containing the first $n-1$ data points \underline{x}_u , $u = 1, \dots, n-1$, and \underline{j}_n is the n th data point \underline{x}_n . If the model is nonlinear in the parameters, the variance is often calculated in the same way by linearizing the model about the point estimate of the parameters $\hat{\underline{\theta}}_i$. When the model is linearized, \mathbf{J} becomes the Jacobian of the model with respect to the parameters evaluated at the data points \underline{x}_u , $u = 1, \dots, n-1$, and \underline{j}_n becomes the Jacobian evaluated at \underline{x}_n .

The process of discriminating between competing models is typically a sequential process which involves repeating two steps. The first step is the design step in which a discrimination criterion is used to choose the next experiment. The discrimination criterion is an objective function which reflects the information content

of all possible experimental conditions. It is used to pick the experimental condition which should provide the most information for model discrimination. After the next experiment is performed, the second step, data analysis, is performed. Based on the analysis, a stopping rule is used to decide if one model can be judged significantly better than the rest. If none of the models can be deemed "best", then the two-step process is repeated.

Most of the model discrimination criteria used in the design step have a common basis. For any experiment it is expected that the "best" model will provide the most accurate prediction of the observed measurement. Therefore, it seems logical that the "best" model would be most easily identified by performing the next experiment at the point \underline{x}_n where the average difference in model predictions is largest. The experimental point \underline{x}_n should be chosen using the criterion:

$$\max \sum_{i=1}^{m-1} \sum_{j=i+1}^m (\hat{y}_i - \hat{y}_j)^2 \quad (5)$$

Normally only a finite number of experimental conditions is considered in order to make the problem of searching for the maximum more tractable. If the points considered are evenly spaced over the range of possible \underline{x}_n values and the number of points is large, the results will approximate a continuous search.

An improvement on eq 5 can be made by considering the variance associated with individual predictions. To achieve maximum discrimination, the n th experiment should be performed at a point where the average difference in model predictions is large relative to the predictions variance. The design criterion then takes the form:

$$\max \sum_{i=1}^{m-1} \sum_{j=i+1}^m \frac{(\hat{y}_i - \hat{y}_j)^2}{\text{var}(\hat{y}_i - \hat{y}_j)} \quad (6)$$

All of the design criteria used in model discrimination methods are based on ideas similar to eqs 5 and 6 although the exact functional forms may be different.

The analysis used in the second step usually takes one of two forms. However, one method, the Bayesian analysis of model probabilities, seems to be the more common in model discrimination methods which contain both design and analysis steps. In the Bayesian analysis, prior probabilities are initially assigned to reflect our belief in the correctness of the competing models. The initial prior probability of the i th model is represented by $Pr(M_{i,0})$ and the total probability is restricted such that

$$\sum_{i=1}^m Pr(M_{i,0}) = 1 \quad (7)$$

The prior probabilities can be set based on existing knowledge about which of the models seems most reasonable, or the prior probabilities can be set to equal values if there is little to no existing knowledge. Model discrimination experiments are then designed and carried out. After the n th experiment is performed, the prior probabilities are updated based on the observation y_n using Bayes' theorem:

$$Pr(M_{i,n}) = Pr(M_{i,n-1}) L(M_i | y_n) \quad (8)$$

where $L(M_i|y_n)$ is the likelihood of model i given the observation y_n . The prior probabilities once updated are referred to as posterior probabilities, but it is simpler to use the subscripts $n-1$ and n to identify the model probabilities before and after the n th experiment. This process of picking a new experimental point, performing the experiment, and updating the model probabilities is continued until the probability of one model, for example, model j , becomes sufficiently large that model j is judged to be the "best".

All other analysis methods can be grouped together because they all use statistical tests to judge the adequacy of competing models. These tests may be based on several different quantities, including the sum of squared residuals (SSR_{*i*}) for the i th model,

$$\text{SSR}_i = \sum_{u=1}^n (y_{i,u} - \hat{y}_{i,u})^2 \quad (9)$$

the estimated variance

$$\frac{\text{SSR}_i}{n - k_i} \quad (10)$$

and the maximum likelihood $L(\hat{\theta}_i)$ function (assuming that $\hat{\theta}_i$ is the maximum likelihood estimate of the model parameters for model i).

Several methods exist in the statistical and engineering literature for the design and analysis of model discrimination experiments. All of the methods employ the basic concepts discussed above, but each method uses a unique design criterion and/or unique analysis method. After reviewing the literature, three of these methods stood out as having the most potential with respect to the general model discrimination problem. These are the exact entropy method (Reilly (1970)), the Hsiang and Reilly (1971) method, and the Buzzi-Ferraris and Forzatti (1983) method. However, to the best of the authors' knowledge, these methods have never been extensively compared to discern their relative merits. For this reason, we set out to apply all three methods to the problem of discriminating between copolymerization models (the terminal and penultimate models in particular). The equations for the three model discrimination methods are presented in the following subsections.

Exact Entropy Method. Box and Hill (1967) developed a criterion which has been used successfully in chemical engineering studies. Although they used reasoning different from that used in developing eq 6, the form of their criterion is similar.

Box and Hill (1967) introduced the use of entropy ζ , where

$$\zeta = - \sum_{i=1}^m \text{Pr}(M_i) \ln \text{Pr}(M_i) \quad (11)$$

The maximum entropy value occurs when there is no information as to which model is best, $\text{Pr}(M_i) = 1/m$, and the minimum value occurs when it is certain that model j is best, $\text{Pr}(M_j) = 1$. Therefore, the n th experiment should be chosen to maximize the change in ζ which is given by R ,

$$R = \zeta_{n-1} - \zeta_n \quad (12)$$

Using the expression for entropy, R can be written as

$$R = \sum_{i=1}^m \text{Pr}(M_{i,n-1}) \int p_i \ln \frac{p_i}{q(y_n)} dy \quad (13)$$

where p_i is the probability density function of y_n assuming σ^2 is known, and $q(y_n)$ is given by

$$q(y_n) = \sum_{i=1}^m \text{Pr}(M_{i,n-1}) p_i \quad (14)$$

In order to evaluate the integral in eq 13, Box and Hill (1967) used an inequality to simplify the integrand and assumed a normal distribution for the observed response y_n . This resulted in an expression for the maximum change in entropy.

Reilly (1970) developed the exact entropy criterion based on the earlier method of Box and Hill (1967). Reilly (1970) showed that numerical methods could be used to calculate the exact value of the change in entropy R , which is given by

$$R = -\frac{1}{2}(1 + \ln 2\pi) - \sum_{i=1}^m \text{Pr}(M_{i,n-1}) \left\{ \frac{1}{2} \ln(\sigma^2 + \sigma_i^2) + E_i(\ln q(y_n)) \right\} \quad (15)$$

where $E_i(\ln q(y_n))$ is the expected value of $\ln q(y_n)$, assuming model i to be correct. The function $q(y_n)$ is still defined as in eq 14. The value of $E_i(\ln q(y_n))$ in eq 15 can be evaluated using a Gauss-Hermite quadrature. A Gauss-Hermite quadrature can be used to evaluate the expected value of a function $f(w)$ where w is a variable with mean μ and variance v . For example,

$$E[f(w)] = \frac{1}{\sqrt{\pi}} \sum_{k=1}^n H_k f(\mu + z_k \sqrt{2v}) \quad (16)$$

where H_k and z_k are the weights and zeros of the n th-order Gauss-Hermite quadrature. Assuming model i to be correct, y_n has an estimated mean of $\hat{y}_{i,n}$ and a variance of $\sigma^2 + \sigma_i^2$. Therefore, eq 16 becomes

$$E_i(\ln q(y_n)) = \frac{1}{\sqrt{\pi}} \sum_{k=1}^n H_k \ln \left(\sum_{j=1}^m \text{Pr}(M_j) p_j \right) \quad (17)$$

where

$$p_j = \frac{1}{\sqrt{2\pi(\sigma^2 + \sigma_j^2)}} \exp \left(-\frac{1}{2(\sigma^2 + \sigma_j^2)} (\hat{y}_{i,n} + z_k \sqrt{2(\sigma^2 + \sigma_i^2)} - \hat{y}_{j,n})^2 \right) \quad (18)$$

Substitution of eq 17 into eq 15 allows the evaluation of R . Model discrimination experiments can then be designed by finding the point \underline{x}_n which maximizes the value of R .

After the n th experiment is performed, the prior probabilities are updated using

$$\text{Pr}(M_{i,n}) = \frac{\text{Pr}(M_{i,n-1}) L(M_i|y_n)}{\sum_{i=1}^m \text{Pr}(M_{i,n-1}) L(M_i|y_n)} \quad (19)$$

where $L(M_i|y_n)$ is the likelihood of the i th model based on the observation y_n . If the observation is assumed to be normally distributed, the likelihood is written as

$$L(M_i|y_n) = \frac{1}{\sqrt{2\pi(\sigma^2 + \sigma_i^2)}} \exp\left(-\frac{1}{2(\sigma^2 + \sigma_i^2)}(y_n - \hat{y}_{i,n})^2\right) \quad (20)$$

The multiple-response exact entropy equations can be derived by starting from the basic expressions and assumptions of Box and Hill (1967). Box and Hill (1967) give the change in entropy as

$$R = \sum_{i=1}^m Pr(M_{i,n-1}) \int p_i \ln \frac{p_i}{q(y_n)} dy_n \quad (21)$$

where $q(y_n)$ is still defined by eq 14 except that the observation is now the vector y_n . If the observation is assumed to have a multivariate normal distribution, for example, under model i ,

$$p_i(y_n|\Sigma) = \frac{1}{(2\pi)^{p/2}|\Sigma + \mathbf{W}_i|^{1/2}} \exp\left\{-\frac{1}{2}(y_n - \hat{y}_{i,n})(\Sigma + \mathbf{W}_i)^{-1}(y_n - \hat{y}_{i,n})^T\right\} \quad (22)$$

then the multivariate analogue of eq 15 can be derived as

$$R = -\frac{1}{2}(p + \ln(2\pi)^p) - \sum_{i=1}^m Pr(M_{i,n-1}) \left\{ \frac{1}{2} \ln|\Sigma + \mathbf{W}_i| + E_i(\ln q(y_n)) \right\} \quad (23)$$

where Σ is the $p \times p$ covariance matrix of the p responses and \mathbf{W}_i is the $p \times p$ covariance matrix of the model predictions. (The definition of \mathbf{W}_i is given elsewhere (Burke et al. (1994b)) and the symbol T used in eq 22 denotes matrix transposition. The full derivation of eq 23 is presented by Burke (1994).) In the multivariate case, the expectation in eq 23 is given by

$$E_i(\ln q(y_n)) = \int_{-\infty}^{\infty} \ln q(y_n) p_i(y_n|\Sigma) dy_n \quad (24)$$

where the integral is over the p -dimensional space containing y_n . Therefore, under the multivariate exact entropy method the next experiment y_n is chosen by maximizing R as given by the combination of eqs 22–24.

After the n th experiment has been performed, the results are analyzed by updating the model probabilities. The equation used is still eq 19, except that the observation is now a vector y_n and the likelihood is

$$L(M_i|y_n) = \frac{1}{(2\pi)^{p/2}|\Sigma + \mathbf{W}_i|^{1/2}} \times \exp\left\{-\frac{1}{2}(y_n - \hat{y}_{i,n})(\Sigma + \mathbf{W}_i)^{-1}(y_n - \hat{y}_{i,n})^T\right\} \quad (25)$$

assuming the observation follows a multivariate normal distribution.

Normally the covariance matrix Σ is not known and is replaced by an estimate \mathbf{S} , from replicate observations or from the smallest estimated covariance matrix produced by regressing the m models.

The strengths of the exact entropy method are the consideration of the prediction variance and the use of

the exact value of R instead of an approximation. As with the Box and Hill (1967) method, the exact entropy method requires the linearization of the model to calculate σ_i^2 or \mathbf{W}_i , and the variance σ^2 of Σ is replaced by some estimate.

The Hsiang and Reilly Method. In several model discrimination methods, including the exact entropy method (Reilly (1970)), the variances of parameter estimates and model predictions are calculated based on a linear approximation of the models about the point estimates of the parameters.

Hsiang and Reilly (1971) proposed a method in which they eliminated the need to linearize nonlinear models. In this method, uncertainty in the parameter estimates is expressed in the form of discrete parameter probability distributions. The symbol $\tilde{\theta}_i$ is used to represent a particular combination of parameter values being considered for the i th model.

The first step in the method is to assign prior probabilities, both to the models and to all parameter vectors denoted by $\tilde{\theta}_i$. Prior model probabilities $Pr(M_i)$ are assigned based on our belief that the i th model is correct. Similarly, prior probabilities for parameter values are assigned based on previous knowledge. For model i , a range of values with nonnegligible probability is defined for each parameter. Each parameter is then represented by a reasonable number of discrete values over the range, for example, 10–50 values. The probability corresponding to a specific combination of the discrete values is represented by $Pr(\tilde{\theta}_i|M_i,y)$, and the set of prior parameter probabilities is stored in a matrix. For the single-response case, the m rival models are written in the form:

$$y_{i,n} = f_i(x_n, \tilde{\theta}_i) + \epsilon_{i,n} \quad i = 1, 2, \dots, m \quad (26)$$

The errors are assumed to have mean zero and the form of the distribution is assumed known (e.g., normal, gamma, uniform, etc.), although the error variance, σ^2 , may not be known. From the error distribution, the distribution of y is derived, which, in turn, allows the calculation of the model likelihoods $L(M_i|\tilde{\theta}_i,y)$.

