# Parameter Estimation in Multiresponse Problems for the Modelling of Multicomponent Polymerization Reactions

by

Emma Kathleen Daly Hauch

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# Abstract

Over the years a great volume of work has been published on copolymer and more recently terpolymer and multi-component systems. Reactivity ratio estimation for polymer systems is of particular interest, to both industry and academia, as these parameters can be utilized to predict polymer properties. Researchers have estimated these parameters via a number of statistical methods and using various data sources, such as copolymer composition and triad fractions data (also referred to as sequence length data). At this point, there is still an ongoing discussion about the validity of some statistical methods in use and the supposedly correct models that have been identified for particular systems. Furthermore, with the advancement of computing power, the potential for estimating reactivity ratios from full conversion polymerization data using cumulative models has increased. Cumulative models are of particular importance given that some multiple component systems being studied today are so fast that instantaneous models are no longer valid.

The objectives of this work: examine the potential benefit, in the estimation of reactivity ratios, from using multiple response copolymer models (such as triad fractions); identify improvements in reactivity ratio estimates using cumulative copolymer models over the full conversion range, for both triad fractions and composition data; and examine the use of terpolymer composition data in the error in variables model reactivity ratio estimation technique.

In the first phase of this research, the potential improvement in reactivity ratio estimation using triad fractions data in place of and in addition to composition data is considered for low conversion studies modeled by instantaneous models. Initially triad fractions are utilized in the error in variables model (EVM) and Box Draper Determinant Criterion method, to compare the effectiveness of the two parameter estimation techniques. The error levels and structure are also investigated, to determine the impact that these assumptions can have on the location of the point estimates. The conclusions drawn from this work showed that the performance of the instantaneous triad fractions model is superior to that of the instantaneous composition model, which can be explained from an information content point of view. In contrast, the potential

benefit of combining composition and triad fractions data was seen to be minimal and thus measurement of copolymer composition data is not necessary if triad fraction data is obtainable.

In the subsequent phase of study, the error in variables model (EVM) for copolymer reactivity ratio estimation is extended to cumulative composition and triad fraction models for the full conversion range. The cumulative models considered for the full conversion copolymer composition data studies were the analytically integrated cumulative copolymer composition model (referred to as the Meyer-Lowry model) and the numerically integrated cumulative copolymer composition model (ODECCC). The reactivity ratio estimates from the cumulative composition model were compared to the instantaneous composition model estimates to show the deviation of the instantaneous estimates when moderate-high conversion data is used. That is, at low conversions the case studies in this work show that the reactivity ratio estimates from the instantaneous model and the cumulative models agree; however in moderate-high conversion experiments, there is deviation in the estimates obtained and thus the appropriate cumulative (ODECCC) model should be used.

Finally, the numerically integrated cumulative copolymer triad fractions (ODECCTF) model was considered. The comparison of the instantaneous triad fractions and cumulative models was limited to low conversion data (thus insignificant feed composition drift) due to the lack of published work on moderate-high conversion triad data. Consequently, it was anticipated that the instantaneous and cumulative models would have overlapping joint confidence regions, indicating agreement of the model reactivity ratio estimates, in the low conversion case studies. Yet this was not always the case. As a result, the issues involved with drawing conclusions from joint confidence regions (for multiple response - small sample size problems) were discussed and recommendations of further study on moderate to high conversion data were proposed.

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# Chapter 1

# Introduction

Reactivity ratios are important parameters which describe composition and sequence length characteristics of copolymer chains. Researchers have estimated these parameters via a number of statistical methods and using various data sources (i.e., copolymer composition and sequence length data) in an attempt to estimate the reactivity ratios for specific systems. With respect to models used to estimate reactivity ratios, the terminal and penultimate model are typically used along with variations of these when applied to different data sources. At this point, there is still an ongoing discussion about the validity of the statistical methods in use and models that have been identified for particular systems, due to contradictory values of the resulting parameters.

The first and most basic mechanistic model used is the Mayo-Lewis equation, based on the terminal mechanism. In the past, in order to bypass the non linear nature of the equation, investigators resorted to graphical and linear regression methods to estimate the reactivity ratios. The linear methods used after transforming the original non linear equation include techniques such as Fineman-Ross, Kelen-Tudos, extended Kelen-Tudos, etc. However, these approaches had inherent faults and subsequently provided poor reactivity ratio estimates. It has been shown by previous researchers that the linear methods are antiquated and frequently do not provide acceptable estimates for the parameters (Rossignoli and Duever, 1995; Polic et al., 1998). Despite this, in a recent detailed literature review it was evident that these linear regression and graphical methods are still commonly used.

In order to combat the faults present in the linear regression of the Mayo-Lewis model a new approach to estimating the reactivity ratios emerged. Tidwell et al. (1965) proposed the use of non linear least squares (NLLS) regression on the Mayo-Lewis model to obtain more precise estimates of the "true" value of the reactivity ratios. Patino-Leal et al. (1980) extended the NLLS technique and applied the Error-in-Variables Model (EVM). As the name would suggest the EVM method ensures that the error in every variable used by the model is accounted for in the parameter estimation procedure. Rossignoli and Duever (1995) compared and contrasted these two methods and further discussed the improvement in the reactivity ratio estimates accuracy when compared with the linear methods. Consequently, with the introduction of faster and easy to use computing tools, both non linear methods have gained in popularity as they enabled the researcher to account for the nonlinear nature of the Mayo-Lewis model structure.

The main limitation with using instantaneous models (i.e., Mayo-Lewis model) for copolymer data is the fact that the model relates instantaneous variables to one another, despite the fact that these variables are rarely those measured. Typically, the measured variables are the feed composition at the start of the reaction and the copolymer composition or triad fractions (sequence length distribution) peak area at the end. Thus, in order to apply the model, the user must assume that the feed composition does not change significantly for the duration of the reaction. Generally, it is considered that there is insignificant feed composition drift at low conversions (<5%) and hence most experiments are operated below this limit, although in some fast reacting systems this is not always possible. Therefore, if there is drift in the feed composition as the reaction proceeds, then the instantaneous model fails to capture this and instead a cumulative model should be used. Cumulative models used to analyze composition data include the analytically integrated model (otherwise referred to as the Meyer-Lowry model) and the numerically integrated model. In contrast, only one cumulative model for triad fractions data has been developed and is referred to as the numerically integrated cumulative triad fractions model in this work.

The application of the correct statistical technique and data source for parameter estimation should improve our ability to estimate the true reactivity ratio values of copolymerization systems. An accurate estimate of reactivity ratios is important due to the use of these values in both accurately representing the copolymer system and discriminating between mechanistic models. Subsequently, the first step in this research was to re-demonstrate that the estimation of reactivity ratios using the linear methods does not provide an accurate estimate of the true values for all systems and thus caution should be heeded before using these simple methods. Following from this is the analysis of systems using sequence length data (triad fractions) to determine reactivity ratios. In this area it will be important to address the following question: Which copolymer measurements, copolymer composition or triad fractions, will provide the most information with respect to parameter estimation and thus obtain a better estimate? Additionally, does combining the data sets further improve the accuracy of the reactivity ratio estimates? The next stage was then to consider determining the reactivity ratios from both copolymer composition and triad fractions cumulative models. In researching this area it is also hoped to further develop the RREVM program, which is based on the EVM statistical method of parameter estimation, to incorporate the full conversion range for composition data. Over the full conversion range there are a number of issues which can be present including composition drift, depropagation and autoacceleration. So thus the question becomes whether EVM can be applied to all copolymer systems over the full conversion range and give accurate estimates for the reactivity ratios? Lastly, it is hoped to further the parameter estimation package to include terpolymer and multicomponent systems, first using instantaneous models. Recently, experimental data has started to become available for these complex systems and thus estimation methods need to be evaluated and analyzed in order to accurately determine reactivity ratios for these systems.

## Chapter 2

# Copolymerization Models

As an introduction to the modeling of copolymerization systems an overview of polymerization reaction kinetics is first required. There are four stages in free radical chain growth polymerization,

i) initiation
ii) propagation
iii) termination
iv) transfer

As the focus of this research is on the estimation of monomer reactivity ratios it is apparent that the stage that is of most interest is the propagation stage. The reason for this is that the consumption of monomer in reactions other than propagation can be neglected, according to the Long Chain Approximation (Type I) (Odian, 1933). The reaction steps during the propagation stage of free radical copolymerization then depend upon the mechanism selected to represent the system. There are two general models of the propagation stage in free radical chain polymerization, the terminal model and the penultimate model.

## 2.1 The Terminal and Penultimate Models

The terminal and penultimate models were both developed to describe the reaction of two monomers, $M_1$ and $M_2$, to form a copolymer. For a free radical polymerization the growing radical of length *n* is represented by $Rn\cdot$. The type of model and data source selected influences the model structure used in the estimation of the reactivity ratios.

The terminal model, as the name suggests, assumes that only the last unit on the growing radical chain influences the subsequent monomer addition. That is, if $R_{n,i}\cdot$ is a radical of chain length *n* ending in monomer *i*, there would be four possible steps during the propagation stage of free radical copolymerization, represented by Equations 2.1 to 2.4.

$$R_{n,1}\cdot + M_1 \xrightarrow{k_{11}} R_{n+1,1}\cdot \qquad (2.1)$$

$$R_{n,1}\cdot + M_2 \xrightarrow{k_{12}} R_{n+1,2}\cdot \qquad (2.2)$$

$$R_{n,2}\cdot + M_1 \xrightarrow{k_{21}} R_{n+1,1}\cdot \qquad (2.3)$$

$$R_{n,2}\cdot + M_2 \xrightarrow{k_{22}} R_{n+1,2}\cdot \qquad (2.4)$$

Although there are four rate constants, $k_{i,j}$ for the addition of monomer *j* to a radical ending in unit *i*, the overall polymerization/propagation rate, $R_p$, is typically expressed in terms of the two homopolymerization rate constants $k_{11}$ and $k_{22}$, and two monomer reactivity ratios,

$$r_1 = \frac{k_{11}}{k_{12}}; \qquad r_2 = \frac{k_{22}}{k_{21}} \qquad (2.5\ \&\ 2.6)$$

In contrast, the penultimate model assumes that the last two units on the growing radical chain influence the subsequent monomer addition. That is, if $R_{n,ij}\cdot$ is a radical with terminal unit *j* and penultimate unit *i,* the eight possible propagation reactions are represented by Equations 2.7 to 2.14.

$$R_{n,11}\cdot + M_1 \xrightarrow{k_{111}} R_{n+1,11}\cdot \qquad (2.7)$$

$$R_{n,11}\cdot + M_2 \xrightarrow{k_{112}} R_{n+1,12}\cdot \qquad (2.8)$$

$$R_{n,22}\cdot + M_1 \xrightarrow{k_{221}} R_{n+1,21}\cdot \qquad (2.9)$$

$$R_{n,22}\cdot + M_2 \xrightarrow{k_{222}} R_{n+1,22}\cdot \tag{2.10}$$

$$R_{n,12}\cdot + M_1 \xrightarrow{k_{121}} R_{n+1,21}\cdot \tag{2.11}$$

$$R_{n,12}\cdot + M_2 \xrightarrow{k_{122}} R_{n+1,22}\cdot \tag{2.12}$$

$$R_{n,21}\cdot + M_1 \xrightarrow{k_{211}} R_{n+1,11}\cdot \tag{2.13}$$

$$R_{n,21}\cdot + M_2 \xrightarrow{k_{212}} R_{n+1,12}\cdot \tag{2.14}$$

Here 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

$$r_{11} = \frac{k_{111}}{k_{112}}; \quad r_{21} = \frac{k_{211}}{k_{212}}; \quad r_{22} = \frac{k_{222}}{k_{221}}; \quad r_{12} = \frac{k_{122}}{k_{222}} \tag{2.15 – 2.18}$$

and two radical reactivity ratios

$$s_1 = \frac{k_{211}}{k_{111}}; \quad s_2 = \frac{k_{122}}{k_{222}} \tag{2.19 \& 2.20}$$

Equations for composition, triad fractions and the overall propagation rate constant can be derived for both the terminal and penultimate model. However, each of these equations for the different data sources can be further classified into either instantaneous or cumulative models. For example, using composition as the data source the instantaneous model describes the composition variation from time *t* to *t+dt*, while the cumulative model describes the composition variation from time zero to time *t*.

### 2.1.1 Copolymer Composition

The most widely used copolymerization model is the Mayo-Lewis model (1944) which expresses the terminal model using instantaneous composition data. The model relates the instantaneous mole fraction of monomer 1 bound in the copolymer, $F_1$, with the mole fractions of unbound (free) monomer 1 and 2 ($f_1$ and $f_2$, respectively) via the reactivity ratios $r_1$ and $r_2$. The terminal model equation is thus given by:

$$F_1 = \frac{r_1 f_1^2 + f_1(1-f_1)}{r_1 f_1^2 + 2f_1(1-f_1) + r_2(1-f_1)^2} \tag{2.21}$$

One limitation of the Mayo-Lewis model is that the model variables are considered to be truly *instantaneous* values, which is rarely the case as feed and copolymer composition are determined at the beginning and completion of the experiment, respectively. Therefore as in most cases one monomer is consumed at a greater rate, the initial feed concentration does not necessarily remain constant for the duration of the copolymerization. In order to minimize the potential impact of composition drift, reactivity ratio experiments are conducted at low conversions, typically below five percent conversion.

Furthermore, an alternate expression that is sometimes used to represent the Mayo-Lewis model is in the derivative form given by:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \times \frac{r_1[M_1]+[M_2]}{[M_1]+r_2[M_2]} \tag{2.22}$$

$$F_1 = \frac{d[M_1]}{d[M_1]+d[M_2]} \tag{2.23}$$

$$f_1 = \frac{[M_1]}{[M_1]+[M_2]} \tag{2.24}$$

$[M_1]$ and $[M_2]$ are the concentrations of monomer 1 and 2 in the reactor. A more detailed discussion of the development of the Mayo-Lewis model can be found in Hamielec et al. (1989).

The instantaneous penultimate model equation, using copolymer composition data, is given by:

$$F_1 = \frac{r_{21}f_1^2\left(\frac{r_{11}f_1+f_2}{r_{21}f_1+f_2}\right)+f_1f_2}{r_{21}f_1^2\left(\frac{r_{11}f_1+f_2}{r_{21}f_1+f_2}\right)+2f_1f_2+r_{12}f_2^2\left(\frac{r_{22}f_2+f_1}{r_{12}f_2+f_1}\right)} \tag{2.25}$$

Similar to the instantaneous terminal model, the issues of truly instantaneous variables and composition drift are also present.

There are two models that express the cumulative composition situation, the analytically integrated model and the numerically integrated model. The analytically integrated model, commonly referred to as the Meyer-Lowry equation, relates the change in feed composition with molar conversion by the following equation:

$$X_n = 1 - \left(\frac{f_1}{f_{1,0}}\right)^{\alpha} \left(\frac{1-f_1}{1-f_{1,0}}\right)^{\beta} \left(\frac{f_{1,0}-\delta}{f_1-\delta}\right)^{\gamma} \qquad (2.26)$$

where

$$\alpha = \frac{r_2}{1-r_2}; \quad \beta = \frac{r_1}{1-r_1}; \quad \gamma = \frac{1-r_1 r_2}{(1-r_1)(1-r_2)}; \quad \delta = \frac{1-r_2}{2-r_1-r_2} \qquad (2.27\text{-}2.30)$$

And

$$X_n = 1 - \frac{N_1+N_2}{N_{1,0}+N_{2,0}}; \quad f_{1,0} = \frac{N_{1,0}}{N_{1,0}+N_{2,0}}; \quad f_1 = \frac{N_1}{N_1+N_2} \qquad (2.31\text{-}2.33)$$

Where $N_1$ and $N_{1,0}$ are the number of moles in the final monomer feed solution and initial monomer feed solution, respectively. Similarly for $N_2$ and $N_{2,0}$. In most of the cases in the literature, the above expressions (2.31-2.33) are expressed as functions of $[M_{1,0}]$, $[M_{2,0}]$ and $[M_1]$, $[M_2]$, which are the molar concentrations of the initial monomer feed solution and final monomer feed solution, respectively (see Section 6.1). This direct substitution of variables is only valid for constant volume of the polymerizing mixture, which is an acceptable assumption at reasonably low, and possibly moderate, conversion levels.

The measured variables implied by Equation 2.26 are the initial and final mole fraction of monomer one in the feed solution. However, these are not the variables typically measured in the lab; rather the final copolymer composition and the initial feed composition are recorded. The final feed composition, $f_1$, can then be expressed as

$$f_1 = \frac{f_{1,0} - \overline{F}_1 X_n}{1 - X_n} \qquad (2.34)$$

Therefore the Meyer Lowry mole conversion form can be rewritten to eliminate the final feed composition, $f_1$, variable by substituting Equation 2.34 into Equation 2.26 to give

$$1 - X_n = \left(\frac{f_{10} - \overline{F}_1 X_n}{f_{1,0}(1-X_n)}\right)^{\alpha} \left(\frac{1 - X_n - f_{10} - \overline{F}_1 X_n}{(1-f_{1,0})(1-X_n)}\right)^{\beta} \left(\frac{(\delta - f_{1,0})(1-X_n)}{\delta - \delta X_n - f_{10} + \overline{F}_1 X_n}\right)^{\gamma} \qquad (2.35)$$

where the mole fraction of monomer in the copolymer, $\overline{F}_1$ is defined as

$$\overline{F}_1 = \frac{N_{1,0} - N_1}{N_{1,0} + N_{2,0} - N_1 - N_2} \tag{2.36}$$

Furthermore, the conversion recorded by experimenters is typically not the molar conversion but rather the weight fraction conversion. The weight fraction conversion is defined as

$$X_w = 1 - \frac{MW_1 N_1 + MW_2 N_2}{MW_1 N_{1,0} + MW_2 N_{2,0}} \tag{2.37}$$

where $MW_1$ and $MW_2$ are the molecular weights of monomer 1 and 2, respectively.

Using this definition along with the definitions of $f_{1,0}$, $\overline{F}_1$ and $X_n$ a new expression relating the molar conversion with mass conversion can be derived as

$$X_n = X_w \frac{MW_1 f_{1,0} + (1 - f_{1,0}) MW_2}{MW_1 \overline{F}_1 + (1 - \overline{F}_1) MW_2} \tag{2.38}$$

As a result, if the weight fraction conversion is given as a measured variable then the above equation can be substituted into Equation 2.35 to give the mass conversion form of the Meyer-Lowry model.

It is also important to note here that the Meyer-Lowry model assumes that the reactivity ratios *do not* change over the *entire* conversion range. However, reactivity ratios may change at high conversion due to diffusion effects on the propagation rate constants.

The numerically integrated cumulative copolymer composition model, referred to in this thesis as ODECCC, is based on equations relating final copolymer composition with initial feed composition and conversion. That is, the final mole fraction of monomer one in the copolymer, $\overline{F}_1$ can be obtained by rewriting Equation 2.34 as

$$\overline{F}_1 = \frac{f_{1,0}}{X_n} - \frac{(1 - X_n) f_1}{X_n} \tag{2.39}$$

In the ODECCC model the variation in the feed composition as the reaction proceeds is evaluated by numerically integrating the differential equation given by:

$$\frac{df_1}{dX_n} = \frac{f_1 - F_1}{1 - X_n} \tag{2.40}$$

where $F_1$ for the terminal model is given by Equation 2.21.

### 2.1.2 Triad Fractions

Measuring triad fractions, i.e., chain sequence length characteristics, is another common method to characterize polymer chain microstructure. Mole fractions of the diad and the triad fractions are $A_{ij}$, $A_{ijk}$ respectively (i, j, k = 1, 2). Monomer-1-centered triads are denoted by $A_{111}$, $A_{211}$, $A_{112}$ and $A_{212}$. The instantaneous terminal model predictions can be found in Koenig (1980) and can be seen in Equations 2.41-2.44.

$$A_{111} = \frac{r_1^2 f_1^2}{r_1^2 f_1^2 + 2r_1 f_1 f_2 + f_2^2} \tag{2.41}$$

$$A_{212} = \frac{f_2^2}{r_1^2 f_1^2 + 2r_1 f_1 f_2 + f_2^2} \tag{2.42}$$

$$A_{211} = A_{112} = \frac{r_1 f_1 f_2}{r_1^2 f_1^2 + 2r_1 f_1 f_2 + f_2^2} \tag{2.43}$$

thus,

$$A_{211+112} = \frac{2r_1 f_1 f_2}{r_1^2 f_1^2 + 2r_1 f_1 f_2 + f_2^2} \tag{2.44}$$

The penultimate model in triad fractions form is given by:

$$A_{111} = \frac{r_{21} r_{11} f_1^2}{r_{21} r_{11} f_1^2 + 2r_{21} f_1 f_2 + f_2^2} \tag{2.45}$$

$$A_{211+112} = \frac{2r_{21} f_1 f_2}{r_{21} r_{11} f_1^2 + 2r_{21} f_1 f_2 + f_2^2} \tag{2.46}$$

$$A_{212} = \frac{f_2^2}{r_{21} r_{11} f_1^2 + 2r_{21} f_1 f_2 + f_2^2} \tag{2.47}$$

The expressions for monomer-2-centred triads can be obtained by simply interchanging subscripts 1 and 2 in Equations 2.41 to 2.47. The reason for combining the $A_{211}$ and $A_{112}$ triad fractions is that typically the NMR peaks, where the triads are calculated from, overlap and thus the fractions are represented by combining the equations.

The definition of cumulative triad fractions is via Equation 2.48, which relates instantaneous monomer feed mole fraction, molar conversion and cumulative triad fractions.

$$\frac{d\left(X_n \overline{A_{ijk}}\right)}{dX_n} = A_{ijk} \tag{2.48}$$

Example,

$$\frac{d\left(X_n \overline{A_{211+112}}\right)}{dX_n} = A_{211+112} = \frac{2r_1 f_1 f_2}{r_1^2 f_1^2 + 2r_1 f_1 f_2 + f_2^2}$$

Similarly, the triad fractions centered on monomer 2 have similar equations, with their respective instantaneous triad fraction equations.

## 2.2 Extensions to Terpolymerization

Reactivity ratio estimation from low conversion terpolymerization composition data was also studied in this thesis. The composition of the monomer and polymer phases of a ternary system may be represented by the following equations, based on the analysis of Alfrey and Goldfinger (1944):

$$\frac{P_1}{P_3} = \frac{M_1(M_1 r_{23} r_{23} + M_2 r_{31} r_{23} + M_3 r_{32} r_{21})(M_1 r_{12} r_{13} + M_2 r_{13} + M_3 r_{12})}{M_3(M_1 r_{12} r_{23} + M_2 r_{13} r_{21} + M_3 r_{12} r_{21})(M_3 r_{31} r_{32} + M_1 r_{32} + M_2 r_{31})} \tag{2.49}$$

$$\frac{P_2}{P_3} = \frac{M_2(M_1 r_{32} r_{13} + M_2 r_{13} r_{31} + M_3 r_{12} r_{31})(M_2 r_{21} r_{23} + M_1 r_{23} + M_3 r_{21})}{M_3(M_1 r_{12} r_{23} + M_2 r_{13} r_{21} + M_3 r_{12} r_{21})(M_3 r_{31} r_{32} + M_1 r_{32} + M_2 r_{31})} \tag{2.50}$$

$M_i$ are the instantaneous mole fractions of monomer $i$ in the feed solution and $P_i$ are the instantaneous mole fractions of monomer $i$ in the polymer phase. The definition of reactivity ratios is the same as that of the copolymer system, thus the reactivity ratios of the constituent copolymer pairs are also applied to the terpolymer system.

Walling and Briggs (1945) extended the analysis of reactivity ratios beyond ternary systems with the equations for multi-component systems with $n$ monomers. For the case of terpolymers it can be shown that the Walling-Briggs equations are equivalent to the Alfrey Goldfinger equations. That is, the Walling-Briggs equations simplified for the terpolymer case are given by:

$$\begin{aligned} & = [M_1]D_1\left\{[M_1]+\frac{[M_2]}{r_{12}}+\frac{[M_3]}{r_{13}}\right\} \\ d[M_1]:d[M_2]:d[M_3] & :[M_2]D_2\left\{\frac{[M_1]}{r_{21}}+[M_2]+\frac{[M_3]}{r_{23}}\right\} \\ & :[M_3]D_3\left\{\frac{[M_1]}{r_{31}}+\frac{[M_2]}{r_{32}}+[M_3]\right\} \end{aligned} \qquad (2.51)$$

where $[M_i]$ are the instantaneous molar concentrations of monomer $i$ in the feed solution and the determinants, D, are given by:

$$D_1 = \begin{vmatrix} -\dfrac{1}{r_{31}} & \dfrac{1}{r_{21}} \\ -\dfrac{[M_2]}{r_{32}} & -\left(\dfrac{[M_3]}{r_{23}}+\dfrac{[M_1]}{r_{21}}\right) \end{vmatrix}$$

$$D_2 = \begin{vmatrix} -\dfrac{1}{r_{12}} & \dfrac{1}{r_{32}} \\ -\dfrac{[M_3]}{r_{13}} & -\left(\dfrac{[M_1]}{r_{31}}+\dfrac{[M_2]}{r_{32}}\right) \end{vmatrix}$$

$$D_3 = \begin{vmatrix} -\dfrac{1}{r_{23}} & \dfrac{1}{r_{13}} \\ -\dfrac{[M_1]}{r_{21}} & -\left(\dfrac{[M_2]}{r_{12}}+\dfrac{[M_3]}{r_{13}}\right) \end{vmatrix} \qquad (2.52\text{-}2.54)$$

Therefore, when the Walling-Briggs determinants are substituted into Equation 2.51 they are equivalent to the Alfrey Goldfinger equations:

$$\begin{aligned} & = [M_1]\left\{\frac{[M_1]}{r_{31}r_{21}}+\frac{[M_2]}{r_{21}r_{32}}+\frac{[M_3]}{r_{31}r_{23}}\right\}\left\{[M_1]+\frac{[M_2]}{r_{12}}+\frac{[M_3]}{r_{13}}\right\} \\ d[M_1]:d[M_2]:d[M_3] = & :[M_2]\left\{\frac{[M_1]}{r_{12}r_{31}}+\frac{[M_2]}{r_{12}r_{32}}+\frac{[M_3]}{r_{32}r_{13}}\right\}\left\{\frac{[M_1]}{r_{21}}+[M_2]+\frac{[M_3]}{r_{23}}\right\} \\ & :[M_3]\left\{\frac{[M_1]}{r_{13}r_{21}}+\frac{[M_2]}{r_{23}r_{12}}+\frac{[M_3]}{r_{13}r_{23}}\right\}\left\{\frac{[M_1]}{r_{31}}+\frac{[M_2]}{r_{32}}+[M_3]\right\} \end{aligned} \qquad (2.55)$$

As an additional example, for a 4-mer multicomponent system, $D_1$ would be expressed as:

$$D_1 = \begin{vmatrix} -\dfrac{1}{r_{41}} & -\dfrac{1}{r_{21}} & -\dfrac{1}{r_{31}} \\ -\dfrac{[M_2]}{r_{42}} & -\left(\dfrac{[M_1]}{r_{21}}+\dfrac{[M_3]}{r_{23}}+\dfrac{[M_4]}{r_{24}}\right) & \dfrac{[M_2]}{r_{32}} \\ -\dfrac{[M_3]}{r_{43}} & \dfrac{[M_3]}{r_{23}} & -\left(\dfrac{[M_1]}{r_{31}}+\dfrac{[M_2]}{r_{32}}+\dfrac{[M_4]}{r_{34}}\right) \end{vmatrix}$$

with $D_2$, $D_3$ and $D_4$ developed in a symmetrical way.

## Chapter 3

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# Parameter Estimation Techniques

### 3.1 Multiple Response Parameter Estimation Problems

In chemical engineering many experimental studies lead to multiresponse parameter estimation problems. This refers to the situation where it is possible to measure more than one response for a particular experimental condition. Thus the multiresponse model expresses multiple responses as a function of the experimental conditions or input variates and a set of parameters to be estimated. In the analysis of copolymer experiments, the use of all the measured responses can result in more precise parameter estimates.

The objective in nonlinear parameter estimation for a multiresponse problem is to obtain a set of parameter values that are robust and have the least possible uncertainty and correlation. The parameter estimation techniques, specifically involving reactivity ratios, have been studied by many authors over the years including the well cited Kelen and Tudos (1975) and Fineman and Ross (1950). These authors used general linear estimation techniques and applied them to the polymerization system using certain assumptions and manipulation of equations.

For example, the Fineman and Ross method rearranges the Mayo-Lewis model to make it linear in the reactivity ratios (parameters). Once the equation is rearranged, simple standard graphical methods or ordinary linear regression are applied to estimate the reactivity ratios.

However, as pointed out by Rossignoli and Duever (1995), from a statistical point of view, these linear techniques are incorrect and can lead to erroneous point estimates. In addition it is not possible to obtain information regarding the uncertainty in these estimates. Therefore despite the fact that these methods are still in use today (refer to Section 4.1), it is our recommendation that they be abandoned in favour of more modern, and statistically correct methods. At best the linear methods can be used to get initial starting values for use in the appropriate nonlinear estimation technique.

The least squares criterion is the most widely accepted by researchers for parameter estimation in nonlinear models (NLLS). Another well known estimation technique is the Box Draper Determinant Criterion (Box and Draper, 1965), which is the most popular criterion for multiresponse problems. More recently, the error in variables model (EVM) has been applied to reactivity ratio estimation. In contrast to the NLLS and the Determinant Criterion, EVM takes into account errors in all the variables, thus providing for a general estimation framework.

## 3.2 Nonlinear Least Squares (NLLS)

In this section, nonlinear least squares (NLLS) will be described, which is the most common method used to solve single-response nonlinear regression problems. In subsequent sections, extension to multiresponse problems and problems with errors in all the variables will be discussed. The use of NLLS for estimating reactivity ratios from composition data was first discussed by Behnken (1964) and Tidwell and Mortimer (1965).

The model structure of NLLS is

$$y_i = f(\underline{x}_i, \underline{\theta}) + \varepsilon_i \tag{3.1}$$

where $y_i$ is the experimental measurement for the ith trial, $f(\underline{x}_i, \underline{\theta}^*)$ is the predicted value of the measurement, $\underline{x}_i$ as the vector of values of the independent variable describing the reaction conditions, $\underline{\theta}^*$ as the true value of the parameters, and $\varepsilon_i$ is the random error.

The basic goal of the NLLS method is to minimize the sum of square difference between the predicted value of the measurement, $f(\underline{x}_i, \underline{\theta}^*)$, and the measurement $y_i$. That is, to minimize the sum of the squared residuals, given by Equation 3.2.

$$S(\underline{\theta}) = \sum_i (y_i - f(\underline{x}_i, \underline{\theta}))^2 \tag{3.2}$$

The values of $\underline{\theta}$ that minimizes $S(\underline{\theta})$ are known as the least squares parameter estimates, $\hat{\underline{\theta}}$. Note the underlined characters indicate vectors or matrices.

The three assumptions of the NLLS technique are,

i) The model perfectly describes the system.
ii) The errors in the independent variables are negligible (the errors are negligible compared with the error in the dependent variable).
iii) The error associated with the dependant variable is independent (i.e., from run to run) and of constant variance.

If the error distribution is identically normally distributed $N(0,\sigma^2)$, a maximum likelihood estimate can be used and thus enable the construction of confidence regions. However, if there is non constant variance, then the third assumption is violated. In the case of reactivity ratio estimation using the NLLS estimation technique, the independent variable is the monomer feed composition, $f_1$. Therefore, if the error associated with the monomer feed composition measurement is not negligible, then the second assumption would be violated. Consequently, with significant error in all the variables other nonlinear methods like EVM must be used in order to determine statistically precise reactivity ratio estimates from copolymer composition and triad fractions data.

## 3.3 Box Draper Determinant Criterion

A parameter estimation criterion for multiresponse data based on a Bayesian approach, was proposed by Box and Draper (1965). The Box and Draper determinant criterion is based on the assumption that the errors in the measurements are uncorrelated, from trial to trial, while the disturbance terms for different responses in the same trial have a fixed, but unknown variance -

covariance matrix. As highlighted by Stewart (1992), it is this fact that the error covariance matrix is rarely precisely known, that prevents the least squares method from being used in multiresponse problems. Consequently, the determinant criterion by Box and Draper is typically utilized in multiresponse problems, as no assumptions regarding the error covariance matrix are required. The general problem consist of *k* responses measured on each of *n* experimental trials and that the models for the *k* responses depend on a total of *p* parameters, $\underline{\theta}$, given by

$$\underline{y}_i = f(\underline{x}_i, \underline{\theta}) + \underline{\varepsilon}_i \tag{3.3}$$

where, *i = 1,2...,n is the number of trials.*

$\underline{y}_i$, *is a kx1 vector of responses for the ith trial; there are n such vectors.*

$\underline{x}_i$, *is a mx1 vector of independent variables for the ith trial.*

$\underline{\theta}$, *is a px1 vector of unknown parameters.*

$\underline{\varepsilon}_i$, *is a kx1 vector of errors for each of the k responses.*

Using the Bayesian approach the posterior probability density function of the parameters given the measured responses is shown to be

$$p(\underline{\theta}^*|\underline{y}) \propto \left|\sum_{i=1}^{n} \underline{z}_i \underline{z}_i'\right|^{-n/2} \tag{3.4}$$

where,

$$\underline{z}_i = (\underline{y}_i - f(\underline{x}_i, \underline{\theta})) \tag{3.5}$$

Therefore, maximizing the probability density function for the parameters given the measured responses is equivalent to choosing $\underline{\theta}$ to minimize the following determinant,

$$\min\left|\sum_{i=1}^{n} \underline{z}_i \underline{z}_i'\right| \tag{3.6}$$

The minimization is achieved in this research using MATLAB fminsearch strategy which is a simplex search method (i.e. it does not use numerical or analytical gradients).

## 3.4 Error in Variables Model (EVM)

The error-in-variables model (EVM) is a relatively recent approach to solving parameter estimation multiresponse problems. The following is a condensed version of the derivation of the EVM technique. Further discussion and analysis can be found in Reilly and Patino-Leal (1981), Seber and Wild (1989), Reilly et al. (1993) and Rossignoli and Duever (1995). A great benefit of using the EVM model is that the algorithm yields not only estimates of the true parameter values, but also estimates of the true values of the variables.

The EVM model consists of two statements. First, the *vx1* vector of measurements $\underline{x}_i$ is equated to the *vx1* vector of true values $\underline{\xi}_i$, at the $i^{th}$ of *n* conditions, and an additive error $\underline{\varepsilon}_i$

$$\underline{x}_i = \underline{\xi}_i + \underline{\varepsilon}_i \qquad where\ i = 1,2,....,n \tag{3.7}$$

The error vector $\underline{\varepsilon}_i$ may be assumed to be normally distributed with a mean vector of $\underline{0}$, and a *vxv* covariance matrix $\underline{V}$, which is non-singular and may be known or unknown (Keeler and Reilly, 1991). The second statement relates the true values of the parameters and variables...a model,

$$\underline{f}(\underline{\xi}_i, \underline{\theta}^*) = 0 \qquad where\ i = 1,2,....,n \tag{3.8}$$

The above vector of functions is *mx1*, and may be linear or nonlinear in the elements of $\underline{\xi}_i$ and $\underline{\theta}$. Reilly and Patino-Leal (1981) show, using a Bayesian approach, that a point estimate $\hat{\underline{\theta}}$, can be found by minimizing

$$\phi = \frac{1}{2}\sum_{i=1}^{n} r_i \left( \underline{\bar{x}}_i - \hat{\underline{\xi}}_i \right)' \underline{V}^{-1} \left( \underline{\bar{x}}_i - \hat{\underline{\xi}}_i \right) \tag{3.9}$$

where, $r_i$ is the number of replicates at the $i^{th}$ trial.

The algorithm published by Reilly et al. (1993), which uses a Newton's method similar to Fisher's method of scoring to minimize $\phi$, is the EVM approach used in this research. The routine to solve the EVM algorithm is a nested-iterative scheme, as discussed by Reilly et al. (1993). The inner iteration aims to estimate the true values of the variables, $\underline{\xi}$, whilst keeping the parameter values constant. Conversely, the outer iteration aims to estimate the true values of the parameters, $\underline{\theta}$, whilst keeping the variables, $\underline{\xi}$, constant.

The algorithm starts by using the initial parameter estimates (supplied by the user) and the $\underline{\xi}^0$ set equal to the measured variables $\underline{x}_i$. The inner scheme uses the following equation iteratively to update the estimates of the variables,

$$\underline{\xi}_i^{(k+1)} = \bar{\underline{x}}_i - \underline{V}\,\underline{B}_i'(\underline{B}_i\underline{V}\,\underline{B}_i')^{-1}[f(\underline{\xi}^{(k)},\underline{\theta})) + \underline{B}_i(\underline{x}_i - \underline{\xi}^{(k)})] \qquad (3.10)$$

where $\underline{B}_i$ is the *vx1* vector of partial derivatives of the function with respect to the variables,

$$\underline{B}_i = \left[\frac{df(\underline{\xi}_i,\underline{\theta})}{d(\underline{\xi}_i)_t}\right]_{\underline{\xi}_i=\underline{\xi}_i^{(k)}} \qquad \textit{for the } t^{th} \textit{ element} \qquad (3.11)$$

and $\underline{V}$ is the *vxv* error covariance matrix for the measurements. Note that $\underline{V}$ must either be supplied by the user or must be estimated from sufficient replicates.

The outer scheme uses the following equation iteratively to update the estimates of the parameters,

$$\underline{\theta}^{(u+1)} = \underline{\theta}^{(u)} - \underline{G}^{-1}\underline{q} \qquad (3.12)$$

where $\underline{G}$ is the *pxp* expected information matrix given by,

$$\underline{G} = E\left[\frac{d^2\phi}{d\theta_i d\theta_j}\right] \qquad \textit{i, j element}$$

$$= \sum_{i=1}^{n} r_i \underline{Z}_i'(\underline{B}_i\underline{V}\,\underline{B}_i')^{-1}\underline{Z}_i \qquad (3.13)$$

and $\underline{q}$ is the *px1* gradient vector

$$\underline{q} = \left[\frac{d\phi}{d\theta_j}\right] \qquad i^{th} \textit{ element}$$

$$= \sum_{i=1}^{n} r_i \underline{Z}_i'(\underline{B}_i\underline{V}\,\underline{B}_i')^{-1}\underline{B}_i(\bar{\underline{x}}_i - \hat{\underline{\xi}}_i) \qquad (3.14)$$

and $\underline{Z}_i$ is the *1xp* vector of partial derivatives with respect to the parameters,

$$\underline{Z}_i = \left[\frac{df(\underline{\xi}_i,\underline{\theta})}{d\theta_k}\right] \qquad \text{k}^{\text{th}} \text{ element} \qquad (3.15)$$

As the EVM algorithm is based on a Newton type search method, convergence problems can occur if poor initial parameter estimates are provided, or large errors in the data exist. As discussed in Rossignoli and Duever (1995) the solution to this problem is to apply a more robust optimization routine, such as the Marquardt-Levenberg algorithm, such as that outlined by Bard (1974).

The only assumption required for EVM is that of model adequacy, while the construction of the confidence regions requires that the errors are independent and identically normally distributed. Generally, to quantify the uncertainty in the parameter estimates the 95% joint probability contour is determined via either of the following two methods. The first is a relatively rough approximation to the joint posterior probability region for the estimated parameters, and is given by (Keeler, 1989),

$$(\underline{\theta} - \hat{\underline{\theta}})'\underline{G}(\underline{\theta} - \hat{\underline{\theta}}) \le \chi^2_{(p,1-\alpha)} \tag{3.16}$$

where the "^" indicates estimates of the parameters $\underline{\theta}$, $\underline{G}$ is the expected information matrix of the parameter estimates, and $\chi^2_{(p,1-\alpha)}$ is the value of the chi-squared distribution having p degrees of freedom, exceeded with probability $\alpha$. Here the assumption of multivariate normalality is made and the elliptical posterior probability contour, commonly referred to as the elliptical joint confidence region (or the Ellipse JCR as abbreviated in this thesis), is determined. It is important to note that both the shape and probability content of these types of contours are approximate.

The second method is a somewhat better alternative to approximate the joint posterior probability region, and is based on (Keeler, 1989),

$$\phi(\underline{\theta}) = \phi(\hat{\underline{\theta}}) + \frac{1}{2}\chi^2_{(p,1-\alpha)} \tag{3.17}$$

where $\phi$ is given by Equation 3.9 and the values of $\underline{\theta}$ on this contour are found by using Equation 3.10 to find the corresponding values of $\underline{\xi}$. This approximation has the interesting property that it gives contours of the correct shape (not in general elliptical) but of approximate probability content. Hence this contour is commonly referred to as the exact shaped, approximate probability joint confidence region (or the Exact JCR for brevity in this thesis). For further discussion on these approximate joint posterior probability regions refer to Polic et al. (1998). It is also important to note here that the EVM posterior distribution is not exactly multivariate normal and thus, neither of the above approximations are perfect.

In order to perform the algorithm iterations involved in the EVM model, MATLAB script and function files were developed. The MATLAB code for applying the EVM algorithm to the different cases can be found in Appendix A.

## 3.5 Error Structure of the Data

Analysis of the variables of a model and their error structure is an important aspect of parameter estimation. Whether the model is based on the Mayo-Lewis composition equation or the Koenig triad fractions equations, typically the error structure must first be considered before a suitable parameter estimation technique is applied.

Error structure refers to (1) the size of the error associated with each measured variable, (2) the distribution of the error, and (3) the errors relation to the variable.

The variance or the standard deviation quantifies the size of the error; thus allowing one to determine whether the error of a particular variable is negligible relative to the other variables. In the case of the EVM technique, the user is required to specify the measurement covariance matrix, $\underline{V}$. In NLLS, the error size dictates whether the NLLS method is appropriate.

The distribution of the error must be considered, and is often unknown. It is very common for experimenters to give only the error limits (i.e., ±5%). The distribution must thus be of a specific type, including normal, uniform, binomial, etc. The distribution assumed for this research, where error limits are only indicated, is the uniform distribution. Furthermore, if the model variables are calculated from actual measured variables (i.e., mole fraction composition from NMR peaks) the error structure of the actual measured variables is considered. The subsequent variance of the calculated variable can then be found by using the propagation of variance analysis, as discussed in Garcia-Rubio (1981).

Lastly, the errors relation to the variable is defined by being either additive or multiplicative. In this research we have analyzed both cases and discussed both error relationships to the EVM model (refer to Section 3.5.1 and 3.5.2).

### 3.5.1 Additive Error

Consider a measurement $x$, which has an additive error structure and follows a uniform distribution, given by

$$x = x^* + k\varepsilon \tag{3.18}$$

Where, $x^*$ is the true value of the measured quantity; $k$ is a constant multiplier; and $\varepsilon$ is a random variable uniformly distributed in the interval from -1 to +1. Therefore, the error can be said to be plus or minus $k$ units, the same units used to measure the variable $x$. The variance of $x$, $V(x)$, is thus calculated as follows

$$\begin{aligned} V(x) &= V(x^* + k\varepsilon) \\ &= k^2 V(\varepsilon) \end{aligned} \tag{3.19}$$

Where the variance of a uniformly distributed error, $V(\varepsilon)$, is calculated using standard distribution theory as

$$\begin{aligned} V(\varepsilon) &= E(\varepsilon^2) - E(\varepsilon)^2 \\ &= \int_{-1}^{1} \frac{\varepsilon^2}{2} d\varepsilon \\ &= 1/3 \end{aligned} \tag{3.20}$$

and thus the variance of x follows to be

$$V(\varepsilon) = k^2/3$$

### 3.5.2 Multiplicative Error

Again consider a measurement $x$, which now has a multiplicative error structure and follows a uniform distribution, given by

$$x = x^* (1 + k\varepsilon) \tag{3.21}$$

To use a multiplicative error, the transformation of the variable by logarithms can be used, as

$$\ln x = \ln x^* + \ln(1 + k\varepsilon) \tag{3.22}$$

Thus if $k < 0.1$ then,

$$\ln(1 + k\varepsilon) \approx k\varepsilon \tag{3.23}$$

The variance of the transformed variable, $V(\ln(x))$, is then given as

$$V(\ln(x)) = k^2/3 \tag{3.24}$$

## Chapter 4

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# Literature Update of Reactivity Ratio Estimation and Selected Case Studies

### 4.1 Reactivity Ratio Estimation: 1997 to date

Reactivity ratio estimation has been discussed extensively in the literature, due to its numerous applications to copolymerization studies. A detailed literature review was last completed by Polic et al. (1998). In this chapter we will build upon his review. Consequently, this literature update focuses on publications that were published post 1997, which include reactivity ratio estimates.

Numerous publications state the value of the estimates for the reactivity ratios for the specific system, yet do not indicate the statistical method used to obtain the estimate. Furthermore, some cases, where the estimation procedure is given, refer to rather simplistic linear regression methods (e.g., Fineman and Ross (1950)).

Typically, reactivity ratios are estimated using the instantaneous copolymer composition equation, based on low conversion (<5%) copolymer composition data, which is relatively easy to obtain. However, obtaining triad fractions data can involve greater experimental complications, thus the number of publications on the use of this data type in estimating reactivity ratios is minimal. Recently there has been an increase in efforts to use sequence length (triad fractions) data for estimation of the reactivity ratios and this is reflected when comparing the literature review conducted by Polic et al. (1998) to the current update (see Table 4.2).

## 4.2 Reactivity Ratio Estimation Techniques

Table 4.1 is an extensive list of articles that published an estimate of the reactivity ratios for a particular system. Table 4.2 is a summary of articles that have provided triad fractions data and whilst some may not have necessarily directly estimated reactivity ratios from the sequence length data there has been attempts at comparing copolymer composition and triad data analysis results. The abbreviations for the statistical parameter estimation methods and the monomers used in the copolymerization are explained in Tables 4.3 and 4.4, respectively. However, if no statistical method was explicitly stated then the parameter estimation method box is empty to indicate this lack of explanation for the published values.

**Table 4.1: Listing of recent articles (1997 to date) where reactivity ratio estimates are given.**

| Reference | Year | Method | Description |
|---|---|---|---|
| Aguilar et al. | 2002 | NLLS | HEMA/acrylamido-methyl-propane sulfonate (AMPS), DMA/AMPS, low conversion, integrated model. |
| Ahmad et al. | 2004 | | HEMA with NVP; crosslinking. |
| Ajzenberg and Ricard | 2001 | NLO | HEMA with ethylene glycol dimethacrylate. |
| Al-Arbash et al. | 1999 | FR, KT, NLLS | STY with dicyclohexyl fumarate; diisopropyl Fumarate. MMA with dicyclohexyl fumurate. |
| Ameduri and Bauduin | 2003 | TM | VDF with muramyldipeptide. |
| Amosova et al. | 2001 | | N-(vinyloxyethyl)dithiocarbamoylethylcarbonitrile with MAnh, VAc and STY. |
| Anand et al. | 2004 | KT, EVM | MMA with N-(o-/m-/p-chlorophenyl) itaconimide; H-NMR analysis. |
| Anand and Choudhary | 2003 | | MMA and N-(phenyl/p-tolyl)itaconimides. |
| Anand and Choudhary | 2001 | | MMA and N-(O/M/P-chlorophenyl) itaconimides. |
| Annenkov et al. | 2004 | | 1-vinylimidazole with sodium acrylate and sodium methacrylate. |
| Appelt and Schmidt-Naake | 2004 | | STY with N-acryloyl morpholine, 2-ethoxyethyl acrylate and isobornyl acrylate. |
| Arun and Reddy | 2003 | KT, ex-KT | EA with pentadiene-hydroxyphenyl-phenyl methacrylate at 70°C. |
| Arun and Reddy | 2004 | FR, KT, ex-KT | Hydroxybenzoic acid with MA, STY; using nitrogen atm. |
| Arun and Reddy | 2004 | FR, KT, ex-KT | 4-[5-(4-hydroxyphenyl)-3-oxopenta-1,4-dienyl]phenyl-2-methacrylate (HPPMA) with vinylcyclohexane at 70°C. |
| Atta and Arndt | 2001 | FR, KT | Sulfopropyl MA potassium salt with 2-acrylamido-2-methyl propane sulfonic acid. |
| Azab | 2004 | | Pentachlorophenyl MA and AN; nitrogen analysis. |
| Azimipour and Reibel | 2002 | | potassium 4-vinyl biphenyl-sulfonyl imide and a series of oligo(oxyethylene) methacrylates. |
| Badawy and Dessouki | 2002 | | AN with STY; radiation polym.; NMR analysis. |
| Bajpai and Srivastava | 2001 | FR | MMA with STY; using triphenylbismuthoniumylide initiator. |
| Balaji et al. | 2004 | FR, KT, ex-KT, EVM | GMA with acrylic monomers. |
| Balaji et al. | 2001 | FR, KT | 2-(n-phthalimido)-2-methylpropyl acrylate with MMA. |

| | | | |
|---|---|---|---|
| Balaji and Nanjundan | 2002 | FR, KT, ex-KT | 4-methyacryloyloxyphenyl-3 prime , 4 prime -dimethoxystyryl ketone (MPDMSK) with GMA; photosensitive polymers. |
| Baradie and Shoichet | 2002 | EVM | Flurocarbon-VAc copolymers in carbon dioxide. |
| Barner-Kowollik et al. | 2001 | Q-e scheme | STY with itaconic acid; kinetic study. |
| Bartsch and Schmidt-Naake | 2004 | KT | STY and bis(ethylenodithio)tetrathiafulvalene) alpha-cyanocinnamate at 125 and 135°C. |
| Belleney et al. | 2002 | FR, KT, TM | MMA, poly(ethylene glycol) methyl ether methacrylate (PMEM), poly(ethylene glycol) ethyl ether methacrylate (PEEM) / MA; and MMA, PMEM, PEEM, MA / with sodium styrene sulfonate (NaSS) for terpolymer MMA/PMEM(PEEM)/MA (NaSS). |
| Bernhardt et al. | 2001 | NLO | Influence of methylated ß-cyclodextrin as host on the free radical copolymerization reactivity ratios of hydrophobic acrylates as guest monomers in aqueous medium. |
| Bevington et al. | 2001 | | MMA, STY and AN with allyl ethers and related compounds. |
| Bhawal and Devi | 2002 | | EA and MMA; true vs. real reactivity ratios. |
| Bisht et al. | 2003 | FR, in-FR, KT, ex-KT, NLLS | BA with a series of alkyl 4-vinylbenzoates (AVBs). |
| Bisht et al. | 2003 | FR,KT,NLLS | Octyl acetate and STY at 80 and 130°C. |
| Bisht et al. | 2002 | ML, KT, FR | Dodecyl-4-vinyl benzoate with dodecyl acrylate. |
| Bokias and Hourdet | 2001 | | Positively charged amphiphilic water soluble polymers based on poly(N-isopropylacrylamide). |
| Boteiller | 1999 | KT | STY with fluorinated polystyrenes. |
| Bourgeat-Lami et al. | 2002 | | 3-(trimethoxysilyl)propyl methacrylate with STY, MMA and BA. |
| Bouquey et al. | 2001 | | Anionic ring-opening copolymerization of cyclodisilazanes. |
| Brar and Dutta | 1998 | KT, EVM | AN/Hexyl methacrylate; low conversion. |
| Brar and Dutta | 1999 | KT, EVM | AN with pentyl acrylate in solution polymerization. |
| Brar and Hekmatyar | 2001 | KT, EVM | STY and MMA. |
| Brar and Hekmatyar | 1999 | EVM | AN/STY/MMA; microstructure determination. |
| Brar and Hekmatyar | 1999 | EVM | AN with STY in photopolymerization. |
| Brar and Kaur | 2002 | KT, EVM | MA with N-vinylcarbazole. |
| Brar and Kumar | 2002 | KT, EVM | NVP with BA. |
| Brar and Kumar | 2002 | KT, EVM | NVP with MMA. |
| Brar and Kumar | 2002 | KT, EVM | NVP with GMA. |
| Brar and Kumar | 2002 | KT, EVM | NVP with AN. |
| Brar and Kumar | 2002 | KT, EVM | NVP with VAc. |
| Brar and Kumar | 2002 | KT, EVM | NVP with MA. |
| Brar and Pradhan | 2001 | KT, EVM | MAN and MMA; complete 1H and 13C NMR spectra. |
| Brar and Thiyagarajan | 2001 | KT, EVM | Trans-4-methacryloyloxyazobenzene with STY. |
| Brar and Thiyagarajan | 1998 | KT, EVM | Trans-4-acryloyloxyazobenzene with MMA. |
| Brar and Thiyagarajan | 1999 | KT, EVM | Trans-4-methacryloyloxyazobenzene with vinylidene chloride in solution polymerization. |
| Brar and Yadav | 2003 | KT, EVM | GMA with vinylidene chloride. |
| Brar and Yadav | 2002 | KT, EVM | GMA with MAN. |
| Brar and Yadav | 2001 | KT, EVM | GMA with VAc. |
| Brar et al. | 2002 | KT, EVM | GMA with STY. |
| Brar et al. | 2004 | KT, EVM | MAN/BA using benzoyl peroxide as initiator. |
| Braun and Hu | 2004 | KT | Terpolymerization of maleic anhydride (MSA), trans-anethole (ANE) and vinyl-iso-butylether (VIBE) at 60°C |

| | | | |
|---|---|---|---|
| Braun et al. | 2001 | | Terpolymerization of three non-homopolymerizable monomers. |
| Brown et al. | 2001 | | Poly[(vinyloxy)cyclophosphazenes]. |
| Buback and Wittkowski | 2000 | NLO | Ethene with AA and MAA; high pressures and temperatures. |
| Buback et al. | 1999 | NLO | Ethene with AA and MAA; high pressure. |
| Buback et al. | 2001 | ML | MA, DMA, BA with MMA, (dodecyl acrylate)-DMA, (dodecyl acrylate)-MMA. |
| Buback et al. | 2001 | NLLS | Ethene and MMA; high-pressure. |
| Bulai et al. | 1999 | TM | DMA with para-acryloyloxyacetanilide. |
| Cao et al. | 1999 | EVM | Cyclic ketene acetals via cationic 1,2-vinyl addition copolymerization. |
| Carlotti et al. | 2004 | | Butadiene and STY; retarded anionic polymerization. |
| Catalgil-Giz et al. | 2002 | EVM | STY/MMA; online monitoring issues. |
| Catalgil-Giz and Giz | 1994 | Linearized methods | Compensating composition drift with copolymerization to high conversions. |
| Cazalis et al. | 2002 | | Several cycloalkenes initiated by Mo-based Schrock complexes. |
| Chambard et al. | 1999 | NLLS | STY with BA. |
| Chang et al. | 1998 | KT | HEMA with MAA. |
| Cheetham et al. | 1994 | KT | AN with VAc. |
| Cheetham et al. | 1994 | | AN with VAc; microstructural observations. |
| Chen et al. | 2002 | NLLS | HEMA and STY; mathematical model. |
| Cheong and Penlidis | 2004 | | AMS with MMA; high temperatures. |
| Chiang | 2000 | FR | N-(4-carboxyphenyl)-maleimide with AN. |
| Chiu et al. | 2003 | | 2-methoxy-5-2'-ethyl-hexyloxy-1,4-phenylenevinylene with 2,3-diphenyl-5-octyl-1,4-phenylenevinylene. |
| Chojnowski et al. | 2002 | ML, KT | 2-vinyl-2,4,4,6,6-pentamethylcyclotrisiloxane (VD2) with hexamethylcyclotrisiloxane (D3). |
| Choudhary et al. | 2004 | FR | N-iso-Pr acrylamide with GMA using AIBN at 60°C. |
| Chung and Lu | 1998 | KT | Ethylene with p-methylstyrene. |
| Cianga and Yagci | 2002 | KT, ex-KT | N-(4-{[2-(3-thienyl)acetyl]oxyphenyl}oxycarbonylphenyl) maleimide (MIThi)i with STY; room temperature. |
| Coote et al. | 1997 | | STY/MMA; pulsed laser polymerization study. |
| Coote et al. | 1997 | | STY/MMA; kinetic analysis. |
| Coskun and Ilter | 2002 | FR, KT | (2-Phenyl-1,3-dioxolane-4-yl)methyl methacrylate with MMA; EMA; BMA at 60°C. |
| Coskun et al. | 2002 | KT, in-FR, ML | STY with phthalimido-2-hydroxypropyl methacrylate (PHPMA); 60°C, low conversions. |
| Coskun et al. | 2002 | KT, in-FR, YBR | 4-bromobenzyl methacrylate and EMA. |
| Couvreur et al. | 2003 | | STY and AA. |
| Covolan et al. | 2000 | KT | STY with Boc-p-aminostyrene (Boc-AMST). |
| Cuervo-Rodriguez et al. | 2002 | ex-KT | STY with BMA at 125°C. |
| Czerwinski | 1998 | NLLS, KT | MMA with NVP for both low and high conversion. |
| Czerwinski | 1998 | KT | STY with methyl alpha-cyanocinnamate. |
| D'Agosto et al. | 2001 | | N-acryloylmorpholine with N-acryloxysuccinimide. |
| Daniel and Srivastava | 2002 | KT | STY and VAc; p-acetylbenzylidene triphenylarsonium ylide. |
| Daniel and Srivastava | 2001 | KT | p-Acetylbenzylidene triphenylarsonium ylide with STY. |
| Davidenko et al. | 1998 | FR, KT, TM | Furfuryl methacrylate and N,N-dimethyl acrylamide at 40°C. |
| Davis | 2001 | | Review of the mechanism of propagation in free radical copolym. |
| De and Sathyanarayana | 2002 | KT | STY with AMS at high pressures. |
| De and Sathyanarayana | 2002 | | Indene and alkyl acrylates. |
| De and Sathyanarayana | 2002 | | Indene with MMA or MAN. |

| | | | |
|---|---|---|---|
| De and Sathyanarayana | 2002 | | Indene with p-tert-butylstyrene; thermal degradation; Tg studies. |
| De and Sathyanarayana | 2002 | | Indene with STY, AMS and alpha-phenylstyrene. |
| De and Sathyanarayana | 2002 | | Indene with VAc and isopropenyl acetate. |
| De and Sathyanarayana | 2002 | | Terpolymer of MMA, VAc and molecular oxygen. |
| Debling and Teymour | 2002 | | Binary copolymerization in a CSTR; new arithmetic for linear free radical copolymerization. |
| Demirelli et al. | 1999 | FR, KT | 2-(3-Phenyl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate and AN copolymers. |
| Demirelli et al. | 2001 | FR, KT | Benzyl methacrylate with EMA at 60°C. |
| Demirelli et al. | 2000 | FR, KT | 2-(3-Phenyl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate and AN copolymers. |
| Dettmer et al. | 2004 | | exo-5-(benzyloxy)norbornene and exo-5-[(4-tert-butyl)benzyloxy]norbornene via ring-opening metathesis polymerization. |
| Devasia et al. | 2003 | | AN with itaconic acid; effect of triethylamine. |
| Devasia et al. | 2002 | KT, ex-KT | AN with itaconic acid; solvent effects. |
| Devasia et al. | 2002 | KT, ex-KT | AN with maleimidobenzoic acid. |
| Dincer et al. | 2002 | KT, NLO | N-isopropylacrylamide with anhydrides of maleic and citraconic acids. |
| Duc and Petit | 1999 | KT, NLLS | Phenylacetylene with 1-hexyne. |
| Dudmun | 2001 | | STY and MMA, STY and 2-vinylpyridinie. |
| El-Ghaffar et al. | 2002 | | AA with BA, BMA and STY; emulsion. |
| El-Nagger et al. | 2001 | | AN/STY and acrylamide/STY onto polyester; radiation graft. |
| Elvira et al. | 1999 | FR, KT, TM | MMA with methacrylic monomers derived from salicylic acid. |
| Elvira et al. | 2000 | FR, KT, TM | Vinyl pyrrolidone with methacrylic monomers derived from salicylic acid at 50°C. |
| Elvira et al. | 2001 | NLLS | Salicylic acid derivatives to hydrophilic copolymer systems. |
| Endo and Yuichi | 1999 | NLLS | STY with butadiene with methylalumoxane (MAO) catalyst. |
| Erbil et al. | 2000 | FR, KT, TM | Itaconic acid with acrylamide. |
| Erceg et al. | 2001 | KT | N-acryl-N, N'-dicyclohexylurea and N-methacryl-N,N'-dicyclohexylurea with STY. |
| Erol and Soykan | 2002 | FR, KT | 2-methylbenzyl methacrylate (2-MBZMA) and 4-methylbenzyl methacrylate (4-MBZMA) with MMA at 60°C. |
| Erol et al. | 2002 | FR, KT, YBR | 2-(3-Mesityl-3-methylcyclobutyl)-2-hydroxyethyl MA with STY at 60°C. |
| Faragalla et al. | 2002 | NLLS | NVP with HEMA. |
| Feldermann et al. | 2004 | ML | MMA with STY; MA with STY;and MMA with BA. |
| Ferbitz and Mormann | 2003 | | tert-BMA with trimethylsilyl methacrylate and MAA. |
| Ferbitz and Mormann | 2003 | | tert-BMA with 2-propenyl isocyanate; photoresist applications. |
| Ferbitz and Mormann | 2002 | | MAnh with tert-BMA and trimethylsilyl MA. |
| Fernandez-Garcia et al. | 2000 | TM | STY and BA at 50°C (low conversion). |
| Fernandez-Garcia et al. | 2001 | | STY and BA; solvent effects. |
| Fernandez-Monreal et al. | 2000 | TM | HEMA with tert-BA in DMF solvent. |
| Fernandez-Monreal et al. | 2001 | TM | HEMA with tert-BA at 50°C. |
| Fernia et al. | 2000 | TM | HEMA and BMA. |
| Filley et al. | 2002 | | Ethylene with VAc; transition state theory. |
| Fujiwara et al. | 2003 | | Novel amphiphilic telechelic polyoxetanes. |
| Fujiwara et al. | 2001 | Q-e scheme | Trialkylsilyl acrylates and methacrylates. |
| Galimberti et al. | 1999 | | Ethene/propene with metallocenes; correlation between reactivity ratio and zirconocene structure. |
| Galimberti et al. | 2001 | | Ethene/propene; metallocene based catalytic systems. |

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| Gallardo et al. | 2003 | | Metacryloyloxyethyl [2-(acetyloxy)-4-(trifluoromethyl)]benzoate (THEMA) and acrylamido-methyl-propane sulfonate (AMPS). |
| Gatica et al. | 1998 | FR, KT | 2-vinylpyridine and 4-vinylpyridine with NVP. |
| Gatica et al. | 2003 | FR, KT, EVM | vinyltrimethoxysilane (VTMOS)-coMMA, tBA-co-NVP, and and vinyltriethoxysilane (VTEOS)-co-NVP. |
| Gatica et al. | 2004 | | poly(2-vinylpyridine-co-NVP), poly(4-vinylpyridine-co-NVP), poly(vinyltrimethylsilane-co-NVP) and poly(vinylcyclohexane-co-NVP). |
| Gatica et al. | 2002 | FR, KT | Vinylcyclohexane with NVP. |
| Gauthier et al. | 2002 | EVM, NLLS | Sulfobetaine zwitterionomers based on n-BA and 2-exthoxyethyl acryalte; low and high conversions. |
| Ghi et al. | 1999 | NLLS | HEMA with tetrahydrofurfuryl methacrylate at 50°C. |
| Ghim et al. | 2003 | | VPi and VAc at 30°C. |
| Giz | 1998 | ex-KT | |
| Godwin et al. | 2004 | FR, KT, ex-KT, EVM | 4-Propanoylphenyl methacrylate with GMA in MEK solution at 70°C. |
| Goiti et al. | 2001 | | STY with furfuryl methacrylate. |
| Goksel et al. | 1997 | ex-KT | MAnh and N-vinylimidazole (NVIM). |
| Gonzalez et al. | 2003 | FR, KT, TM | MMA with ethyl pyrrolidone [2-ethyl-(2-pyrrolidone) methacrylate (EPM) and ethyl pyrrolidine [2-ethyl-(2-pyrrolidine) methacrylate (EPyM). Full conversion range. |
| Glockner and Ritter | 1999 | | Methylated b-cyclodextrim with isoboruyl acrylate and BA in aqueous medium. |
| Grishin et al. | 2001 | KT | Tricarbonylchromium complexes of STY. |
| Grunden and Sung | 2003 | | STY with vinylene at 75°C; analyzed by near-IR. |
| Guiot et al. | 2002 | TM | 2,3,3-trifluoroprop-2-enol (FA1) with VDF at 50°C. |
| Guiot et al. | 2003 | TM | 2-benzoyloxypentafluoropropene (BPFP) with VDF. |
| Guo et al. | 2002 | FR, KT, YBR | tert-butyl 3-isopropenylcumylperoxide with STY; grafting MMA onto copolymers. |
| Guo et al. | 2001 | FR | STY with MMA; 1,1,2,2-teraphenyl-1,2-bis(trimetylsilyloxy) ethane as initiator. |
| Gupta and Khandekar | 2003 | ML | Graft copolym. of acrylamide and MMA onto cellulose. |
| Gupta and Khandekar | 2002 | ML | Graft copolym. of acrylamide and MMA onto cellulose. |
| Gupta and Sahoo | 2001 | ML | Graft copolym. of AN and EMA onto cellulose. |
| Habibi et al. | 2003 | NLLS | Iso-BMA with LMA at 70°C. |
| Habibi et al. | 2003 | FR, KT, ex-KT, MH, YBR | LMA with iso-BMA at 70°C. |
| Habibi et al. | 2004 | NLLS, NLO | Full conversion data for copolymerization of LMA with iso-BMA using NLLS based on both Marquardt optimization and van Herk methods. |
| Haddleton et al. | 1997 | | MMA and BMA in anionic radical and living radical polym. |
| Hagiopol and Frangu | 2003 | NM | Several systems with different characters of reactivity ratios. |
| Hakim et al. | 2000 | EVM, NLLS | BA/MMA; solution polymerization; elevated temperatures; depropagation. |
| Harrison et al. | 2002 | | Ring-opening cyclic allylic sulfid monomers with MMA and STY. |
| Harrison et al. | 2001 | | 7-methylene-2-methyl-1,5-dithiacyclooctane with STY and MMA. |
| Hasegawa et al. | 2002 | FR | MMA and STY; initiated by grinding quartz. |
| Hatada et al. | 2002 | Q-e scheme | Vinyl monomers. |
| Hill et al. | 1989 | NLLS | Styrene-acrylonitrile; compares penultimate and terminal reactivity |

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| | | | ratio estimates using both composition and triad fractions data. |
| Hong et al. | 2003 | | MMA with BA. |
| Hong et al. | 2002 | | Poly(BA)-graft-branched polyethylene with BA. |
| Hongo et al. | 1999 | FR, KT | Methyl α-acryloxyacrylates with vinyl monomers at 60°C. |
| Hooda and Brar | 2001 | KT, EVM | 4-vinylpyridine with EMA. |
| Hou et al. | 2003 | KT | AN/N-vinylpyrrolidone; copolymerization system. |
| Hsu et al. | 2001 | | MMA with STY; semibatch emulsion; composition control. |
| Huafang and Hunkeler | 1997 | NLO | High conversion; uses an artificial neural network. |
| Huang et al. | 2000 | FR | Norbornene with ethylene. |
| Huang et al. | 2004 | | tert-BMA and norbornene with nickel-based methylaluminoxane catalysts. |
| Hull and Kennedy | 2001 | TM, H | Isobutylene with STY. |
| Hung et al. | 2003 | | Ethylene-propylene with ethylene-1-hexene. |
| Ilter et al. | 2003 | FR, KT, TM | (2-cyclopentylidene-1,3-dioxolane-4-yl)methyl methacrylate (CPDMMA) with STY; and AN at 60°C. |
| Ilter et al. | 2001 | FR, KT | MMA with AN and STY at 60°C. |
| Ishizu | 2003 | | (N,N-diethyldithiocarbamyl)methylstyrene with maleimide under UV irradiation. |
| Ishizu et al. | 2004 | KT | 2-(N,N-diethylaminodithiocarbamoyl)-ethyl methacrylate with ethyl methacrylate under UV irradiation. |
| Ishizu et al. | 2003 | | MMA with STY; hyperbranched. |
| Ishizu et al. | 2001 | Curve fitting | MAnh and N,N-diethylaminodithiocarbamoylmethylstyrene. |
| Isusi et al. | 2002 | EVM | N-vinylcarbazole with BA and Ethyl, Butyl, and cyclohexyl MA. |
| Ito et al. | 2000 | KT | Hydroxystyrene derivatives with t-BMA and t-BA. |
| Ito et al. | 2004 | KT, NLLS | Radical copolymerization of 2-trifluoromethylacrylic monomers. |
| Ito et al. | 2004 | KT, NLLS | Trifluoromethylacetylene (TFMA) with norbornene and with ethyl vinyl ether. |
| Jaimes et al. | 1998 | KT | Butyrolactone with caprolactone and valerolactone. |
| Jansen et al. | 2004 | | Fumarate/vinyl ether, maleate/vinyl ether, fumarate/allyl ether, maleate/allyl ether, fumarate/methacrylate, fumarate/acrylate, methacrylate/vinyl ether, methacrylate/allyl ether, methacrylate/acrylate, methacrylate/N-vinylcaprolactam, acrylate/N-vinylcap. |
| Janus et al. | 2003 | | Characterization of new cyclodextrin derivative with 1-vinyl-2-pyrrolidinone. |
| Jenkins and Jenkins | 2001 | "Patterns" | Any copolymerization of a monomer; provided it has been characterized with STY and AN. |
| Jia et al. | 1998 | YBR | Maleimide with ethyl α-(hydroxymethyl) acrylate. |
| Jiang et al. | 2000 | ex-KT | MMA with N-cyclohexylmaleimide. |
| Jiang et al. | 2000 | ex-KT | STY with N-cyclohexylmaleimide (NCMI) at 110°C to higher conversion. |
| Johnson et al. | 2001 | | 1-alkylvinazenes with STY. |
| Jone Selvamalar et al. | 2004 | FR, KT, ex-KT, EVM | 4-benzyloxycarbonylphenyl acrylate with GMA. |
| Jone Selvamalar et al. | 2003 | FR, KT, ex-KT, EVM | 4-benzyloxycarbonylphenyl methacrylate with GMA. |
| Jone Selvamalar et al. | 2003 | FR, KT, ex-KT, EVM | 4-benzyloxycarbonylphenyl methacrylate with MMA in MEK at 70°C. |
| Kaim | 2000 | NLO | STY with AN. |
| Kaim | 1998 | | STY/AN in bulk. |
| Kaim and Oracz | 1999 | NM, NLO | STY/MMA; solvent effect. |
| Kaim and Oracz | 1998 | NM | STY/AN terminal and penultimate model; solvent effect. |
| Kaim and Oracz | 1998 | NM | STY/MMA; bulk. |
| Kaita et al. | 1997 | KT | STY with MMA, STY with p-methoxySTYY (PMOS), STY with |

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| | | | p-methylSTY, and STY with p-chloroSTY (PCS). |
| Karanikolopoulos et al. | 2004 | FR, in-FR, KT | MMA with other methacrylate monomers; zirconocene catalyzed. |
| Kavousian et al. | 2004 | FR, in-FR, YBR, KT, ex-KT, MH, ML, TM, EVM | STY with 2-ethylhexylacrylate at 80°C. |
| Kim et al. | 2003 | KT | Synthesis of photocrosslinkable polymers using abietic acid and their characterization. |
| Kobayashi et al. | 1998 | FR | Isoprene and STY; butadiene and STY. |
| Koch and Yaacoub | 2003 | FR, KT, TM | BA with 3-o-methacryloyl-1,2:5,6-di-o-isopropylidene-α-D-glucofuranose (3-MDG). |
| Kostov et al. | 2004 | TM, Q-e scheme | Bulk copolymerization of tetrafluoroethylene (TFE) with 4,5,5-trifluoro-4-ene pentyl acetate (FAc). |
| Kothandaraman and Sangeetha | 2001 | KT | STY and MMA; Effect of catalyst |
| Kucharski and Lubczak | 1997 | FR, KT | Hydroxyalkyl methacrylates with acrylamide and methacrylamide; low conversion. |
| Kumar et al. | 2002 | FR | [L]-Lactide and pentofuranose. |
| Kunisada et al. | 2001 | | Isopropenyl-1,3,5-triazines with STY. |
| Kuzmic et al. | 2001 | KT | N(p-phenoxy-phenyl)acrylamide and copolymers with STY. |
| Lad et al. | 2003 | | MMA with dimethylaminoethyl methacrylate and (tert-butylamino)ethyl methacrylate. |
| Larraz et al. | 2003 | FR, KT, TM | Novel acrylic macromonomer with amphiphilic character derived from triton X-100, with MMA. |
| Lebedeva et al. | 2001 | | Vinyl chloride with 1-vinyl-1,2,4-triazole. |
| Lee et al. | 2000 | KT | Cholesteryl (ChMOC) with STY; MMA; N-cyclohexylmaleimide and N-phenylmaleimide. |
| Lee et al. | 2003 | Q-e scheme | (S)-(+)-1-cyclohexylethyl-(2-methacryloyloxyethyl)urea (CEMOU) with STY or MMA. |
| Lee et al. | 2003 | | DMAEMA with BMA by atom transfer radical polymerization. |
| Lee et al. | 2003 | Q-e scheme | (R)-(-)-1-(1-Naphthyl)ethyl(2-methacryloyloxyethyl)urea (NEMOU) with STY or MMA. |
| Lee et al. | 2002 | Q-e scheme | Novel chiral poly(methacrylate)s bearing urethane and cinchoa alkaloid moieties with STY and MMA. |
| Lee et al. | 2002 | Q-e scheme | Chiral methacrylates with STY or BMA. |
| Lee et al. | 2001 | Q-e scheme | Novel chiral polymethacrylate bearing urethane and 1,1'-binaphthlene moieties with MMA. |
| Li and Berner | 1997 | FR, KT, NLLS | 2-ethylhexyl acrylate and 3-[3,3,3-trimethyl-1,1-bis (trimethylsiloxy) disiloxanyl] propyl methacrylate. |
| Li et al. | 2004 | KT | Pinene with isobutylene. |
| Li et al. | 2002 | FR | 3-Morpholinone (M) and caprolactone (CL) at 120°C. |
| Li et al. | 2001 | FR, KT, YBR | Tert-butyl 3-isopropenylcumyl peroxide with butyl acrylate and grafting of STY onto copolymer. |
| Liaw et al. | 1999 | KT | Radical polymerization of new functional monomers derived from methacryloyl isocyanate and urea with MMA at 90°C. |
| Liaw and Liaw | 2000 | FR | 4-chloro-1-phenol (CPHMAI) with STY at 60°C. |
| Liaw et al. | 2000 | FR, KT | Methacrylamide with cationic or zwitterionic monomers. |
| Lin et al. | 1998 | KT | AN with D-lactose-o-(p-vinylbenzyl)-hydroxime. |
| Lin et al. | 2000 | YBR | Synthesis of a new monomer N prime -(β-methacryloyloxyethyl)-2-pyrimidyl-(p-benzyloxycarbonyl)aminobenzenesulfonamide and its copolymerization with N-phenyl maleimidel at 60°C. |
| Ling and Shen | 2002 | | Lanthanum tris(2,6-di-tert-butyl-4-methylphenolate) with caprolactone and trimethylene carbonate. |
| Litvinenko et al. | 2001 | | Self-condensing vinyl copolymerization. |

