Demystifying the Estimation of Reactivity Ratios for Terpolymerization Systems

Niousha Kazemi, Thomas A. Duever, and Alexander Penlidis
Dept. of Chemical Engineering, Institute for Polymer Research (IPR),
University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

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In typical practice for terpolymerizations so far, binary reactivity ratios have been used directly in the instantaneous Alfrey and Goldfinger (AG) model, effectively ignoring the presence of the third monomer. In addition, the use of the AG model leads to severe estimation problems, if one would like to estimate reactivity ratios from experimental data. Due to the above reasons, the AG model was recast and was subsequently used with terpolymerization data directly to estimate ternary reactivity ratios under the error-in-variables-model framework, based both on instantaneous (low conversion) and cumulative composition data (medium and high conversions). Several examples and counter examples highlight such important issues as the choice of the correct number of responses, accounting for the appropriate error structure, and incorporating the right information content, all with diagnostic checks whose target is the eventual reliability of the reactivity ratio estimates. © 2014 American Institute of Chemical Engineers *AIChE J*, 60: 1752–1766, 2014
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Introduction

Polymeric materials with new and optimized properties are being produced with an ever increasing frequency by the use of multicomponent polymerization techniques. The simplest case of a multicomponent polymerization is a binary copolymerization, which is the starting point for a more complex polymeric molecule. Terpolymerization systems with three monomers are being utilized to generate polymeric materials with tailor-made properties. For such products, one needs to describe (among other characteristics) the composition of the terpolymer, which is directly linked to its physical properties. This composition is also linked to the kinetics of the polymerization, which can be studied by the use of powerful mathematical models that have been developed. Due to the practical impact and versatility of the properties of terpolymers, understanding the kinetics of ternary systems is not only advantageous for exploring strategies for advanced technologies but also necessary for producing terpolymers with desirable physicochemical properties in pilot-plant and/or industrial scales.

Polymerization rate controls polymer composition, strongly influenced by the relative reactivities of the monomers present in the reaction medium. These relative reactivities govern monomer reactivity ratios, which play a very important role, as they describe the rate of incorporation of each monomer in the polymer chain. The impact of polymer chain composition on chemical, physical, and mechanical properties clearly indicates how important it is to be able to predict and, furthermore control polymer composition from the knowledge of monomer concentrations and reactivity ratios. Despite the importance of these terpolymerization reactivity ratios, not a lot of research has been conducted to estimate and study these parameters in terpolymerization modeling. This is partly due to the complexity of the developed mathematical models and their poor performance in predicting real data. It is more importantly related to the fact that, based on an analogy between copolymerization and terpolymerization mechanisms, reactivity ratios obtained for binary pairs from copolymerization experiments have commonly (albeit misleadingly) been used in models dealing with terpolymerizations.

From even a quick screening of the literature regarding binary reactivity ratios, it can be realized that there are many ambiguities and inconsistencies around these reactivity ratios, even for the same copolymerization system. The inaccuracies in these reactivity ratios can simply propagate into the terpolymerization composition model (consisting of more than one equations, unlike the simpler and single-equation Mayo–Lewis model for copolymerization), thus becoming a much more serious (than in copolymerization) source of error in parameter estimation and prediction variance. Using binary reactivity ratios in terpolymerization studies also treats the ternary system as separate and unrelated binary pairs and the interactions between three monomers are ignored. This past approach is therefore an unjustified simplification that could have been acceptable at a time when computation power was very limited, but not nowadays.

The correct approach for determining ternary reactivity ratios is to use the experimental data directly from terpolymerization and estimate reactivity ratios for each system.

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Correspondence concerning this article should be addressed to A. Penlidis at penlidis@uwaterloo.ca.

Correction added on March 21, 2014, after first online publication: Best Presentation footnote.

Such studies based on ternary experimental data are very limited and quite unclear with respect to experimental descriptions, which has led to very little use of their data in estimation schemes in ternary investigations.[1,2] Therefore, our goal is to conduct a thorough study of this problem, from the terpolymerization composition equations to the statistical approaches that have been implemented in this regard.

The current study is presented in four parts. First, the related literature is reviewed and information about existing techniques and their potential problems are discussed. Second, our approach and the most appropriate statistical procedure for this problem are explained. This involves recasting of the traditional terpolymerization composition equations and implementing the error-in-variables-model (EVM) framework (Kazemi et al.[3]) for parameter estimation. In the third part, we highlight important details about our findings and observations, along with more detailed explanations about the implementation of our approach, with examples and counter examples. This section also contains a summary table that presents several studied systems with their reactivity ratios. Finally, the last part discusses how the results of reactivity ratio estimation from different sources can be evaluated to "weigh" the reliability of these reactivity ratios for terpolymerization systems.

Related Work

Terpolymer composition equations

A typical terpolymerization in which three monomers are polymerized simultaneously was mathematically described originally by Alfrey and Goldfinger[4] (AG model), who derived the first composition equations for ternary systems. This approach is based on the assumption that three active growing radicals in the terpolymerization of three monomers, M_1, M_2, and M_3, participate in nine chain propagation reactions, based on the terminal model, as shown below

$$\begin{array}{lll} -R_{r,1}{}^{*}+M_1\xrightarrow{k_{11}}R_{r+1,1}{}^{*} & -R_{r,1}{}^{*}+M_2\xrightarrow{k_{12}}R_{r+1,2}{}^{*} & -R_{r,1}{}^{*}+M_3\xrightarrow{k_{13}}R_{r+1,3}{}^{*} \\ -R_{r,2}{}^{*}+M_1\xrightarrow{k_{21}}R_{r+1,1}{}^{*} & -R_{r,2}{}^{*}+M_2\xrightarrow{k_{22}}R_{r+1,2}{}^{*} & -R_{r,2}{}^{*}+M_3\xrightarrow{k_{23}}R_{r+1,3}{}^{*} \\ -R_{r,3}{}^{*}+M_1\xrightarrow{k_{31}}R_{r+1,1}{}^{*} & -R_{r,3}{}^{*}+M_2\xrightarrow{k_{32}}R_{r+1,2}{}^{*} & -R_{r,3}{}^{*}+M_3\xrightarrow{k_{33}}R_{r+1,3}{}^{*} \end{array} \quad (1)$$

k_{ij} represents the rate constant of the reaction between radical i and monomer j, $R_{r,i}*$ denotes a radical of chain length r ending in monomer i, and M_i denotes monomer i. Based on the rate of disappearance for each monomer and considering the steady-state approximation for radicals, a set of three differential equations (Eqs. 2–4) can be derived, where f_i is the mole fraction of unbound monomer i in the polymerizing mixture and df_i is the mole fraction of monomer i incorporated (bound) into the terpolymer chains.

$$\frac{df_1}{df_2}=\frac{F_1}{F_2}=\frac{f_1\left(\frac{f_1}{r_{21}r_{31}}+\frac{f_2}{r_{21}r_{32}}+\frac{f_3}{r_{31}r_{23}}\right)\left(f_1+\frac{f_2}{r_{12}}+\frac{f_3}{r_{13}}\right)}{f_2\left(\frac{f_1}{r_{12}r_{31}}+\frac{f_2}{r_{21}r_{32}}+\frac{f_3}{r_{13}r_{32}}\right)\left(f_2+\frac{f_1}{r_{21}}+\frac{f_3}{r_{23}}\right)} \quad (2)$$

$$\frac{df_1}{df_3}=\frac{F_1}{F_3}=\frac{f_1\left(\frac{f_1}{r_{21}r_{31}}+\frac{f_2}{r_{21}r_{32}}+\frac{f_3}{r_{31}r_{23}}\right)\left(f_1+\frac{f_2}{r_{12}}+\frac{f_3}{r_{13}}\right)}{f_3\left(\frac{f_1}{r_{13}r_{21}}+\frac{f_2}{r_{23}r_{12}}+\frac{f_3}{r_{13}r_{23}}\right)\left(f_3+\frac{f_1}{r_{31}}+\frac{f_2}{r_{32}}\right)} \quad (3)$$

$$\frac{df_2}{df_3}=\frac{F_2}{F_3}=\frac{f_2\left(\frac{f_1}{r_{12}r_{31}}+\frac{f_2}{r_{21}r_{32}}+\frac{f_3}{r_{13}r_{32}}\right)\left(f_2+\frac{f_1}{r_{21}}+\frac{f_3}{r_{23}}\right)}{f_3\left(\frac{f_1}{r_{13}r_{21}}+\frac{f_2}{r_{23}r_{12}}+\frac{f_3}{r_{13}r_{23}}\right)\left(f_3+\frac{f_1}{r_{31}}+\frac{f_2}{r_{32}}\right)} \quad (4)$$

The instantaneous form of the AG model (Eqs. 2–4) applies to low conversion data, where df_i is substituted by F_i, the instantaneous mole fraction of monomer i incorporated (bound) in the terpolymer, owing to the assumption that compositional drift at that very early stage of the polymerization is negligible. The composition of a terpolymer can thus be calculated by using any two equations of the three combinations shown above for the AG model. To find the terpolymer composition, knowledge of six reactivity ratios is required and none of these values can be infinite or equal to zero. These important monomer reactivity ratios are defined as

$$r_{12}=\frac{k_{11}}{k_{12}}, r_{13}=\frac{k_{11}}{k_{13}}, r_{21}=\frac{k_{22}}{k_{21}}, r_{23}=\frac{k_{22}}{k_{23}}, r_{31}=\frac{k_{33}}{k_{31}}, r_{32}=\frac{k_{33}}{k_{32}} \quad (5)$$

The visualization of the composition of a terpolymerization system has been done by the use of a triangular plot. This approach was first proposed by Slocombe,[5] whereby sides of a triangle represent the mole fraction of the monomer assigned to those sides, the corners of the triangle represent 100% concentration of each monomer, and the sides describe the corresponding binary mixtures. Experimental compositions of the polymer chains can be represented as points inside the triangle and the drift in the terpolymer composition mixture can be illustrated by arrows (the head of the arrow indicates the instantaneous composition of the resulting polymer and its tail the composition of the monomer mixture). An example of such a triangular plot is shown in the results and discussion section.