The discrimination criterion states that the n th experiment should be chosen to maximize:

$$C = \sum_{i=1}^m \sum_{j=i+1}^m |\hat{y}_i - \hat{y}_j| [Pr(M_{i,n-1}) + Pr(M_{j,n-1})] \quad (27)$$

where \hat{y}_i is the expected value of y given by model i . The value of \hat{y}_i is calculated by taking the expectation of y_i over all possible values of the parameters and is written as

$$\hat{y}_i = \sum_{\tilde{\theta}_i} f_i(x_n, \tilde{\theta}_i) Pr(\tilde{\theta}_i|M_i,y) \quad (28)$$

Once the n th experiment has been carried out, the model multivariate probabilities are updated using

$$Pr(M_{i,n}) = \frac{Pr(M_{i,n-1}) \sum_{\tilde{\theta}_i} Pr(\tilde{\theta}_i|M_i) L(M_i|\tilde{\theta}_i,y_n)}{\sum_{i=1}^m Pr(M_{i,n-1}) \sum_{\tilde{\theta}_i} Pr(\tilde{\theta}_i|M_i) L(M_i|\tilde{\theta}_i,y_n)} \quad (29)$$

and the parameter probabilities are updated using

$$Pr(\tilde{\theta}_i|M_p, y_n) = \frac{Pr(\tilde{\theta}_i|M_p) L(M_i|\tilde{\theta}_i, y_n)}{\sum_{\tilde{\theta}_i} Pr(\tilde{\theta}_i|M_p) L(M_i|\tilde{\theta}_i, y_n)} \quad (30)$$

If the distribution of the errors is assumed to be normal, the likelihood $L(M_i|\tilde{\theta}_i, y_n)$ is given by

$$L(M_i|\tilde{\theta}_i, y_n) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{1}{2\sigma^2}(y_n - f_i(x_n, \tilde{\theta}_i))^2\right) \quad (31)$$

After the probabilities have been updated, some parameter combinations may have negligible probabilities. The matrix of parameter probabilities can then be rescaled to eliminate combinations with negligible probability, thus allowing more probable parameter values to be examined in greater detail.

In the multivariate case, we have used the extension (Burke (1994))

$$C = \sum_{i=1}^m \sum_{j=i+1}^m (\hat{y}_i - \hat{y}_j)(\hat{y}_i - \hat{y}_j)^T [Pr(M_{i,n-1}) + Pr(M_{j,n-1})] \quad (32)$$

where

$$\hat{y}_i = \sum_{\tilde{\theta}_i} f_i(x_n, \tilde{\theta}_i) Pr(\tilde{\theta}_i|M_p, y) \quad (33)$$

The vector product in eq 32 gives the distance between \hat{y}_i and \hat{y}_j just as the absolute difference in eq 27 gives the distance between \hat{y}_i and \hat{y}_j . However, when there are large differences in the variances of the p responses, the response with the largest variance will dominate the criterion. Therefore, to make sure the next experiment is performed at the point with the maximum difference in predictions, the responses should be scaled to have roughly equal variances, or, alternatively, the criterion should be variance-scaled, e.g.,

$$C = \sum_{i=1}^m \sum_{j=i+1}^m (\hat{y}_i - \hat{y}_j) \Sigma^{-1} (\hat{y}_i - \hat{y}_j)^T [Pr(M_{i,n-1}) + Pr(M_{j,n-1})] \quad (34)$$

After the next experiment is performed, the model probabilities are still updated using eqs 29 and 30. The difference is that the observation is now a vector \underline{y}_n and the likelihood, assuming the observation is multivariate normal, is given by

$$L(M_i|\tilde{\theta}_i, \underline{y}_n) = \frac{1}{(2\pi)^{p/2} |\Sigma|^{1/2}} \times \exp\left\{-\frac{1}{2}(\underline{y}_n - f_i(x_n, \tilde{\theta}_i)) \Sigma^{-1} (\underline{y}_n - f_i(x_n, \tilde{\theta}_i))^T\right\} \quad (35)$$

The Hsiang and Reilly (1971) method has not been used widely in engineering studies because of its need for a large amount of computer storage space. However, with the advances in computers that have occurred since the method was introduced, this should no longer be a constraint.

The method has two major advantages. The first is that all previous knowledge of the parameters can be included in the form of probability distributions. Parameter information can also be updated and prediction variances can be calculated without linearizing the model. This is an improvement over other methods

which assume a normal distribution characterized by the point estimate $\hat{\theta}_r$. In addition, σ or Σ can be treated as a parameter. This is more realistic than using a point estimate because experimental error is never known in real situations, and a point estimate may be a poor estimate if the number of experiments is relatively small compared with the number of model parameters.

The Buzzi-Ferraris and Forzatti Method. Although the Hsiang and Reilly (1971) criterion is different from the exact entropy (Reilly (1970)) method, they both employ a Bayesian analysis. An alternative approach was taken by Buzzi-Ferraris and co-workers (Buzzi-Ferraris and Forzatti (1983), Buzzi-Ferraris et al. (1984, 1990)).

Buzzi-Ferraris and Forzatti developed a design criterion that is similar to eq 6. They proposed that the n th experiment be chosen to maximize:

$$T(\underline{x}_n) = \frac{\sum_{i=1}^{m-1} \sum_{j=i+1}^m (\hat{y}_i - \hat{y}_j)^2}{(m-1)(ms^2 + \sum_{i=1}^m s_i^2)} \quad (36)$$

An independent estimate of variance s^2 is used instead of σ^2 , and the estimated prediction variances s_i^2 is used instead of σ_i^2 . This criterion is a simple ratio of the average squared difference between predictions to the average variance in the predictions. Since the form of the criterion $T(\underline{x}_n)$ is similar to an F -statistic, the value of $T(\underline{x}_n)$ can be used to judge the ability to discriminate between the models. For example, if it is possible to discriminate between models at a given experimental condition, the value of $T(\underline{x}_n)$ should be greater than 1. If $T(\underline{x}_n)$ is less than 1 at all possible experimental points, no discrimination can be gained and an experimenter may wish to temporarily switch to parameter estimation experiments in order to decrease the prediction variance, thus improving the possibility of achieving model discrimination. This property of the Buzzi-Ferraris and Forzatti criterion makes it somewhat simpler to interpret than the other model discrimination criteria discussed.

The Buzzi-Ferraris and Forzatti method also takes a different approach to data analysis. In their first paper, Buzzi-Ferraris and Forzatti (1983) suggest that the adequacy of all competing models should be checked and only models shown to be adequate should be used in the next evaluation of $T(\underline{x}_n)$. To check the adequacy of each model, they proposed an F -test on the variance estimate s^2 produced by regression and some independent estimate $\hat{\sigma}^2$. Alternatively, they suggested a Hartley F max test (Hartley (1940)) or Bartlett's χ^2 test (Bartlett (1937)). However, since the terminal and penultimate models are nested, we can use a general form of the F -test which is used with nested models. For example, for a pair of nested models, where model 2 is nested in model 1, the F -statistic is

$$F = \frac{(SSR_2 - SSR_1)/(k_1 - k_2)}{SSR_1/(n - k_1)} \quad (37)$$

where SSR is the sum of squared residuals produced by regression analysis. The F -statistic is compared to the F distribution with $k_1 - k_2$ and $n - k_1$ degrees of freedom to determine whether the extra parameters in

model 1 provide a significantly better fit to the data. Only models judged to be an adequate description of the system are used in the next evaluation of $T(\underline{x}_n)$. Buzzi-Ferraris and Forzatti (1983) and Buzzi-Ferraris et al. (1984, 1990) suggest this is an improvement over the Bayesian analysis which may be negatively affected by poor variance estimates.

In the multiple-response case with two competing models, Buzzi-Ferraris et al. (1984) proposed that the next experiment should be chosen to maximize

$$T_{ij}(\underline{x}_n) = (\hat{\underline{y}}_i - \hat{\underline{y}}_j)(\mathbf{S}_{ij}(\underline{x}_n))^{-1}(\hat{\underline{y}}_i - \hat{\underline{y}}_j)^T \quad (38)$$

where

$$\mathbf{S}_{ij}(\underline{x}_n) = 2\mathbf{S} + \mathbf{W}_i + \mathbf{W}_j \quad (39)$$

Buzzi-Ferraris et al. (1984) suggest that discrimination is possible if

$$\max T_{ij}(\underline{x}_n) > p \quad (40)$$

and if this is not true, parameter estimation experiments are needed to reduce prediction variance. This is a reasonable extension of the univariate rule that $\max T(\underline{x}_n)$ should be greater than 1.

After the n th experiment is performed, the results are analyzed. Buzzi-Ferraris et al. (1984) suggest that the adequacy of the i th model be tested by applying a χ^2 test to the test statistic

$$\Phi_i = \sum_{u=1}^n (\underline{y}_u - \hat{\underline{y}}_i(\underline{x}_u))\mathbf{\Sigma}^{-1}(\underline{y}_u - \hat{\underline{y}}_i(\underline{x}_u))^T \quad (41)$$

where $\mathbf{\Sigma}$ is the known covariance matrix (or an independent estimate). However, $\mathbf{\Sigma}$ is rarely known with certainty.

As an alternative, the multivariate analogue of the F -test can be used. For example, for a pair of nested models, where model 2 is nested in model 1, we are really testing the hypothesis

$$\begin{array}{ll} H_0 & \mathbf{K}\hat{\underline{\theta}}_1 = \underline{0} \\ & \text{(model 2)} \end{array} \quad \begin{array}{ll} H_a & \mathbf{K}\hat{\underline{\theta}}_1 \neq \underline{0} \\ & \text{(model 1)} \end{array} \quad (42)$$

The matrix $\mathbf{K}_{q \times k_1}$ in the null hypothesis expresses the restrictions on model 1 needed to reduce it to model 2. In the univariate case, this hypothesis is tested using eq 37 where $q (=k_1 - k_2)$ denotes the degrees of freedom associated with the null hypothesis. In the multivariate case, the sums of squared residuals are also compared, but these are now $p \times p$ matrices. The multivariate hypothesis can be tested using the test statistic U (Muirhead (1982), chapter 10, and Anderson (1984), chapter 8) written as

$$U = \frac{|\mathbf{Y} - \hat{\mathbf{Y}}_1|^T(\mathbf{Y} - \hat{\mathbf{Y}}_1)|}{|\mathbf{Y} - \hat{\mathbf{Y}}_2|^T(\mathbf{Y} - \hat{\mathbf{Y}}_2)|} = \frac{|\text{SSR}_{H_a}|}{|\text{SSR}_{H_0}|} \quad (43)$$

where \mathbf{Y} is the $n \times p$ matrix containing the data for n experiments and $\hat{\mathbf{Y}}_1$ contains the predictions from model 1.

The distribution of U can be expressed in terms of the more common F distribution if either $q \leq 2$ or $p \leq 2$. Fortunately, we have been able to capitalize on these simplifications. For example, when discriminating between the terminal and penultimate models using triad fraction data, $q = 2$ (and $p = 4$ because we have chosen

to use four of the available six triad fractions). The value of q is 2 because two restrictions are applied to the penultimate model ($r_{11} = r_{21}$, $r_{22} = r_{12}$) in order to obtain the terminal model. For $q = 2$ the distribution of U is given by

$$\left(\frac{1 - \sqrt{U}}{\sqrt{U}} \right) \frac{n - k_1 - p + 1}{p} \sim F(2p, 2(n - k_1 - p + 1)) \quad (44)$$

where k_1 is the number of parameters in the unrestricted model (in our case, the unrestricted model is the penultimate model). Therefore, after the n th experiment has been performed, the test statistical F_{test} is calculated as

$$F_{\text{test}} = \left(\frac{1 - \sqrt{U}}{\sqrt{U}} \right) \frac{n - k_1 - p + 1}{p} \quad (45)$$

and its upper tail probability is found. If the upper tail probability is less than 5%, the restricted model is rejected at the 95% confidence level, and if the upper tail probability is greater than 95%, we can be fairly certain that the restricted model is the better model for the system.

Similarly, copolymer composition and rate data have been used together, enabling us to use the simplification for $p = 2$. For $p = 2$, the distribution of U is given by

$$\left(\frac{1 - \sqrt{U}}{\sqrt{U}} \right) \frac{n - k_1 - 1}{q} \sim F(2q, 2(n - k_1 - 1)) \quad (46)$$

Although the form of the statistic is the same, the constant multiplier is different in terms of p and q , and the degrees of freedom for the F distribution are different. Thus, in the case of copolymer composition and rate data, the test statistic used in the modified Buzzi-Ferraris and Forzatti method is

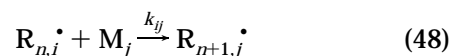
$$F_{\text{test}} = \left(\frac{1 - \sqrt{U}}{\sqrt{U}} \right) \frac{n - k_1 - 1}{q} \quad (47)$$

Since the analysis proposed here is different from that proposed by Buzzi-Ferraris et al. (1984), this method will henceforth be referred to as the modified Buzzi-Ferraris and Forzatti method (Burke (1994)).

Past Work on Copolymerization Modeling

Terminal and Penultimate Models. In the current work, the focus is on the problem of discriminating between the terminal and penultimate models for copolymerization kinetics. Both the terminal and penultimate models were developed to describe the reaction of two monomers M_1 and M_2 to form a copolymer. For a free-radical polymerization, R_n^\bullet represents a growing radical of chain length n .