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| Liu and Wilen | 2001 | | Hyperbranched polymers with maleic functional groups as radical crosslinkers. |
| Liu et al. | 2003 | | Alternating radical copolymerization systems. |
| Liu et al. | 2002 | NLO | 5-fluorouracil derivatives with N-vinylpyrrolinone. |
| Longo et al. | 2002 | | Ethene and propene in presence of Cs sym group 4 metallocenes. |
| Loos et al. | 2003 | | Ambident reactivity of the thiocyanate anion revisited. |
| Lousenberg and Shoichet | 2000 | EVM | Trifluorovinyl ether with ethyl vinyl ether (EVE) and VAc. |
| Lovell et al. | 1999 | | Triethylene glycol dimethacrylate (TEGDMA) with bis-GMA. |
| Madruga | 2002 | | Solvent effects on reactivity ratios; a review. |
| Mahrholz et al. | 2003 | | Poly(sodium carboxylate) with MAnh and itaconic acid. |
| Mao and Huglin | 1992 | MH | New linear method for high conversion copolymerization data. |
| Marcu et al. | 2003 | | Vinyltriethoxysilane with n-Bu acrylate. |
| Martin-Gomes et al. | 2003 | TM | HEMA with DMAEMA; and 2-ethylhexyl methacrylate (EHMA) with DMAEMA at 50°C. |
| Martinez-Pina et al. | 1998 | FR, KT | N-vinylimidazole (VI) with NVP. |
| Martinez et al. | 2002 | TM | HEMA with 2-diethylaminoethyl methacrylate at 50°C. |
| Martinez et al. | 2000 | TM | 2- HEMA and tert-butyl acrylate. |
| Masuda et al. | 1999 | KT | Methacryloylglycine (Mgly) with STY. |
| Masuda et al. | 2002 | | Methyl 2-acetamidoacrylate and STY in stannic chloride. |
| Mathakiya et al. | 2003 | FR, KT | VAc, cyclohexyl acrylate and benzyl acrylate. |
| Mathakiya et al. | 1997 | FR, KT | Solution terpolymerization of acrylamide, AA, and AN in dimethylformamide and water at 85°C. |
| Mathias et al. | 2001 | | 4-Adamantylphenyl methacrylate derivatives with MMA and STY. |
| Matsumoto and Mohri | 1999 | NLLS | Di-isopropyl fumarate (DiPF) with STY, (DiPF) with vinyl benzoate (VB), STY with MMA. |
| Matsumoto et al. | 2002 | | 2,2 prime-azobis[N-(2-propenyl)-2-methylpropionamide] (APMPA) with vinyl benzoate; crosslinking. |
| Matyjaszewski | 2002 | | Copolymerization processes with intermittent activation; factors affecting rate of comonomer consumption. |
| Mav and Zigon | 2001 | KT | 2-Methoxyaniline with 3-aminobenzenesulfonic acid. |
| Mav and Zigon | 2002 | KT | 2-Methoxyaniline with acidic substituted anilines. |
| McManus et al. | 1999 | EVM | BA/MMA; bulk elevated temperature. |
| McManus et al. | 1998 | EVM | AN/VAc; bulk. |
| McManus et al. | 1998 | EVM | STY/HEA; STY/HEA/EA. |
| McManus et al. | 2002 | EVM | AMS/BA; bulk. |
| McManus et al. | 2002 | NLLS, EVM | BA, MMA and AMS. |
| Mi et al. | 2003 | | STY with norbornene. |
| Mignard et al. | 2004 | | STY with butyl acrylate; automatic continuous online monitoring of polymerization reactions (ACOMP). |
| Miyagawa et al. | 2001 | FR, Q-e scheme | 2,2-dimethyl-5-methylene-1,3-dioxolan-4-one with common monomers. |
| Mohammed et al. | 1998 | KT, NLLS | Dimethyl meta-isopropenyl benzyl isocyanate with STY, MMA and BA. |
| Mokhtar et al. | 2000 | FR, KT, NLLS | 1-cyanoethanoyl-4-acryloyl-thiosemicarbzide (CEATS) with VAc, MMA and AN. |
| Mokhtar et al. | 2001 | Q-e scheme | Itaconic acid with BA. |
| Monnet et al. | 2002 | FR, KT, TM, GA | MMA with maleic anhydride-vinyl ether (MVE); low conversion. |
| Mormann and Ferbitz | 2003 | | MAA and trimethylsilyl methacrylate. |
| Mormann and Ferbitz | 2003 | | tert-Bu methacrylate and itaconic anhydride. |
| Motheo et al. | 2004 | | Aniline and o-methoxyaniline; elemental analysis. |
| Naguib et al. | 2003 | NLLS | Bromophenylmaleimide with ethyl or BMA. |
| Naguib et al. | 2003 | KT, NLLS | Terpolymerisation of ethyl methacrylate (EMA), N-phenylmaleimide (NPMI) and itaconic acid (IA). Used KT to get |

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| | | | intial estimates used in NLLS. |
| Naguib et al. | 2003 | | Vinylimidazole and AA. |
| Nair et al. | 1999 | KT | Ethyl-2-(2-cyano-2-ethylthio)-ethyl-propenoate (ECEP) with MMA and STY. |
| Nath et al. | 2002 | FR | 1,3-Butadiene with isoprene at 0°C. |
| Neugebauer and Matyjaszewski | 2003 | | N,N-Dimethylacrylamide with n-BA. |
| Nguyen et al. | 2003 | ML, FR, KT | Hydrogenated cardanyl acrylate, cardanyl acetate and STY. |
| Nishida et al. | 2002 | YIO | Octafluorocyclopentene (OFCPE) with ethyl vinyl ether (EVE). |
| Nishida et al. | 2003 | YIO | OFCPE with cyclohexyl vinyl ether (CHVE). |
| Nomura et al. | 2001 | | Ethylene and alpha-olefin copolymerization. |
| Nurkeeva et al. | 2002 | | Novel cationic copolymers based on vinyl ethers of monoethanolamine and ethyleneglycol. |
| Ochiai et al. | 2001 | Q-e scheme | 4-Monosubstitiuted and 2,4 disubstituted enyne with MMA. |
| Oliva et al. | 1997 | | Ethylene/STY with zirconocene-based catalyst. |
| Oracz and Kaim | 2001 | | Maximum likelihood methodology; general copolymer system. |
| Ortiz et al. | 1998 | FR, KT, TM, NLLS | Methacrylic derivative of alpha-tocopherol with 2-hydroxy HEMA. |
| Pack et al. | 2002 | | Glycolide and caprolactone at high temps. |
| Palacios et al. | 2003 | | AA and N-isopropylacrylamide. |
| Palmer et al. | 2000 | NLLS | AMS with MMA between temps 60-140°C and full conversion range; uses Wittmer and Kruger equations. |
| Palmer et al. | 2001 | NLLS | AMS with MMA. |
| Pandey and Srivastava | 2002 | KT | Citronellol with VAc at 60°C. |
| Pandey and Srivastava | 2003 | KT | Citronellol with AN in xylene at 75°C. |
| Pandey and Srivastava | 2002 | KT | Terpolymer of citronellol, STY and MMA. |
| Pang et al. | 2004 | KT | DMAEMA with MMA, BMA, MA, BA. |
| Pasquale and Long | 2004 | ML | MAnh with norbornene; free radical; conversion data obtained insitu FTIR. |
| Patel et al. | 2003 | FR | 2,4-DMA and N-vinylpyrrolidone at 70°C. |
| Patel et al. | 2003 | FR | VAc and 2,4-DMA; UV spectroscopy. |
| Patel et al. | 2004 | FR | 2,4-DMA and 8-quinolinyl methacrylate. |
| Pekel et al. | 2004 | NLO, KT, FR | N-vinylimidazole with AN at 70°C in nitrogen atmosphere. |
| Pekel et al. | 2001 | FR, KT | N-vinylimidazole and ethyl methacrylate. |
| Perry et al. | 2003 | | Free radical frontal copolymerization; analysis of dependence on reactivity ratios. |
| Pierik and Van Herk | 2003 | | MMA and BA in different solvent concentrations. |
| Pittman and Lee | 2003 | KT | STY with methyl-methylene-butyrolactone (MMBL) at 60°C. |
| Prevost et al. | 1999 | ex-KT | Oxidative of aniline with alkoxysulfonated anilines. |
| Rachkov et al. | 2003 | | p-Phenylazoacrylanilide and MAA. |
| Rainaldi et al. | 2000 | KT | AA/HEMA; template polymerization. |
| Reddy and Balasubramanian | 2002 | | Novel activated acrylates with MMA and GMA. |
| Reddy et al. | 2002 | FR, KT, ML | MMA with AN; microemulsion and conventional emulsion. |
| Reddy et al. | 2003 | FR, KT | N-Ph methacrylamide and MMA at 70°C. |
| Reddy et al. | 2002 | FR, KT | MA with MMA and with AN; FTIR analysis. |
| Restrepo et al. | 2004 | KT | Terpolymerization of MAA, methoxy poly(ethylene glycol) methacrylate, and lauryl methacrylate. |
| Rodriguez et al. | 2004 | NLLS | Hydrophillic polymer drug from derivative of salicylic acid. |
| Roos et al. | 1999 | | BA/MMA and poly(MMA) macromers; comparison of reactivity ratios in conventional and atom transfer radical copolymerization. |
| Rutkaite et al. | 2001 | | Carbazoylalkyl(meth)acrylates with MAA. |
| Ryttel | 1999 | FR, KT, ML | EMA with halophenyl maleimides. |
| Rzaev | 1998 | FR, KT | Tri-n-butylstannyl methacrylate (TBSM) with allyl chloroacetate. |

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| Rzaev et al. | 2002 | ex-KT | Terpolymerization of MAnh, trans-stilbene and acrylic monomers. |
| Sahloul and Penlidis | 2004 | EVM | STY and EA; high temperatures. |
| Saidi et al. | 2002 | FR, KT | Fluorinated acrylates with STY at 80°C. |
| Sakai et al. | 2002 | | Vinylidene with MMA; emulsion polymerization. |
| Sanchez-Chaves et al. | 1999 | ML | HEMA and STY in N,N'-dimethylformamide solution. |
| Sanchez-Chaves et al. | 2002 | TM | GMA with NVP at 50 °C. |
| Sanghvi et al. | 2000 | FR, KT, TM | STY/AN; microemulsion; low conversions. |
| Sanghvi et al. | 2002 | | STY with HEMA; microemulsion rectivity ratios. |
| Sannigrahi et al. | 1997 | KT | MMA with LMA. |
| Santhosh et al. | 2004 | FR, KT | Diphenylamine with m-toluidine. |
| Santhosh et al. | 2003 | FR, KT | Diphenylamine with ortho-methoxy aniline. |
| Sarmah and Baruah | 2003 | ex-KT | Behenyl (docosyl) acrylate with behenyl fumarate at 70°C. |
| Sarzotti et al. | 2002 | ML | Ethylene/1-hexene. |
| Sato et al. | 1998 | NLLS | Ortho-(1,2-dioxolan-2-yl) phenyl ethyl fumarate (DOPEF) with STY. |
| Sato et al. | 1998 | NLLS | Copolymerization of p-tert-butoxystyrene (TBOSt) and di-n-butyl maleate (DBM) with dimethyl 2,2'-azobisisobutyrate (MAIB). |
| Sato et al. | 2001 | YIO | N-methyl-α-fluoroacrylamide with STY at 50°C. |
| Sayyah et al. | 2002 | | Benzylidenemalononitrile with MMA; nitrogen atmosphere. |
| Schaverien et al. | 2001 | | Alpha-Olefins; disastereomeric metallocenes catalysts. |
| Schue et al. | 2000 | KT | Butyrolactone with caprolactone and valerolactone. |
| Scorah et al. | 2001 | EVM | MMA/VAc; bulk/solution; low conversions. |
| Se and Aoyama | 2004 | | MMA and methacryl-terminated poly(n-hexyl isocyanate). |
| Selvam et al. | 2004 | FR, KT, ex-KT, EVM | 4-(3',4'-Dimethoxycinnamoyl)phenyl acrylate and MMA at 70°C. |
| Selvamalar et al. | 2003 | FR, KT, ex-KT, EVM | 4-Benzyloxycarbonylphenyl methacrylate with GMA. |
| Senel et al. | 2003 | KT, NLLS | N-Phenylmaleimide with 2-hydroxyHEMA at 65°C. |
| Seno et al. | 2003 | Q-e scheme | Novel quinone methide ketals with STY at 60°C. |
| Senthilkumar et al. | 2001 | FR, KT | (Phthalimido) EMA/GMA. |
| Senthilkumar et al. | 2003 | FR, KT | Phenylethyl acrylate (PEA) with phenylethyl methacrylate. |
| Senthilkumar et al. | 2001 | FR, KT | 2-(N-Phthalimido)ethyl methacrylate and STY. |
| Seridou-Karayannidou and Seretoudi | 1999 | ex-KT | N-Vinylcarbazole with N,N-dimethylaminoethyl acrylate at 60°C. |
| Shah et al. | 2004 | FR | 2,4-Dichlorophenyl methacrylate and BMA in toluene as solvent; AIBN initiator at 70°C. |
| Shaikh et al. | 2002 | ML, KT, NLLS | Isobutylene with isoprene. |
| Shan et al. | 2000 | | STY with poly(1-vinyl-2-methylimidazole). |
| Sharma and Srivastava | 2004 | KT | Limonene with STY at 80°C; FTIR analysis. |
| Sharma and Srivastava | 2004 | KT | Terpolymerization of limonene, STY and MMA at 80°C. |
| Sharma and Srivastava | 2003 | KT, Q-e scheme | Limonene with AN in DMF at 70°C; FTIR analysis. |
| Sharma and Srivastava | 2003 | KT | Limonene with MMA at 80°C; FTIR analysis. |
| Shi et al. | 2000 | KT | Maleimide with ethyl α-propylacrylate. Full conversion range. |
| Shiho et al. | 2000 | KT | 1,1-Dihydroperfluorooctyl methacrylate (FOMA) with methacryloxypropyl-terminated polydimethylsiloxane (M-PDMS) to high conversion. |
| Shiho and Desimone | 2000 | KT | 3-[Tris(trimethylsilyloxy)silyl] propyl methacrylate (SiMA) with MMA; FOMA; and STY at high conversions. |
| Shinoda et al. | 2001 | | Methacryloyl-terminated poly(dimethylsiloxane) macromonomer with MMA. |
| Shu et al. | 2003 | FR, KT | Poly(STY-co-phosphate-containing maleimide) in toluene at 70°C. |

| | | | |
|---|---|---|---|
| Shukla and Srivastava | 2004 | KT | Linalool and VAc; benzoyl peroxide at 60°C. |
| Shukla and Srivastava | 2003 | KT | Linalool and AN. |
| Shukla and Srivastava | 2003 | KT | Linalool and acrylamide at 75°C. |
| Shukla and Srivastava | 2002 | KT | Terpolymer linalool-STY-MMA. |
| Smith and Klier | 1998 | FM | MAA with poly(ethylene glycel) mono methacrylate. |
| Song et al. | 2003 | | Synthesis and thermal properties of a new cholic acid-containing copolymer. |
| Souzy et al. | 2004 | TM | Alpha-trifluoromethylacrylic acid with VDF and VDF/hexafluoropropene. |
| Souzy et al. | 2003 | TM | VDF with methyl trifluoroacrylate. |
| Soykan et al. | 2000 | FR, KT | Phenacyl methacrylate (PAMA) with AN at 70°C. |
| Soykan and Erol | 2004 | FR, KT, NLLS | MMA with 2-(4-tert-butylphenoxy)-2-oxo-ethyl MA. |
| Soykan and Erol | 2003 | FR, KT | MMA or AN with [(4-isopropylphenyl) oxycarbonyl] methyl methacrylate (IP-POMMA) in $CHCl_3$ solution at 60°C. |
| Soykan and Erol | 2003 | FR, KT | 2-[(5-Methylisoxazol-3-yl)amino]-2-oxo-ethyl methacrylate with STY and MMA. |
| Srivastava and Pandey | 2001 | FR | STY with citronellol at 80°C. |
| Srivastava et al. | 2002 | KT | Terpolymerization of AN-STY-linalool. Gives reactivity ratios of AN and (linalool + STY). |
| Stancu et al. | 2004 | | Methacryloyloxyethyl phosphate wth Et methacrylate and 1-vinyl-2-pyrrolidinone. |
| Stanek et al. | 2003 | FR, in-FR, KT, ex-KT, TM | MMA with 2-vinyl-4,4'-dimethylazlactone (VDMA) at both low and high conversions. |
| Stergiou et al | 2002 | FR, KT | STY/alkyl methacrylates; thermal properties. |
| Subramanian and Reddy | 2002 | KT | 4-(4'-nitrocinnamoyl)phenyl acrylate and GMA. |
| Sun et al. | 2003 | ML | MA with 2-methylene-1,3-dioxepane at varying temperatures. |
| Sünbül et al. | 2004 | EVM | A new error-in-variables method; data obtained from automatic, continuous, on-line monitoring of polymerization systems. |
| Szczubialka et al. | 2001 | FR, KT, ex-KT | N-Isopropylacrylamide with sodium 2-acrylamido-2-methyl-1-propanesulphonate. |
| Taden et al. | 2002 | | 5-(Methacrylamido)tetrazole and acrylamide. |
| Tanaka et al. | 1997 | FR, KT | Methyl α-trifluoroacetoxyacrylate (MTFAA) and STY. |
| Thamizharasi and Reddy | 2001 | | N-substituted maleimide with alkyl acrylate. |
| Thamizharasi et al. | 1999 | FR, KT, ex-KT | 4-Nitrophenyl acrylate with MMA. |
| Thamizharasi et al. | 1999 | FR, KT, ex-KT | MA with 4-chlorophenyl acrylate; applications in leather industry. |
| Thamizharasi et al. | 1997 | FR, KT, ex-KT | MMA and BMA with acetylphenyl acrylate. |
| Thamizharasi et al. | 1997 | FR, KT, ex-KT | GMA with nitrophenyl acrylate. |
| Thamizharasi et al. | 2003 | FR, KT, ex-KT | BMA with 4-nitrophenyl acrylate. |
| Tritto et al. | 2002 | FM | Ethylene and norbornene; metallocene based catalysts. |
| Tronc et al. | 2003 | | STY and BMA with hydroxy fluorescent dyed cetyl methacrylate. |
| Valdebenito et al. | 2001 | FR, KT, NLO | MMA-(4-hexyloxy-1-phenyloxycarbonyl)-1,4-phenylene ethylene copolymers. |
| Van Den Brink et al | 1999 | NLLS | General copolymerization system. |
| Van Den Brink et al | 1999 | NLLS | MMA/alpha-methylene gamma-butyrolactone (MBL); online raman spectroscopy. |
| Van Herk and Droge | 1997 | NLLS | General copolymerization system. |
| Vazquez et al. | 1997 | FR, KT, TM | Monomethacrylate/MMA at 70°C. |
| Venkatesh et al. | 2004 | | MA with 1-octene using atom transfer radical copolymerization. |

| | | | |
|---|---|---|---|
| Veron et al. | 2004 | | N,N-dimethylaminoethyl methacrylate and 2-methylacrylic acid 2-(3-imidazol-l-yl-propionyloxy)ethyl ester at 60°C. |
| Vijayanand et al. | 2002 | FR, KT, ex-KT | 3,5-DMPA with GMA. |
| Vijayanand et al. | 2002 | FR, KT, ex-KT | 3,5-DMPMA with GMA. |
| Vijayanand et al. | 2002 | FR, KT, ex-KT, EVM | 3,5-DMPA with MMA at 70°. |
| Vijayanand et al. | 2003 | FR, KT, ex-KT, EVM | 3,5-DMPA with MMA at 70°C. |
| Vijayanand et al. | 2003 | FR, KT, ex-KT, EVM | 4-(Benzyloxycarbonyl)phenyl acrylate with MMA. |
| Vijayaraghavan et al. | 1999 | | 4-Clorophenyl acrylates and GMA copolymers. |
| Vijayaraghavan et al. | 1996 | FR, KT, ex-KT | 4-Methyl and 4-methoxyphenyl acrylates with GMA at 70°C. |
| Vijayaraghavan et al. | 2003 | FR, KT | STY-MMA, STY-EMA, and STY-BMA. |
| Virtanen and Tenhu | 2001 | FR, ex-KT | N-Isopropylacrylamide with GMA at 70°C. |
| Vosloo et al. | 2004 | | BMA with N-acryloxysuccinimide. |
| Wamsley et al. | 2004 | FR, KT, NLLS | Leucine with beta-benzyl aspartate, beta benzyl aspartate with valine, and valine with leucine. |
| Wan et al. | 1998 | YBR | N-Phenylmaleimide with ethyl α-phenylacrylate. |
| Wan and Huang | 1999 | FR | Ethyl phenylacrylate (EPA) with N-phenylmaleimide (NPMI). |
| Wang et al. | 1999 | NLLS | Octene-1 and ethylene with metallocene catalyst using Behnken approach. |
| Wang et al. | 2001 | FR | Various cyclic phosphates and cyclic carbonates. |
| Wang et al. | 2004 | EVM | AMS with BA; parameter considerations. |
| Wen and Zhuo | 1998 | KT | Lactide with ethylene mathyl phosphate. |
| Wickel and Agarwal | 2003 | KT | BMDO with STY. |
| Wickel et al. | 2003 | KT | BMDO with MMA. |
| Williamson et al. | 2004 | ML | STY with 1,3-cyclohexadiene; insitu FTIR spectroscopy. |
| Wiles et al. | 2004 | ML, TM, | AN and MA. |
| Wu et al. | 1998 | EVM, TM | Used EVM in combination with TM to provide optimal experimental [M1]/[M2] ratios for cationic copolymerization of cyclic ketene acetals. |
| Wu and Sheares | 2001 | ML | 2-(N-Benzyl-N-methylamino)methyl-1,3-butadiene with STY at 75°C. |
| Xie et al. | 2001 | | Epichlorohydrin with other alkylene oxide. |
| Xu and Cheng | 2001 | | 4-Methyl-1-pentene and ethylene with group 4 ansa-cyclopentadienylamido complexes. |
| Xu et al. | 2001 | FM | Propylene with various higher α-olefins. |
| Xu et al. | 2001 | | Polymerizable anionic surfactants and STY; emulsion copolym. |
| Xue et al | 2000 | ex-KT | N-Isopropylacrylamide with AA, MAA and acrylamido-methyl-propane sulfonate (AMPS). |
| Yadav and Srivastava | 2002 | KT | MMA with α-terpineol. |
| Yadav and Srivastava | 2003 | KT | STY with α-terpineol at 80°C. |
| Yaegashi et al. | 2004 | Curve fitting | N,N-diethyl-2-methylene-3-butenamide (DEA) with STY and with chloroprene. |
| Yaegashi et al. | 2003 | Q-e scheme | N-(2-methylene-3-butenoyl)piperidine with STY. |
| Yan et al. | 2001 | FR | BA with (methacrylamido)propyl]trimethylammonium chloride. |
| Yang et al. | 2004 | FR | MMA with N-p-tolymaleimide. |
| Yang et al. | 2002 | FR, KT | DL-lactide with 3-benzyloxymethyl-1,4-dioxane-2,5-dione. |
| Yamada et al. | 2000 | KT | VAc, VPi and vinyl 2,2-bis(trifluoromethyl)propionate (VF6Pi)i in fluoroalcohols as solvents. |
| Yamada et al. | 2001 | S | Amphiphilic block and statistical copolymers with pendant glucose residues |

| | | | |
|---|---|---|---|
| Yamada et al. | 2003 | | Me a-(chloromethyl)acrylate with STY. |
| Yamamoto et al. | 2000 | NLLS | N-vinylformamide and N-vinylisobutyramide (NVIBA); used curve fitting method based on nonlinear least squares procedure. |
| Yamamoto et al. | 2003 | | N-vinylacetamide (NVA) and N-vinylformamide copolymerization with VAc. |
| Yan-Ming et al. | 2001 | | STY and poly(tetrahydrofuran) macromer. |
| Ydens et al. | 2003 | | HEMA with MMA; high MMA conversion. |
| Yoon et al. | 2003 | | Bis(3-hydroxypropyl)terephthalate (BHPT) and bis(2-hydroxyethyl) terephthalate (BHET). |
| Zaldivar et al. | 1998 | KT, TM, FR, ML | AA with VAc. |
| Zerroukhi et al. | 1999 | KT, TM, ML | Substituted styrenes - MAnh copolymers; high conversions. |
| Zetterlund et al. | 2002 | NLO | STY and cyclohexyl methacrylate in benzene at 60°C. |
| Zhang et al. | 2001 | S | STY with 2-[(perfluorononenyl)oxy] ethyl methacrylate at 100°C. |
| Zhang et al. | 2003 | | STY and MMA in room temperature ionic liquid. |
| Zhang et al. | 2002 | | Butadiene with STY; using dialkylmagnesium- halohydrocarbon catalytic system. |
| Zhang et al. | 2001 | | Isoprene and STY; neodymium catalyst and alkylmagnesium cocatalyst. |
| Zhang and Easteal | 2003 | FR, KT | N-isopropylacrylamide with 2-acrylamido-2-methyl-1-propanesulfonic acid at 70°C. |
| Zhao et al. | 2001 | KT | N-Phenylmaleimide with STY. |
| Zhao et al. | 2002 | FR, KT | N-Hexylmaleimide with STY at 110°C. |
| Zhao et al. | 2002 | | N-butyl maleimide and STY; charge transfer complex. |
| Zhao et al. | 2002 | | N-phenylmaleimide and STY. |
| Zhou et al. | 1999 | FR, KT, TM | Acrylamidolatamine (LAM) with N-isopropylacrylamide. |
| Zhu et al. | 2001 | | Ethylene and butylenes. |
| Ziaee and Nekoomanesh | 1998 | ML, KT, ex-KT, FR, in-FR, TM, MH | STY with BA at 80°C. |
| Ziegler and Matyjaszewski | 2001 | NLLS | MMA and n-BA. |

**Table 4.2: Listing of articles (1980 to date) which give triad fractions/sequence length data and reactivity ratio estimates.**

| Reference | Year | Method | Description |
|---|---|---|---|
| Brar and Dutta | 1998 | KT, EVM | AN-Pentyl MA. Uses composition data to determine reactivity ratio values, which are used in a model to compare predicted vs. experimental triad fractions data. |
| Brar and Dutta | 1998 | KT, EVM | AN-AA. Uses composition data to determine reactivity ratio values, which are used in a model to compare predicted vs. experimental triad fractions data. |
| Brar et al. | 1994 | | AN-alkyl MA. |
| Brar and Kaur | 2003 | KT, EVM | N-vinylcarbazole and MMA. |
| Brar and Kaur | 2003 | KT, EVM | N-vinylcarbazole and BMA. |
| Brar and Pradhan | 2003 | | Terpolymer AN-STY-GMA. |
| Brar and Pradhan | 2003 | | Terpolymer MAN-STY-MMA. |
| Brar et al. | 2003 | KT, EVM | NVP and MAN. |
| Brown and Fujimori | 1994 | | STY with citraconic anhydride. |
| Burke et al. | 1994 | Box-Draper | STY-AN; discusses penultimate and terminal model discrimination. |
| de la Fuente et al. | 2001 | | MMA and BA; sequence distribution. |
| Erol et al. | 2004 | FR, KT | STY with 2-oxo-2-(4-methyl)phenylamino]ethylene methacrylate at 65°C; used infrared, $C^{13}$ and H-NMR techniques. |
| Escher and Galland | 2004 | | Terpolymerization of ethylene-propylene-1-hexene. |
| Ferando and Aldo | 1997 | | STY and AN; no parameter estimation. |
| Fernandez-Monreal et al. | 1999 | TM | 2-HEMA/STY in DMF solvent. |
| Galimberti et al. | 1998 | | Ethene/propene. |
| Ha, N | 1998 | NLLS | STY-co-citraconic anhydride-polymers; terminal and penultimate discussion. |
| Ha et al. | 1999 | NLLS | STY and citraconic anhydride; terminal and penultimate discussion. |
| Hill et al. | 1989 | NLLS | STY-AN; compares penultimate and terminal reactivity ratio estimates using both composition and triad fractions data. |
| Hill et al. | 1992 | NLLS | STY-AN; compares penultimate and terminal reactivity ratio estimates using triad fractions data. |
| Hooda and Brar | 2003 | KT, EVM | 4-vinyl pyridine with MAN. |
| Kim and Harwood | 2002 | | MMA with MA. |
| Kim et al. | 2003 | | Dimethyl(1-ethoxycarbonyl)vinyl phosphate with STY; $C^{13}$, $P^{31}$ and H-NMR analysis. |
| Klumperman and Kraeger | 1994 | NLLS | STY and AN; discusses only penultimate model. |
| Kramer et al. | 1999 | | STY and EA; high conversion data. |
| Maxwell | 1993 | NLLS | STY-MMA; compares predicted vs. experimental triad fractions. |
| Mukherjee et al. | 1999 | KT, EVM | Acrylamide-AN. Uses composition data to determine reactivity ratio values, which are used in a model to compare predicted vs. experimental triad fractions data. |
| Nguyen, T | 1997 | NLLS | STY-co-maleic anhydride polymers; terminal and penultimate discussion. |
| O'Driscoll et al. | 1980 | | Infrared for obtaining sequence distribution contains a bias that causes the apparent reactivity ratios to show a trend with composition. |
| O'Leary | 2004 | | Copolymers of poly(n-alkyl acrylates) at low conversion. |
| Pazhanisamy et al. | 1997 | FR, KT | AMS with N-cyclohexylacrylamide in toluene at 60°C; characterized by H-NMR and C-NMR spectroscopy. |
| Rudin et al. | 1981 | | Vinyl compounds. |

| | | | |
|---|---|---|---|
| Selvamalar et al. | 2004 | FR, KT, ex-KT, EVM | BCPA with GMA at 70°C; FTIR, 1H-NMR, 13C-NMR spectrometry. |
| Soykan and Erol | 2004 | FR, KT | N-(4-acetylphenyl)-maleimide and STY; FTIR, 1H and 13C NMR analysis. |
| Sundarrajan et al. | 2003 | | Ethylene dibromide or methylene dibromide with styrne dibromide and sodium sulfide; H-NMR and 13C-NMR analysis. |
| Wharry | 2004 | | Ethylene with 1-hexene. |
| Zhao et al. | 2001 | | N-butyl maleimide with STY. |

**Table 4.3: Abbreviations of monomers/chemicals.**

| Abbreviations | Description |
|---|---|
| AA | Acrylic acid |
| AIBN | 2,2'-Azo-diisobutyronitrile |
| AMS | Alpha-methyl styrene |
| AN | Acrylonitrile |
| BA | Butyl acrylate |
| BCPA | Benzyloxycarbonylphenyl acrylate |
| BCPM | 4-benzyloxycarbonylphenyl |
| BMA | Butyl methacrylate |
| BMDO | 5,6-Benzo-2-methylene-1,3-dioxepane |
| CPA | Chlorophenyl acrylate |
| DCPA | Di-cinnamoyl phenyl acrylate |
| DMA | N,N-dimethylacrylamide |
| DMF | N,N'-dimethylformamide |
| DMAEMA | poly(N,N-dimethylamino)ethyl methacrylate |
| DMPM | Di-methoxyannamoyl phenyl methacrylamide |
| DMPMA | 3,5-Dimethylphenyl methacrylate |
| DMPA | 3,5-Dimethylphenyl acrylate |
| EA | Ethyl acrylate |
| EMA | Ethyl methacrylate |
| GMA | Glycidyl methacrylate |
| HEA | Hydroxyethyl acrylate |
| HEMA | 2-hydroxyethyl methacrylate |
| HPMA | Hydroxypropyl methacrylate |
| LMA | Lauryl methylacrylate |
| MA | Methyl acrylate |
| MAA | Methacrylic acid |
| MAN | Methacrylonitrile |
| MAnh | Maleic anhydride |
| MBL | α-methylene-γ-butyrolactone |
| MEK | Methyl ethyl ketone |
| MMA | Methyl methacrylate |
| MSMPK | Methacryloyl styryl methoxy phenyl ketone |
| NAS | N -acryloyloxysuccinimide |
| NVP | N-vinyl-2-pyrrolidone |
| PCPA | Propanoyl cinnamoyl phenyl acrylate |
| STY | Styrene |
| VAc | Vinyl acetate |
| VPi | Vinyl piralate |
| VDF | Vinylidene fluoride |

**Table 4.4: Abbreviations of estimation techniques.**

| Abbreviations | Description |
|---|---|
| Box Draper | Box Draper Determinant Criterion |
| EVM | Error in Variables Model |
| ex-KT | Extended Kelen Tudos |
| FM | First Order Markovian Statistics |
| FR | Fineman-Ross |
| H | Harwood Excel Program |
| in-FR | Inverted Fineman Ross |
| KT | Kelen Tudos |
| MH | Mao-Huglin |
| ML | Mayo-Lewis |
| NLLS | Nonlinear Least Squares |
| NLO | Nonlinear Optimization |
| NM | Nelder and Mead Simplex method |
| S | Skeist |
| TM | Tidwell-Mortimer |
| YBR | Yezuilev-Brokhina-Roskin |
| YIO | Yamada-Itahashi-Otsu Nonlinear Least Squares Method |

## 4.3 Literature Case Studies Reviewed

In this analysis we used the program RREVM developed by Dube et al. (1991) and updated by Polic et al. (1998), which is based on the EVM estimation technique using copolymer composition data at low conversion. Furthermore, in the following case studies the exact shaped 95% approximate probability joint confidence region and the approximate shape and 95% probability joint confidence region of the reactivity ratio estimates are referred to as the exact JCR and the ellipse JCR, respectively.

### 4.3.1 DMPA-MMA Case Study

The first case to be analyzed was that of a well behaved system. That is, the reactivity ratio point estimates from a number of parameter estimation techniques agree with one another for a particular copolymer system, in this case 3,5-dimethylphenyl acrylate (DMPA) and methyl methacrylate (MMA).

Data was published by Vijayanand et al. (2003) for the DMPA-MMA copolymerization, see Table 4.5. The aim of the analysis was to demonstrate that for a well behaved system point estimates from other parameter estimation techniques are contained within the RREVM exact shaped 95% approximate probability joint confidence region and the calculated copolymer compositions, using the point estimates, at varying feed compositions, are in good agreement with experimental results.

**Table 4.5: Data used in analysis of DMPA-MMA bulk system (Vijayanand et al. 2003).**

| Initial Feed Composition (Mol frac DMPA) $f_1$ | Copolymer Composition (Mol frac DMPA) $F_1$ |
|---|---|
| 0.1506 | 0.0702 |
| 0.3445 | 0.1928 |
| 0.5009 | 0.2958 |
| 0.6311 | 0.4201 |
| 0.8092 | 0.6197 |
| 0.9023 | 0.7908 |

In order to conduct the analysis in RREVM, the feed data was assumed to have a measurement error of 3% while the copolymer data was assumed to have a 10% measurement error. The estimates of the reactivity ratios from RREVM and those given by Vijayanand et al. (2003) can be seen in Table 4.6. In the RREVM analysis the initial estimates used for the reactivity ratios were those provided by the original data source group (Vijayanand et al., 2003) using the Kelen-Tudos parameter estimation method.

**Table 4.6: Reactivity ratio estimation results for the data of Vijayanand et al. (2003).**

| | Estimation Method | $r_1$ | $r_2$ |
|---|---|---|---|
| Vijayanand et al. (2003) | Fineman Ross (FR) | 0.3942 | 2.325 |
| Vijayanand et al. (2003) | Kelen Tudos (KT) | 0.3848 | 2.2584 |
| Current work | EVM | 0.3889 | 2.2657 |

The exact JCR for the reactivity ratio estimates of the DMPA-MMA system was also completed using RREVM (refer to Figure 4.1).

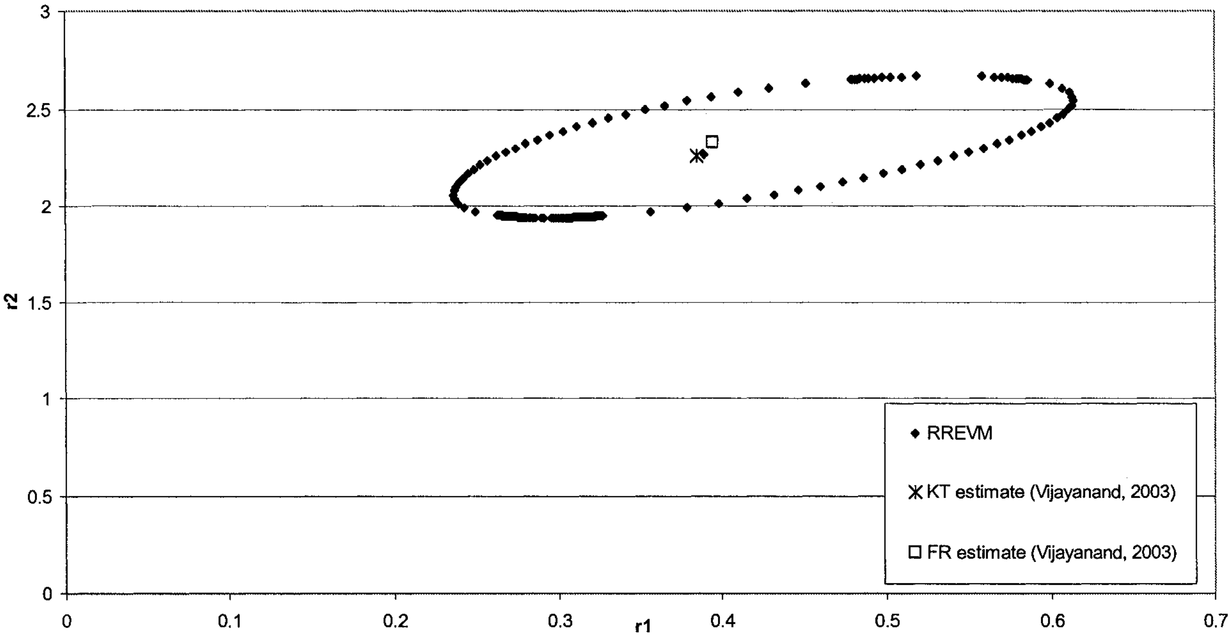


**Figure 4.1: Exact JCR for DMPA-MMA copolymerization system using RREVM.**

As can be seen in Figure 4.1, the point estimates are similar in location and are contained within the EVM exact JCR. Consequently, when the estimates were used to produce plots of the instantaneous copolymer composition, using the Mayo-Lewis equation (Equation. 2.21), it was anticipated that the curves would be similar (refer to Figure 4.2). The experimental values were also plotted on the figure as copolymer composition versus feed composition. As can be seen in Figure 4.2, there is good agreement between the curves.

The points shown as black circles on Figure 4.2 were from point estimates obtained by sampling from within the exact JCR of Figure 4.1. They were used to create a mock confidence band to show that the confidence region can be translated into an anticipated copolymer band. That is, using the confidence band (created by the sampling of the joint confidence region) and a given feed composition one can anticipate at a 95% confidence level that the copolymer composition will fall within the band at that feed condition. This would be particularly helpful for a quick reference guide for the anticipated copolymer composition in an industrial system that concentrates on a select copolymer system.

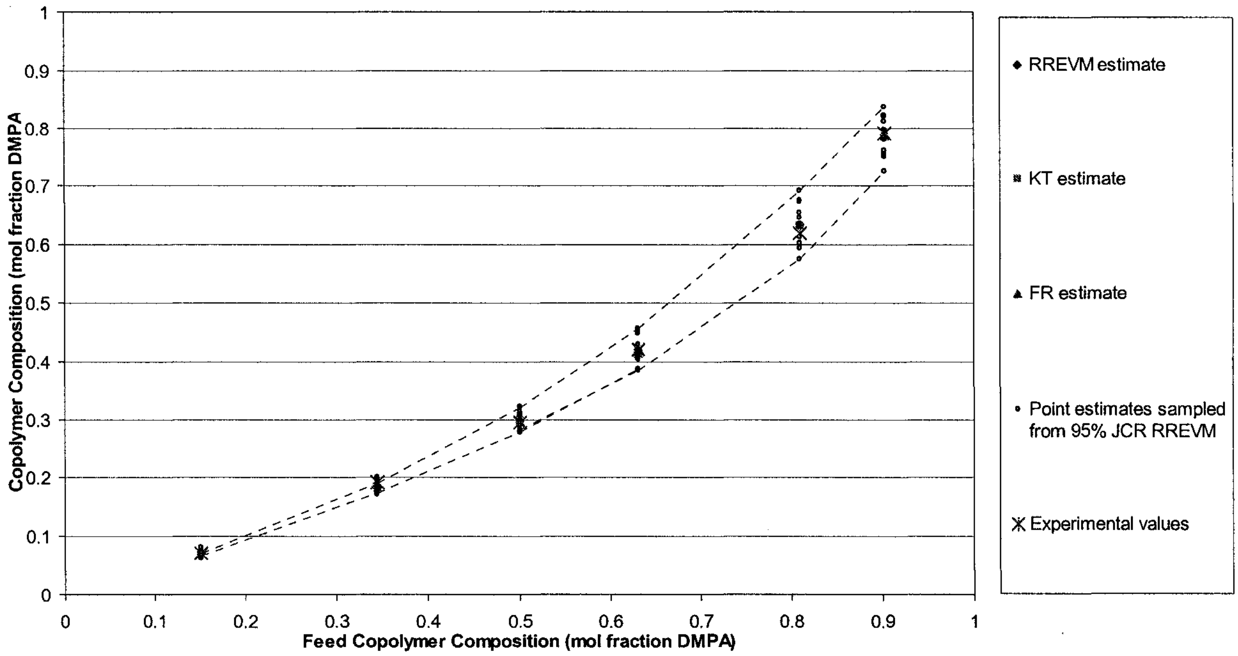


**Figure 4.2: Instantaneous copolymer composition curves of DMPA-MMA system.**

This is equivalent to perturbing the values of the reactivity ratios using reasonable magnitudes of variation, and looking at the corresponding effect on the predicted values of copolymer composition (i.e., looking at the variance of the predicted values). We can then compare the magnitude of the band with typical measurement (experimental) errors and therefore have a better appreciation of the effect of uncertainty in the parameter estimates.

### 4.3.2 STY-AN (Bulk) Case Study

Analysis of the styrene (STY) and acrylonitrile (AN) copolymer system was conducted using data collected by Hill et al. (1989), refer to Table 4.7. Determination of the reactivity ratios was completed by Hill et al. (1989) and also recalculated by Kaim and Oracz (1998). In the article by Kaim and Oracz (1998) model discrimination between the terminal and penultimate models is performed by using the reactivity ratios estimated from the two models to calculate copolymer composition at various feed fractions and subsequently show the results on the instantaneous copolymer composition curve. However, in the following analysis it is shown that visual inspection of the instantaneous copolymer composition curves is not sufficient for model discrimination.

**Table 4.7: Data used in analysis of STY-AN bulk system (Hill et al. 1989).**

| Initial Feed Composition (Mol frac STY) $f_1$ | Copolymer Composition (Mol frac STY) $F_1$ |
|---|---|
| 0.021 | 0.234 |
| 0.023 | 0.248 |
| 0.047 | 0.323 |
| 0.053 | 0.333 |
| 0.072 | 0.36 |
| 0.104 | 0.406 |
| 0.221 | 0.476 |
| 0.314 | 0.51 |
| 0.416 | 0.542 |
| 0.53 | 0.582 |
| 0.631 | 0.627 |
| 0.696 | 0.649 |
| 0.802 | 0.705 |
| 0.889 | 0.772 |
| 0.939 | 0.829 |

In order to conduct the analysis in RREVM, the feed data was assumed to have a measurement error of 3% while the copolymer data was assumed to have a 10% measurement error. The estimates of the reactivity ratios for the terminal and penultimate model, given by Kaim and Oracz (1998) and Hill et al. (1989), can be seen in Table 4.8. In the RREVM analysis the initial reactivity ratio estimates were those provided by the original data source group, Hill et al. (1989).

**Table 4.8: Reactivity ratio estimation results for the data of Hill et al. (1989).**

| | Estimation Method | $r_1$ | $r_2$ | $r_{11}$ | $r_{22}$ | $r_{21}$ | $r_{12}$ |
|---|---|---|---|---|---|---|---|
| Hill et al. (1989) | NLLS | 0.34 | 0.05 | | | | |
| Kaim and Oracz (1998) (Terminal model) | NLLS | 0.34 | 0.054 | | | | |
| Kaim and Oracz (1998) (Penultimate model) | NLLS | | | 0.223 | 0.038 | 0.652 | 0.098 |
| Current work | EVM | 0.3522 | 0.0523 | | | | |

The reactivity ratio exact JCR for the STY-AN system was also completed using RREVM, refer to Figure 4.3. It can be seen in the figure that the system is well behaved as the literature reactivity ratio estimates fall within the exact JCR obtained from RREVM.

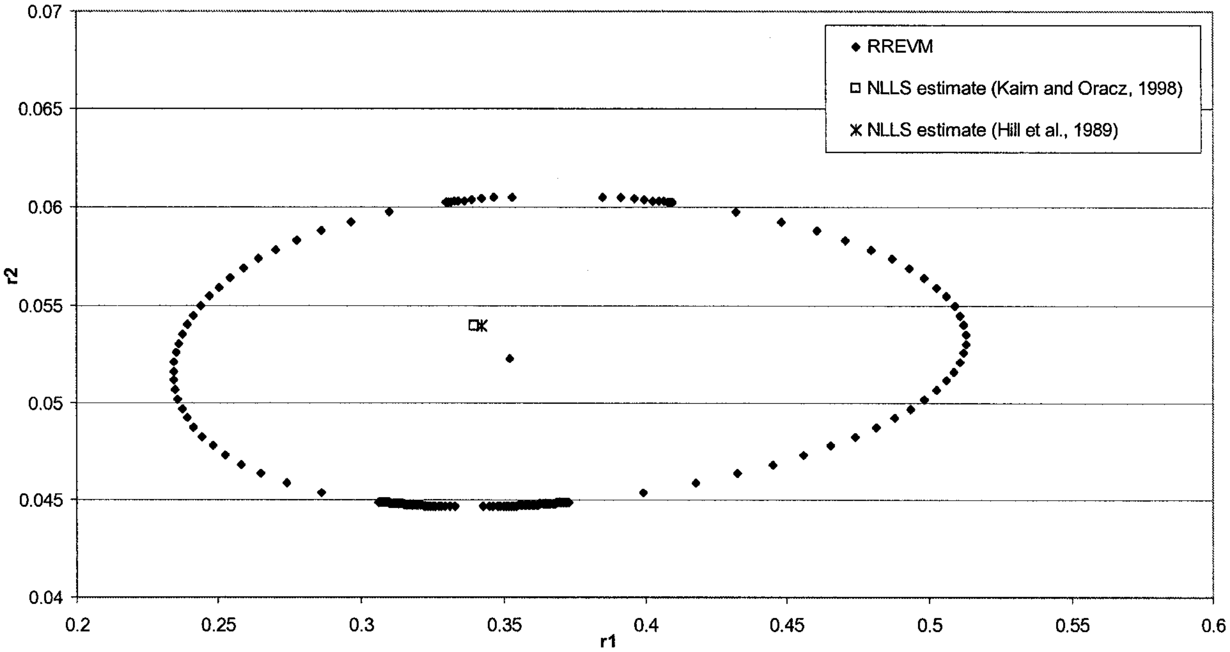


**Figure 4.3: Exact JCR for STY-AN bulk system using RREVM.**

Similar to the previous case study, the plots of the instantaneous copolymer composition curves were obtained by using the reactivity ratio estimates in the Mayo-Lewis equation (Equation 2.21). Furthermore, the penultimate reactivity ratio estimates by Kaim and Oracz (1998) were used in a similar equation for the instantaneous copolymer composition, according to the penultimate model, to plot the subsequent penultimate estimate of the copolymer composition curve. As can be seen in Figure 4.4, there does not appear to be considerable differences in the curves, despite the fact that one curve uses penultimate reactivity ratio estimates. However, enlarging a region of the plot in the same way as that in Kaim and Oracz (1998), slight variations amongst the estimates can be seen, refer to Figure 4.4.

From the enlarged plot in Figure 4.4 Kaim and Oracz (1998) stated that from visual inspection, the terminal model is not able to describe the variation of the copolymer composition with the monomer in an exact way. And after analysis with the penultimate parameters the article further states that the results confirm the known fact that the penultimate model is the more appropriate of the models. However, it is important to note that it is extremely difficult to prove such hypothesis without the use of error levels or replicates. In other words, using one data set without error bars, but rather visual inspection of a selected region on the graph is very misleading as the basis of discrimination between models is dependent on that data set and whether one subjectively considers the deviation from measurements to be beyond the expected measurement errors. That is, model discrimination can not occur unless there is a quantifiable deviation from the measured values which is beyond the extent of typical measurement errors. There is a considerable volume of literature specifically detailing the method of model discrimination in copolymer systems, such as Burke et al. (1994).

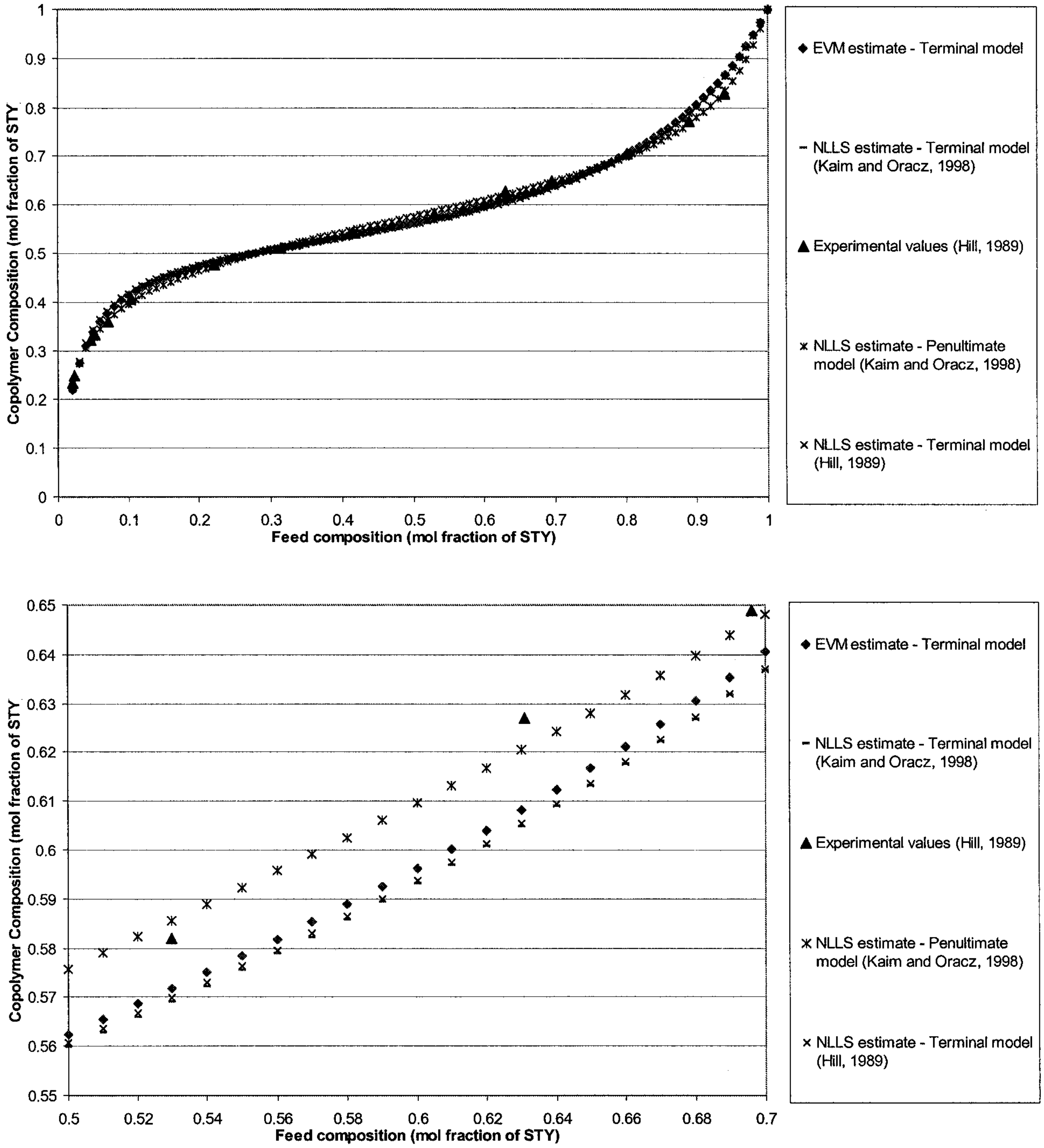


**Figure 4.4: Instantaneous copolymer composition curves of STY-AN system.**

### 4.3.3 STY-AN (Solution) Case Study

A relatively recent article by Kaim (2000), focused on determining whether a solvent effect, on reactivity ratio estimates, exists in the styrene (STY) and acrylonitrile (AN) copolymerization system. In order to be able to determine the existence of a potential solvent effect in the STY/AN copolymerization system, copolymer composition data sets, with different solvents, were used to estimate reactivity ratios. Kaim's (2000) research however, did not involve experimental work and thus utilized data from Hill et al. (1992) and Klumperman and Kraeger (1994). Consequently in this work the aim was to re-analyze the data using EVM as the parameter estimation method, to determine whether a solvent effect could be statistically said to exist.

Firstly, Klumperman et al. (1994) provided the data for the STY/AN copolymerization using toluene and DMF solvent systems (refer to Table 4.9), while Hill et al. (1992) provided data for the bulk, toluene solvent and acetonitrile solvent systems (refer to Table 4.10).

**Table 4.9 Data for toluene and DMF solvent STY/AN systems at 60°C (Klumperman et al. 1994).**

| | Copolymer Composition (Mol frac STY) $F_1$ | |
|---|---|---|
| **Initial Feed Composition (Mol frac STY) $f_1$** | **Toluene solvent** | **DMF solvent** |
| 0.0149 | | 0.101 |
| 0.015 | | 0.094 |
| 0.0151 | 0.092 | 0.113 |
| 0.0152 | 0.092 | |
| 0.0155 | | |
| 0.0377 | 0.233 | |
| 0.0406 | | 0.231 |
| 0.0531 | | |
| 0.1037 | | |
| 0.1084 | | 0.336 |
| 0.1085 | | 0.337 |
| 0.1091 | | 0.333 |
| 0.1095 | | |
| 0.1101 | 0.366 | |
| 0.111 | 0.361 | |
| 0.1899 | 0.434 | |
| 0.2214 | | |
| 0.2639 | | 0.452 |
| 0.3241 | 0.496 | |
| 0.4182 | | 0.495 |
| 0.5009 | 0.566 | |
| 0.5727 | 0.591 | |
| 0.5763 | 0.594 | |
| 0.5765 | | 0.556 |
| 0.5769 | | 0.587 |
| 0.5861 | | |
| 0.6198 | | |
| 0.7503 | | 0.596 |
| 0.7555 | 0.67 | |
| 0.8006 | | |
| 0.8303 | | 0.698 |
| 0.9317 | | 0.788 |
| 0.9334 | 0.818 | |
| 0.9348 | | 0.821 |
| 0.9349 | 0.827 | |
| 0.9392 | | |

**Table 4.10: Data for bulk, toluene solvent and acetonitrile solvent STY/AN systems at 60°C (Hill et al. 1992).**

| | **Copolymer Composition (Mol frac STY) $F_1$** | | |
|---|---|---|---|
| **Initial Feed Composition (Mol frac STY) $f_1$** | **Bulk** | **Toluene solvent** | **Acetonitrile solvent** |
| 0.021 | 0.234 | | |
| 0.023 | 0.248 | | |
| 0.035 | | 0.135 | 0.27 |
| 0.047 | 0.323 | | 0.3 |
| 0.053 | 0.333 | | |
| 0.072 | 0.360 | 0.275 | 0.365 |
| 0.104 | 0.406 | | |
| 0.125 | | 0.375 | 0.419 |
| 0.212 | | 0.44 | 0.475 |
| 0.221 | 0.476 | | |
| 0.276 | | 0.485 | 0.5 |
| 0.314 | 0.510 | | |
| 0.364 | | 0.52 | 0.542 |
| 0.416 | 0.542 | | |
| 0.462 | | 0.55 | 0.577 |
| 0.53 | 0.582 | | |
| 0.596 | | 0.6 | 0.629 |
| 0.631 | 0.627 | | |
| 0.696 | 0.649 | 0.645 | 0.674 |
| 0.802 | 0.705 | | |
| 0.808 | | 0.7 | 0.74 |
| 0.889 | 0.772 | | |
| 0.9 | | 0.78 | 0.84 |
| 0.939 | 0.829 | | |

Using the different data sets in RREVM, the plots of the reactivity ratios exact JCRs were generated and can be seen in Figure 4.5. In the plot the abbreviations (Hill, 1992 data) and (Klumperman, 1994 data) refer to use of the data sets provided by Hill et al. (1992) and Klumperman and Kraeger (1994), respectively.

Firstly, the literature point estimates by Kaim (2000) can be seen in Figure 4.5 to be outside the exact JCRs for the toluene and DMF solvent cases. The figure also shows that for the toluene solvent system, the collection of the data set can impact the location of the reactivity ratios significantly. That is, the RREVM analysis performed on the toluene data from Hill et al. (1992) does not agree with the analysis performed on the toluene data from Klumperman and Kraeger (1994), even though the temperature during both copolymerization experiments was the same.

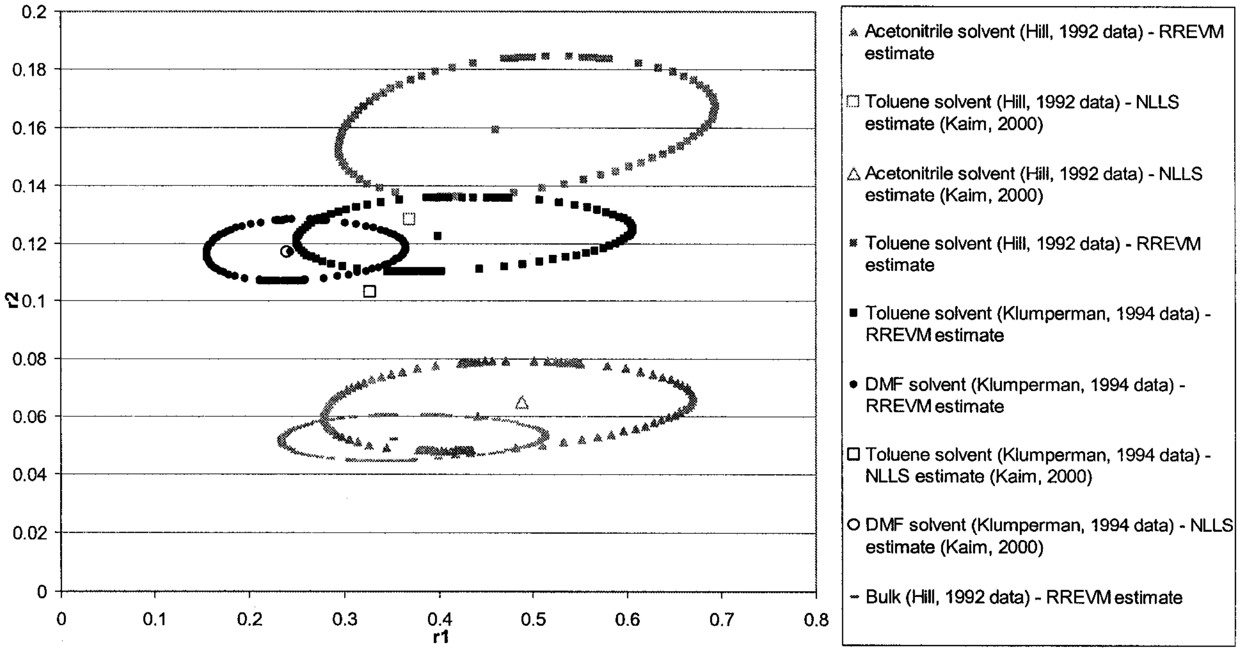


**Figure 4.5: Exact JCRs for the STY/AN copolymerization system with different solvents.**

Furthermore, it can be seen in Figure 4.5 that the variation (from the bulk case) in the reactivity ratios when the toluene and DMF solvents are used, is greater than the shift when acetonitrile solvent is used. The variation could be considered to be a possible solvent effect, provided that the variation can not be attributed to experimental errors. The solvent effect however can not be statistically proven unless the error levels were known and specific feed regions, which ensured that the precipitation of polyAN did not affect the copolymerization, were used. Consequently, further work is required to find feed regions and conditions that would limit the degree of precipitation of polyAN and then parameter estimation analysis redone on the new experimental data collected at the optimum feed/system conditions.

### 4.3.4 MMA-AM Case Study

The copolymer composition data at low conversions for the methyl methacrylate (MMA) and acrylamide (AM) copolymerization was collected by Talpur et al. (1996), for two systems with different solvents; dioxane and cyclohexane (refer to Table 4.11).

The article by Talpur et al. (1996) suggests that EVM was the parameter estimation method used and references the article by Dube et al. (1991). However, analysis of Talpur et al. (1996) data set with the program RREVM, which is the EVM program developed by Dube et al. (1991), results in reactivity ratio estimates that are quite different from the literature values (refer to Table 4.12). The RREVM analysis was completed twice as seen in the table, due to the fact that some of the data obtained by Talpur et al. (1996) exceeds conversions of 5%. The conversion limit of 5% is set to avoid issues of composition drift which can distort the reactivity ratio estimates, as the model used (Mayo-Lewis) deals with instantaneous properties. It can be seen that removing the data that contains conversions higher than 5% has a considerable impact on the estimates obtained.

**Table 4.11: Data used in analysis of MMA-AM system (Talpur et al. 1996).**

| | Cyclohexane solvent | | Dioxane solvent | |
|---|---|---|---|---|
| **Initial Feed Composition (Mol frac MMA) $f_1$** | **Copolymer Composition (Mol frac MMA) $F_1$** | **Conversion (wt%) $X_w$** | **Copolymer Composition (Mol frac MMA) $F_1$** | **Conversion (wt%) $X_w$** |
| 0.9 | 0.954 | 7.43 | 0.9 | 2.027 |
| 0.8 | 0.922 | 7.32 | 0.874 | 1.716 |
| 0.7 | 0.876 | 7.258 | 0.787 | 1.547 |
| 0.6 | 0.756 | 5.234 | 0.615 | 1.632 |
| 0.5 | 0.598 | 6.813 | 0.465 | 1.461 |
| 0.4 | 0.453 | 6.724 | 0.344 | 1.381 |
| 0.3 | 0.33 | 6.816 | 0.258 | 1.253 |
| 0.2 | 0.235 | 5.073 | 0.186 | 1.202 |
| 0.9 | 0.954 | 2.994 | 0.942 | 6.225 |
| 0.8 | 0.86 | 3.451 | 0.893 | 6.635 |
| 0.7 | 0.992 | 3.672 | 0.784 | 6.741 |
| 0.6 | 0.494 | 3.59 | 0.686 | 6.667 |
| 0.5 | 0.386 | 3.563 | 0.566 | 6.307 |
| 0.4 | 0.289 | 3.261 | 0.436 | 7.839 |
| 0.3 | 0.227 | 3.249 | 0.328 | 7.768 |
| 0.2 | 0.137 | 2.873 | 0.256 | 6.577 |

**Table 4.12: Reactivity ratio estimation results for the data of Talpur et al. (1996).**

| | Cyclohexane solvent | | Dioxane solvent | |
|---|---|---|---|---|
| | $r_1$ | $r_2$ | $r_1$ | $r_2$ |
| Talpur et al. (1996) | 2.72 | 1.05 | 1.99 | 1.84 |
| RREVM (all data points) | 2.0241 | 1.7276 | 1.3946 | 1.1148 |
| RREVM (only data points with conversion below 5%) | 1.4842 | 2.1373 | 1.3061 | 1.3811 |

In the RREVM program the initial estimates used were the literature values of Talpur et al. (1996). Also, the feed data was assumed to have a measurement error of 5% while the copolymer data was assumed to have a 10% measurement error. The copolymer composition error was set to 10% due to the nature of obtaining the copolymer composition being quite error prone; while Talpur et al. (1998) set it to an unreasonably low value of 1%.

The JCRs for the dioxane and cyclohexane solvent systems were also completed using RREVM and can be seen in Figures 4.6 and 4.7, respectively.

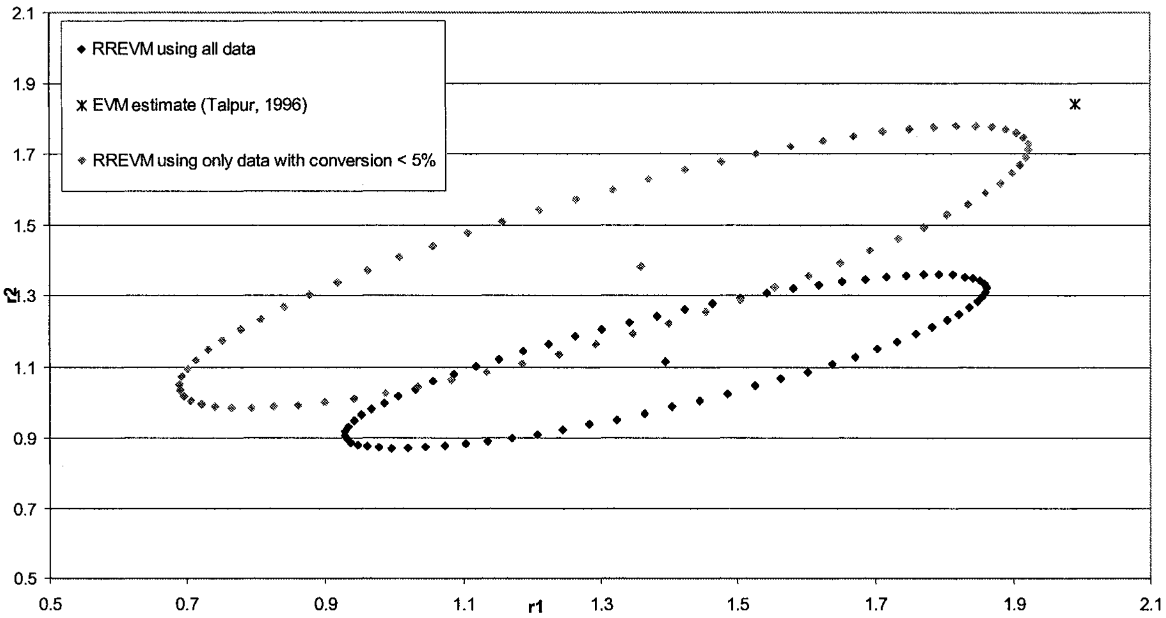


**Figure 4.6: Ellipse JCRs for MMA-AM (dioxane solvent) copolymerization system using RREVM (assumed feed and copolymer measurement errors of 5 and 10%, respectively).**

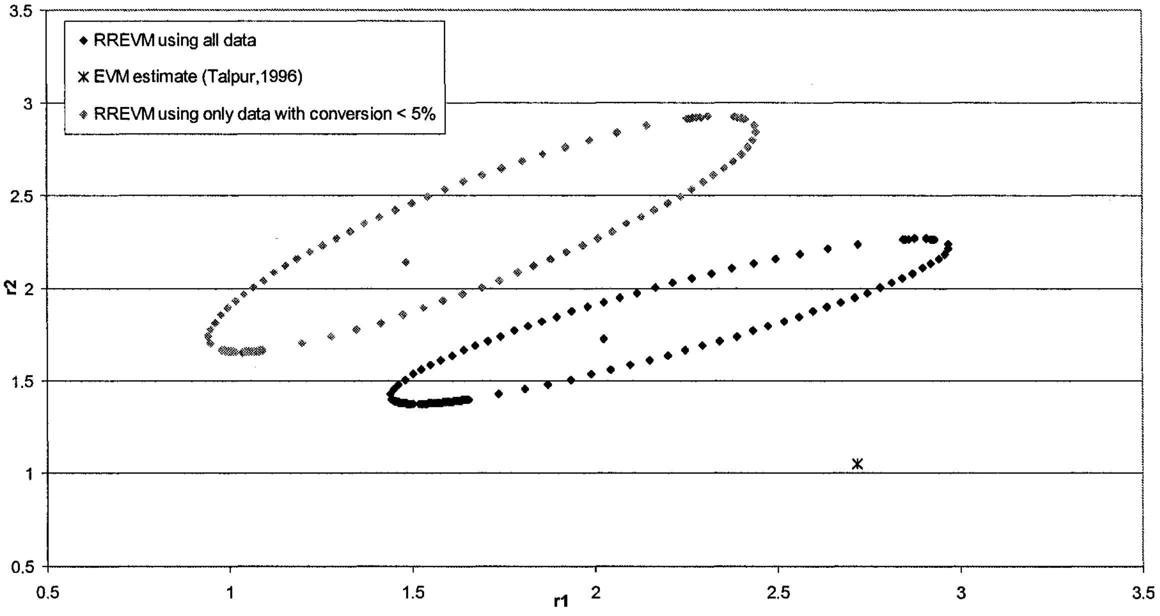


**Figure 4.7: Exact JCRs for MMA-AM (cyclohexane solvent) system using RREVM (assumed feed and copolymer measurement errors of 5 and 10%, respectively).**

In Figure 4.6, the ellipse JCRs are shown rather than the exact JCRs, as the exact JCR calculations in RREVM could not converge for the case where all the data is used. However, regardless of which JCR is analyzed the important point to be seen from both figures is that the estimates provided by Talpur et al. (1996) lie outside the JCRs.

In order to ensure that the assumed level of error in the copolymer composition measurement was not the source of difference between the Talpur et al. (1996) and the current RREVM estimate, analysis was completed using the error levels outlined in the paper (5% for feed composition and 1% for copolymer composition). However, the JCRs obtained from the new analysis still show that the point estimates, referenced in the article, fall outside the JCRs (see Figures 4.8 and 4.9). The case of Figure 4.9, where only data with conversion levels below 5% were input to RREVM, resulted in the program not converging and hence JCRs could not be shown. Therefore, it can only be presumed that the method used by the group was not in fact the EVM method outlined in the paper by Dube et al. (1991).