The calculations with the AG model and therefore its usage are quite simple nowadays. However, at the time that these equations were proposed, computational tasks were not as simple and this motivated researchers to devise even simpler forms of these composition equations. A probabilistic approach was developed by Fordyce et al.[6] and Fordyce and Ham[7] that still involved six reactivity ratios but with simpler mathematical expressions. Valvassori and Sartori[8] also proposed the same simpler forms by extending the steady-state assumption of binary copolymerizations to ternary systems. Later on, Hocking and Klimchuk[9] presented yet another form of the terpolymer composition equations which was based on the Valvassori and Sartori model, but with symmetrical characteristics. Also, Kahn and Horowitz[10] were the first to develop the integrated form of the AG model for prediction of higher conversion level data, given the values of the six reactivity ratios.

Despite all these attempts to predict terpolymer composition, it has often been observed that the prediction results do not have an acceptable agreement with experimental data. To resolve such issues, some have suggested that for systems where one of the monomers is unreactive toward itself or other monomers, modified forms of the AG model should be used.[1] These types of adjustments are rather arbitrary and, while eliminating some of the reactivity ratios, introduce other parameters as ratios of remaining rate constants. These new parameters, however, have unclear physical meaning and so these modified equations neither have the extensive usage nor the applicability of the original AG model.

In addition to the special forms of the AG model, other attempts have been made by considering at different mechanisms for developing the terpolymerization composition equation. While the AG model (or its simplified forms) is based on the terminal mechanism in the propagation steps, the penultimate mechanism can also be used to derive the

terpolymerization composition equations. This approach has been rarely used or even studied mainly due to the cumbersome calculations and even larger number of unknown parameters in the model.[11] Another suggested mechanism for some ternary systems is the charge-transfer complex participation mechanism, which can be valid for systems where complexes are formed between two out of three monomers.[12] That is, the system can be treated as a binary case between two complexes. Discussions about whether the penultimate model versus the terminal model or the free-radical propagation versus the complex participation model can perform better with ternary data belong to ongoing research which is out of the scope of this article.

Conventional approaches for reactivity ratio estimation

The assumptions involved in the development of the AG model are similar to those used for describing copolymerization systems. Therefore, studies about the ternary composition equations were initially based on the reactivity ratios extracted from binary systems. Based on this analogy, a ternary system is treated as a "mixture" of three binary copolymerizations, instead of one specific ternary system, and the effect of the interactions between all three monomers on their reactivity toward each other is overlooked. This approach, even though established as common practice, is neither reliable nor precise for predicting ternary compositions. In fact, several issues with prediction results of the terpolymer composition equations are simply due to the usage of binary reactivity ratios instead of reactivity ratios based directly on terpolymerization experimental data.

It is also worth considering that even if the analogy between binary and ternary mechanisms allows the utilization of binary reactivity ratios, the database of binary reactivity ratios in the literature is very dubious and inconsistent, suffering over many years from the implementation of several incorrect binary reactivity ratio estimation techniques and/or poorly designed experimental data sets. These inaccuracies propagate in the ternary composition model, and result in serious deviations between predictions of terpolymerization composition and experimental data. A simple example of this problem is that there are several differing (often widely) reactivity ratio values for the same copolymerization system in the literature, and so the question becomes which set of values should be used (averaging and any random selection between the existing sets of reactivity ratios would definitely increase the uncertainty level of the calculations).

In one of the early applications of estimation techniques with terpolymerization models, Duever et al.[2] pointed out some problems in earlier methodologies, while illustrating the application of the EVM parameter estimation method with the AG model for estimation of ternary reactivity ratios. Some efforts tried to handle terpolymerization data directly (see, e.g., Luft et al.[13] and Iglesias et al.[14]), but given the paucity of actual terpolymerization data and studies, these efforts were overall just too few and vague to get the attention of people studying ternary systems. As a result, using binary reactivity ratios became the *de facto* procedure in ternary kinetic studies. Our premise in the current article is that using binary reactivity ratios is an oversimplification, not only with respect to the reliability of the values themselves, but also with respect to not including measures (and, hence, the effect) of their uncertainty.

In addition to the inaccurate conventional estimation approach, the AG model itself can be a source of error for the problem of reactivity ratio estimation. In preliminary studies, we looked at several ternary case studies where reactivity ratios were estimated using the AG model and pointed out that the results were not reliable for all cases, which can be directly attributed to either the lack of information in the existing data sets (usually, very few experimental points are reported), or large experimental error associated with the data, and/or issues with the formulation of the AG model itself. In these preliminary studies,[15] we showed that selecting different combinations of ratios of mole fractions in the AG model (e.g., F_1/F_2 and F_1/F_3 vs. F_1/F_2 and F_2/F_3) can affect the precision of the reactivity ratio estimates. This observation revealed that this model suffers from symmetry issues and thus final results depend on the arbitrary choice of different combinations of copolymer mole fractions into the parameter estimation scheme. Hence, the question becomes, which set of copolymer mole fraction ratios amongst (F_1/F_2, F_1/F_3), (F_1/F_2, F_2/F_3), and (F_1/F_3, F_2/F_3) should be used in the AG model?

In addition to the asymmetry problem with the AG model, it can also be easily seen that this model uses ratios of copolymer mole fractions as responses in the parameter estimation problem. This is done despite the fact that in ternary reactivity ratio estimation studies, as in other copolymerization or multicomponent polymerization studies, it is the individual copolymer mole fractions that are measured directly, say, from NMR analysis. In other words, what is measured directly is F_1 or F_2, and not F_1/F_2. This violates the well known and practical recommendation in parameter estimation schemes that the model be written directly relating a measured response y_i with the right-hand side function, which involves the independent variables and unknown parameters. In other words, it is highly recommended that the measured F_1, and not the ratio (F_1/F_2), be related directly to a model right-hand side function, as the right-hand side appearing in Eqs. 2–4. This is recommended to avoid distorting the error structure of the measured responses during estimation. A certain error structure corresponds to the measured F_1, and this error structure will be distorted or transformed if a ratio like (F_1/F_2) is used instead. This distortion, when using mole fraction ratios, can have severe effects on the reliability of the parameter estimates (reactivity ratios), even if one knows *a priori* which set of mole fractions to use.

In our approach, as explained in the next section, the remedy for such difficulties and the appropriate parameter estimation scheme for obtaining ternary reactivity ratios from an instantaneous model and ternary data are presented. This approach also extends directly to usage of a cumulative model and including both composition and conversion values in the procedure of finding more reliable ternary reactivity ratios.

A Correct Approach for Parameter Estimation

We now present a complete approach for estimating reactivity ratios in ternary systems. The first step in this regard is to resolve the issue with the instantaneous AG model stemming from its inherent derivation and the use of copolymer mole fraction ratios, by simply recasting the form of the model and isolating each of the terpolymer composition mole fractions as an individual response. The second step is about the implementation of the EVM parameter estimation technique, which is the most appropriate technique for the

problem of reactivity ratio estimation (see, e.g., Ref. 3 and 16). In the third step, we estimate ternary reactivity ratios using the cumulative composition model. This can potentially include medium to high conversion data for the parameter estimation procedure (analogous work for copolymerization can be found in Kazemi et al.[17]).

Model recasting

A new form of the terpolymerization equations is rederived in our work, where each one of the terpolymer composition mole fractions is formulated explicitly, as shown in Eqs. 6–8. This new formulation is symmetrical and does not deal with ratios of different copolymer mole fractions (as F_i/F_j and F_i/F_k). Therefore, the model responses are direct measurements from the system and their error structures are not distorted by the use of mole fraction ratios. One only needs to select any two mole fractions out of F_1, F_2, and F_3, as responses for the parameter estimation problem, and due to the symmetrical nature of this model (unlike the original AG model), the results are consistent regardless of the selection. Of course, the new formulation is in agreement with the AG model, in terms of predictions, once the six reactivity ratios are known and fixed.

$$F_1-\frac{f_1\left(\frac{f_1}{r_{21}r_{31}}+\frac{f_2}{r_{21}r_{32}}+\frac{f_3}{r_{31}r_{23}}\right)\left(f_1+\frac{f_2}{r_{12}}+\frac{f_3}{r_{13}}\right)}{f_1\left(\frac{f_1}{r_{21}r_{31}}+\frac{f_2}{r_{21}r_{32}}+\frac{f_3}{r_{31}r_{23}}\right)\left(f_1+\frac{f_2}{r_{12}}+\frac{f_3}{r_{13}}\right)+f_2\left(\frac{f_1}{r_{12}r_{31}}+\frac{f_2}{r_{21}r_{32}}+\frac{f_3}{r_{13}r_{32}}\right)\left(f_2+\frac{f_1}{r_{21}}+\frac{f_3}{r_{23}}\right)+f_3\left(\frac{f_1}{r_{13}r_{21}}+\frac{f_2}{r_{23}r_{12}}+\frac{f_3}{r_{13}r_{23}}\right)\left(f_3+\frac{f_1}{r_{31}}+\frac{f_2}{r_{32}}\right)}=0 \quad (6)$$

$$F_2-\frac{f_2\left(\frac{f_1}{r_{12}r_{31}}+\frac{f_2}{r_{21}r_{32}}+\frac{f_3}{r_{13}r_{32}}\right)\left(f_2+\frac{f_1}{r_{21}}+\frac{f_3}{r_{23}}\right)}{f_1\left(\frac{f_1}{r_{21}r_{31}}+\frac{f_2}{r_{21}r_{32}}+\frac{f_3}{r_{31}r_{23}}\right)\left(f_1+\frac{f_2}{r_{12}}+\frac{f_3}{r_{13}}\right)+f_2\left(\frac{f_1}{r_{12}r_{31}}+\frac{f_2}{r_{21}r_{32}}+\frac{f_3}{r_{13}r_{32}}\right)\left(f_2+\frac{f_1}{r_{21}}+\frac{f_3}{r_{23}}\right)+f_3\left(\frac{f_1}{r_{13}r_{21}}+\frac{f_2}{r_{23}r_{12}}+\frac{f_3}{r_{13}r_{23}}\right)\left(f_3+\frac{f_1}{r_{31}}+\frac{f_2}{r_{32}}\right)}=0 \quad (7)$$

$$F_3-\frac{f_3\left(\frac{f_1}{r_{13}r_{21}}+\frac{f_2}{r_{23}r_{12}}+\frac{f_3}{r_{13}r_{23}}\right)\left(f_3+\frac{f_1}{r_{31}}+\frac{f_2}{r_{32}}\right)}{f_1\left(\frac{f_1}{r_{21}r_{31}}+\frac{f_2}{r_{21}r_{32}}+\frac{f_3}{r_{31}r_{23}}\right)\left(f_1+\frac{f_2}{r_{12}}+\frac{f_3}{r_{13}}\right)+f_2\left(\frac{f_1}{r_{12}r_{31}}+\frac{f_2}{r_{21}r_{32}}+\frac{f_3}{r_{13}r_{32}}\right)\left(f_2+\frac{f_1}{r_{21}}+\frac{f_3}{r_{23}}\right)+f_3\left(\frac{f_1}{r_{13}r_{21}}+\frac{f_2}{r_{23}r_{12}}+\frac{f_3}{r_{13}r_{23}}\right)\left(f_3+\frac{f_1}{r_{31}}+\frac{f_2}{r_{32}}\right)}=0 \quad (8)$$