The terminal model assumes only the *last* unit on the growing chain influences monomer addition. If $R_{n,i}^\bullet$ is a radical ending in monomer i , the four propagation reactions can be summarized as

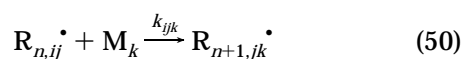


where the first subscript on R denotes the radical chain length, i and j are used to denote monomer units (1 or 2), and k_{ij} is the rate constant for addition of monomer j to a radical ending in unit i . Although there are four

propagation rate constants k_{ij} , the polymerization rate is usually expressed in terms of the two homopolymerization rate constants k_{11} and k_{22} and two monomer reactivity ratios

$$r_1 = \frac{k_{11}}{k_{12}}; \quad r_2 = \frac{k_{22}}{k_{21}} \quad (49)$$

The penultimate model assumes that the last *two* monomer units on the growing radical chain influence monomer addition. If $R_{n,ij}$ is a radical with terminal unit j and penultimate unit i , the eight propagation reactions can be summarized as



The rate of polymerization is usually expressed in terms of the two homopolymerization rate constants k_{111} and k_{222} , along with four monomer reactivity ratios

$$\begin{aligned} r_{11} &= \frac{k_{111}}{k_{112}}; & r_{21} &= \frac{k_{211}}{k_{212}} \\ r_{22} &= \frac{k_{222}}{k_{221}}; & r_{12} &= \frac{k_{122}}{k_{121}} \end{aligned} \quad (51)$$

and two radical reactivity ratios

$$s_1 = \frac{k_{211}}{k_{111}}; \quad s_2 = \frac{k_{122}}{k_{222}} \quad (52)$$

The terminal model is nested within the penultimate model. One can see that if an attempt is made to fit the penultimate model to a system best described by the terminal model, joint confidence regions for the reactivity ratio estimates will include the points

$$\begin{aligned} \hat{r}_{11} &= \hat{r}_{21} \\ \hat{r}_{22} &= \hat{r}_{12} \\ \hat{s}_1 &= \hat{s}_2 = 1 \end{aligned} \quad (53)$$

Equations for instantaneous composition, triad fractions, and the overall propagation rate constant can be derived based on the reactions given in eqs 48 and 50. These equations, along with the equations for cumulative copolymer composition, have been presented elsewhere (Burke et al. (1994)).

Design of Model Discrimination Experiments. To the best of the author's knowledge, statistical model discrimination methods have not been previously applied to the problem of discriminating between the terminal and penultimate models. A review of the copolymerization literature has been performed in order to show that the application of statistical model discrimination techniques has the potential to improve discrimination between the terminal and penultimate models. Most existing research on discrimination between the terminal and penultimate models shares common characteristics with respect to the planning of experiments, modeling assumptions, and analysis of results. For this reason, these steps will be discussed in turn with reference to specific papers where appropriate.

The work of Hill et al. (1982), on the styrene/acrylonitrile system, is typical of previous research on model

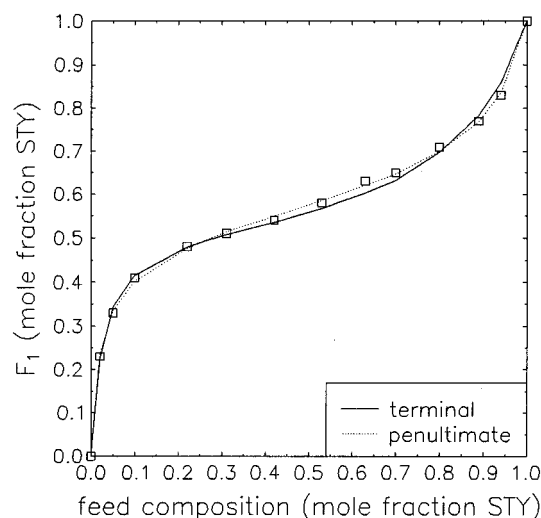


Figure 1. Copolymer composition data for STY/AN from Hill et al. (1982).

discrimination. Ampule experiments were performed over the entire range of feed compositions to conversions of less than 5%. The copolymer compositions were measured and used to estimate terminal and penultimate reactivity ratios using instantaneous composition equations. Figure 1 is a plot of the data and the fitted curves. Since the terminal and penultimate models are nested, an *F*-test was used to determine whether or not the penultimate model provides a significantly better fit of the data.

These experiments do not seem to be optimal for either parameter estimation or model discrimination. At the beginning of a study very little may be known about the model parameters, but if discrimination is to be achieved, the variance of parameter estimates must be such that prediction variance is of the same order of magnitude or smaller than the average difference between model predictions. Therefore, it is usually necessary to perform some initial parameter estimation experiments. Tidwell and Mortimer (1965) used the *D*-optimal criterion to design terminal model parameter estimation experiments. Their results are summarized in terms of two approximate formulas, which give two optimum experimental conditions. For an azeotropic system, the feed compositions will be on opposite sides of the azeotrope. (The *D*-optimal criterion can also be used to design experiments for the estimation of penultimate model reactivity ratios, but it does not seem possible to express this information as simple formulas similar to those given by Tidwell and Mortimer (Burke et al. (1993)).) These feed compositions are very different from the range of compositions shown in Figure 1 (from the work of Hill et al. (1982)), and this is why we state that the experiments do not seem to be optimal for parameter estimation.

The experiments also do not seem to be designed for the purpose of model discrimination. As mentioned in the previous section, the maximum amount of information with respect to discrimination is usually gained by performing experiments where there is a maximum average difference in model predictions. From Figure 1 it can be seen that there is a noticeable difference in model predictions at feed compositions between 0.4 and 0.7 mole fraction styrene and some difference at approximately 0.9 mole fraction styrene. The experiments performed at other feed compositions provide very little information with respect to discrimination. What the

Table 1. Composition Measurements for Copolymers Containing Styrene

experimental error	method	source
±1.75 wt%	¹ H-NMR	Garcia-Rubio and Ro (1985)
±5.0%	¹ H-NMR	Garcia-Rubio et al. (1985)
±1.0%	¹ H-NMR	Johnson et al. (1978)
±2.0	¹ H-NMR	Ebdon (1982)
±0.4%	UV	Garcia-Rubio and Ro (1985)
±1.0%	UV	Johnson et al. (1978)
±5.0%	IR	Garcia-Rubio et al. (1985)

researchers might have been trying to accomplish is parameter estimation and model discrimination in one set of experiments, but since their experiments are not optimal for either purpose, a two-stage approach should make experimentation more efficient, thus reducing the number of experiments required to reach conclusions with some given level of confidence. It should also be pointed out that a sequential experimental design is an improvement over doing several experiments at once, since information gained from one experiment can be used to plan the next experiment more effectively.

Although the work of Hill et al. (1982) has been given as a typical example, many other researchers have spread experiments over the entire feed composition range and then fit competing models to the data. Examples in which copolymer composition was the measured variable include the work of Brown and Fujimori (1994) and Fukuda et al. (1982). Examples in which triad fractions were measured include Brown et al. (1993) and Maxwell et al. (1993). Finally, studies involving the propagation rate constant as the measured variable include Davis et al. (1989a, 1990), Fukuda et al. (1985a), and Olaj et al. (1989).

Additional problem relate to the equations and analysis methods used. Most researchers use instantaneous equations because conversion is typically low (<10 wt %). However, if the differences between model predictions are small, as they typically are for copolymer composition data, the bias introduced by using instantaneous equations could affect model discrimination. Thus, it would be better to use cumulative equations, even for low conversion data. It is also true that not all authors use statistically sound analysis methods. In many cases, for example, the work of Fukuda et al. (1985a,b) and Ma et al. (1985), the analysis seems to be overly influenced by plots of the data in which there is no indication of experimental error or prediction variance. In other cases where statistically sound analysis methods have been used, the conclusions drawn may be weakened by the poor experimental design.

Measured Copolymer Characteristics. Past work seems to indicate that rate measurements have the greatest potential for achieving discrimination, followed by sequence distribution and composition, respectively. However, these inferences are based mainly on differences in model predictions. Clearer conclusions as to which of these three variables is best suited for discrimination studies would be gained by considering how experimental error propagates through the calculations involved and how this error compares with the average difference in model predictions.

There is a great variation in the precision with which polymer characteristics can be measured. Tables 1–3 give estimates of experimental error. For instance, composition can be measured with a relative error of as low as ±1.0% (Johnson et al. (1978)), while triad fractions can only be measured with a relative error of ±10% (Schaefer (1971)). There is also a difference in

Table 2. Error in Triad Fraction Measurements

experimental error	source
±10%	Schaefer (1971)
±0.03 mole fraction	Hill et al. (1982)
±0.05 mole fraction	Hill et al. (1989)

Table 3. Experimental Error in the Overall Propagation Rate Constant

error in \bar{k}_p	experimental method	source
±20.0%	rotating sector	Stickler (1987)
±10.0–15.0%	spatially intermittent polymerization	O'Driscoll and Mahabadi (1976)
±5.0%	pulsed laser	Olaj et al. (1987)
±3.0–13.0%	pulsed laser	Davis et al. (1989b)
±10.0%	pulsed laser	Schnöll-Bitai and Olaj (1990)
±40.0%	electron spin resonance	Ballard et al. (1986)
±20.0%	electron spin resonance	Lau et al. (1987)

the precision obtained for the same characteristic using various experimental techniques. This is evident for measurements of the propagation rate constant where estimates of error range from ±5.0% for the pulsed laser method (Olaj et al. (1987)) to ±20% or more for the electron spin resonance method (Lau et al. (1987)).

Error in all measurements will affect the variance of the estimated model parameters and the variance of model predictions. When we consider that rate and sequence distribution measurements typically involve 10 times the error involved in composition measurements, the advantages of rate and sequence distribution are diminished. Therefore, although rate and sequence distribution measurements still seem to have the most potential for discrimination, it is worth reconsidering all measurements using statistical model discrimination techniques.

Formulation of Objectives: Our Approach

A great deal of time and energy has been expended in attempts to identify the “best” copolymerization model for specific pairs of monomers. Unfortunately, previous studies do not share the characteristics of designed model discrimination experiments. The literature review has pointed out that, although certain past studies have employed a rigorous statistical analysis, most work has involved poorly designed experiments. The combined use of designed parameter estimation and statistical model discrimination experiments should improve our ability to discriminate between competing models.

Our objective in this study is to address several issues systematically by applying model discrimination methods to the problem of discriminating between the terminal and penultimate models for copolymerization. This objective is very broad in scope. It involves the application of three model discrimination methods (Buzzi-Ferraris and Forzatti (1983), Reilly (1970), Hsiang and Reilly (1971)) to several copolymerization systems along with studies to compare available measurements.

It would take years to meet this objective using only laboratory studies. Computer simulations were thus proposed for the first stage of the research as a way of efficiently using available resources. The idea was to develop a computer program which could simulate the “true” behavior of a copolymer system, including random measurement error, and thus produce the same type of measurements that we would obtain in the laboratory. Developing such a program requires an initial investment of effort to ensure realistic results, after which

many model discrimination methods and copolymer systems can be studied in a relatively short time.

Simulation of Model Discrimination Experiments

Steps in the Simulation Program. The computer program developed to study model discrimination methods contains all the steps that would be used to design and analyze real experiments, except that experimental data are generated using a computer simulation. These are the same steps that were mentioned in the literature review on model discrimination methods. Unless good parameter estimates are available, the first step is to design and perform parameter estimation experiments. Model discrimination experiments are then designed, performed, and analyzed sequentially until the analysis shows that one model is "best" or until resources for performing experiments are exhausted. It is simplest to explain these steps in detail by referring to a specific example. Here we will explain how these steps have been programmed to study the application of the exact entropy method to a copolymer system based on copolymer composition as the measured variable.

All model discrimination methods, including the exact entropy method, require initial parameter estimates for both the terminal and penultimate models. At the beginning of a study, reliable estimates may not be available. Therefore, the first step in the program is to design parameter estimation experiments. Since the terminal model is nested within the penultimate model, parameter estimation experiments for the penultimate model should lead to good initial estimates for the parameters of both models.

In the case of copolymer composition data, the D -optimal criterion is used to pick four optimal feed compositions $f_{1,1}$, $f_{1,2}$, $f_{1,3}$, and $f_{1,4}$ for estimating the four penultimate reactivity ratios, r_{11} , r_{21} , r_{22} , and r_{12} . The D -optimal criterion is

$$\varphi = \max [\det(\mathbf{J}^T \mathbf{J})] \quad (54)$$

where \mathbf{J} is the Jacobian at the four feed compositions. For composition data, the i th row of the Jacobian contains the derivatives of the copolymer composition F_1 with respect to the parameters evaluated at the i th feed composition $f_{1,i}$. For example, the first row of the Jacobian is

$$\left[\frac{\partial F_1}{\partial r_{11}}, \frac{\partial F_1}{\partial r_{21}}, \frac{\partial F_1}{\partial r_{22}}, \frac{\partial F_1}{\partial r_{12}} \right] \quad (55)$$

where $f_1 = f_{1,1}$. Initial guesses of the four reactivity ratios are needed to evaluate the Jacobian. These initial guesses are input to the program, and a simplex optimization technique is used to find the optimal experimental conditions.

Optimizing the D -optimal criterion will produce four optimal experimental conditions, but more than four parameter estimation experiments are simulated. Six parameter estimation experiments are simulated so that the four penultimate reactivity ratios can be estimated with 2 degrees of freedom for the estimate of variance produced by the model s_{pent}^2 . Simulating six experiments will also allow the two terminal model reactivity ratios to be estimated with 4 degrees of freedom for the terminal model estimate of variance s_{term}^2 . The first four parameter estimation experiments are assigned the four feed compositions picked by the D -optimal criterion.

The fifth and sixth experiments are assigned the first and third compositions picked by the D -optimal criterion, so they are actually replicate experiments. All six experiments are assigned target conversions between 0 and 10 mol % in order to reflect the range of conversions typically used in low-conversion composition studies.

Once the conditions for the parameter estimation experiments have been assigned, they are simulated one at a time. Based on the initial feed composition for an experiment f_{10} and the target conversion x , the simulation generates an experimental measure of the cumulative composition \bar{F}_1 . More details on the simulation model are given in the following section.