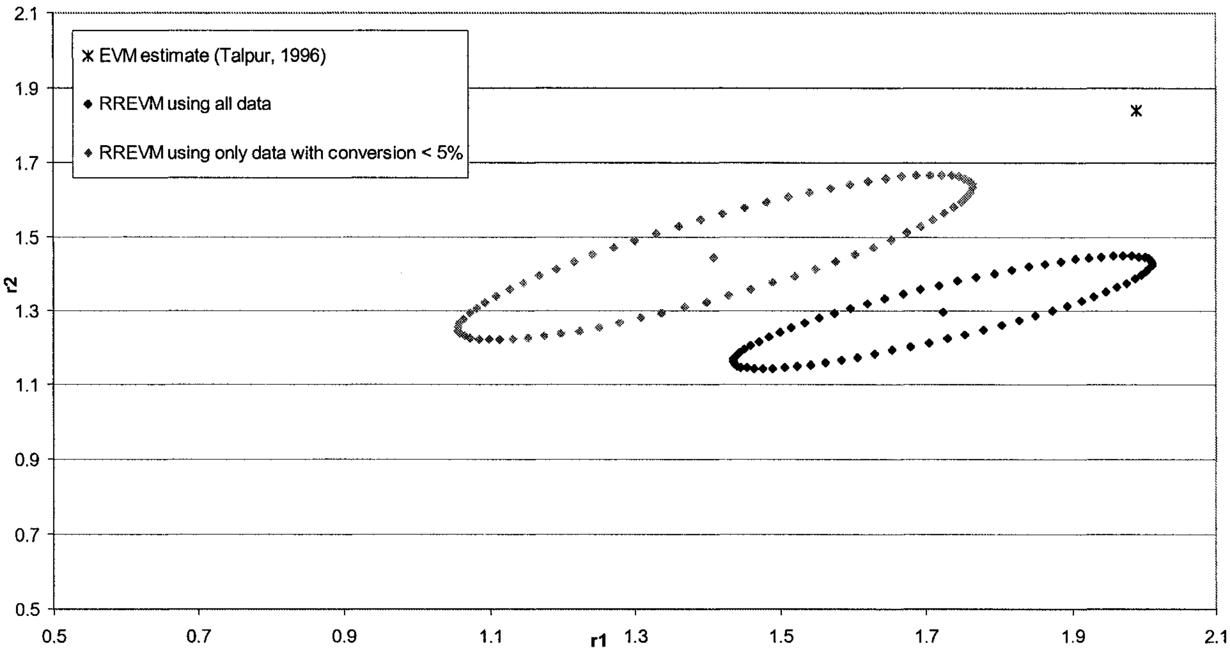


**Figure 4.8: Ellipse JCRs for MMA-AM (dioxane solvent) system using RREVM (assumed feed and copolymer measurement errors of 5 and 1%, respectively).**

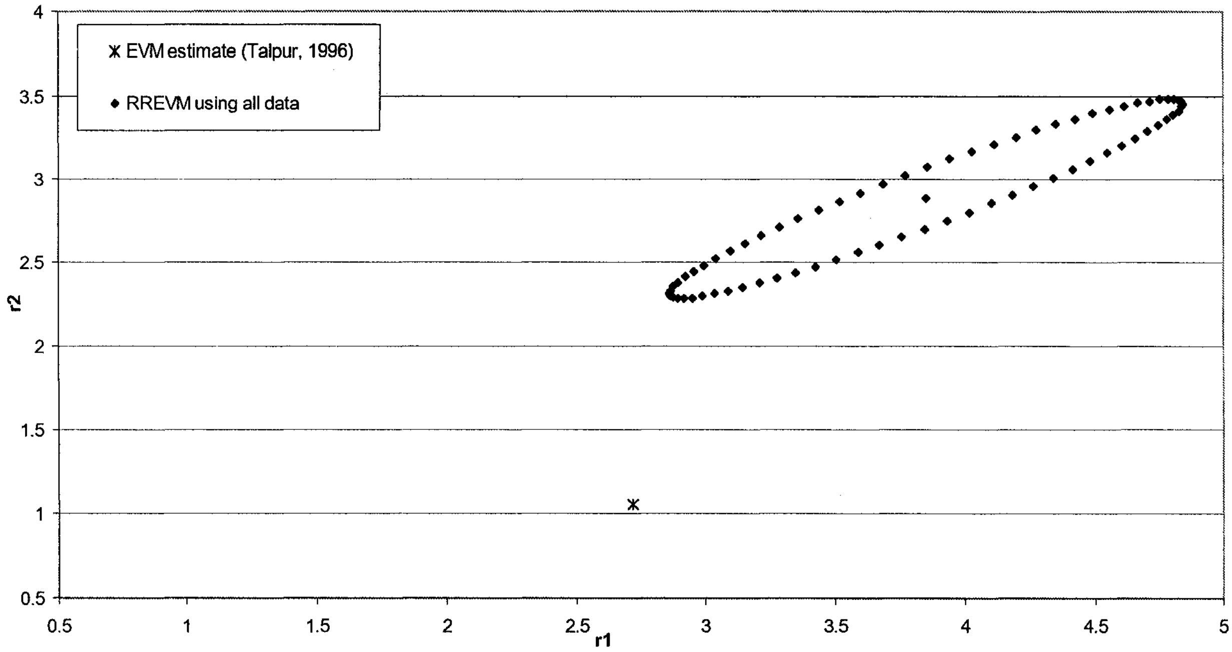


**Figure 4.9 Ellipse JCRs for MMA-AM (cyclohexane solvent) system using RREVM (assumed feed and copolymer measurement errors of 5 and 1%, respectively).**

### 4.3.5 Case Studies with New Experimental Data

Tables 4.13 to 4.17 cite new copolymer composition experimental data for several functionalized systems (Penlidis, 2005) for photonic/electronic/automotive protective coatings applications. Only abbreviations of the monomer names are used in the following discussion; however the full chemical names of the monomers can be found in Table 4.3.

In the RREVM analysis of these case studies, a number of scenarios were run in order to see the effect of the initial estimate and the measurement errors on the reactivity ratios. Using these scenarios it was seen that when the initial estimates of reactivity ratios were varied, the point estimates of the parameters remained constant. Furthermore, when the measurement errors in the feed and copolymer were varied, the effect on the point estimates was negligible; suggesting the systems are well behaved.

**Table 4.13: Data used in analysis of NAS-DMA system.**

| Initial Feed Composition (Mol frac NAS) $f_1$ | Copolymer Composition (Mol frac NAS) $F_1$ |
|---|---|
| 0.8503 | 0.8726 |
| 0.848 | 0.8749 |
| 0.6703 | 0.6859 |
| 0.6629 | 0.6933 |
| 0.5038 | 0.5088 |
| 0.4936 | 0.5131 |
| 0.3234 | 0.2796 |
| 0.2998 | 0.3032 |
| 0.0899 | 0.0597 |
| 0.0857 | 0.0639 |

**Table 4.14: Data used in analysis of PCPA-GMA system.**

| Initial Feed Composition (Mol frac PCPA) $f_1$ | Copolymer Composition (Mol frac PCPA) $F_1$ |
|---|---|
| 0.1495 | 0.1061 |
| 0.3575 | 0.2569 |
| 0.5011 | 0.3848 |
| 0.6493 | 0.5241 |
| 0.8071 | 0.6961 |
| 0.9007 | 0.8280 |

**Table 4.15: Data used in analysis of DCPA-GMA system.**

| Initial Feed Composition (Mol frac DCPA) $f_1$ | Copolymer Composition (Mol frac DCPA) $F_1$ |
|---|---|
| 0.1497 | 0.0731 |
| 0.352 | 0.1827 |
| 0.4989 | 0.2793 |
| 0.6507 | 0.3931 |
| 0.8012 | 0.5348 |
| 0.8993 | 0.6812 |

**Table 4.16: Data used in analysis of DMPM-GMA system.**

| Initial Feed Composition (Mol frac DMPM) $f_1$ | Copolymer Composition (Mol frac DMPM) $F_1$ |
|---|---|
| 0.1493 | 0.0672 |
| 0.3496 | 0.1853 |
| 0.5010 | 0.2864 |
| 0.6498 | 0.4307 |
| 0.8012 | 0.6211 |
| 0.9002 | 0.7805 |

**Table 4.17: Data used in analysis of MSMPK-MMA system.**

| Initial Feed Composition (Mol frac MSMPK) $f_1$ | Copolymer Composition (Mol frac MSMPK) $F_1$ |
|---|---|
| 0.1503 | 0.2729 |
| 0.3012 | 0.4010 |
| 0.5032 | 0.5791 |
| 0.6518 | 0.7029 |
| 0.7998 | 0.8211 |
| 0.9012 | 0.9016 |

The point estimates found by using the RREVM program with assumed error levels of 5% and 10% for feed monomer one fraction and copolymer monomer one fraction respectively, can be seen in Table 4.18. Additionally, the estimation techniques used by the research group included Fineman-Ross (FR), Inverted FR (Inv-FR), Kelen-Tudos (KT) and extended KT (ex-KT), which can also be seen in Table 4.18 for the respective system.

**Table 4.18: Reactivity ratio point estimates for the copolymerization systems.**

| System | Estimation Method | $r_1$ | $r_2$ |
|---|---|---|---|
| NAS-DMA | EVM | 1.6738 | 1.5707 |
| | FR | 1.36 | 1.38 |
| | Inv-FR | 1.55 | 1.55 |
| | KT | 1.44 | 1.49 |
| PCPA-GMA | EVM | 0.5061 | 1.4514 |
| | FR | 0.5045 | 1.4482 |
| | KT | 0.5056 | 1.4508 |
| | ex-KT | 0.4836 | 1.4631 |
| DCPA-GMA | EVM | 0.1948 | 2.1235 |
| | FR | 0.183 | 2.075 |
| | KT | 0.190 | 2.112 |
| | ex-KT | 0.168 | 2.176 |
| DMPM-GMA | EVM | 0.3957 | 2.4076 |
| | FR | 0.398 | 2.383 |
| | KT | 0.393 | 2.404 |
| | ex-KT | 0.366 | 2.466 |
| MSMPK-MMA | EVM | 0.9043 | 0.3901 |
| | FR | 0.9439 | 0.3656 |
| | KT | 0.9726 | 0.4172 |
| | ex-KT | 0.9731 | 0.4055 |

It is interesting to note here that in the NAS-DMA copolymerization case the linear estimates suggest $r_2$ to be slightly greater than $r_1$ (refer to Table 4.18). This suggests that radicals with monomer two (DMA) terminal units have a greater affinity for adding their own monomer than radicals with monomer one (NAS) terminal units have for adding their respective monomer (i.e., that radicals with a DMA monomer terminal unit add more DMA monomers to the growing copolymer chain, compared to radicals with a NAS monomer terminal unit adding NAS monomer). Consequently, the linear parameter estimates would suggest that the copolymer would have a lower mole fraction of NAS than the initial feed, as DMA is preferentially added by the growing radical chain. However, when the raw data is analyzed, this is not the case. Rather, from inspecting the data there appears to be a trend that when a certain mole fraction of NAS in the feed is given, the copolymer formed is slightly richer in NAS than the feed concentration. Consequently, the data suggests that $r_1$ should be slightly greater than $r_2$, which is in agreement with the EVM result, refer to Table 4.18.

Furthermore, the result of obtaining both reactivity ratios to be greater than unity in the NAS-DMA case is very rare and indicates a certain copolymer pattern. That is, when a reactivity ratio is greater than unity, this suggests that a radical with a certain monomer terminal unit preferentially adds the same monomer. Consequently, when both reactivity ratios are greater than unity this suggests that both radicals with opposing monomer terminal units preferentially add their own monomer. The result of both reactivity ratios being greater than unity is then a tendency to form blocks of both monomers in the chain. The reactivity ratios thus indicate the formation of block copolymers and that the statistical "chance" of forming one block of monomer one to be slightly greater than forming a block of monomer two, hence the trend of slightly greater concentrations of monomer one (NAS) in the copolymer than the concentration given in the feed (refer to Table 4.13).

The exact JCRs for the reactivity ratios for these copolymerization systems were also generated using RREVM and plotted alongside the respective point estimates from the other parameter estimation techniques; refer to Figures 4.10 - 4.14. The figures show that the linear estimates fall within the RREVM exact JCRs for all the different copolymerization systems. Consequently, it is reasonable to suggest that the systems are well behaved.

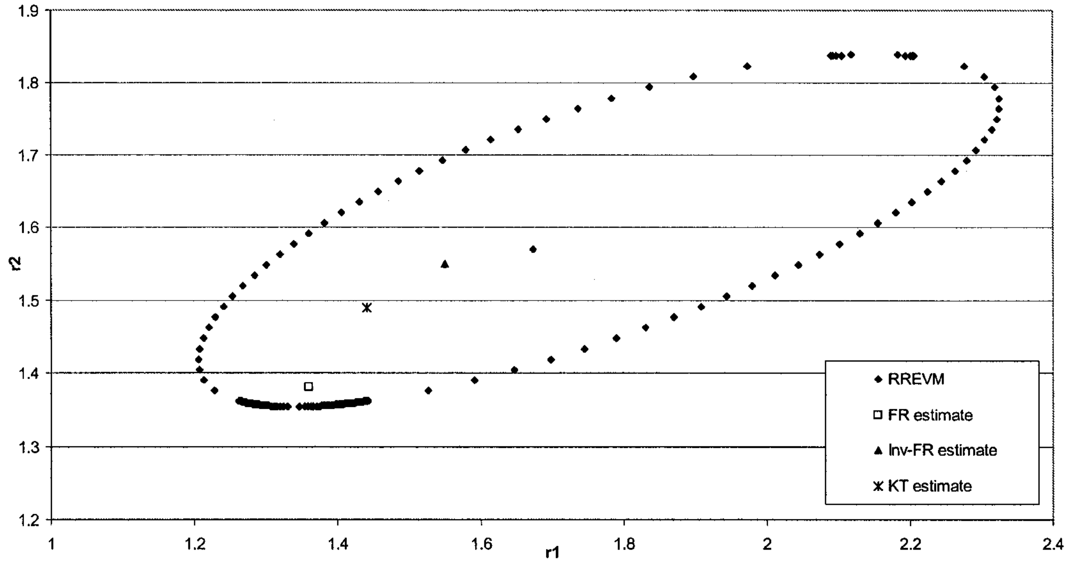


**Figure 4.10: Exact JCR for NAS-DMA system and point estimates.**

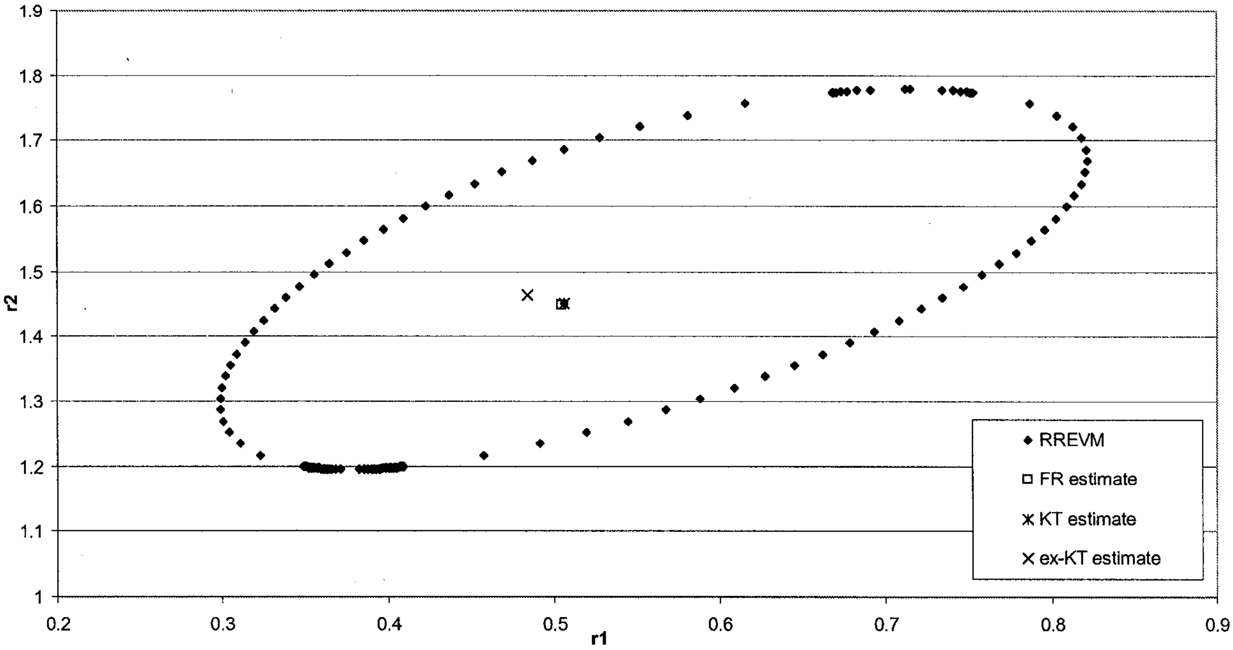


Figure 4.11: Exact JCR for PCPA-GMA system and point estimates.

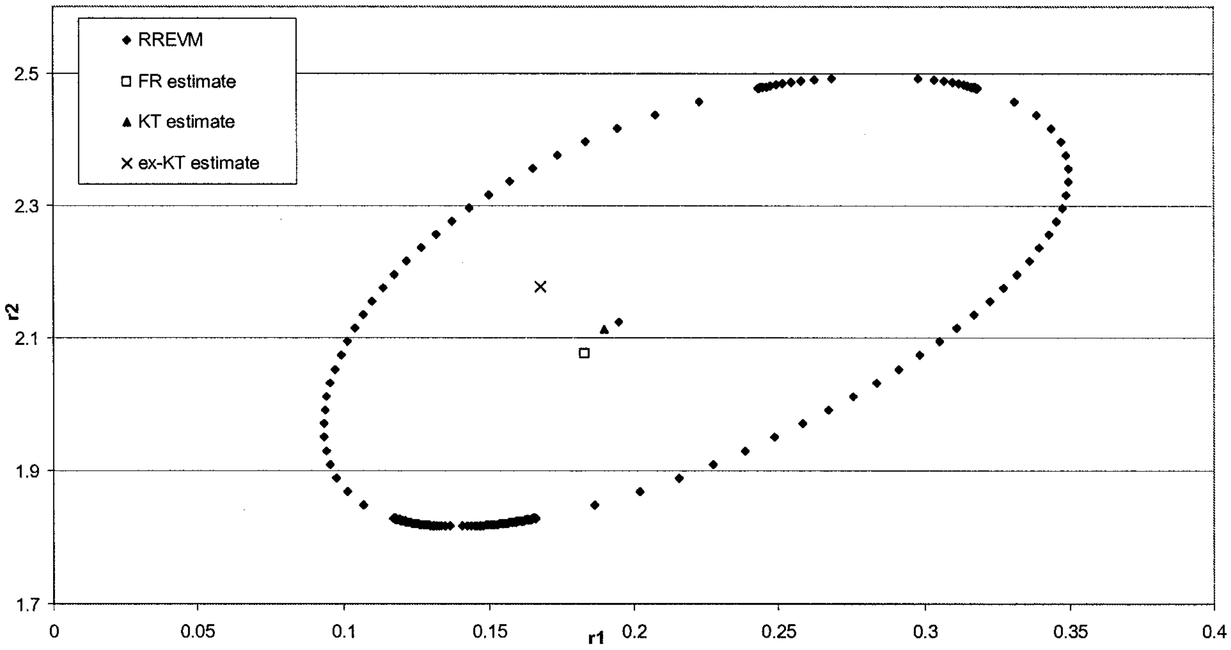


Figure 4.12: Exact JCR for DCPA-GMA system and point estimates.

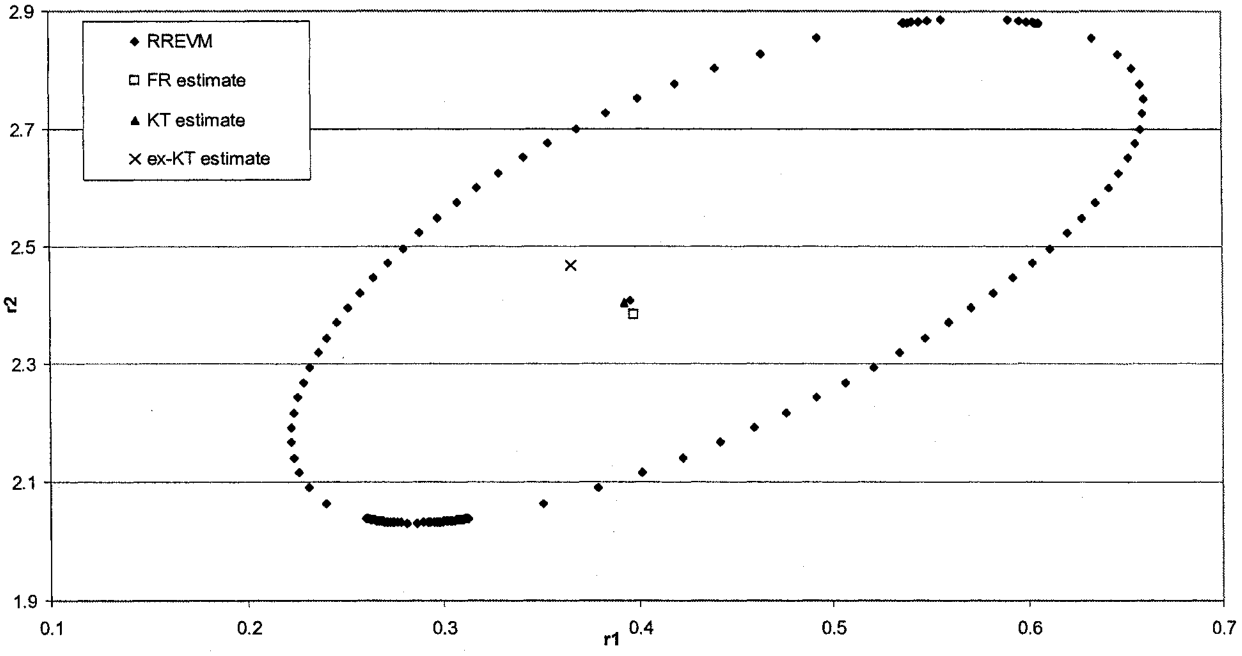


Figure 4.13: Exact JCR for DMPM-GMA system and point estimates.

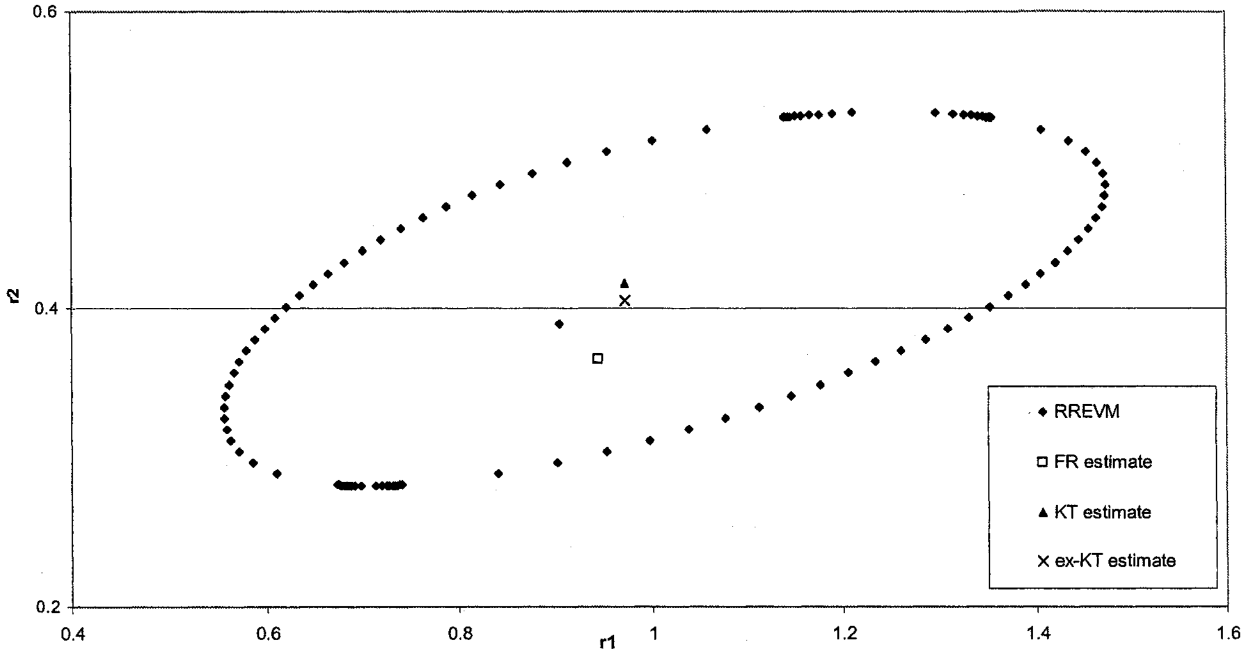


Figure 4.14: Exact JCR for MSMPK-MMA system and point estimates.

# Chapter 5

# Estimation of Reactivity Ratios from Instantaneous Data

## 5.1 Reactivity Ratio Estimation from Instantaneous Data

Typically, reactivity ratio estimates are obtained from analyzing instantaneous models of either triad fractions or copolymer composition data.

Triad fractions are sequences of three consecutive monomer units in a copolymer chain. The fractions are categorized as either monomer-1-centered triads or monomer-2-centered triads. The triads are denoted by $A_{ijk}$, where *i, j* and *k* are either monomer units 1 or 2. The six triad fractions as stated in Koenig (1980) can be related to the reactivity ratios through the following equations:

$$
\begin{aligned}
A_{111} &= \frac{r_1^2 f_1^2}{r_1^2 f_1^2 + 2r_1 f_1 f_2 + f_2^2} & A_{222} &= \frac{r_2^2 f_2^2}{r_2^2 f_2^2 + 2r_2 f_1 f_2 + f_1^2} \\
A_{211} + A_{112} &= \frac{2r_1 f_1 f_2}{r_1^2 f_1^2 + 2r_1 f_1 f_2 + f_2^2} & A_{122} + A_{221} &= \frac{2r_2 f_1 f_2}{r_2^2 f_2^2 + 2r_2 f_1 f_2 + f_1^2} \\
A_{212} &= \frac{f_2^2}{r_1^2 f_1^2 + 2r_1 f_1 f_2 + f_2^2} & A_{121} &= \frac{f_1^2}{r_2^2 f_2^2 + 2r_2 f_1 f_2 + f_1^2}
\end{aligned}
\tag{5.1}
$$

where $f_1$ and $f_2$ represent the mole fraction of monomer 1 and 2 in the feed, respectively. It is also well established that the sum of the monomer-1-centered triad fractions is one and similarly with the monomer-2-centered fractions. Therefore, a reactivity ratio estimation scheme which uses all six triad fractions will lead to highly correlated parameter estimates (Burke, 1994). As a result, in this research $A_{111}$ and $A_{222}$, unless otherwise stated, were arbitrarily eliminated in order to avoid the issue of linear dependency.

It is also important to note here that triad fractions are not measured directly, but rather are linearly related to C$^{13}$-NMR spectral data (Burke, 1994). That is, the normalized peak areas in the NMR spectral data are related to the triad fractions by:

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} 0 & 0 & (1-\sigma_{12})^2 \\ 1 & 1-\sigma_{12} & 2\sigma_{12}(1-\sigma_{12}) \\ 0 & \sigma_{12} & \sigma_{12}{}^2 \end{bmatrix} \begin{bmatrix} A_{111} \\ A_{112+211} \\ A_{212} \end{bmatrix} \tag{5.2}$$

$$\begin{bmatrix} A \\ B+C \\ D \end{bmatrix} = \begin{bmatrix} \sigma_{12}{}^2 & \sigma_{22}\sigma_{12} & \sigma_{22}{}^2 \\ 1-\sigma_{12}{}^2 & 1-\sigma_{22}\sigma_{12} & 2\sigma_{22}(1-\sigma_{22}) \\ 0 & 0 & (1-\sigma_{22})^2 \end{bmatrix} \begin{bmatrix} A_{121} \\ A_{122+221} \\ A_{222} \end{bmatrix} \tag{5.3}$$

where X, Y, Z, A, B+C and D are relative peak areas in the C$^{13}$-NMR spectrum with the known calibration parameters, $\sigma_{12}$ and $\sigma_{22}$ (i.e., coisotacticity and tacticity parameters, respectively). As a result, in the literature the NMR normalized peak areas may be given or the calculated triad fractions explicitly stated. Thus use of either form of the triad fractions data or the NMR normalized peak areas data was made possible in the EVM program.

In contrast, the copolymer composition is the mole fraction of monomer one incorporated in the copolymer. Typically, the instantaneous copolymer composition model is referred to as the Mayo-Lewis model. It relates the monomer feed composition with the copolymer composition, $F_1$, by the following equation:

$$F_1 = \frac{r_1 f_1^2 + f_1(1-f_1)}{r_1 f_1^2 + 2f_1(1-f_1) + r_2(1-f_1)^2} \tag{5.4}$$

## 5.2 Program Development and Error Structure

The main method used in this work for estimating reactivity ratios is the error in variables model (EVM), as it has been shown that this model is a better statistical method for parameter estimation in copolymerization systems (Rossignoli and Duever, 1995). As EVM is the routine developed in the MATLAB program, the error structure of the data must be considered in order to be able to create the covariance matrix, $\underline{V}$. While copolymer composition data is considered by most to have a multiplicative error structure, the triad fractions data error structure has not been studied or reported in the literature in any great detail and thus whether or not the error structure is additive or multiplicative is unclear. Consequently, the following case studies were analyzed for both multiplicative and additive error, to illustrate the impact the error structure of the data may have on the reactivity ratio estimates.

The error levels and subsequent covariance matrix used in the EVM program, was obtained using the approach outlined by Rossignoli and Duever (1995). In Section 3.5, a summary of this approach can be reviewed. An important conclusion from Section 3.5 showed that the variance of the variable $x$, ($V(x)$) when an additive error structure is imposed, is the same as the variance of the transformed variable ($V(\ln x)$), when a multiplicative error structure is imposed; provided that the error can be said to be below ±10%. As a result the covariance matrix for copolymer composition data, assuming there is no covariance between feed and copolymer compositions, is given by:

$$\underline{V} = \begin{bmatrix} \frac{k_{f1}^{2}}{3} & 0 \\ 0 & \frac{k_{F1}^{2}}{3} \end{bmatrix} \tag{5.5}$$

Where the errors of the mole fraction of monomer one in the feed and copolymer can be said to be $\pm k_{f1}$ and $\pm k_{F1}$ units, respectively (where $\pm k$ units is the same units as the measured variable $x$ and as we are measuring mole fractions it thus becomes $\pm k$ percent).

Similarly for triad fractions data (or NMR normalized peak areas) the covariance matrix used in the EVM model is obtained by:

$$\underline{V} = \begin{bmatrix} \frac{k_{f1}^{2}}{3} & 0 & 0 & 0 & 0 \\ 0 & \frac{k_{A112}^{2}}{3} & 0 & 0 & 0 \\ 0 & 0 & \frac{k_{A212}^{2}}{3} & 0 & 0 \\ 0 & 0 & 0 & \frac{k_{A221}^{2}}{3} & 0 \\ 0 & 0 & 0 & 0 & \frac{k_{A121}^{2}}{3} \end{bmatrix} \tag{5.6}$$

In the following chapter case studies, unless otherwise stated, the feed composition and triad fractionss/NMR normalized peak areas errors were assumed to follow a uniform distribution of

±5%, while copolymer composition error was uniformly distributed in the interval ±10%. Therefore, using the assumed error levels the covariance matrix for copolymer composition and triad fractions are given by:

$$\underline{V}\,(\text{copolymer composition}) = \begin{bmatrix} \frac{0.05^2}{3} & 0 \\ 0 & \frac{0.1^2}{3} \end{bmatrix} \tag{5.7}$$

$$\underline{V}(\text{triad fractions or NMR normalized peak areas}) = \begin{bmatrix} \frac{0.05^2}{3} & 0 & 0 & 0 & 0 \\ 0 & \frac{0.05^2}{3} & 0 & 0 & 0 \\ 0 & 0 & \frac{0.05^2}{3} & 0 & 0 \\ 0 & 0 & 0 & \frac{0.05^2}{3} & 0 \\ 0 & 0 & 0 & 0 & \frac{0.05^2}{3} \end{bmatrix} \tag{5.8}$$

The EVM program used in this thesis was developed in the MATLAB programming environment. Preliminary work carried out by Dalvi (2003) converted the EVM program described in Reilly et al. (1993) from Fortran to MATLAB. The first case study analyzed in this section is the Burke (1994) NMR normalized peak areas data which was used to troubleshoot and validate the EVM program in MATLAB. Subsequent case studies were used to (1) determine the potential improvement in reactivity ratio estimation using either triad fractions or NMR normalized peak areas data in place of and in addition to composition data, (2) illustrate the impact the selected error structure of the data can have on the reactivity ratio estimates, and lastly (3) demonstrate the importance of residual plot analysis as a statistical tool for determining lack of model fit.

It is also important to note that similar to previous chapters the exact shape, 95% approximate probability joint confidence region and the approximate shape, 95% approximate probability joint confidence region will be referred to as the exact JCR and the ellipse JCR, respectively. Furthermore, in some cases where multiplicative error structure was used data points that contained values of zero had to be removed, as the natural logarithm of the variables could not be found at these points.

## 5.3 Case Study I: Troubleshooting MATLAB EVM

Burke (1994) provided experimental NMR normalized peak areas data for the styrene (STY)/methyl methacrylate (MMA) system in bulk at 60°C. The $C^{13}$-NMR spectral data provided by Burke (1994) can be seen in Table 5.1.

**Table 5.1: NMR normalized peak areas data (Burke, 1994).**

| **Feed Composition f1 (mol frac of STY)** | **NMR Normalized Peak Areas** | | | | | |
|---|---|---|---|---|---|---|
| | **X** | **Y** | **Z** | **A** | **B+C** | **D** |
| 0.21232 | 0.17477 | 0.54829 | 0.27695 | 0.09908 | 0.68361 | 0.21731 |
| 0.22490 | 0.20291 | 0.53759 | 0.25950 | 0.08317 | 0.71368 | 0.20315 |
| 0.39255 | 0.16945 | 0.60578 | 0.22477 | 0.08787 | 0.78201 | 0.13012 |
| 0.39715 | 0.15556 | 0.53333 | 0.31112 | 0.11592 | 0.75007 | 0.13401 |
| 0.51690 | 0.11864 | 0.62423 | 0.25713 | 0.11206 | 0.81746 | 0.07048 |
| 0.51701 | 0.12033 | 0.60967 | 0.27000 | 0.11255 | 0.77942 | 0.10803 |
| 0.79132 | 0.04592 | 0.74733 | *0.20676* | 0.13330 | 0.78146 | 0.08524 |
| 0.79186 | 0.05760 | 0.76525 | 0.17715 | 0.15984 | 0.74077 | 0.09938 |

The reactivity ratio parameter estimation problem, with the above data, using two approaches; the multiresponse Box Draper determinant criterion and the error in variables model (EVM), was studied.

### 5.3.1 Multiresponse Determinant Criterion

In the first case using the Box Draper determinant criterion, the parameter estimation is a multi-response problem where NMR normalized peak areas are responses and the monomer feed, $f_1$ is an independent variable. The response variables are assumed to have an additive error structure in the determinant criterion, due to the nature of the model being in the form of Equation 3.3. The development of the determinant criterion used in the multiresponse problem is shown in Section 3.3. The end result is that a point estimate, $\underline{\boldsymbol{\theta}}$, in this case the reactivity ratios $r_1$ and $r_2$, can be found by choosing $\underline{\boldsymbol{\theta}}$ to minimize

$$\left|\sum_{i=1}^{n} Z_i Z_i'\right| . \tag{5.9}$$

Due to the fact that the $C^{13}$-NMR data is normalized, both the fractions (i.e., the monomer-1-centered triads and the monomer-2-centered triads) sum to equal one. As discussed by Burke

(1994), if all the data is used in the parameter estimation problem then issues involving colinearity will be present. Colinearity problems cause the solution to be very unstable and the variance of the parameter estimates to be quite large. Consequently, to avoid the colinearity issues the two redundant variables eliminated for this data set were those same variables selected by Burke (1994), namely X and D peaks. Burke (1994) selected these peaks as the X peak is the smallest of the first three peaks (X, Y, and Z) and the peak D was excluded because it should go to zero for comonomer feeds rich in styrene monomer.

The parameter estimation was carried out using the multiresponse determinant criterion coded in MATLAB (refer to Appendix A). The initial estimates used for the reactivity ratios were those given by Burke (1994). The parameter estimates obtained from running the MATLAB program can be seen in Table 5.2, along with the estimate found by Burke (1994). The estimates obtained in this work show slight deviation from Burke's (1994) result. This deviation can be attributed to a mistake in the original data set used by Burke (refer to italicized entry in Table 5.1).

**Table 5.2: Parameter estimates of $r_1$ and $r_2$ using the Box Draper determinant criterion method.**

| | $r_1$ | $r_2$ |
|---|---|---|
| Current work | 0.6207 | 0.6884 |
| Burke (1994) | 0.6761 | 0.58624 |

### 5.3.2 Error in Variables Model (EVM)

The EVM case was solved by troubleshooting the previously developed MATLAB model where all variables were considered to have error. The MATLAB file was based on an original FORTRAN EVM code to solve the numerous inner and outer loop iterations. The theory of EVM can be seen in Section 3.4, while the coding files used in the program can be seen in Appendix A.

The data used in the EVM program was the $C^{13}$-NMR normalized peak areas data set (refer to Table 5.1) provided by Burke (1994) and like the previous analysis, only four out of the six responses were used to avoid the problems with colinearity. The eliminated responses were the same as those previously selected, namely X and D. The model was run for both an additive and multiplicative error structure, to illustrate the impact it may have on the parameter point estimates and confidence regions.

Table 5.3 shows the parameter estimates of the reactivity ratios found using the MATLAB EVM program for the NMR normalized peak areas data (assuming the error of the peak areas follow a uniform distribution of ±5%). A sensitivity analysis was then performed to determine the effect on the estimates when the inputted covariance matrix was altered. There was negligible effect when the covariance matrix values were halved and when increased by one order of magnitude.

**Table 5.3: Parameter estimates of $r_1$ and $r_2$ using EVM.**

| | $r_1$ | $r_2$ |
|---|---|---|
| Additive error | 0.6763 | 0.4874 |
| Multiplicative error | 0.8213 | 0.7272 |

Figure 5.1 shows the exact JCRs, for the different imposed error structures, obtained from the EVM analysis of the NMR normalized peak areas data. Theoretically, one would anticipate that there would be significant overlap of the exact JCRs, as the same data set is used; yet this is not the case. One potential explanation for the separation of contours is the effect of insufficient data (i.e., small data sample size), which will later be shown to influence the location of the point estimate significantly, particularly when a multiplicative error structure is imposed (refer to Section 5.3.4.3).

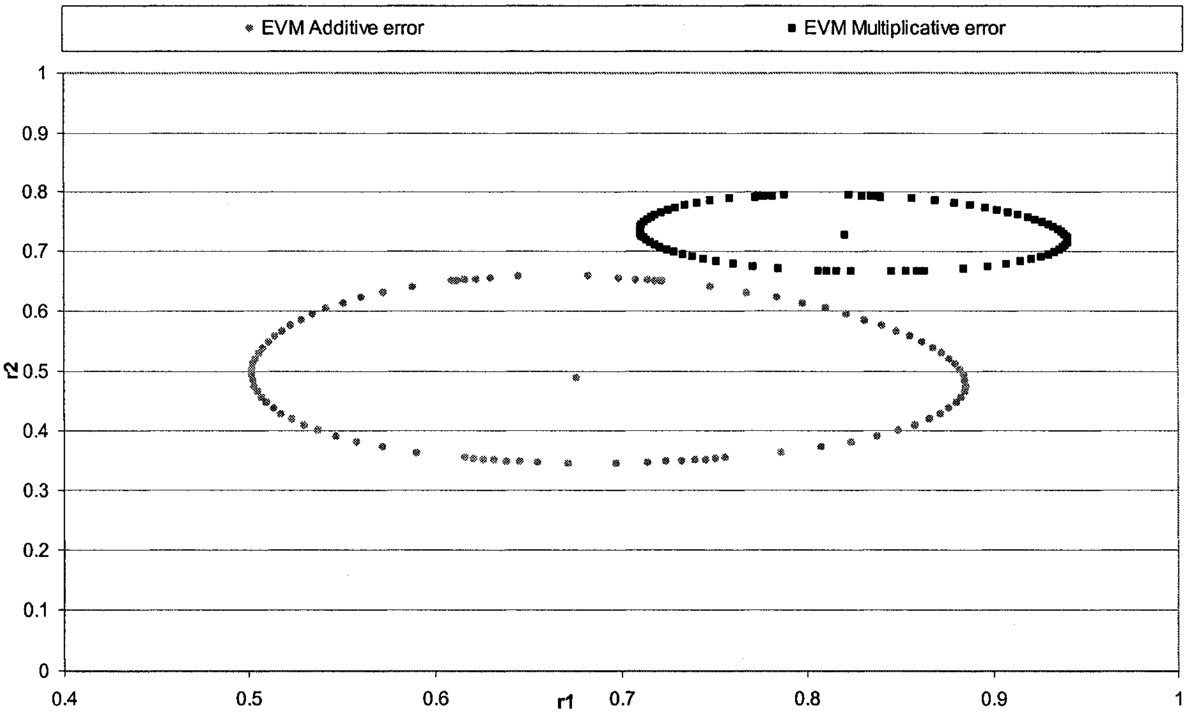
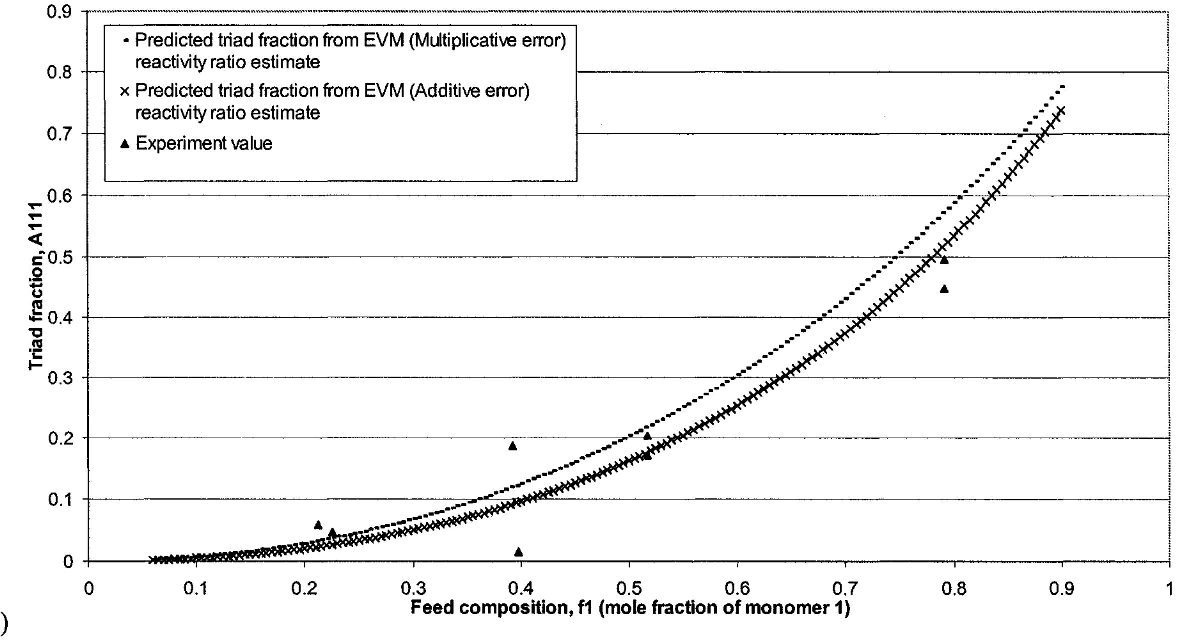


**Figure 5.1: Exact JCRs for EVM analysis of Burke (1994) STY-MMA NMR normalized peak areas data.**

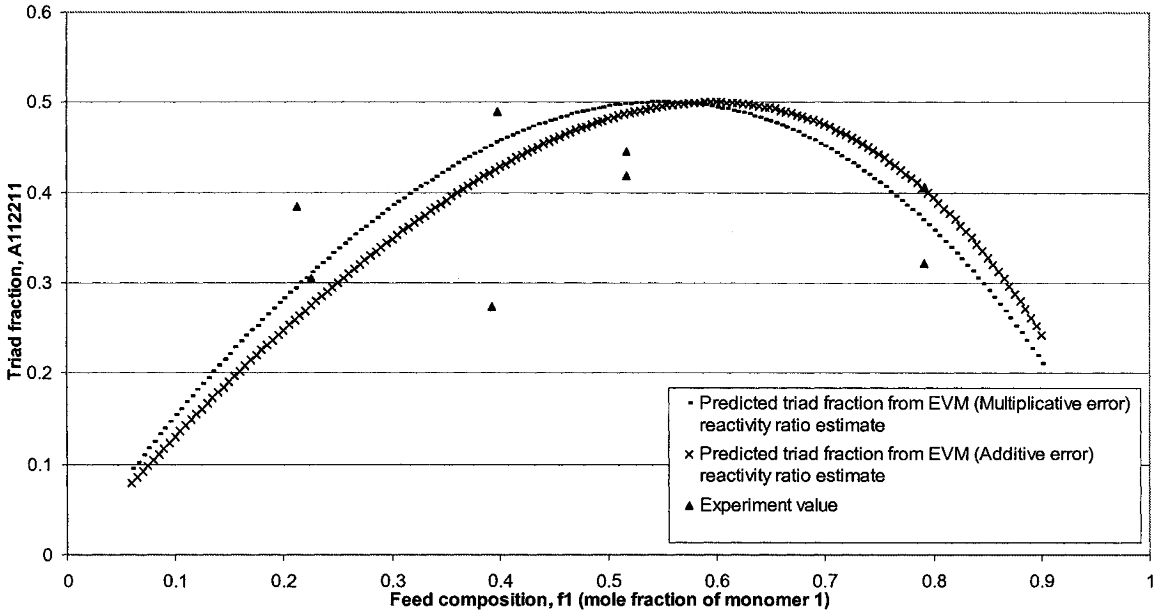
### 5.3.3 Diagnostic Checking of EVM results

Diagnostic checking is performed in order to ensure that the reactivity ratio estimates in fact model the experimental results accurately. The reactivity ratio estimates, obtained from the EVM analysis (refer to Table 5.4), were used in the triad fractions equations reported by Koenig (1980) to compare the 'predicted' triad fractions with the 'experimental' triad fractions. As Burke (a994) did not state explicitly the triad fractions results, rather the NMR normalized peak areas, the 'experimental' triad fractions were those transformed by Equations 5.2 and 5.3, using the known calibration parameters, $\sigma_{12}$ and $\sigma_{22}$ to be 0.24 and 0.44, respectively (Burke, 1994).

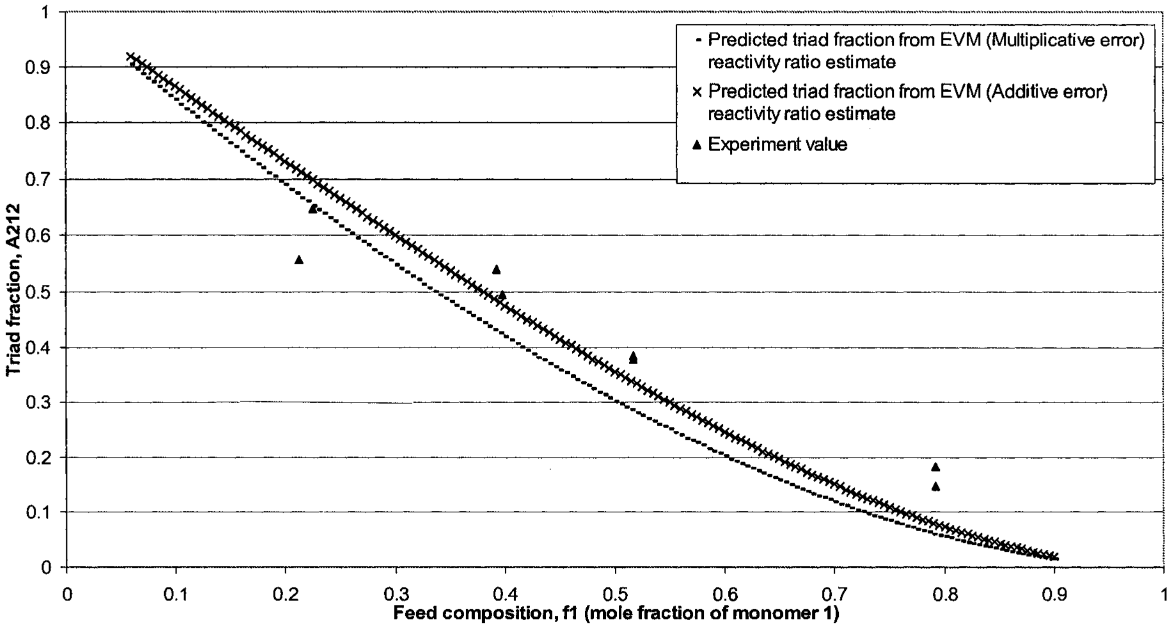
Figures 5.2 a) – f) show the triad fractions 'predicted' from the triad fractions equations, using the EVM reactivity ratio estimates (for both additive and multiplicative errors), and the 'experimental' triad fractions. Note that styrene (STY) is monomer 1 and methyl methacrylate (MMA) is monomer 2.



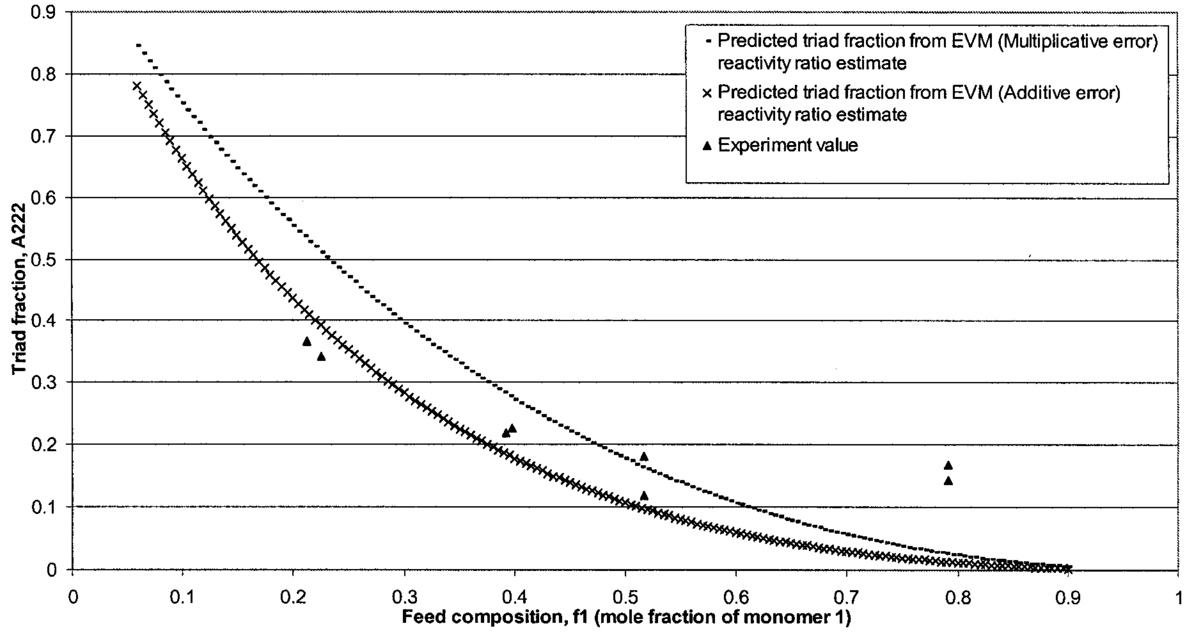
a)


0.6
0.5
0.4
0.3
0.2
0.1
0
Triad fraction, A112211
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Feed composition, f1 (mole fraction of monomer 1)
- Predicted triad fraction from EVM (Multiplicative error) reactivity ratio estimate
× Predicted triad fraction from EVM (Additive error) reactivity ratio estimate
▲ Experiment value

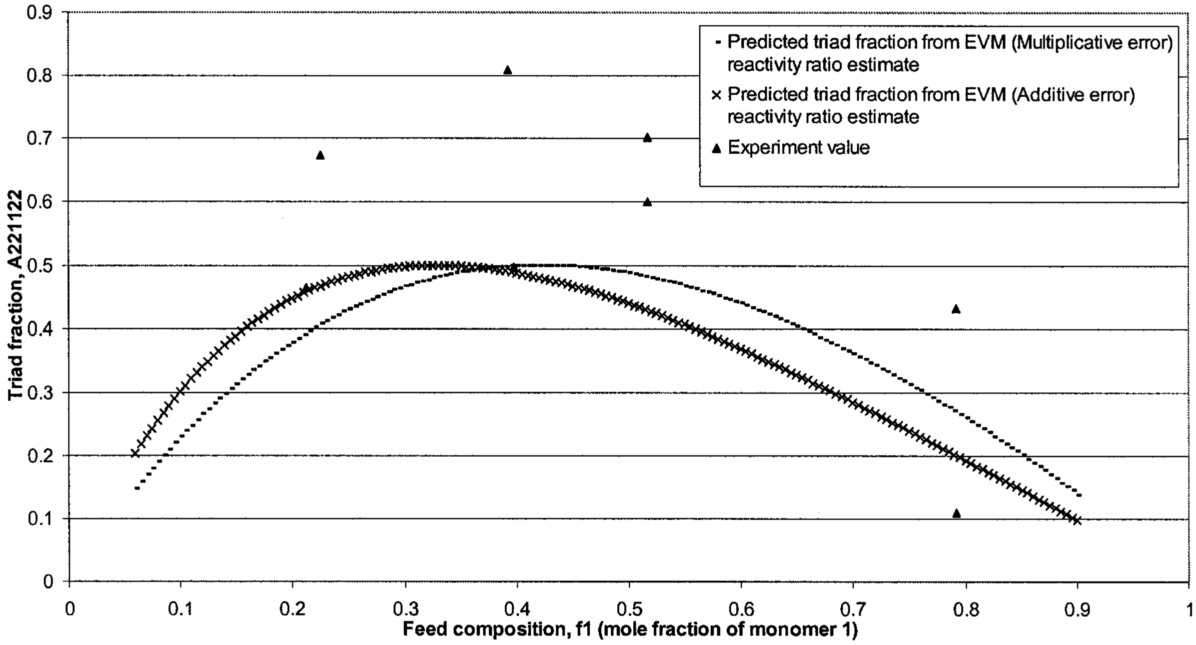
b)


1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Triad fraction, A212
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Feed composition, f1 (mole fraction of monomer 1)
- Predicted triad fraction from EVM (Multiplicative error) reactivity ratio estimate
× Predicted triad fraction from EVM (Additive error) reactivity ratio estimate
▲ Experiment value

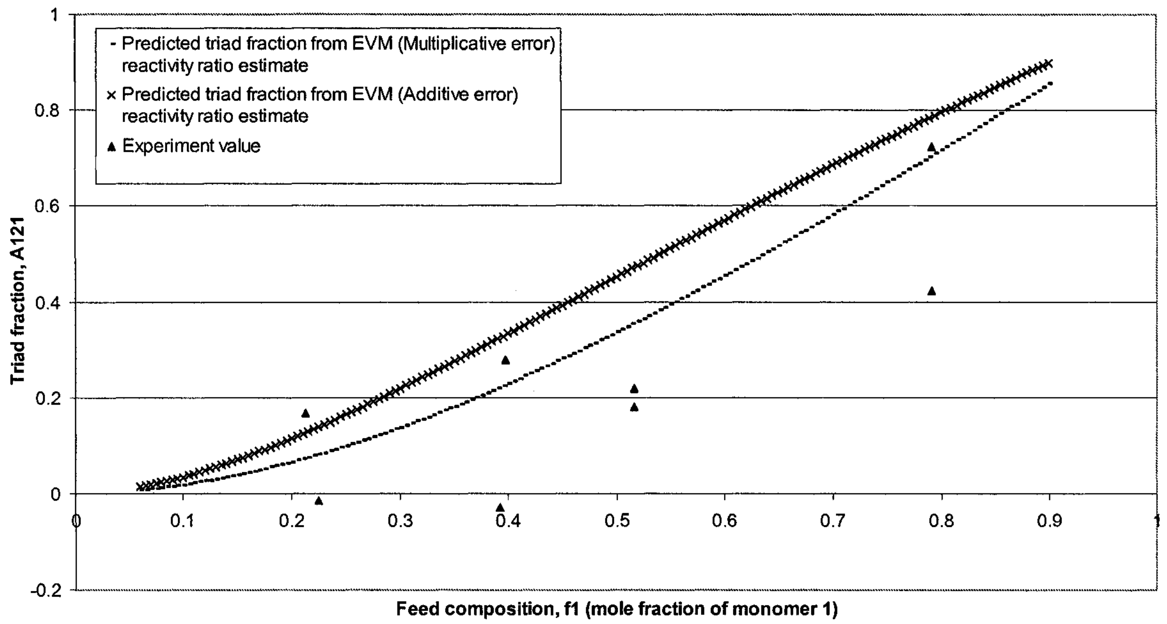
c)


0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Triad fraction, A222
- Predicted triad fraction from EVM (Multiplicative error) reactivity ratio estimate
× Predicted triad fraction from EVM (Additive error) reactivity ratio estimate
▲ Experiment value
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Feed composition, f1 (mole fraction of monomer 1)

d)


0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Triad fraction, A221122
- Predicted triad fraction from EVM (Multiplicative error) reactivity ratio estimate
× Predicted triad fraction from EVM (Additive error) reactivity ratio estimate
▲ Experiment value
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Feed composition, f1 (mole fraction of monomer 1)

e)



f)

**Figure 5.2 a) – f): Predicted triad fractions using the reactivity ratio estimates obtained from EVM (multiplicative error) analysis of the NMR normalized peak areas in Equation 5.1 and the 'experimental' triad fractions obtained from transforming the measured NMR normalized peak areas.**

It can be seen from Figures 5.2 a) - f) that the 'predicted' triad fractions obtained from using the EVM (multiplicative error) reactivity ratio estimates and the EVM (additive error) reactivity ratio estimates are in somewhat good agreement with the transformed 'experimental' results. The separation of the two 'predicted' trend lines, obtained from using the different reactivity ratio estimates, was anticipated given that there was no overlap of the exact JCRs in the original analysis (refer to Figure 5.1). However, there does not appear to be one reactivity ratio estimate (i.e., the EVM additive error estimate or the EVM multiplicative error estimate) that results in 'predicted' triads consistently in better agreement with the transformed 'experimental' results. In other words, we could say that the obvious dissagreement in reactivity ratio estimates (seen in the separation of the exact JCRs) obtained from imposing different error structures, is not translated to a considerable difference in the 'predicted' triad fractions. One potential explanation for this is that the diagnostic testing should not be performed on transformed 'experimental' results, but rather the true measured variable (i.e., NMR normalized peak areas); which is discussed in the following case study in Section 5.4.2. Another explanation may be attributed to the fact that the exact JCR is in fact only an approximation of the joint posterior probability region and thus may not be accurately representing the true nature of the estimates (discussed in Section 6.3.2.1).

### 5.3.4 Comparison of EVM and Box Draper Determinant Criterion Estimates

Comparison of the two parameter estimation methods can be seen when the point estimates and the exact JCRs for the EVM cases are plotted (refer to Figure 5.3).

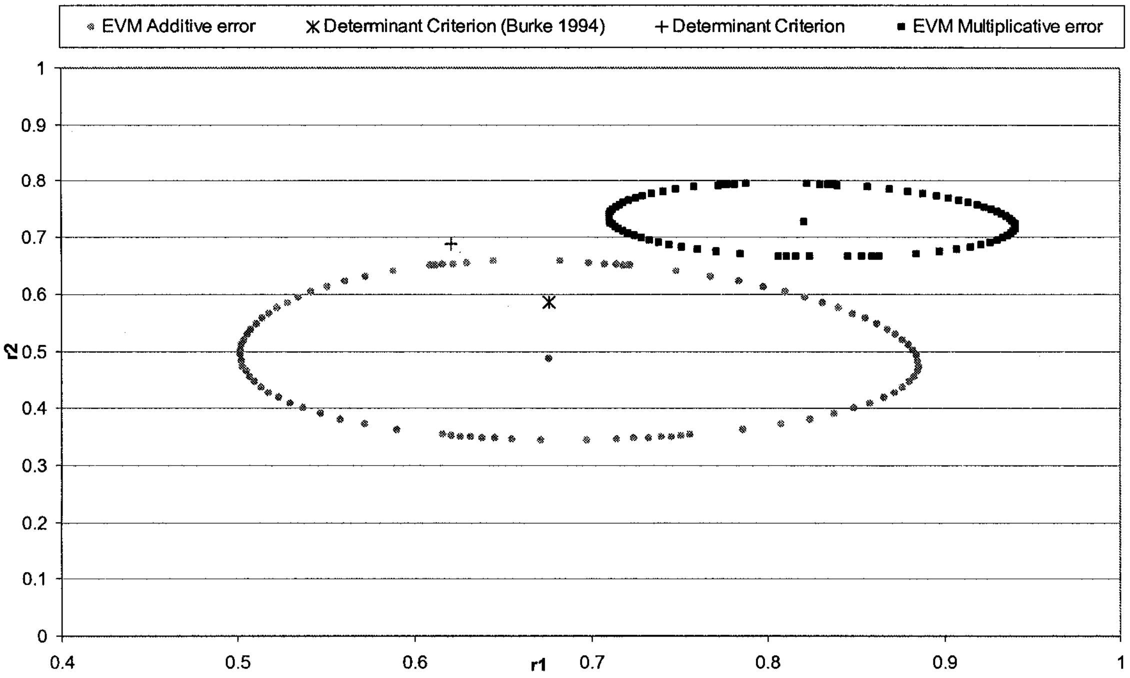


**Figure 5.3: Comparing the Exact JCRs obtained from EVM to the determinant criterion point estimates for the Burke (1994) STY-MMA NMR normalized peak areas data.**

As can be seen in Figure 5.3 the determinant criterion estimate falls outside the exact JCRs of both the additive error EVM case and the multiplicative error EVM case. There are three possible sources for the dissagreement in point estimates. The first is based on the difference in assumptions between the two parameter estimation approaches, namely that the feed composition in the determinant criterion is considered an independent variable with negligible error. The second is the simplification in EVM that there is no correlation between the normalized peak areas, where as the determinant criterion implicitly estimates the covariance matrix and thus may allow for correlation. Lastly, the difference in point estimates from the two parameter estimation methods may be due to the Box Draper determinant criterion being highly dependent on the data sample size (Oxby et al., 2003).

### *5.3.4.1 Considering feed composition to be perfectly known*

The source of the difference between the parameter estimation methods point estimates may be attributed to the determinant criterion assumption that the error associated with the feed composition is negligible compared to the error in the triad fractions measurements. Therefore, to test this hypothesis the EVM model was adapted to not include $f1$, the feed monomer composition, as a random variable with error. That is, when the EVM model is altered to exclude the feed composition as a random variable by assuming it to be perfectly known, this mimics the assumption of the determinant criterion. Figure 5.4 shows the exact JCR when the $f_1$ variable is assumed to be perfectly known in the EVM routine, for both an additive and multiplicative error structure.

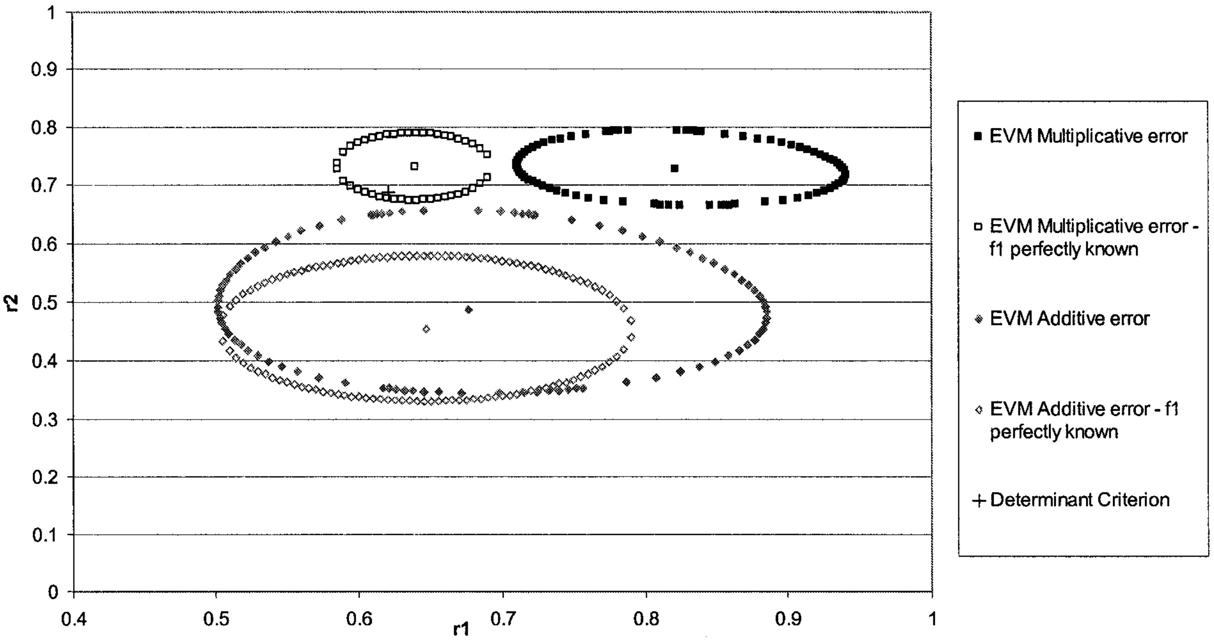


**Figure 5.4: Exact JCRs for EVM analysis of Burke (1994) STY-MMA NMR normalized peak areas data when feed composition is considered perfectly known (not a random variable).**

Figure 5.4 shows that the determinant criterion estimate falls within the exact JCR of the multiplicative error structure case when the EVM model is adapted to mimic the assumption of the determinant criterion (i.e., $f_1$ assumed perfectly known, not a random variable). Therefore, assuming the feed composition measurement has negligible error appears to be incorrect, due to the fact that the variable's presence as a random variable has shown to affect the location of the reactivity ratio point estimates significantly.

However, when the additive error structure in EVM is imposed on the data the determinant criterion estimate still falls outside the exact JCR. This is of particular importance given that the determinant criterion models an additive error structure. Thus, the other hypotheses for the dissagreement in parameter estimates, obtained from the EVM and determinant criterion methods, must be considered.

#### *5.3.4.2 Considering correlation amongst the triad fractions*

The next hypothesis to account for the difference in point estimates from the two parameter estimation techniques (EVM and the Box Draper determinant criterion) is the effect of imposing correlation between the triads. That is, in the original EVM method the covariance matrix was specified to have zero correlation between the normalized peak areas and the feed composition (i.e., all the off diagonal elements in the covariance matrix, $\underline{V}$, were zero). However, the Box Draper determinant criterion estimates the covariance matrix as part of the estimation routine and thus could potentially be estimating correlation. As a result the EVM model, assuming a multiplicative error structure, was re-run for a number of different levels of covariance (*Cov*).

The covariance values of the NMR normalized peak areas implemented to the EVM model were evaluated using set correlation coefficients ($\rho$) of ±0.2, ±0.5, and ±0.9, and the assumed variance ($V$) of the NMR normalized peak areas. For example,

$$\rho_{Y,Z} = \frac{Cov(Y,Z)}{\sqrt{V(Y)V(Z)}} \tag{5.10}$$

E.g. $$Cov(Y,Z) = 0.2 * \sqrt{\left(\frac{0.05^2}{3}\right) * \left(\frac{0.05^2}{3}\right)}$$

At the correlation coefficients of ±0.2, +0.5 and +0.9 the EVM program was able to evaluate the exact JCRs for the reactivity ratio estimates, seen in Figure 5.5. However the correlation coefficients of -0.5 and -0.9 could not be evaluated by the EVM program, as the covariance matrix is required to be positive definite.

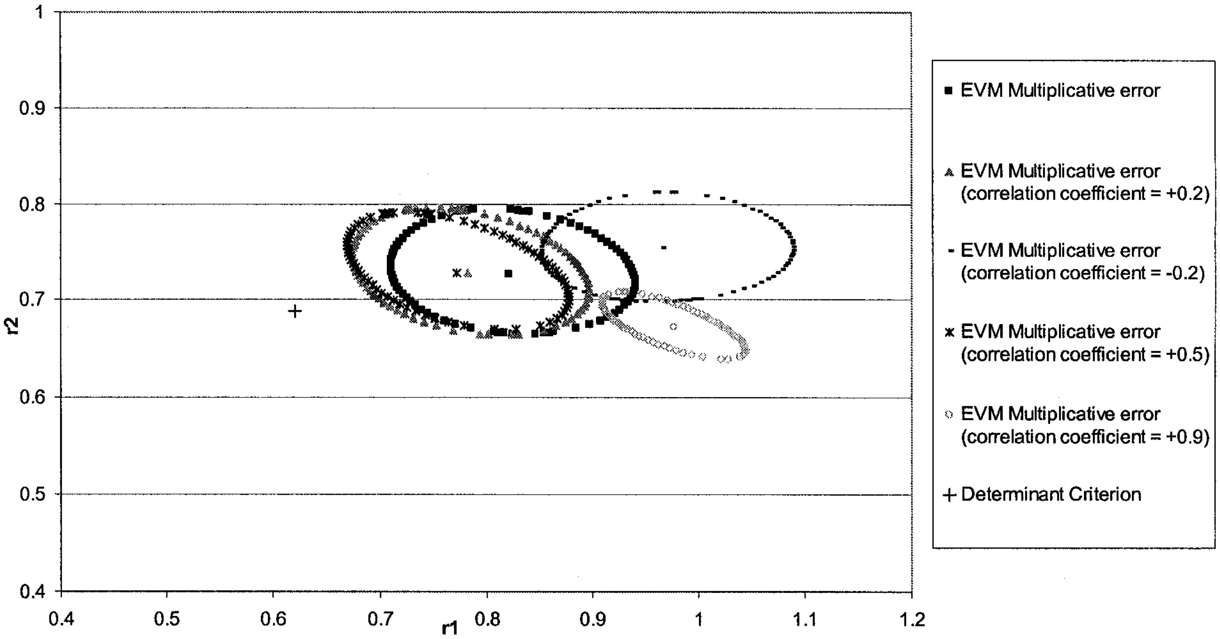


**Figure 5.5: Exact JCRs from EVM models using differing levels of correlation between the NMR normalized peak areas.**

Considering Figure 5.5 it can be said that reasonable levels of correlation amongst triads does not greatly affect the location of the point estimates. Only the correlation coefficient of +0.9 and -0.2 resulted in a significant shift in the point estimates, though there is still a degree of overlap of the exact JCRs.

Most importantly, in all of the cases the Box Draper determinant criterion still does not fall within the exact JCRs of the EVM estimates. Therefore, it can be presumed that the difference in the parameter estimation methods reactivity ratio estimates is not due to the simplification, used in EVM, of insignificant covariance amongst the NMR normalized peak areas.

### *5.3.4.3 Considering influence of data sample size*

It has been shown by Oxby et al. (2003) that the Box Draper determinant criterion method for parameter estimation is highly dependent on the data sample size and it is believed this is the main cause for the difference in the methods point estimates. In order to show the data sample size effect here, simulated data was used to increase the data sample size.

Eight simulated points were used in conjunction with the experimental data provided by Burke (1994) to create a sixteen point data set. Error was incorporated into the simulated data points by using a normal random number generation in Excel to generate normally distributed errors with a mean of 0 and variance of 0.0008 (i.e., N(0,SQRT($0.05^2$/3)). Thus, the simulated measured feed mole fraction values were obtained by using 'true values' plus the generated random error. The 'true' values of the feed mole fraction were taken as approximate replicates of the data points Burke (1994) designed. That is, the simulated feed mole fractions 'true' values were replicates of 0.22, 0.39, 0.51 and 0.79. The simulated triad fractions 'true' values were then found by using the equations that relate triad fraction, feed mole fraction and reactivity ratios (refer to Equation 5.1). The reactivity ratios used to evaluate the triad fractions were those obtained by the previous work on Burke's data using EVM additive error ($r_1 = 0.67626$, $r_2 = 0.4874$). The triad fractions 'true' values were then used in Equations 5.2 and 5.3 to obtain the 'true' values of the NMR normalized peak areas. The tacticity constants used to evaluate the NMR peaks were those published by Burke (1994) of $\sigma_{12} = 0.44$, $\sigma_{22}$=0.24. The NMR peaks were then simulated as experimental data by adding the generated random normalized error, N(0,SQRT($0.05^2$/3)). The resulting data set can be seen in Table 5.4. The entries that are in italics are those experimental values determined by Burke (1994), while the remaining values are simulated.

**Table 5.4: Experimental and simulated data.**

| **Feed Composition f1 (mol frac of STY)** | **NMR Normalized Peak Areas** | | | | | |
|---|---|---|---|---|---|---|
| | **X** | **Y** | **Z** | **A** | **BC** | **D** |
| 0.25280 | 0.25577 | 0.51523 | 0.21804 | 0.10522 | 0.70693 | 0.28179 |
| 0.21276 | 0.20125 | 0.51541 | 0.24817 | 0.12978 | 0.63871 | 0.18296 |
| *0.21232* | *0.17477* | *0.54829* | *0.27695* | *0.09908* | *0.68361* | *0.21731* |
| *0.22490* | *0.20291* | *0.53759* | *0.25950* | *0.08317* | *0.71368* | *0.20315* |
| *0.39255* | *0.16945* | *0.60578* | *0.22477* | *0.08787* | *0.78201* | *0.13012* |
| *0.39715* | *0.15556* | *0.53333* | *0.31112* | *0.11592* | *0.75007* | *0.13401* |
| 0.38739 | 0.13646 | 0.51402 | 0.25159 | 0.10262 | 0.70583 | 0.09642 |
| 0.37079 | 0.19161 | 0.57123 | 0.26926 | 0.11551 | 0.75628 | 0.10562 |
| 0.52279 | 0.17660 | 0.60656 | 0.26523 | 0.19847 | 0.82470 | 0.03985 |
| *0.51690* | *0.11864* | *0.62423* | *0.25713* | *0.11206* | *0.81746* | *0.07048* |
| *0.51701* | *0.12033* | *0.60967* | *0.27000* | *0.11255* | *0.77942* | *0.10803* |
| 0.50315 | 0.16342 | 0.65990 | 0.23349 | 0.15709 | 0.82575 | 0.05631 |
| *0.79132* | *0.04592* | *0.74733* | *0.20676* | *0.13330* | *0.78146* | *0.08524* |
| *0.79186* | *0.05760* | *0.76525* | *0.17715* | *0.15984* | *0.74077* | *0.09938* |
| 0.80475 | 0.02953 | 0.76626 | 0.21315 | 0.16293 | 0.84033 | 0.01746 |
| 0.78651 | 0.01565 | 0.73745 | 0.18318 | 0.17300 | 0.81927 | 0.07095 |

The analysis was conducted on the augmented data, using both the EVM and determinant criterion approaches for parameter estimation. Additive and multiplicative error structures were examined in EVM for the augmented data set, producing the exact JCRs seen in Figure 5.6.