For the purpose of ternary reactivity ratio estimation, Eqs. 9–12 represent an example of the instantaneous ternary model that the EVM program works with. Among the true values of terpolymer and feed mole fractions, there are two linear relations as shown in Eqs. 11 and 12. Given these two relations, not all three mole fractions can be used in the model for parameter estimation purposes, and any two of the mole fractions along with the linear relations can represent the terpolymerization model.

$$F_1-\frac{f_1\left(\frac{f_1}{r_{21}r_{31}}+\frac{f_2}{r_{21}r_{32}}+\frac{f_3}{r_{31}r_{23}}\right)\left(f_1+\frac{f_2}{r_{12}}+\frac{f_3}{r_{13}}\right)}{f_1\left(\frac{f_1}{r_{21}r_{31}}+\frac{f_2}{r_{21}r_{32}}+\frac{f_3}{r_{31}r_{23}}\right)\left(f_1+\frac{f_2}{r_{12}}+\frac{f_3}{r_{13}}\right)+f_2\left(\frac{f_1}{r_{12}r_{31}}+\frac{f_2}{r_{21}r_{32}}+\frac{f_3}{r_{13}r_{32}}\right)\left(f_2+\frac{f_1}{r_{21}}+\frac{f_3}{r_{23}}\right)+f_3\left(\frac{f_1}{r_{13}r_{21}}+\frac{f_2}{r_{23}r_{12}}+\frac{f_3}{r_{13}r_{23}}\right)\left(f_3+\frac{f_1}{r_{31}}+\frac{f_2}{r_{32}}\right)}=0 \quad (9)$$

$$F_2-\frac{f_2\left(\frac{f_1}{r_{12}r_{31}}+\frac{f_2}{r_{21}r_{32}}+\frac{f_3}{r_{13}r_{32}}\right)\left(f_2+\frac{f_1}{r_{21}}+\frac{f_3}{r_{23}}\right)}{f_1\left(\frac{f_1}{r_{21}r_{31}}+\frac{f_2}{r_{21}r_{32}}+\frac{f_3}{r_{31}r_{23}}\right)\left(f_1+\frac{f_2}{r_{12}}+\frac{f_3}{r_{13}}\right)+f_2\left(\frac{f_1}{r_{12}r_{31}}+\frac{f_2}{r_{21}r_{32}}+\frac{f_3}{r_{13}r_{32}}\right)\left(f_2+\frac{f_1}{r_{21}}+\frac{f_3}{r_{23}}\right)+f_3\left(\frac{f_1}{r_{13}r_{21}}+\frac{f_2}{r_{23}r_{12}}+\frac{f_3}{r_{13}r_{23}}\right)\left(f_3+\frac{f_1}{r_{31}}+\frac{f_2}{r_{32}}\right)}=0 \quad (10)$$

$$F_1+F_2+F_3-1=0 \quad (11)$$

$$f_1+f_2+f_3-1=0 \quad (12)$$

EVM estimation

The problem of reactivity ratio estimation, among several other nonlinear parameter estimation problems, encountered frequently in science and engineering, has variables (both dependent and independent) that are subject to error. For such problems, results from basic nonlinear regression, where only dependent variables contain considerable amounts of error, would yield imprecise and biased parameter estimates. A relatively recent approach is the EVM that is probably the most complete approach for situations where the dependent and independent variables cannot be distinguished. This feature makes EVM the perfect method for estimating reactivity ratios in multicomponent polymerizations. The basis of the EVM parameter estimation method was proposed originally by Reilly and Patino-Leal.[18] This algorithm was specifically applied on the problem of estimating reactivity ratios for copolymerization systems by Dube et al.[16] and Polic et al.,[19] and further detailed explanations about it can be found in Kazemi et al.,[3] where the latest methodology for using this algorithm for estimating copolymerization reactivity ratios is highlighted.

An EVM program that estimates ternary reactivity ratios based on terpolymerization data has been developed in our research group, initiated by Duever et al.[2] for the original form of the instantaneous AG model and later on tested on other case studies by Hauch[20] and Kazemi.[15] These sources point toward potential problems in the results attributed to

the structure of the AG model and also the lack of adequate information in the terpolymerization literature. In this work, the EVM procedure has been modified in several parts based on the computational requirements of the ternary problem and the problematic nature of the original form of the AG model. In the following, a brief explanation of the EVM algorithm is presented along with extensive details about the particular implementation on the ternary case.

All variables in the EVM context are treated as if they have an unknown true value and an added error term. The first statement of EVM equates the vector of measurements $\underline{x}_i$ to the vector of true (yet unknown) values $\underline{\xi}_i$, plus a multiplicative error term, $k\underline{\varepsilon}_i$, as shown in Eq. 13, where i refers to the trial number, k is a constant, and $\underline{\varepsilon}_i$ is a random variable, which, in the simplest case, has a uniform distribution in the interval from -1 to 1.

$$\underline{x}_i = \underline{\xi}_i\left(1+k\underline{\varepsilon}_i\right) \qquad where\ i=1,2,\ldots,n \tag{13}$$

The magnitude of the error is quantified by the variance of the measurements, determined through independent replication. The distribution of the error is generally unknown, but it is commonly assumed to be normal. The measurement errors for all the variables appear in the variance-covariance matrix of the measurements, $\underline{V}$ (to be discussed shortly), which is nonsingular and known. In addition, for multiresponse problems, if measurements have interrelated dependencies, correlation terms should be considered in the error structure and $\underline{V}$ matrix, as well. In this article, we present the solution for nonlinear parameter estimation with a known and nonsingular variance-covariance matrix, shown in Eq. 14. The diagonal elements of $\underline{V}$ are $\sigma^2_{x_i}$, the variances of the measurements, whereas the off-diagonal elements, $\sigma^2_{x_i x_j}$, represent the covariances between measurements. The values of the constant k (as shown in Eq. 13) for different variables in a problem could be different, as the amount of uncertainty in data coming from different sources may be different. A log transformation on the variables in Eq. 13 is also necessary so that the error term becomes additive. Taking logarithms of both sides, $ln(1+k\varepsilon)$ can be replaced by $k\varepsilon$, provided that the magnitude of the error does not exceed 10% ($k<0.1$). The error structure is chosen to be multiplicative (relative) due to the nature of the actual (physical) measurements in the reactivity ratio estimation problem. As simple algebra can show, for each variable, the corresponding diagonal element in $\underline{V}$ (Eq. 14) is $k^2/3$.

$$\underline{V}=\begin{bmatrix} \sigma^2_{x_1} & \sigma^2_{x_1x_2} & \cdots & \sigma^2_{x_1x_v} \\ \sigma^2_{x_2x_1} & \sigma^2_{x_2} & \cdots & \sigma^2_{x_2x_v} \\ \vdots & \vdots & \cdots & \vdots \\ \sigma^2_{x_vx_1} & \sigma^2_{x_vx_2} & \cdots & \sigma^2_{x_v} \end{bmatrix} \tag{14}$$

In addition to Eq. 13, EVM has a statement that relates the true (yet unknown) values of the parameters, $\underline{\theta}^*$, and variables, $\underline{\xi}_i$, via the mathematical model, represented by Eq. 15. In a multiresponse problem, $\underline{g}_i$ is a vector of responses. In the case of terpolymerization, the terpolymerization composition equations (Eqs. 9–12) are the responses that are considered for the vector $\underline{g}$.

$$\underline{g}\left(\underline{\xi}_i,\underline{\theta}^*\right)=0 \qquad Where\ i=1,2,\ldots,n \tag{15}$$

Using a Bayesian approach, the objective function for minimization to find the point estimates, $\underline{\hat{\theta}}$, is given by equation 16, where r_i is the number of replicates at the ith trial, $\underline{\bar{x}}_i$ is the average of the r_i measurements $\underline{x}_i$, and $\underline{\hat{\xi}}_i$ denotes estimates of the true values of the variables $\underline{\xi}_i$.

$$\phi=\frac{1}{2}\sum\nolimits_{i=1}^{n} r_i\left(\underline{\bar{x}}_i-\underline{\hat{\xi}}_i\right)'\underline{V}^{-1}\left(\underline{\bar{x}}_i-\underline{\hat{\xi}}_i\right) \tag{16}$$

The minimization of the EVM objective function (Eq. 16) is a nonlinear constrained optimization problem, in which the objective function minimization is subject to constraints consisting of a nonlinear model that relates the variables and parameters (Eq. 15), and lower and upper bounds on the magnitudes of the parameters. The original EVM algorithm[18] uses a quasi-Newton optimization algorithm that works very effectively only in the vicinity of the given initial guesses. Also, based on the size of the variable space and the number of parameters in the problem, the magnitude of this search problem increases and several difficulties can arise in the process of locating the parameter estimates. We have modified the EVM procedure by using a global optimization algorithm, called the Shuffled Complex Evolutionary (SCE) algorithm, which belongs to the evolutionary class of optimization algorithms. The SCE method was proposed originally by Duan et al.[21] In our research, we have used the SCE method via the SCE library in MATLAB.[22]

A very important component of the EVM objective functions, calculated within the numerical procedure, is the information matrix for the parameters (the second derivatives of the objective function ϕ). The information matrix, which is the inverse of the variance-covariance matrix for the parameters, is shown in Eq. 17 and can be calculated by Eq. 18. $\underline{B}_i$ is the vector of partial derivatives of the function, $\underline{g}(\underline{\xi}_i,\underline{\theta})$ with respect to the variables, whereas $\underline{Z}_i$ is the vector of partial derivatives of the (model) function, $\underline{g}(\underline{\xi}_i,\underline{\theta})$, with respect to the parameters, given by Eqs. 19 and 20, respectively.