After the parameter estimation experiments have been simulated, the values of f_{10} , x , and \bar{F}_1 are used to estimate the reactivity ratios for both the terminal and penultimate models. The models are fitted using a Levenberg–Marquardt regression as described by Press et al. (1989) or Himmelblau (1970). Regression requires model predictions for both models. For the terminal model, the Meyer–Lowry equation is used to obtain a prediction for the final feed composition f_1 based on the values of f_{10} and x . This, in turn, is used to obtain a prediction of \bar{F}_1 . Similarly, for the penultimate model, the integrated composition equation is solved numerically to obtain a prediction of the final feed composition f_1 based on the values of f_{10} and x . The prediction f_1 is then used to obtain a prediction of \bar{F}_1 .

At this point the program picks the first model discrimination experiment. The value of R given by eqs 15, 17, and 18 is maximized to find the optimum values of the feed composition f_{10} and target conversion x . The values of \hat{y}_i and \hat{y}_j in eq 18 are replaced by the terminal and penultimate predictions of cumulative composition \bar{F}_1 . To find the maximum, R is evaluated at all compositions from 0.02 to 0.98 mole fraction monomer 1 (at intervals of 0.02 mole fraction) and all conversions from 5 to 25 mol % (at intervals of 5 mol %). Note that when R is evaluated, the variance σ^2 is replaced by the penultimate regression estimate s_{pent}^2 , which should be smaller or equal to the estimate based on the terminal model. Note also that when the exact entropy method is being used, model probabilities are needed to evaluate R . The model probabilities are both set to 50% before the six parameter estimation experiments are picked.

The seventh experiment is then simulated at the chosen values of feed composition f_{10} and target conversion x , and the value of cumulative composition \bar{F}_1 is recorded. The reactivity ratios are then reestimated using the Levenberg–Marquardt regression based on the first seven experiments. After the reactivity ratios have been reestimated, the model probabilities are updated using eq 19. If one of the model probabilities exceeds 95%, then that model is declared best and experimentation stops. If neither of the model probabilities exceeds 95%, then an eighth experiment is picked by maximizing R . Experiments will continue to be designed and analyzed sequentially until one of the model probabilities exceeds 95% or until the maximum number of experiments (arbitrarily set at 20) is reached.

When the Buzzi-Ferraris and Forzatti method or the Hsiang and Reilly method is used instead of the exact entropy method, the only differences in the simulation program are the equations used for experimental design and analysis.

Simulation of Experimental Data. The general simulation model was developed as a set of ordinary

Table 4. Homopolymerization Constants for Styrene

constant		units ^c	source
MW	104.1512	g/mol	
k_p	$1.09 \times 10^7 \exp(-7051/RT)$	L/(mol·s)	<i>a</i>
k_t	$1.703 \times 10^9 \exp(-2268/RT)$	L/(mol·s)	<i>a</i>
k_{IM}	$1.096\,482 \times 10^7 \exp(-134268.8/RT)$	L/(mol·s)	<i>b</i>
ρ_M	$0.924-9.18 \times 10^{-4}(T-273.15)$	g/cm ³	<i>b</i>
ρ_P	$1.084-6.05 \times 10^{-4}(T-273.15)$	g/cm ³	<i>b</i>
γ	0.00		<i>b</i>

^a Buback et al. (1988). ^b Kuindersma (1992). ^c All activation energies are stated in cal/mol, and the temperature *T* is in Kelvin.

Table 5. Homopolymerization Constants for Methyl Methacrylate

constant		units ^c	source
MW	100.1162	g/mol	
k_p	$5.365\,859 \times 10^5 \exp(-4353/RT)$	L/(mol·s)	<i>a</i>
k_t	$9.8 \times 10^7 \exp(-701/RT)$	L/(mol·s)	<i>b</i>
k_{IM}	$1.557\,243 \times 10^3 \exp(-7475.06/RT)$	L/(mol·s)	<i>b</i>
ρ_M	$0.966\,471-1.16 \times 10^{-3}(T-273.15)$	g/cm ³	<i>b</i>
ρ_P	$1.193\,43-2.8 \times 10^{-4}(T-273.15)$	g/cm ³	<i>b</i>
γ	0.84		<i>b</i>

^a Based on the expression presented by Kuindersma (1992) as being a reasonable description for available data sets. It was modified to obtain a better fit to the data set presented by Huang (1988). (See text). ^b Kuindersma (1992). ^c All activation energies are stated in cal/mol, and the temperature *T* is in Kelvin.

differential equations describing low-conversion (0–20 mol %) ampule experiments. The equations include a balance on the total moles of radicals, the moles of monomers 1 and 2 being consumed, and the moles of monomer incorporated in the copolymer. The equations also include the change of conversion with time, the change in volume with time, the moments of the molecular weight distribution, and the change in the triad fractions with time.

The general simulation model was then customized for each of the three copolymer systems studied by hard-coding rate constants and physical properties such as monomer and polymer densities. The three systems studied are styrene–acrylonitrile (STY/AN), styrene–methyl methacrylate (STY/MMA), and styrene–butyl acrylate (STY/BA). The resulting simulations were then checked against existing experimental data and fine tuned until the simulation models could accurately predict existing data.

For example, consider the development of the simulation for the copolymerization of styrene and methyl methacrylate. The homopolymerization constants used for styrene and methyl methacrylate are given in Tables 4 and 5. To simulate copolymerization, values were also needed for reactivity ratios, the overall termination rate constant, the transfer to monomer rate constant, and the copolymer density.

The reactivity ratios for STY/MMA were taken from O'Driscoll and Huang (1989). In the simulation all equations have been written in terms of penultimate monomer and radical reactivity ratios. For STY/MMA, which is thought to be best described by an implicit penultimate model (Fukuda et al. (1985a) and Davis et al. (1989a)), this means that parameters are assigned with the simplifications $r_{11} = r_{21}$ and $r_{22} = r_{12}$ as given in Table 6. In fact, since the terminal model is nested within the penultimate model, the simulation as designed can be adapted to reproduce terminal model kinetics, implicit penultimate effects, or explicit penultimate effects.

Finally, the overall termination rate constant, the overall transfer to monomer rate constant, and the

Table 6. Reactivity Ratios for the Modeling of STY/MMA

parameter	value	source	parameter	value	source
r_{11}	0.472	<i>a</i>	r_{12}	0.454	<i>a</i>
r_{21}	0.472	<i>a</i>	s_1	0.412	<i>a</i>
r_{22}	0.454	<i>a</i>	s_2	0.170	<i>a</i>

^a O'Driscoll and Huang (1989). The value of s_2 was reported as 0.153 by O'Driscoll and Huang (1989) and has been modified to 0.170. (See text.)

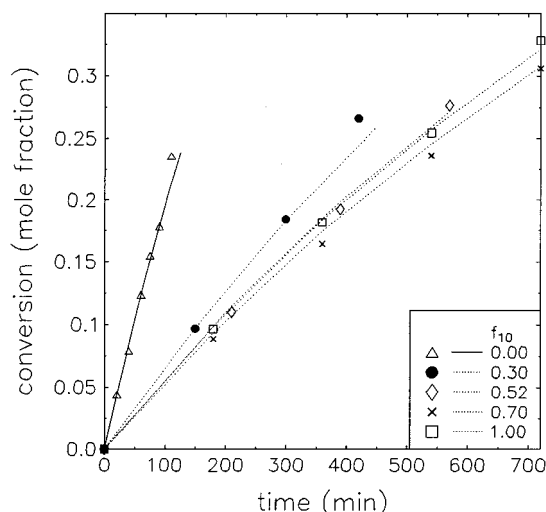


Figure 2. Conversion versus time data for STY/MMA. Symbols represent the experimental data of Huang (1988) at 60 °C; [I] = 0.01 mol/L of AIBME. The lines are model predictions. f_{10} is the mole fraction of styrene in the feed.

copolymer density were all estimated as averages of the homopolymer values.

After including expressions for these constants, the simulation was checked using the experimental data of Huang (1988) and Fukuda et al. (1985a). The simulation was first tested on the data of Huang (1988). Huang (1988) used the initiator 2,2'-azobis(isobutyromethyl ether) (AIBME), and so kinetic data for AIBME (O'Driscoll and Huang (1989)) were used in order to obtain the model predictions. (Data for 2,2'-azobis(isobutyronitrile) (AIBN) have been used in all other simulations.) The simulation predicted conversion and cumulative composition well except for slight overpredictions of conversion for MMA-rich copolymers. In order to improve the predictions for this particular data set, the MMA homopolymerization rate constant was decreased by a factor of 1.09 and the value of s_2 was increased to 0.170 from the value of 0.153 reported by O'Driscoll and Huang (1989). Figures 2 and 3 show the experimental data and model predictions. Note that the predictions shown in the figures are simulations of the "true" system behavior. No random error has been added to the predictions. The simulation seems to predict conversion and copolymer composition adequately at all feed compositions.

Conditions for Simulation Runs. The simulations for STY/MMA, STY/AN, and STY/BA can all reliably simulate the type of data that would be obtained in the laboratory. When these simulations are combined with computer code which designs and analyzes model discrimination experiments, each run of the program can simulate a total of up to 20 sequentially designed parameter estimation and model discrimination experiments. The simulations were designed to study the application of each model discrimination method (exact entropy, Hsiang and Reilly and Buzzi-Ferraris and Forzatti) to the three copolymer systems (STY/MMA,

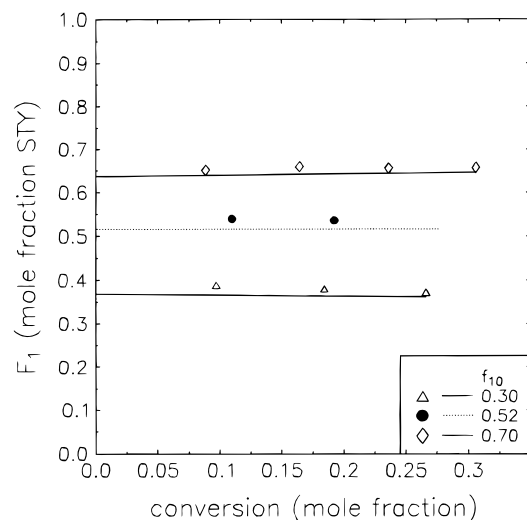


Figure 3. Composition versus conversion data for STY/MMA. Symbols represent the experimental data of Huang (1988) at 60 °C; $[I] = 0.01$ mol/L of AIBME. The lines are model predictions. f_{10} as in Figure 2.

Table 7. Error Levels for STY/AN

	level		
	low	medium	high
feed composition	0.005	0.005	0.005
polymer composition	0.005	0.010	0.015
triad fraction (mole fraction)	0.00833	0.01677	0.03333
chain length (% error)	1.666	3.333	6.666
conversion (mole fraction)	0.0067	0.0067	0.0067

STY/AN, and STY/BA). This results in nine combinations of the model discrimination method and copolymer system for each of the three measurements (copolymer composition, triad fractions, and copolymerization rate).

For each of these nine combinations, there are several other variables that affect the results of model discrimination experiments. For example, *initial* guesses of *reactivity ratios* are input into the program and used to design the initial parameter estimation experiments. If the initial reactivity ratio estimates are changed, the effect on the initial parameter estimation experiments will affect the overall results of the model discrimination experiments. The magnitude of the *experimental error* added in the simulation will also affect discrimination since increasing the error makes model discrimination more difficult. Finally, the “true” nature of the copolymer system, terminal or penultimate, will affect the results. In real life we can never know the “true” model with 100% certainty, but by using simulations the level of penultimate effect can be arbitrarily changed by changing the reactivity ratios in the *simulation model*, which is the “true” model for the purpose of the simulation.

These last three variables, the initial reactivity ratios, the level of experimental error, and the simulation model, were investigated by assigning three levels to each variable for each copolymer system. For example, Tables 7–9 show the levels that were assigned for the study of the system STY/AN based on copolymer composition data.

Table 7 contains the three levels of experimental error. The errors were assumed to be normally distributed and have been expressed in terms of standard deviations. For example, it was estimated from literature data (e.g., Garcia-Rubio and Ro (1985), Garcia-Rubio et al. (1985), Johnson et al. (1978), Ebdon (1982))

Table 8. Simulation Parameters for STY/AN

	level		
	terminal	strong penultimate	small penultimate
r_{11}	0.400	0.230	0.331
r_{21}	0.400	0.634	0.533
r_{22}	0.065	0.039	0.052
r_{12}	0.065	0.091	0.078
s_1	0.700	0.700	1.000
s_2	0.700	0.700	1.000

Table 9. Initial Reactivity Ratio Estimates for STY/AN

	level		
	poor	neutral	good
\hat{r}_{11}	0.600	0.350	0.200
\hat{r}_{21}	0.200	0.450	0.600
\hat{r}_{22}	0.100	0.060	0.050
\hat{r}_{12}	0.050	0.080	0.100
\hat{r}_1	0.100	0.300	0.450
\hat{r}_2	0.450	0.200	0.100
\hat{s}_1	1.000	0.850	0.850
\hat{s}_2	1.000	0.850	0.850

that the typical error in cumulative composition is approximately ± 0.03 mole fraction and that this represents 3 standard deviations. Therefore, the medium level of polymer composition error was assigned a standard deviation of $0.03/3 = 0.010$ mole fraction. Since this may be too high, a low error level was created with a standard deviation of 0.005 mole fraction and a high error level was also used with a standard deviation of 0.015 mole fraction. The error in feed composition was assumed to be approximately ± 0.015 mole fraction and was assigned a standard deviation of $0.015/3 = 0.005$. Errors are also given for triad fractions and chain length in a pulsed laser experiment (which is a measure of copolymerization rate). The error in conversion was assumed to be approximately ± 0.020 mole fraction and was assigned a standard deviation of 0.0067.