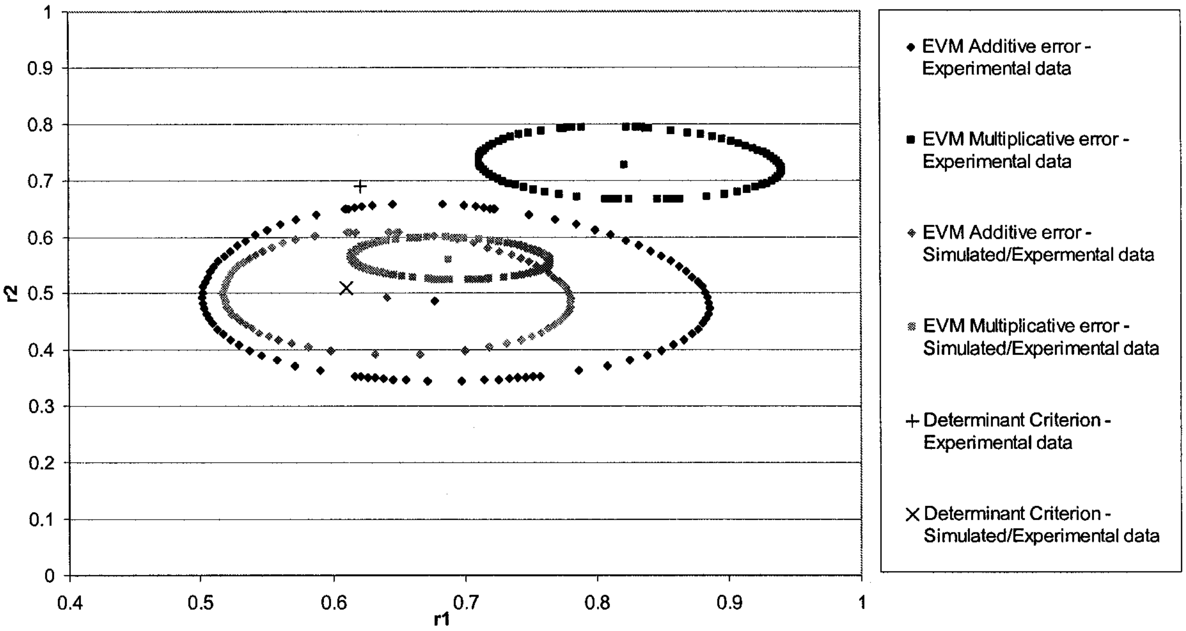


**Figure 5.6: Exact JCRs for EVM analysis of experimental and 'simulated/experimental' NMR normalized peak areas data.**

Figure 5.6 shows that the augmented data results in the reactivity ratio estimates by the determinant criterion and the EVM method being in agreement with one another. That is, the determinant criterion estimate using the augmented data falls within both the EVM additive error (Experimental) and the EVM additive error (Simulated/Experimental) exact JCRs. It was anticipated that the additive error EVM cases would agree with the determinant criterion estimate, due to the determinant criterion assumption of an additive error structure. Therefore, this indicated that the determinant criterion estimate may be highly dependent on the size of the data set, while the EVM (additive error structure) is not. Furthermore, the EVM (multiplicative error structure) appears to be dependent on the size of the data set, as when the data size increases the exact JCR shifts to be significantly overlapping both the EVM additive error (Simulated/Experimental) and the EVM additive error (Experimental) case. Prior to the augmentation of the data (i.e., only using the experimental data) there was significant separation of the EVM contours for the different imposed error structures; which can now be attributed to the EVM normalized peak areas data being dependent on sample size when a multiplicative error structure is imposed.

Additionally, the size of the exact JCR is affected by sample size for both the additive and multiplicative imposed error structures. This was to be expected as when the data sample size increases, more information is given to the EVM routine; thus reducing the uncertainty in the parameter estimates.

## 5.4 Case Study II: Styrene/Methyl Methacrylate

Maxwell et al. (1993) studied the styrene (STY) and methyl methacrylate (MMA) system at 40°C in bulk copolymerization and presented extensive experimental data on both copolymer composition and NMR normalized peak areas. Therefore, both data types were analyzed in order to: (1) determine whether the point estimates are influenced by the data type used; (2) determine if one data type results in a smaller confidence region (less uncertainty); and (3) evaluate the potential improvement of using both data types combined.

### 5.4.1 Using NMR Normalized Peak Areas or Composition Data?

In order to illustrate the use of NMR normalized peak areas data in comparison to copolymer composition data the Maxwell et al. (1993) case was analyzed using the EVM MATLAB program. The data set provided by Maxwell et al. (1993) can be seen below in Table 5.5.

**Table 5.5: NMR normalized peak areas data and copolymer composition data from Maxwell et al. (1993).**

| Feed Composition f1 (mol frac of STY) | Copolymer Composition F1 (mol frac of STY) | NMR Normalized Peak Areas | | | | | |
|---|---|---|---|---|---|---|---|
| | | X | Y | Z | A | B+C | D |
| 0.073 | 0.135 | 0.191 | 0.557 | 0.252 | 0.069 | 0.503 | 0.428 |
| 0.109 | 0.198 | 0.243 | 0.524 | 0.232 | 0.079 | 0.56 | 0.361 |
| 0.199 | 0.307 | 0.203 | 0.528 | 0.269 | 0.106 | 0.651 | 0.243 |
| 0.262 | 0.355 | 0.187 | 0.561 | 0.252 | 0.148 | 0.681 | 0.171 |
| 0.377 | 0.419 | 0.155 | 0.542 | 0.303 | 0.113 | 0.767 | 0.12 |
| 0.458 | 0.489 | 0.148 | 0.558 | 0.293 | 0.154 | 0.771 | 0.075 |
| 0.557 | 0.539 | 0.116 | 0.633 | 0.241 | 0.135 | 0.803 | 0.062 |
| 0.705 | 0.648 | 0.08 | 0.624 | 0.296 | 0.166 | 0.808 | 0.025 |

Similar to the previous case study, the eliminated NMR responses, to avoid the issues of colinearity, were X and D. The parameter estimation was conducted using either copolymer composition data or the NMR normalized peak areas data. The analysis of the data required the further sub-categorization to be either an imposed additive error structure or multiplicative error structure.

### *5.4.1.1 Additive Error Structure*

The point estimates from using the different data sets along with the point estimates published by Maxwell et al. (1993), can be seen in Table 5.6.

**Table 5.6: Point estimates for NMR normalized peak areas and composition data with an imposed additive error structure and the literature values published by Maxwell et al. (1993).**

| | Data Source | Estimation Method | $r_1$ | $r_2$ |
|---|---|---|---|---|
| Maxwell et al. (1993) | NMR normalized peak areas | NLLS | 0.51 | 0.52 |
| Maxwell et al. (1993) | Composition | NLLS | 0.48 | 0.42 |
| Current work | Maxwell NMR normalized peak areas | EVM | 0.526 | 0.5078 |
| Current work | Maxwell composition | EVM | 0.479 | 0.4182 |

The exact JCRs of the NMR normalized peak areas case versus the copolymer composition case demonstrates that the use of the NMR normalized peak areas data significantly reduces the area of the contour and thus uncertainty in the parameter estimates (refer to Figure 5.7).

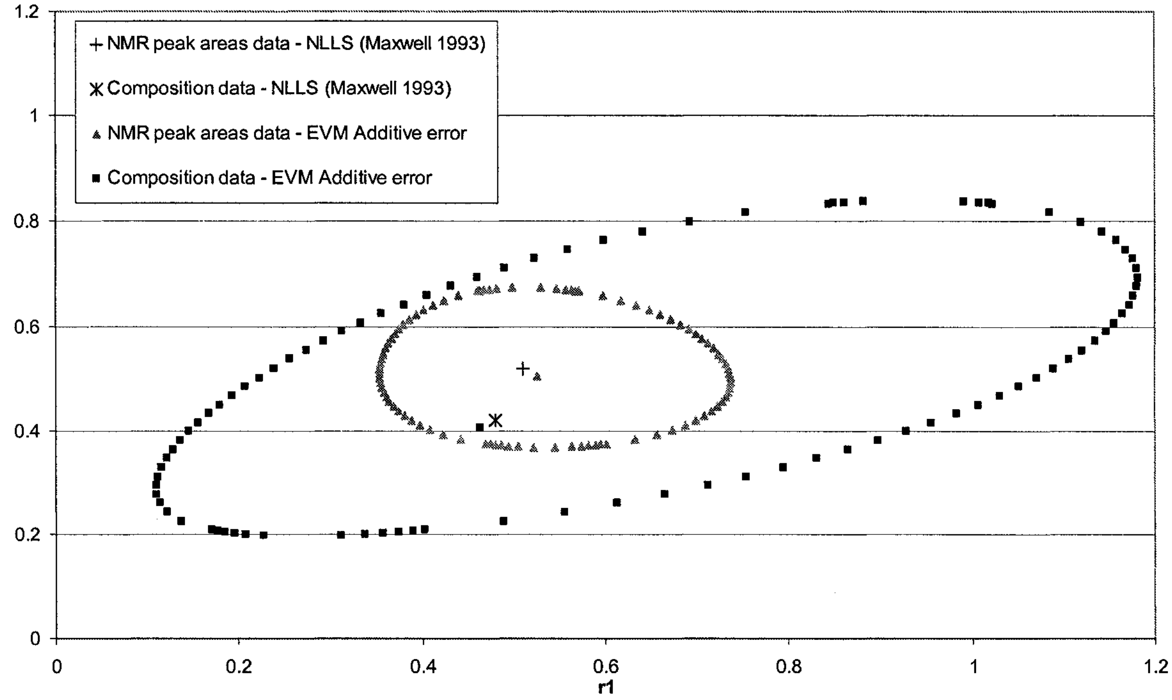


**Figure 5.7: Exact JCRs for EVM analysis of Maxwell et al. (1993) NMR normalized peak areas data and composition data cases (additive error structure).**

Figure 5.7 clearly shows that the point estimates given by Maxwell et al. (1993) fall within the exact JCRs of both data source cases. It can then be said that the literature values are in good agreement with the EVM results when an additive error structure is imposed on the data sets.

### *5.4.1.2 Multiplicative Error Structure*

The point estimates from using either NMR normalized peak areas data or copolymer composition data, with imposed multiplicative error structures, along with the point estimates published by Maxwell et al. (1993), can be seen in Table 5.7.

**Table 5.7: Point estimates for the NMR normalized peak areas data and composition data, with imposed multiplicative error structures, and the literature values published by Maxwell et al. (1993).**

| | Data Source | Estimation Method | $r_1$ | $r_2$ |
|---|---|---|---|---|
| Maxwell et al. (1993) | NMR normalized peak areas | NLLS | 0.51 | 0.52 |
| Maxwell et al. (1993) | Composition | NLLS | 0.48 | 0.42 |
| Current work | Maxwell NMR normalized peak areas | EVM | 0.6512 | 0.3683 |
| Current work | Maxwell composition | EVM | 0.4787 | 0.418 |

The exact JCRs of the NMR normalized peak areas case and the copolymer composition case can be seen in Figure 5.8. Furthermore, in order to show that the MATLAB EVM program was calculating the point estimates and joint confidence regions correctly, the composition data for this case study was analyzed using the program RREVM (Polic et al., 1998). The resulting exact JCR and pointe estimates obtained from the RREVM program can also be seen in Figure 5.8.

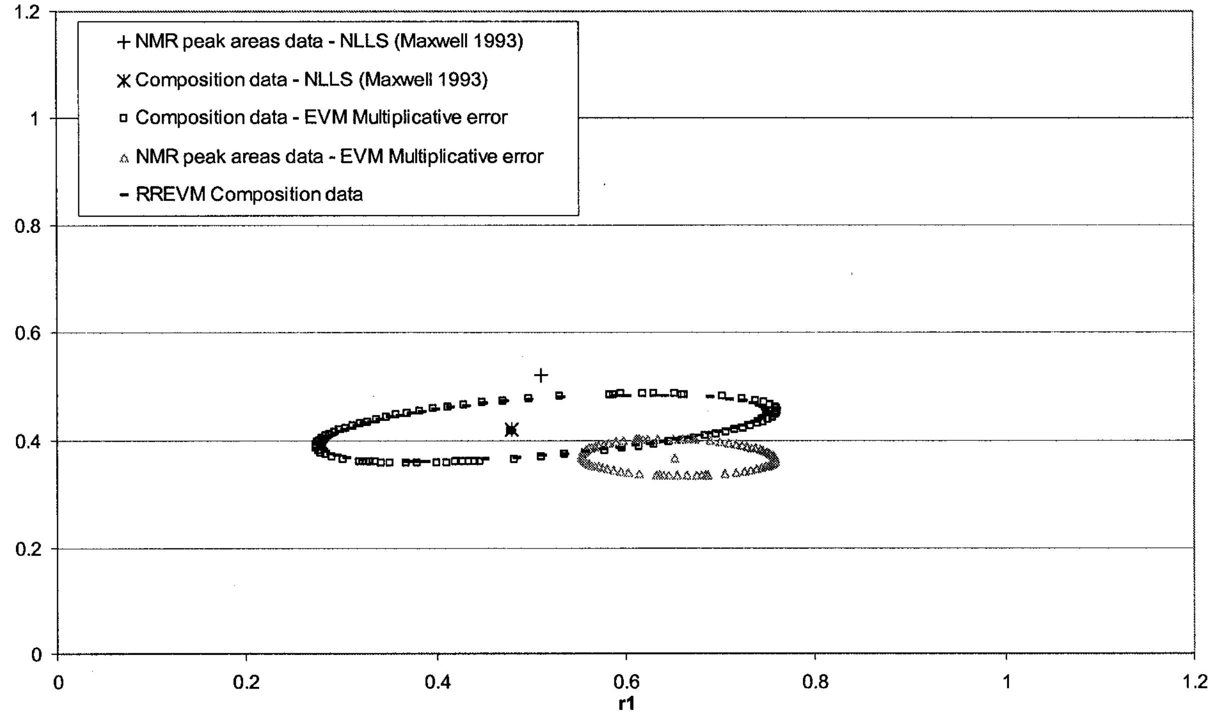


**Figure 5.8: Exact JCRs for EVM analysis of Maxwell et al. (1993) NMR normalized peak area data and composition data cases (multiplicative error).**

Figure 5.8 clearly shows that the point estimates and exact JCR obtained from the RREVM program agree with the result obtained using the EVM MATLAB program (for composition data with multiplicative error at the same error levels 5 and 10% for feed and copolymer composition measurements, respectively) and thus validate the effectiveness of the developed EVM MATLAB program.

Furthermore, similar to the previous additive error structure analysis, in Figure 5.8 it is apparent that the use of the NMR normalized peak areas data resulted in a smaller exact JCR compared to that obtained from the analysis of the composition data. Therefore, it can be said that the use of the NMR normalized peak areas data results in less uncertainty in the parameter estimates, regardless of the error structure imposed.

A difference to the previous additive error structure case however is that the NLLS point estimate by Maxwell et al. (1993) for the NMR normalized peak areas data lies outside the exact JCR obtained using the peak areas data in EVM (multiplicative error structure), refer to Figure 5.8. However, further inspection of the parameter estimation methodology used by Maxwell et al. (1993) showed that the estimated parameters were based on analysis of all six peak areas (which contain two near linear dependencies), whereas we used four of the six peak areas to avoid the issues of colinearity. Furthermore, Maxwell et al. (1993) uses the NLLS estimation approach, which is considered to be a statistically invalid parameter estimation technique for reactivity ratio parameter estimation.

The additive and multiplicative error structure cases can be directly compared in Figure 5.9 for the NMR normalized peak area data and composition data EVM analysis. It is apparent in the figure that when a multiplicative error structure is imposed on the NMR normalized peak areas data in EVM, that the resulting exact JCR shifts away from the exact JCR obtained when analyzing the same data, but imposing an additive error structure. The lack of overlap between the two exact JCRs (for the different error structures) is similar to what was seen in Case Study I (Section 5.3.2) and may be again due to the small sample size factor.

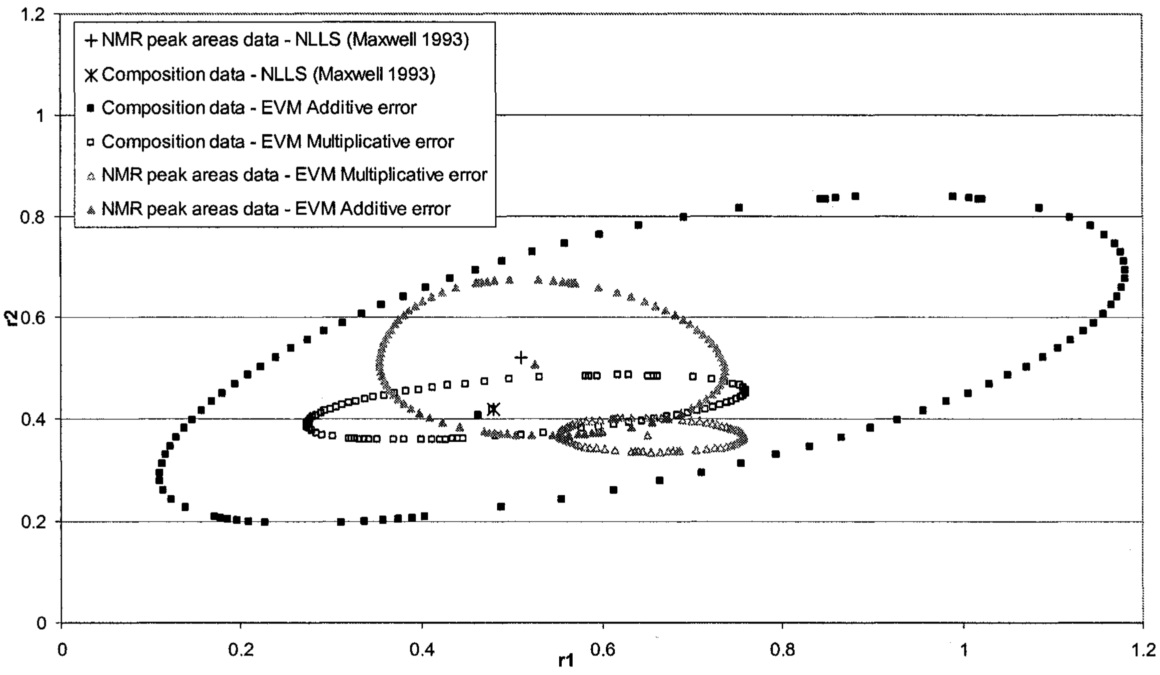


**Figure 5.9: Exact JCRs for EVM analysis of Maxwell et al. (1993) NMR normalized peak area data and composition data cases (additive and multiplicative error).**

By considering the previous discussion and figures the following overall statements can then be made:

i) The use of NMR normalized peak areas data results in less uncertainty in the parameter estimates (reactivity ratios) than using the conventional copolymer composition data.

ii) The use of either multiplicative or additive error structure to copolymer composition data does not significantly affect the location of the point estimates obtained; however the uncertainty in the parameter estimates is significantly smaller when using a multiplicative error structure.

iii) The use of either multiplicative or additive error structure with the NMR normalized peak areas data does significantly affect the location of the point estimates and the confidence region (uncertainty) of the parameters.

iv) There is little overlap and thus agreement between the NMR normalized peak areas data (multiplicative error) EVM exact JCR and the copolymer composition data (multiplicative error) EVM exact JCR.

v) There is overlap and thus agreement between the NMR normalized peak areas data (additive error structure) EVM exact JCR and the copolymer composition data (multiplicative and additive error structure) EVM exact JCR.

vi) There is little overlap and thus agreement between the NMR normalized peak areas data (multiplicative error structure) EVM exact JCR and the NMR normalized peak areas data (additive error structure) EVM exact JCR.

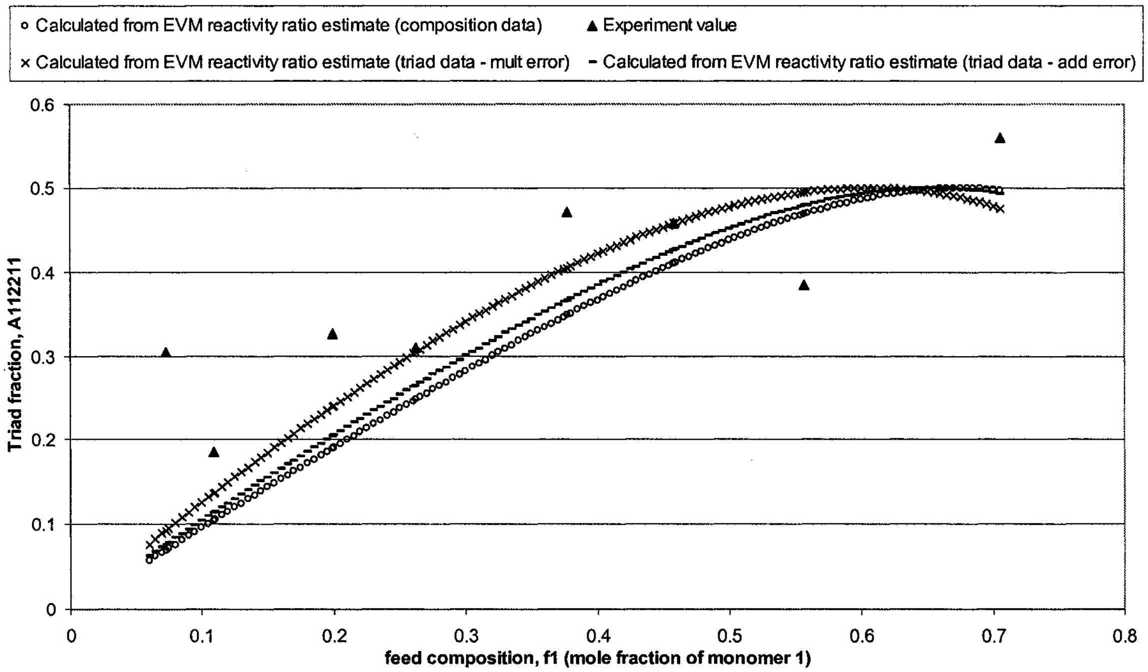
The question then becomes, is multiplicative error structure the incorrect structure for NMR normalized peak areas data, or is the separation/shift of the exact JCR due to small sample size issues. As a result, it is recommended for future studies that the true error structure of triad fractions data be determined (refer to Section 7.2, point 1 - error structure study) and the effect of data sample size studied in greater detail.

### 5.4.2 Diagnostic Checking

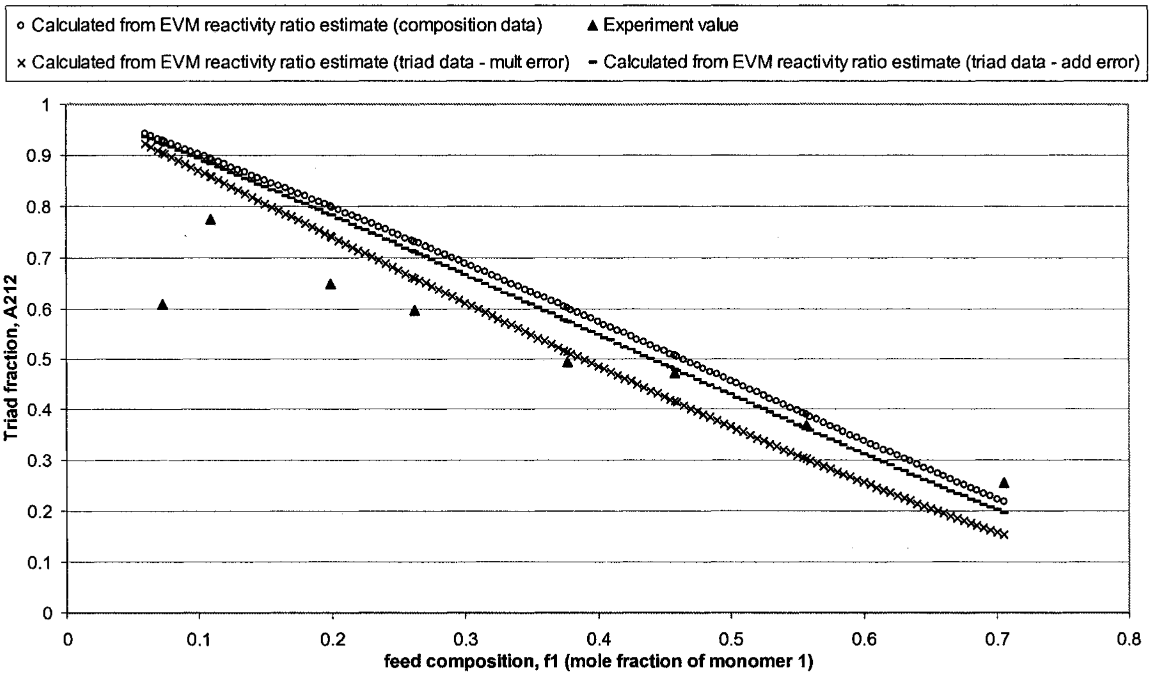
In order to determine whether the reactivity ratio estimates in fact model the experimental results accurately, diagnostic checking is performed. The EVM reactivity ratio estimates used in this section were obtained from analysis of Maxwell et al. (1993) normalized peak areas data with an imposed multiplicative error structure ($r_1 = 0.6512$, $r_2 = 0.3683$), normalized peak areas with an imposed additive error structure ($r_1 = 0.526$, $r_2 = 0.5078$), and composition data with an imposed multiplicative error structure ($r_1 = 0.4787$, $r_2 = 0.418$).

The reactivity ratio estimates were used in the equations for triad fractions (Equation 5.1) to obtain 'predicted' triad fractions, which were compared to 'experimental' triad fractions. As Maxwell det al. (1993) did not state explicitly the triad fractions results, rather the NMR normalized peak areas, the 'experimental' triad fractions were obtained by transforming the peak areas into triads via Equations 5.2 and 5.3. The reactivity ratios were also used in the Mayo-Lewis model to provide 'predicted' copolymer composition values to compare to the experimental values collected by Maxwell et al. (1993).

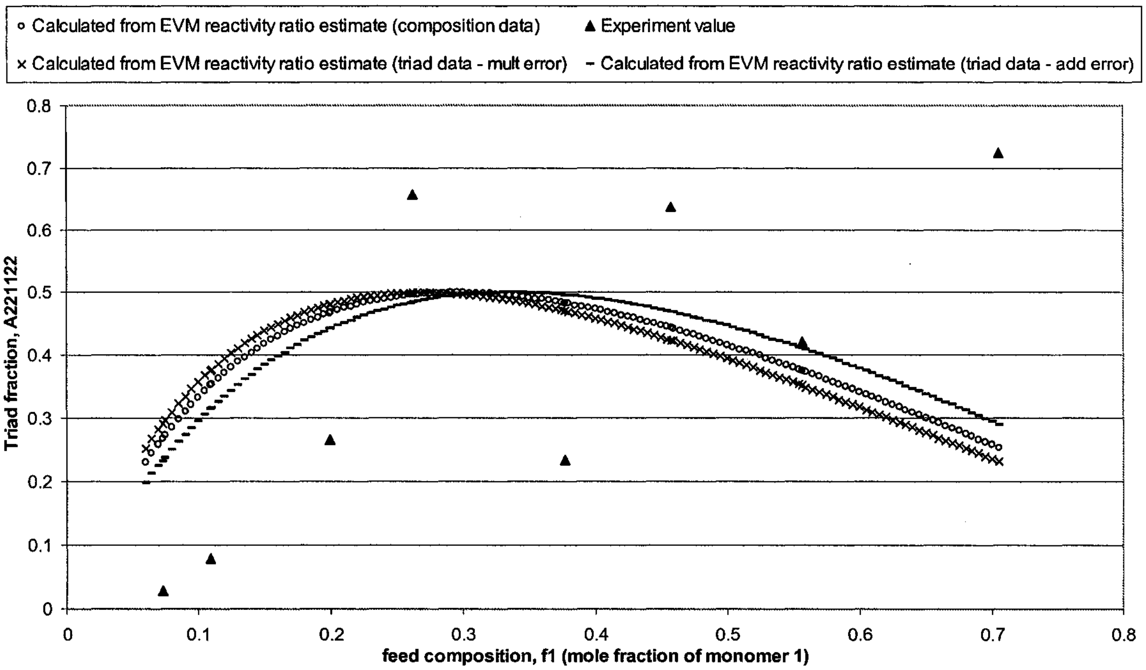
Figures 5.10 a)- d) show the selected triad fractions predicted from the triad fractions equations, using the EVM reactivity ratio estimates of the NMR normalized peak areas data (referred to in the figures as 'triad data') and composition data, and the so called 'experimental' triad fractions. Figure 5.10 e) shows the copolymer composition predicted from the Mayo-Lewis equation and the copolymer composition experimental values recorded by Maxwell et al. (1993).



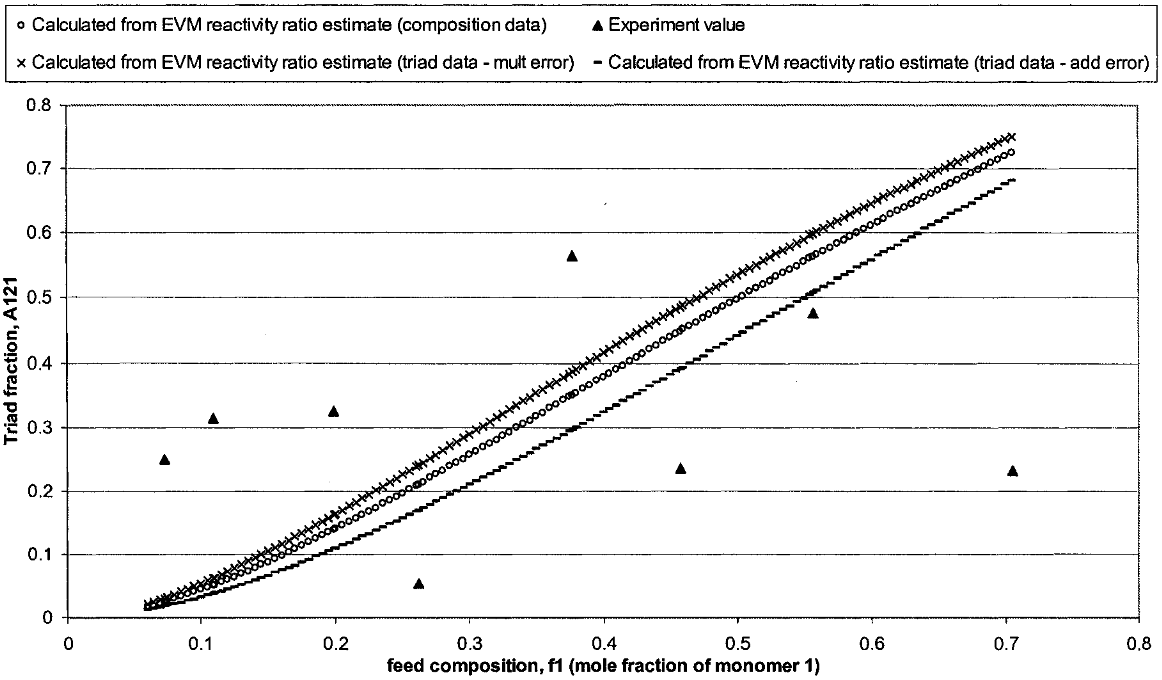
a)



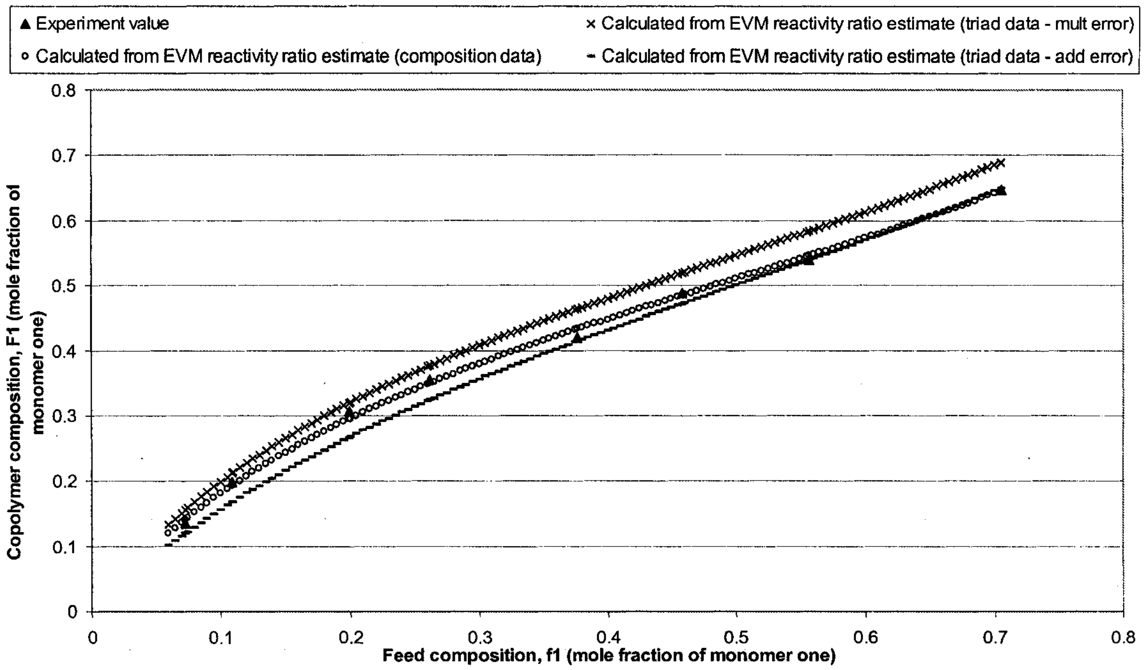
b)


○ Calculated from EVM reactivity ratio estimate (composition data)
▲ Experiment value
× Calculated from EVM reactivity ratio estimate (triad data - mult error)
- Calculated from EVM reactivity ratio estimate (triad data - add error)
Triad fraction, A221122
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
feed composition, f1 (mole fraction of monomer 1)

c)


○ Calculated from EVM reactivity ratio estimate (composition data)
▲ Experiment value
× Calculated from EVM reactivity ratio estimate (triad data - mult error)
- Calculated from EVM reactivity ratio estimate (triad data - add error)
Triad fraction, A121
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
feed composition, f1 (mole fraction of monomer 1)

d)

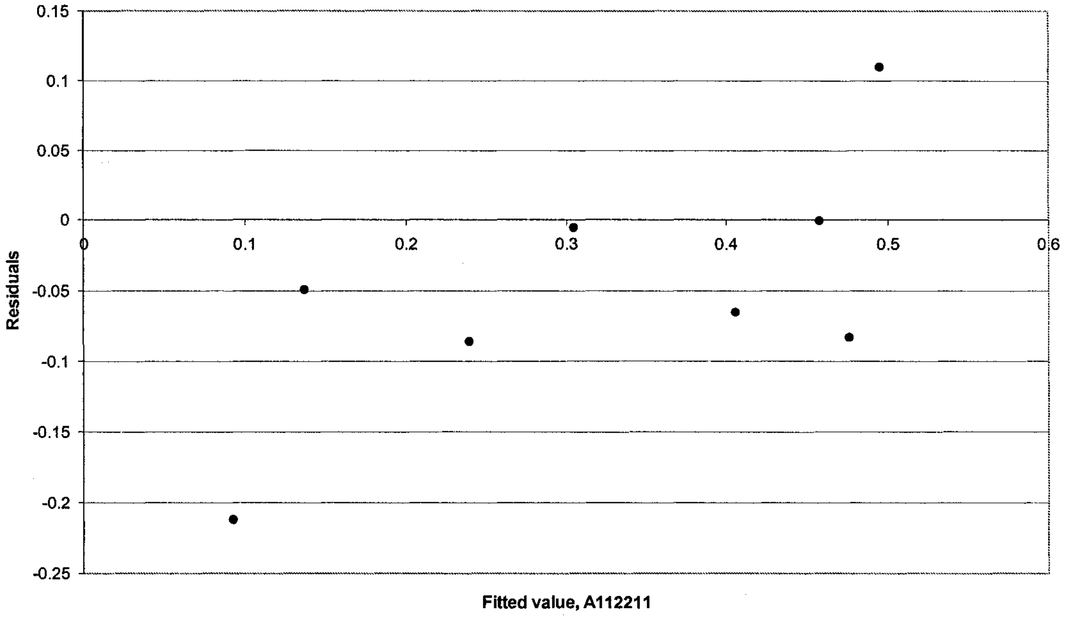


e)

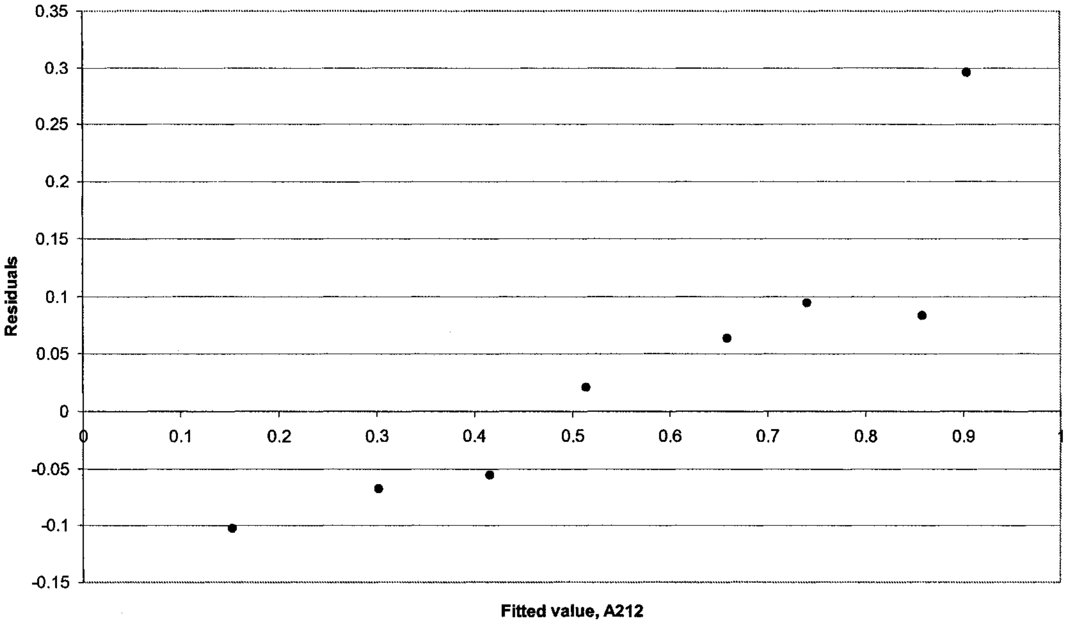
**Figure 5.10 a) - d): Predicted triad fractions using the reactivity ratio estimates obtained from EVM (multiplicative error) analysis of the NMR normalized peak areas (triad data) and composition data in Equation 5.1 and the 'experimental' triad fractions obtained from transforming the measured NMR normalized peak areas. e) Predicted copolymer composition using the EVM (multiplicative error) reactivity ratio estimates, obtained from analyzing NMR normalized peak areas (triad data) and composition data, in the Mayo-Lewis equation and the published copolymer composition measurements.**

As can be seen from Figures 5.10 a) - d) the 'predicted' triad fractions are not in agreement with the calculated 'experimental' triad fractions results (particularly for monomer-2-centered triads); regardless of whether the triads were calculated using either reactivity ratio estimates from the triads or composition data. The difference between the 'predicted' triad fractions and the 'experimental' results indicates there may be lack of fit by the model.

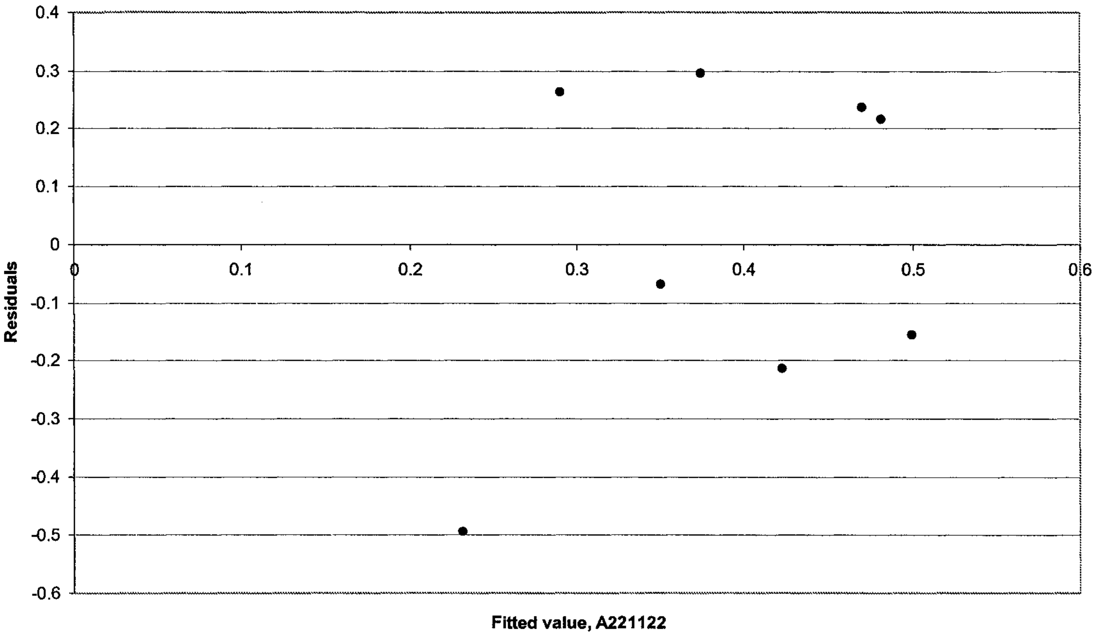
To determine lack of fit, residual analysis is performed by plotting the residuals (i.e., 'predicted'minus 'experimental') against the fitted ('predicted') values for the triad fractions, as seen in Figure 5.11 a) to d). In the below analysis the fitted values are the triads calculated from Equation 5.1 with EVM reactivity ratio estimates obtained from analyzing the NMR normalized peak areas ($r_1$ = 0.6512 and $r_2$ = 0.3683), while the 'experimental' values are obtained by transformation of the measured NMR peaks into triads via Equation 5.2 and 5.3.


0.15
0.1
0.05
0
-0.05
-0.1
-0.15
-0.2
-0.25
Residuals
0
0.1
0.2
0.3
0.4
0.5
0.6
Fitted value, A112211

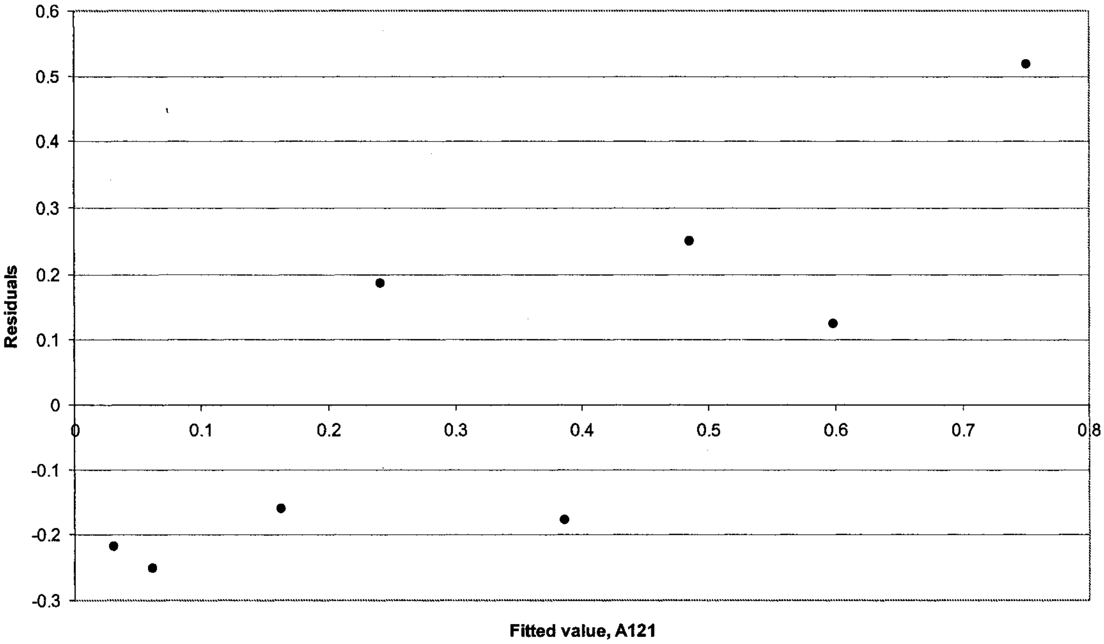
a)


0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
-0.05
-0.1
-0.15
Residuals
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Fitted value, A212

b)



c)

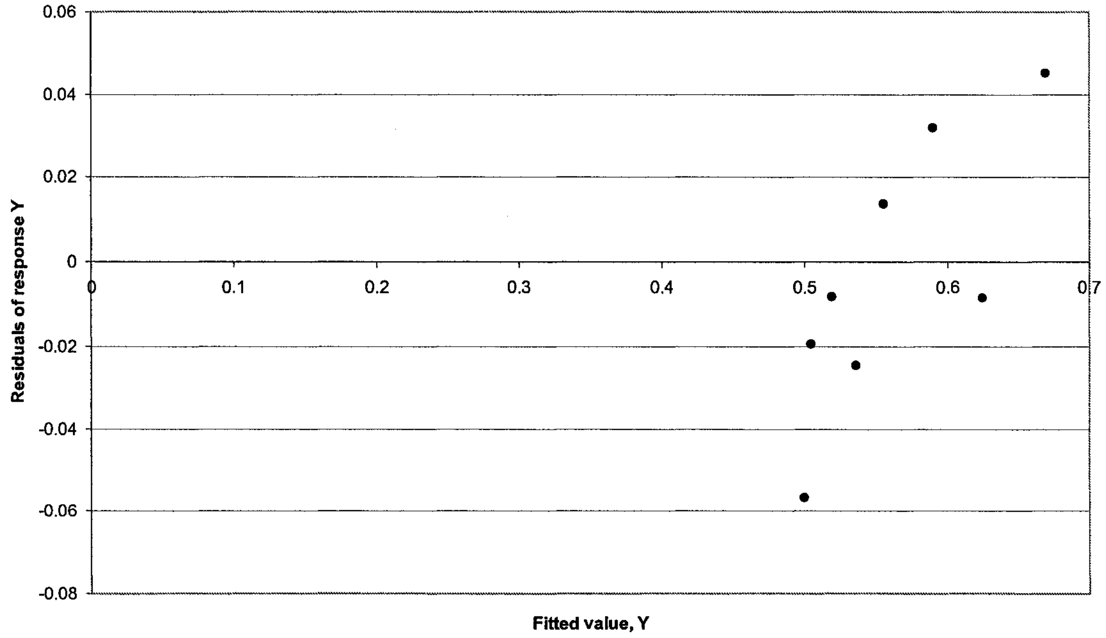


d)

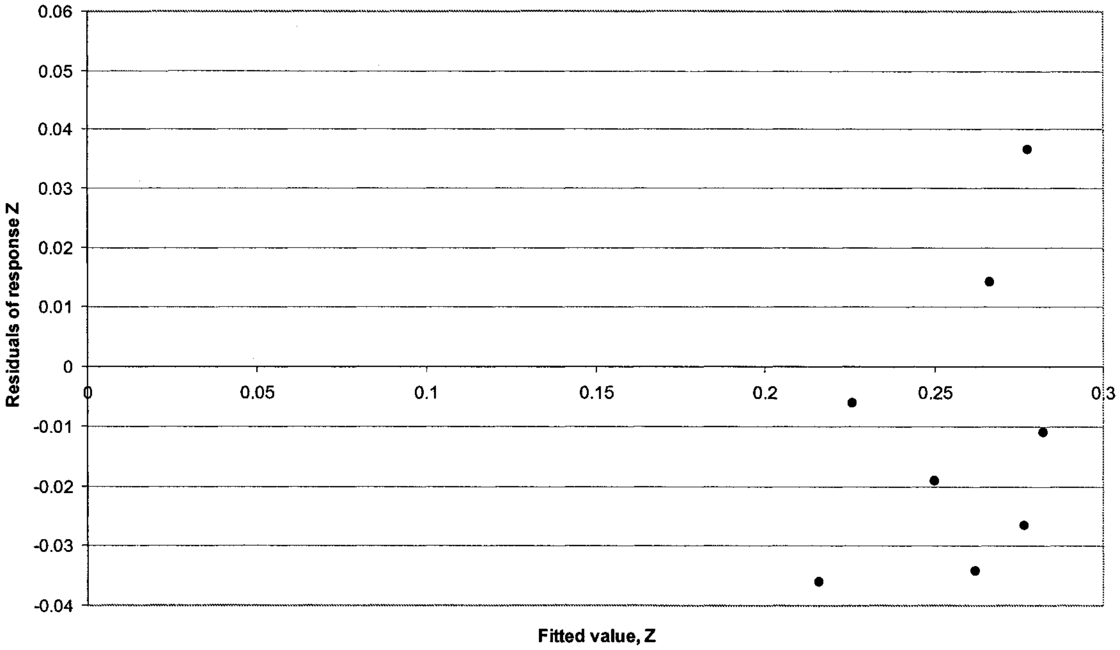
**Figure 5.11 a)-d): Residual analysis for each predicted triad fraction.**

It can be seen from Figures 5.11 a) – d) the residuals are random except for the triad fractions, $A_{212}$ and $A_{121}$ which appear to have linear trends. However, residual analysis should really be performed on the actual measured variable (i.e., normalized peak areas X, Y, Z, A, BC, and D), rather than transformed experimental results. That is, the 'experimental' values used in the above residual analysis were in fact calculated triad fractions, obtained by transformation of the true measured response (peak areas) via Equations 5.2 and 5.3. Therefore, trends in the residuals may in fact be illustrating the triad fractions equations inability to represent the data, or the tacticity parameter equations (Equation 5.2 and 5.3) inability to correctly transform the peak areas into triad fractions.

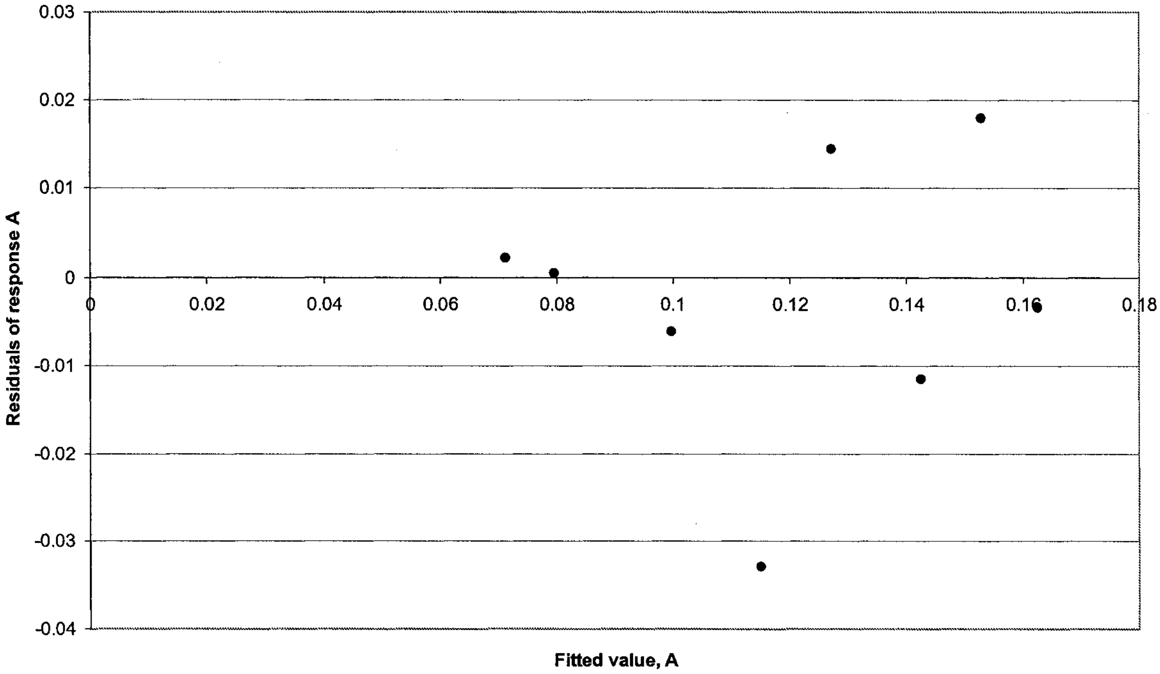
Subsequently, the residual analysis was redone using the true measured response as the variable under consideration. That is, the residuals were calculated by using the EVM estimates of the true values of the normalized peak areas and the experimentally measured normalized peak areas recorded by Maxwell et al. (1993). Due to the fact that the EVM analysis only uses four out of the six available normalized peak area responses, only those responses used in the analysis can be shown (namely Y, Z, A and BC). For example, the residual for peak Y was calculated by subtracting the experimentally recorded normalized area for peak Y from the estimate of the true value of the normalized area for peak Y by EVM, at a certain feed composition. Therefore, comparing the actual experimentally measured values to those directly estimated by EVM yields the following residual plots seen in Figures 5.12 a) - d).



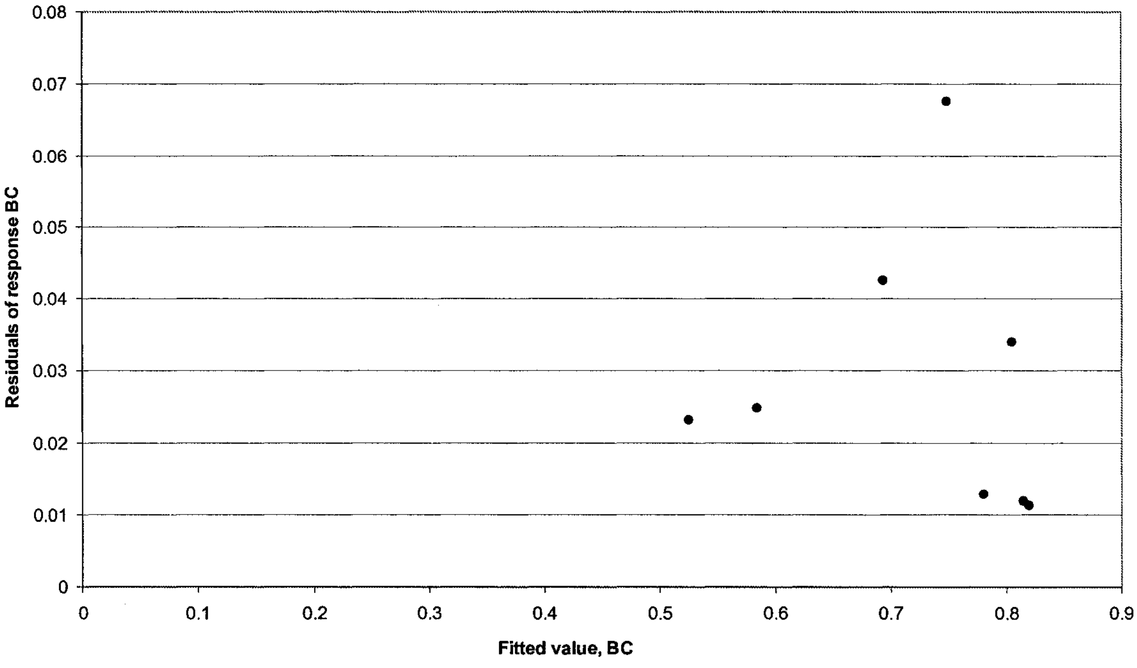
a)


0.06
0.05
0.04
0.03
0.02
0.01
0
-0.01
-0.02
-0.03
-0.04
Residuals of response Z
0
0.05
0.1
0.15
0.2
0.25
0.3
Fitted value, Z

b)


0.03
0.02
0.01
0
-0.01
-0.02
-0.03
-0.04
Residuals of response A
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
0.18
Fitted value, A

c)



d)

**Figure 5.12 a)-d): Residual analysis for each estimate of the true value of the measured response in EVM.**

It can be seen in Figures 5.12 a) – d) when the NMR normalized peak areas are considered there are no trends present in the residuals. This suggests that the transformation of the peak areas into triad fractions using the tacticity equations (Equations 5.2 and 5.3) induces the trend in the residuals seen in $A_{121}$ and $A_{212}$. Understandably then, the transformation of normalized peak areas into triads needs further consideration and analysis; along with the inclusion of the tacticity variables as parameters in the EVM estimation routine.

### 5.4.3 NMR Normalized Peak Areas Data and Composition Data Combined vs. NMR Normalized Peak Areas Data

The next stage of analysis was to determine whether using all the available information in the EVM program would result in a further reduction of uncertainty in the parameter estimates. In other words, the EVM MATLAB program was run using the combined composition and NMR normalized peak areas data to determine whether a significant improvement in the degree of uncertainty in the parameter estimates, compared to using only NMR normalized peak areas data, was possible. In this analysis only an imposed multiplicative error structure was considered. Figure 5.13 shows the exact JCR obtained.

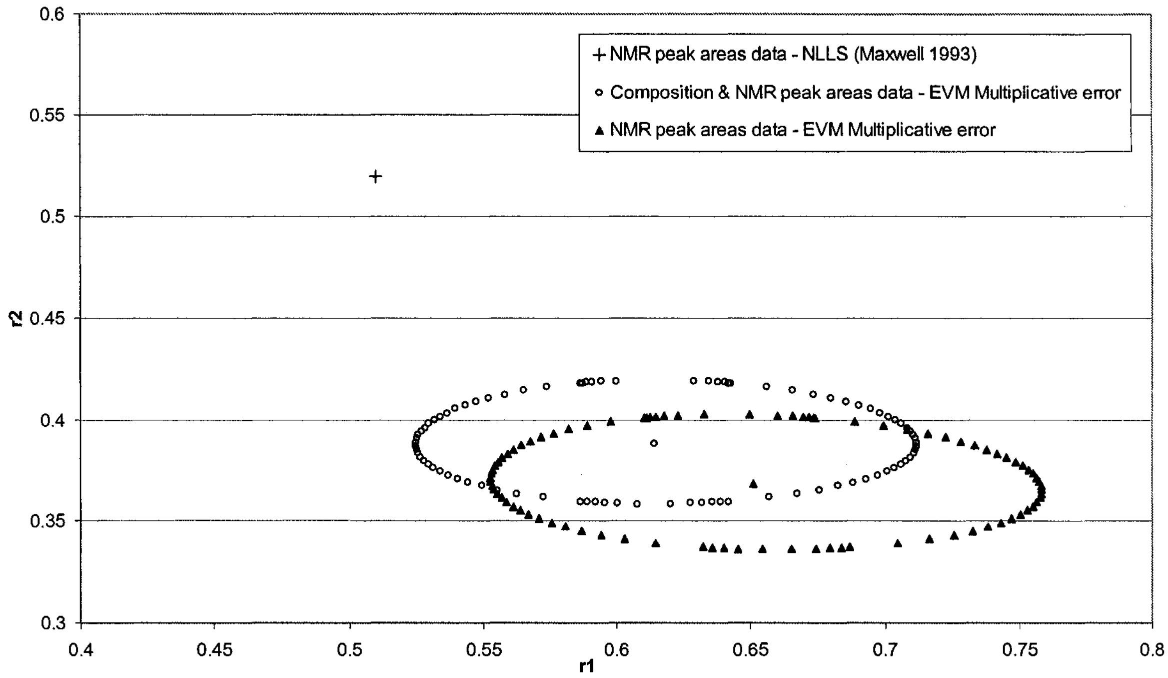


**Figure 5.13: Exact JCRs for EVM (Multiplicative error structure) analysis of Maxwell et al. (1993) NMR normalized peak areas and composition data combined vs. only NMR normalized peak areas data.**

The additional use of the copolymer composition data with the NMR normalized peak areas data does not appear to have a dramatic improvement in the confidence of the estimates (refer to Figure 5.13), compared to the increase in confidence seen between using composition data to NMR normalized peak areas data (see Figure 5.8). That is, by comparing Figures 5.8 and 5.13, the decrease in area of the exact JCR when both data sets are used (i.e., combining the copolymer and peak areas data) does not seem sufficiently significant to warrant the need for conducting the measurements of the copolymer composition, but rather only obtaining the NMR normalized peak areas triad data.

## 5.5 Case Study III: Acrylamide/ Acrylonitrile

Mukherjee et al. (1998) studied the acrylamide/acrylonitrile (AN) system at 65°C in bulk copolymerization and presented experimental data for both copolymer composition and triad fractions. Minor changes were made to adapt the EVM MATLAB program to explicitly use triad fractions data as the input, rather than normalized NMR peak areas data.

Both data types were then analyzed in order to: (1) demonstrate the influence of the data type on the point estimates; (2) determine if one data type resulted in less uncertainty in the parameter estimates; and (3) evaluate the potential improvement in the estimates when the data sets are combined. Also, as in the prior case studies, the influence of the error structure on the parameter estimates was examined.

### 5.5.1 Using Triad Fractions or Composition Data?

In order to then demonstrate the potential improvement in estimates obtained from analysis of triad fractions data compared to copolymer composition data, the Mukherjee et al. (1998) case was analyzed using the EVM MATLAB program. The data set provided by Mukherjee et al. (1998) can be seen below in Table 5.8.

**Table 5.8: Data set of Mukherjee et al. (1998) acrylamide/acrylonitrile in bulk at 65°C.**

| **Feed Composition f1 (mol frac of Acrylamide)** | **Copolymer Composition F1 (mol frac of Acrylamide)** | **Triad Fractions** | | | | | |
|---|---|---|---|---|---|---|---|
| | | $A_{111}$ | $A_{112+211}$ | $A_{212}$ | $A_{121}$ | $A_{122+221}$ | $A_{222}$ |
| 0.3 | 0.3 | 0 | 0.25 | 0.75 | 0.09 | 0.42 | 0.49 |
| 0.4 | 0.4 | 0.05 | 0.32 | 0.63 | 0.15 | 0.51 | 0.34 |
| 0.5 | 0.5 | 0.06 | 0.38 | 0.56 | 0.23 | 0.51 | 0.26 |
| 0.55 | 0.55 | 0.11 | 0.42 | 0.47 | 0.31 | 0.47 | 0.22 |
| 0.6 | 0.6 | 0.14 | 0.46 | 0.4 | 0.36 | 0.49 | 0.14 |
| 0.65 | 0.65 | 0.17 | 0.47 | 0.36 | 0.44 | 0.45 | 0.11 |
| 0.7 | 0.7 | 0.21 | 0.49 | 0.3 | 0.47 | 0.44 | 0.09 |
| 0.75 | 0.75 | 0.27 | 0.5 | 0.23 | 0.57 | 0.38 | 0.05 |
| 0.8 | 0.8 | 0.33 | 0.52 | 0.15 | 0.66 | 0.3 | 0.04 |

#### *5.5.1.1 Additive vs. Multiplicative Error Structure*

In the article by Mukherjee et al. (1998) reactivity ratio point estimates were obtained by using the Kelen-Tudos and EVM (multiplicative error) parameter estimation method on copolymer composition data (refer to Table 5.9). Once the reactivity ratios were evaluated by Mukherjee et al. (1998) the estimates were then used by the group to predict values for the triad fractions. These triad fractions model predictions were then said to be in good agreement with the 'experimentally' determined triad fractions, by determining the correlation coefficient value R. A more statistically accurate method for determining whether the composition and triad fractions data result in similar estimates of the reactivity ratios, and thus highly correlated, is to determine the reactivity ratios using each data set in EVM. That is, the EVM reactivity ratio estimates were found using either composition data or triad fractions data, for both additive and multiplicative error structures (see Table 5.9).

**Table 5.9: Point estimates published by Mukherjee et al. (1998) and the estimates obtained by EVM MATLAB analysis of the composition and triad fractions data sets for the Acrylamide/AN BULK system at 65°C.**

| | Data Source | Estimation Method | Error Structure | $r_1$ | $r_2$ |
|---|---|---|---|---|---|
| Mukherjee et al. (1998) | Composition | KT | | 0.37 | 1.03 |
| Mukherjee et al. (1998) | Composition | EVM | Multiplicative | 0.36 | 1.01 |
| Current work | Composition | EVM | Additive | 0.3715 | 1.0285 |
| Current work | Composition | EVM | Multiplicative | 0.3469 | 0.9762 |
| Current work | Triad fractions | EVM | Additive | 0.3646 | 0.9948 |
| Current work | Triad fractions | EVM | Multiplicative | 0.3668 | 1.0138 |

The exact JCRs for the different data types and error structure can be seen in Figure 5.14. The point estimates published by Mukherjee et al. (1998) fall within the exact JCRs and thus can be said to be in good agreement with the results obtained from using both the triad fractions and composition data.

Also, the exact JCRs for the EVM composition analysis (with either an imposed multiplicative or additive error structure) are larger than those obtained when using triad fractions data (see Figure 5.14). Therefore, it can be said that the use of triad fractions data for this system results in less uncertainty in the reactivity ratio parameter estimates, regardless of the error structure implemented.

Furthermore, the exact JCR obtained from triad fractions analysis, with multiplicative error structure, falls within the exact JCR obtained from analysis of the triad fractions data with an imposed additive error structure. It can therefore be said that this system is well behaved and that the use of triad fractions data to determine reactivity ratio estimates will give good point estimates with the least uncertainty.

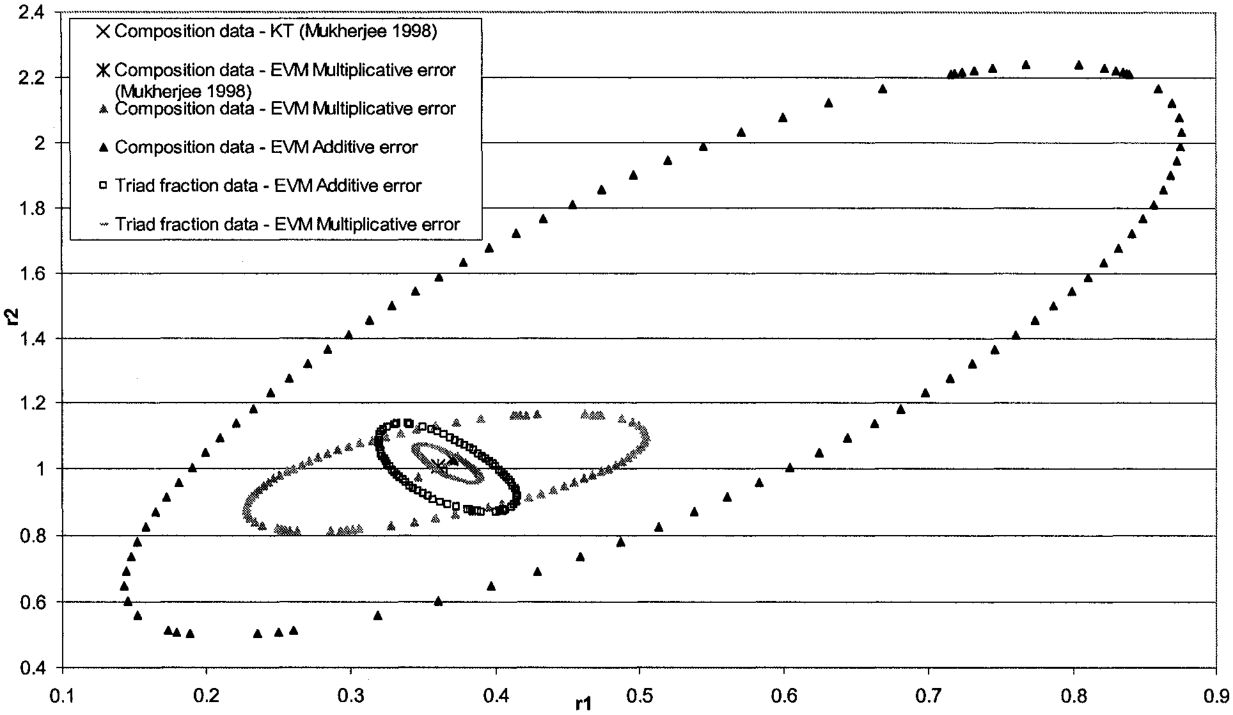
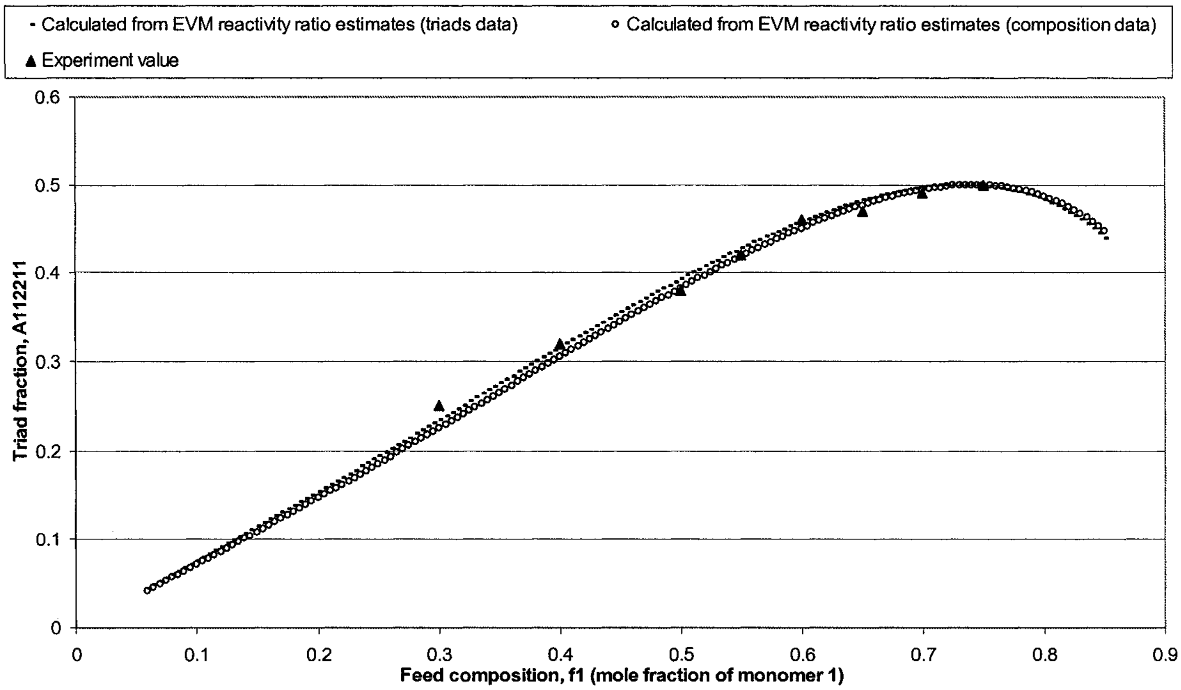


**Figure 5.14: Exact JCRs for EVM (additive and multiplicative error) analysis of Mukherjee et al. (1998) triad fractions vs. composition data for the Acrylamide/AN BULK system at 65°C.**

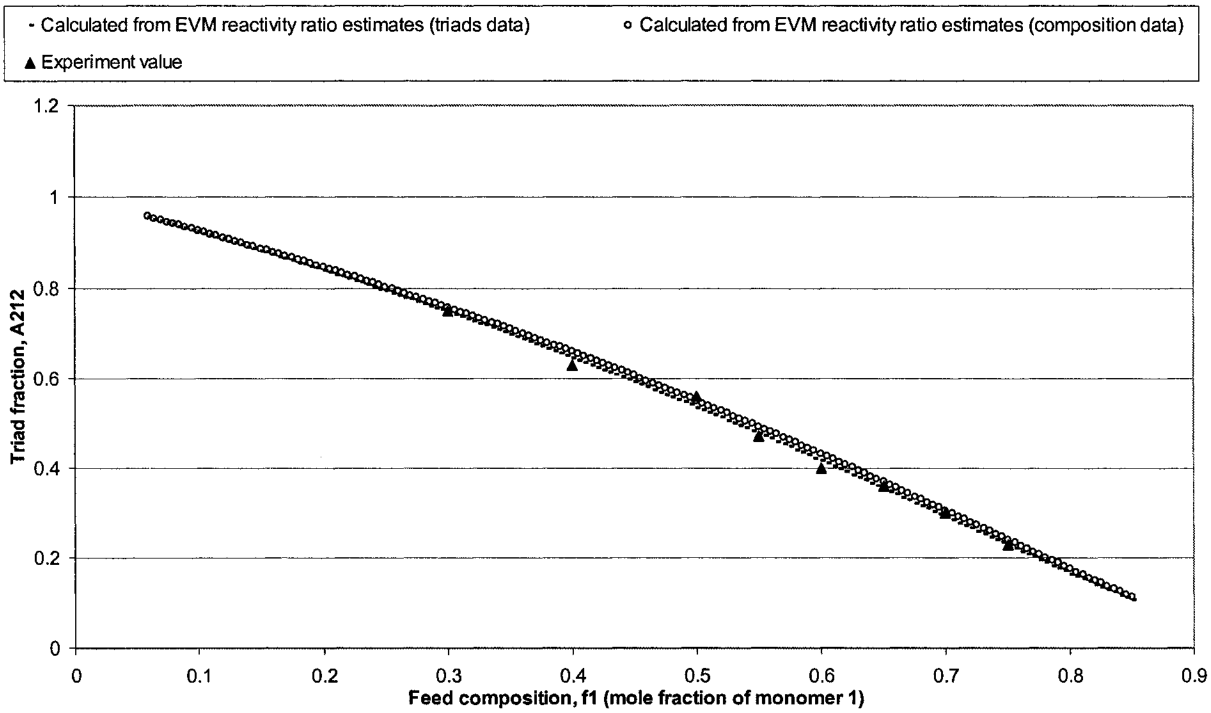
### 5.5.2 Diagnostic Checking

Diagnostic checking was performed in order to determine whether the reactivity ratio estimates in fact model the experimental results accurately. The EVM (multiplicative error) reactivity ratio estimates, obtained from analyzing Mukherjee et al. (1998) triad fractions and composition data, were used in the triad fractions equations (Equation 5.1) to compare the 'predicted' triad fractions with the published 'experimental' triad fractions.