$$\underline{G}=E\left[\frac{d^2\phi}{d\theta_i d\theta_j}\right] \quad i,j\ elements \tag{17}$$

$$\underline{G}=\sum\nolimits_{i=1}^{n} r_i\underline{Z}_i'\left(\underline{B}_i\underline{V}\underline{B}_i'\right)^{-1}\underline{Z}_i \tag{18}$$

$$\underline{B}_i=\left[\frac{\partial g\left(\underline{\xi}_i,\underline{\theta}\right)}{\partial\underline{\xi}_i}\right] \tag{19}$$

$$\underline{Z}_i=\left[\frac{\partial g\left(\underline{\xi}_i,\underline{\theta}\right)}{\partial\theta_m}\right] \quad m^{th}\ element \tag{20}$$

The evaluation of the parameter estimation results is a crucial task in any parameter estimation procedure, almost as important as estimating the parameters themselves. There are some indicators that quantitatively define the uncertainty of the results, allowing us to decide whether the results are reliable or not. Confidence intervals are common indicators for this objective. However, for cases where there are more than one parameter, being simultaneously estimated, a joint confidence region (JCR) should be presented that quantifies and visualizes the measure of uncertainty in the estimated parameters by presenting a contour/JCR. Values of the parameters inside or on the contour represent plausible values of the parameters at the specified confidence level, and the smaller the JCR the higher the precision of the results.

The basis of constructing JCRs for parameter estimates is their information matrix, as given in Eq. 18. For the problem

of estimating reactivity ratios of a ternary system, we have six parameters and therefore the information matrix is a 6 by 6 matrix, where we have to select certain rows and columns to plot the JCRs for the different pair combinations (e.g., r_{12} and r_{21} for M_1 and M_2). Considering the variance to be known and the distribution of the errors to follow a normal distribution, the confidence regions can be constructed using the formula for elliptical JCRs, given in Eq. 21. $\chi^2_{(p,1-\alpha)}$ on the right-hand side of Eq. 21 stands for the chi-squared statistic with p parameters and probability of $(1-\alpha)$, where α is the usual 5% significance level.

$$(\underline{\theta}-\underline{\hat{\theta}})' \underline{G} (\underline{\theta}-\underline{\hat{\theta}}) \leq \chi^2_{(p,1-\alpha)} \tag{21}$$

From low conversion to high conversion

One of the major limitations in reactivity ratio estimation studies in the literature, for both binary and ternary systems, has been about using the instantaneous composition model. To use the instantaneous model, the experimental data must be collected at very low conversion levels (less than 5%), based on the assumption that up to such a conversion level, the compositional drift of the system is negligible; therefore, the cumulative composition that is being measured is actually equal to its instantaneous value (F_1 instead of $\bar{F}_1$) and the initial feed compositions have remained the same (f_{10} instead of f_1). These assumptions may not hold for many cases and thus using low conversion data introduce immediately experimental error and hence becomes a source of bias in reactivity ratio estimates. In addition, the error during low conversion experimental procedures is accentuated. For copolymerization systems, the potential problems with this approach have been discussed and an alternative procedure for estimation of reactivity ratios based on full conversion experimental data has been developed (see Kazemi et al.[3,17]).

The ternary model (Eqs. 9 and 10) is originally in differential equation form, where we substitute df_i with F_i, assuming that we can collect F_i at low conversion levels. This is while most of the reactions are run up to higher conversion levels, and all this valuable information is usually discarded simply because the estimation approach/model cannot incorporate this into the analysis. Even though using higher conversion level data for estimating binary reactivity ratios has gained more attention in the literature these days, there has been no attempt at estimating ternary reactivity ratios using the cumulative ternary composition model. Therefore, a necessary extension to our approach for estimating ternary reactivity ratios is to include the full conversion trajectory into our program.

This approach consists of a model that relates cumulative terpolymer composition for each monomer ($\bar{F}_i$) to the mole fraction of unreacted monomer (f_i) in the polymerizing mixture and molar conversion, X_n. This relation is the so-called Skeist equation given by Eq. 22, where f_{i0} and f_i are mole fractions of monomer i ($i = 1$, 2, and 3 for three monomers) in the initial and remaining mixtures, and F_i and $\bar{F}_i$ are instantaneous and cumulative compositions. As the reaction proceeds with time, X_n changes, and f_i is evaluated by the numerical solution of the differential copolymer composition equation, given by Eq. 23, given the initial conditions of $f_i = f_{i0}$ when $X_n = 0$. The set of differential equations for all three unreacted monomer compositions f_1, f_2, and f_3 versus conversion (X_n) is being integrated over the course of conversion. The unreacted monomer mixture composition, f_i, is then used in Eq. 22 to evaluate the corresponding cumulative copolymer compositions, $\bar{F}_1$, $\bar{F}_2$, and $\bar{F}_3$. Also, as the measured conversion is usually on a mass (weight) basis, a weight conversion (X_w), as in Eq. 24, should be used to relate X_n to X_w (in this equation, M_{wi} is the molecular weight of monomer i, for $i = 1$, 2, or 3).

$$\bar{F}_l = \frac{f_{i0} - f_i(1-X_n)}{X_n} \quad \text{for } i = 1, 2, \text{ and } 3 \tag{22}$$

$$\frac{df_i}{dX_n} = \frac{f_i - F_i}{1-X_n} \quad \text{for } i = 1, 2, \text{ and } 3 \tag{23}$$

$$X_n = X_w \frac{Mw_i f_{i0} + Mw_j f_{j0} + Mw_k f_{k0}}{Mw_i \bar{F}_i + Mw_j \bar{F}_j + Mw_k \bar{F}_k} \quad i, j, \text{ and } k = 1, 2, \text{ and } 3 \tag{24}$$

The performance of this approach, which is referred to as direct numerical integration (DNI), without resorting to any analytical integration, was recently evaluated and discussed in detail for copolymerization systems in Kazemi et al.[17] Using the DNI approach and medium and high conversion data points for estimating reactivity ratios can significantly improve the quality of the results by (simply) including more information in the analysis as well as avoiding (practical) limitations of collecting low conversion data (with their inherent sources of errors). This extension completes our approach for estimating ternary reactivity ratios directly based on terpolymerization experimental data. By using the EVM method, we utilize the most statistically appropriate parameter estimation technique for this problem and by implementing the DNI approach we use all the available information in the system for the determination of its parameters. Therefore, the results can be considered to be the most reliable ones in the literature to date.

Results and Discussion

Overview of case studies

To compare our work with prior information, we first looked into the literature for existing terpolymerization experimental publications with reactivity ratio estimation studies. In all these publications, almost with no exception, binary reactivity ratios were estimated (as per normal practice) with classical linear/nonlinear approaches. A condensed summary of our literature review is compiled in Table 1, where these reactivity ratios are shown for each system with labels of "binary" (B) or "ternary" (T). Additional explanations for the entries of Table 1 are given at the bottom of the table. In our work, these published terpolymerization systems were analyzed and ternary reactivity ratios were estimated using our approach with the instantaneous ternary model and the EVM methodology. These reactivity ratios are presented in Table 1 for each system as well. For the publications where the conversion values were provided, the cumulative model was also used to determine reactivity ratios, and these values are also listed in Table 1.

Several important points can now be made concerning our observations, based on our estimation results, as summarized in Table 1.

- Our methodology does not use approximate binary reactivity ratios when ternary data are directly available.
- The methodology is not restricted to any simplifying assumptions regarding the error structure.

Table 1. Values of Reactivity Ratios Estimated Based on Terpolymerization Experimental Data

	M_1[a]	M_2[a]	M_3[a]	Type[b]	Model[c]	Source[d]	r_{12}	r_{21}	r_{13}	r_{31}	r_{23}	r_{32}
1	Maleic anhydride	Acrylonitrile	Styrene	T	Inst.	EVM	2.40	0.40	0.07	0.05	0.14	0.58
				B	Inst.	Ref. 23	0.0001	6.00	0.0001	0.04	0.04	0.41
2	Indene	MMA	Acrylonitrile	T	Inst.	EVM	0.0001	0.40	0.0001	2.87	0.24	0.99
				B	Inst.	Ref. 24	0.03	0.40	0.02	3.82	0.15	1.2
3	Ethyl methacrylate	N-phenylmaleimide	Itaconic acid	T	Inst.	EVM	0.33	0.43	3.48	0.21	0.08	1.83
				B	Inst.	Ref. 25	0.37	0.11	2.12	0.59	0.08	1.08
4	Acrylonitrile	Styrene	2,3-dibromopropyl acrylate	T	Inst.	EVM	0.19	0.23	0.99	1.98	0.39	0.16
				B	Inst.	Ref. 26	0.16	0.3	0.87	0.75	0.41	0.22
5	DMAEM[e]	MMA	DDMA	T	Inst.	EVM	0.80	0.75	0.80	0.80	1.09	1.20
				T	Cum.	EVM	0.80	0.75	0.80	0.80	1.09	1.20
				B	Inst.	Ref. 27	0.85	0.86	0.79	0.75	1.12	1.19
6	DMAEM	Styrene	DDMA	T	Inst.	EVM	0.45	1.50	0.78	1.06	3.07	0.55
				T	Cum.	EVM	0.43	1.50	0.77	1.06	3.07	0.55
				B	Inst.	Ref. 27	0.43	1.79	0.79	0.75	2.19	0.45
7	Leucine-NCA[f]	β-benzyl aspartate-NCA	Valine-NCA	T	Inst.	EVM	0.45	1.65	1.03	0.72	3.12	0.41
				B	Inst.	Ref. 28	0.40	1.46	1.37	0.55	2.34	0.34
8	Acrylonitrile	Styrene	MMA	T	Inst.	EVM	0.07	0.29	0.20	1.32	0.57	0.55
				B	Inst.	Ref. 29	0.04	0.31	0.17	1.45	0.47	0.52
9	$Ethylene_{(P=1900,T=180)}$[g]	Methyl acrylate	Vinyl acetate	T	Inst.	EVM	0.05	2.29	0.90	0.82	3.34	0.35
				T	Inst.	Ref. 13	0.05	2.07	0.89	0.92	3.23	0.39
10	$Ethylene_{(P=1100,T=180)}$	Methyl acrylate	Vinyl acetate	T	Inst.	EVM	0.05	3.67	0.73	0.90	3.47	0.08
				T	Inst.	Ref. 13	0.09	2.01	0.92	0.78	3.89	0.24
11	$Ethylene_{(P=1100,T=230)}$	Methyl acrylate	Vinyl acetate	T	Inst.	EVM	0.09	2.44	0.95	0.64	4.00	0.12
				T	Inst.	Ref. 13	0.05	3.34	0.71	0.79	3.25	0.07
12	MMA	NPGMA[h]	HEMA[i]	T	Inst.	EVM	1.05	1.16	1.07	1.86	0.93	1.31
				T	Inst.	Ref. 14	1.03	1.55	1	1.19	0.88	1.25
				B	Inst.	Ref. 14	0.94	1	0.60	0.77	0.98	1.40
13	Fumaronitirle	Dodecyl vinyl ether	β-Chloroethyl acrylate	T	Inst.	EVM	0.009	1.0e-4	0.043	7.03	0.006	0.134
				B	Inst.	Ref. 12	0.019	0.004	0.11	10.2	0.013	1.97
14	Methacylonitrile	Styrene	α-Methylstyrene	T	Inst.	EVM	0.44	0.37	0.39	0.55	1.12	0.64
				B	Inst.	Ref. 30	0.44	0.37	0.38	0.53	1.12	0.63
15	Styrene	Acrylonitrile	MMA	T	Inst.	EVM	0.42	0.02	0.65	0.61	0.07	0.98
				B	Inst.	Ref. 31	0.41	0.04	0.64	0.55	0.16	1.24
16	Maleic anhydride	MMA	Styrene	T	Inst.	EVM	0.0001	7.04	0.0001	0.41	0.40	3.52
				B	Inst.	Ref. 32	0.046	3.496	0.064	0.078	0.530	0.534