Table 8 contains the reactivity ratios for the three levels of the simulation model. The first level is the implicit penultimate model. Here the implicit penultimate model will be referred to as the terminal model since the implicit penultimate model cannot be distinguished from the terminal model using composition data alone. The values of the monomer reactivity ratios for the terminal model were set based on the terminal model reactivity ratios given by Garcia-Rubio (1981) and Hill et al. (1982). The values of the radical reactivity ratios (s_1 , s_2) were set arbitrarily to produce what should be a noticeable penultimate effect in the studies based on copolymerization rate. The second level is a “strong” explicit penultimate effect. The reactivity ratios were set using the penultimate estimates of Hill et al. (1982), and the radical reactivity ratios were set to be the same as those in the terminal model. This penultimate effect is termed a strong penultimate effect because STY/AN is one of the few systems for which the penultimate model has been shown to provide a better description of copolymer composition data than the terminal model. Thus, the differences between reactivity ratios (e.g., $|r_{11} - r_{21}|$) are probably larger than those of other systems. However, this level of penultimate effect is unusually large, and it would be useful to investigate cases where the penultimate effect is smaller than that found by Hill et al. (1982) for STY/AN. Thus, the third level is a “small” explicit penultimate effect which should be much harder to detect than the strong penultimate effect. For this third level, the reactivity ratios were set so that

Table 10. Experimental Design for Simulation Runs^a

run	simulation model	initial reactivity ratio estimates	error level
1	terminal	poor	low
2	terminal	poor	medium
3	terminal	poor	high
4	terminal	neutral	low
5	terminal	neutral	medium
6	terminal	neutral	high
7	terminal	good	low
8	terminal	good	medium
9	terminal	good	high
10	strong penultimate	poor	low
11	strong penultimate	poor	medium
12	strong penultimate	poor	high
13	strong penultimate	neutral	low
14	strong penultimate	neutral	medium
15	strong penultimate	neutral	high
16	strong penultimate	good	low
17	small penultimate	good	medium
18	small penultimate	good	high
19	small penultimate	poor	low
20	small penultimate	poor	medium
21	small penultimate	poor	high
22	small penultimate	neutral	low
23	small penultimate	neutral	medium
24	small penultimate	neutral	high
25	small penultimate	good	low
26	small penultimate	good	medium
27	small penultimate	good	high

^a The values used for the simulation model, the initial reactivity ratios, and the error level are given for STY/AN in Tables 7–9.

the differences in reactivity ratios ($r_{11} - r_{21}$ and $r_{22} - r_{12}$) are half of what they are in the strong penultimate effect.

Table 9 contains the three levels for initial reactivity ratio estimates. The initial reactivity ratio estimates have been set with reference to the strong penultimate case in Table 8. The first column of Table 9 contains the poor initial estimates. They are called poor estimates because they would be poor reactivity ratio estimates if the strong penultimate effect in Table 8 was the "true" simulation model. The third column contains good estimates in that they would be good estimates if the strong penultimate effects was the "true" simulation model. The neutral estimates in the second column would not be particularly good nor particularly bad estimates if the strong penultimate effect was the "true" model for the system.

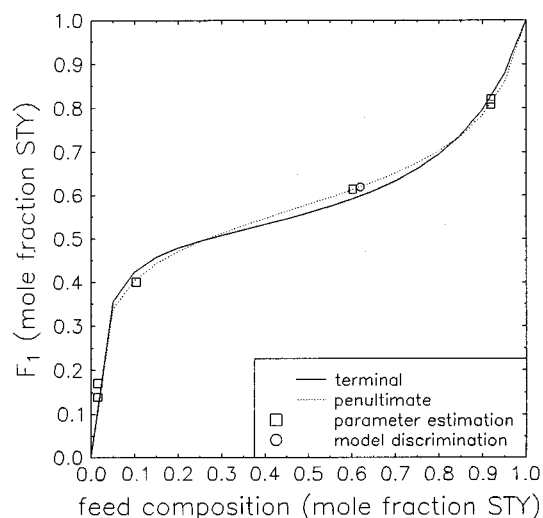
The variable levels for STY/MMA and STY/BA were set in a similar manner. For both STY/MMA and STY/BA, the error levels are the same as those given in Table 7. The simulation parameters for STY/MMA and STY/BA were assigned based on literature values.

The most efficient way to study the effect of the three variables is to design a set of simulation runs for each combination of model discrimination method and copolymer system in the form of a 3^3 factorial experiment. Table 10 shows the combinations of simulation model, initial reactivity ratio estimates, and error level for each run. For example, the seventh run would be set up with the terminal model as the "true" simulation model, "good" initial reactivity ratio estimates, and the low level of experimental error.

Results

Results Based on Copolymer Composition Data.

One of the questions that we wanted to address with this research was whether or not designed experiments would be more reliable and efficient than equally spaced

**Figure 4.** Application of the Buzzi-Ferraris and Forzatti method to STY/AN, run 13.**Table 11. Results Based on Copolymer Composition Data**

simulation model	model chosen as "best" at 95% confidence (number of simulation runs)		
	terminal	penultimate	neither
A. Buzzi-Ferraris and Forzatti Method			
terminal	7	4	16
strong penultimate	3	22	2
small penultimate	3	16	8
B. Exact Entropy Method			
terminal	19	6	2
strong penultimate	21	4	2
small penultimate	22	3	2
C. Hsiang and Reilly Method			
terminal	23	3	1
strong penultimate	17	8	2
small penultimate	25	2	0

experiments. The simulations in which copolymer composition was the measured variable provided a clear answer. Figure 4 shows the results of run 13 (conditions given in Table 10) in which the Buzzi-Ferraris and Forzatti method was applied to the system STY/AN. In this run, the simulation model was the strong penultimate effect with model parameters $r_{11} = 0.230$, $r_{21} = 0.634$, $r_{22} = 0.039$, and $r_{12} = 0.091$. The initial parameter estimates were $\hat{r}_{11} = 0.350$, $\hat{r}_{21} = 0.450$, $\hat{r}_{22} = 0.060$, and $\hat{r}_{12} = 0.080$, and the standard deviation of the error in cumulative composition was 0.005 mole fraction. The conditions used for this simulation run are almost identical to the conditions under when the experiments in Figure 1 were performed. In this simulation run, the penultimate model was chosen as the best model for composition data at 98.3% confidence using just 7 experiments, whereas in the work of Hill et al. (1982) shown in Figure 1, 14 experiments were performed and the penultimate model was chosen as best with 99.5% confidence. In general, by using the Buzzi-Ferraris and Forzatti method on the system STY/AN, it was possible to discriminate between the terminal and penultimate models in fewer experiments than would be required if experiments were evenly spread over the full range of feed compositions. Thus, it seems possible to reduce the number of experiments required to identify the best model for the system by using a combination of parameter estimation and model discrimination experiments.

Table 11 summarizes all of the simulation results. The results for the copolymer systems STY/MMA, STY/

AN, and STY/BA have been combined together in order to provide a concise overview of the data. The first row of Table 11A shows that when the terminal model was used to generate copolymer composition data, the Buzzi-Ferraris and Forzatti method picked the terminal models in 7 runs and the penultimate model in 4 runs, and neither model was picked as "best" at 95% confidence in 16 out of 27 runs.

The results show that the Buzzi-Ferraris and Forzatti method is most likely to correctly discriminate between the two models based on copolymer composition data and that penultimate effects can be detected despite the small differences between model predictions. The Buzzi-Ferraris and Forzatti method was able to correctly discriminate in 81.5% (22 out of 27) of the runs in which the strong penultimate model was used to generate data and 59.3% of the runs in which the small penultimate model was used to generate the data. This is important when we consider that the simulated small penultimate effect is smaller than penultimate effects that have been reported in the literature. This indicates that, if penultimate effects exist, they can be detected using designed experiments. In contrast, when the terminal model was used to generate data, neither model was picked as "best" in 16 of the runs and in 4 of the runs the penultimate model was falsely chosen as the best model for the system. Picking neither model when the terminal model is actually correct is not that serious since the two models are nested and we would by default use the more parsimonious terminal model. Falsely choosing the penultimate model is more serious. An analysis of the results leads to the conclusion that with only one response the extra parameters in the penultimate model allowed the penultimate model to "overfit" the data. This "overfitting" caused the penultimate model to be incorrectly chosen. This type of variance estimation problem could be overcome in the single-response case by incorporating independent replicates of the model discrimination experiments. For example, when the simulations were re-run with replicate model discrimination experiments, only 1 run in 27 remained in which the penultimate model was falsely chosen.

Table 11B shows the results for the exact entropy method. The exact entropy method tends to choose the terminal model as "best" regardless of which model was used to generate the data. In many runs, the conditions chosen for model discrimination experiments were similar to those chosen by the Buzzi-Ferraris and Forzatti method. Therefore, the difference in reliability seems to be due to the difference in the analysis step. The F -test used in the Buzzi-Ferraris and Forzatti method may be better able to discriminate in the case of small differences between model predictions because it is specifically designed to analyze nested models. The similarity between the two analysis methods is how they respond to poor estimates of experimental variance. There were 6 runs in which the terminal model was used to generate the data and the penultimate model was falsely picked as the "best" model. Once again, this seems to be due to the ability of the penultimate model to overfit the data.

The results for the Hsiang and Reilly method, shown in Table 11C, are similar to the results for the exact entropy method. The differences between the Hsiang and Reilly results and the Buzzi-Ferraris and Forzatti results are partly caused by the difference in the analysis step and partly due to the fact that the design

criterion in eq 27 chooses different feed compositions from the Buzzi-Ferraris and Forzatti criterion.

Results Based on Triad Fraction Data. As with composition data, triad fractions depend only on monomer reactivity ratios. However, although there is only one composition measurement, either F_1 or F_2 , there are six triad fractions (A_{111} , $A_{211+112}$, A_{212} , A_{222} , $A_{122+221}$, and A_{121}). Of course, one cannot use all six triad fraction measurements. Since triad fractions are customarily normalized, e.g.

$$A_{111} + A_{211+112} + A_{212} = 1 \quad (56)$$

$$A_{222} + A_{122+221} + A_{121} = 1 \quad (57)$$

the use of all six triad fractions will create two linear dependencies in the data. Even if triad fraction data are not normalized, eqs 56 and 57 will still hold approximately, and this will create two near-linear dependencies in the data. Box et al. (1973) explain how linear or near-linear dependencies in experimental data lead to high correlations among estimated model parameters. In order to avoid a linear dependency in the data, only two of the monomer-1-centered triads and two of the monomer-2-centered triads should be used. The four triads used in the simulations were $A_{211+112}$, A_{212} , $A_{122+221}$, and A_{121} . The triad fractions A_{111} and A_{222} have been excluded because their concentrations are small except at feed compositions close to the homopolymerization conditions. Since four triad fractions were used, the multiresponse forms of the model discrimination methods were used in the simulations.

The simulation results show that the use of model discrimination experiments based on triad fraction data should improve our ability to correctly and efficiently identify the best copolymerization model for a given system. For example, parts a and b of Figure 5 show the results of run 14 (conditions given in Table 10) in which the modified Buzzi-Ferraris and Forzatti method was applied to the system STY/AN. The conditions used to simulate the data in parts a and b of Figure 5 closely duplicate the experimental conditions used by Hill et al. (1989) in parts a and b of Figure 6. The data in parts a and b of Figure 5 were simulated using the strong penultimate model as the "true" model with reactivity ratios $r_{11} = 0.230$, $r_{21} = 0.634$, $r_{22} = 0.039$, and $r_{12} = 0.091$ ($s_1 = s_2 = 0.700$). The initial reactivity ratios were $\hat{r}_{11} = 0.350$, $\hat{r}_{21} = 0.450$, $\hat{r}_{22} = 0.06$, and $\hat{r}_{12} = 0.08$ ($\hat{s}_1 = \hat{s}_2 = 0.850$), and the standard error of triad fraction measurements was 0.01667 mole fraction. In the simulation, the modified Buzzi-Ferraris and Forzatti method was able to pick the penultimate model as "best" at a 99.99% confidence level using 8 parameter estimation and 1 model discrimination experiments. In the work of Hill et al. (1989), 13 experiments were required to pick the penultimate model as "best" at greater than 99.0% confidence. In general, the use of model discrimination methods leads to discrimination in a total of about 10 experiments at the 95% confidence level when discrimination is possible. This is an improvement over previous work in which experiments were typically spread over the entire range of feed compositions.

Table 12 provides a summary of the simulations based on triad fraction data. (More detailed results are given in Burke et al. (1995b).) The first row of the table shows that when the terminal model was used to simulate data, the Buzzi-Ferraris and Forzatti method picked the terminal model as "best" in 26 runs, the penultimate

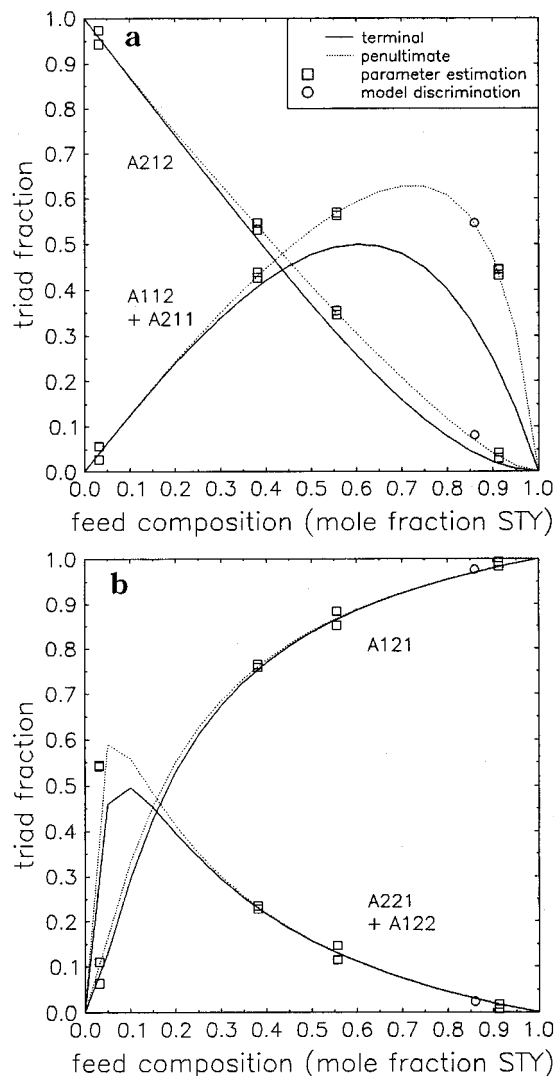


Figure 5. Application of the Buzzi-Ferraris and Forzatti method to STY/AN based on triad fraction data (run 14): (a) monomer-1-centered triads; (b) monomer-2-centered triads.

model was not picked in any run, and neither model was picked as "best" at 95% confidence in 1 run.