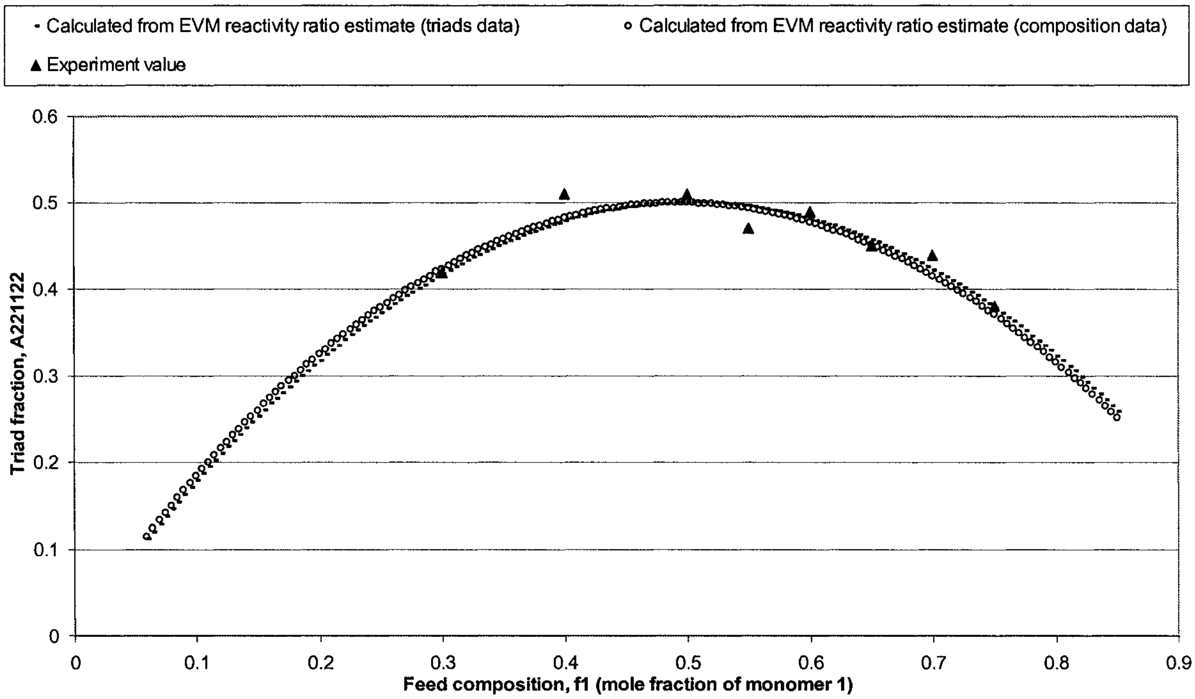
Figures 5.15 a) - d) show the selected triad fractions predicted from the equations, using the EVM (multiplicative error) reactivity ratio estimates, obtained from analysis of both the triad fractions and composition data. While Figure 5.15 e) shows the copolymer composition predicted from the Mayo-Lewis equation, using the EVM (multiplicative error) reactivity ratio estimates of the triad fractions and composition data.


- Calculated from EVM reactivity ratio estimates (triads data)
○ Calculated from EVM reactivity ratio estimates (composition data)
▲ Experiment value
Triad fraction, A112211
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
Feed composition, f1 (mole fraction of monomer 1)

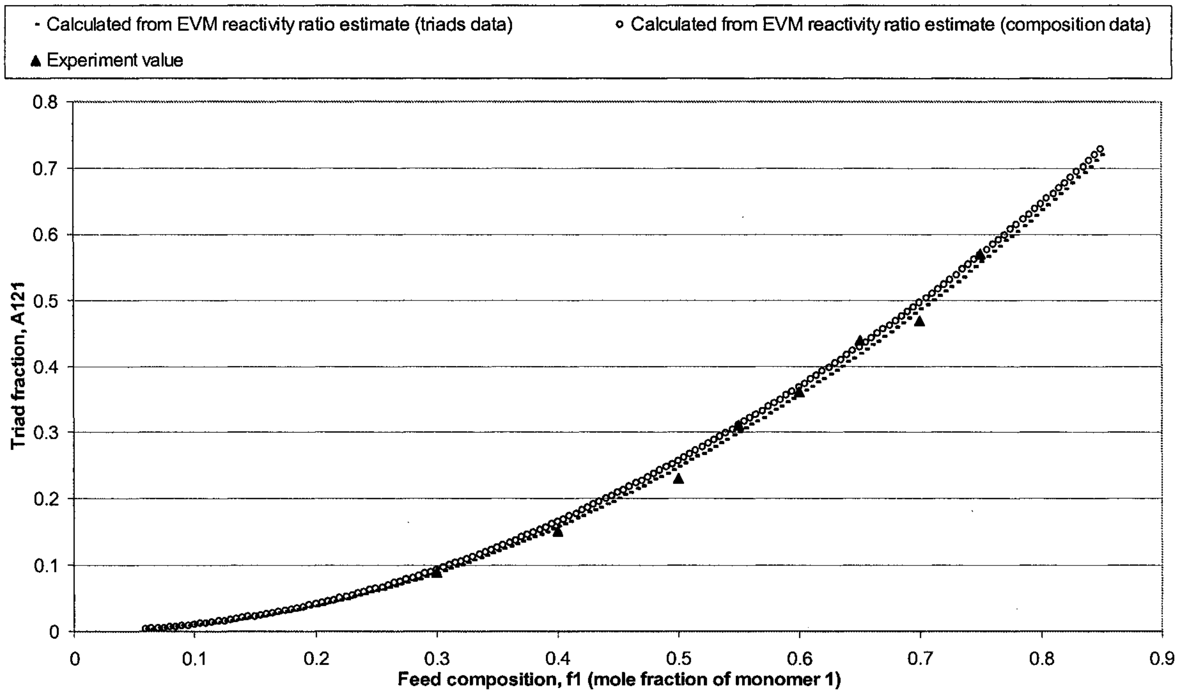
a)


- Calculated from EVM reactivity ratio estimates (triads data)
○ Calculated from EVM reactivity ratio estimates (composition data)
▲ Experiment value
Triad fraction, A212
1.2
1
0.8
0.6
0.4
0.2
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
Feed composition, f1 (mole fraction of monomer 1)

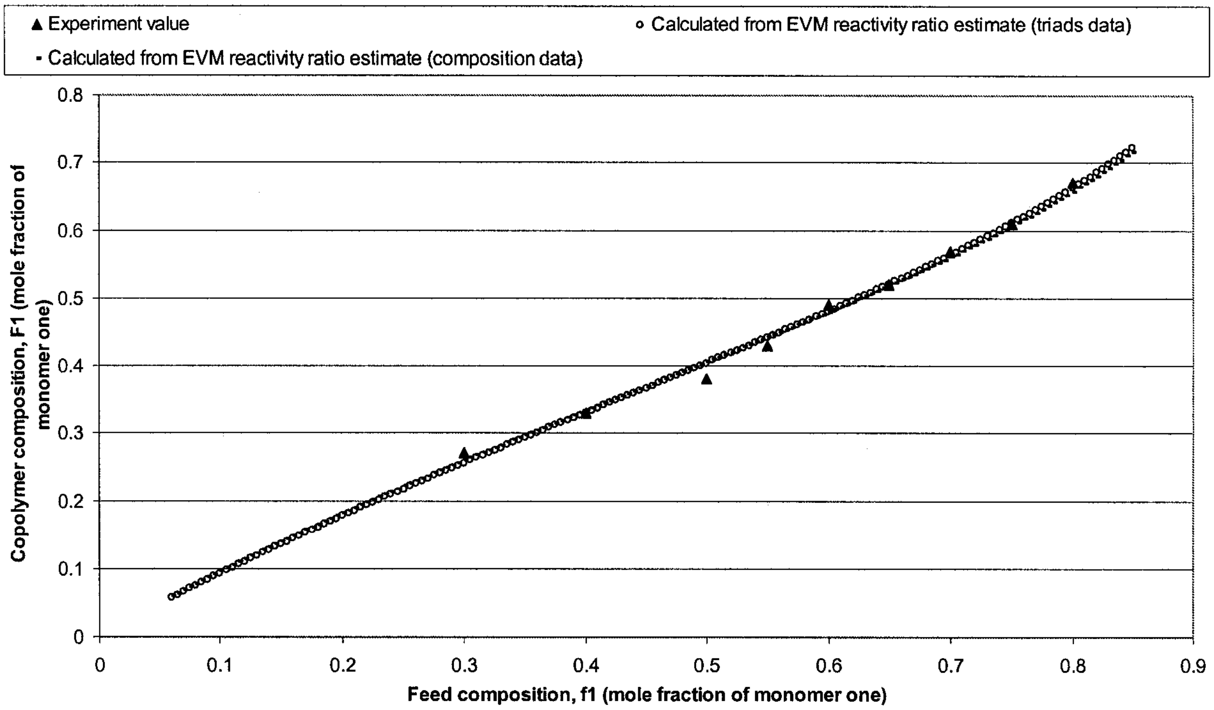
b)


- Calculated from EVM reactivity ratio estimate (triads data)
○ Calculated from EVM reactivity ratio estimate (composition data)
▲ Experiment value
Triad fraction, A221122
0
0.1
0.2
0.3
0.4
0.5
0.6
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
Feed composition, f1 (mole fraction of monomer 1)

c)


- Calculated from EVM reactivity ratio estimate (triads data)
○ Calculated from EVM reactivity ratio estimate (composition data)
▲ Experiment value
Triad fraction, A121
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
Feed composition, f1 (mole fraction of monomer 1)

d)



e)

**Figure 5.15 a) - d): Predicted triad fractions using EVM (multiplicative error) reactivity ratio estimates, obtained from analyzing triad fractions and composition data, in the triad fractions equations (Equation 5.1) and the published 'experimental' triad fractions. e) Predicted copolymer composition using the EVM (multiplicative error) reactivity ratio estimates, obtained from analyzing triad fractions and composition data, in the Mayo-Lewis equation and the published copolymer composition measurements.**

As can be seen from Figures 5.15 a) – d) the predicted triad fractions, calculated by using the EVM (multiplicative error) reactivity ratio estimates from analyzing the triad fractions and composition data, are in agreement with the 'experimental' triad fractions results. Furthermore, the copolymer composition can be predicted well with reactivity ratios that are estimated from either composition data or triad fractions data, as seen in Figure 5.15 e). These results were expected as in this case study the reactivity ratio estimates, from the different data sources, were in agreement and thus the model predictions were expected to be very similar.

### 5.5.3 Triad Fractions and Composition Data Combined vs. Triad Fractions Data

In order to determine whether using all the information available in the EVM program would result in a further reduction of uncertainty in the parameter estimates, analysis was conducted on using triad fractions with composition data versus triad fractions data only. Figure 5.16 thus illustrates the exact JCRs of the Acrylamide/AN system when using triad fractions and composition data in EVM compared to only triad fractions data, for a multiplicative error structure.

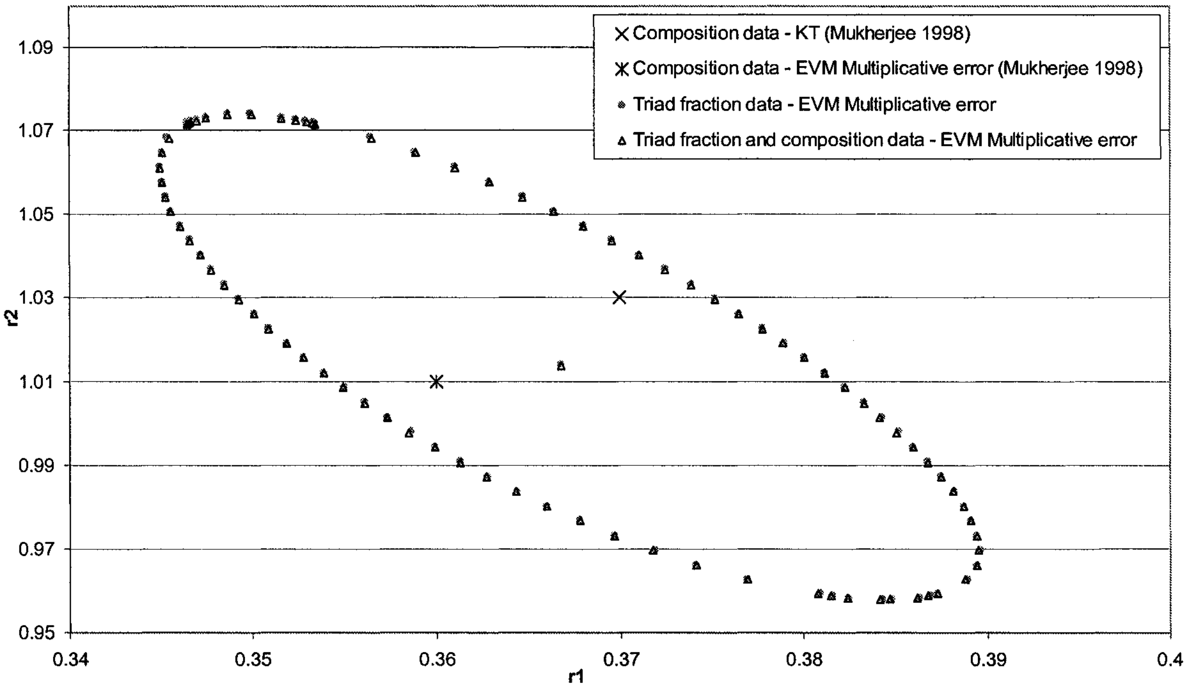


**Figure 5.16: Exact JCRs for EVM (multiplicative error) analysis of Mukherjee et al. (1998) triad and composition data vs. only triad fractions data for the Acrylamide/AN BULK system at 65°C.**

Considering the axis of the diagram in Figure 5.16 have been reduced considerably, it can be said that that the use of composition data in conjunction with the triad fractions data does not result in a decrease in uncertainty, compared to simply using triad fractions data. Subsequently, the effort to obtain the copolymer composition data is not warranted for parameter estimation experiments; rather the collection of triad fractions data is a better statistical data set.

## 5.6 Case Study IV: Acrylonitrile/Acrylic Acid

Brar et al. (1998) studied the acrylonitrile (AN)/acrylic acid (AA) system at room temperature (27°C) in bulk photo-initiated copolymerization and presented experimental data on both copolymer composition and triad fractions. Therefore, both data types were analyzed to determine whether different systems result in the same conclusion regarding the improvement in reactivity ratio estimates when triad fractions data is used. Also, similar to the prior case studies, the effect of the error structure on the parameter estimates was examined.

### 5.6.1 Using Triad Fractions or Composition Data?

In order to compare the use of triad fractions data to copolymer composition data for parameter estimation, the Brar et al. (1998) case was analyzed using the EVM MATLAB program. The data set provided by Brar et al. (1998) can be seen below in Table 5.10.

**Table 5.10: Data set of Brar et al. (1998) AN/AA BULK system at 27°C.**

| Feed Composition f1 (mol frac of AN) | Copolymer Composition F1 (mol frac of AN) | Triad Fractions | | | | | |
|---|---|---|---|---|---|---|---|
| | | $A_{111}$ | $A_{112+211}$ | $A_{212}$ | $A_{121}$ | $A_{122+221}$ | $A_{222}$ |
| 0.95 | 0.94 | | | | | | |
| 0.9 | 0.88 | | | | | | |
| 0.85 | 0.82 | 0.704 | 0.242 | 0.054 | 0.371 | 0.456 | 0.173 |
| 0.8 | 0.76 | 0.624 | 0.306 | 0.07 | 0.247 | 0.499 | 0.253 |
| 0.75 | 0.62 | 0.542 | 0.377 | 0.081 | 0.188 | 0.501 | 0.311 |
| 0.7 | 0.57 | 0.462 | 0.413 | 0.125 | 0.16 | 0.467 | 0.373 |
| 0.6 | 0.4 | 0.326 | 0.518 | 0.156 | 0.075 | 0.437 | 0.488 |
| 0.55 | | 0.284 | 0.477 | 0.238 | 0.084 | 0.328 | 0.588 |
| 0.5 | 0.19 | 0.229 | 0.526 | 0.245 | 0.058 | 0.339 | 0.602 |
| 0.45 | | 0.153 | 0.507 | 0.339 | 0.064 | 0.286 | 0.65 |
| 0.4 | 0.19 | | | | | | |
| 0.3 | 0.17 | | | | | | |

#### 5.6.1.1 *Additive vs. Multiplicative Error Structure*

In the article by Brar et al. (1998) analysis of the composition data to obtain reactivity ratio point estimates, was conducted using the KT and EVM (multiplicative error) (refer to Table 5.11). Once the reactivity ratios were evaluated by Brar et al. (1998) the estimates were then used to obtain predicted values for the triad fractions. These model predictions were then said to be in good agreement with the 'experimentally' determined triad fractions, by evaluating the correlation coefficient value R, the same procedure as that used by Mukherjee et al. (1998). A more statistically accurate method for determining whether the composition and triad fractions data are highly correlated, is to directly compare the different data sources reactivity ratio estimates from EVM (see Table 5.11).

**Table 5.11: Point estimates published by Brar et al. (1998) and the estimates obtained from EVM analysis of the data for AN/AA BULK system at 27°C.**

| | Data Source | Estimation Method | Error Structure | $r_1$ | $r_2$ |
|---|---|---|---|---|---|
| Brar et al. (1998) | Composition | KT | | 0.93 | 3.64 |
| Brar et al. (1998) | Composition | EVM | Multiplicative | 0.98 | 3.79 |
| Current work | Composition | EVM | Additive | 1.0226 | 3.6521 |
| Current work | Composition | EVM | Multiplicative | 0.784 | 2.9036 |
| Current work | Triad fractions | EVM | Additive | 0.9444 | 3.7904 |
| Current work | Triad fractions | EVM | Multiplicative | 0.9074 | 3.2291 |

The exact JCRs for the different data sources and error structures produced by the EVM MATLAB program and the point estimates published by Brar et al. (1998) can be seen in Figure 5.17.

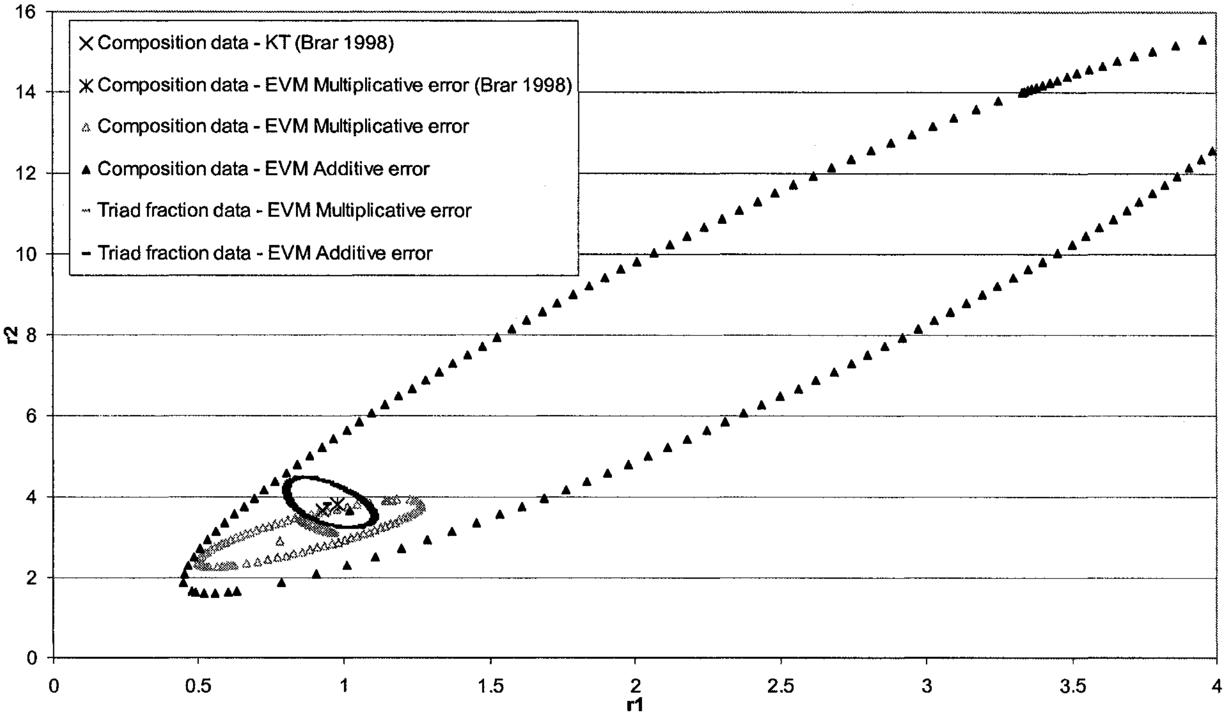


**Figure 5.17: Exact JCRs for EVM (additive and multiplicative error) analysis of Brar et al. (1998) triads and composition data sets for the AN/AA BULK system at 27°C.**

Due to the large range that the composition data (additive error) exact JCR covers, Figure 5.17 was zoomed in to show the point estimates and other exact JCRs in more detail.

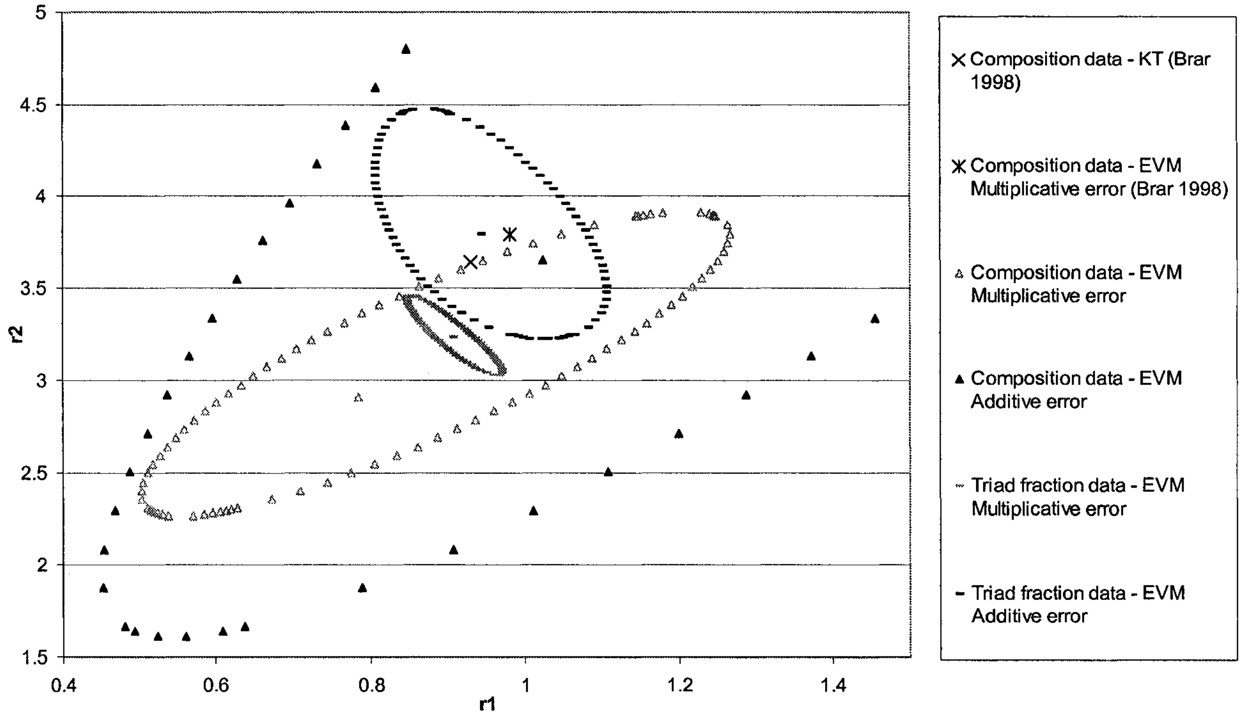


**Figure 5.17 (zoomed in): Exact JCRs for EVM (additive and multiplicative error) analysis of Brar et al. (1998) triad and composition data sets for the AN/AA BULK system at 27°C.**

From Figure 5.17 it can be seen that the exact JCRs of the triad fractions analysis are smaller than the composition exact JCRs, regardless of error structure. Therefore, this is another case that shows the use of triad fractions data results in less uncertainty in the reactivity ratio estimates, than those obtained from using composition data.

Furthermore, Figure 5.17 shows the point estimates published by Brar et al. (1998) fall within the exact JCR of the additive cases and not the multiplicative cases, despite the fact that Brar et al. (1998) states that a multiplicative error structure was used. Interestingly, Brar et al. (1998) also refers to the EVM copolymer composition method outlined by the same research group that this EVM MATLAB coding was developed from. In the article they also state that the assumed feed composition measurement error was 1% and the copolymer composition was 3%. Thus, the EVM MATLAB program was run with these proposed error levels in an attempt to mimic the results published in the literature. However, when the assumed error levels were reduced to that stated by Brar et al. (1998) the exact JCR obtained still does not include the point estimates that research group state are obtained by the same method (refer to Figure 5.18).

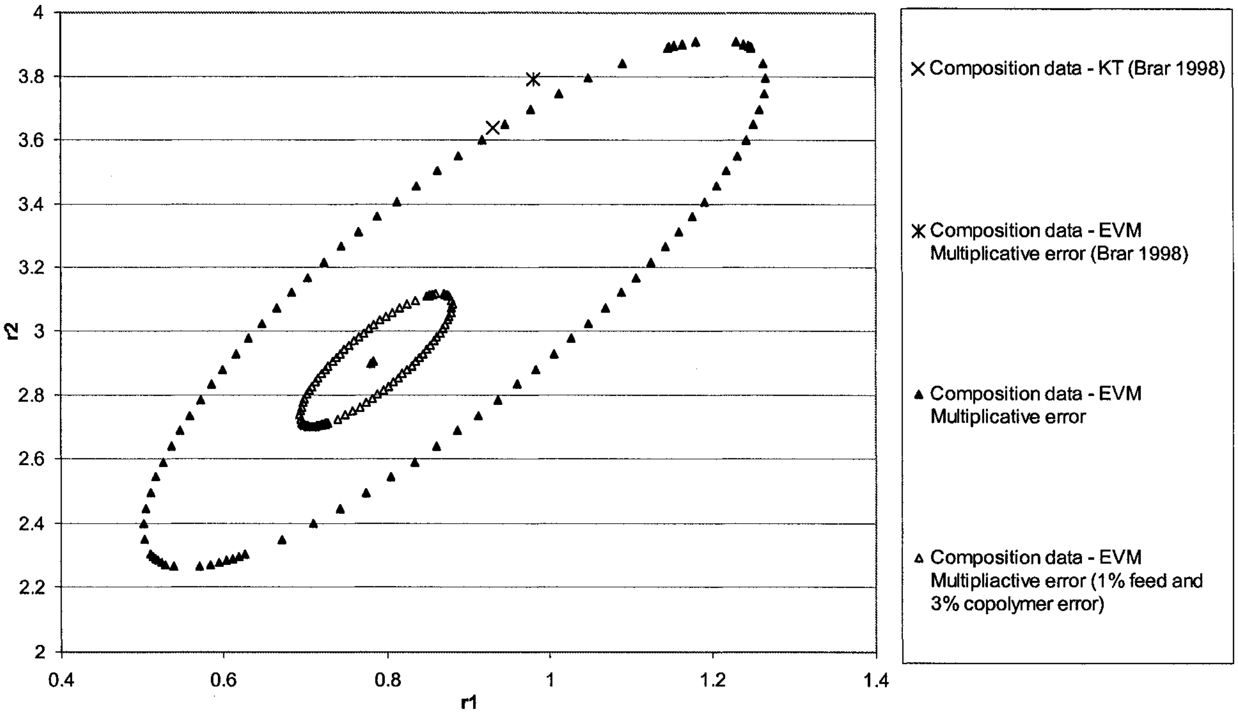


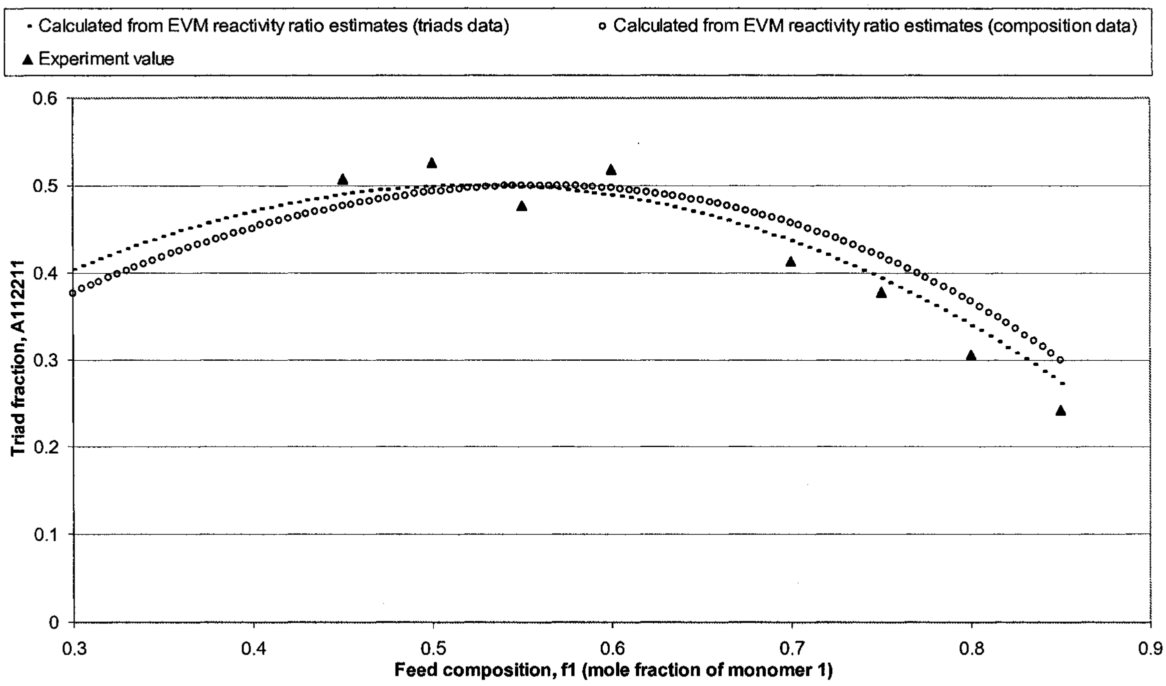
**Figure 5.18: Exact JCRs for EVM (multiplicative error) analysis of Brar et al. (1998) composition data set for the AN/AA BULK system at 27°C.**

It therefore can only be presumed that the EVM method used by Brar et al. (1998) is not the indicated research group's method, as the program that this analysis was based upon originated from a FORTRAN coding that the research group in question developed.

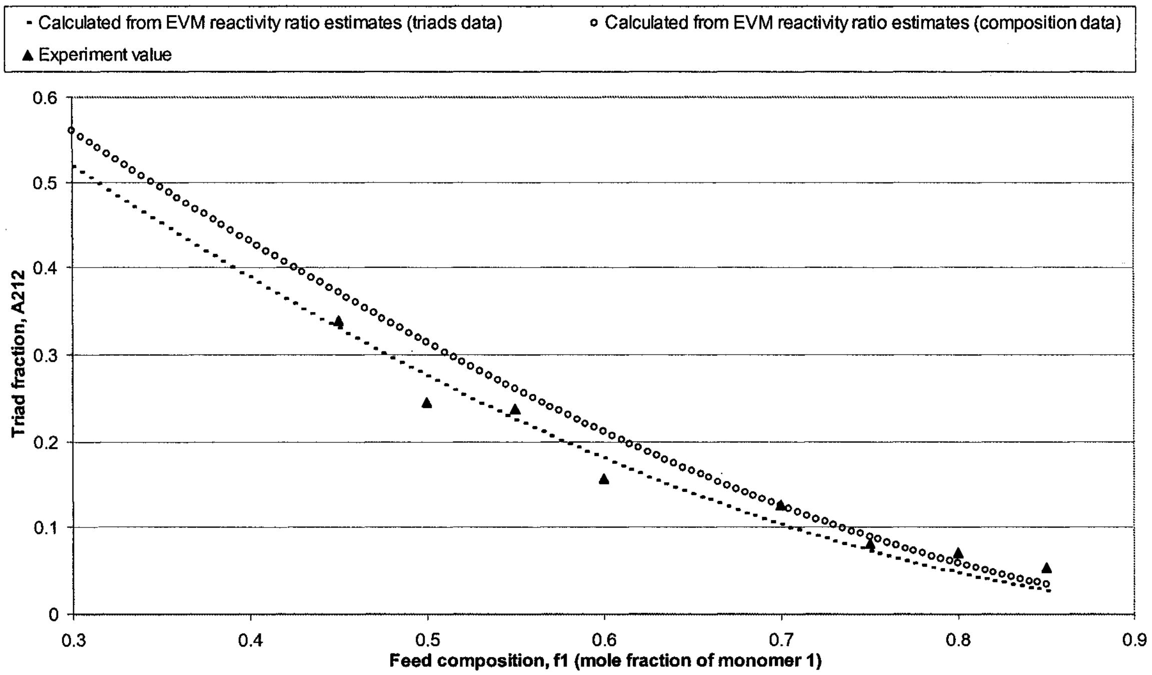
### 5.6.2 Diagnostic Checking

Diagnostic checking was performed in order to determine whether the reactivity ratio estimates in fact model the experimental results accurately. The reactivity ratio estimates, obtained from analyzing Brar et al. (1998) triad fractions and composition data with the EVM multiplicative error model, were used in the triad fractions equations to compare the 'predicted' triad fractions with the published 'experimental' triad fractions.

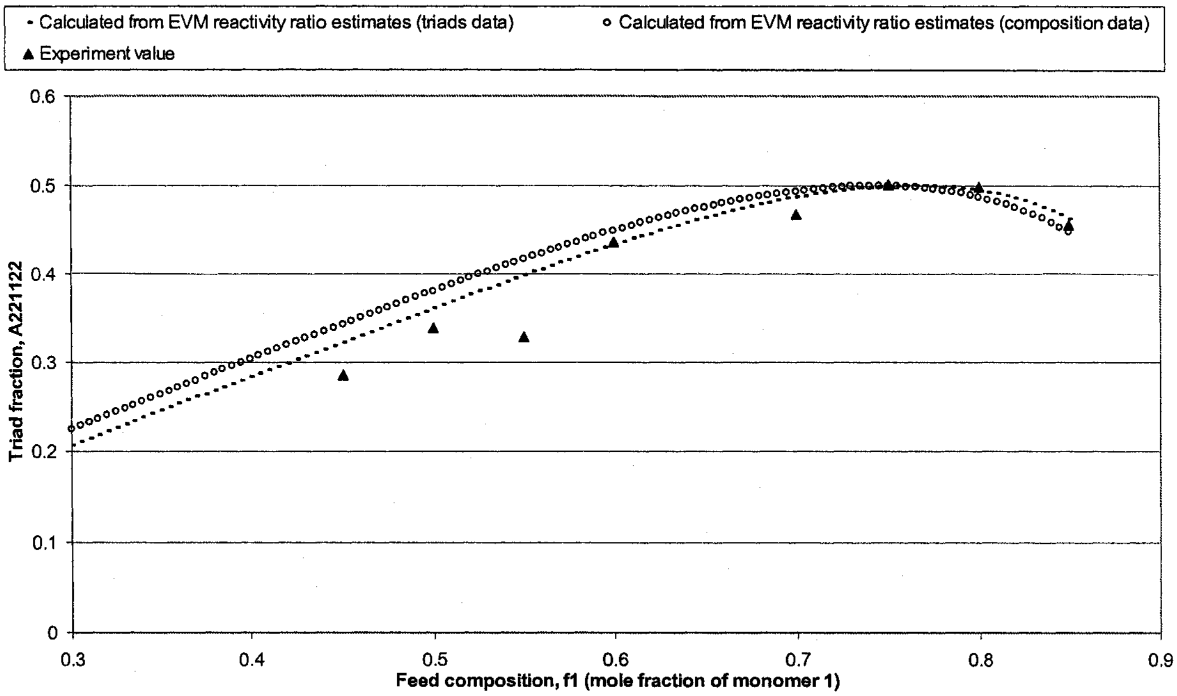
Figures 5.19 a) - d) shows the selected triad fractions predicted from Equations 5.1, using the EVM (multiplicative error) reactivity ratio estimates of the triad fractions and composition data. While Figure 5.19 e) shows the copolymer composition predicted from the Mayo-Lewis equation, using the EVM (multiplicative error) reactivity ratio estimates of the triad fractions and composition data.



a)

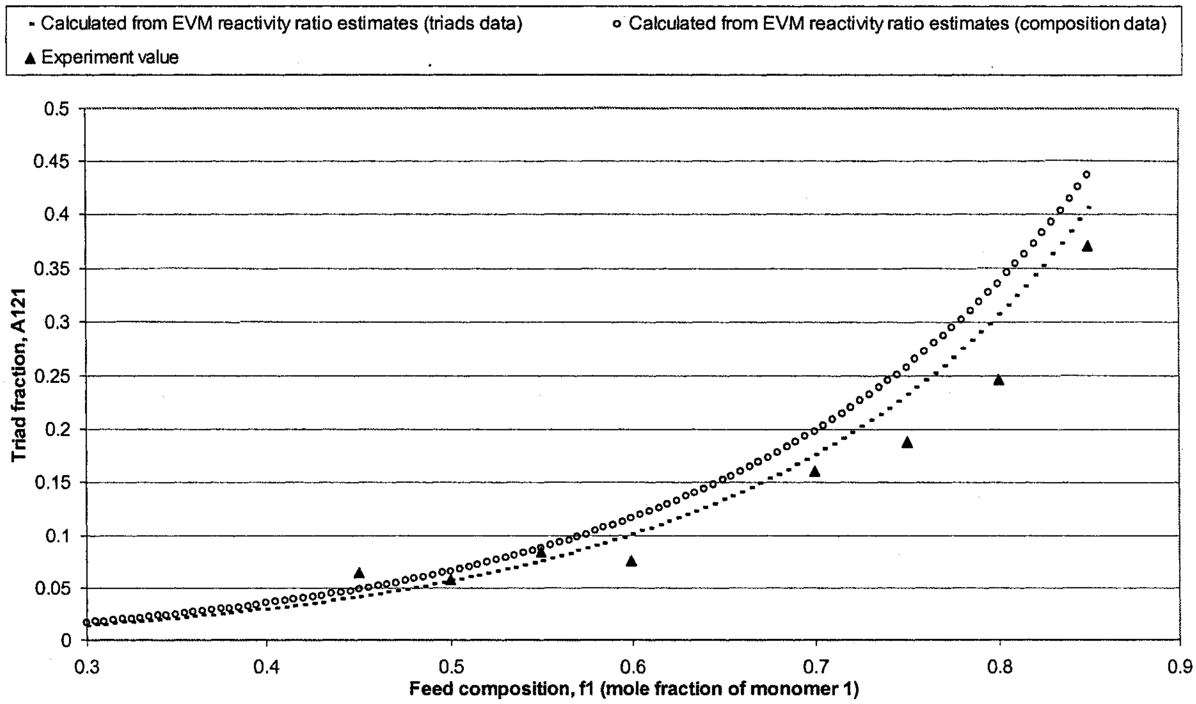


b)



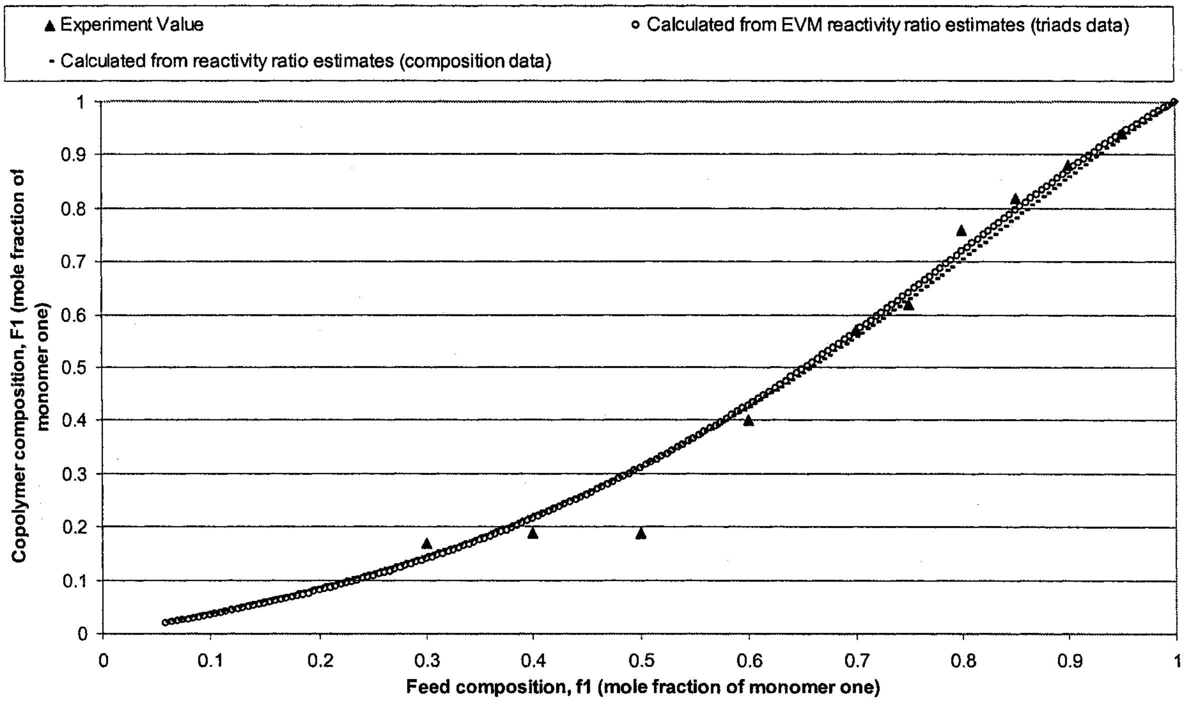
- Calculated from EVM reactivity ratio estimates (triads data)
○ Calculated from EVM reactivity ratio estimates (composition data)
▲ Experiment value
Triad fraction, A221122
0
0.1
0.2
0.3
0.4
0.5
0.6
0.3
0.4
0.5
0.6
0.7
0.8
0.9
Feed composition, f1 (mole fraction of monomer 1)

c)



- Calculated from EVM reactivity ratio estimates (triads data)
○ Calculated from EVM reactivity ratio estimates (composition data)
▲ Experiment value
Triad fraction, A121
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
0.5
0.3
0.4
0.5
0.6
0.7
0.8
0.9
Feed composition, f1 (mole fraction of monomer 1)

d)



e)

**Figure 5.19 a) - d): Predicted triad fractions using the EVM (multiplicative error) reactivity ratio estimates, obtained from analyzing triad fractions and composition data, in the triad fractions equations and the published 'experimental' triad fractions. e) Predicted copolymer composition using the EVM (multiplicative error) reactivity ratios, obtained from analyzing triad fractions and composition data, in the Mayo-Lewis equation and the published copolymer composition measurements.**

As can be seen from the Figures 5.19 a) – d) the predicted triad fractions obtained from using the EVM (multiplicative error) reactivity ratio estimates (which were from analyzing the triad fractions and composition data) are in agreement with the experimental triad fractions results published by Brar et al. (1998). Furthermore, it has again been shown that the copolymer composition can be predicted well with reactivity ratios that are estimated from either composition data or triad fractions data (refer to Figure 5.19 e)). As in the previous case, the results were expected as in this case study the reactivity ratio estimates, from the different data sources, were in agreement and thus the model predictions were expected to be very similar.

### 5.6.3 Triad Fractions and Composition Data Combined vs. Triad Fractions Data

In order to determine whether using all the information available in the EVM program would result in a further reduction of uncertainty in the parameter estimates, analysis was conducted on using triad fractions with composition data and triad fractions data only. The following diagram is the exact JCRs of the system using triad fractions and composition data compared to only triad fractions data, when a multiplicative error structure is imposed (see Figure 5.20).

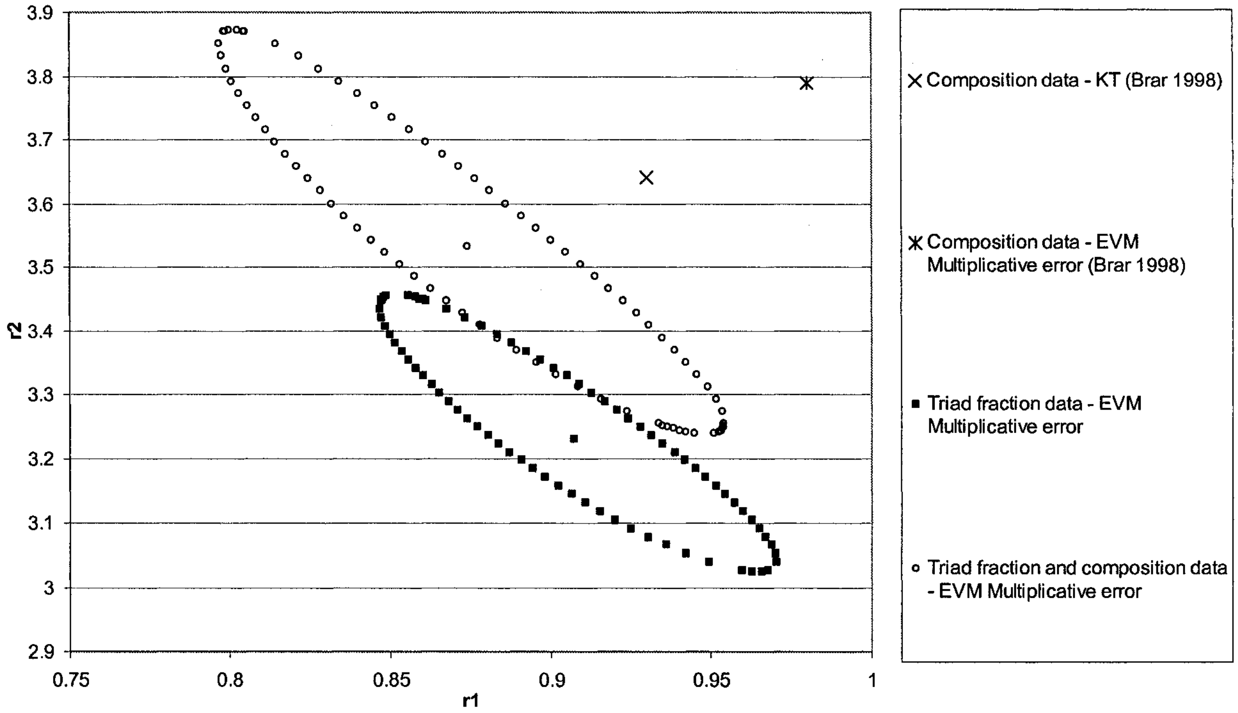


**Figure 5.20: Exact JCRs for EVM (multiplicative error) analysis of Brar et al. (1998) triad and composition data vs. only triad fractions data for the AN/AA BULK system at 27°C.**

It appears from Figure 5.20 that the use of composition and triad fractions data together results in a slight increase in area and a shift in the exact JCR. The reason for this shift and increase can be attributed to the fact that in order to perform analysis on the combined triad fractions and composition data set, half the data points had to be eliminated as there was missing copolymer composition data at certain feeds. Therefore, the analysis using the combined triad fractions and composition data had a reduced data set than when using only the triad fractions data and thus the comparison between the two exact JCRs is not entirely fair. As a result, this case study can not provide any conclusions regarding the use of combined data versus using only triad fractions data, for parameter estimation as the number of data points in the data set biases the results obtained.

## 5.7 Case Study V: Acrylonitrile/Pentyl Methacrylate

Brar et al. (1998) studied the acrylonitrile (AN)/ pentyl methacrylate (PMA) system at room temperature in bulk copolymerization and presented experimental data on both copolymer composition and triad fractions. Therefore, both data source types were analyzed to further support the conclusions drawn from the previous case studies.

### 5.7.1 Using Triad fractions or Composition Data?

The data set provided by Brar et al. (1998) can be seen below in Table 5.12. As in the prior case studies, the parameter estimation was conducted using either copolymer composition data or triad fractions data for both an additive and multiplicative error structure.

**Table 5.12: Data set of Brar et al. (1998) AN/PMA BULK system at room temperature.**

| Feed Composition f1 (mol frac of AN) | Copolymer Composition F1 (mol frac of AN) | Triad Fractions | | | | | |
|---|---|---|---|---|---|---|---|
| | | $A_{111}$ | $A_{112+211}$ | $A_{212}$ | $A_{121}$ | $A_{122+221}$ | $A_{222}$ |
| 0.95 | 0.82 | | | | | | |
| 0.9 | 0.67 | 0.45 | 0.44 | 0.11 | 0.06 | 0.4 | 0.53 |
| 0.85 | 0.6 | 0.27 | 0.47 | 0.26 | 0.11 | 0.45 | 0.44 |
| 0.8 | 0.52 | 0.21 | 0.47 | 0.32 | 0.17 | 0.45 | 0.38 |
| 0.75 | 0.47 | 0.17 | 0.47 | 0.36 | 0.17 | 0.53 | 0.3 |
| 0.7 | 0.41 | 0.13 | 0.41 | 0.46 | 0.25 | 0.52 | 0.23 |
| 0.6 | 0.32 | 0.09 | 0.34 | 0.57 | 0.41 | 0.46 | 0.13 |
| 0.5 | 0.18 | 0.06 | 0.26 | 0.68 | 0.52 | 0.41 | 0.07 |

#### *5.7.1.1 Additive vs. Multiplicative Error Structure*

In the article by Brar et al. (1998) analysis of the composition data is conducted using the KT and EVM (multiplicative error) method to obtain reactivity ratio point estimates, refer to Table 5.14. Similar to Mukherjee et al. (1998) the estimates obtained by Brar et al. (1998) were used to obtain predicted values for triad fractions. These model predictions were then said to be in good agreement with the 'experimentally' determined triad fractions, by evaluating the correlation coefficient value R. As discussed in Case III and IV a more statistically accurate method for determining whether the two different data sources are highly correlated, is to determine if there is good agreement between the reactivity ratio estimates obtained by using each data set independently in the EVM MATLAB program. The point estimates obtained by the analysis of the different data sets and error structure implemented in the EVM MATLAB program can be seen in Table 5.13.

**Table 5.13: Point estimates published by Brar et al. (1998) and the estimates obtained by EVM MATLAB analysis.**

| | Data Source | Estimation Method | Error Structure | $r_1$ | $r_2$ |
|---|---|---|---|---|---|
| Brar et al. (1998) | Composition | KT | | 0.21 | 2.65 |
| Brar et al. (1998) | Composition | EVM | Multiplicative | 0.2 | 2.62 |
| Brar et al. (1998) | Triad fractions | Conditional probability slope measurements | | 0.21 | 2.56 |
| Current work | Composition | EVM | Additive | 0.2432 | 3.3056 |
| Current work | Composition | EVM | Multiplicative | 0.356 | 4.4471 |
| Current work | Triad fractions | EVM | Additive | 0.209 | 3.5189 |
| Current work | Triad fractions | EVM | Multiplicative | 0.217 | 3.7125 |

The exact JCRs obtained by the EVM MATLAB program for the different data types and the point estimates published by Brar et al. (1998) can be seen in Figure 5.21.

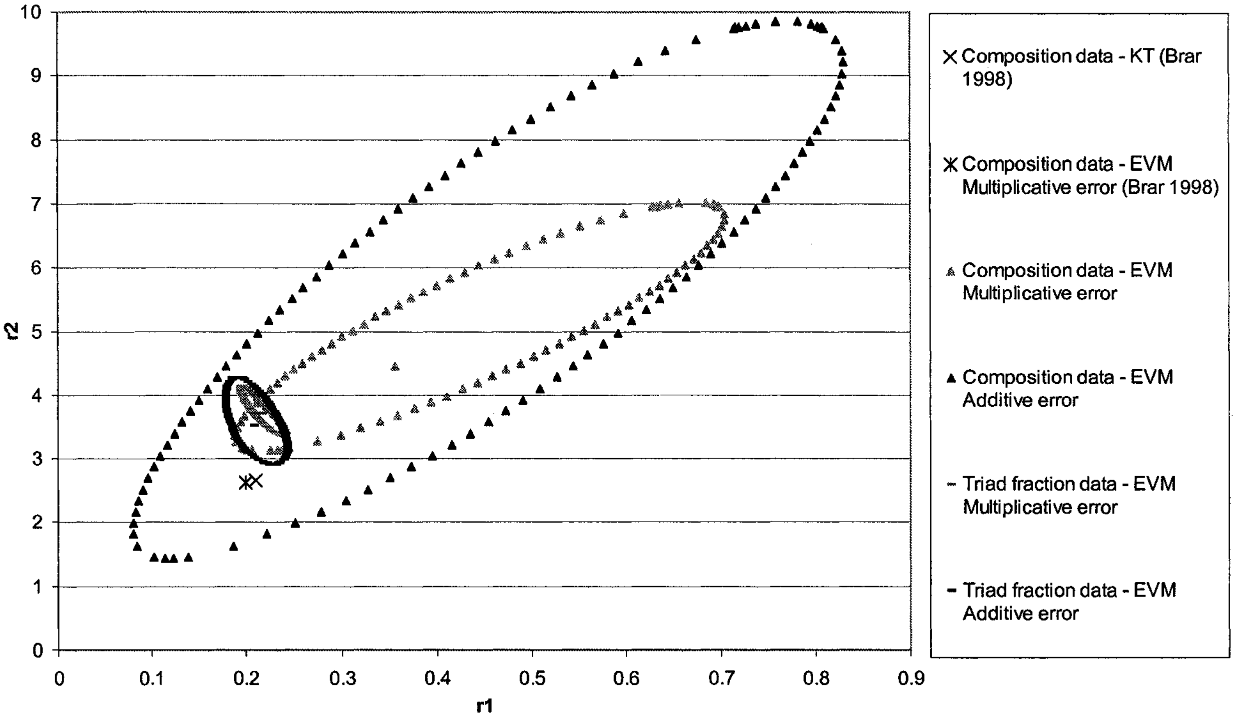


**Figure 5.21: Exact JCRs for EVM (additive and multiplicative error) analysis of Brar et al. (1998) triad fractions and composition data for the AN/PMA BULK system at room temperature.**

Figure 5.21 shows the exact JCR from the EVM analysis of composition data to be larger than the exact JCR from the EVM analysis of triad fractions data, regardless of error structure. That is, the above diagram is further testimony to the fact that the use of triad fractions data results in less uncertainty in the reactivity ratio parameter estimates, regardless of error structure.

The overlapping of the exact JCRs in Figure 5.21 also indicates good agreement between the estimated reactivity ratios from the different data sources. Furthermore, as expected the exact JCRs for an imposed multiplicative error structure on the composition data or triad fractions analysis, fall within the respective exact JCRs for an imposed additive error structure; indicating a well behaved system.

The point estimates published by Brar et al. (1998) do not fall within any of the exact JCRs, with the exception of the contour obtained from analyzing the composition data set with an imposed additive error structure. However, the error structure of composition data is generally considered to be more closely represented by a multiplicative error structure. Therefore, the point estimates published by Brar et al. (1998) are not in agreement with the analysis conducted here, for either composition or triad fractions data. Despite this Brar et al. (1998) refers to the EVM copolymer composition method that this EVM MATLAB model was developed from. Similar to the previous case, the EVM program was rerun with the same error levels as stated in the paper, in order to try to replicate the published results. Once again the exact JCRs using the error levels, as indicated by Brar et al. (1998), do not contain the point estimates published in the paper, refer to Figure 5.22.

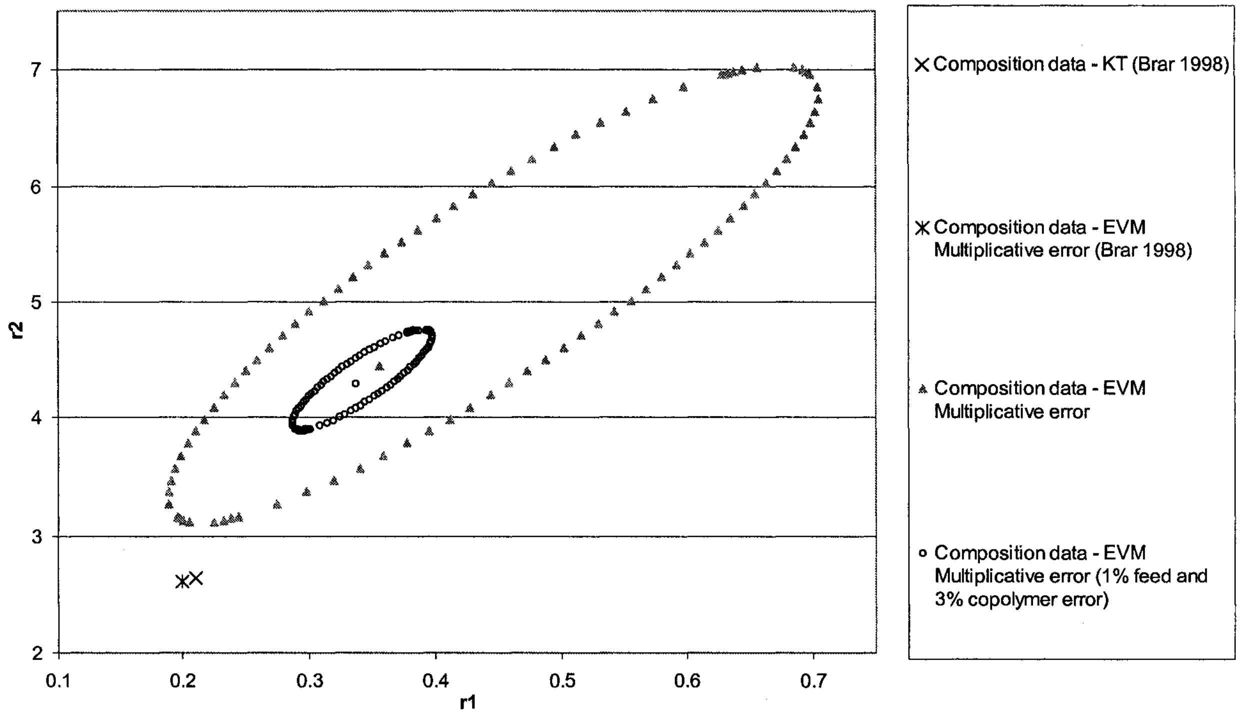
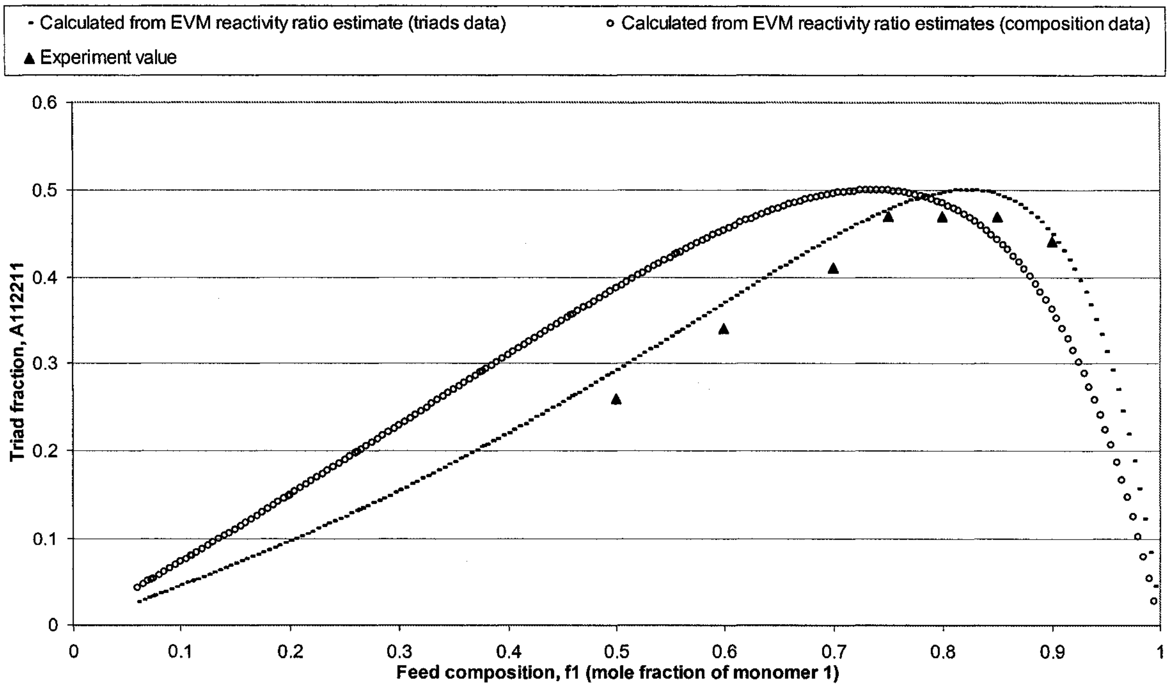


**Figure 5.22: Exact JCRs for EVM (multiplicative error) analysis of Brar et al. (1998) composition data set for the AN/PMA BULK system at room temperature.**

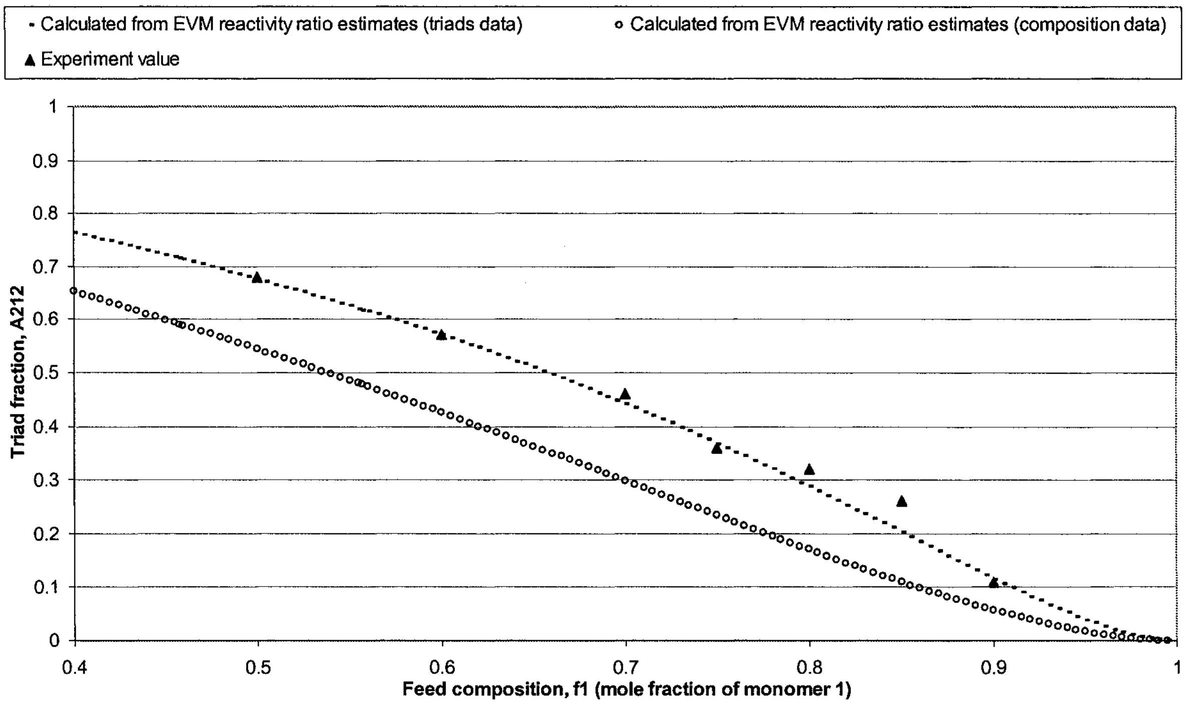
Similar to the previous case study (Case IV) it can be presumed that the EVM method used by Brar et al. (1998) is not the indicated research group's method, as the program that this analysis was based upon originated from a FORTRAN coding that the research group in question developed.

### 5.7.2 Diagnostic Checking

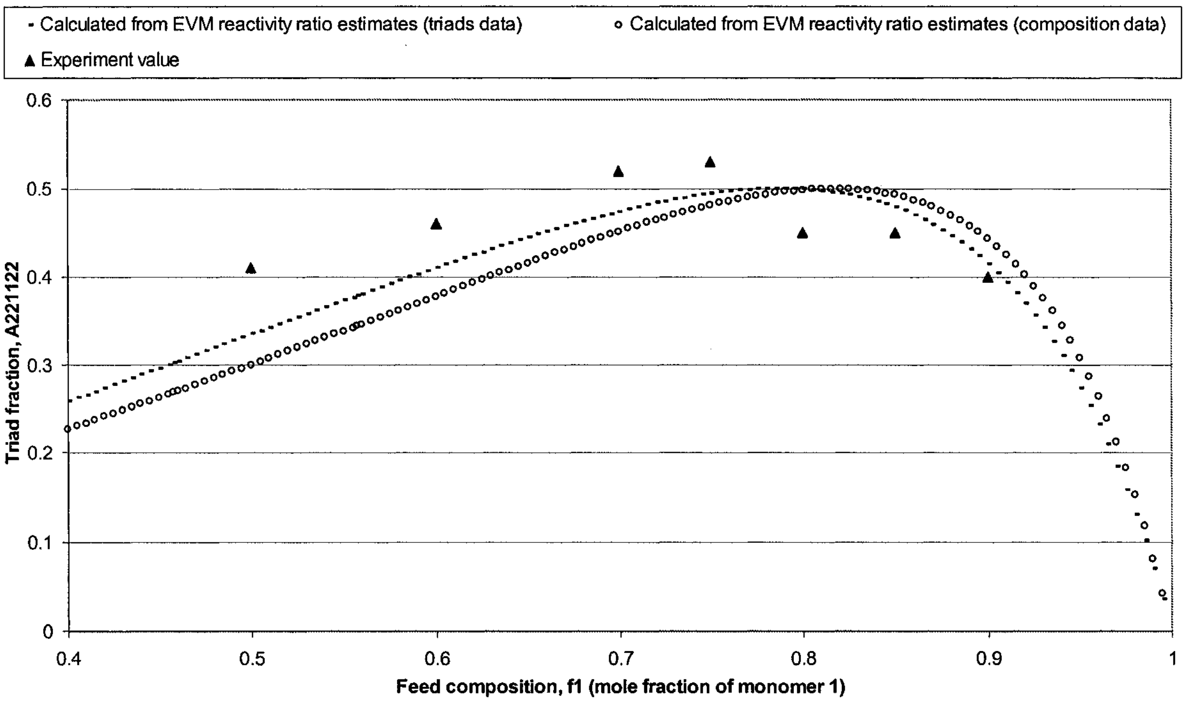
Similar to the other case studies, diagnostic checking was performed to ensure the fit of the model to the experiment results. The reactivity ratio estimates, obtained from EVM analysis of Brar et al. (1998) triad fractions and composition data (imposed multiplicative error), were used in the triad fractions equations to compare the 'predicted' triad fractions with the published 'experimental' triad fractions. Figures 5.23 a) - d) show the predicted triad fractions obtained from the equations, when using the EVM reactivity ratio estimates of the triad fractions and composition data (multiplicative error) analysis. While Figure 5.23 e) shows the copolymer composition predicted from the Mayo-Lewis equation, using the same reactivity ratio estimates as those used to predict the triad fractions.