[a]M_1, M_2, and M_3 denote the three monomers in each terpolymerization system.
[b]Type indicates whether reactivity ratios are obtained from terpolymerization (ternary) data, denoted as "T," or from (binary) copolymerization data, denoted as "B."
[c]Model refers to the terpolymerization model used for parameter estimation; "Inst." and "Cum." stand for instantaneous and cumulative models, respectively.
[d]Source indicates whether the results are obtained in the current work, denoted by "EVM," or reported in the reference articles, denoted by "Ref."
[e]DMAEM: N,N-dimethylaminoethyl methacrylate.
[f]NCA: N-carboxyanhydride.
[g]Operating conditions are given as degrees Celsius and atm.
[h]NPGMA: 3-hydroxyneopentyl methacrylate.
[i]HEMA: 2-hydroxyethyl methacrylate.

• The approach can apply to any terpolymer data set at any conversion level.

• Overall, the methodology provides reliable reactivity ratios, as will be shown in more detail with the case studies that follow.

• Ternary reactivity ratios differ from binary ones; differences ranging from slight to considerable have been observed, depending on the values of the reactivity ratios.

• The basic premise of our investigations, based on the case studies that follow, is that use of binary reactivity ratios may reduce the reliability of terpolymerization model predictions.

In the three subsections that follow, we concentrate on specific cases (examples and counter examples) and offer more information about different aspects of our investigations. The first subsection evaluates the performance of our approach while pointing out differences with earlier and alternative methodologies. Also, within the context of these results, we focus on the error structure of the measurements that mimics real experimental settings. The second subsection is about using the DNI approach and higher conversion values for estimation of ternary reactivity ratios. Finally, the third and last subsection shows how our results can be evaluated and provides justifications as to why binary reactivity ratios should not be used in terpolymerization system studies.

Old pitfalls versus the correct approach for estimating ternary reactivity ratios

For the estimation of ternary reactivity ratios, the EVM structure can include all variables that are subject to error for the purpose of determining values for these parameters. In this multiresponse problem, the number of variables that could be involved in the parameter estimation procedure is six. That is, f_1, f_2, and f_3 for the mole fractions of the feed composition, and F_1, F_2, and F_3 for the mole fractions of the terpolymer composition. For these variables, we can consider three kinds of dependencies, commonly existing among variables of multiresponse problems.[33]

The first kind is the linear dependencies among true (expected) values of the mole fractions in the feed and terpolymer compositions. These dependencies, as shown earlier in Eqs. 11 and 12, are stoichiometric, stating that the sum of mole fractions in the feed or in the terpolymer is always unity. In this case, data sets in which all these six variables are measured can be used. In fact, this type of data set is the most preferred one, because it contains more information about the system. The composition model handled by the EVM program (as shown in Eq. 15) should also be selected, and for the case where all six variables are available, we can choose any two out of three terpolymer mole fractions, shown in Eqs. 6–8, along with the two mole fraction relations in Eqs. 11 and 12.

The second kind of linear dependencies is among the measurements (observed data). This happens when the experimenter forces the stoichiometric relation between the mole fractions to become true for the observed mole fractions either by normalizing the mole fraction values or by measuring only two out of three mole fractions and calculating the third one based on the summation expression. If not all six variables are directly measured from the experiments, then only two out of three variables in both feed and terpolymer compositions are random variables and hence included in the EVM structure. The EVM model (Eq. 15) should again be selected according to the measured variables.

The third and last kind of dependencies is among the errors. This relation refers to the correlation among variables, which translates into the correlation among the error components in the variance-covariance matrix of measurements ($\underline{V}$). This $\underline{V}$ matrix, as shown previously in Eq. 14, consists of variances and covariances of the variables involved. The dimensions of this matrix are also defined by the number of variables involved in the EVM structure. For the case where all six variables (i.e., all six mole fractions) are available, the $\underline{V}$ matrix can be constructed as shown in Eq. 25. As the feed composition mole fractions are usually obtained by gravimetery, the measurements are independent. Therefore, in the $\underline{V}$ matrix, we have $\sigma_{f_i}^2$ as the diagonal elements (i.e., variances of f_i), yet the off-diagonal elements (i.e., covariances among the measured f_i's) are all zero. On the other hand, for the mole fractions of the terpolymer composition, every two out of three terms are correlated. The reason is that all these mole fractions (F_i's) are obtained from one measurement (e.g., via NMR) and therefore, they are not independent. In this work, to describe these covariances, we use Eq. 26, which uses the correlation coefficient factor (ρ) to determine the magnitude and direction of the correlations among each two variables.

$$\underline{V}=\begin{bmatrix} \sigma_{f_1}^2 & 0 & 0 & 0 & 0 & 0 \\ 0 & \sigma_{f_2}^2 & 0 & 0 & 0 & 0 \\ 0 & 0 & \sigma_{f_3}^2 & 0 & 0 & 0 \\ 0 & 0 & 0 & \sigma_{F_1}^2 & \sigma_{F_1F_2}^2 & \sigma_{F_1F3}^2 \\ 0 & 0 & 0 & \sigma_{F_1F_2}^2 & \sigma_{F_2}^2 & \sigma_{F_2F_3}^2 \\ 0 & 0 & 0 & \sigma_{F_1F3}^2 & \sigma_{F_2F_3}^2 & \sigma_{F_3}^2 \end{bmatrix} \tag{25}$$

$$\sigma_{F_iF_j}^2=\rho * \sqrt{\sigma_{F_i}^2 * \sigma_{F_j}^2} \tag{26}$$

In a way analogous to Eq. 25, if there are only four random variables in the system, that is, for instance, if only f_1, f_2, F_1, and F_2 are measured and hence available, then the $\underline{V}$ matrix can be given by Eq. 27.

$$\underline{V}=\begin{bmatrix} \sigma_{f_1}^2 & 0 & 0 & 0 \\ 0 & \sigma_{f_2}^2 & 0 & 0 \\ 0 & 0 & \sigma_{F_1}^2 & \sigma_{F_1F_2}^2 \\ 0 & 0 & \sigma_{F_1F_2}^2 & \sigma_{F_2}^2 \end{bmatrix} \tag{27}$$

To calculate the variances of each measurement/variable, data from extensive and independently replicated experiments must be collected. In the absence of an extensive database, one can resort to "expert" opinions about the amount of expected error in certain measurements, with the recognition that the quality of information in this case is of a lower grade than in the former case. Relating now the elements of the $\underline{V}$ matrix in Eq. 25 or 27 with the constant k of Eq. 13 and the discussion between Eqs. 13 and 14 earlier, the variances of these measurements ($\sigma_{f_i}^2$ and $\sigma_{F_i}^2$) can be expressed based on the variability in the data reflected by the constant multiplier k which has common values of $\pm 1\%$ for feed and $\pm 5\%$ for terpolymer compositions (i.e., $\sigma_{f_i}^2=\frac{k_{f_i}^2}{3}$ and $\sigma_{F_i}^2=\frac{k_{F_i}^2}{3}$).

As mentioned earlier, published experimental data in the literature are not usually accompanied by adequate

Table 2. Terpolymerization Data for DMAEM (M_1), MMA (M_2), DDMA (M_3), Soljic et al.

Feed composition			Experimental terpolymer composition			Calculated terpolymer composition, Soljic et al.[27]			Calculated terpolymer composition, current work		
M_1	M_2	M_3	M_1	M_2	M_3	M_1	M_2	M_3	M_1	M_2	M_3
0.100	0.100	0.800	0.114	0.084	0.802	0.126	0.086	0.788	0.1198	0.0867	0.7935
0.100	0.400	0.500	0.125	0.381	0.494	0.128	0.377	0.495	0.1256	0.3764	0.498
0.100	0.700	0.200	0.128	0.690	0.182	0.125	0.686	0.189	0.126	0.683	0.191
0.200	0.200	0.600	0.243	0.118	0.569	0.237	0.179	0.584	0.2309	0.1805	0.5886
0.200	0.500	0.300	0.237	0.476	0.287	0.236	0.476	0.288	0.2355	0.4754	0.289
0.400	0.100	0.500	0.422	0.090	0.488	0.424	0.089	0.487	0.417	0.0915	0.4915
0.400	0.400	0.200	0.423	0.378	0.199	0.425	0.381	0.194	0.4237	0.3836	0.1927
0.600	0.200	0.200	0.599	0.195	0.206	0.600	0.196	0.204	0.5975	0.1996	0.2029
0.800	0.100	0.100	0.310	0.118	0.099	0.782	0.106	0.110	0.7809	0.1097	0.1094

information about measuring procedures and therefore it is not possible for such cases to decide whether six variables are indeed directly measured or only two! Based on existing information in the literature, it seems more likely that either only two out of three compositions are measured and/or the mole fraction data are normalized after the fact by imposing that the summation of all three mole fractions is unity. Therefore, our goal in this section is to illustrate the performance of EVM with a certain representative system with typically available information. For this system, we want to point out some of the problems with the original AG model and also advantages and disadvantages of having six or four independently measured variables in the ternary problem.