Table 12A shows that the Buzzi-Ferraris and Forzatti method was able to pick the model used to generate the data in 98.8% of the simulations including all of the simulation in which the penultimate model was used to generate the data.

The exact entropy method, shown in Table 12B, was able to discriminate as well when the penultimate model was used to generate data. The difference between the two methods is that the exact entropy method cannot reliably identify terminal model kinetics. The penultimate model variance estimates were examined, since poor estimates could cause this type of problem. However, the penultimate model variance estimates were reasonably close to the true simulation values. It is possible that the difference between the exact entropy and Buzzi-Ferraris and Forzatti results is due to the Bayesian analysis which is not specifically designed to discriminate between nested models.

Table 12C shows that the Hsiang and Reilly method was also able to discriminate when the penultimate model was used to generate triad fraction data. When the strong penultimate model was used to generate data, the Hsiang and Reilly method correctly picked the penultimate model as "best" in all of the runs. When

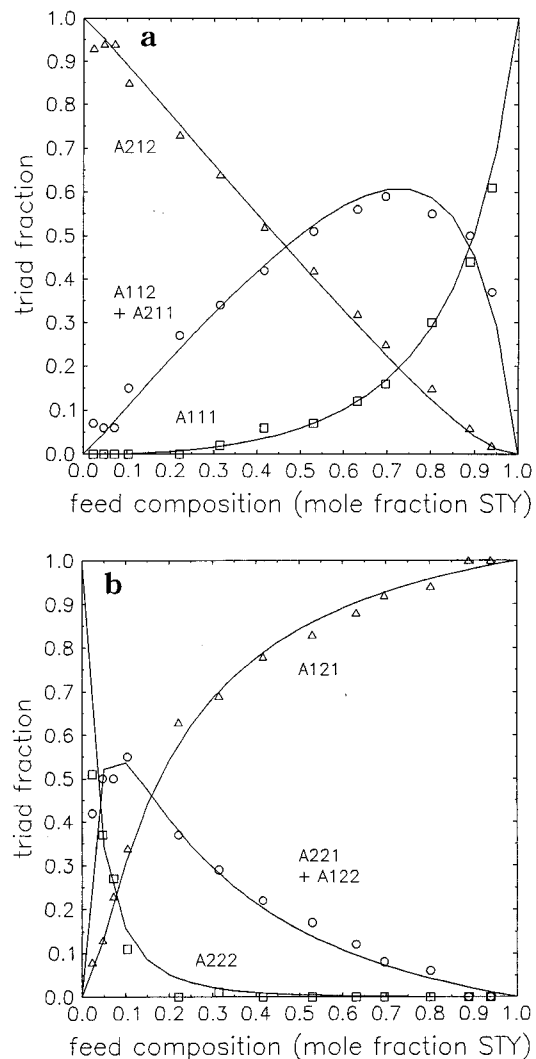


Figure 6. Triad fraction data of Hill et al. (1989) for STY/AN. The simulation predictions were calculated using the penultimate reactivity ratios $\hat{r}_{11} = 0.230$, $\hat{r}_{21} = 0.634$, $\hat{r}_{22} = 0.039$, and $\hat{r}_{12} = 0.091$. (a) Monomer-1-centered triads. (b) Monomer-2-centered triads.

Table 12. Results Based on Triad Fraction Data

simulation model	model chosen as "best" at 95% confidence (number of simulation runs)		
	terminal	penultimate	neither
A. Buzzi-Ferraris and Forzatti Method			
terminal	26	0	1
strong penultimate	0	27	0
small penultimate	0	27	0
B. Exact Entropy Method			
terminal	8	7	12
strong penultimate	0	27	0
small penultimate	0	27	0
C. Hsiang and Reilly Method			
terminal	17	9	1
strong penultimate	0	27	0
small penultimate	4	23	0

the terminal model was used to generate data, the terminal model was picked more often than in the case of the exact entropy method, but the penultimate model was falsely picked more often as well. An examination of the runs in which the penultimate model was falsely picked showed that the penultimate maximum likelihood estimate of the error covariance matrix was smaller on an element by element basis than the

terminal model estimate. Therefore, the problem might be due to problems with the covariance estimates, although this was not anticipated. In fact, the replication in the parameter estimation experiments should improve the covariance estimates.

However, the results from the Hsiang and Reilly method do suggest that the penultimate maximum likelihood estimate of the covariance matrix may underestimate the true value when the terminal model is used to simulate experimental data. If, in fact, the covariance estimate is causing the difficulty in discrimination, it may be possible to eliminate the problem by eliminating the need for a covariance estimate. For example, Box and Draper (1965), in their work on multivariate parameter estimation, showed how the covariance matrix could be integrated out of the posterior probability distribution of the model parameters. It should be possible to eliminate the covariance matrix from the model likelihoods using similar arguments and thus develop a Bayesian analysis that does not depend on the estimate of the covariance matrix. Once the new model likelihoods are derived, a few of the simulations can be repeated to determine whether or not poor covariance estimates were at the root of the problem in Table 12C.

The results are overall very positive and somewhat surprising. For example, the Buzzi-Ferraris and Forzatti method was able to correctly identify small penultimate effects in only 59.3% of the simulations in which copolymer composition was the measured variable, but the same method correctly identified penultimate effects in 100% of the simulations in which triad fractions were the measured variable. The use of triad fraction data resulted in more reliable discrimination than copolymer composition despite the fact that both measurements depend on the same reactivity ratios. Why does the use of triad fraction data result in more reliable model discrimination?

There are two reasons why the use of triad fraction data allows the correct model to be more readily identified than the use of copolymer composition data. First, there is more replication within the parameter estimation experiments based on triad fraction data. There are four optimal parameter experiments for estimating the penultimate reactivity ratios. The feed compositions for these experiments will be different for experiments based on polymer composition versus experiments based on triad fraction data, but the fact remains that there are four optimal experiments for each. In the work on copolymer composition data, six parameter estimation experiments were performed, including two replicates, in order to estimate all four penultimate reactivity ratios and have 2 degrees of freedom left for the penultimate estimate of variance. In the triad fraction simulations, all four optimal experiments were simulated twice in order to estimate all four penultimate reactivity ratios and have 4 degrees of freedom left for the 4×4 estimate of the covariance matrix Σ . The additional replication used in the triad fraction simulations may help provide a more reliable variance estimate than was obtained in the composition studies. Second, there are four linearly independent triad fractions compared to one composition measurement. Duever (1987) and Hill et al. (1989) have previously shown that the use of diad and triad measurements, respectively, improve the precision in reactivity ratio estimates. Thus, the use of four measurements instead of one should improve the precision of reactivity ratio estimates and lead to improvements in model

discrimination. The benefits of using four triad fraction measurements are shared by all three model discrimination methods.

Results Based on Copolymer Composition and Chain-Length Data. In our third set of simulation studies, we set out to use rate data (in the form of chain-length measurements from pulsed-laser experiments) to discriminate between the terminal and penultimate models for copolymerization, just as copolymer composition and triad fraction data had been used in the previous two studies. However, we discovered that the penultimate parameter estimates based on rate data alone are so highly correlated that it makes it virtually impossible to accurately estimate all penultimate parameters for rate data (Burke et al. (1995)). In order to estimate all model parameters and discriminate between the two models, one has to use either copolymer composition data or triad fraction data together with chain-length data. We have chosen to use copolymer composition data.

In our simulation studies involving chain-length data, we have also increased the number of simulation models. In the studies on copolymer composition and triad fraction data, the simulation models were the terminal model (which was really an implicit penultimate model), the strong explicit penultimate model, and the small explicit penultimate model. Since rate data can be used to distinguish between implicit and explicit penultimate effects, it was necessary to add a fourth true terminal model. Thus, in the simulations involving rate data, the implicit penultimate model has been referred to as such and a true terminal model has been added by setting the radical reactivity ratios in the implicit penultimate model to 1 (e.g., $s_1 = s_2 = 1$).

Parts a and b of Figure 7 show an example of simulation results based on copolymer composition and chain length as the measured variables. The results are from run 14 (conditions given in Table 10) in which the modified Buzzi-Ferraris and Forzatti method was applied to the system STY/AN. A total of 15 experiments was simulated, and the penultimate model was picked as best at >99.9% confidence. Parts a and b of Figure 7 are typical of the simulation results for all three copolymer systems and all three model discrimination methods.

Table 13 summarizes the simulation results. For example, Table 13A gives the results for the application of the modified Buzzi-Ferraris and Forzatti method based on copolymer composition and chain-length data. The first row shows that when the implicit penultimate model was used to generate simulated data, the penultimate model was picked at $\geq 95\%$ confidence in 27 out of 27 runs. Overall, the Buzzi-Ferraris and Forzatti method correctly discriminated between the terminal and penultimate models in 96% of the simulations.

The data in Table 13B show that the exact entropy method was also able to correctly discriminate between the terminal and penultimate models based on copolymer composition and rate data. The difference between the modified Buzzi-Ferraris and Forzatti method and the exact entropy method is that the exact entropy method usually chooses neither model as "best" when the terminal model is used to generate simulated data. We would have expected, as did Box and Hill (1967), that the exact entropy method would be able to identify cases where the simpler of the two nested models was the "best" model. However, just as in the case of triad fraction data, it seems that the Bayesian analysis may

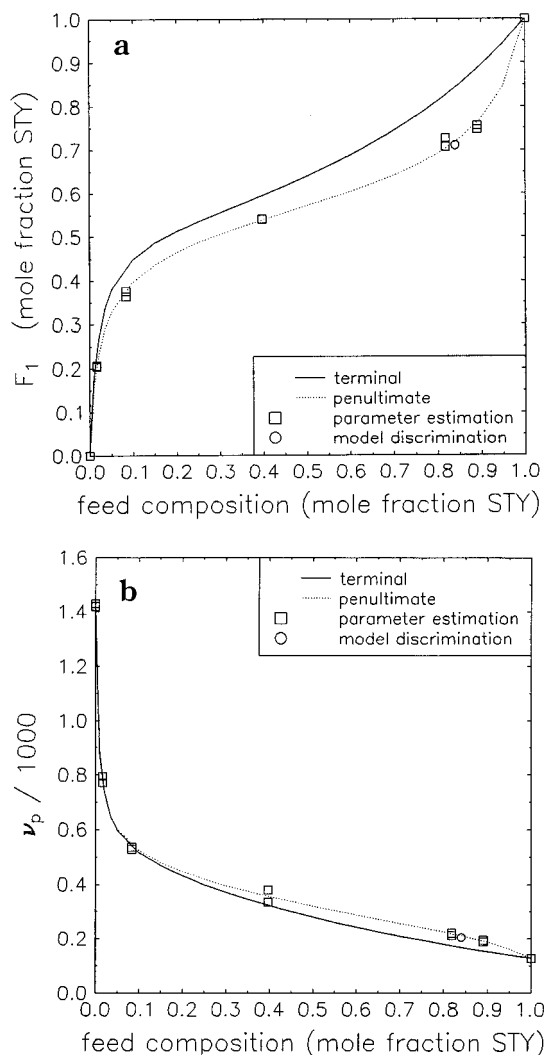


Figure 7. Application of the modified Buzzi-Ferraris and Forzatti method to STY/AN based on copolymer composition and chain length data. (a) Copolymer composition for run 14. (b) Chain length for run 14.

Table 13. Results Based on Copolymer Composition and Chain-Length Data

simulation model	model chosen as "best" at 95% confidence (number of simulation runs)		
	terminal	penultimate	neither
A. Buzzi-Ferraris and Forzatti Method			
implicit penultimate	0	27	0
strong penultimate	0	27	0
small penultimate	2	25	0
terminal	25	0	2
B. Exact Entropy Method			
implicit penultimate	0	26	1
strong penultimate	0	27	0
small penultimate	0	25	2
terminal	0	4	23
C. Hsiang and Reilly Method			
implicit penultimate	2	25	0
strong penultimate	0	27	0
small penultimate	1	26	0
terminal	16	11	0

not be able to discriminate as effectively as the use of the F -statistic which is specifically designed to discriminate between nested models.