- Calculated from EVM reactivity ratio estimate (triads data)
○ Calculated from EVM reactivity ratio estimates (composition data)
▲ Experiment value
Triad fraction, A112211
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Feed composition, f1 (mole fraction of monomer 1)

a)

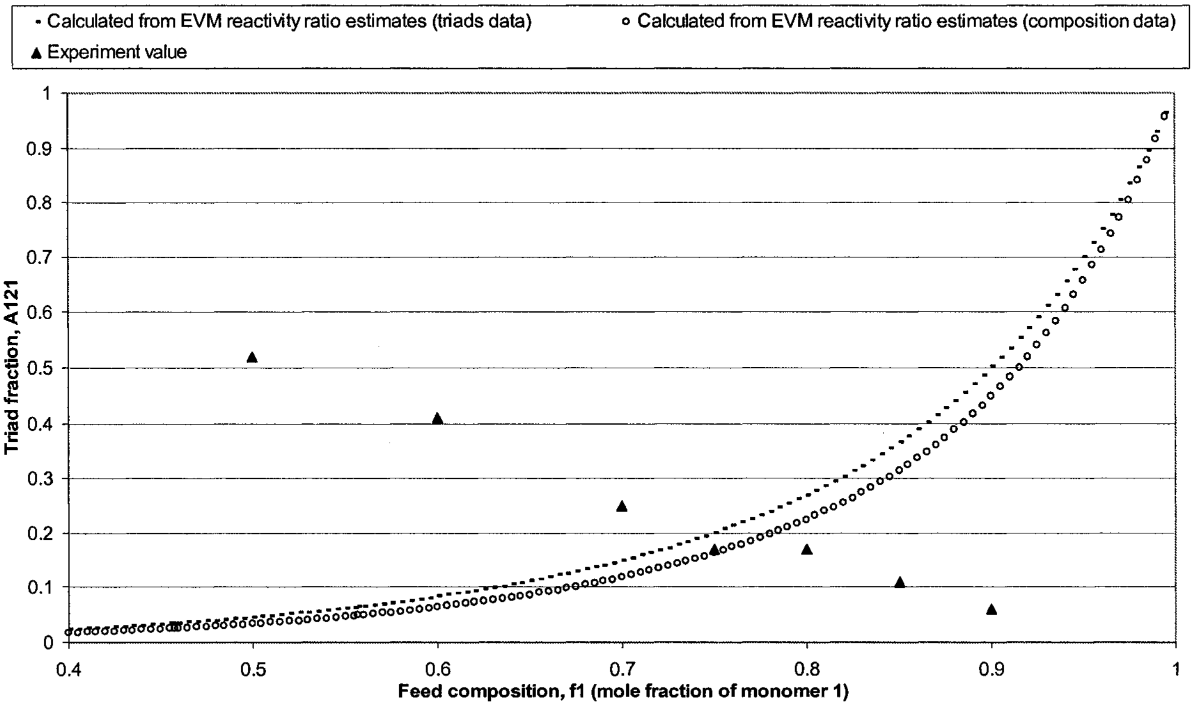

- Calculated from EVM reactivity ratio estimates (triads data)
○ Calculated from EVM reactivity ratio estimates (composition data)
▲ Experiment value
Triad fraction, A212
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.4
0.5
0.6
0.7
0.8
0.9
1
Feed composition, f1 (mole fraction of monomer 1)

b)



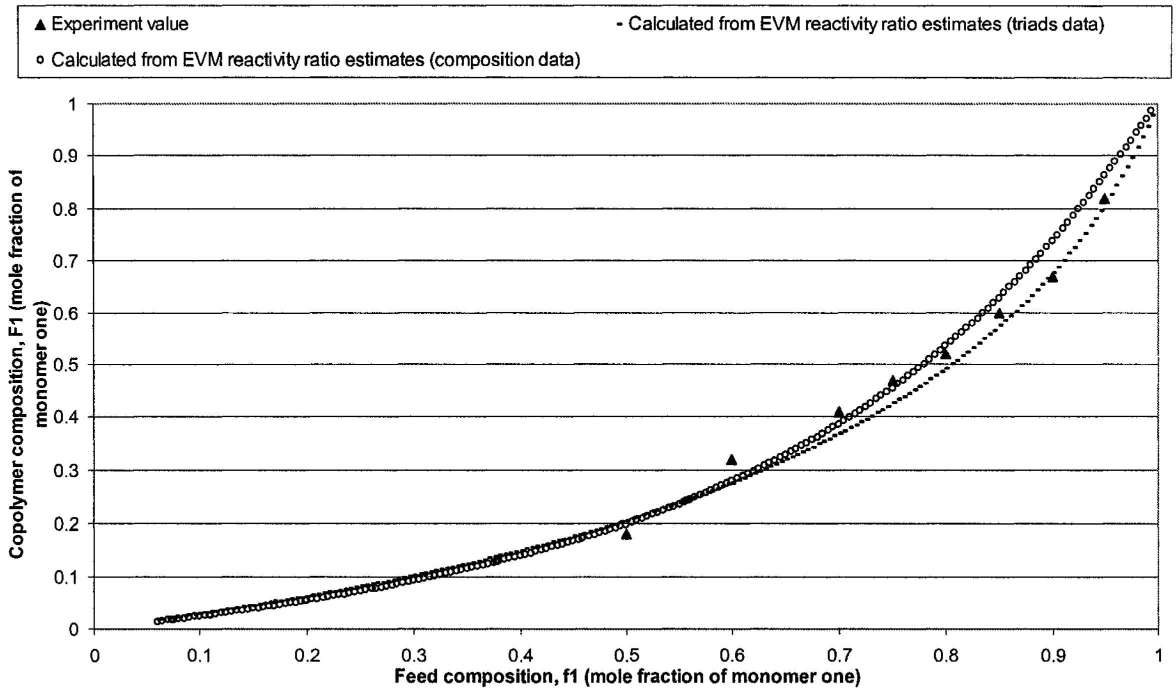
- Calculated from EVM reactivity ratio estimates (triads data)
o Calculated from EVM reactivity ratio estimates (composition data)
▲ Experiment value
Triad fraction, A221122
0.6
0.5
0.4
0.3
0.2
0.1
0
0.4
0.5
0.6
0.7
0.8
0.9
1
Feed composition, f1 (mole fraction of monomer 1)

c)



- Calculated from EVM reactivity ratio estimates (triads data)
o Calculated from EVM reactivity ratio estimates (composition data)
▲ Experiment value
Triad fraction, A121
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.4
0.5
0.6
0.7
0.8
0.9
1
Feed composition, f1 (mole fraction of monomer 1)

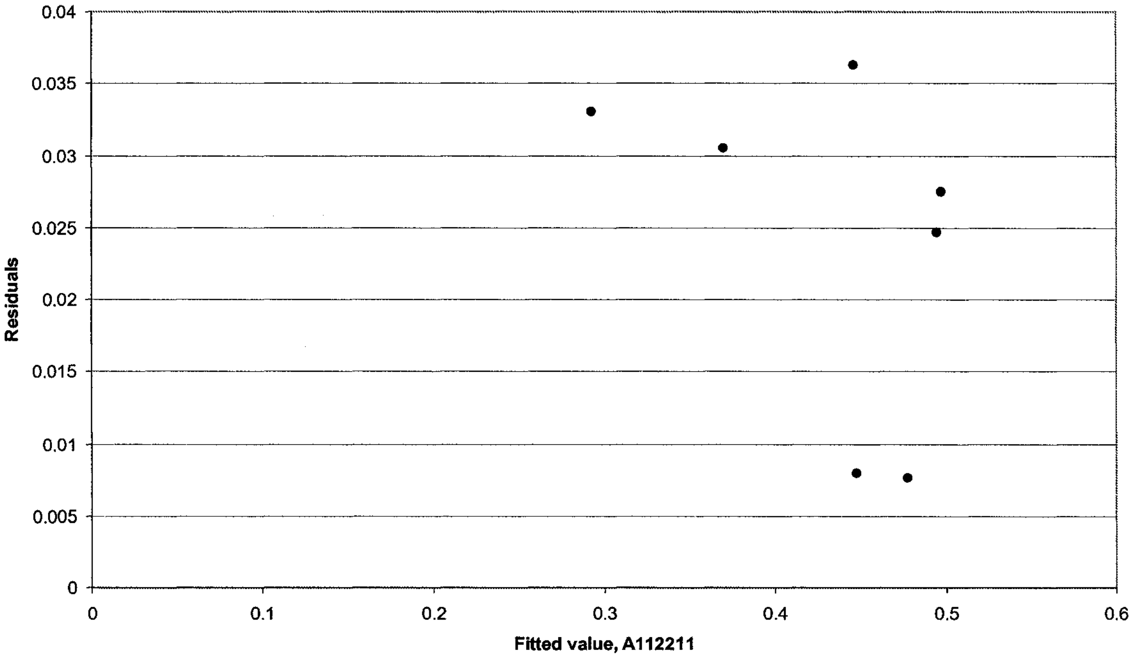
d)



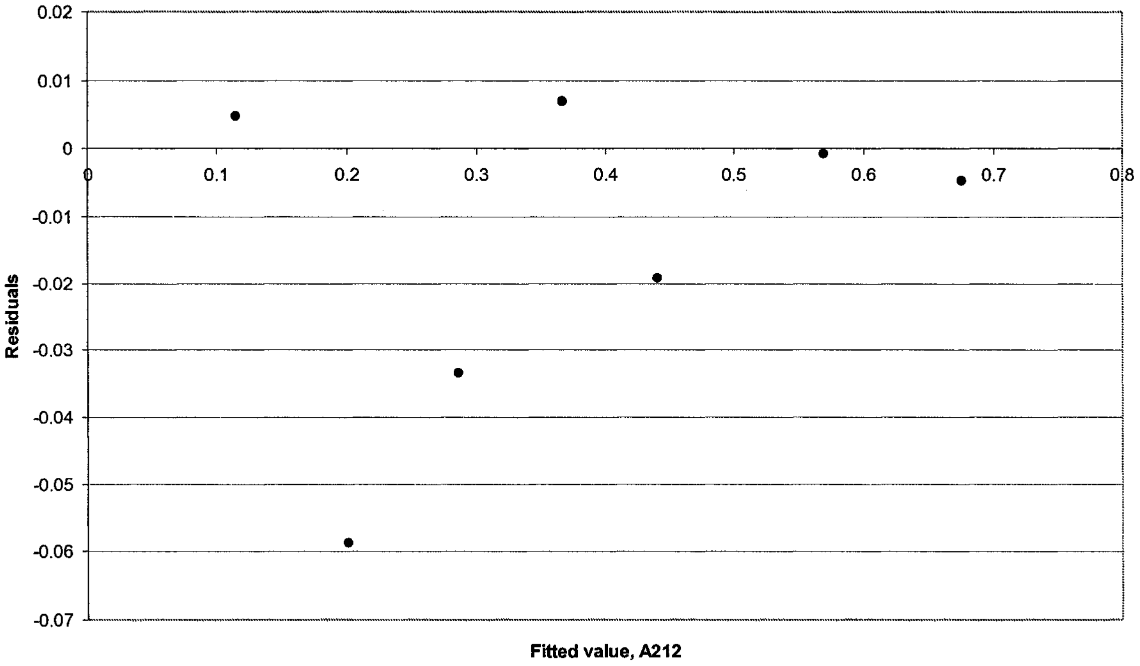
e)

**Figure 5.23: a) - d) Predicted triad fractions using the EVM (multiplicative error) reactivity ratio estimates, obtained from analyzing triad fractions and composition data, in the triad fractions equations and the published 'experimental' triad fractions. e) Predicted copolymer composition using the EVM (multiplicative error) reactivity ratio estimates, obtained from analyzing triad fractions and composition data, in the Mayo-Lewis equation and the published copolymer composition measurements.**

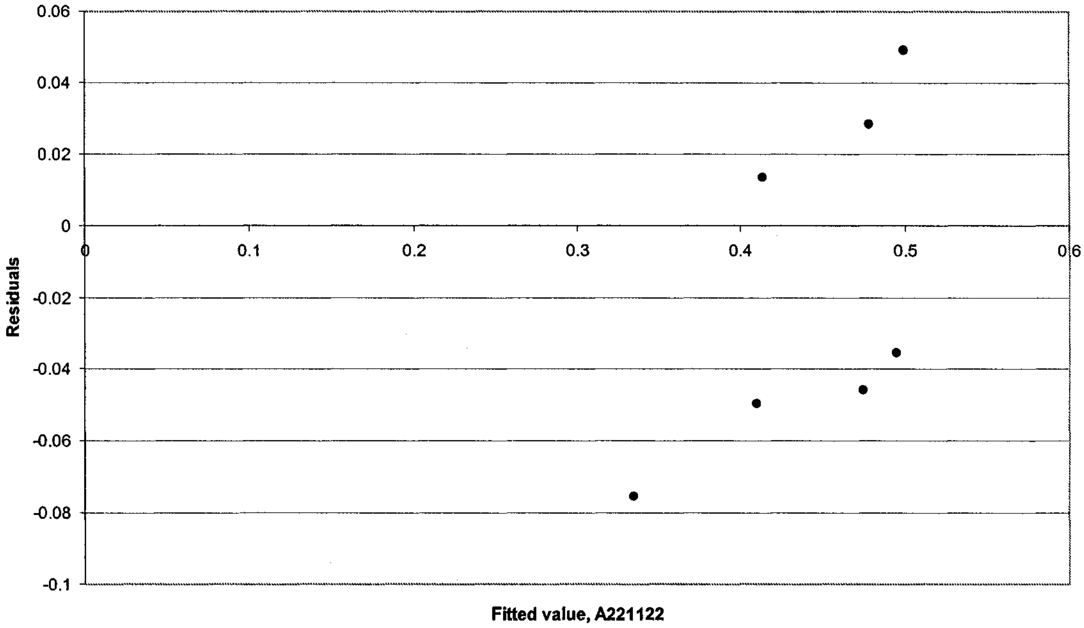
As can be seen from Figures 5.23 a) – d) the predicted triad fractions obtained from using the EVM reactivity ratio estimates (triad fractions data analysis) are in fairly good agreement with the 'experimental' triad fractions results, except $A_{121}$. While the predicted triad fractions, obtained from using the EVM reactivity ratio estimates (composition data analysis), are not as good at predicting the 'experimental' triad fractions results. Furthermore, looking at the triad fraction $A_{121}$ specifically, both of the trend lines of 'predicted' triads (i.e., both data sources) are not in agreement with the 'experimental' triad trend. In fact, the trends are opposite. The difference in the model triad fraction predictions to the 'experimental' results indicate that the experiment was either poorly designed for parameter estimation or large experimental errors are present. Therefore, it is of the utmost importance that residual analysis of the triad fraction $A_{121}$ is considered along with the residuals of the other triad fractions, as seen in Figure 5.24 a) - d).


0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
Residuals
0
0.1
0.2
0.3
0.4
0.5
0.6
Fitted value, A112211

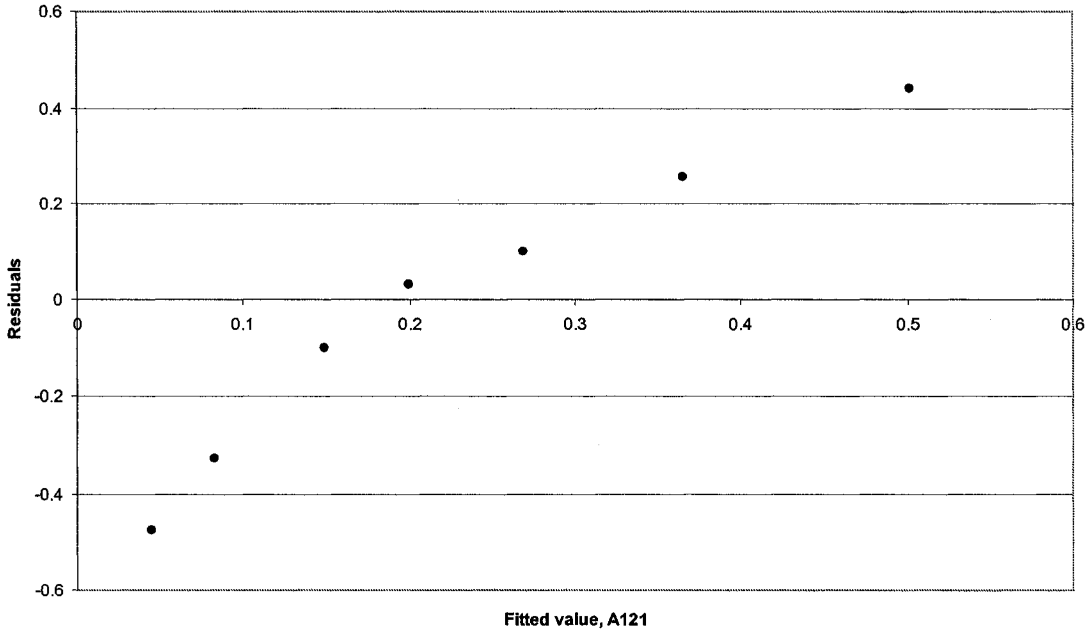
a)


0.02
0.01
0
-0.01
-0.02
-0.03
-0.04
-0.05
-0.06
-0.07
Residuals
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
Fitted value, A212

b)



c)



d)

**Figure 5.24 a) - d): Residual analysis for each predicted triad fraction.**

It can be seen from Figures 5.24 a) – d) that the residuals are random except for the triad fraction, $A_{121}$, which appears to have a linear trend. The explanation for this is similar to that presented in Maxwell et al. (1993) STY-MMA case study (refer to Section 5.4.2). Basically, the true measurement variable that would have been recorded by Brar et al. (1998) would have been the NMR normalized peak areas and then certain equations would have been used to transform these peak areas into triad fractions. The triad fractions were the only data reported in the article and no mention of the equation and tacticity parameter values used to transform the data were given. Therefore, it is believed that the trend in the triad fractions residuals could be related to the issue of transformation of the true measured response variable (peak areas) into triad fractions, similar to that seen in the diagnostic testing of Maxwell et al. (1993) STY-MMA case study. As a result, the equations used to transform peak areas into triad fractions require further study and in particular the effect it can have on the accuracy of the parameter estimates.

### 5.7.3 Triad Fractions and Composition Data vs. Triad Fractions Data

Once again the use of the amalgamated data set of both data sources (composition and triad fractions data) in the EVM MATLAB program is shown to result in an insignificant improvement in the uncertainty of the parameter estimates, compared to using only the triad fractions data in the analysis. Figure 5.25 thus shows the exact JCR of the system using combined triad fractions and composition data, compared to the exact JCR when only triad fractions data is analyzed (both with imposed multiplicative error structures).

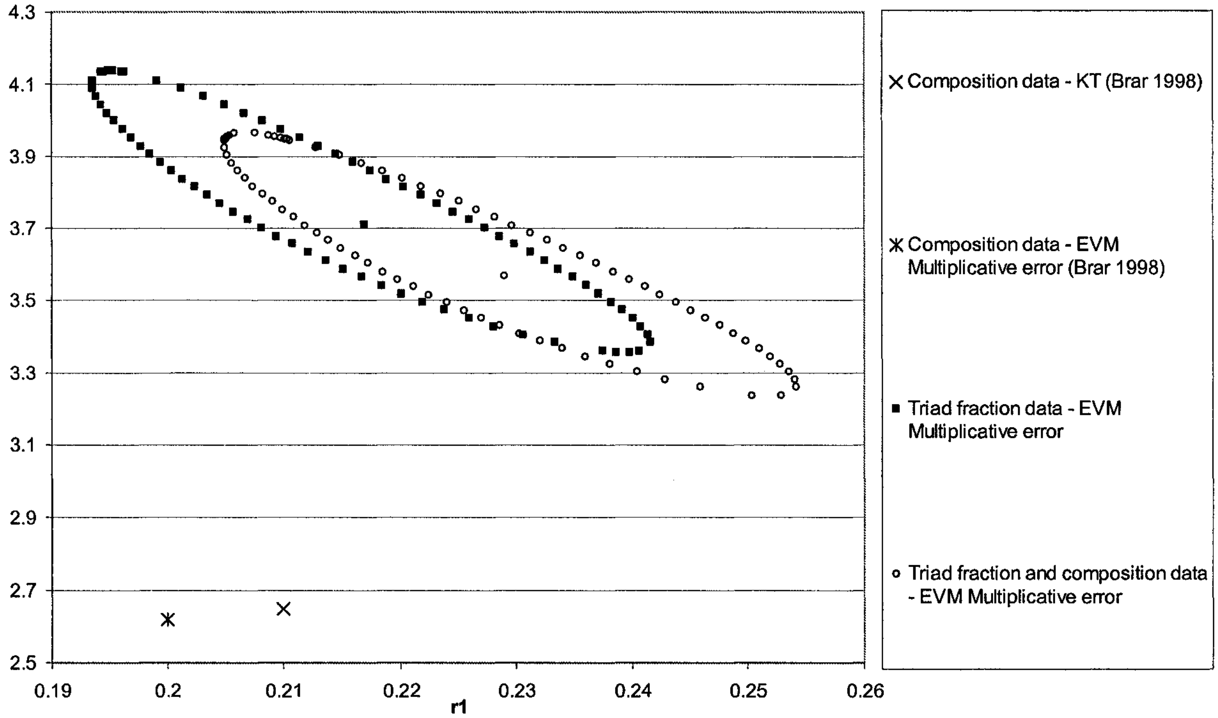


**Figure 5.25: Exact JCRs for EVM (multiplicative error) analysis of Brar et al. (1998) triad fractions and composition data vs. only triad fractions data for the AN/PMA BULK system at room temperature.**

Figure 5.25 shows a shift in the exact JCR when the combined data set is used. The shift is due to the reduced data set for the combined case, as at certain feed points there were no values recorded for one of the data sources and thus the feed point had to be eliminated (thus reducing the total number of data points analyzed). Furthermore, there appears to be insignificant change to the level of uncertainty when the combined composition and triad fractions data is used, compared to the uncertainty of simply using the triad fractions data. Subsequently, the effort to obtain the copolymer composition data is unwarranted for parameter estimation experiments; rather the collection of triad fractions data is a better statistical data set.

## 5.8 Case Study VI: Styrene/Acrylonitrile

A number of groups have published work on the styrene (STY) - acrylonitrile (AN) system for both bulk and solvent copolymerization. Here we analyzed data from the groups of Hill et al. (1989) and (1992) and Klumperman and Kraeger (1994).

Hill et al. (1989) analyzed the STY/AN bulk copolymerization system at 60°C and then later again in 1992 adding this time the toluene solvent and acetonitrile solvent systems. Klumperman and Kraeger (1994) also analyzed the potential solvent effect at 60°C of STY/AN in toluene, butanone and N, N'-dimethylformamide (DMF), whilst also providing data for the bulk system. However, as Klumperman and Kraeger (1994) published only reactivity ratio estimates for the penultimate model case and not the terminal model, only the toluene and bulk data is used from the Klumperman and Kraeger (1994) paper, so as to be able to compare against the results obtained using the Hill et al. groups data sets. Consequently, as there are three data sets available for the bulk system and two data sets for the toluene solvent system, sensitivity of the reactivity ratio estimates to data sets and thus experimental design is also able to be analyzed to some extent.

### 5.8.1 Using Triad Fractions or Composition Data?

In order to illustrate the use of triad fractions data in comparison to copolymer composition data the Hill et al. (1989 and 1992) and Klumperman and Kraeger (1994) cases were analyzed using the EVM MATLAB program. The data sets for the Hill et al. systems can be seen in Tables 5.14 to 5.17, while the Klumperman and Kraeger (1994) data sets can be seen in Table 5.18 and 5.19.

The parameter estimation was conducted using either copolymer composition data or the triad fractions data from the different groups. As in the prior case studies, both the additive error structure and multiplicative error structure were considered.

**Table 5.14: Data set of Hill et al. (1989) styrene/acrylonitrile in bulk at 60°C.**

| Feed Composition f1 (mol frac of STY) | Copolymer Composition F1 (mol frac of STY) | Triad Fractions | | | | | |
|---|---|---|---|---|---|---|---|
| | | $A_{111}$ | $A_{112+211}$ | $A_{212}$ | $A_{222}$ | $A_{221+122}$ | $A_{121}$ |
| 0.023 | 0.248 | 0 | 0.07 | 0.93 | 0.51 | 0.42 | 0.08 |
| 0.047 | 0.323 | 0 | 0.06 | 0.94 | 0.37 | 0.5 | 0.13 |
| 0.072 | 0.36 | 0 | 0.06 | 0.94 | 0.27 | 0.5 | 0.23 |
| 0.104 | 0.406 | 0 | 0.15 | 0.85 | 0.11 | 0.55 | 0.34 |
| 0.221 | 0.476 | 0 | 0.27 | 0.73 | 0 | 0.37 | 0.63 |
| 0.314 | 0.51 | 0.02 | 0.34 | 0.64 | 0.01 | 0.29 | 0.69 |
| 0.416 | 0.542 | 0.06 | 0.42 | 0.52 | 0 | 0.22 | 0.78 |
| 0.53 | 0.582 | 0.07 | 0.51 | 0.42 | 0 | 0.17 | 0.83 |
| 0.631 | 0.627 | 0.12 | 0.56 | 0.32 | 0 | 0.12 | 0.88 |
| 0.696 | 0.649 | 0.16 | 0.59 | 0.25 | 0 | 0.08 | 0.92 |
| 0.802 | 0.705 | 0.3 | 0.55 | 0.15 | 0 | 0.06 | 0.94 |
| 0.889 | 0.772 | 0.44 | 0.5 | 0.06 | 0 | 0 | 1 |
| 0.939 | 0.829 | 0.61 | 0.37 | 0.02 | 0 | 0 | 1 |

**Table 5.15: Data set of Hill et al. (1992) styrene/acrylonitrile in bulk at 60°C.**

| Feed Composition f1 (mol frac of STY) | Copolymer Composition F1 (mol frac of STY) | Triad Fractions | | | | | |
|---|---|---|---|---|---|---|---|
| | | $A_{111}$ | $A_{112+211}$ | $A_{212}$ | $A_{222}$ | $A_{221+122}$ | $A_{121}$ |
| 0.023 | 0.248 | 0 | 0.07 | 0.93 | 0.41 | 0.5 | 0.09 |
| 0.047 | 0.323 | 0 | 0.06 | 0.94 | 0.24 | 0.55 | 0.21 |
| 0.072 | 0.36 | 0 | 0.06 | 0.94 | 0.12 | 0.57 | 0.31 |
| 0.104 | 0.406 | 0 | 0.15 | 0.85 | 0.11 | 0.55 | 0.34 |
| 0.221 | 0.476 | 0 | 0.27 | 0.73 | 0 | 0.37 | 0.63 |
| 0.314 | 0.51 | 0.02 | 0.34 | 0.64 | 0.01 | 0.29 | 0.69 |
| 0.416 | 0.542 | 0.06 | 0.42 | 0.52 | 0 | 0.22 | 0.78 |
| 0.53 | 0.582 | 0.07 | 0.51 | 0.42 | 0 | 0.17 | 0.83 |
| 0.631 | 0.627 | 0.12 | 0.56 | 0.32 | 0 | 0.12 | 0.88 |
| 0.696 | 0.649 | 0.16 | 0.59 | 0.25 | 0 | 0.08 | 0.92 |
| 0.802 | 0.705 | 0.3 | 0.55 | 0.15 | 0 | 0.06 | 0.94 |
| 0.889 | 0.772 | 0.44 | 0.5 | 0.06 | 0 | 0 | 1 |
| 0.939 | 0.829 | 0.61 | 0.37 | 0.02 | 0 | 0 | 1 |

**Table 5.16: Data set of Hill et al. (1992) styrene/acrylonitrile in toluene at 60°C.**

| Feed Composition f1 (mol frac of STY) | Copolymer Composition F1 (mol frac of STY) | Triad Fractions | | | | | |
|---|---|---|---|---|---|---|---|
| | | $A_{111}$ | $A_{112+211}$ | $A_{212}$ | $A_{222}$ | $A_{221+122}$ | $A_{121}$ |
| 0.035 | 0.135 | 0 | 0.034 | 0.966 | 0.665 | 0.283 | 0.052 |
| 0.035 | 0.135 | 0 | 0.05 | 0.95 | 0.707 | 0.261 | 0.033 |
| 0.072 | 0.275 | 0 | 0.08 | 0.92 | 0.364 | 0.536 | 0.1 |
| 0.125 | 0.375 | 0 | 0.11 | 0.89 | 0.144 | 0.534 | 0.322 |
| 0.212 | 0.44 | 0.015 | 0.225 | 0.76 | 0.08 | 0.42 | 0.5 |
| 0.212 | 0.44 | 0.03 | 0.24 | 0.73 | 0.07 | 0.43 | 0.5 |
| 0.276 | 0.485 | 0.022 | 0.3 | 0.678 | 0.034 | 0.358 | 0.608 |
| 0.364 | 0.52 | 0.029 | 0.385 | 0.586 | 0.038 | 0.258 | 0.703 |
| 0.364 | 0.52 | 0.024 | 0.385 | 0.591 | 0.021 | 0.284 | 0.695 |
| 0.463 | 0.55 | 0.057 | 0.463 | 0.48 | 0.009 | 0.201 | 0.79 |
| 0.596 | 0.6 | 0.11 | 0.552 | 0.337 | 0 | 0.141 | 0.859 |
| 0.596 | 0.6 | 0.114 | 0.551 | 0.335 | 0.011 | 0.133 | 0.856 |
| 0.696 | 0.645 | 0.193 | 0.574 | 0.233 | 0 | 0.086 | 0.914 |
| 0.808 | 0.7 | 0.297 | 0.564 | 0.138 | 0 | 0.052 | 0.948 |
| 0.9 | 0.78 | 0.496 | 0.439 | 0.065 | 0 | 0 | 1 |
| 0.9 | 0.78 | 0.473 | 0.477 | 0.05 | 0 | 0.033 | 0.967 |

Table 5.17: Data set of Hill et al. (1992) styrene/acrylonitrile in acetonitrile at 60°C.

| Feed Composition f1 (mol frac of STY) | Copolymer Composition F1 (mol frac of STY) | Triad Fractions | | | | | |
|---|---|---|---|---|---|---|---|
| | | $A_{111}$ | $A_{112+211}$ | $A_{212}$ | $A_{222}$ | $A_{221+122}$ | $A_{121}$ |
| 0.035 | 0.27 | 0 | 0.05 | 0.95 | 0.37 | 0.52 | 0.11 |
| 0.047 | 0.3 | 0 | 0.07 | 0.28 | 0.28 | 0.57 | 0.15 |
| 0.72 | 0.365 | 0 | 0.09 | 0.91 | 0.23 | 0.56 | 0.21 |
| 0.125 | 0.419 | 0 | 0.17 | 0.83 | 0.09 | 0.5 | 0.41 |
| 0.212 | 0.475 | 0 | 0.25 | 0.75 | 0.09 | 0.42 | 0.48 |
| 0.276 | 0.5 | 0.02 | 0.32 | 0.66 | 0.06 | 0.33 | 0.61 |
| 0.364 | 0.542 | 0.03 | 0.37 | 0.6 | 0.05 | 0.27 | 0.68 |
| 0.462 | 0.577 | 0.06 | 0.48 | 0.46 | 0.01 | 0.22 | 0.78 |
| 0.596 | 0.629 | 0.12 | 0.58 | 0.3 | 0.01 | 0.12 | 0.87 |
| 0.696 | 0.674 | 0.21 | 0.59 | 0.2 | 0 | 0.08 | 0.92 |
| 0.808 | 0.74 | 0.35 | 0.54 | 0.12 | 0 | 0.04 | 0.97 |
| 0.9 | 0.84 | 0.6 | 0.38 | 0.02 | 0 | 0.03 | 0.97 |

Table 5.18: Data set of Klumperman and Kraeger (1994) styrene/acrylonitrile in bulk at 60°C.

| Feed Composition f1 (mol frac of STY) | Copolymer Composition F1 (mol frac of STY) | Triad Fractions | | | | | |
|---|---|---|---|---|---|---|---|
| | | $A_{111}$ | $A_{112+211}$ | $A_{212}$ | $A_{222}$ | $A_{221+122}$ | $A_{121}$ |
| 0.0151 | 0.138 | 0 | 0 | 1 | 0.74 | 0.24 | 0.02 |
| 0.0155 | 0.147 | 0 | 0 | 1 | 0.75 | 0.23 | 0.02 |
| 0.0531 | 0.318 | 0 | 0.06 | 0.94 | 0.24 | 0.62 | 0.14 |
| 0.1037 | 0.393 | 0.02 | 0.14 | 0.85 | 0.11 | 0.56 | 0.38 |
| 0.1095 | 0.371 | 0 | 0.09 | 0.91 | 0.13 | 0.57 | 0.3 |
| 0.2214 | 0.466 | 0.02 | 0.27 | 0.71 | 0.05 | 0.39 | 0.56 |
| 0.5861 | 0.598 | 0.13 | 0.55 | 0.32 | 0 | 0.13 | 0.87 |
| 0.6198 | 0.632 | 0.18 | 0.54 | 0.28 | 0 | 0.12 | 0.88 |
| 0.8006 | 0.693 | 0.29 | 0.58 | 0.13 | 0 | 0.08 | 0.92 |
| 0.9392 | 0.832 | 0.62 | 0.34 | 0.04 | 0 | 0.05 | 0.95 |

Table 5.19: Data set of Klumperman and Kraeger (1994) styrene/acrylonitrile in toluene at 60°C.

| Feed Composition f1 (mol frac of STY) | Copolymer Composition F1 (mol frac of STY) | Triad Fractions | | | | | |
|---|---|---|---|---|---|---|---|
| | | $A_{111}$ | $A_{112+211}$ | $A_{212}$ | $A_{222}$ | $A_{221+122}$ | $A_{121}$ |
| 0.0151 | 0.092 | 0 | 0 | 1 | 0.84 | 0.15 | 0.01 |
| 0.0152 | 0.092 | 0 | 0.03 | 0.97 | 0.83 | 0.16 | 0.01 |
| 0.0377 | 0.233 | 0 | 0.03 | 0.97 | 0.52 | 0.45 | 0.03 |
| 0.1101 | 0.366 | 0 | 0.09 | 0.91 | 0.16 | 0.57 | 0.27 |
| 0.111 | 0.361 | 0 | 0.08 | 0.92 | 0.19 | 0.57 | 0.24 |
| 0.1899 | 0.434 | 0.01 | 0.23 | 0.76 | 0.07 | 0.46 | 0.47 |
| 0.3241 | 0.496 | 0.03 | 0.35 | 0.62 | 0.03 | 0.31 | 0.66 |
| 0.5009 | 0.566 | 0.07 | 0.5 | 0.43 | 0.01 | 0.18 | 0.81 |
| 0.5727 | 0.591 | 0.11 | 0.53 | 0.36 | 0 | 0.15 | 0.85 |
| 0.5763 | 0.594 | 0.1 | 0.55 | 0.35 | 0.01 | 0.14 | 0.85 |
| 0.7555 | 0.67 | 0.24 | 0.58 | 0.18 | 0 | 0.08 | 0.92 |
| 0.9334 | 0.818 | 0.61 | 0.36 | 0.03 | 0 | 0.03 | 0.97 |
| 0.9349 | 0.827 | 0.62 | 0.36 | 0.03 | 0 | 0.03 | 0.97 |

### 5.5.1.1 *Additive Error Structure*

The point estimates published by Hill et al. (1989 and 1992) can be seen in Table 5.20, along with the point estimates found using the EVM MATLAB analysis of the data sets. The Klumperman and Kraeger (1994) article did not publish reactivity ratio estimates for the terminal model, as they only considered the penultimate model. Consequently, analysis of the Klumperman and Kraeger (1994) data was performed to determine the sensitivity of the parameter estimates to the data set and subsequent experimental design (refer to Table 5.21).

**Table 5.20: Point estimates published by Hill et al. (1989 & 1992) and the EVM estimates (additive error).**

| | Solvent | Temp (°C) | Data Source | Estimation Method | $r_1$ | $r_2$ |
|---|---|---|---|---|---|---|
| Hill et al. (1989) | Bulk | 60 | Triad fractions | NLLS | 0.47 | 0.08 |
| Hill et al. (1989) | Bulk | 60 | Composition | NLLS | 0.34 | 0.05 |
| Current work | Bulk | 60 | Hill et al. (1989) triad fractions | EVM | 0.4814 | 0.1034 |
| Current work | Bulk | 60 | Hill et al. (1989) composition | EVM | 0.3503 | 0.0576 |
| Hill et al. (1992) | Bulk | 60 | Triad fractions | NLLS | 0.394 | 0.063 |
| Current work | Bulk | 60 | Hill et al. (1992) triad fractions | EVM | 0.4817 | 0.0995 |
| Hill et al. (1992) | Toluene | 60 | Triad fractions | NLLS | 0.423 | 0.118 |
| Current work | Toluene | 60 | Hill et al. (1992) triad fractions | EVM | 0.5371 | 0.1236 |
| Current work | Toluene | 60 | Hill et al. (1992) composition | EVM | 0.3646 | 0.1112 |
| Hill et al. (1992) | Acetonitrile | 60 | Triad fractions | NLLS | 0.485 | 0.081 |
| Current work | Acetonitrile | 60 | Hill et al. (1992) triad fractions | EVM | 0.4816 | 0.1632 |
| Current work | Acetonitrile | 60 | Hill et al. (1992) composition | EVM | 0.2802 | 0.0582 |

**Table 5.21: EVM (additive error) point estimates from analyzing Klumperman & Kraeger (1994) data.**

| Solvent | Temp (°C) | Data Source | Estimation Method | $r_1$ | $r_2$ |
|---|---|---|---|---|---|
| Bulk | 60 | Triad fractions | EVM | 0.5133 | 0.1069 |
| Bulk | 60 | Composition | EVM | 0.3551 | 0.0755 |
| Toluene | 60 | Triad fractions | EVM | 0.4973 | 0.1191 |
| Toluene | 60 | Composition | EVM | 0.3394 | 0.0968 |

A clearer picture of the estimates can be seen when the data is grouped together by system (i.e., bulk, toluene solvent, and acetonitrile solvent) and the exact JCRs shown (refer to Figures 5.26-5.28). Note here that in the figures if the data set used in the analysis is taken from Hill et al.

(1989), Hill et al. (1992) or Klumperman and Kraeger (1994) it is referred to in the figure as (Hill, 1989), (Hill, 1992) or (Klumperman, 1994) , respectively.

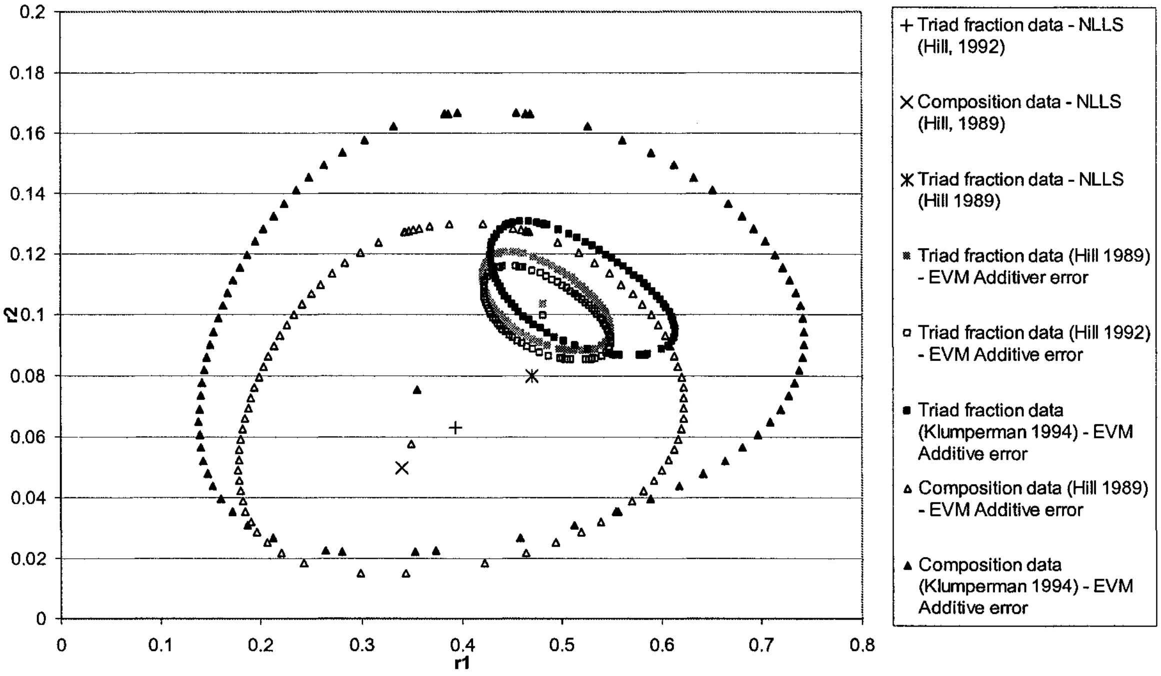


**Figure 5.26: Exact JCRs for EVM (additive error) analysis of Hill et al. (1989), Hill et al. (1992) and Klumperman & Kraeger (1994) triad and composition data for the STY/AN BULK system at 60°C.**

Figure 5.26 shows a relatively well behaved system, when an additive error structure is imposed to both composition and triad fractions data sets. That is, the EVM exact JCRs obtained from analysis of both the Hill et al. (1989 and 1992) and Klumperman and Kraeger (1994) data sets, overlap significantly. Furthermore, both of the composition data exact JCRs contain the respective literature NLLS point estimate by Hill et al. (1989).

Now considering the triad fractions data analysis, when an additive error structure is imposed, the exact JCRs from the different literature groups can be seen to also overlap significantly for this bulk copolymerization system (refer to Figure 5.26). Therefore, confidence in the point estimates is warranted as the parameter estimates do not appear to be significantly influenced by different data sets (i.e., consistent results from independent analysis). Most interesting is the fact that the exact JCR obtained from analyzing the triad fractions data (Hill et al., 1992) is slightly shifted in a SW direction away from the exact JCR obtained from analyzing the triad fractions data (Hill et al., 1989); mimicking the same trend in the literature groups NLLS estimates.

However, the shift in the contour is less pronounced than that seen in the shift in the NLLS point estimates. This is of particular importance as it indicates that EVM is more robust and consistent at estimating reactivity ratio estimates than NLLS (i.e., consistent estimates obtained despite using different data sets); and thus another reason for EVM to be the parameter estimation method of choice for reactivity ratio estimation problems.

Not surprisingly, the exact JCRs (seen in Figure 5.26) obtained from analysis of the Klumperman and Kraeger (1994) triad fractions and composition data sets result in larger contours than those obtained from the analysis of Hill et al. (1989 and 1992) data sets. The reason for the larger contours, and thus more uncertainty in the parameter estimates, is due to the fact that the Klumperman and Kraeger (1994) data set had less data points than the Hill et al. (1989 and 1992) data sets. That is, there is less information supplied to the EVM routine in the Klumperman and Kraeger (1994) analysis and subsequently more uncertainty in the parameter estimates.

In Figure 5.27 the exact JCRs are shown for the toluene solvent STY-AN system. The exact JCRs are obtained from EVM analysis of Hill et al. (1992) and Klumperman and Kraeger (1994) data sets for both triad fractions and composition.

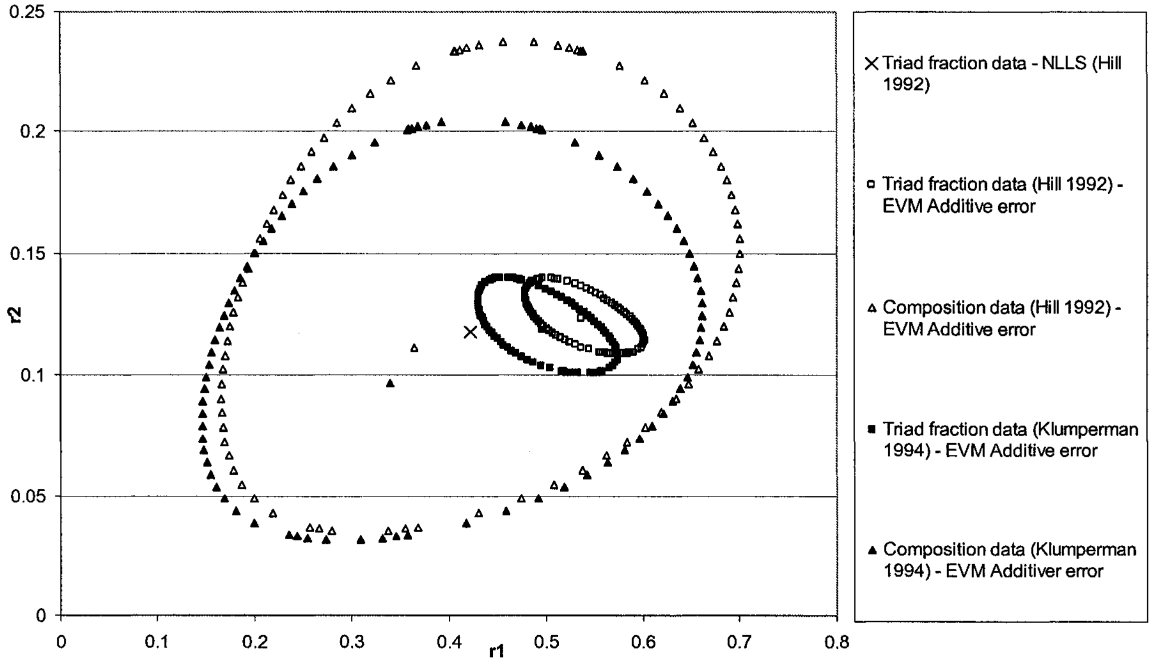


**Figure 5.27: Exact JCRs for EVM (additive error) analysis of Hill et al. (1992) and Klumperman & Kraeger (1994) triad and composition data for the STY/AN TOLUENE solvent system at 60°C.**

Similar to the previous figure, Figure 5.27 shows that exact JCRs obtained from analyzing triad fractions data overlap considerably with the exact JCRs obtained from analyzing composition data; thus indicating good agreement between the two data sources when an additive error structure is imposed. Furthermore, the contours and point estimates appear to be robust to changes in the data set used. That is, using different literature group data sets yields very similar exact JCRs for the respective triad fractions or composition data analysis.

In Figure 5.28 however, the exact JCRs obtained from the analysis of the STY/AN acetonitrile solvent system composition and triad fractions data sets are seen to be quite different to the previous results. That is, the exact JCR obtained from analysis of triad fractions data is not overlapping the exact JCR obtained from the analysis of composition data. Theoretically, one would expect triad fractions and composition to lead to similar estimates, yet this is not the case. The cause of the contour separation may be attributed to: 1) the model used by Hill et al. (1992) to transform the NMR peak areas into triads is not a correct representation of the system (i.e., incorrect tacticity parameters or equations); 2) that the use of triad fractions data lacks the ability to accurately represent reactivity ratio estimates (although unlikely, as in the previous case studies the contours generally overlapped); or 3) the precipitation of acrylonitrile in the copolymerization system may be more pronounced in an acetonitrile solvent and thus influencing the results.

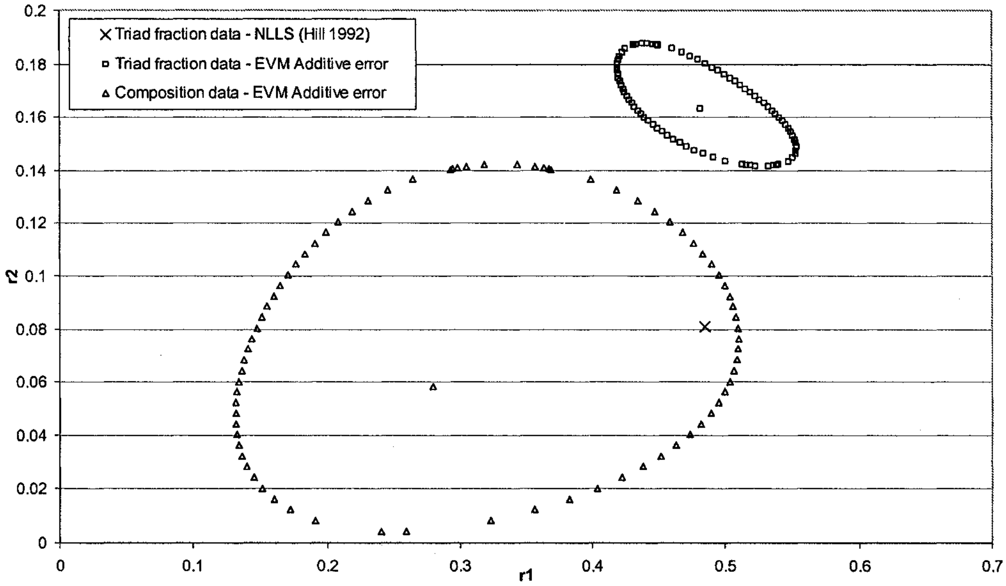


**Figure 5.28: Exact JCRs for EVM (additive error) analysis of Hill et al. (1992) triad and composition data for the STY/AN ACETONITRILE solvent system at 60°C.**

Some points to be made that are common to all of the STY/AN composition and triad fractions data EVM parameter estimation analysis (with imposed additive error structures), by referring to Figures 5.26-5.28, are the following:

- The exact JCR is smaller when using triad fractions data than when composition data is used, which can be explained from an information content point of view (i.e., more responses per data point for triad fractions data sets). Consequently, it can be said that the use of triad fractions data results in less uncertainty in the parameter estimates than when using copolymer composition data.
- The NLLS estimates provided by the Hill et al. (1989 and 1992) group fall outside the exact JCRs when the triad fractions data is used. Therefore, one can say that either the point estimates by the authors are incorrect (due to the use of a statistically incorrect estimation method not accounting for the error in the feed fraction), or that the triad fractions data does not give accurate estimates (perhaps due to insufficient sample size).
- The uncertainty in $r_1$ (the reactivity ratio estimate of the styrene monomer) is significantly greater than the uncertainty in $r_2$ (reactivity ratio estimate of the acrylonitrile monomer). This may be attributed to the precipitation of acrylonitrile during the copolymerization or due to poor experimental design.

### *5.5.1.2 Multiplicative Error Structure*

The analysis of the STY/AN solvent systems when imposing a multiplicative error structure, in the EVM program, was completed. The point estimates of the new analysis and the estimates provided by the Hill et al. (1989 and 1992) group can be seen in Table 5.22. While the reactivity ratio estimates obtained from the analysis of the Klumperman and Kraeger (1994) data set (imposing a multiplicative error structure) for the STY/AN bulk and toluene solvent systems can be seen in Table 5.23.

**Table 5.22: Point estimates published by Hill et al. (1989 and 1992) and the estimates obtained by EVM (multiplicative error) analysis of the data.**

| | Solvent | Temp (°C) | Data Source | Estimation Method | $r_1$ | $r_2$ |
|---|---|---|---|---|---|---|
| Hill et al. (1989) | Bulk | 60 | Triad fractions | NLLS | 0.47 | 0.08 |
| Hill et al. (1989) | Bulk | 60 | Composition | NLLS | 0.34 | 0.05 |
| Current work | Bulk | 60 | Hill et al. (1989) triad fractions | EVM | 0.6517 | 0.0841 |
| Current work | Bulk | 60 | Hill et al. (1989) composition | EVM | 0.358 | 0.0531 |
| Hill et al. (1992) | Bulk | 60 | Triad fractions | NLLS | 0.394 | 0.063 |
| Current work | Bulk | 60 | Hill et al. (1992) triad fractions | EVM | 0.6658 | 0.0752 |
| Hill et al. (1992) | Toluene | 60 | Triad fractions | NLLS | 0.423 | 0.118 |
| Current work | Toluene | 60 | Hill et al. (1992) triad fractions | EVM | 0.5135 | 0.1262 |
| Current work | Toluene | 60 | Hill et al. (1992) composition | EVM | 0.4674 | 0.1587 |
| Hill et al. (1992) | Acetonitrile | 60 | Triad fractions | NLLS | 0.485 | 0.081 |
| Current work | Acetonitrile | 60 | Hill et al. (1992) triad fractions | EVM | 0.477 | 0.1224 |
| Current work | Acetonitrile | 60 | Hill et al. (1992) composition | EVM | 0.2317 | 0.0627 |

**Table 5.23: Point estimates obtained by EVM (multiplicative error) analysis of Klumperman and Kraeger (1994) data.**

| Solvent | Temp (°C) | Data Source | Estimation Method | $r_1$ | $r_2$ |
|---|---|---|---|---|---|
| Bulk | 60 | Triad fractions | EVM | 0.6204 | 0.1026 |
| Bulk | 60 | Composition | EVM | 0.3765 | 0.0772 |
| Toluene | 60 | Triad fractions | EVM | 0.5081 | 0.1352 |
| Toluene | 60 | Composition | EVM | 0.407 | 0.1223 |

Firstly, in Figure 5.29 the exact JCRs are shown for the Hill et al. (1989) and (1992) triad fractions and composition data sets, with additive and multiplicative error structures, to illustrate the impact the imposed error structure may have on the reactivity ratio point estimates and exact JCR.

By specifically focusing on triad fractions data an interesting trend can be seen when the data sets of Hill et al. (1989) and Hill et al. (1992) are considered. In Figure 5.29 it can be seen that when an additive error structure is imposed to the triad fractions data the exact JCRs of the two data set studies (i.e., Hill 1989 and Hill 1992) overlap. However, when a multiplicative error structure is imposed to the triad fractions the exact JCRs of the two data set studies no longer overlap. In fact, when the multiresponse error structure is imposed to either literature triad fractions data sets, the exact JCRs shift outside the region of all other exact JCRs. Theoretically, the exact JCRs from the analysis of triad fractions data with a multiresponse error structure should be significantly overlapping the exact JCRs of the same triad fractions data set study, but with an additive error structure; similar to that seen in the composition data study (multiplicative always falling within the additive error contour for the respective data set). Yet this is not the case. Consequently, the question becomes whether the multiplicative error is the correct error structure to implement in triad fractions data EVM analysis or whether some other effect specific to this STY/AN system, such as the precipitation of acrylonitrile, is more prominent and thus shifting the JCRs when a multiplicative error structure is imposed? Or alternatively, the triad fractions exact JCR (multiplicative error) separation from the triad fractions exact JCRs (additive error) may be the effect of small data sample size, similar to that seen in Case Study I (refer to Section 5.3).

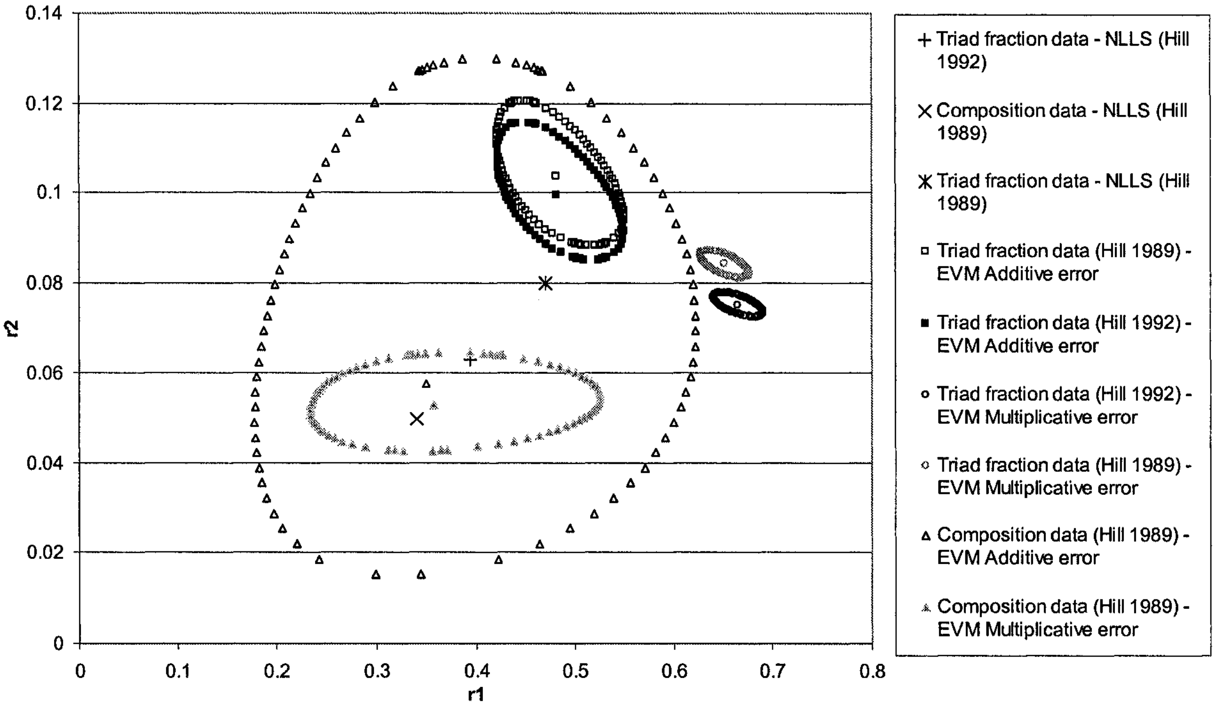


**Figure 5.29: Exact JCRs for EVM (additive and multiplicative error) analysis of Hill et al. (1989 and 1992) triad and composition data for the STY/AN BULK system at 60°C.**

Furthermore, by considering Figure 5.30 with the bulk STY/AN studies from Hill et al. (1992) and Klumperman and Kraeger (1994), it can be seen that the exact JCRs, from the different data sources do not overlap when multiplicative error structure is implemented, for either composition or triad fractions data. Compare this with the case when additive error is used the exact JCRs do in fact overlap (refer to Figure 5.26). Therefore, it becomes apparent that when using a multiplicative error structure for either triad fractions or composition data, the EVM estimates are no longer robust and consistent for different data sources. One possible reason for the inconsistency of estimates, obtained from different data sources, may be the experimental design and quality of data provided for analysis becomes very important in obtaining statistically consistent parameter estimates when a multiplicative error structure is imposed (i.e., bad data results in a more prominent affect to estimates when a multiplicative error structure is imposed). Another possible explanation is that multiplicative error for either triad fractions or composition data is not the correct error structure, which can only be disputed once an error structure study is performed (refer to Section 7.2). Alternatively, the inconsistency could be attributed to issues specific to this particular system, namely the precipitation of acrylonitrile, which may result in a more prominent affect to the reactivity ratio point estimates and exact JCR when a multiplicative error structure is imposed.

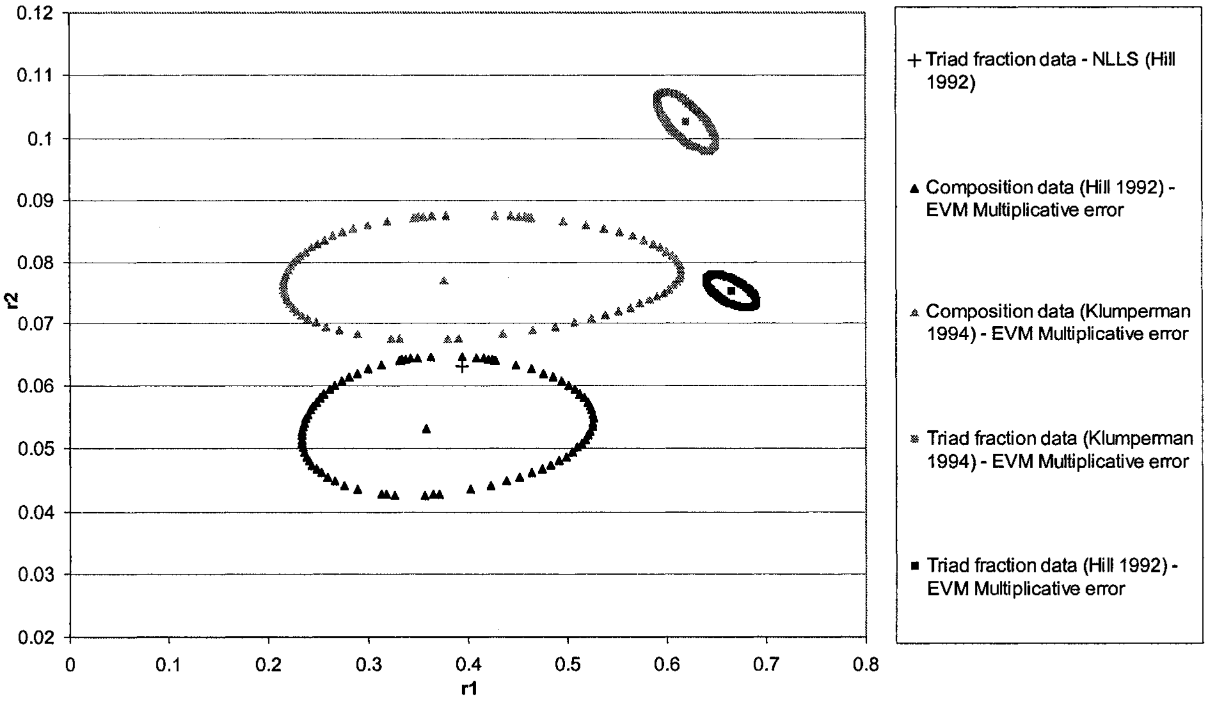


**Figure 5.30: Exact JCRs for EVM (multiplicative error) analysis of Hill et al. (1992) and Klumperman and Kraeger (1994) triad and composition data for the STY/AN BULK system at 60°C.**

The same trends are again seen when considering the toluene solvent STY/AN studies from Hill et al. (1992) and Klumperman and Kraeger (1994), refer to Figure 5.31. That is, when considering the composition data set studies, the exact JCRs from different data sources (i.e., Hill vs. Klumperman) do not overlap when multiplicative error structure is implemented. Similarly, when considering the triad fractions data set studies, the exact JCRs from different data sources do not overlap. Thus supporting the fact that in this case study for STY/AN the EVM estimates obtained from either triad fractions or composition data (when a multiplicative error structure is imposed) are inconsistent when using different data sets (refer to previous discussion).

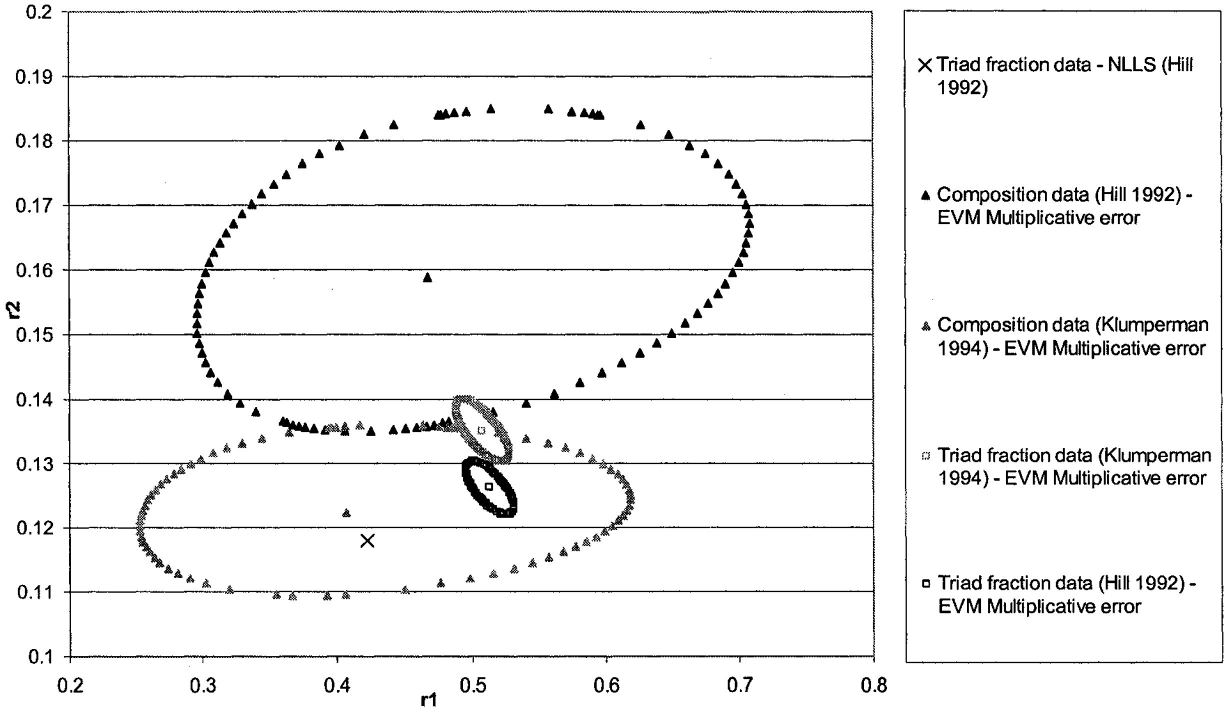


**Figure 5.31: Exact JCRs for EVM (multiplicative error) analysis of Hill et al. (1992) and Klumperman and Kraeger (1994) triad and composition data for the STY/AN TOLUENE solvent system at 60°C.**

In contrast to the result seen in Figure 5.30, in Figure 5.31 the exact JCRs obtained from analysis of the triad fractions data, of either Hill et al. (1992) or Klumperman and Kraeger (1994) data sources, significantly overlap the exact JCR obtained from analysis of the composition data provided by Hill et al. (1992). That is, the exact JCR of Hill composition data (multiplicative error) significantly overlaps with both exact JCRs of Hill triad fractions data (multiplicative error) and Klumperman triad fractions data (multiplicative error). Consequently, when only considering the toluene STY/AN system one could suggest that the data provided by

Klumperman and Kraeger (1994) may not be the best quality data or have a good experimental design. As theoretically, the exact JCRs obtained from analysis of triad fraction and composition data should significantly overlap.

In Figures 5.32 and 5.33 the toluene solvent case studies, with both data sets analysis and different imposed error structures, are considered for each of the literature groups. That is, in Figure 5.32 the exact JCRs obtained from analyzing Hill et al. (1992) groups triad fractions or composition data (toluene solvent), with imposed additive and multiplicative error structures, are shown.

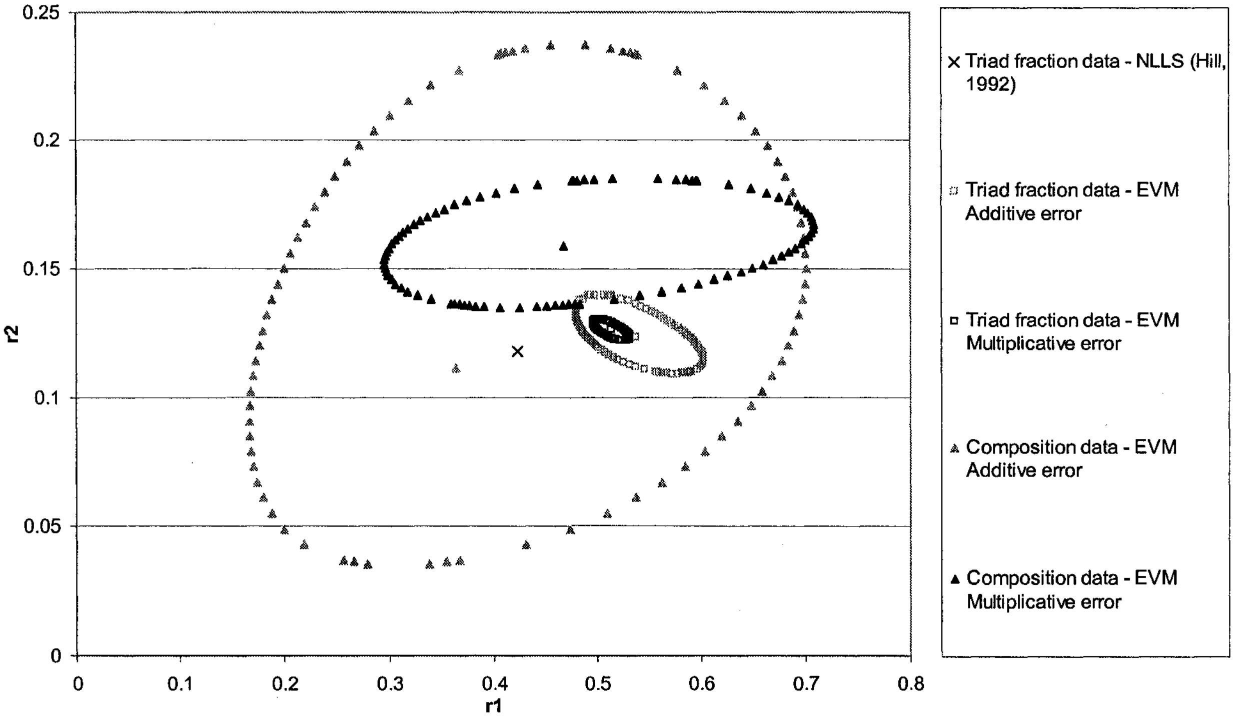


**Figure 5.32: Exact JCRs for EVM (additive and multiplicative error) analysis of Hill et al. (1992) triad and composition data for the STY/AN TOLUENE solvent system at 60°C.**

It can be seen in Figure 5.32 that when the multiplicative error structure is imposed on the composition data the point estimate shifts quite a considerable amount away from the point estimate obtained when an additive error structure was imposed on the same data set. However, when a multiplicative error structure is imposed to triad fractions data the shift is not as pronounced. Although, it can be said from studying Hill et al. (1992) toluene solvent data that the error structure does not significantly affect the reactivity ratio estimates when studying either composition or triad fractions, as the exact JCRs overlap considerably for the different error structures.

In Figure 5.33 the same concept is shown for Klumperman and Kraeger (1994) data for the toluene solvent system. It is most interesting to then compare the Figures 5.32 and 5.33 as it can be seen in Figure 5.33 that the use of different error structures on the triad fractions data resulted in the exact JCRs no longer significantly overlapping. However, both the exact JCRs obtained from analyzing the triad fractions data (additive and multiplicative error) overlap with both the exact JCRs obtained from analyzing the composition data. Therefore, the estimates obtained from the different data sets can be said to still be in agreement.

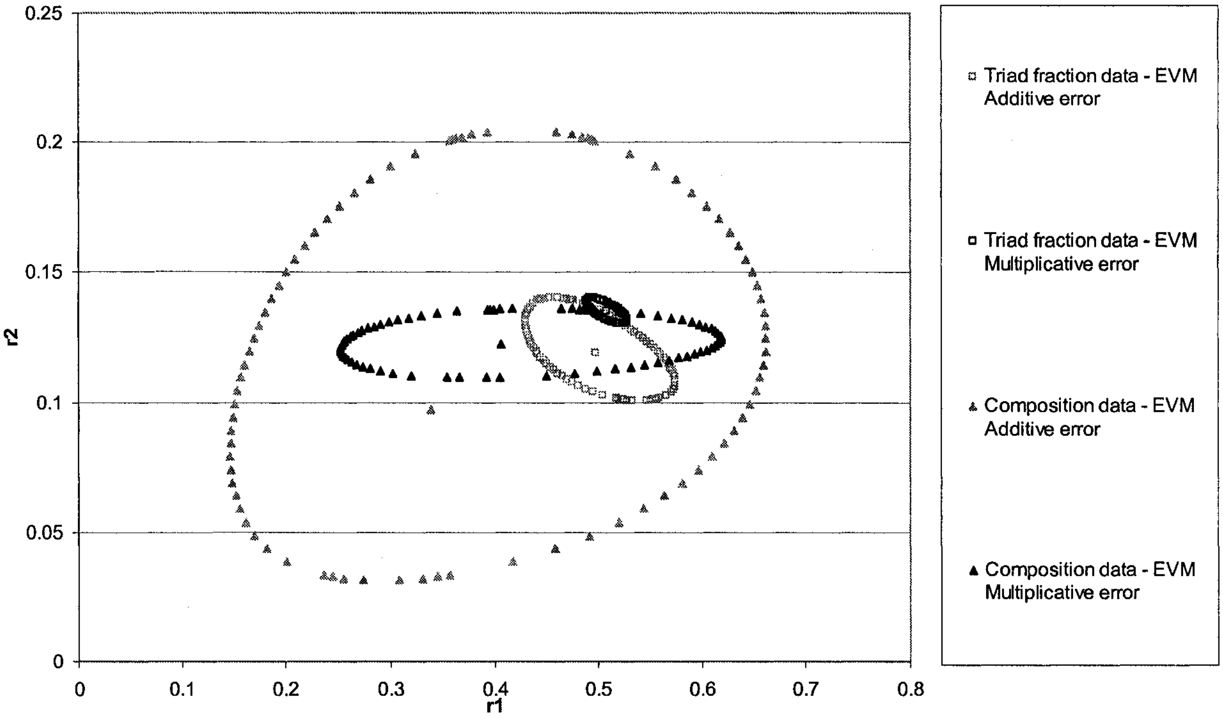


**Figure 5.33: Exact JCRs for EVM (additive and multiplicative error) analysis of Klumperman and Kraeger (1994) triad and composition data for the STY/AN TOLUENE solvent system at 60°C.**

Note that in the case of acetonitrile solvent using triad fractions data, with multiplicative error structure, neither the exact JCR nor the ellipse JCR could be evaluated even after >300 inner and outer iterations. Therefore, in Figure 5.34 the exact JCRs for both analysis of triad fractions and composition data, when an additive error structure was imposed, are shown along with the exact JCR for the analysis of composition data, when a multiplicative error structure is imposed.

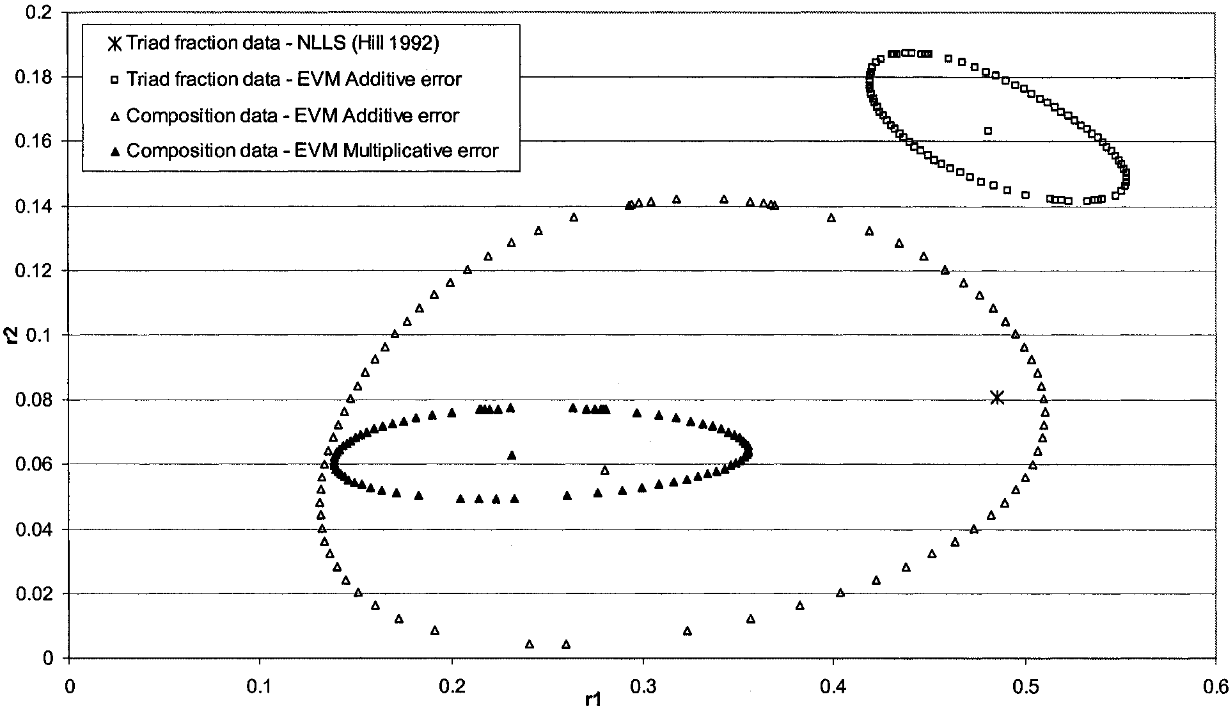


**Figure 5.34: Exact JCRs for EVM (additive and multiplicative error) analysis of Hill et al. (1992) triad and composition data for the STY/AN ACETONITRILE solvent system at 60°C.**

It can be seen in Figure 5.34 that once again the exact JCR for triad fractions data (imposed additive error structure) analysis does not significantly overlap the exact JCRs obtained from composition data analysis, regardless of error structure imposed.