The terpolymerization system of N,N-dimethylaminoethyl methacrylate (DMAEM, M_1), methyl methacrylate (MMA, M_2), and dodecyl methacrylate (DDMA, M_3) was investigated by Soljic et al.[27] Terpolymerizations were performed at isothermal conditions at low conversion levels, in toluene solution. Experimental and calculated data sets are shown in Table 2. The authors used binary reactivity ratios that were estimated based on copolymerization data from separate binary copolymerization trials (i.e., DMAEM/MMA, DDMA/MMA, and DMAEMA/DDMA).[27,34] Those reactivity ratio estimates were averaged between estimates from both linear and nonlinear regression. These values are cited in Table 1 as binary reactivity ratios. For this system, we used the terpolymerization experimental data to estimate ternary reactivity ratios with:

1. The original AG model in all possible combinations (Eqs. 2–4),
2. The recast terpolymer composition model with six variables (Eqs. 9–12),
3. The recast terpolymer composition model with four variables (only, Eqs. 9 and 10), and
4. Different amounts of correlation between the terpolymer composition mole fractions.

The representative reactivity ratio estimates for this system, cited in the 5th row of Table 1, were obtained from Case 2.

In the first part of the analysis (Case 1 above), we used the EVM method with the three combinations of the AG model, meaning that the model was described as the ratios of (F_2/F_1 and F_3/F_1), (F_1/F_3 and F_2/F_3), and (F_1/F_2 and F_2/F_3). The results from parameter estimation for the reactivity ratio pairs of (r_{12} and r_{21}), (r_{13} and r_{31}), and (r_{23} and r_{32}) along with their corresponding JCRs are shown in Figures 1–3, respectively. In these figures, the line styles ——, - - - -, and -.-.-.- refer to different combinations of (F_2/F_1 and F_3/F_1), (F_1/F_3 and F_2/F_3), and (F_1/F_2 and F_2/F_3), respectively. Also, the reported values of reactivity ratios by Soljic et al.[27] and the EVM point estimates are shown in these figures with "o" and "x," respectively.

As can be seen in Figures 1–3, the EVM point estimates are always the same regardless of the AG model combinations, as all these point estimates overlap at a single point. However, the visualization of the JCRs in these figures illustrates how the choice of different combinations in the AG

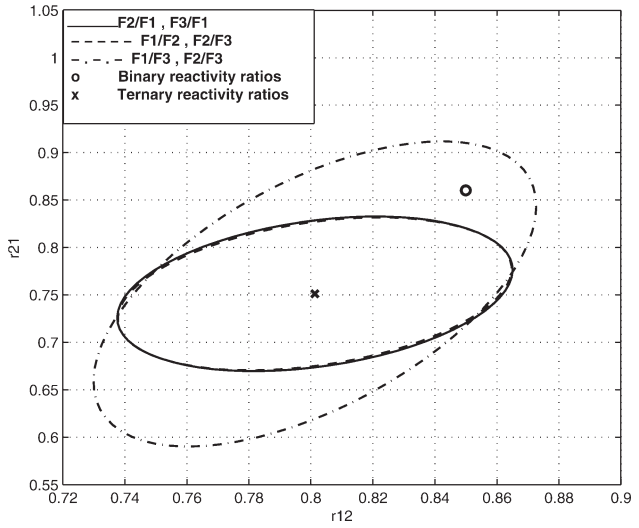

Figure 1. r_{12} and r_{21} estimation results for different combinations of the AG model.

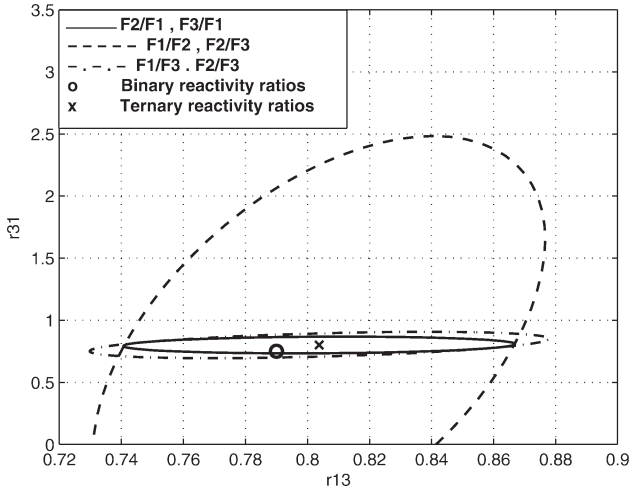

Figure 2. r_{13} and r_{31} estimation results for different combinations of the AG model.

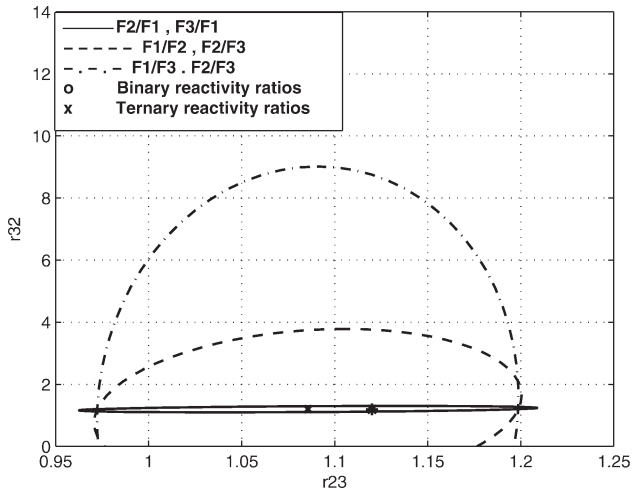

Figure 3. r_{23} and r_{32} estimation results for different combinations of the AG model.

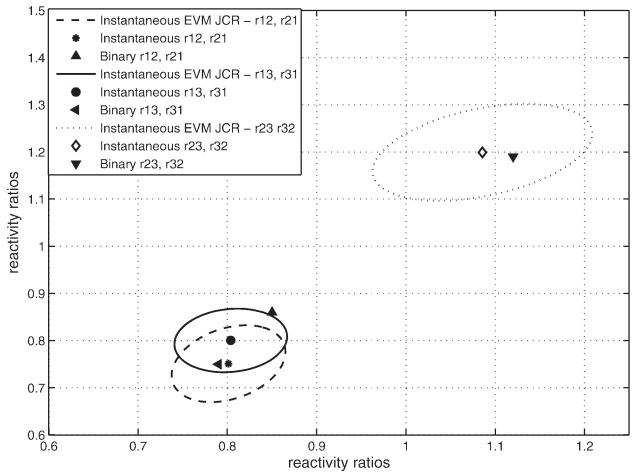

Figure 4. Reactivity ratio estimates and JCRs based on the recast composition model with six variables.

model [e.g., (F_2/F_1 and F_3/F_1) vs. (F_1/F_2 and F_2/F_3)] affects the precision of these results. In particular for this system, it can be seen that the (F_2/F_1 and F_3/F_1) combination gives the smallest JCRs for all three pairs of reactivity ratios (see Figures 1–3); meanwhile, for the (r_{13}, r_{31}) and (r_{23}, r_{32}) pairs of reactivity ratios (Figures 2 and 3), the (F_1/F_3 and F_2/F_3) combination results in JCRs crossing inside the negative region. The changes in the level of uncertainty in our parameter estimation results, when one combination is taken into account versus another, are affected either by the choice of the specific combination or by experimental error associated to the data. Hence, these observations indicate that the estimation results from the AG model are very much combination specific and should be used with great caution.

In the second step of the analysis, we used the recast expression of the terpolymer composition model (Eqs. 9–12) to estimate ternary reactivity ratios for this terpolymerization system based on the same data as before (see Table 2). For this procedure, the most general scenario is selected first, with six variables (all three composition mole fractions are considered as measured in both feed and terpolymer) and no correlation between any of the measurements. The $\underline{V}$ matrix in this case would be similar to Eq. 25 for the diagonal elements (variances), whereas the off-diagonal elements (covariances) are all zero. The results from parameter estimation are shown in Figure 4, where all six reactivity ratios are shown in pairs with their JCRs. This figure shows that for all three pairs of reactivity ratios, we have reasonable JCRs indicating that these reactivity ratio estimates have acceptable level of precision.

The symmetrical nature of the recast form of the composition model allows us to choose any two responses out of three without affecting the results. The same results were obtained for all combinations of (F_1, F_2, and F_3) in pairs. The point estimates of Figure 4 are the ones cited in Table 1. Figure 4 also shows the reported binary reactivity ratios in the reference paper and it can be seen (almost) all of those estimates are included inside the EVM JCRs. The results from this estimation represent a "best case" scenario, as ternary reactivity ratios are in good agreement with their respected binary values. This is not necessarily the case for many other terpolymerization systems, as is evident from Table 1.

In the third step of the analysis of DMAEM/MMA/DDMA, a different number of measured variables was chosen (four in this case) for the EVM parameter estimation problem (e.g., f_1, f_2, F_1, and F_2). Figures 5–7 show the results for the reactivity ratios pairs of (r_{12} and r_{21}), (r_{13} and r_{31}), and (r_{23} and r_{32}). For each pair of reactivity ratios [e.g., (r_{12} and r_{21}) in Figure 5], the line styles ——, - - - -, and -.-.-.- represent the JCRs of the cases where (F_1 and F_3), (F_2 and F_3), and (F_1 and F_2) are selected as the measured responses (and hence, as the EVM variables). Their corresponding point estimates are shown as an open circle, "o," in the center of each JCR. In addition to these results, the reactivity ratio estimates and their JCRs from Case 2 (the "best case" scenario) for (r_{12} and r_{21}), (r_{13} and r_{31}), and (r_{23} and r_{32}) are included in Figures 5–7, respectively. For example, in Figure 5, this JCR is shown with line style –x-x-x and the corresponding point estimates are indicated with an open square, "□," in the center of the JCR. This formatting is used in Figures 6 and 7 as well. The binary reactivity ratios from the reference paper[27] are also included in Figures 5–7 for each reactivity ratio pair, denoted with a filled star, "*."