The data in Table 13C show that the Hsiang and Reilly criterion can correctly discriminate between the copolymerization models when either the implicit or

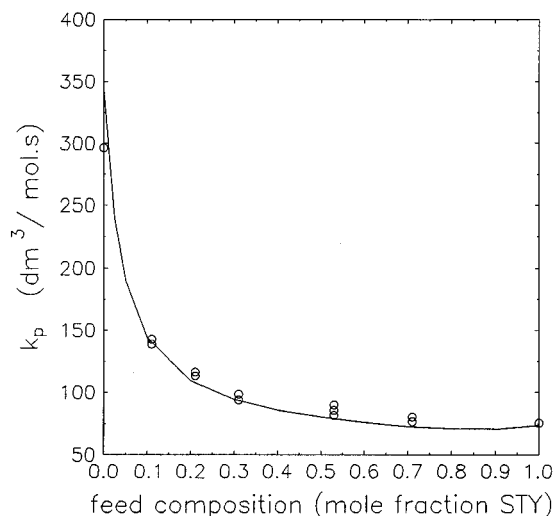


Figure 8. Model predictions of the k_p data for STY/MMA. Symbols represent the data of Davis et al. (1989a). The line is the penultimate prediction based on $\hat{r}_{11} = \hat{r}_{21} = 0.472$, $\hat{r}_{22} = \hat{r}_{12} = 0.454$, $\hat{s}_1 = 0.412$, and $\hat{s}_2 = 0.170$.

explicit penultimate model is used to generate data. When the terminal model is used to generate simulated data, the Hsiang and Reilly method correctly picks the terminal model more often than the exact entropy method but falsely picks the penultimate model as "best" more often as well. This is similar to the results obtained based on triad fraction data. A closer examination of the results showed that the penultimate maximum likelihood estimate of the covariance matrix was smaller than the terminal model estimate in all the runs in which the penultimate model was falsely picked. In other words, the penultimate model provides a lower variance estimate than the terminal model. This is quite unexpected. The replication in the parameter estimation experiments should lead to a good covariance estimate for both models. However, as suggested previously, the only solution to this problem may be to integrate the covariance matrix out of the posterior distribution of the parameters, which will, in turn, eliminate it from the likelihood expression in eq 35.

Comparison to Past Work. The simulations show that the use of designed experiments should allow one to correctly discriminate based on composition and rate data. How does this compare to past work based on rate data? In work performed by other researchers on rate data, such as the work of Davis et al. (1989a) shown in Figure 8 (along with the work of O'Driscoll (1992) and Fukuda et al. (1992)), a total of 9–17 experiments was used to pick the penultimate model as the "best" model. In our simulations, a total of 15 experiments was typically used to discriminate between the two models. Therefore, the number of experiments per se has not been reduced considerably. However, the use of designed experiments should increase the information content of the data and allow successful discrimination for systems with smaller penultimate effects. If we compare Figure 8 with parts a and b of Figure 7, we see that our designed experiments put more emphasis on the feed composition range from $f_1 = 0.0$ to 0.1 presumably because both copolymer composition and chain length are changing rapidly in this range. This should improve the precision and accuracy of the estimated reactivity ratios and lead to reliable model discrimination in cases where the implicit penultimate effect is smaller than that in systems previously studied in the literature. As an example, the implicit penulti-

Table 14. Radical Reactivity Ratios for Copolymer Systems Containing Styrene

system	temp (°C)	s_1	s_2	$s_1 s_2$	source
styrene/methyl methacrylate	40	0.30	0.53	0.159	Fukuda et al. (1985a)
styrene/methyl methacrylate	25	0.466	0.175	0.082	Davis et al. (1989a)
styrene/ethyl methacrylate	25	0.62	0.21	0.130	Davis et al. (1990)
styrene/butyl methacrylate	25	0.56	0.63	0.353	Davis et al. (1990)
styrene/methyl acrylate	25	1.10	0.26	0.286	Davis et al. (1991)
styrene/butyl acrylate	50	0.90	0.11	0.099	Davis et al. (1991)

mate model used to generate data for the system STY/AN contains a smaller implicit penultimate effect than other systems previously studied. The relative magnitude of the implicit penultimate effect is given by the product $s_1 s_2$. Strong implicit penultimate effects are indicated by $s_1 s_2 \ll 1.0$, whereas the terminal model is represented by $s_1 = s_2 = 1.0$. Some typical values of $s_1 s_2$ from the literature are given in Table 14. The implicit penultimate model used for STY/AN (referred to as the terminal model in Table 8) has radical reactivity ratios of $s_1 = s_2 = 0.7$, which gives a product of $s_1 s_2 = 0.49$. This represents a smaller implicit penultimate effect than all of the systems in Table 14. Despite this, all three of the model discrimination methods were able to correctly identify the penultimate model as "best" in at least 7 out of 9 runs in which the implicit penultimate model was used to generate data for the system STY/AN. These results indicate that designed experiments would, in principle, allow us to identify penultimate effects that are smaller than those already identified in the literature.

Concluding Remarks

For each set of simulation studies (copolymer composition, triad fractions, and rate), the simulation results were first compared to past work in the area of copolymerization modeling. In the case of copolymer composition data, we found that when penultimate unit effects exist, a combination of parameter estimation and model discrimination experiments can correctly detect these effects in fewer experiments than have typically been used. For example, when the penultimate model was used to simulate data for STY/AN, the Buzzi-Ferraris and Forzatti method picked the penultimate model as "best" in half the number of experiments used by Hill et al. (1982). The simulations showed that when the small penultimate model was used to generate data, the Buzzi-Ferraris and Forzatti method could correctly identify the penultimate model as "best" in 59.3% of the simulations. This is significant since the small penultimate effect is smaller than the penultimate effect found by Hill et al. (1982) for STY/AN and thus is small enough that most researchers would have thought it to be undetectable. The simulations also demonstrated that discrimination can be achieved reliably and efficiently based on the triad fraction and the combination of copolymer composition and rate data. In the case of copolymer composition and rate data, the penultimate effects that can be detected are smaller than any that have been reported in the literature. Thus, for all three measurements, it was found that the use of designed experiments decreased the number of experiments required and/or improved the quality of the information being gathered about the models.

Comparison of Model Discrimination Techniques. The Buzzi-Ferraris and Forzatti method (1983) performed the best on the problem of discriminating between the terminal and penultimate models for copolymerization. It could successfully discriminate based

on copolymer composition data and when the terminal model was used to generate simulated data. These were situations in which the exact entropy method had difficulty achieving discrimination. The superior performance of the Buzzi-Ferraris and Forzatti method seems to be due to the analysis step involving an F -test specifically designed for testing nested models. The design criterion used in the Buzzi-Ferraris and Forzatti method was not better or worse than other design criteria, but the values of the criterion are simpler to interpret.

The exact entropy method (Reilly (1970)) performed almost as well except for problems discriminating based on composition data and problems identifying terminal model kinetics. We had originally thought, as did Box and Hill (1967), that the Bayesian analysis would be able to correctly identify cases in which the simpler of the two nested models is the "best" model. This hypothesis is based on the fact that if the simpler model is "best", both models will have approximately equal residuals and the simpler model will have a smaller prediction variance s^2 due to the smaller number of estimated parameters. This should cause the simpler model to have a higher model likelihood and therefore a higher model probability $Pr(M)$. However, in our simulations, both model probabilities fluctuated around 50% when the terminal model was used to simulate data. This needs to be investigated further to determine whether the problem stems from imprecise estimates of error variance due to the small number of experiments or whether it stems from some other aspect in the implementation of the method.

The Hsiang and Reilly (1971) method did not perform as well as either of the other two methods, despite the fact that it enables nonlinear models to be analyzed without using a linear approximation. The poor performance could be due to the absence of a prediction variance term in the design criterion, the effect of poor variance estimates on the Bayesian analysis, or challenges in implementing the discrete parameter probability distribution.

Comparison of Copolymer Measurements. Three copolymer measurements, copolymer composition, triad fractions (or sequence distribution), and copolymerization rate, have been used in past attempts at copolymerization modeling, but very little information was provided on the relative merits of these measurements.

Researchers had begun to think that copolymer composition data are best described by the terminal model for most systems or that it was practically too difficult to discriminate due to the small difference between model predictions. Our simulation studies showed that when there is indeed a penultimate unit effect on copolymer composition, it is much more likely to be detected if the experiments are designed for the purpose of model discrimination. Using designed experiments (Buzzi-Ferraris and Forzatti method), the correct model could be picked based on composition in 55.6% of the simulations compared with 30.9% of the simulations based on equally spaced experiments. The

reason why both numbers are relatively low is that, based on composition data, both designed and undesigned experiments have difficulty identifying cases of terminal model kinetics at 95% confidence. However, the simulations did show that the use of designed experiments provides more information than was previously thought possible.

Triad fractions are based on the same terminal and penultimate reactivity ratios as copolymer composition data. However, there are four linearly independent triad fraction measurements, compared to one copolymer composition measurement. As a result, triad fractions provide more detailed information on the copolymerization, and this leads to improved discrimination compared to copolymer composition data. In the simulations based on triad fraction data, the Buzzi-Ferraris and Forzatti method was able to identify the correct model in 99% of the simulations at the 95% confidence level. The exact entropy method performed almost as well except for problems identifying terminal model kinetics. The extra information provided by triad fraction measurements may justify the effort required to accurately assign peaks in the ^{13}C -NMR spectra.

Finally, the simulations also showed that the combination of copolymer composition and rate data has great potential for model discrimination. Based on copolymer composition and copolymerization rate data, the Buzzi-Ferraris and Forzatti method was able to discriminate between the terminal and penultimate models in 96% of the simulations. Again, the exact entropy method provided results similar to the Buzzi-Ferraris and Forzatti method except for problems identifying terminal model kinetics.

Both the combination of copolymer composition/rate data and triad fractions were able to correctly discriminate in over 95% of the simulations. The main difference between the two measurements is that triad fraction data are only capable of detecting explicit penultimate effects. Based on this observation, triad fractions would be the measurement of choice if one is only interested in predicting structural information, and the combination of copolymer composition and rate data would be preferred in the more general case. However, the other difference between the two measurements is that the penultimate parameter estimates based on rate data are very highly correlated. Thus, along with the potential of copolymer composition and rate data to achieve successful discrimination, there are additional challenges with respect to parameter estimation. Extreme care must be taken to ensure parameter estimation algorithms converge to a true minimum, and the error in all estimates must be accounted for when comparing models.

Nomenclature

A_{ijk} = instantaneous fraction of monomer- j -centered triads with sequence ijk
 E_i = expectation of a function assuming model i to be the correct representation of the system
 $f_{1,0}$ = initial mole fraction of monomer 1 in the comonomer feed
 f_1, f_2 = mole fractions of monomers 1 and 2 in the comonomer feed
 f_i, f_j = functional form of the i th model for the single- and multiple-response cases, respectively
 F_1, F_2 = instantaneous mole fractions of monomers 1 and 2 in the copolymer

\bar{F}_1, \bar{F}_2 = cumulative mole fraction of monomers 1 and 2 in the copolymer
 F = F -statistic
 $\dot{J}_n = 1 \times k$ Jacobian matrix for a single response at \underline{x}_n
 \mathbf{J} = Jacobian matrix for a single response with dimensions $(n - 1) \times k$ (it contains the derivatives of the model predictions with respect to the parameters for the last $n - 1$ experiments)
 \mathbf{J}_i = Jacobian matrix for the i th response where $i = 1, 2, \dots, P$
 k_{TM} = overall rate constant for transfer to monomer (L/(mol·s))
 k_i = number of parameters in model i (it is sometimes used without a subscript when referring to models in general)
 k_{ij} = terminal model rate constant for the addition of monomer j to a radical ending in unit i (L/(mol·s))
 k_{ijk} = penultimate model rate constant for the addition of monomer k to a radical ending in units ij (L/(mol·s))
 k_p = overall propagation rate constant (L/(mol·s))
 k_t = overall termination rate constant (L/(mol·s))
 $L(M_i|y_n)$ = likelihood of model i given the observation y_n
 $L(M_i|\underline{y}_n)$ = likelihood of model i given the multiple response observation \underline{y}_n
 m = number of competing models
 M_j = monomer j
 n = total number of experiments (when the next experiment is being designed, it is referred to as the n th experiment)
 p = number of measurements or responses available from a single experiment
 $p(y_n|\hat{y}_i, \sigma^2)$ = probability of the observation y_n given the prediction of the i th model \hat{y}_i and some estimate of the error variance σ^2
 $p_i(\underline{y}_n|\hat{\underline{y}}_i, \Sigma)$ = probability of the multiple-response observation \underline{y}_n given the prediction of the i th model $\hat{\underline{y}}_i$ and some estimate of the error covariance matrix Σ
 $Pr(M_{i,n})$ = probability that model i is the "best" model for the system after the n th experiment
 q = used in conjunction with the testing of two nested models (q is the number of restrictions that must be placed on the parameters of the more complex model to reduce it to the simpler model)
 r_1, r_2 = reactivity ratios in the terminal model
 $r_{11}, r_{21}, r_{22}, r_{12}$ = monomer reactivity ratios in the penultimate model
 R_n^\bullet = free-radical chain containing n monomer units
 $R_{n,ij}^\bullet, R_{n,ijk}^\bullet$ = free-radical chains of length n ending in monomer units ij and ijk , respectively
 s_1, s_2 = radical reactivity ratios in the penultimate model
 s^2 = estimated measurement variance (the subscripts term and pent have been used to denote the estimates produced by the terminal and penultimate models, respectively)
 s_i^2 = estimated variance of the average prediction given by the i th model
 \mathbf{S} = estimated $p \times p$ covariance matrix (once again, the subscripts term and pent have been used to denote the estimates produced by the terminal and penultimate models, respectively)
 \mathbf{S}_i = estimated covariance of an individual $1 \times p$ prediction given by the i th model (note $\mathbf{S}_i = \mathbf{S} + \mathbf{W}_i$)
 $S_{ij}(\underline{x}_n)$ = estimated covariance of the difference $(\hat{y}_i - \hat{y}_j)$
 SSR = sum of squared residuals
 v = number of experimental conditions
 \mathbf{W}_i = estimated covariance of the $1 \times p$ average prediction given by the i th model
 \underline{x}_n = vector containing the conditions for the n th experiment
 x = monomer conversion (in this work conversion is mole fraction or mole percent conversion unless otherwise stated)

y_n = scalar containing the observation for the n th experiment in the case of one measured response
 $Y_n = 1 \times p$ vector containing the observations for the n th experiment
 \hat{y}_i , $\hat{y}_{i,n}$ = scalar containing the prediction given by the i th model for the n th experiment in the case of one measured response
 \hat{Y}_i , $\hat{Y}_{i,n} = 1 \times p$ vector containing the prediction given by the i th model for the n th experiment
 \mathbf{Y} = matrix containing the observations for all n experiments
 $\hat{\mathbf{Y}}_i$ = matrix containing the prediction of the i th model for all n experiments