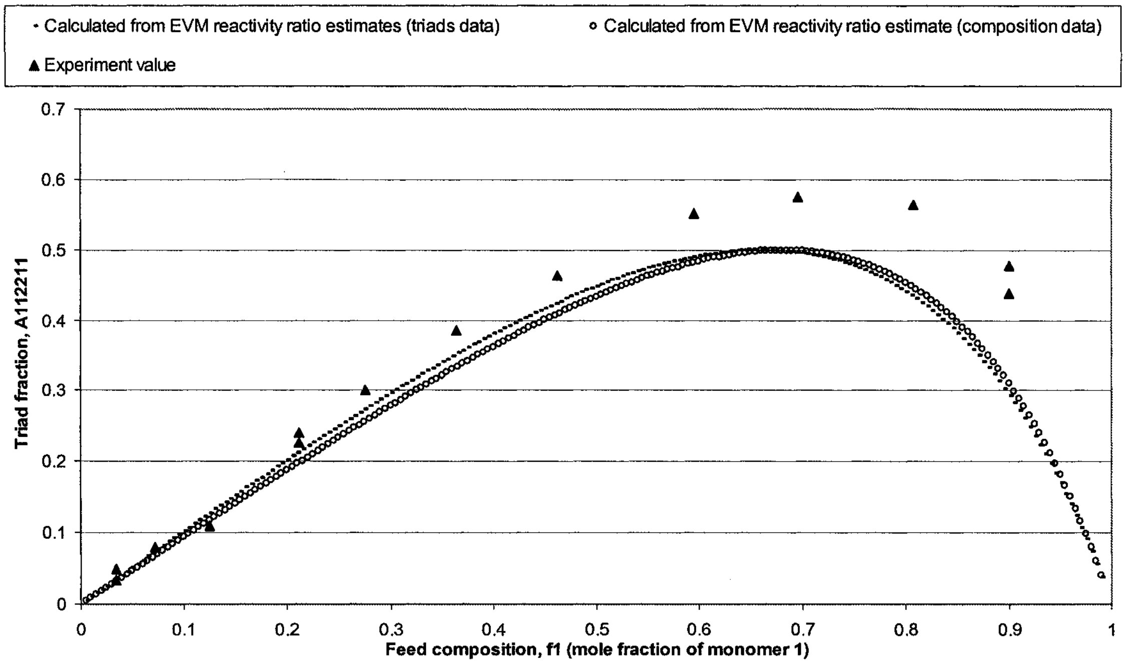
It is also interesting to note, that regardless of error structure all the exact JCRs for the STY/AN composition and triad fractions data EVM parameter estimation analysis (Figures 5.26-5.34) showed that the exact JCR is smaller when using triad fractions data than when composition data is used. Thus, it can be said that there is less uncertainty in reactivity ratio estimates obtained from triad fractions data than in those obtained from composition data.

## 5.8.2 Diagnostic Checking

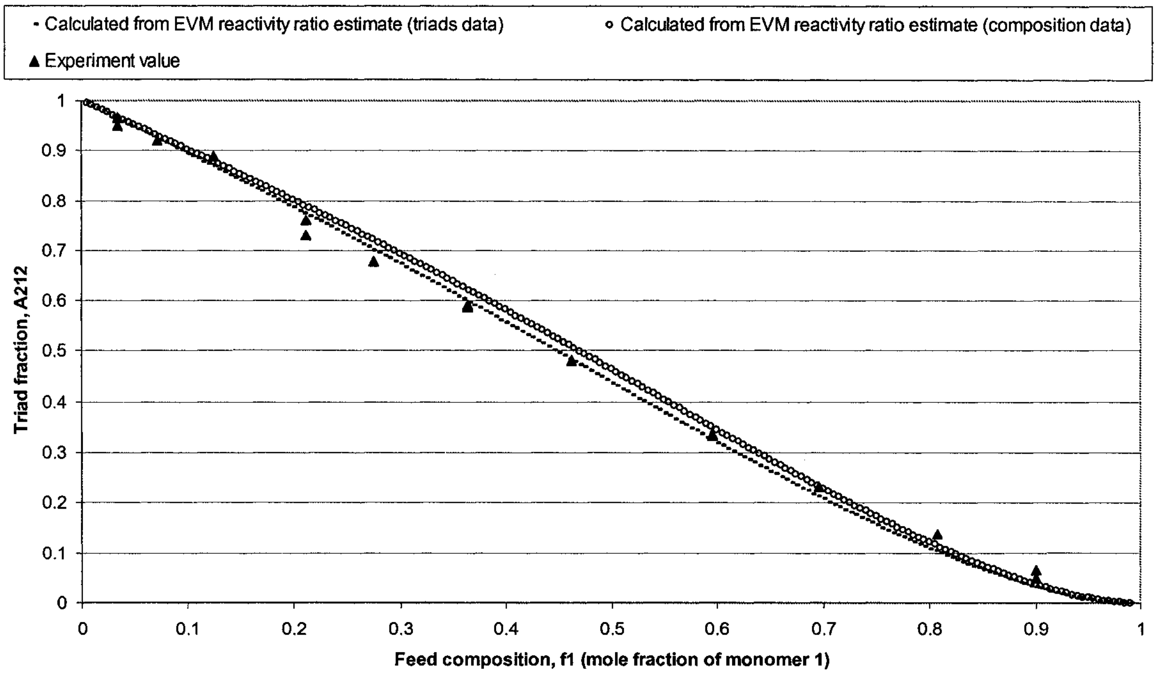
In order to determine whether the reactivity ratio estimates in fact model the experimental results accurately the toluene solvent STY/AN system data from Hill et al. (1992) was selected to be studied in more detail. The EVM (multiplicative error) reactivity ratio estimates, obtained from analyzing Hill's triad fractions and composition data, were used in the triad fractions equations

(Equation 5.1) to compare the ‘predicted’ triad fractions with the recorded ‘experimental’ triad fractions.

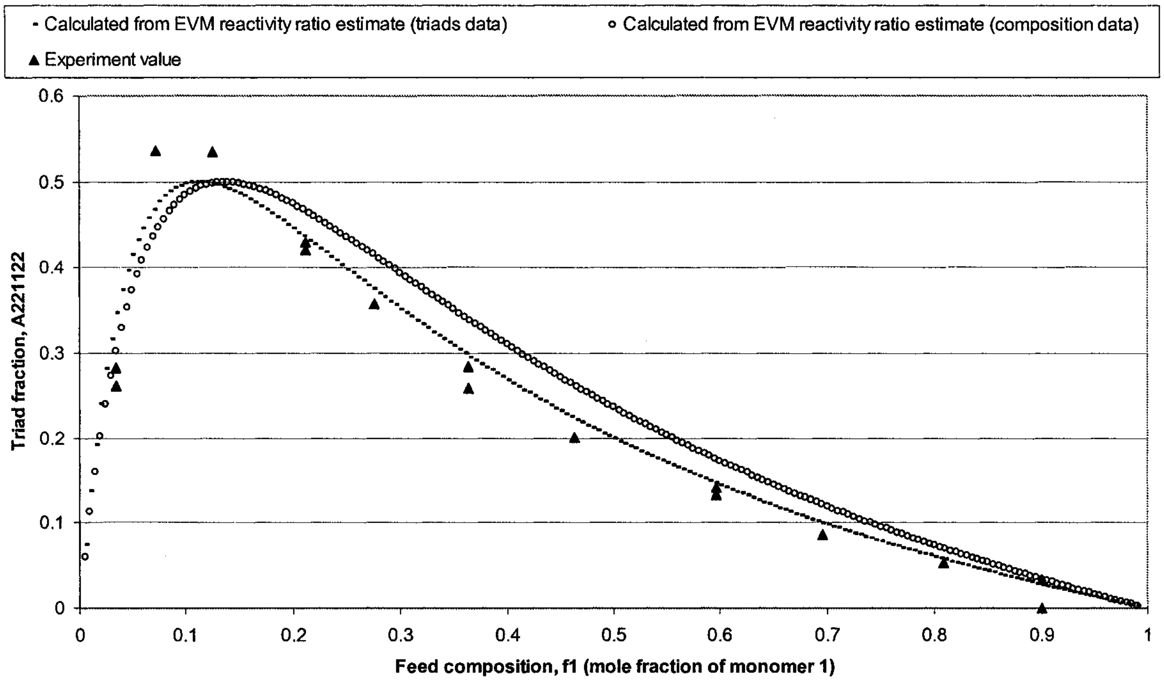
Figures 5.35 a) - d) show the triad fractions predicted from the equations, using the EVM (multiplicative error) reactivity ratio estimates of the triad fractions and composition data. Note only the four triad fractions used in the EVM analysis are shown in the diagnostic testing. While Figure 5.33 e) shows the copolymer composition predicted from the Mayo-Lewis equation, using the EVM (multiplicative error) reactivity ratio estimates of the triad fractions and composition data.



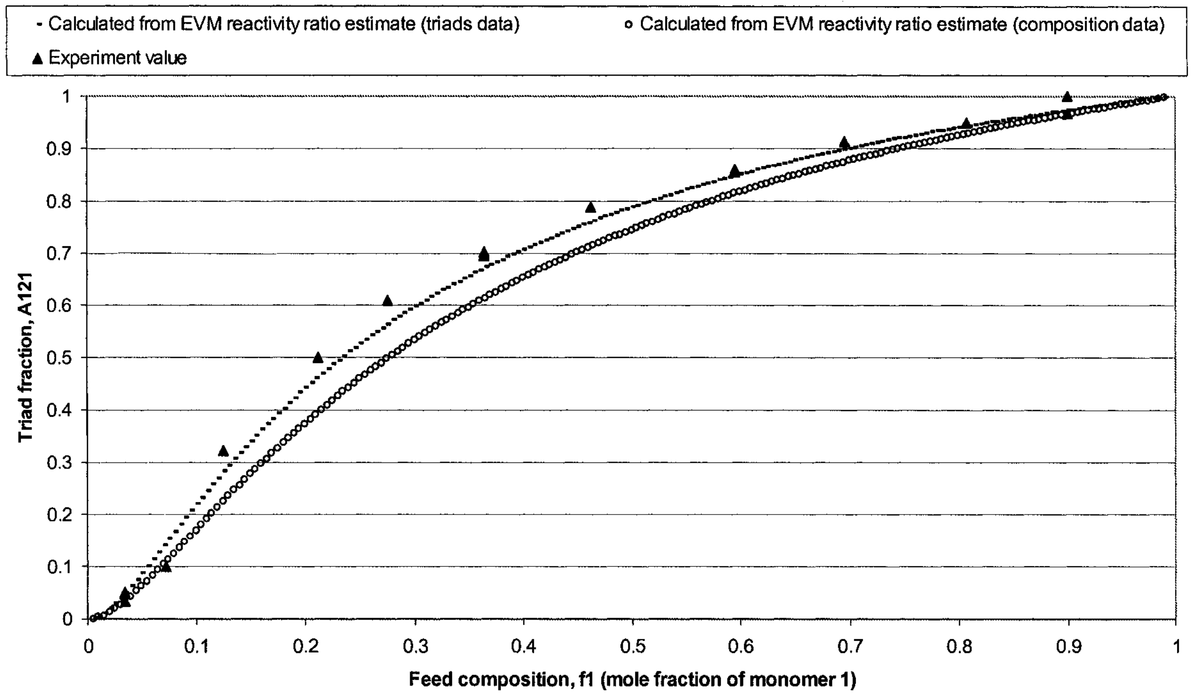
a)


- Calculated from EVM reactivity ratio estimate (triads data)
○ Calculated from EVM reactivity ratio estimate (composition data)
▲ Experiment value
Triad fraction, A212
Feed composition, f1 (mole fraction of monomer 1)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1

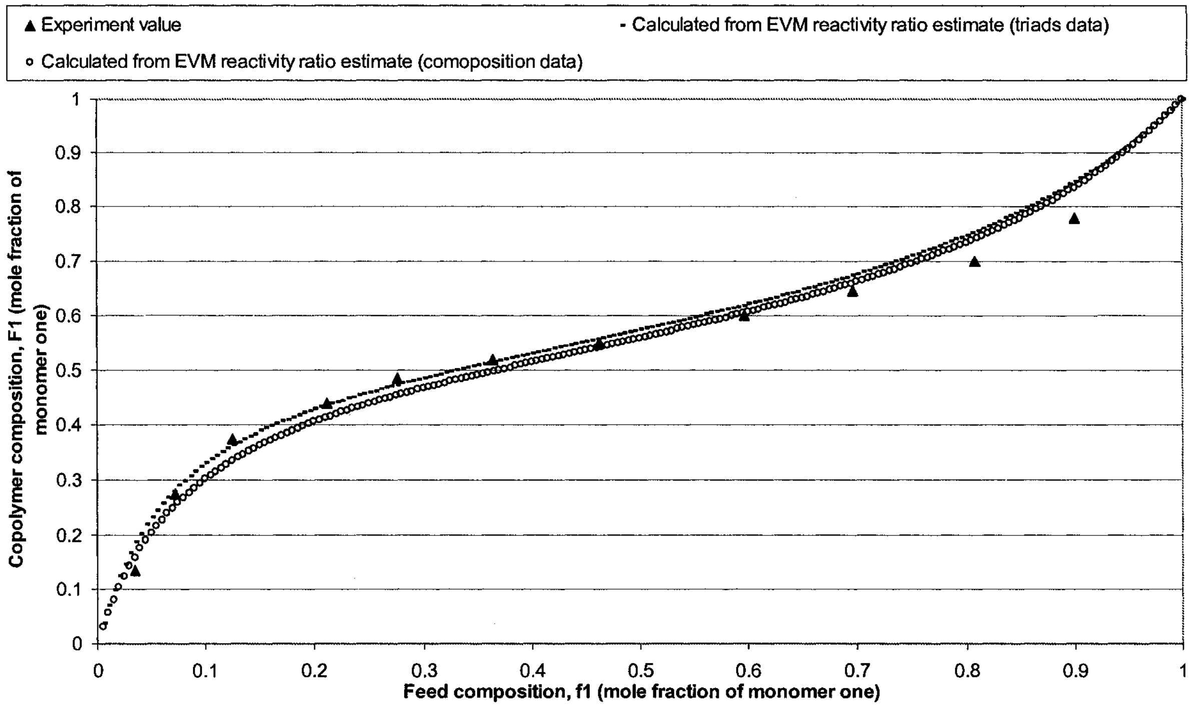
b)


- Calculated from EVM reactivity ratio estimate (triads data)
○ Calculated from EVM reactivity ratio estimate (composition data)
▲ Experiment value
Triad fraction, A221122
Feed composition, f1 (mole fraction of monomer 1)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1

c)



d)



e)

**Figure 5.35 a) - d): Predicted triad fractions using the reactivity ratio estimates obtained from EVM (multiplicative error) analysis of the NMR normalized peak areas in Equation 5.1 and the 'experimental' triad fractions obtained from transforming the measured NMR normalized peak areas. e) Predicted copolymer composition using the EVM (multiplicative error) reactivity ratio estimates, obtained from analyzing triad fractions and composition data, in the Mayo-Lewis equation and the published copolymer composition measurements.**

As can be seen from Figures 5.35 a) –d) the predicted triad fractions obtained from using the EVM (multiplicative error) reactivity ratio estimates from analyzing the triad fractions and composition data are in agreement with the published 'experimental' triad fractions results. Furthermore, the diagram shows that the copolymer composition can be predicted well with reactivity ratios that are estimated from either composition data or triad fractions data.

### 5.8.3 Triad Fractions and Composition Data Combined vs. Triad Fractions Data

The next stage of analysis, as in the previous case study, was to determine whether using all the information available in the EVM program would result in a further reduction of uncertainty in the parameter estimates. The following diagrams are the exact JCRs of the solvent systems using triad fractions and composition data compared to only triad fractions data, imposing a multiplicative error structure. The data sets selected for this analysis were those published by Hill et al. (1992) for bulk and toluene solvent system (refer to Figures 5.36 and 5.37 respectively) as the other data sets for STY-AN followed the same trends.

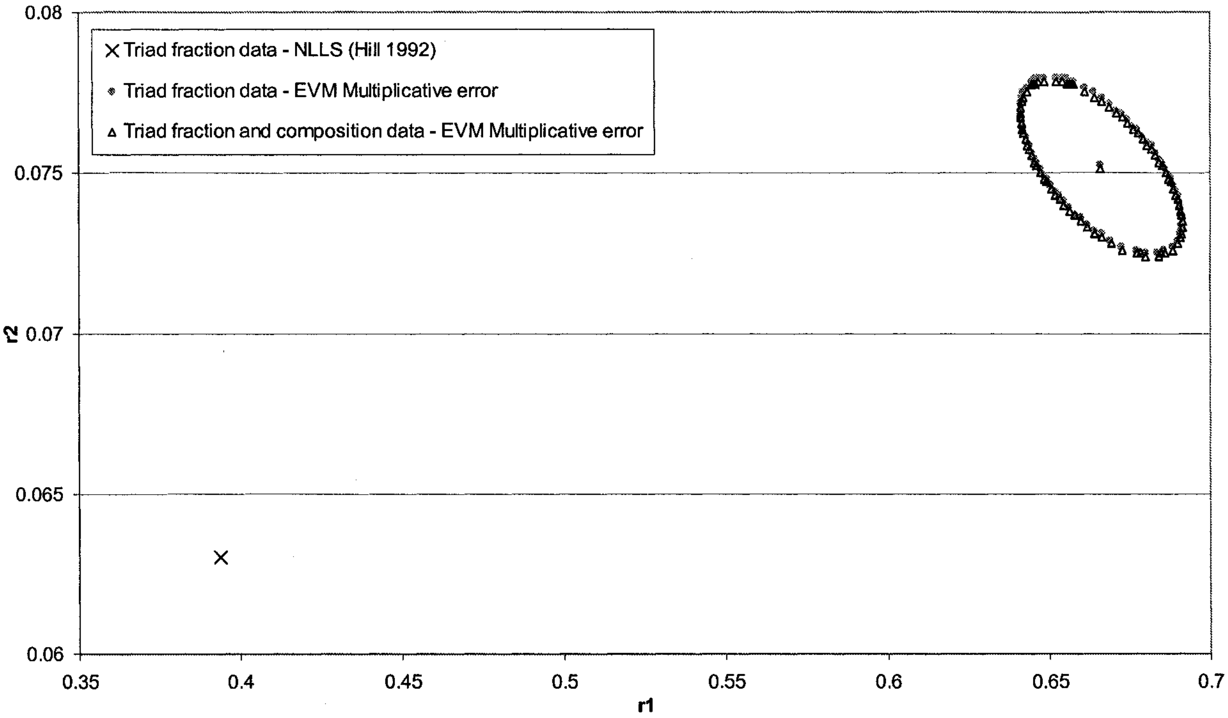


Figure 5.36: Exact JCR for EVM (multiplicative error) analysis of Hill et al. (1992) triad and composition data vs. only triad fractions data for the STY/AN BULK system at 60°C.

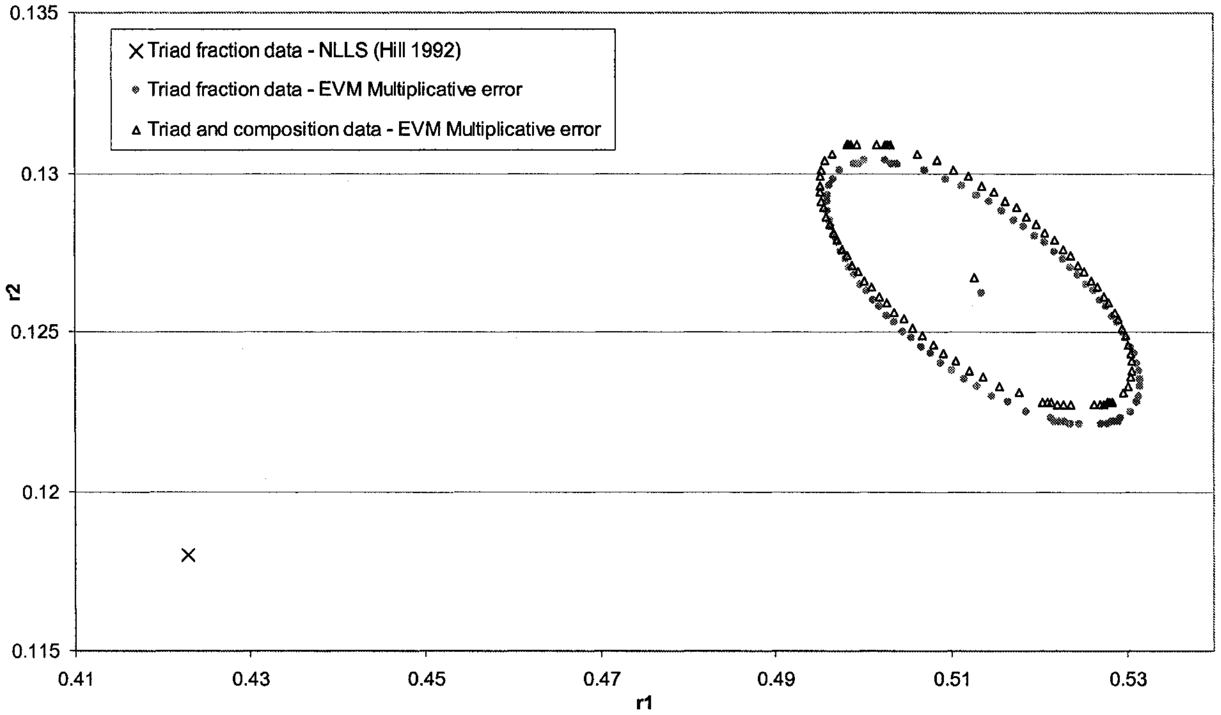


**Figure 5.37: Exact JCR for EVM (multiplicative error) analysis of Hill et al. (1992) triad and composition data vs. only triad fractions data for the STY/AN TOLUENE solvent system at 60°C.**

Considering Figures 5.36 and 5.37, it can be noted that the decrease in area of the exact JCR, when the augmented data sets are used (i.e., combining the copolymer and triads data), does not seem sufficiently significant compared to the exact JCR obtained when using only triad fractions data. Therefore, this case study once again demonstrates that conducting measurements of copolymer composition is not needed, provided reliable triad fractions data can be obtained.

## 5.9 Summary of Results from Analysis of Case Studies I – VI

The main objective of this chapter was to address the following questions by analyzing instantaneous data from a variety of copolymerization systems: 1) Are triad fractions/NMR normalized peak areas based reactivity ratio estimates in agreement with those obtained from composition data; regardless of error structure; 2) When using triad fractions/NMR normalized peak areas do the resulting JCRs show less uncertainty in the parameter estimates than those obtained when using composition data, for either an additive or multiplicative error structure; 3) When using triad fractions/NMR normalized peak areas and composition data together do the resulting JCRs show less uncertainty in the parameter estimates than those obtained when using only triad fractions data; and lastly 4) Does error structure affect the location of the JCR when studying either composition or triad fractions/NMR normalized peak areas data?

The following Table 5.24 was thus created to summarize the analysis of the instantaneous case studies, so as to be able to easily identify the results from each study with reference to the aims of this chapter. However, it is important to realize that each individual case study does deserve more detailed attention (by referring to the appropriate section), as further discussion can be found on results that are of interest, yet may only be relevant to that specific system and not explicitly related to the general objectives of this chapter.

Some general points to be made from Table 5.24 include:

- The use of triad fractions/NMR normalized peak areas data consistently results in less uncertainty in the parameter estimates, compared to when composition data is used; regardless of the error structure imposed.
- Using combined data sets (triad fractions and composition) consistently did not improve the uncertainty in the reactivity ratio estimates, compared to when only triad fractions data is used.
- The imposed error structure does not significantly affect the reactivity ratio estimates (i.e., significant to complete overlapping of exact JCRs exists) when composition data is used.

- The imposed error structure may influence the reactivity ratio estimates (i.e., separate exact JCRs obtained from analyzing the data with different imposed error structures) when triad fractions/NMR normalized peak areas data is used.
- The reactivity ratio estimates may not agree for the same system, when different data types are used. That is, the parameter estimates obtained from analyzing triad fractions/NMR normalized peak areas data is not always in agreement (i.e., overlapping exact JCRs) with the estimates obtained from analyzing composition data, particularly when a multiplicative error structure is imposed.

**Table 5.24: Summary of important results from analyzing Case Studies I – VI.**

| (Case Study) Copolymerization System | | Composition data | Triad fractions data | NMR normalized peak areas data | Triads and composition estimate agrees | | Triads has less uncertainty in estimate than composition | | Combined has less uncertainty in estimate than triads | Error structure significantly effects location of estimates | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Additive error | Multi error | Additive error | Multi error | Multi error | Comp data | Triads data |
| (I)<br>STY-MMA | | X | X | √ | | | | | | | √ |
| (II)<br>STY-MMA | | √ | X | √ | √ | X | √ | √ | X | X | √ |
| (III)<br>Acrylamide-AN | | √ | √ | X | √ | √ | √ | √ | X | X | X |
| (IV)<br>AN-Acrylic Acid | | √ | √ | X | √ | √ | √ | √ | Inconclusive due to deletion of data points | X | √ |
| (V)<br>AN-Pentyl Methacrylate | | √ | √ | X | √ | √ | √ | √ | X | X | X |
| (VI)<br>STY-AN<br>(bulk) | Hill (1989) | √ | √ | X | √ | X | √ | √ | | X | √ |
| | Hill (1992) | √* | √ | X | √ | X | √ | √ | X | X* | √ |
| | Klump (1994) | √ | √ | X | √ | X | √ | √ | | X | √ |
| (VI)<br>STY-AN<br>(Toluene) | Hill (1992) | √ | √ | X | √ | X | √ | √ | X | X | X |
| | Klump (1994) | √ | √ | X | √ | √ | √ | √ | | X | √ |
| (VI)<br>STY-AN<br>(Acetonitrile) | Hill (1992) | √ | √ | X | X | X | √ | Unable to obtain JCR for triads multi error | | X | Unable to obtain JCR for triads multi error |

* The composition data presented in Hill et al. (1992) was the same data set as presented in Hill et al. (1989).

NOTE: √ = Yes, X = No.

The following abbreviations are used in the table: Multi = Multiplicative; Comp = Composition; Klump = Klumperman and Kraeger (1994); Hill = Hill et al. (1992) and (1989). Also, in the last three columns of the table, triad data refers to either use of triad fraction data or NMR normalized peak area data. Blank spaces in the table indicate that the analysis was not performed for that particular system.

## 5.10 Case Study VII: Acrylonitrile/Styrene/Methyl Methacrylate

There are a multitude of literature sources for the terpolymerization composition data of acrylonitrile (AN), styrene (STY) and methyl methacrylate (MMA), including: Hocking and Klimchuk (1996); Shukla and Srivastava (1994); and Brar and Hekmatyar (1999). However, when terpolymer data is used there are in fact six parameters (reactivity ratios) that are estimated and thus there is a minimum of six data points required for the analysis (to satisfy the $n=p$ requirement of parameter estimation, where $n$ is the number of data points and $p$ is the number of parameters). Consequently, the data sets provided by Hocking and Klimchuk (1996), and Shukla and Srivastava (1994) were not used independently, due to insufficient number of data points for the system. Therefore, a recommendation from this work is that future studies need to focus on well designed multicomponent polymerization experiments with many replicates, so that parameter estimation from these types of systems can be thoroughly examined (refer to Section 7.2).

In order to analyze the available terpolymer data the EVM MATLAB program had to be updated to account for the terpolymer equations, based on the differential equations of Alfrey and Goldfinger (Equations 2.49 and 2.50) at low conversions, seen below for reference

$$\begin{aligned}
\frac{P_1}{P_3} &= \frac{M_1(M_1r_{23}r_{23}+M_2r_{31}r_{23}+M_3r_{32}r_{21})(M_1r_{12}r_{13}+M_2r_{13}+M_3r_{12})}{M_3(M_1r_{12}r_{23}+M_2r_{13}r_{21}+M_3r_{12}r_{21})(M_3r_{31}r_{32}+M_1r_{32}+M_2r_{31})} \\
\frac{P_2}{P_3} &= \frac{M_2(M_1r_{32}r_{13}+M_2r_{13}r_{31}+M_3r_{12}r_{31})(M_2r_{21}r_{23}+M_1r_{23}+M_3r_{21})}{M_3(M_1r_{12}r_{23}+M_2r_{13}r_{21}+M_3r_{12}r_{21})(M_3r_{31}r_{32}+M_1r_{32}+M_2r_{31})}
\end{aligned} \tag{5.11}$$

where, $M_i$ are the instantaneous mole fractions of monomer $i$ in the feed solution and $P_i$ are the instantaneous mole fractions of monomer $i$ in the polymer phase.

Implementing the EVM procedure and model equations to the terpolymer case required further adaptation of the EVM program. As discussed previously in Section 3.4 the EVM routine is based on estimating parameters by minimizing the function $\varphi$. In the copolymerization experiments this minimization was achieved by a Newton's method similar to that of Fisher's method of scoring, as outlined by Reilly et al. (1993). However, in the terpolymer case this particular minimization routine had convergence issues; thus a more robust optimization routine was selected. The optimization routine chosen is based on the Simplex method and was implemented into EVM by using the 'fminunc' code command (refer to Appendix A).

It is also important to note here that only the implementation of a multiplicative error structure was considered, due to the EVM variables being composition measurements (which are generally considered to have a multiplicative error structure). Furthermore, the error associated with the feed composition was assumed to be ±1%, while the terpolymer composition was assumed to be ±5%.

### 5.10.1 Brar and Hekmatyar (1999) STY-MMA-AN Data Set

Brar and Hekmatyar (1999) provided experimental data for the AN-STY-MMA system at six different feed composition points and measured terpolymer compositions. The terpolymers were prepared by photopolymerization using uranyl ion as initiator, whilst maintaining the conversion to below 10% to avoid significant composition drift. The AN-STY-MMA terpolymer data set provided by Brar and Hekmatyar (1999) can be seen in Table 5.25.

**Table 5.25: Data set of Brar and Hekmatyar (1999) AN/STY/MMA system.**

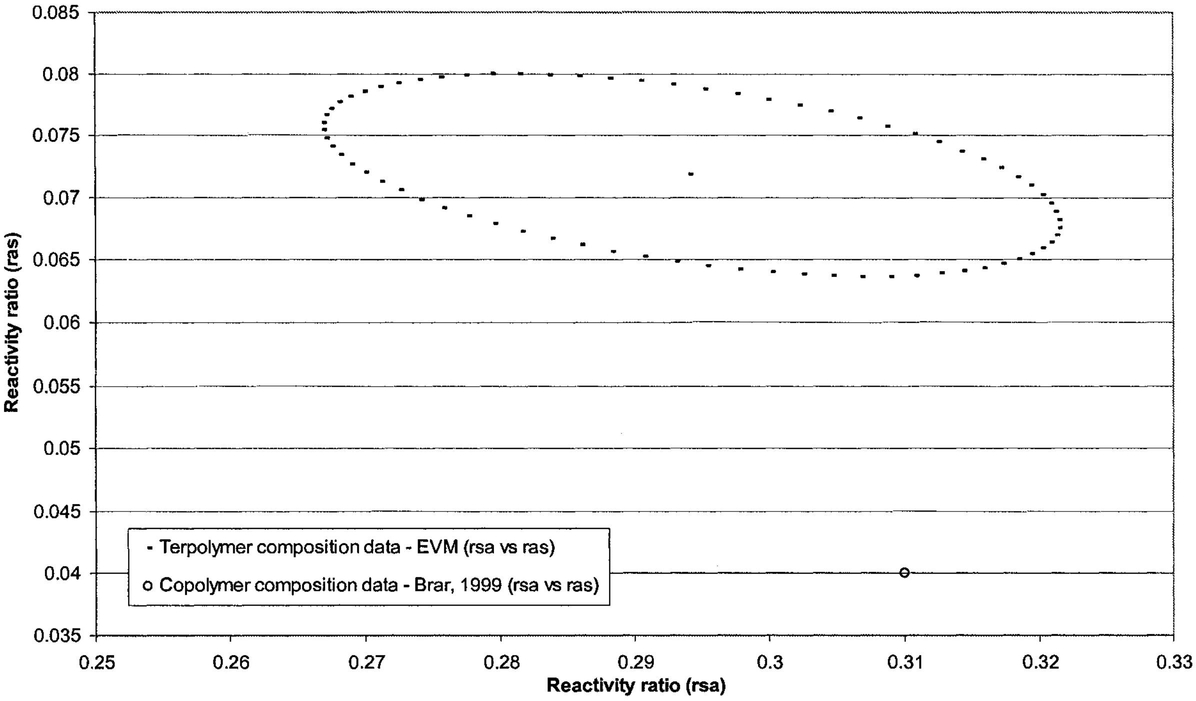
| Mole fraction of monomer in feed | | | Mole fraction of monomer in terpolymer | | |
|---|---|---|---|---|---|
| AN | STY | MMA | AN | STY | MMA |
| 0.63 | 0.22 | 0.15 | 0.46 | 0.40 | 0.14 |
| 0.42 | 0.36 | 0.22 | 0.37 | 0.46 | 0.17 |
| 0.23 | 0.53 | 0.24 | 0.27 | 0.53 | 0.20 |
| 0.41 | 0.16 | 0.43 | 0.32 | 0.29 | 0.39 |
| 0.29 | 0.08 | 0.63 | 0.22 | 0.15 | 0.63 |
| 0.29 | 0.44 | 0.27 | 0.30 | 0.48 | 0.22 |

Using the EVM program, estimation of the six reactivity ratio parameters was then conducted. The initial estimates for the EVM procedure were those given by Brar and Hekmatyar (1999), which were from prior work by Brar et al. (1998), where copolymerization data for different pairs of the three monomers were analyzed. The reactivity ratio estimates given in the literature (using copolymerization data) and those obtained from EVM analysis of the terpolymer data can be seen in Table 5.26.

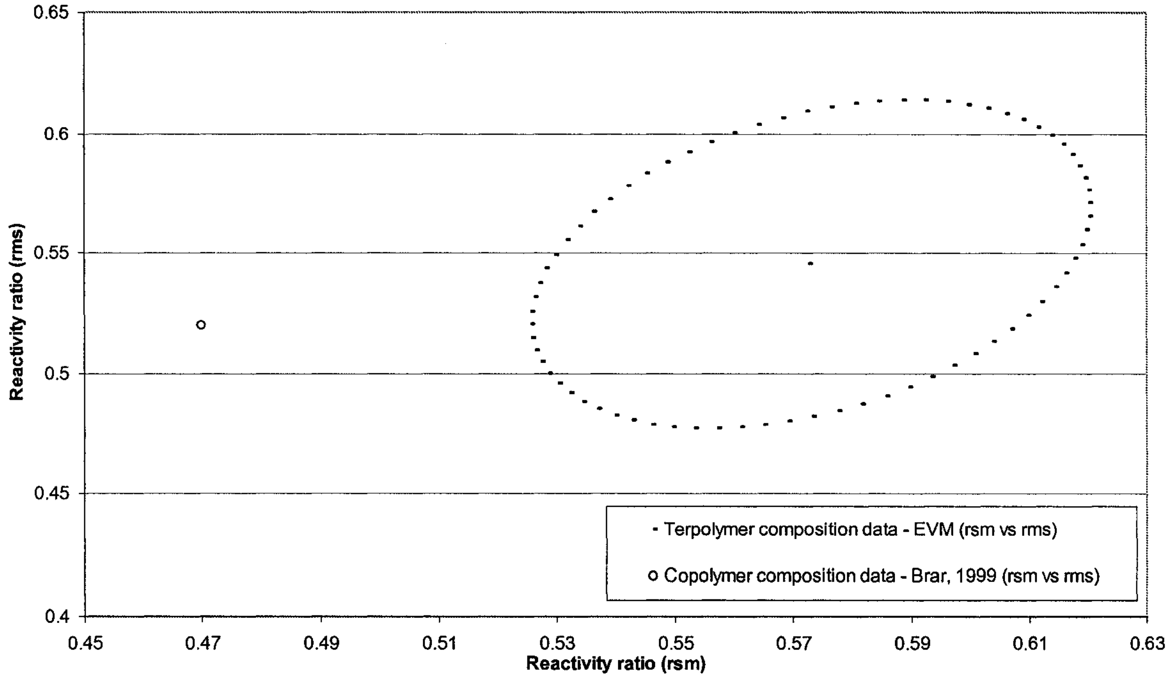
**Table 5.26: Point estimates published by Brar and Hekmatyar (1999) and the estimates obtained by EVM MATLAB, where STY = S, MMA =M and AN = A.**

| | $r_{AS}$ | $r_{AM}$ | $r_{SA}$ | $r_{SM}$ | $r_{MA}$ | $r_{MS}$ |
|---|---|---|---|---|---|---|
| Brar and Hekmatyar (1999) | 0.04 | 0.17 | 0.31 | 0.47 | 1.45 | 0.52 |
| Current work | 0.0718 | 0.2023 | 0.2941 | 0.5729 | 1.3243 | 0.5455 |

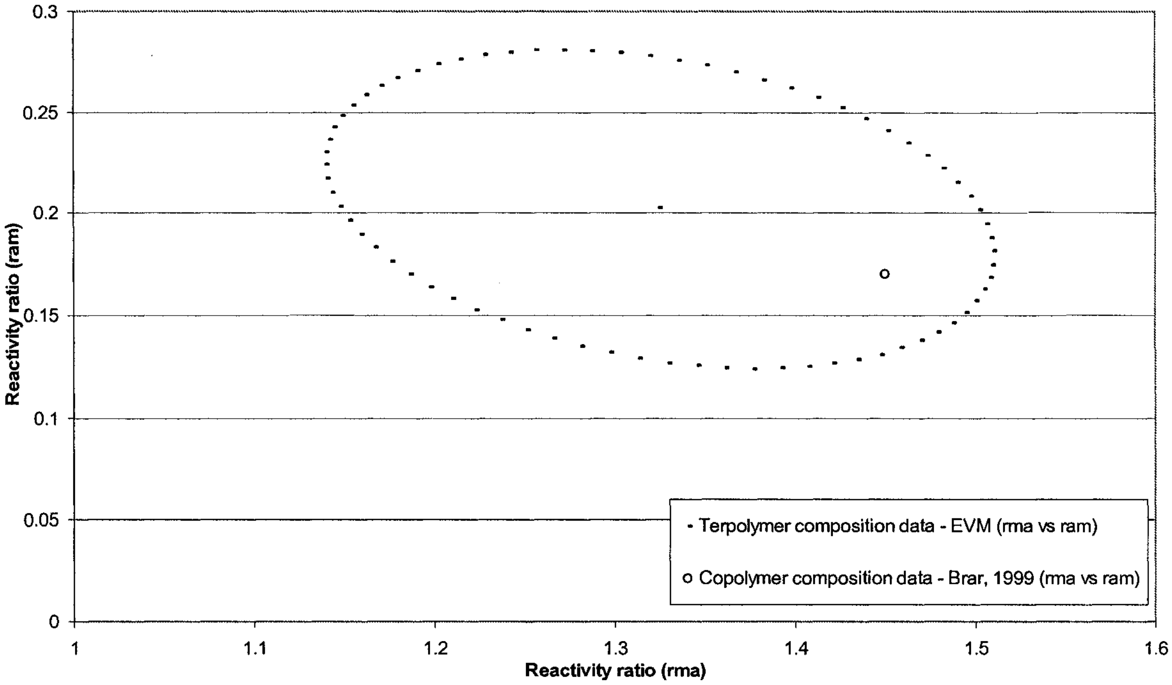
In order to determine whether the point estimates provided by Brar and Hekmatyar (1999) were in agreement, the ellipse JCRs of the reactivity ratios in their respective copolymer pairs (i.e. $r_{SA}$ vs. $r_{AS}$) were analyzed, refer to Figures 5.38 a) - d).



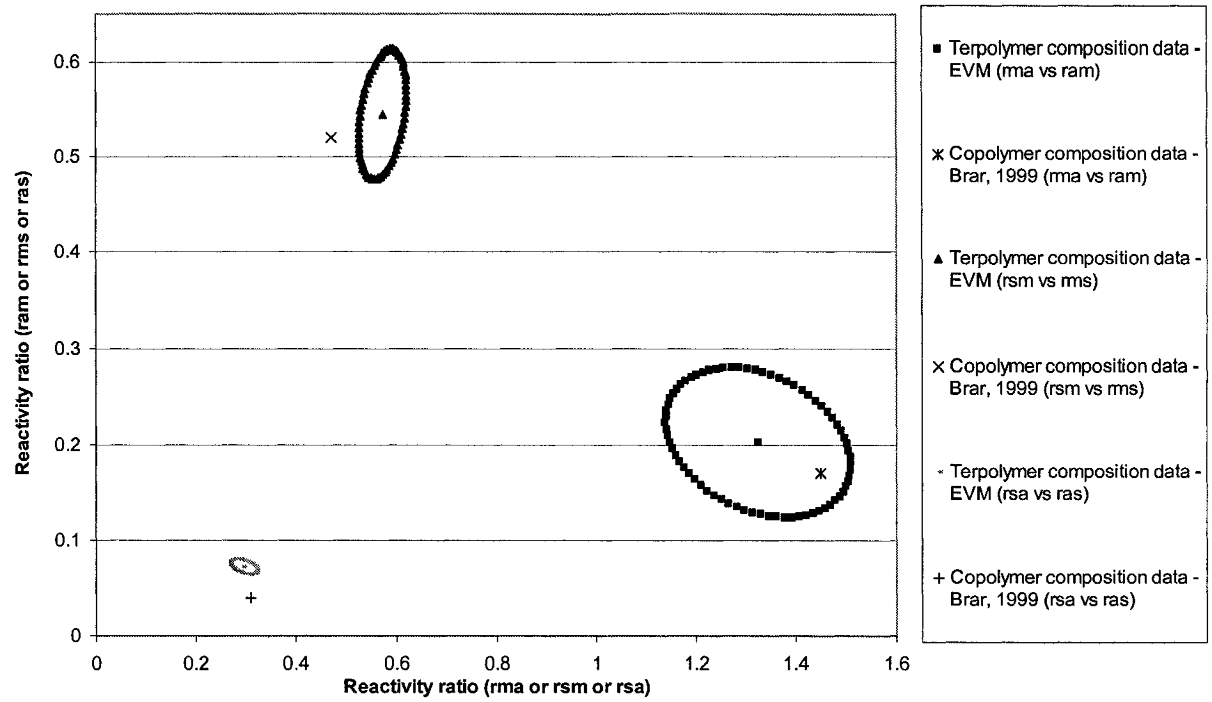
a)


0.65
0.6
0.55
0.5
0.45
0.4
Reactivity ratio (rms)
0.45
0.47
0.49
0.51
0.53
0.55
0.57
0.59
0.61
0.63
Reactivity ratio (rsm)
- Terpolymer composition data - EVM (rsm vs rms)
o Copolymer composition data - Brar, 1999 (rsm vs rms)

b)


0.3
0.25
0.2
0.15
0.1
0.05
0
Reactivity ratio (ram)
1
1.1
1.2
1.3
1.4
1.5
1.6
Reactivity ratio (rma)
- Terpolymer composition data - EVM (rma vs ram)
o Copolymer composition data - Brar, 1999 (rma vs ram)

c)



d)

**Figure 5.38a) – d): Ellipse JCRs for EVM analysis of Brar and Hekmatyar (1999) terpolymer composition data for the AN/STY/MMA system.**

It can be seen in Figure 5.38 d) that the reactivity ratio estimates by Brar and Hekmatyar (1999) fall outside the ellipse JCR of the respective pair, except the acrylonitrile and methyl methacrylate interaction pair. It is also interesting to note the varying sizes of the ellipse JCRs and thus uncertainty in the reactivity ratio estimates for the different monomer pairs. The varying uncertainty in the pairs may be attributed to poor experimental design and insufficient data. That is, the terpolymer data set provided by Brar and Hekmatyar (1999) was not extensive, but rather only met the minimum number of data points required for a six parameter estimation problem and thus may not have been sufficient for the accurate estimation of all the parameters. As a result the inclusion of the point estimates from Brar and Hekmatyar (1999) in the ellipse JCR of the AN-MMA interaction is believed to be due to poor experimental design affecting the uncertainty in the EVM estimates obtained for the AN-MMA interaction (hence this monomer pair has the largest contour). Therefore, it is believed that future study of a well designed terpolymer experiment will show that reactivity ratios from copolymer composition data do not necessarily accurately represent the terpolymer reaction kinetics.

## 5.10.2 Amalgamated STY-MMA-AN Data Set

As stated previously, the STY-MMA-AN data set published in Hocking and Klimchuk (1996) had insufficient feed points to use in the parameter estimation routine; however when this data is combined with the Brar and Hekmatyar (1999) STY-MMA-AN data, the resulting amalgamated data set has 10 experimental points. The amalgamated STY-MMA-AN terpolymer data set can be seen in Table 5.27.

**Table 5.27: Amalgamated data set using the published data from Brar and Hekmatyar (1999) and Hocking and Klimchuk (1996).**

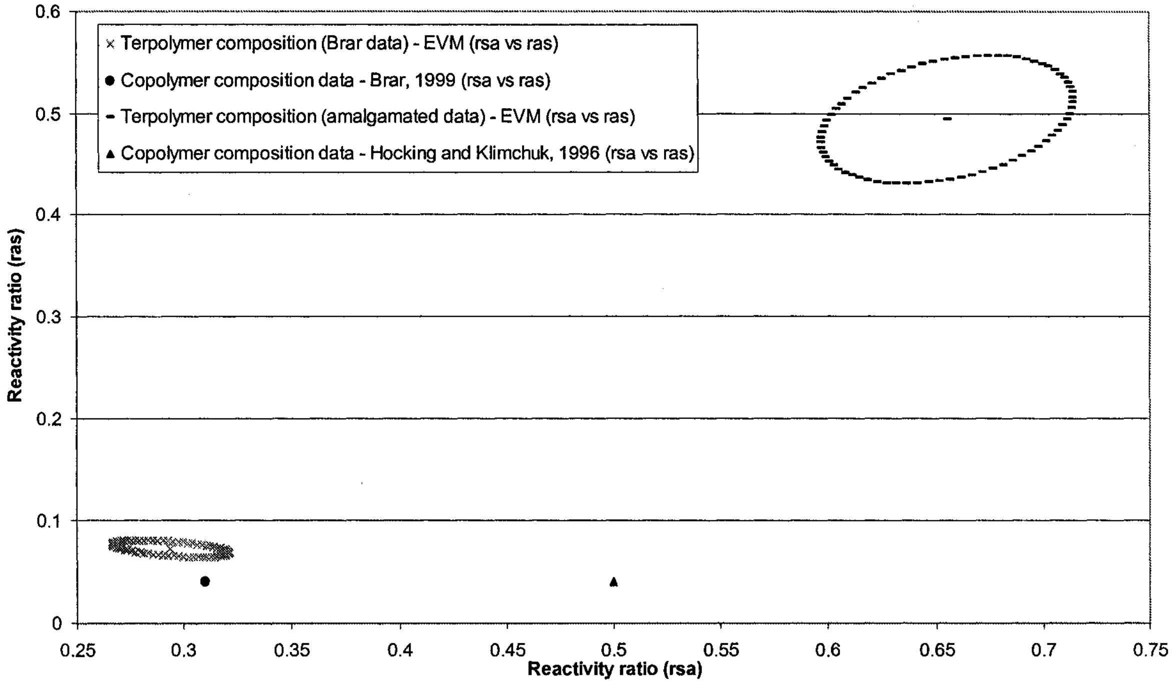
| Mole fraction of monomer in feed | | | Mole fraction of monomer in terpolymer | | |
|---|---|---|---|---|---|
| AN | STY | MMA | AN | STY | MMA |
| 0.63 | 0.22 | 0.15 | 0.46 | 0.40 | 0.14 |
| 0.42 | 0.36 | 0.22 | 0.37 | 0.46 | 0.17 |
| 0.23 | 0.53 | 0.24 | 0.27 | 0.53 | 0.20 |
| 0.41 | 0.16 | 0.43 | 0.32 | 0.29 | 0.39 |
| 0.29 | 0.08 | 0.63 | 0.22 | 0.15 | 0.63 |
| 0.29 | 0.44 | 0.27 | 0.30 | 0.48 | 0.22 |
| 0.2805 | 0.3592 | 0.3603 | 0.2920 | 0.4470 | 0.2610 |
| 0.2026 | 0.5323 | 0.2651 | 0.2720 | 0.5260 | 0.2020 |
| 0.4344 | 0.2832 | 0.2824 | 0.3860 | 0.3840 | 0.2300 |
| 0.2028 | 0.2776 | 0.5206 | 0.2300 | 0.3640 | 0.4060 |

Using the EVM program, estimation of the six reactivity ratio parameters was then conducted for the amalgamated data case. The initial estimates for the EVM procedure were those given by Brar and Hekmatyar (1999). The reactivity ratio estimates given in the literature (using copolymerization data) and those obtained from the EVM analysis of the amalgamated terpolymer data and the previous EVM analysis on the Brar and Hekmatyar (1999) data can be seen in Table 5.28.

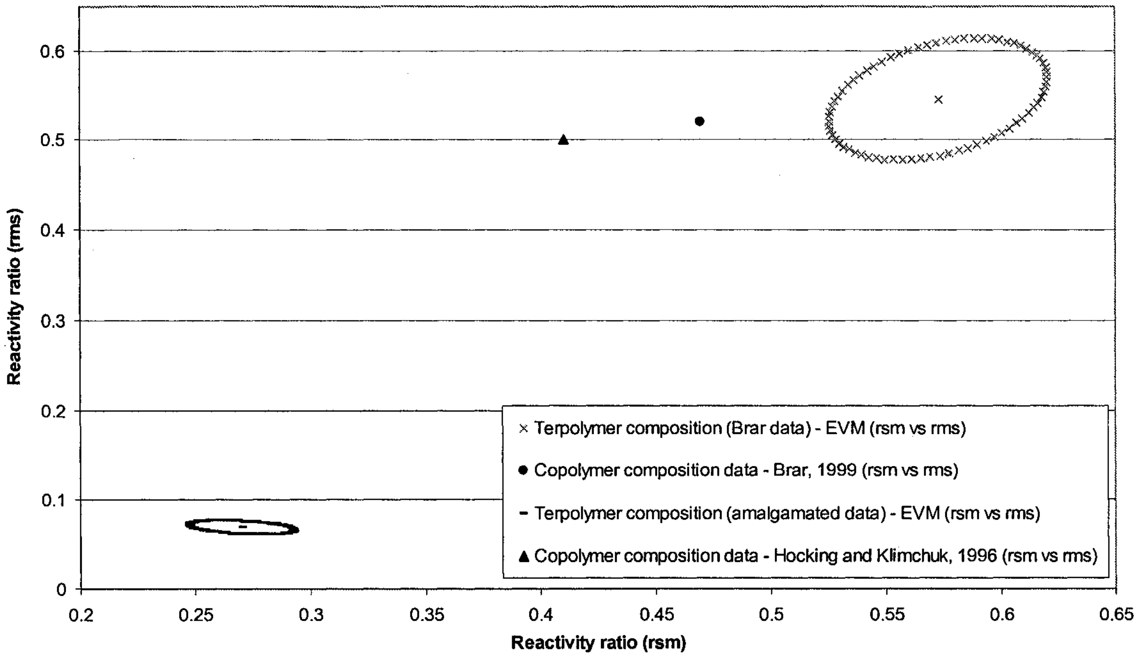
**Table 5.28: Point estimates published by Brar and Hekmatyar (1999), and Hocking and Klimchuk (1996), and the estimates obtained by EVM MATLAB on the amalgamated data set. Where STY = S, MMA =M and AN = A.**

| | $r_{AS}$ | $r_{AM}$ | $r_{SA}$ | $r_{SM}$ | $r_{MA}$ | $r_{MS}$ |
|---|---|---|---|---|---|---|
| Brar and Hekmatyar (1999) | 0.04 | 0.17 | 0.31 | 0.47 | 1.45 | 0.52 |
| Hocking and Klimchuk (1996) | 0.04 | 0.15 | 0.5 | 0.41 | 1.2 | 0.5 |
| Current work | 0.0684 | 0.1637 | 0.2703 | 0.6557 | 1.2785 | 0.494 |

In order to determine whether similar results were obtained from the amalgamated data set and the original Brar and Hekmatyar (1999) data set, the ellipse JCRs of the reactivity ratios in their respective copolymer pairs (i.e. $r_{SA}$ vs. $r_{AS}$) were analyzed, refer to Figures 5.39 a) -c).


× Terpolymer composition (Brar data) - EVM (rsa vs ras)
● Copolymer composition data - Brar, 1999 (rsa vs ras)
- Terpolymer composition (amalgamated data) - EVM (rsa vs ras)
▲ Copolymer composition data - Hocking and Klimchuk, 1996 (rsa vs ras)
Reactivity ratio (ras)
0
0.1
0.2
0.3
0.4
0.5
0.6
Reactivity ratio (rsa)
0.25
0.3
0.35
0.4
0.45
0.5
0.55
0.6
0.65
0.7
0.75

a)


× Terpolymer composition (Brar data) - EVM (rsm vs rms)
● Copolymer composition data - Brar, 1999 (rsm vs rms)
- Terpolymer composition (amalgamated data) - EVM (rsm vs rms)
▲ Copolymer composition data - Hocking and Klimchuk, 1996 (rsm vs rms)
Reactivity ratio (rms)
0
0.1
0.2
0.3
0.4
0.5
0.6
Reactivity ratio (rsm)
0.2
0.25
0.3
0.35
0.4
0.45
0.5
0.55
0.6
0.65

b)

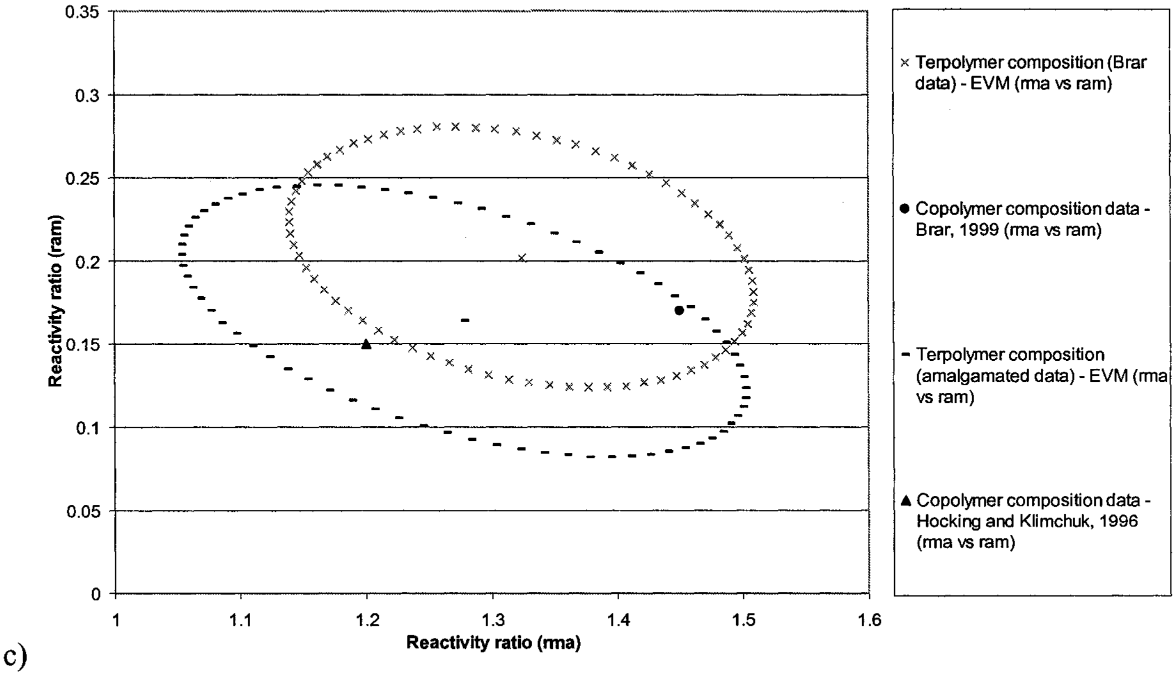


**Figure 5.39 a) –c): Ellipse JCRs for EVM analysis of amalgamated terpolymer composition data for the AN/STY/MMA system compared to the Ellipse JCRs from EVM analysis of Brar and Hekmatyar (1999) data.**

It can be seen in Figures 5.39 a) – c) that the reactivity ratio estimates published by Brar and Hekmatyar (1999) and by Hocking and Klimchuk (1996) fall outside the ellipse JCR of the respective pair, except for the acrylonitrile-methyl methacrylate interaction. It is also interesting to note the effect of incorporating the Hocking and Klimchuk (1996) data results in a shift in the ellipse JCR for each monomer pair away from the location of the literature point estimates. Consequently, it is reasonable to suggest that the data by Hocking and Klimchuk (1996) has large experimental errors in the four feed point data set which distorts the EVM result.

# Chapter 6

# Estimation of Reactivity Ratios from Cumulative Data

As stated previously in Chapter two, there are two general models used in the estimation of copolymer reactivity ratios; the instantaneous and the cumulative models. The most often used is the instantaneous copolymer composition model, otherwise known as the Mayo-Lewis model. The main issue in using the instantaneous model is that it assumes that all variables are measured over an infinitesimal period of time, which is rarely the case. The monomer feed composition is measured at the beginning of the reaction (time zero), while the copolymer composition is taken after a very small, yet finite, time period. In order to still apply the model however, the assumption that the feed composition does not change significantly throughout the reaction is applied. It is for this reason that the instantaneous model requires that the polymerization experiment be run at low conversion in order to prevent composition drift becoming significant. However, without measuring the feed composition during the experiment one can not truly rely on the feed composition being constant during the reaction. Furthermore, even stopping the reaction at low conversions is hard to achieve in some systems.

In order to not be confined by the assumption that the feed composition does not change during the reaction and thus limited to low conversion data, a model was required that would account for the feed composition at the end of the reaction, whether directly or indirectly. There are two main models discussed in the literature that were developed in order to circumvent the problems that existed with the instantaneous composition model.

The first and most well known is the Meyer-Lowry Model (1965), sometimes referred to as the analytically integrated cumulative copolymer composition model. The second is the numerically integrated cumulative copolymer composition (ODECCC) model.

The triad fractions cumulative model has considerably less discussion in the literature. In this thesis the cumulative model has been employed and is referred to as the numerically integrated cumulative copolymer triad fractions (ODECCTF) model.

## 6.1 Meyer-Lowry Model

The Meyer-Lowry model was developed to obtain reliable estimates of the reactivity ratios from data with moderate conversion levels. Typically, the experiments run to conversions of approximately 25% to ensure that the reaction stays within the chemical control regime. Maintaining the copolymerization in the chemical control regime is important to avoid the issues of auto-acceleration and other diffusional limitations (and hence potential variation of the reactivity ratios).

The lack of reliable literature on the application of the Meyer-Lowry model for parameter estimation is due to the complexity of the model. The antiquated computing power of the past thus resulted in the frequent misuse of invalid parameter estimation techniques (e.g. graphical intersection) by researchers. One of the first authors to propose a reliable numerical method for the Meyer-Lowry model was German and Heikens (1971). The authors introduced the idea of an error in variables approach, which later Van der Meer et al. (1978) further refined. Patino-Leal et al. (1980) applied the error in variables model (EVM) very systematically to the Meyer-Lowry model. However in all these articles, the Meyer-Lowry model used is in the following form:

$$\log\left(\frac{M_2}{M_{20}}\right)=\frac{r_2}{1-r_2}\log\left(\frac{M_{20}M_1}{M_{10}M_2}\right)-\frac{1-r_1r_2}{(1-r_1)(1-r_2)}\log\left(\frac{(r_1-1)\frac{M_1}{M_2}-r_2+1}{(r_1-1)\frac{M_{10}}{M_{20}}-r_2+1}\right) \qquad (6.1)$$

where $M_1$ and $M_2$ are the monomer feed concentrations at the end of the reaction and $M_{10}$ and $M_{20}$ are the initial monomer feed concentrations.

From Equation 6.1, it can be seen that the model is based on the conversion of monomer two only and thus contains no information regarding the conversion of the other monomer. As a result, when the reactivity ratios differ greatly, the other monomer may attain a very different conversion level. It is for this reason that models that use a total conversion as a response are a better alternative.

Papers that use total conversion as a response in a form of the Meyer-Lowry model (as given by Equation 2.26) are those of Hautus et al. (1984) and Garcia-Rubio et al. (1985). Equation 2.26 is considered to be the general Meyer-Lowry model and is written below for reference.

$$X_n = 1 - \left(\frac{f_1}{f_{1,0}}\right)^{\alpha} \left(\frac{1-f_1}{1-f_{1,0}}\right)^{\beta} \left(\frac{f_{1,0}-\delta}{f_1-\delta}\right)^{\gamma} \tag{6.2}$$

where,

$$\alpha = \frac{r_2}{1-r_2}; \quad \beta = \frac{r_1}{1-r_1}; \quad \gamma = \frac{1-r_1 r_2}{(1-r_1)(1-r_2)}; \quad \delta = \frac{1-r_2}{2-r_1-r_2}$$

The variables seen in Equation 6.2 are defined in this work, by assuming constant volume of the polymerizing mixture, as functions of molar concentrations (refer to discussion in Section 2.1.1);

$$X_n = 1 - \frac{[M_1]+[M_2]}{[M_{1,0}]+[M_{2,0}]}; \quad f_{1,0} = \frac{[M_{1,0}]}{[M_{1,0}]+[M_{2,0}]}; \quad f_1 = \frac{[M_1]}{[M_1]+[M_2]}$$

The form of Equation 6.2 also suggests that the measured variables be the initial and final feed concentrations of monomer one. However, this is not typically the case as when a measurement of the final mole fraction of one of the monomer in the feed is obtained, then the overall mole fraction conversion cannot be calculated (Rossignoli, 1993). Consequently, a third measurement is usually the final mole fraction of monomer one in the copolymer, $\overline{F_1}$, given by:

$$\overline{F_1} = \frac{[M_{1,0}]-[M_1]}{[M_{1,0}]+[M_{2,0}]-[M_1]-[M_2]} \tag{6.3}$$

This allows a new equation for the molar conversion, $X_n$, as a function of the initial and final feed composition ($f_{10}$ and $f_1$, respectively) to be derived as:

$$X_n = \frac{f_1 - f_{10}}{f_1 - \overline{F_1}} \tag{6.4}$$

As a result the Meyer-Lowry equation can then be expressed in terms of the variables measured, which Rossignoli (1993) termed the **mole conversion form,** given by:

$$f(f_{10},f_1,\overline{F}_1)=\frac{f_1-f_{10}}{f_1-\overline{F}_1}-1+\left(\frac{f_1}{f_{1,0}}\right)^{\alpha}\left(\frac{1-f_1}{1-f_{1,0}}\right)^{\beta}\left(\frac{f_{1,0}-\delta}{f_1-\delta}\right)^{\gamma} \tag{6.5}$$

Papers that include copolymer composition in the Meyer-Lowry model, similar to the above equation, include Shawki and Hamielec (1979), O'Driscoll et al. (1984), and Plaumann and Branston (1989).

It would be best however, if the measurements taken for reactivity ratio estimation problems were the same regardless of whether the Mayo-Lewis or the Meyer-Lowry model is applied. That is, the measurements typically recorded are the initial feed concentration, in terms of monomer one mole fraction ($f_{10}$); the final mole fraction of monomer one incorporated in the copolymer ($\overline{F}_1$) and the weight fraction conversion ($X_w$). The Meyer-Lowry model can be expressed in terms of these three measured variables, $f_{10}$, $X_w$ and $\overline{F}_1$ by using a model outlined by Rossignoli (1993) as the **mass conversion form**, given by (refer to Section 2.1.1):

$$f(f_{10},X_w,\overline{F}_1)=X_n-1+\left(\frac{f_{10}-\overline{F}_1X_n}{f_{1,0}(1-X_n)}\right)^{\alpha}\left(\frac{1-X_n-f_{10}-\overline{F}_1X_n}{(1-f_{1,0})(1-X_n)}\right)^{\beta}\left(\frac{(\delta-f_{1,0})(1-X_n)}{\delta-\delta X_n-f_{10}+\overline{F}_1X_n}\right)^{\gamma} \tag{6.6}$$

where $X_n$ is given in terms of $X_w$ by:

$$X_n=X_w\frac{MW_1f_{10}+(1-f_{10})MW_2}{MW_1\overline{F}_1+(1-\overline{F}_1)MW_2} \tag{6.7}$$

In this thesis, the form of the Meyer-Lowry model used is the **mass conversion form** seen above.

### 6.1.1 Parameter Estimation Technique: EVM or NLLS?

The Meyer-Lowry model is nonlinear in the parameters and subsequently requires a nonlinear parameter estimation technique. In this research, the non linear least squares (NLLS) and error in variables (EVM) techniques were considered for application to the Meyer-Lowry model. As is well known, if NLLS is used, then one of the variables must be considered as the dependent variable and the model cast into the NLLS form. The mole conversion case (i.e. f $(f_{10}, f_1, \overline{F_1})$) can not be used with the NLLS estimation technique, as the $\overline{F_1}$ and $f_1$ variables both have considerable error (Rossignoli, 1993). That is, regardless of whether $\overline{F_1}$ or $f_1$ was selected as the dependent variable, the assumption that the independent variables have insignificant error would be violated. Similarly, the mass conversion case (i.e. f $(f_{10}, X_w, \overline{F_1})$) would be difficult to use with the NLLS parameter estimation technique, as the model can not be easily cast into an explicit NLLS form. Consequently, in this research EVM was the only parameter estimation method used to obtain reactivity ratio values from the mass conversion form of the Meyer-Lowry model.

It is also important to note that in this chapter the initial feed composition, $f_{10}$, and final copolymer composition, $\overline{F_1}$, were assumed to have multiplicative errors of ±1% and ±5%, respectively, unless otherwise stated in the study. The assumed weight fraction conversion error level was based on the fact that it is measured by gravimetry analysis, similar to initial feed composition, and thus has a similar error structure and assumed ±1% level.

Furthermore, for the sake of simplicity and similar to previous chapters, the exact shape, 95% probability joint confidence region is called the exact JCR, while the ellipse shape, 95% probability joint confidence region is called the ellipse JCR. Also, in the cases where the Meyer-Lowry model is used, only the ellipse JCR could be evaluated as the exact JCR would not converge.

### 6.1.2 EVM Using the Mass Conversion Form of the Meyer-Lowry Model

Applying EVM to the mass conversion form of the Meyer-Lowry model is identical to the explanation given in Section 3.5 for the Mayo-Lewis model. Subsequently, only highlights will be given here.

The first step is to take the natural logarithm of the EVM variables (i.e. $f_{10}, X_w, \overline{F_1}$) to account for the multiplicative error structure of the data. Then the main EVM function and the partial derivatives with respect to the parameters and variables are developed. As the derivatives are much more complicated and lengthy, they are not listed here (but can be found in BFCalc and ZCalc, in the respective EVM MATLAB program, refer to Appendix A). The main EVM functions used in the program were the following:

$$f(f_{10}, X_w, \overline{F}_1) = X_n - 1 + \left(\frac{f_1}{f_{1,0}}\right)^{\alpha} \left(\frac{1-f_1}{(1-f_{1,0})}\right)^{\beta} \left(\frac{(f_{1,0}-\delta)}{f_1-\delta}\right)^{\gamma} \tag{6.8}$$

where,

$$f_1 = \frac{f_{10} - \overline{F}_1 X_n}{1 - X_n} \qquad X_n = X_w \frac{MW_1 f_{10} + (1 - f_{10}) MW_2}{MW_1 \overline{F}_1 + (1 - \overline{F}_1) MW_2} \tag{6.9-6.10}$$

and

$$\alpha = \frac{r_2}{1 - r_2}; \quad \beta = \frac{r_1}{1 - r_1}; \quad \gamma = \frac{1 - r_1 r_2}{(1 - r_1)(1 - r_2)}; \quad \delta = \frac{1 - r_2}{2 - r_1 - r_2} \tag{6.11-6.14}$$

A number of case studies were run using this Meyer-Lowry mass conversion form model to obtain reactivity ratio estimates. Some case studies selected were used to demonstrate the Meyer-Lowry reactivity ratio estimates agreement to the instantaneous Mayo-Lewis estimates for low conversion data. Others show that for moderate conversion data where composition drift is significant, the Mayo-Lewis reactivity ratio estimates deviate from those obtained using the Meyer-Lowry model.

### 6.1.3 Case Study I: STY- MMA System

O'Driscoll et al. (1984) studied the styrene (STY) / methyl methacrylate (MMA) system at 60°C and presented experimental data for final copolymer composition, initial feed composition and weight fraction conversion (refer to Table 6.1). Rossignoli (1993) also studied the STY/MMA system using simulated data (refer to Table 6.2).

**Table 6.1: O'Driscoll et al. (1984) data set for STY/MMA bulk system at 60°C.**

| Initial Feed Composition (Mole frac STY) | Conversion (wt %) | Copolymer Composition (wt % STY) | Copolymer Composition (Mole frac STY) |
|---|---|---|---|
| 0.6 | 4.5 | 55.1 | 0.5413 |
| 0.6 | 4.7 | 57.4 | 0.5644 |
| 0.6 | 26.1 | 56.2 | 0.5523 |
| 0.6 | 27.3 | 59 | 0.5805 |
| 0.6 | 49.6 | 59.5 | 0.5855 |
| 0.6 | 55.6 | 58.3 | 0.5734 |
| 0.6 | 70 | 59.6 | 0.5865 |
| 0.35 | 4.6 | 40.4 | 0.3946 |
| 0.35 | 24.1 | 42.1 | 0.4115 |
| 0.35 | 69.6 | 40.6 | 0.3966 |

**Table 6.2: Rossignoli (1993) simulated data set for STY/MMA system.**

| Initial Feed Composition (Mole frac STY) | Conversion (wt %) | Copolymer Composition (Mole frac STY) |
|---|---|---|
| 0.111004 | 9.9724 | 0.1894 |
| 0.219854 | 9.9093 | 0.2955 |
| 0.328317 | 9.994 | 0.3874 |
| 0.443518 | 10.0678 | 0.4517 |
| 0.553271 | 10.0253 | 0.5550 |
| 0.666121 | 10.0439 | 0.5769 |
| 0.765762 | 9.9397 | 0.6832 |
| 0.871357 | 9.9057 | 0.7970 |

It can be seen from the data sets that Rossignoli (1993) kept the conversion to a moderately low level (<11%), while O'Driscoll et al. (1984) carried out copolymerization to moderately high conversions (<70%). However, both authors used the same form of the Meyer-Lowry model as was used in this research, namely the mass conversion form, to evaluate reactivity ratio estimates. The point estimates published by O'Driscoll et al. (1984) and the estimates obtained from this research, using different models, can be seen in Table 6.3. Similarly the point estimates published by Rossignoli (1993) and the estimates obtained from this research can be seen in Table 6.4.

**Table 6.3: Point estimates by O'Driscoll et al. (1984) and the estimates obtained by EVM MATLAB analysis of the data for the Meyer-Lowry and Mayo-Lewis models.**

|  | Model | Estimation Method | $r_1$ | $r_2$ |
|---|---|---|---|---|
| O'Driscoll et al. (1984) | Meyer-Lowry | EVM | 0.4317 | 0.4215 |
| Current work | Mayo-Lewis | EVM | 0.4955 | 0.4814 |
| Current work | Meyer-Lowry | EVM | 0.4281 | 0.4183 |

**Table 6.4: Point estimates by Rossignoli (1993) and the estimates obtained by EVM MATLAB analysis of the simulated data for the Meyer-Lowry and Mayo-Lewis models.**

|  | Model | Estimation Method | $r_1$ | $r_2$ |
|---|---|---|---|---|
| Rossignoli (1993) | Meyer-Lowry | EVM | 0.40801 | 0.429389 |
| Current work | Mayo-Lewis | EVM | 0.42726 | 0.44847 |
| Current work | Meyer-Lowry | EVM | 0.40801 | 0.42938 |

The JCRs for the different models are given in Figure 6.1 for the O'Driscoll et al. (1984) data set. The point estimates indicate good agreement between the analysis completed by this research and those published by O'Driscoll et al. (1984).

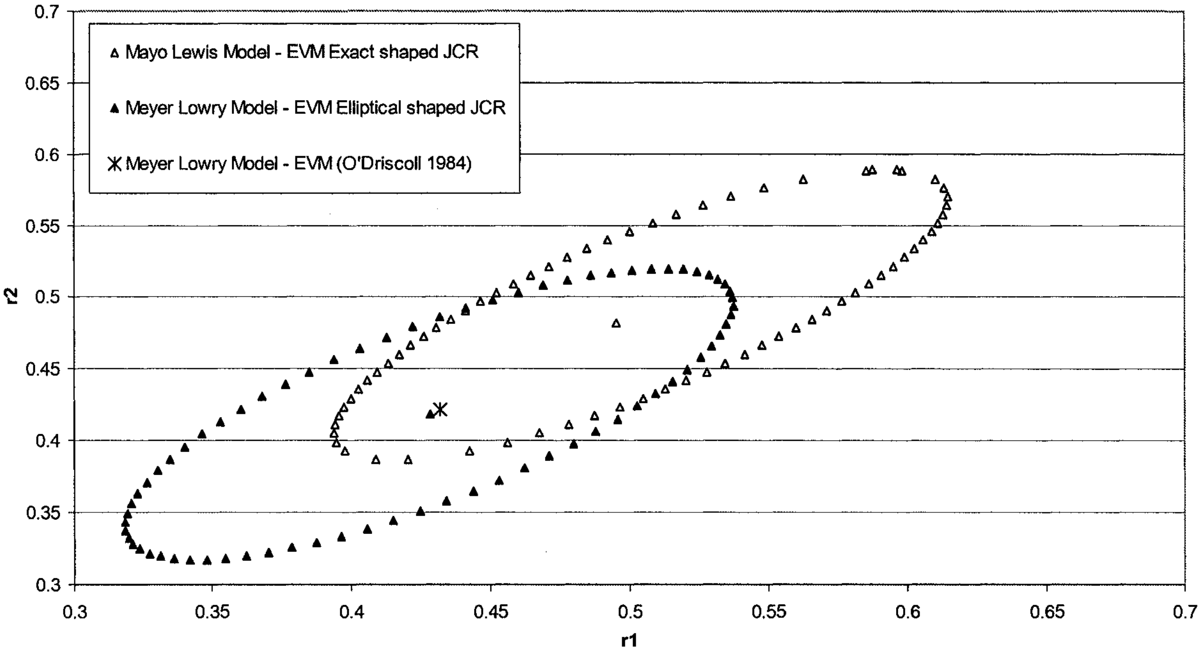


**Figure 6.1: JCRs for the application of EVM parameter estimation to the Meyer-Lowry model and Mayo-Lewis model for the O'Driscoll et al. (1984) STY-MMA bulk system at 60°C.**

From Figure 6.1 it can be seen that the Meyer Lowry model point estimates obtained by both O'Driscoll et al. (1984) and the current work, fall within the Mayo-Lewis model's ellipse JCR. There is a degree of overlap of the JCRs when using the Mayo-Lewis and Meyer-Lowry models, though not as significant as was anticipated. That is, the reactivity ratios are similar and thus the deviation of the Meyer-Lowry model's result from the Mayo-Lewis model's result was anticipated to be minimal (due to insignificant composition drift) and hence the overlap of the JCRs was anticipated to be more significant. However, only two initial feed composition points were analyzed and thus the small sample may have biased the results.