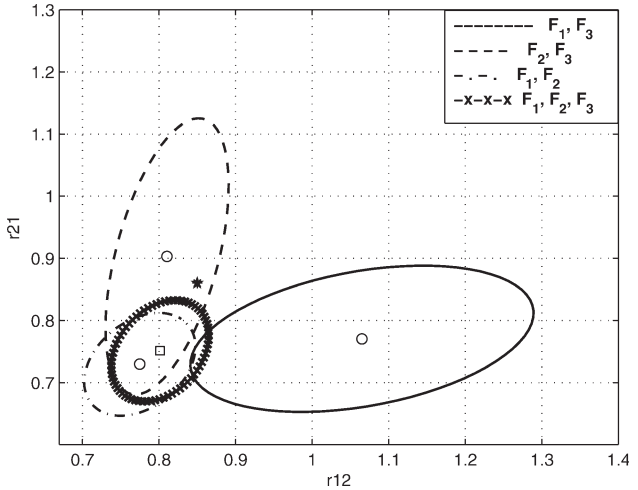

Figure 5. r_{12} and r_{21} estimates for the recast composition model with four variables.

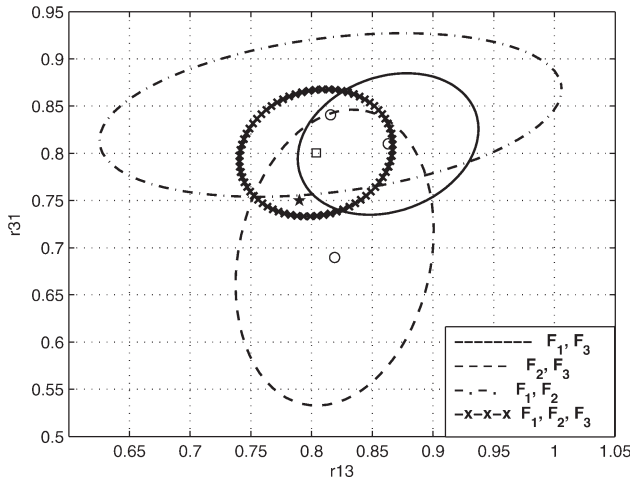

Figure 6. r_{13} and r_{31} estimates for the recast composition model with four variables.

Figures 5–7 clearly show that not only can the point estimates shift with the choice of variables, but also the sizes of the obtained JCRs change considerably. Finding reliable results within this approach needs more information about the measurement procedure, indicating which one of the mole fractions in the feed and terpolymer compositions are actually measured. Those measured responses can then be chosen as the EVM variables, and the reactivity ratio estimation results mimic the real nature of the measurements and offer, in turn, an acceptable level of reliability. In the absence of such information, a pair of mole fractions in the feed and terpolymer compositions should be selected randomly and, therefore, the results may not be truly representative. For instance, as there is no such information available for the ternary system in question, any of the (F_1 and F_3), (F_2 and F_3), and (F_2 and F_3) JCRs for the (r_{12} and r_{21}) pair in Figure 5 can be selected at random. Obviously, this arbitrary choice may lead to a nonrepresentative set of reactivity ratios for this ternary system. Comparing these results with the case where all six variables were involved, it can be suggested that having all six variables measured would provide much more reliable values for the reactivity ratios, as results

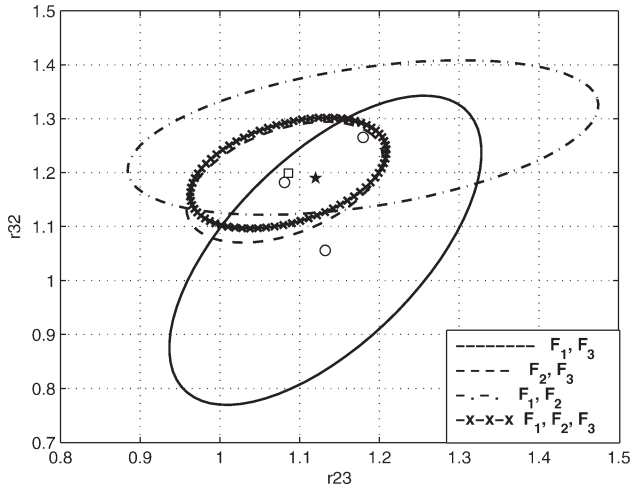

Figure 7. r_{23} and r_{32} estimates for the recast composition model with four variables.

Table 3. Effect of Correlation on the Reactivity Ratio Estimates for DMAEM (M_1), MMA (M_2), DDMA (M_3)

	$\rho = -0.4$	$\rho = -0.2$	$\rho = 0$	$\rho = 0.2$	$\rho = 0.4$
r_{12}	0.82	0.80	0.80	0.79	0.79
r_{21}	0.78	0.76	0.75	0.74	0.74
r_{13}	0.79	0.80	0.80	0.80	0.80
r_{31}	0.80	0.80	0.80	0.79	0.79
r_{23}	1.09	1.09	1.08	1.08	1.07
r_{32}	1.21	1.20	1.19	1.19	1.18

are consistent and with an acceptable level of precision, as can be seen in Figure 4.

So far in the analysis, all measurements were treated as uncorrelated. The last part of the analysis is about the correct error structure, specifically the correlation between the measurements. The effect of different correlations is tested by using different correlation coefficients between the measurements coming from NMR (i.e., different values for the correlation coefficient, ρ, in Eq. 26). The terpolymer composition mole fractions measured from NMR can be assumed to be negatively correlated, as these mole fractions sum up to one and if one of them increases, the other two mole fractions should decrease. Results from the EVM program were obtained with correlation coefficients of -0.2 and -0.4, and also with 0.2 and 0.4, to see the effect of change in the direction of the correlation. The reactivity ratio estimates for these cases are shown in Table 3, along with the correlation coefficient of zero (middle column), which acts as our standard case. Although the true value of the correlation is unknown, the results in Table 3 clearly show that by changing the amount of correlation from -0.4 to 0.4, the change in the values of the reactivity ratios for this system is very minimal and apparently the choice of the correlation coefficient does not affect the general outcome.

The most appropriate approach to find the value of the correlation coefficient is to estimate it from the analysis of residuals of a rich replicated experimental data set. Such an investigation is not possible with existing data sets in the literature due to the limited number of data points. In the absence of this information, looking into the effect of varying the correlation coefficient on the reactivity ratio estimation results can determine whether it is necessary to run the extra step of the analysis of residuals, depending on the significance of the different correlations between the measurements on the estimation results. For this ternary system, the reactivity ratios in Table 3 shift insignificantly so that having a more detailed analysis of residuals may not be justified. While this is true for this case, there might be other terpolymerization systems where the analyses of their NMR data are subject to higher error levels and, in turn, their correlations could have more of a substantial effect.

Combining conversion information with the cumulative terpolymer composition equation

As mentioned before, using the cumulative terpolymer composition model and incorporating conversion values in the parameter estimation process improves the precision of the obtained reactivity ratios, based on trends established for copolymerization systems as well as theoretical explanations supporting this point.[3,17] The key equations for the terpolymerization cumulative composition model are shown in Eqs. 22–24. To show the implementation of EVM, we retained

Table 4. DMAEM (M_1), MMA (M_2), DDMA (M_3), Soljic et al.[27]

Feed composition			Conversion	Experimental terpolymer composition		
M_1	M_2	M_3	X_w%	M_1	M_2	M_3
0.100	0.100	0.800	0.70	0.114	0.084	0.802
0.100	0.400	0.500	0.96	0.125	0.381	0.494
0.100	0.700	0.200	1.32	0.128	0.690	0.182
0.200	0.200	0.600	1.69	0.243	0.118	0.569
0.200	0.500	0.300	2.11	0.237	0.476	0.287
0.400	0.100	0.500	2.97	0.422	0.090	0.488
0.400	0.400	0.200	3.82	0.423	0.378	0.199
0.600	0.200	0.200	5.05	0.599	0.195	0.206
0.800	0.100	0.100	6.85	0.783	0.118	0.099

Table 5. DMAEM (M_1), Styrene (Sty) (M_2), DDMA (M_3), Soljic et al.[27]

Feed composition			Conversion	Experimental terpolymer composition		
M_1	M_2	M_3	X_w%	M_1	M_2	M_3
0.100	0.100	0.800	0.70	0.108	0.181	0.711
0.100	0.400	0.500	0.84	0.095	0.579	0.326
0.100	0.700	0.200	1.09	0.077	0.829	0.094
0.200	0.200	0.600	1.46	0.194	0.330	0.476
0.200	0.500	0.300	1.74	0.160	0.669	0.171
0.400	0.100	0.500	2.66	0.367	0.172	0.461
0.400	0.400	0.200	3.11	0.312	0.557	0.131
0.600	0.200	0.200	4.55	0.509	0.322	0.169
0.800	0.100	0.100	6.43	0.718	0.189	0.093

the same reference as previous section, Soljic et al.,[27] where two terpolymerization systems of DMAEM (M_1)/MMA (M_2)/DDMA (M_3) and DMAEM (M_1)/Styrene (Sty) (M_2)/DDMA (M_3) (as shown in the 5th and 6th rows of Table 1) were studied. Their experimental data including conversion values are shown in Tables 4 and 5. Although these data points were collected at low conversion levels, they can still be used to illustrate how the cumulative terpolymerization model can be incorporated into the EVM ternary reactivity ratio estimation program and how beneficial this can be. These data sets were analyzed and the reactivity ratio estimates are shown in Figures 8 and 9 for each system. These figures also show the point estimates and JCRs from the instantaneous model (Case 2) and the binary reactivity ratios reported in the reference paper.[27]

As can be seen in Figures 8 and 9, the point estimates and their JCRs from the cumulative model are almost identical to those from the instantaneous model. The closeness of the reactivity ratio estimates from both instantaneous and cumulative models is an indication that the cumulative model works perfectly for the ternary systems. Typically, one would expect that the cumulative model adds more information to the parameter estimation procedure and therefore provides more reliable reactivity ratio estimates. However, our results for these two systems indicate that the instantaneous data are of high quality and the assumptions of the

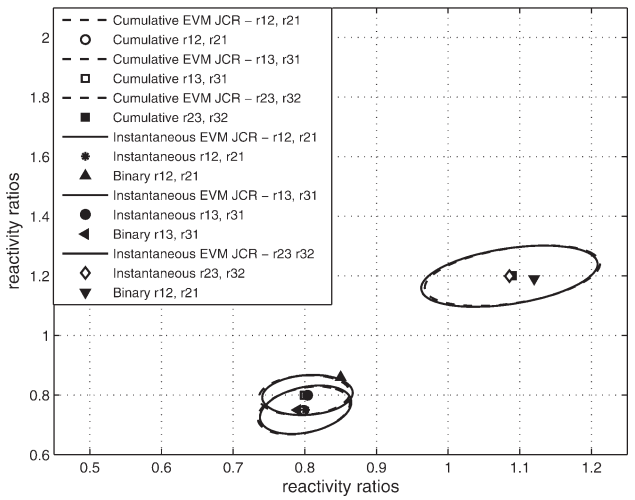

Figure 8. Reactivity ratio estimates from cumulative data for DMAEM (M_1), MMA (M_2), DDMA (M_3).