Greek Letters

γ = proportion of free-radical chains terminating by disproportionation
 $\epsilon_{i,n}$ = scalar containing the prediction error for the n th experiment under the i th model in the single-response case
 $\epsilon_{i,n} = 1 \times p$ vector containing the prediction errors for the n th experiment under the i th model
 Θ^{-1} = covariance of the parameters estimated from p responses
 θ_i = vector of parameters for the i th model
 $\hat{\theta}_i$ = vector of parameter estimates for the i th model
 $\tilde{\theta}_i$ = vector used to represent a particular combination of parameter estimates being considered in the Hsiang and Reilly (1971) method
 ν_p = chain length formed between pulses in pulsed-laser experiments
 ρ_M, ρ_P = densities for the comonomer feed and copolymer, respectively (g/cm^3)
 σ^2 = true measurement variance
 $\hat{\sigma}^2$ = variance estimate
 σ_f^2 = true variance of the average prediction given by the i th model (the variance of an individual prediction is $\text{var}(\hat{y}_i) = \sigma^2 + \sigma_f^2$)
 σ^{ij} = ij th element of the matrix Σ^{-1}
 Σ = true covariance matrix for p responses

Literature Cited

- Anderson, T. W. *An introduction to multivariate statistical analysis*, 2nd ed.; John Wiley & Sons Ltd.: New York, 1984.
- Ballard, M. J.; Gilbert, R. G.; Napper, D. H.; Pomery, P. J.; O'Sullivan, P. W.; O'Donnell, J. H. Propagation coefficients from electron spin resonance studies of the emulsion polymerization of methyl methacrylate. *Macromolecules* **1986**, *19*, 1303.
- Bartlett, M. S. Properties of sufficiency and statistical tests. *Proc. R. Soc. London, Ser. A* **1937**, *160*, 268.
- Box, G. E. P.; Draper, N. R. The Bayesian estimation of common parameters from several responses. *Biometrika* **1965**, *52*, 355.
- Box, G. E. P.; Hill, W. J. Discrimination among mechanistic models. *Technometrics* **1967**, *9* (1), 57.
- Box, G. E. P.; Hunter, W. G.; MacGregor, J. E.; Erjavec, J. Some problems associated with the analysis of multiresponse data. *Technometrics* **1973**, *15* (1), 33.
- Brown, P. G.; Fujimori, K. A mechanistic study of the radical copolymerisation of *p*-chlorostyrene with citraconic anhydride via ^{13}C NMR spectroscopy. *Macromol. Chem. Phys.* **1994**, *195*, 917.
- Brown, P. G.; Fujimori, K.; Brown, A. S.; Tucker, D. J. The applicability of copolymer composition and sequence distribution data to the mechanistic study of the alternating copolymerisation of maleic anhydride with substituted styrene derivatives. *Makromol. Chem.* **1993**, *194*, 1357.
- Buback, M.; Garcia-Rubio, L. H.; Gilbert, R. G.; Napper, N. G.; Guillot, J.; Hamielec, A. E.; Hill, D.; O'Driscoll, K. F.; Olaj, O. F.; Shen, J.; Solomon, D.; Moad, G.; Stickler, M.; Tirrell, M.; Winnik, M. A. Consistent values of rate parameters in free radical polymerization systems. *J. Polym. Sci., Polym. Lett.* **1988**, *26*, 293.
- Burke, A. L. Model Discrimination Techniques for the Modeling of Copolymerization Reactions. Ph.D. Thesis, Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada, 1994.
- Burke, A. L.; Duever, T. A.; Penlidis, A. Revisiting the design of experiments for copolymer reactivity ratio estimation. *J. Polym. Sci., Poly. Chem.* **1993**, *31*, 3065.
- Burke, A. L.; Duever, T. A.; Penlidis, A. Model discrimination via designed experiments: discriminating between the terminal and penultimate models on the basis of composition data. *Macromolecules* **1994a**, *27*, 386.
- Burke, A. L.; Duever, T. A.; Penlidis, A. Model discrimination via designed experiments: discriminating between the terminal and penultimate models based on triad fraction data. *Macromol. Theory Simul.* **1994b**, *3*, 1005.
- Burke, A. L.; Duever, T. A.; Penlidis, A. Model discrimination via designed experiments: discrimination between the terminal and penultimate models based on rate data. *Chem. Eng. Sci.* **1995**, *50*, 1619.
- Buzzi-Ferraris, G.; Forzatti, P. A new sequential experimental design procedure for discriminating among rival models. *Chem. Eng. Sci.* **1983**, *38* (2), 225.
- Buzzi-Ferraris, G.; Forzatti, P.; Emig, G.; Hofmann, H. Sequential experimental design for model discrimination in the case of multiple responses. *Chem. Eng. Sci.* **1984**, *39* (1), 81.
- Buzzi-Ferraris, G.; Forzatti, P.; Canu, P. An improved version of a sequential design criterion of discriminating among rival response models. *Chem. Eng. Sci.* **1990**, *45* (2), 477.
- Davis, T. P.; O'Driscoll, K. F.; Piton, M. C.; Winnik, M. A. Determination of rate constants for the copolymerization of methyl methacrylate and styrene using a pulsed laser technique. *J. Polym. Sci., Polym. Lett.* **1989a**, *27*, 181.
- Davis, T. P.; O'Driscoll, K. F.; Piton, M. C.; Winnik, M. A. Determination of propagation rate constants using a pulsed laser technique. *Macromolecules* **1989b**, *22*, 2785.
- Davis, T. P.; O'Driscoll, K. F.; Piton, M. C.; Winnik, M. A. Copolymerization propagation kinetics of styrene with alkyl methacrylates. *Macromolecules* **1990**, *23* (8), 2113.
- Davis, T. P.; O'Driscoll, K. F.; Piton, M. C.; Winnik, M. A. Copolymerization propagation kinetics of styrene with alkyl acrylates. *Polym. Int.* **1991**, *24*, 65.
- Draper, N. R.; Hunter, W. G. Design of experiments for parameter estimation in multiresponse situations. *Biometrika* **1966**, *53* (3 & 4), 525.
- Duever, T. A. Statistical consideration in the use of Monte Carlo methods with applications. Ph.D. Thesis, Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada, 1987.
- Ebdon, J. R. Microstructural analysis of synthetic organic polymers by high resolution NMR. In *Analysis of polymerization systems*; Bark, L. S., Allen, N. S., Eds.; Applied Science Publishers Ltd.: Oxford, England, 1982.
- Fukuda, T.; Ma, Y. D.; Inagaki, H. Free-radical copolymerization I. Reactivity ratios in bulk-copolymerization of *p*-chlorostyrene and methacrylate. *Polym. J.* **1982**, *14* (9), 705.
- Fukuda, T.; Ma, Y. D.; Inagaki, H. Free-radical copolymerization 3. Determination of rate constants of propagation and termination for the styrene/methyl methacrylate system. A critical test of terminal model kinetics. *Macromolecules* **1985a**, *18*, 17.
- Fukuda, T.; Ma, Y. D.; Inagaki, H. Reexamination of free-radical copolymerization kinetics. *Makromol. Chem. Suppl.* **1985b**, *12*, 125.
- Fukuda, T.; Kubo, K.; Ma, Y. D. Kinetics of free radical copolymerization. *Prog. Polym. Sci.* **1992**, *17*, 875.
- Garcia-Rubio, L. H. An experimental investigation on the free-radical synthesis and characterization of styrene acrylonitrile copolymers. Ph.D. Thesis, McMaster University, Hamilton, Ontario, Canada, 1981.
- Garcia-Rubio, L. H.; Ro, N. Detailed copolymer characterization using ultraviolet spectroscopy. *Can. J. Chem. Eng.* **1985**, *63*, 253.
- Garcia-Rubio, L. H.; Lord, M. G.; MacGregor, J. F.; Hamielec, A. E. Bulk copolymerization of styrene and acrylonitrile: Experimental kinetics and mathematical modeling. *Polymer* **1985**, *26*, 2001.
- Hartley, H. O. Testing the homogeneity of a set of variances. *Biometrika* **1940**, *31*, 249.
- Harwood, H. J. Structures and compositions of copolymers. *Makromol. Chem., Macromol. Symp.* **1987**, *10/11*, 311.
- Hill, P. H. D. A review of experimental design procedures for regression model discrimination. *Technometrics* **1978**, *20* (1), 15.

- Hill, D. J. T.; O'Donnell, J. H.; O'Sullivan, P. W. Analysis of the mechanism of copolymerization of styrene/acrylonitrile. *Macromolecules* **1982**, *15*, 960.
- Hill, D. J.; O'Donnell, J. H.; O'Sullivan, P. W. Methyl methacrylate/chloroprene copolymerization: an evaluation of copolymerization models. *Polymer* **1984**, *25*, 569.
- Hill, D. J. T.; Lang, A. P.; O'Donnell, J. H.; O'Sullivan, P. W. Determination of reactivity ratios from analysis of triad fractions—analysis of the copolymerization of styrene-acrylonitrile as evidence for the penultimate model. *Eur. Polym. J.* **1989**, *25* (9), 911.
- Himmelblau, D. M. *Process analysis by statistical methods*; John Wiley & Sons Ltd.: New York, 1970.
- Hsiang, T.; Reilly, P. M. A practical method for discriminating among mechanistic models. *Can. J. Chem. Eng.* **1971**, *49*, 865.
- Huang, J. The kinetics of styrene/methyl methacrylate free radical copolymerization. M.A.Sc. Thesis, Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada, 1988.
- Johnson, M.; Karmo, T. S.; Smith, R. R. High conversion copolymerization of styrene with methylmethacrylate. *Eur. Polym. J.* **1978**, *14*, 409.
- Kuindersma, M. E. On the modeling of free-radical polymerization reactions: homopolymerization. M.A.Sc. Thesis, Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada, 1992.
- Lau, W.; Westmoreland, D. G.; Novak, R. W. Direct measurement of propagating radical concentration in a semicontinuous emulsion polymerization. *Macromolecules* **1987**, *20*, 457.
- Ma, Y. D.; Fukuda, T.; Inagaki, H. Free-radical copolymerization. 4. Rate constants of propagation and termination for the *p*-chlorostyrene/methyl acrylate system. *Macromolecules* **1985**, *18*, 26.
- Maxwell, I. A.; Aerdt, A. M.; German, A. L. Free radical copolymerization: an NMR investigation of current kinetic models. *Macromolecules* **1993**, *26*, 1956.
- Moad, G.; Solomon, D. H.; Spurling, T. H.; Stone, R. A. How powerful are composition data in discriminating between the terminal and penultimate models for binary copolymerization? *Macromolecules* **1989**, *22* (3), 1145.
- Muirhead, R. J. *Aspects of multivariate statistical theory*; John Wiley & Sons Ltd.: New York, 1982.
- O'Driscoll, K. Modeling copolymerization kinetics. *Makromol. Chem., Macromol. Symp.* **1992**, *53*, 53.
- O'Driscoll, K. F.; Mahabadi, H. R. Spatially intermittent polymerization. *J. Polym. Sci., Polym. Chem.* **1976**, *14*, 869.
- O'Driscoll, K. F.; Huang, J. The rate of copolymerizations of styrene/methyl methacrylate. I. Low conversion kinetics. *Eur. Polym. J.* **1989**, *27* (7/8), 629.
- Olaj, O. F.; Bitai, I.; Hinkelmann, F. The laser-flash initiated polymerization as a tool of evaluating (individual) kinetic constants of free-radical polymerization 2. The direct determination of the rate constant of chain propagation. *Makromol. Chem.* **1987**, *188*, 1689.
- Olaj, O. F.; Schnoll-Bitai, I.; Kremminger, P. Evaluation of individual rate constants from the chain-length distribution of polymer samples prepared by intermittent (rotating sector) photopolymerization—2. The copolymerization system styrene-methyl methacrylate. *Eur. Polym. J.* **1989**, *25* (6), 535.
- Press, W. H.; Flannery, B. P.; Teukolky, S. A.; Vetterling, W. T. *Numerical recipes: The art of scientific computing (FORTRAN version)*; Cambridge University Press: New York, 1989.
- Reilly, P. M. Statistical methods in model discrimination. *Can. J. Chem. Eng.* **1970**, *48*, 168.
- Schaefer, J. High-resolution pulsed carbon-13 nuclear magnetic resonance analysis of the monomer distribution in acrylonitrile-styrene copolymers. *Macromolecules* **1971**, *4* (1), 107.
- Schnoll-Bitai, I.; Olaj, O. F. The laser-flash initiated polymerization as a tool of evaluating (individual) kinetic constants of free-radical polymerization 6. The influence of monomer consumption during sample preparation. *Makromol. Chem.* **1990**, *19*, 2491.
- Schweer, J. Penultimate model description for the free radical copolymerization of styrene and methylmethacrylate. *Makromol. Chem., Theor. Simul.* **1993**, *2* (3), 485.
- Stickler, M. Experimental techniques in free radical polymerization kinetics. *Makromol. Chem., Macromol. Symp.* **1987**, *10/11*, 17.
- Tidwell, P. W.; Mortimer, G. A. An improved method of calculating copolymer reactivity ratios. *J. Polym. Sci., Polym. Chem.* **1965**, *3*, 369.
- Tirrell, D. A. Copolymerization. In *The Encyclopedia of Polymer Science*; Mark, H. I., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; John Wiley & Sons Ltd.: New York, 1986.

Received for review February 15, 1996

Revised manuscript received June 7, 1996

Accepted June 7, 1996*

IE960084D

* Abstract published in *Advance ACS Abstracts*, February 15, 1997.