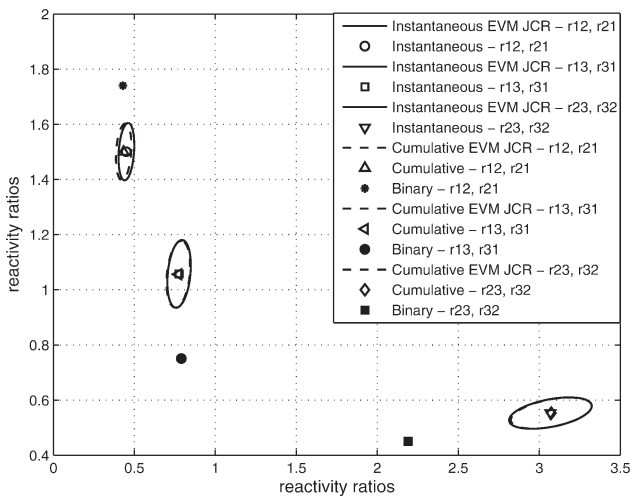

Figure 9. Reactivity ratio estimates from cumulative data for DMAEM (M_1), Styrene (Sty) (M_2), DDMA (M_3).

Table 6. Terpolymerization Experimental Data for the MMA(M_1)/NPGMA(M_2)/HEMA(M_3) Ternary System, Iglesias et al.[14]

Feed composition			Experimental terpolymer composition		
M_1	M_2	M_3	M_1	M_2	M_3
0.32	0.34	0.34	0.28	0.32	0.4
0.21	0.20	0.59	0.2	0.18	0.62
0.2	0.40	0.40	0.16	0.4	0.44
0.2	0.60	0.2	0.14	0.61	0.25
0.41	0.21	0.38	0.4	0.19	0.41
0.62	0.19	0.19	0.58	0.19	0.23
0.1	0.1	0.80	0.05	0.09	0.86
0.79	0.10	0.11	0.78	0.11	0.11
0.41	0.39	0.41	0.37	0.4	0.23
0.10	0.79	0.11	0.1	0.79	0.11

instantaneous ternary model are met to a very good extent. It must be kept in mind, however, that this is not the case for most of the experimental work in the literature as the "so-called" low conversion data often go to higher conversion levels and therefore the error in the instantaneous data cannot be neglected. That is when using cumulative data would be more beneficial.

Evaluation of the reliability of the reactivity ratio estimates

To show the effect of the presence of the third monomer, an example about the evaluation process of the reactivity ratio results is given in this section for the terpolymerization system of MMA (M_1), 3-hydroxyneopentyl methacrylate (NPGMA, M_2), 2-hydroxyethyl methacrylate (HEMA, M_3). This system was investigated by Iglesias et al.[14] where terpolymerization and copolymerizations were performed at low conversion levels and binary reactivity ratios were estimated, albeit with linear estimation techniques. The terpolymerization data were also used with a nonlinear least-squares technique to estimate ternary reactivity ratios (these values are shown in the 12th row of Table 1). In our work, we used the experimental data (as shown in Table 6) and estimated ternary reactivity ratios, using the recast terpolymerization model with six variables, assuming no correlation amongst the measurements. The published binary and ternary reactivity ratios along with our point estimates are given in Table 1 and their JCRs are shown in Figure 10.

As shown in Figure 10, the difference between binary and ternary reactivity ratios in the reference paper is very significant for two of the reactivity ratio pairs (except for r_{23} and r_{32}). With respect to our results, the estimated ternary reactivity ratios do not agree well with neither of the reported reactivity ratios, again with the exception of the pair r_{23} and r_{32}. It is also noted that for both (r_{12} and r_{21}) and (r_{13} and r_{31}) pairs, the reactivity ratio values are greater than one. While such binary systems are not feasible on their own, in this case, the reactivity ratios lie very close to unity and therefore, these results may reflect a large level of error in the experimental data that in turn introduces bias in the ternary reactivity ratio estimates.

The shifts in the values of the reactivity ratios from a binary system to a ternary one clearly illustrates that using binary reactivity ratios can be a grossly incorrect choice as they do not necessarily reflect the actual (true) reactivities of the monomers in the ternary system. The importance of the variation in reactivity ratios values can also be illustrated in

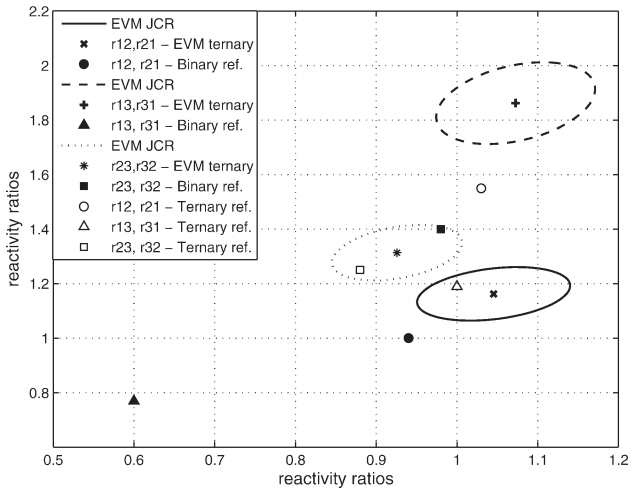

Figure 10. Reactivity ratio estimates for the terpolymerization system of MMA (M_1)/NPGMA (M_2)/HEMA (M_3).

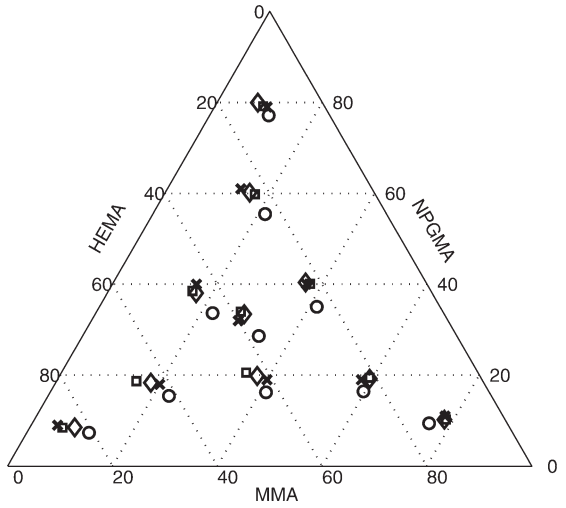

Figure 11. Comparison of experimental and calculated terpolymerization compositions; (X) experimental data; (○) calculated based on binary reactivity ratios[14]; (◇) calculated based on ternary reactivity ratios[14]; (□) calculated based on ternary reactivity ratios in current work.

terms of the prediction of the experimental data, and more specifically, by looking at the agreement between experimental and theoretical terpolymer compositions. Figure 11 shows a triangular plot for the terpolymer composition of this ternary system. The experimental data from the reference paper along with calculated terpolymer compositions based on reported binary, reported ternary and our estimated ternary reactivity ratios are also shown in this figure.

Looking at different sets of predicted compositions in Figure 11, it can be seen that although the experimental and predicted ternary compositions are close, they are quite far from the ternary compositions calculated from binary reactivity ratios. The largest difference, and hence, disagreement, in Figure 11 is indeed between experimental data and calculated compositions based on binary reactivity ratios! Such results can be associated to, firstly, the EVM methodology that was used to obtain these estimated reactivity ratios and, secondly, to including the third monomer and the subsequent changes in the reaction medium in the estimation process compared to binary studies. This influence can be realized with the shifts in the values of ternary and binary reactivity ratios, but it is also noticeable through the change in the predicted composition values.

Using binary reactivity ratios to describe a terpolymerization system is effectively ignoring the presence of the third monomer, and hence the interactions between monomers 1, 2, and 3. These interactions (be it electronic, steric, etc.) are indeed reflected in the process data collected from a terpolymerization system. Therefore, the will in turn be reflected in the values of the determined reactivity ratios, as long as such reactivity ratios are estimated directly from terpolymerization data using the terpolymerization model.

Conclusions

The following points have been made, and justified by our analysis, related to the estimation of ternary reactivity ratios:

a. The recast terpolymerization model, which uses terpolymer composition mole fractions explicitly (and not in ratios), avoids the estimation pitfalls with the original AG model.

b. Estimating ternary reactivity ratios based on terpolymerization data directly protects against unnecessary propagation of errors from badly estimated binary reactivity ratios, at the same time without essentially ignoring the presence of the third comonomer.

c. EVM is the framework to use, especially with terpolymerization systems which contain inherently more error (than copolymerizations) in all variables.

d. Several examples and counter examples with literature ternary experimental data showed how one can go toward consistent and reliable ternary reactivity ratios, when the correct information content is taken into account (with respect to (i) the choice of measurements, (ii) their error structure, and (iii) the correlation between measurements).

Acknowledgments

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