Figure 6.2 is the JCRs for the different models for the simulated Rossignoli (1993) STY-MMA copolymerization data set. From the figure it can be seen that the Mayo-Lewis and Meyer-Lowry models' results are in very good agreement, as there is significant overlap of their respective JCR. As discussed above, the overlap of the JCRs was expected given the reactivity ratios values being very similar. Further analysis of the figure also shows that the point estimates by Rossignoli (1993) lie within both the Mayo-Lewis and Meyer-Lowry JCRs.

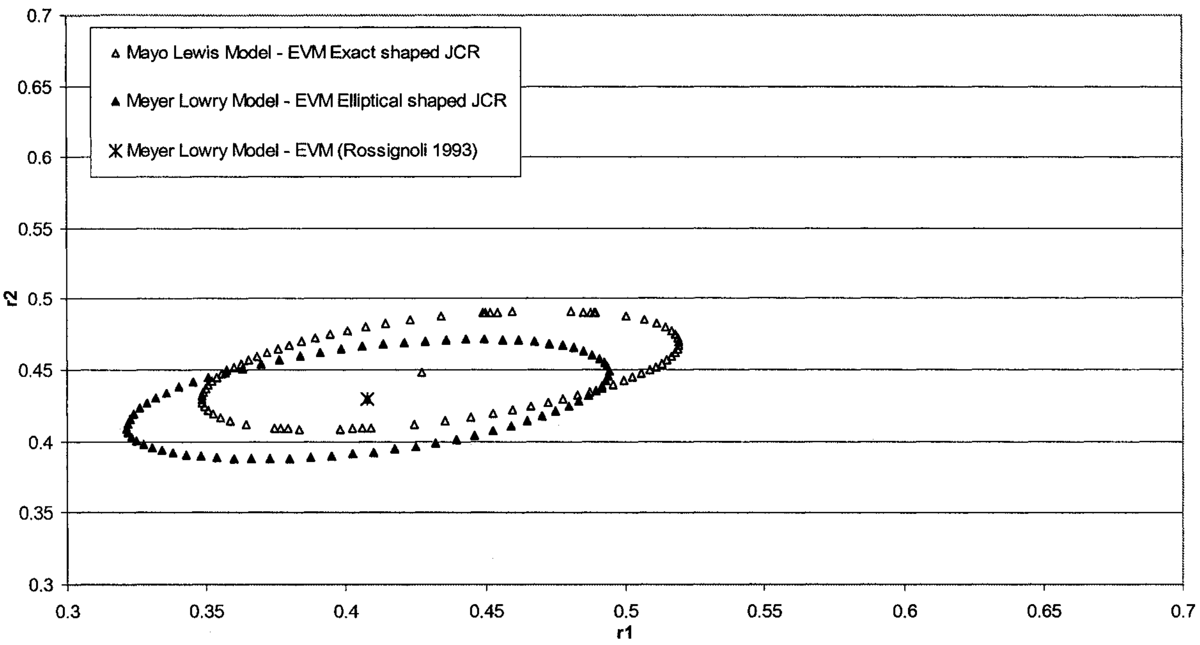


**Figure 6.2: JCRs for the application of EVM parameter estimation to the Meyer-Lowry model and Mayo-Lewis model for the Rossignoli (1993) STY-MMA simulated data set.**

Another observation from the previous figures is that the size of the confidence contours appears to be independent of whether the Mayo-Lewis model or the Meyer-Lowry model is used in the EVM analysis. This is counterintuitive, as given that the Meyer-Lowry model contains more information than the Mayo-Lewis model (three variables instead of two) the size of the confidence contour would be expected to be smaller. As this is not the case, it suggests that while it may be necessary to use the Meyer-Lowry model (due to high conversion data or significant composition drift), the additional information does not contribute to higher confidence in the point estimates.

### 6.1.4 Case Study II: Acrylic Acid- Acrylamide System

Bourdais (1955) and Cabaness et al. (1971) studied the acrylic acid (AAcid) / acrylamide (AM) copolymerization system at low conversion for 25°C and 60°C, respectively (refer to Table 6.5). Similarly, Shawki and Hamielec (1979) studied the system at 40°C and presented experimental data at high conversion (refer to Table 6.6).

**Table 6.5: Experimental data for AAcid/AM system (low conversion).**

| Reference | Temperature (°C) | Feed Composition (Mole % AAcid) | Conversion (wt %) | Copolymer Composition (Mole % AAcid) |
|---|---|---|---|---|
| Bourdais | 25 | 12.5 | 7 | 18.3 |
| | | 25 | 10 | 32.7 |
| | | 37.5 | 6 | 46.6 |
| | | 50 | 6 | 60.7 |
| | | 62.5 | 5 | 71.2 |
| | | 75 | 2 | 81.7 |
| | | 87.5 | 3 | 90.1 |
| Cabaness et al. | 60 | 80 | 3.92 | 87.49 |
| | | 66.7 | 2.54 | 76.88 |
| | | 50 | 4.3 | 64.51 |
| | | 35.1 | 10.7 | 49.97 |
| | | 20 | 4.46 | 33.46 |

**Table 6.6: Experimental data by Shawki and Hamielec (1979) for AAcid/AM system (high conversion).**

| Initial Feed Composition (Mole % AAcid) | Conversion (wt %) | Copolymer Composition (Mole % AAcid) |
|---|---|---|
| 8 | 16.4 | 12.8 |
| | 24.1 | 11.5 |
| | 38 | 11.7 |
| | 50.9 | 11.1 |
| | 58.3 | 10.3 |
| | 68.9 | 9.6 |
| 15 | 23.4 | 21.7 |
| | 31.8 | 20.4 |
| | 47.2 | 21 |
| | 52.1 | 19.4 |
| | 60.2 | 18.6 |
| | 71.1 | 18 |
| 20 | 19.7 | 28.8 |
| | 27.6 | 27.3 |
| | 38.1 | 26.4 |
| | 49 | 26.6 |
| | 58.3 | 25.6 |
| | 62.1 | 23.9 |
| 25 | 22.8 | 33.5 |
| | 34 | 33.4 |
| | 44.9 | 32.3 |
| | 51.2 | 31.3 |
| | 63.8 | 30.9 |
| | 66.1 | 29.7 |

Bourdais (1955) and Cabaness et al. (1971) both used graphical methods to estimate $r_1$ and $r_2$ from the copolymer composition equation; while Shawki and Hamielec (1979) used a nonlinear regression method. The point estimates published by the authors and the estimates obtained from this research using the different model forms can be seen in Table 6.7.

**Table 6.7: Point estimates of reactivity ratio values from literature data of Bourdais (1955), Cabaness et al. (1971) and Shawki and Hamielec (1979).**

| Reference | | Values reported by original authors | Values obtained by Mayo-Lewis model (current work) | Values obtained by Meyer-Lowry model (current work) |
|---|---|---|---|---|
| Bourdais (1955) | $r_1$ | 1.43 | 1.4089 | 1.417 |
| | $r_2$ | 0.6 | 0.6383 | 0.6227 |
| Cabaness et al. (1971) | $r_1$ | 1.473 | 1.5816 | 1.608 |
| | $r_2$ | 0.48 | 0.4469 | 0.4346 |
| Shawki and Hamielec (1979) | $r_1$ | 1.45 | 1.3243 | 1.4608 |
| | $r_2$ | 0.57 | 0.6918 | 0.5715 |

The resulting JCRs for the different models and low conversion data sets are given in Figure 6.3.

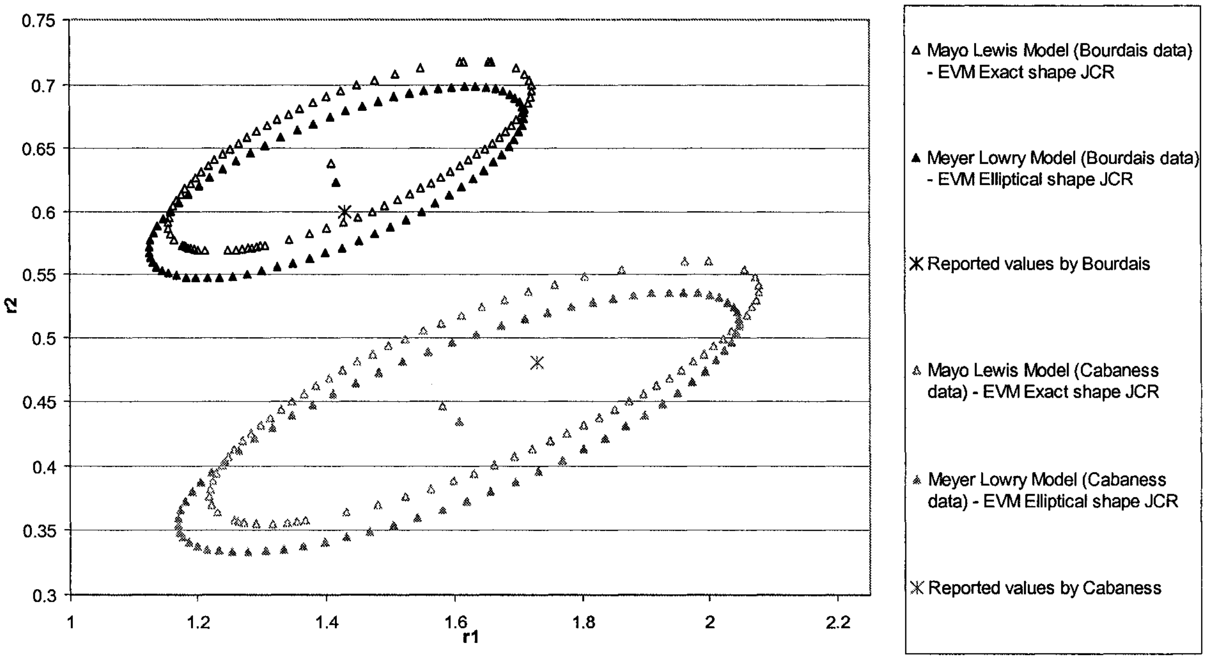


**Figure 6.3: JCRs for the application of EVM parameter estimation to the Meyer-Lowry model and Mayo-Lewis model for the low conversion AAcid/AM data sets.**

From Figure 6.3 it can be seen that the Mayo-Lewis and Meyer-Lowry models' results are in very good agreement, due to the large area of overlap of their confidence regions. The similarity in point estimates from the different models was anticipated as the conversion level, in both data sets, was kept below 11% (thus minimizing potential composition drift effect).

Furthermore, in Figure 6.3 there appears to be a significant separation of the JCRs when the different data sets are used. That is when using the Bourdais (1955) data set the JCRs obtained, from using either the Meyer-Lowry model or the Mayo-Lewis model, are quite separate from the JCRs obtained when using the Cabaness et al. (1971) data set. The separation of the author's JCRs can be attributed to the difference in copolymerization temperature.

In contrast, Figure 6.4 shows the effect on the point estimates when using the different models for high conversion experimental data. It can be seen that not only do the point estimates obtained from the EVM method differ for the models, but also the confidence regions no longer overlap. Additionally, Shawki and Hamielec (1979) reactivity ratio point estimates fall within the Meyer-Lowry model ellipse JCR. This was expected as the authors performed a nonlinear estimation technique on a similar model form to that used in this thesis.

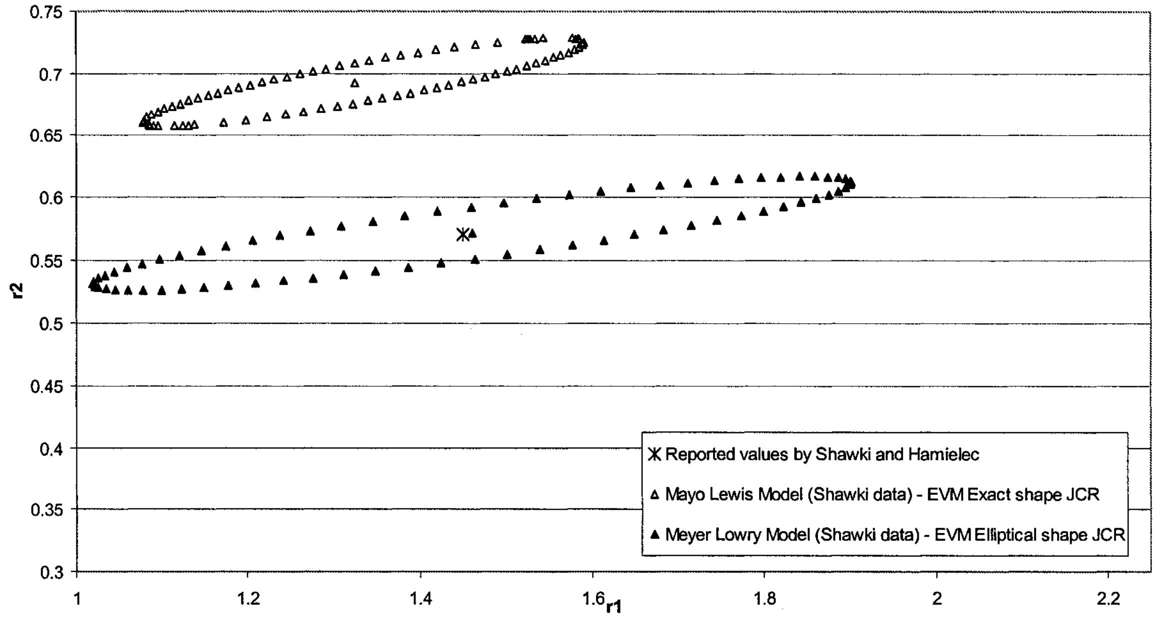


**Figure 6.4: JCRs for the application of EVM parameter estimation to the Meyer-Lowry model and Mayo-Lewis model for the high conversion AAcid/AM data.**

Considering all the previous figures in this case study, it can then be said that the use of the Meyer-Lowry model does not improve the level of confidence in the reactivity ratio estimates, as the JCR does not decrease in size. However, if composition drift is occurring in the system, in high conversion experiments in particular, then the location of the point estimates can be significantly affected by the choice of model used (i.e., applying either the Mayo-Lewis or Meyer-Lowry model).

## 6.2 Numerically Integrated Cumulative Copolymer Composition (ODECCC) Model

There have been many articles published on the issues and problems with using the analytical solution of the integrated copolymer equation (i.e., Meyer-Lowry model). As Hautus et al. (1985) discussed, there are two potential problems when applying the Meyer-Lowry model; the forbidden region and the dangerous region. The forbidden region identified by Hautus et al. (1985) can be present when using the mole conversion form of the Meyer-Lowry model, which is when $f_1$ is one of the measured variables. The region occurs when the values of $f_{10}$ and $f_1$ result in the last quotient of the Meyer-Lowry equation to be negative. These values of $f_{10}$ and $f_1$ that force the quotient to be negative are not physically possible; however they may occur in the iterative estimation scheme as intermediate estimates of the true values of these variables. Of course this forbidden region only occurs for the mole conversion case and not the mass conversion case, which is another reason why the mass conversion form is preferable if the Meyer-Lowry model is to be implemented.

The second region Hautus et al. (1985) discussed is the dangerous region, which refers to the issue when $r_1$ **or** $r_2$ approach one and thus force the α or β term in the Meyer-Lowry equation to approach infinity. Hautus et al. (1985) demonstrated the solution to this problem is to take the limit of the model for $r_1 \rightarrow 1$ at the problem region. However, taking the limit of the model is not simple and can involve a great deal of computational time. Furthermore, if $r_1$ **and** $r_2$ approach one then the Hautus et al. (1985) transformations are not applicable and rather the use of some *ad hoc* method is suggested by the authors. As the likelihood of either reactivity ratio being close to one is highly probable, a model without the need for a transformation or *ad hoc* method is desired. Subsequently, with the improvement in computational capability, the route of the numerically integrated cumulative copolymer composition model (ODECCC) was taken. For reference, ODE stands for ordinary differential equation (model).

The numerically integrated model is based on an equation that relates the cumulative copolymer composition to the initial feed composition and conversion, by:

$$\bar{F}_1 = \frac{f_{10} - f_1(1 - X_n)}{X_n} \tag{6.15}$$

where $f_1$ is given by numerically solving the following ordinary differential equation:

$$\frac{df_1}{dX_n} = \frac{f_1 - F_1}{1 - X_n} \tag{6.16}$$

and $F_1$ is from the instantaneous Mayo-Lewis model written below for reference as,

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \tag{6.17}$$

In order to solve the ordinary differential equation (Equation 6.16) the initial condition $f_1 = f_{10}$ *when* $X_n = 0$ is required.

The objective function used in the EVM analysis of the ODECCC model is thus:

$$f(\overline{F_1}) = \overline{F_1} - \frac{f_{10} - f_1(1 - X_n)}{X_n} \tag{6.18}$$

where $X_n$ is related to the measured variable $X_w$ by Equation 6.7.

The variable used in the EVM analysis is only the cumulative copolymer composition, $\overline{F_1}$, as $X_w$ and $f_{10}$ are unable to be classified as independent as they are used in the solution of the ordinary differential equation. In any case, it is reasonable that $X_w$ and $f_{10}$ be considered as perfectly known as the error associated with the variables measurements (typically from gravimetry analysis) is insignificant compared to the $\overline{F_1}$, which is typically from NMR analysis.

The case studies analyzed with the EVM parameter estimation technique, using the ODECCC model, were those same cases analyzed with the Meyer-Lowry model plus an additional case study. That is, the styrene and methyl methacrylate copolymerization data given by Rossignoli (1993) and O'Driscoll et al. (1984) is Case I; and the acrylic acid and acrylamide copolymerization data given by Bourdais (1955), Cabaness et al. (1971) and Shawki and Hamielec (1979) is Case II. Case Study III was selected as an additional example as the system produced unusual joint confidence regions of the estimated reactivity ratios.

### 6.2.1 Case Study I: STY- MMA System

As outlined in Section 6.1.3 O'Driscoll et al. (1984) presented moderately high conversion experimental data, while Rossignoli (1993) created a simulated moderate-low conversion data set (see Table 6.1 and 6.2, respectively). The point estimates published by O'Driscoll et al. (1984) and Rossignoli (1993), when using the Meyer-Lowry model, can be seen in Table 6.8 along with the estimates obtained from the EVM numerically integrated cumulative copolymer composition (ODECCC) analysis.

**Table 6.8: Point estimates of reactivity ratios using data from O'Driscoll et al. (1984) and Rossignoli (1993).**

| | **Model** | **$r_1$** | **$r_2$** |
|---|---|---|---|
| O'Driscoll et al. (1984) | Meyer-Lowry | 0.4317 | 0.4215 |
| Current work | Meyer-Lowry | 0.4281 | 0.4183 |
| Current work | ODECCC | 0.4403 | 0.4385 |
| Rossignoli (1993) | Meyer-Lowry | 0.40801 | 0.429389 |
| Current work | Meyer-Lowry | 0.40801 | 0.42938 |
| Current work | ODECCC | 0.3986 | 0.4273 |

The JCRs for the different models are given in Figures 6.5 and 6.6 for the O'Driscoll et al. (1984) and Rossignoli (1993) data sets, respectively. It can be seen from Figure 6.5 that the size of the JCR appears to be slightly larger for the ODECCC model than that of the Meyer-Lowry case. This is understandable given that the Meyer-Lowry model contains more information than the ODECCC model (three EVM variables instead of one) and O'Driscoll et al. (1984) data is recorded up to conversions of 70% (i.e., if there is any difference in the models ability in tracking composition drift, it would be more pronounced for higher conversion problems). While in Figure 6.5 the JCRs appear to be in very good agreement, which was expected given the total conversion was maintained below 11%.

Further analysis of the figures also shows that all point estimates fall within both the Meyer-Lowry and ODECCC JCRs. The similarity in point estimates and significant overlap of the contours from the different models demonstrates that the ODECCC model is in good agreement with the Meyer-Lowry model results.

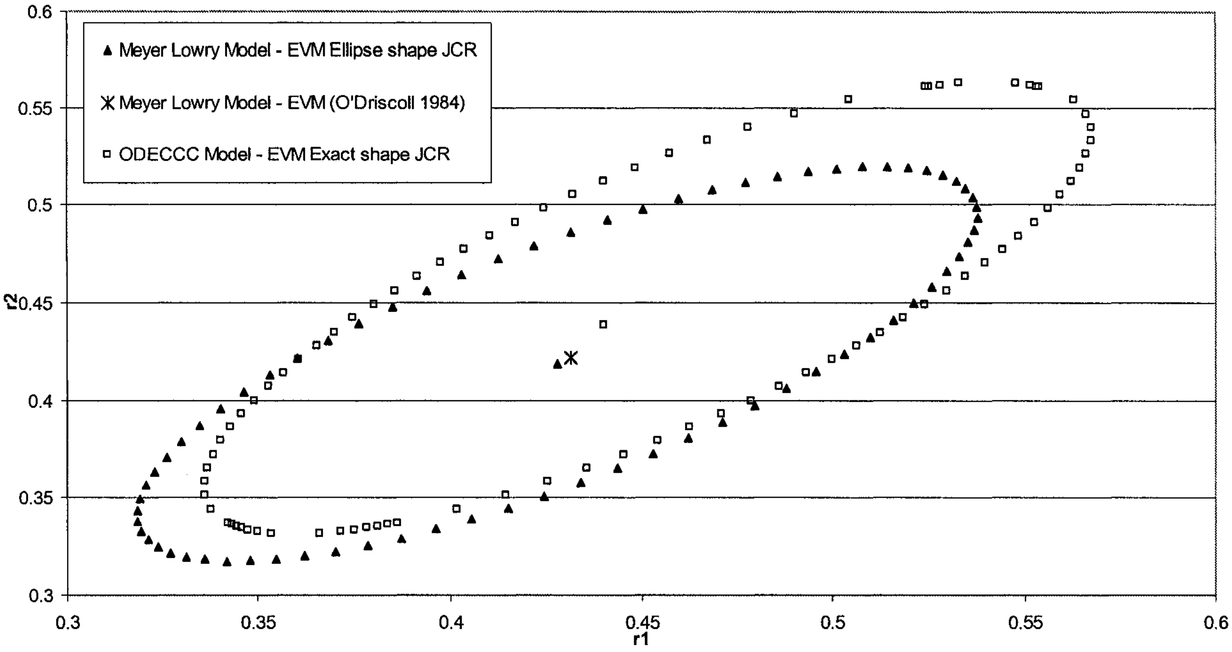


**Figure 6.5: JCRs for the application of the EVM parameter estimation to the ODECCC model for the STY-MMA copolymerization data set given by O'Driscoll et al. (1984).**

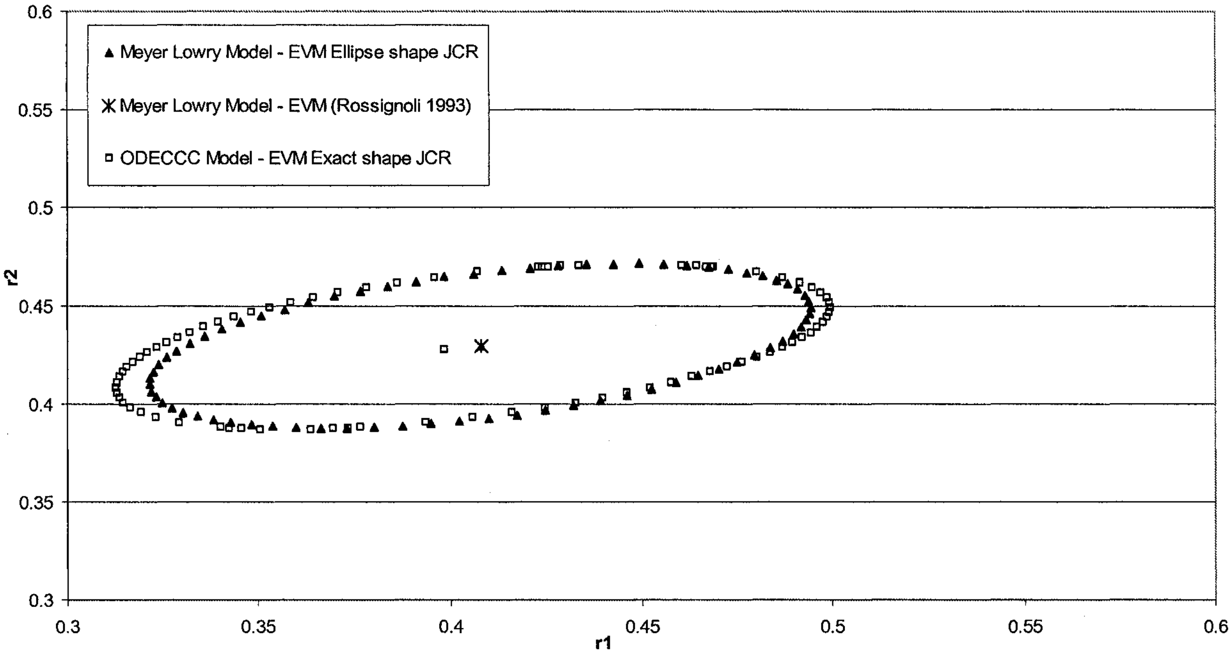


**Figure 6.6: JCRs for the application of the EVM parameter estimation to the ODECCC model for the STY-MMA copolymerization data set given by Rossignoli (1993).**

### 6.2.2 Case Study II: Acrylic Acid- Acrylamide System

The acrylic acid (AAcid)/ acrylamide (AM) copolymerization system has been studied by many authors including Bourdais (1955), Cabaness et al. (1971), and Shawki and Hamielec (1979). While each of the named authors conducted the experiments at different temperatures and level of conversion, all provided measurements for the copolymer composition, weight fraction conversion and initial feed composition (refer to Table 6.5 and 6.6). Bourdais (1955) and Cabaness et al. (1971) both used graphical methods to estimate $r_1$ and $r_2$ from the Mayo-Lewis equation; Shawki and Hamielec (1979) used a nonlinear regression method on the Meyer-Lowry model.

The ODECCC model was used for the three data sets in the EVM MATLAB routine and found the exact JCRs for each of the parameter estimates (obtained from analyzing the different data sets). The exact JCRs, along with point estimates and the ellipse JCRs, found using the Meyer-Lowry model EVM MATLAB routine, for the different data sets, can be seen in Figures 6.7 to 6.9. The exact JCR could not be found for either the Meyer-Lowry model case or the ODECCC model case, when the Cabaness, 1971 data set was used.

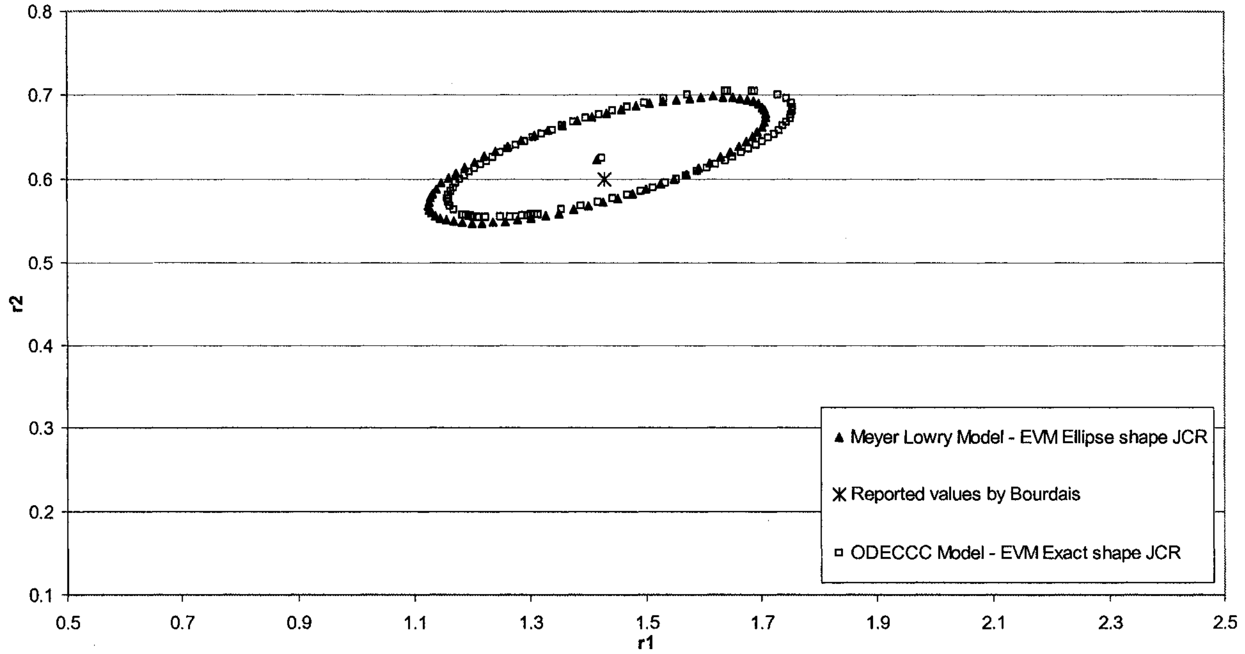


**Figure 6.7: JCRs for the application of EVM parameter estimation to the ODECCC model for the AAcid-AM copolymerization at 25°C, data set given by Bourdais (1955).**

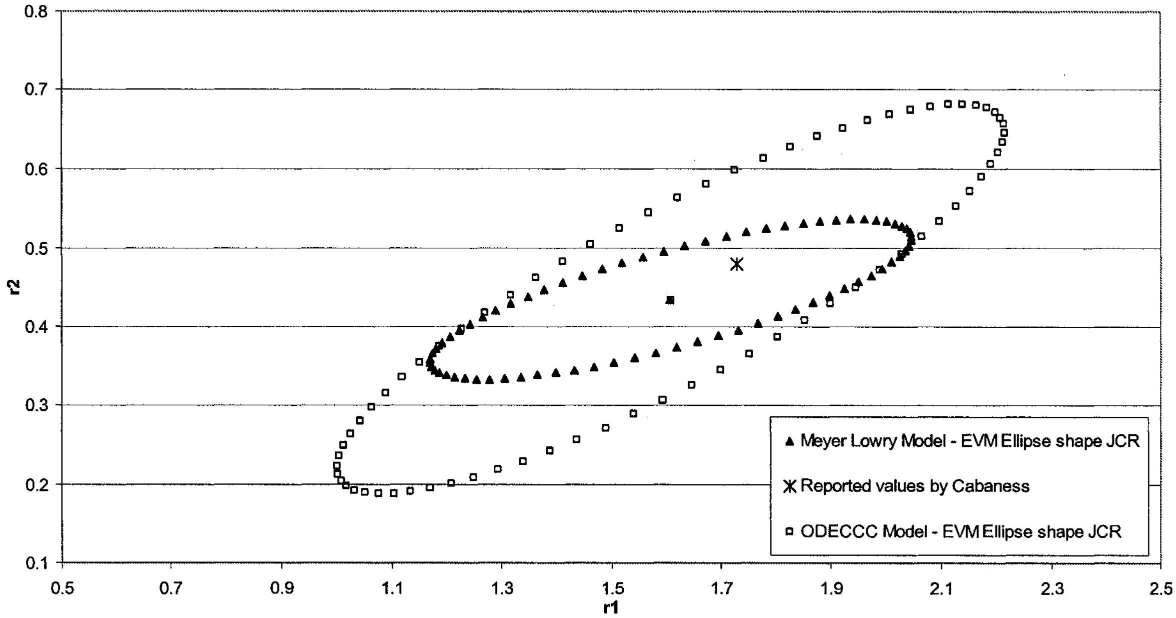


**Figure 6.8: JCRs for the application of EVM parameter estimation to the ODECCC model for the AAcid-AM copolymerization at 40°C, data set given by Cabaness et al. (1971).**

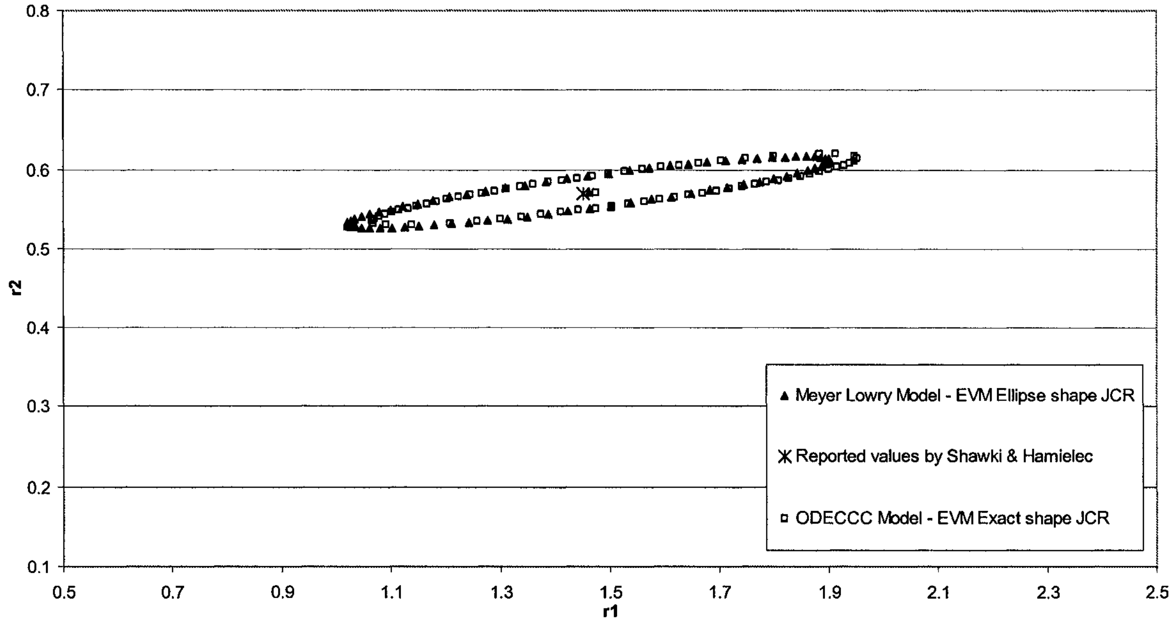


**Figure 6.9: JCRs for the application of EVM parameter estimation to the ODECCC model for the AAcid-AM copolymerization at 60°C, data set given by Shawki and Hamielec (1979).**

Figures 6.7 and 6.9 show that for both the Bourdais (1955) low conversion data set and Shawki and Hamielec (1979) high conversion data set, the Meyer-Lowry model is in very good agreement with the ODECCC model. On the other hand, Figure 6.8 shows that for Cabaness et al. (1971) low conversion data set the Meyer-Lowry model appears to result in a smaller confidence contour than the ODECCC model, which may be due to poor experimental design.

In all the figures however the point estimates, given by the authors, lie within both the Meyer-Lowry and ODECCC JCRs for the respective data sets and thus indicates good agreement between the two models. Therefore, reliable reactivity ratio estimates can be obtained for both low and moderate conversion experiments by using the ODECCC model, which avoids the difficulties associated with the use of the Meyer-Lowry model.

### 6.2.3 Case Study III: N-vinyl pyrrolidone (NVP)/ MMA System

Once it had been shown that the ODECCC model and the Meyer Lowry model gave parameter estimates that were in agreement, an additional case study, with a relatively extensive data set, was analyzed. The selected case study was the N-vinyl pyrrolid-2-one ($M_1$)/methyl methacrylate ($M_2$) system in solvent DMSO for moderate to high conversion data. The data set can be seen in Table 6.9 and was provided by Czerwinski (1998).

**Table 6.9: Experimental data by Czerwinski (1998) for N-vinyl pyrrolidone/MMA DMSO solvent system (moderate - high conversion).**

| Initial Feed Composition (Mole frac NVP) ($f_1$) | Copolymer Composition (Mole frac NVP) ($F_1$) | Conversion (wt %) ($X_w$) |
|---|---|---|
| 0.2 | 0.058 | 16.3 |
| | 0.065 | |
| 0.4 | 0.159 | 63.2 |
| | 0.167 | |
| 0.55 | 0.186 | 18.9 |
| | 0.191 | |
| 0.65 | 0.276 | 24.2 |
| | 0.230 | |
| 0.75 | 0.406 | 41.1 |
| | 0.404 | |
| 0.85 | 0.650 | 43.5 |
| | 0.603 | |
| 0.9 | 0.688 | 22.9 |
| | 0.664 | |
| 0.94 | 0.758 | 40.6 |
| | 0.763 | |
| 0.98 | 0.852 | 38.5 |
| | 0.835 | |

The data was used in the ODECCC and Mayo-Lewis models to show the deviation in the estimates for moderate to high conversion data problems. The point estimates from the two models can be seen in Table 6.10, along with the estimates recorded by Czerwinski (1998). The selected error level for the variables in the EVM routine was 10% due to the fact that Czerwinski indicated large error margins in the parameter estimates published.

**Table 6.10: Point estimates by Czerwinski (1998) and the estimates obtained by EVM MATLAB analysis of the data for different models.**

| | Model | Estimation Method | $r_1$ | $r_2$ |
|---|---|---|---|---|
| Czerwinski (1998) | Meyer-Lowry | KT | 0.127 | 6.184 |
| Czerwinski (1998) | Meyer-Lowry | NLLS | -0.138 | 3.694 |
| Current work | Mayo-Lewis | EVM | 0.0538 | 4.0934 |
| Current work | ODECCC | EVM | 0.008 | 4.24 |

Furthermore, the JCRs obtained from the use of the ODECCC and Mayo-Lewis models in EVM are shown in Figure 6.10.

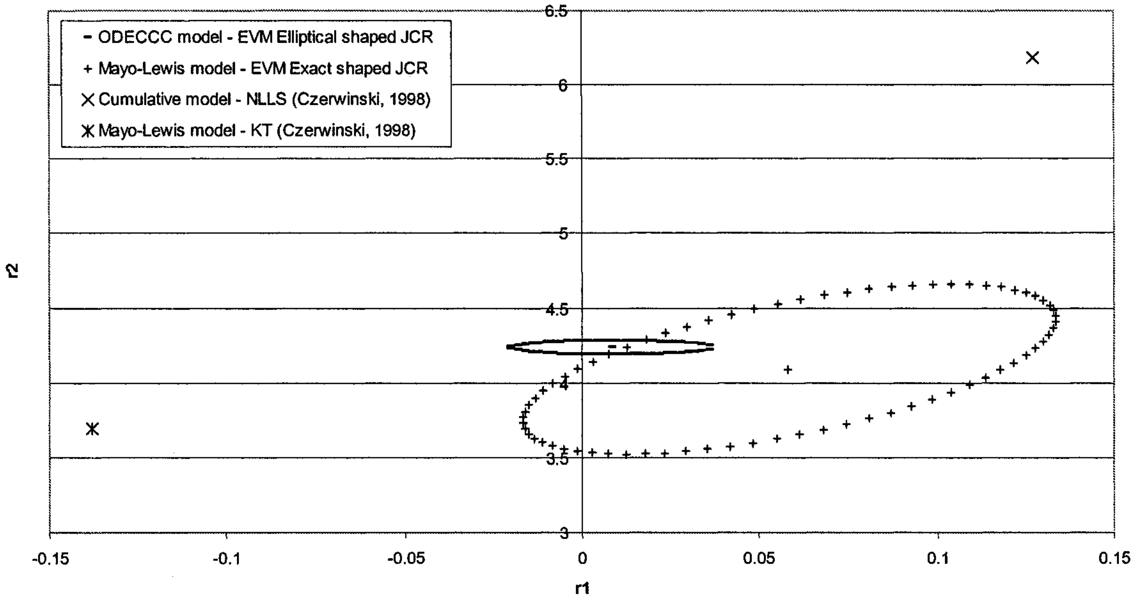


**Figure 6.10: JCRs for the application of EVM parameter estimation to the ODECCC model and Mayo-Lewis model for the Czerwinski (1998) NVP-MMA copolymerization data set.**

It can be seen that the estimates provided by Czerwinski do not agree with those obtained from EVM for either the ODECCC or Mayo-Lewis models. Furthermore, there is some separation of the JCRs from the different models, which was expected given the data was collected for moderate to high conversion levels where composition drift may occur. It is also interesting to note that the models JCRs overlap into the negative region, thus indicating the large degree of uncertainty in the estimation of NVP.

## 6.3 Numerically Integrated Cumulative Copolymer Triad Fractions (ODECCTF) Model

There have been very few articles published on the cumulative triad fractions model. The model used here relates the cumulative triad fractions, $\overline{A_{iji}}$, to the instantaneous triad fractions $A_{iji}$ and conversion by:

$$\frac{d\left(X_n \overline{Ai_{ijk}}\right)}{dX_n} = A_{ijk} \tag{6.19}$$

where i, j and k are the six combinations of monomers 1 and 2. The equation above can be re-written as:

$$\frac{d\left(\overline{Ai_{ijk}}\right)}{dX_n} = \frac{A_{ijk} - \overline{Ai_{ijk}}}{X_n} \tag{6.20}$$

where $A_{ijk}$ is given by the instantaneous triad fraction equations. For reference, the monomer one centered triads are written as:

$$A_{111} = \frac{r_1^2 f_1^2}{r_1^2 f_1^2 + 2r_1 f_1 f_2 + f_2^2}; A_{211+112} = \frac{2r_1 f_1 f_2}{r_1^2 f_1^2 + 2r_1 f_1 f_2 + f_2^2}; \ A_{212} = \frac{f_2^2}{r_1^2 f_1^2 + 2r_1 f_1 f_2 + f_2^2}$$

(6.21-6.23)

while the monomer two centered triads are found by simply interchanging the subscripts.

Also, it is important to note here that only four out of the six triads are used in the analysis in order to avoid the issues of colinearity, as discussed by Burke (1994). In this work the triads eliminated were $A_{222}$ and $A_{111}$, unless otherwise indicated in the case study.

Before Equation 6.20 can be numerically solved the feed composition, $f_1$, is required, and thus Equation 6.16 (re-written below for convenience) must also be numerically solved.

$$\frac{df_1}{dX_n} = \frac{f_1 - F_1}{1 - X_n} \tag{6.24}$$

where $F_1$ is given by the instantaneous Mayo-Lewis model (Equation 6.17) and the weight fraction conversion is related to the molar conversion by Equation 6.7.

In order to then solve the cumulative triads ordinary differential equation (Equation 6.20), the initial condition had to be approximated by $\overline{A_{iji}} \approx 0$ *when* $X_n = 0$. Additionally, the values of the feed, $f_1$, had to evaluated from the ordinary differential equation (Equation 6.24) using the initial condition $f_1 = f_{10}$ when $X_n = 0$.

The objective function used in the EVM analysis of the ODECCTF model is thus,

$$f\left(\overline{A_{iji}}\right) = \overline{A_{iji}}(meas) - \overline{A_{iji}}(calc) \tag{6.25}$$

where $\overline{A_{iji}}$ *(calc)* is the solution obtained from Equation 6.20.

The variables used in the EVM analysis are the four cumulative triad fractions (as two are eliminated to avoid issues of colinearity). The weight fraction conversion, $X_w$ and initial feed composition, $f_{10}$, are not classified as independent as they are used in the solution of the ordinary differential equations. As discussed in Section 6.2, it is reasonable that these variables be considered as perfectly known as the errors associated with the $f_{10}$ and $X_w$ measurements (typically from gravimetry analysis) are insignificant compared to $\overline{A_{iji}}$, which is from $C^{13}$NMR analysis.

Selected literature cases were analyzed with the EVM parameter estimation technique using the above numerically ODECCTF model and the instantaneous triad fractions model in order to be able to compare the results. In these studies the triad fractions and feed composition variables (in the instantaneous model) assumed error levels of 10% and multiplicative error structure.

### 6.3.1 Case Study I: STY- MMA System

Maxwell et al. (1993) presented low conversion experimental data for initial feed composition; weight fraction conversion; and NMR normalized peak areas, which were converted to triad fractions (refer to Table 5.5). The point estimates published by Maxwell et al. (1993), when using the instantaneous model, can be seen in Table 6.11 along with the estimates obtained from the EVM numerically integrated cumulative copolymer triad fractions (ODECCTF) analysis.

**Table 6.11: Point estimates of reactivity ratios using triad fractions data from Maxwell et al. (1993).**

| | Model | Estimation Method | $r_1$ | $r_2$ |
|---|---|---|---|---|
| Maxwell et al. (1993) | Instantaneous | NLLS | 0.51 | 0.52 |
| Current work | Instantaneous | EVM | 0.6512 | 0.3683 |
| Current work | Cumulative (ODECCTF) | EVM | 0.7402 | 0.3192 |

The JCRs for the different models and the literature values given by Maxwell et al. (1993) can be seen in Figure 6.11. The exact JCR could not be found for the ODECCTF case as the information matrix ($G$ in the program) was diagonal, thus the ellipse JCR is shown.

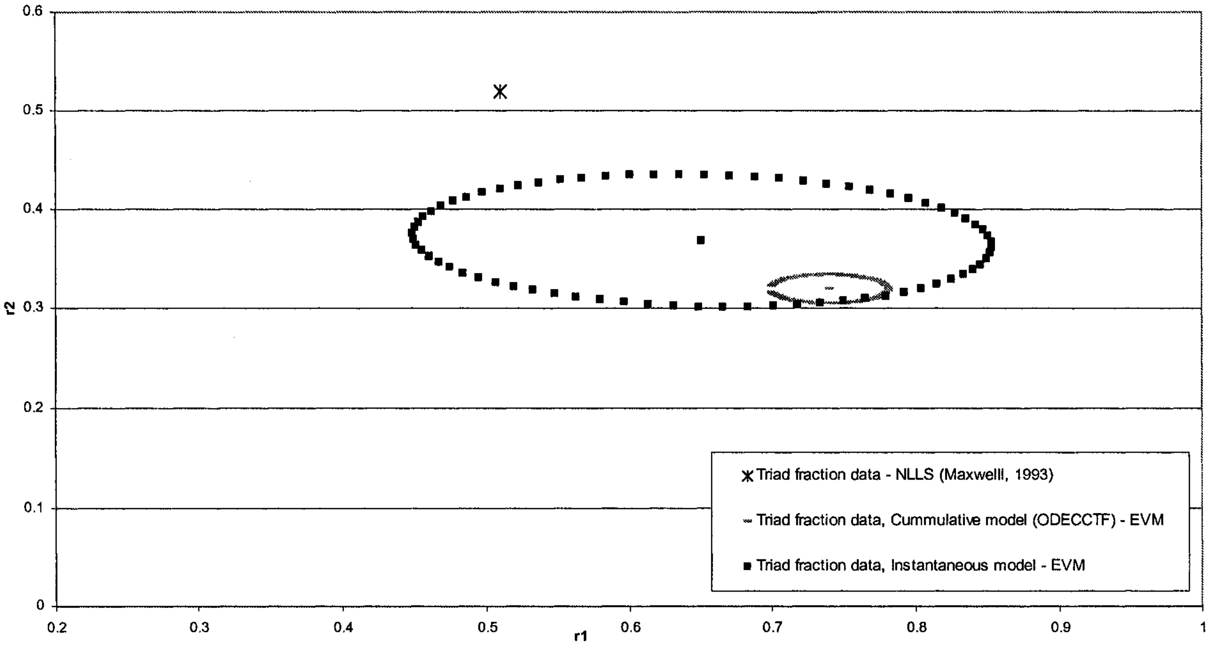


**Figure 6.11: JCRs for the application of the EVM parameter estimation to the instantaneous triad fractions model and ODECCTF model, for the Maxwell et al. (1993) STY-MMA copolymerization data set.**

Given that the data was measured at low conversions where composition drift is considered insignificant, one would anticipate that the JCR of the cumulative model (which accounts for composition drift) would overlap the JCR of the instantaneous model. It can be seen in Figure 6.11 that the ODECCTF JCR indeed overlaps the instantaneous model's JCR. In fact, it can be seen that the size of the ODECCTF model JCR is considerably smaller than that obtained from the instantaneous model; as more process information was input to the model. That is, the ODECCTF has four responses (triad fractions) and two other variables measurements considered to be perfectly known (conversion and initial feed composition), while the instantaneous triad fractions model only has five responses (all considered to have error) thus resulting in less certainty in the reactivity ratio estimates.

Furthermore, it can also be seen in Figure 6.11 that the literature point estimates, found using a NLLS parameter estimation method by Maxwell et al. (1993), are not contained within either JCR. This is not unexpected as the NLLS estimation method for all instantaneous triad fractions cases in Chapter 5 did not agree with the EVM estimate and thus it is believed that applying this estimation procedure is statistically incorrect (due to assumptions required to apply model to triad fractions data).

However, it can be said that the STY-MMA copolymerization is a well behaved system that shows the analysis of triad fractions data using EVM yields reactivity ratio estimates, from either an instantaneous model or cumulative model, that are in good agreement.

### 6.3.2 Case Study II: STY- AN System

Hill et al. (1989) presented low conversion experimental data for styrene- acrylonitrile copolymerization (refer to Table 5.14). The point estimates published by Hill et al. (1989), when using the instantaneous models can be seen in Table 6.12 along with the estimates obtained from the EVM numerically integrated cumulative copolymer composition (ODECCC) and numerically integrated cumulative copolymer triad fractions (ODECCTF) analysis.

**Table 6.12: Point estimates of reactivity ratios using data from Hill et al. (1989).**

| | Data Set | Model | Estimation Method | $r_1$ | $r_2$ |
|---|---|---|---|---|---|
| Hill (1989) | Composition | Instantaneous (Mayo-Lewis) | NLLS | 0.34 | 0.05 |
| Current work | Composition | Instantaneous (Mayo Lewis) | EVM | 0.3671 | 0.0536 |
| Current work | Composition | Cumulative (ODECCC) | EVM | 0.3572 | 0.0473 |
| Hill (1989) | Triad fractions | Instantaneous | NLLS | 0.47 | 0.08 |
| Current work | Triad fractions | Instantaneous | EVM | 0.6517 | 0.0841 |
| Current work | Triad fractions | Cumulative (ODECCTF) | EVM | 0.5767 | 0.0795 |

The JCRs for the different models are given in Figure 6.12. The exact JCR could not be found for the ODECCTF case as the information matrix (*G* in the program) was diagonal.

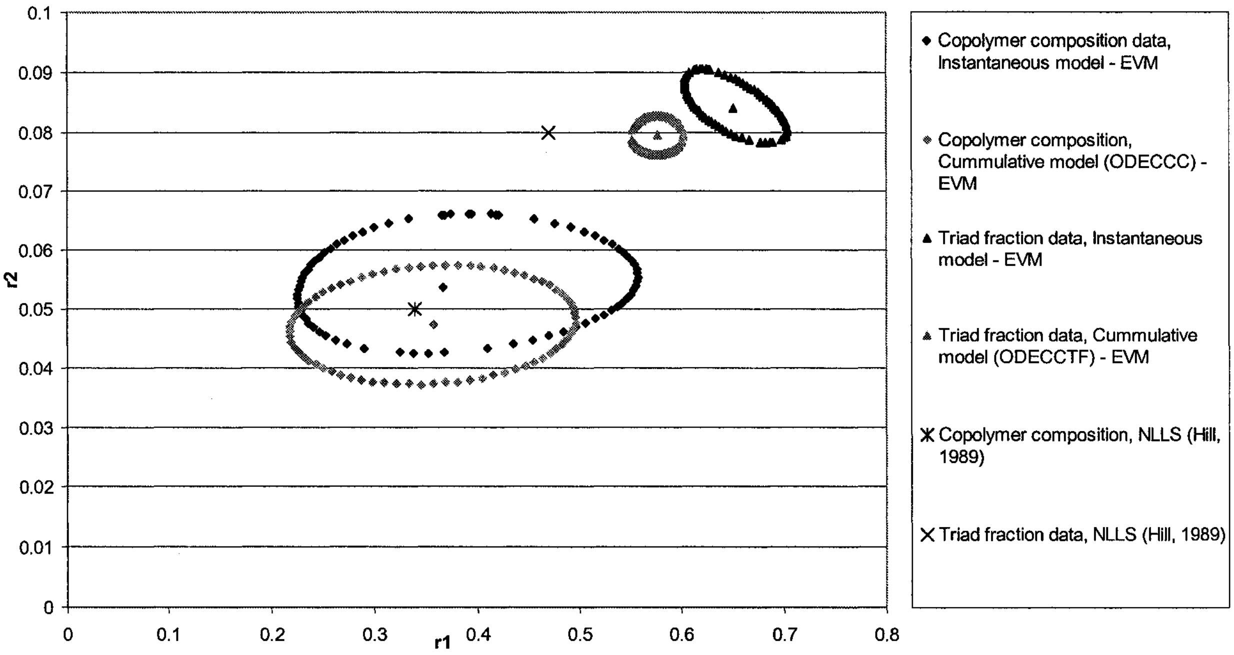


**Figure 6.12: JCRs for the application of the EVM parameter estimation to the ODECCC and ODECCTF models for the Hill et al. (1989) STY-AN copolymerization data sets.**

The first point to note from Figure 6.12 is the uncertainty in the triad fractions instantaneous and cumulative models is less than the uncertainty of the cumulative copolymer composition model and hence less than the instantaneous copolymer composition model. The multiple responses of triad fractions, for both instantaneous and cumulative models, contribute to the improvement in estimation certainty.

Perhaps most interesting is the fact that the triad fractions JCRs of the instantaneous and cumulative model do not overlap. Given that the data was measured at low conversions where composition drift is considered insignificant, one would anticipate that the JCR of the cumulative model (which accounts for composition drift) would be at least overlapping the JCR of the instantaneous model, similar to the previous STY-MMA case study (Section 6.3.1). However, this is not the case for the triad fractions models, nor do they contain the literature point estimates found using the NLLS parameter estimation method as reported by Hill et al. (1989).

Consequently, two potential hypotheses were analyzed in order to account for the difference in the cumulative and instantaneous estimates. The hypotheses focused on the potential correlation between triads and the fact that the ODECCTF model considers the feed composition to be perfectly known, while the instantaneous model includes it as a random variable. Cases were thus re-run to: include covariance in the instantaneous and cumulative models; assume $f_1$ is perfectly known in the instantaneous model; combine the effects of adding covariance to the triads and assuming $f_1$ to be perfectly known. Covariance of the triads was calculated via Equation 5.10, where the correlation coefficient was selected as 0.2 and the variance of the triads was 10%. Figure 6.13 illustrates the effects that the above changes had on the location of the point estimates and JCRs.

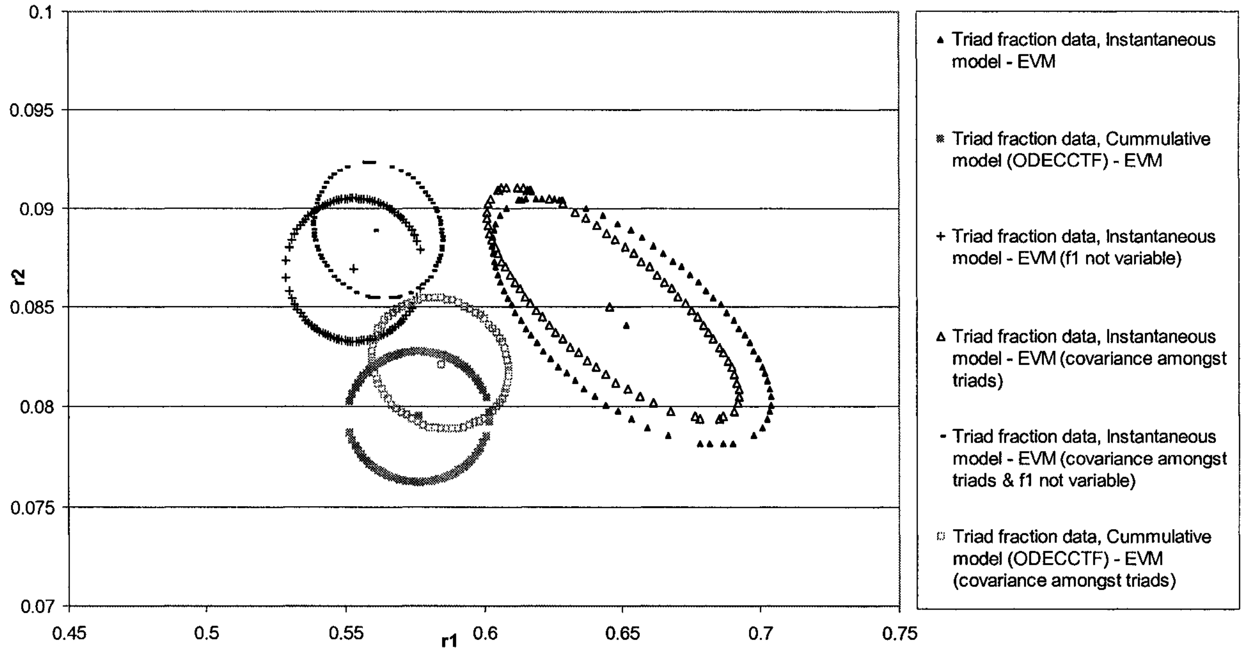


**Figure 6.13: JCRs for the application of the EVM parameter estimation to the ODECCTF model for the Hill et al. (1989) STY-AN copolymerization data sets.**

It can be seen when the feed composition variable, $f_1$, is assumed to be perfectly known (i.e. $f_1$ not a random variable) for the instantaneous model that the point estimates are in better agreement as the random variables used in the models are then the same. That is, when the instantaneous model for triad fractions data was adjusted to only represent the four triad fractions as random variables, this allowed the instantaneous model to have the same comparison basis as the cumulative model. It is therefore a recommendation from this work that the numerical difficulty of incorporating the feed composition and weight fraction conversion as random variables in the ODECCTF EVM program be investigated in greater detail.

Furthermore, when covariance amongst the triads is inputted to the EVM covariance matrix, $\underline{V}$, the JCRs are touching; indicating the possibility of triad fractions data having correlation between the measurements. However, there is still separation of the JCRs and thus the next stage of analysis was to perform diagnostic checking.

### *6.3.2.1 Diagnostic Checking*

Diagnostic checking is performed here in order to be able to determine whether the reactivity ratio estimates, obtained from using either the instantaneous or cumulative models in EVM, give similar triad fractions and copolymer composition predictions, despite having different values.

Firstly, using the estimated reactivity ratios from the cumulative model and the instantaneous model (with $f_1$ assumed to be perfectly known), copolymer compositions at varying feed compositions were calculated using the Mayo-Lewis equation. Consequently, two predicted copolymer composition curves from the instantaneous and cumulative triad reactivity ratio estimates can be seen in Figure 6.14, along with the experimental values. Furthermore, the estimates of the 'true' values of the triad fractions, calculated in the EVM routine, for the ODECCTF and instantaneous triad fractions ($f_1$ assumed perfectly known) models were also plotted against the experimental values (refer to Figures 6.15-6.18).

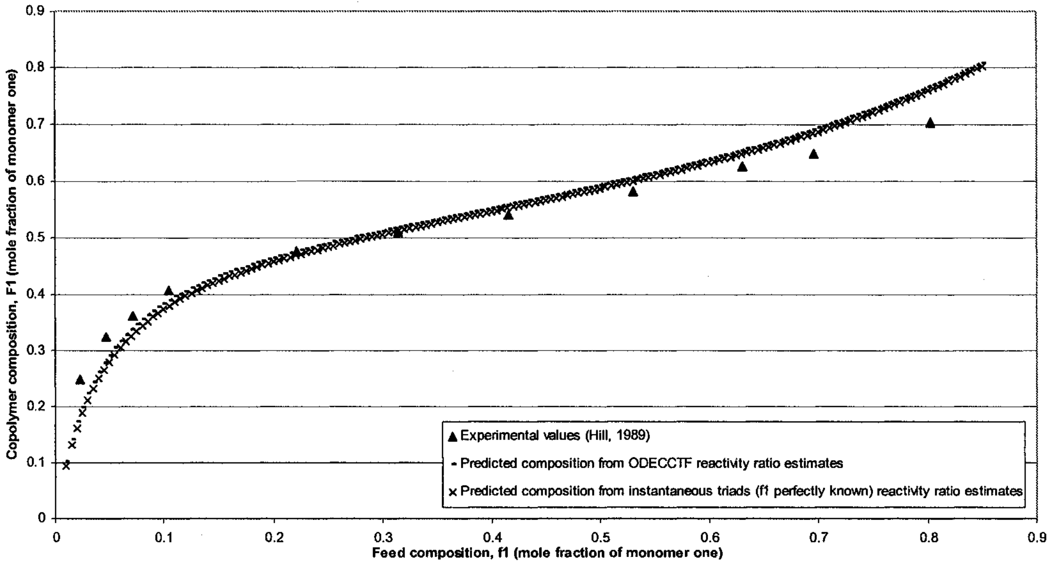


**Figure 6.14: Predicted copolymer composition curves using the Mayo-Lewis equation and reactivity ratio estimates obtained from analyzing triad fractions data with the ODECCTF model and the instantaneous ($f_1$ assumed perfectly known) triad model.**

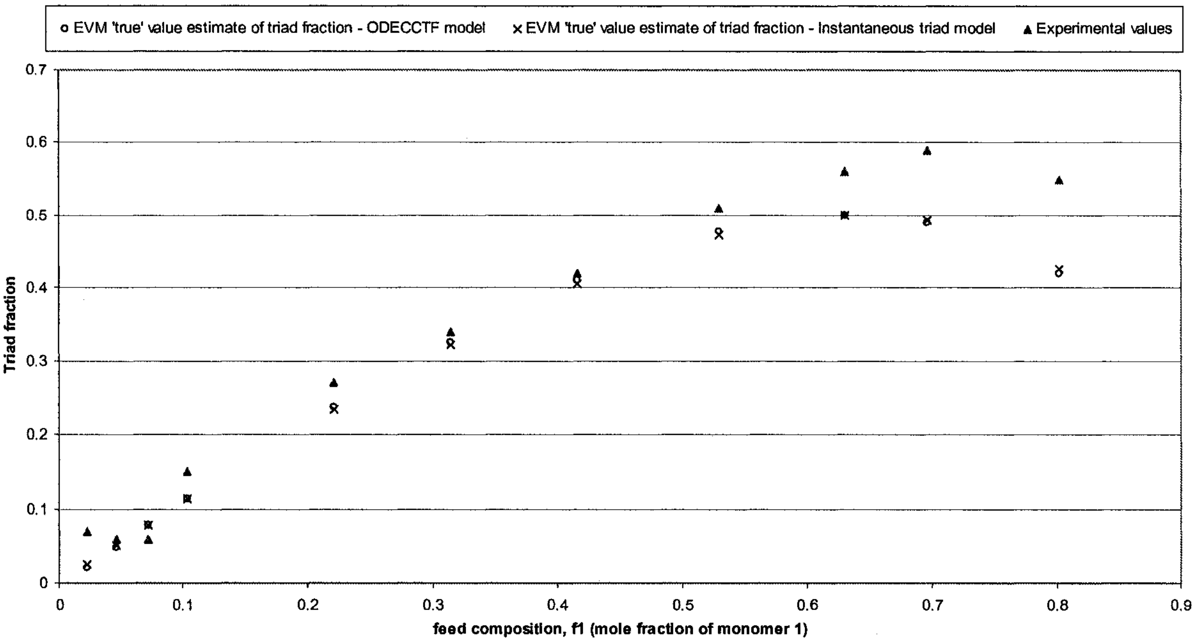


**Figure 6.15: 'True' value estimate of $A_{112+211}$ triad fraction from the ODECCTF model and the Instantaneous triad fractions model ($f_1$ assumed perfectly known) EVM analysis.**

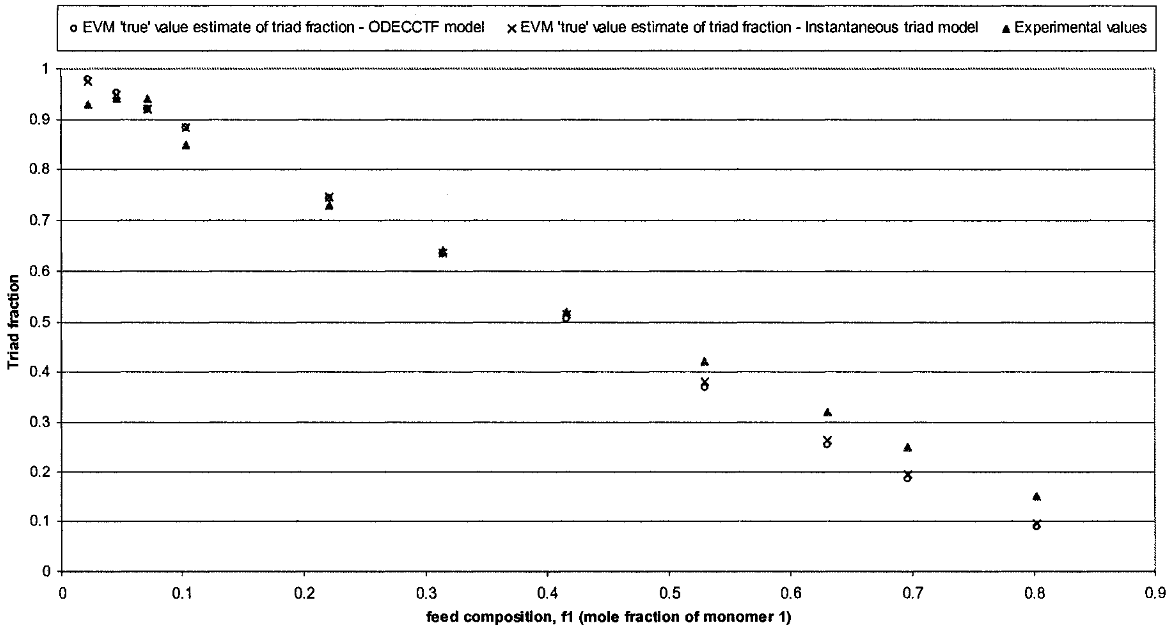


**Figure 6.16: 'True' value estimate of $A_{212}$ triad fraction from the ODECCTF model and the Instantaneous triad fractions model ($f_1$ assumed perfectly known) EVM analysis.**

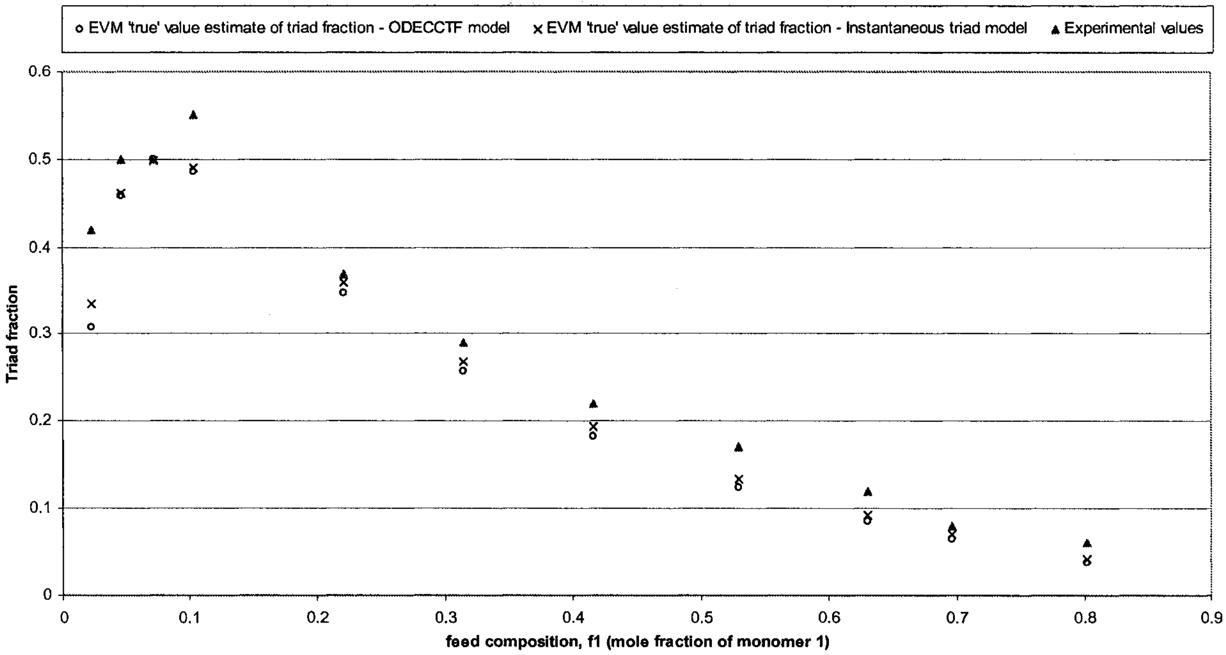


**Figure 6.17: 'True' value estimate of $A_{122+221}$ triad fraction from the ODECCTF model and the Instantaneous triad fractions model ($f_1$ assumed perfectly known) EVM analysis.**

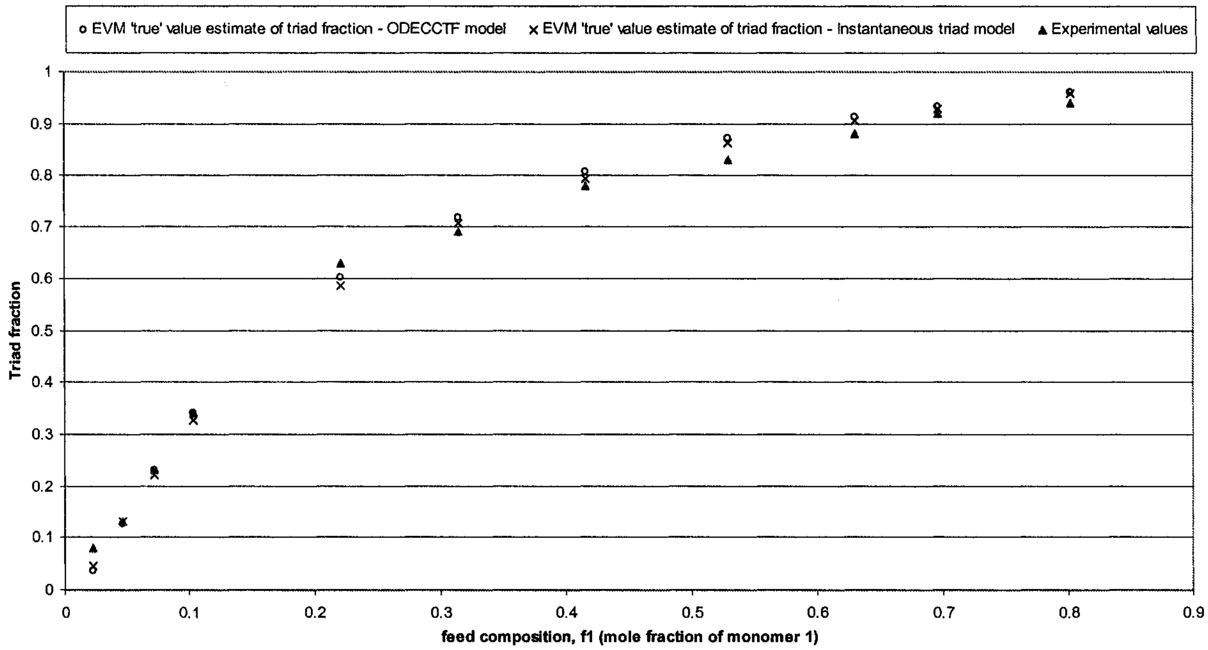


**Figure 6.18: 'True' value estimate of $A_{121}$ triad fraction from the ODECCTF model and the Instantaneous triad fractions model ($f_1$ assumed perfectly known) EVM analysis.**

As can be seen from Figures 6.14 to 6.18, there does not appear to be a significant difference between the two models' precision at predicting the copolymer composition and triad fractions, despite the fact that the models' reactivity ratio JCRs do not overlap.

There are issues in using the JCRs for multiresponse problems and thus the potential for incorrect conclusions to be drawn from analyzing the contours, as discussed in detail in Polic (2001). Whilst it is common to use the parameter estimates JCR to determine the quality of the estimates, a limitation of the exact JCR when multiple responses are used, is that the confidence level of the exact JCR obtained can be significantly different than expected when the sample size is small (Polic, 2001). The difference can be up to 70% as observed in Polic (2001) case studies and can be even greater when the ellipse JCR is used. The JCRs can then fail at accurately representing the uncertainty present in the parameter estimates for multiresponse - small sample size problems.

Consequently, the JCRs seen in Figure 6.13 are believed to be misrepresenting the true nature of the reactivity ratio estimates from the different models, due to the problem being multiresponse and the data set being small (11 data points used). The fact that the estimates of the 'true' value triad fractions are almost identical for the instantaneous and cumulative models supports this idea of a lack of sensitivity. Thus, it is impossible to distinguish between the parameter estimates from the different models. A better alternative to comparing the JCRs would be to use Markov Chain Monte Carlo methods. In fact, generally cases that involve model discrimination or where model parameter estimates are to be compared, Markov Chain Monte Carlo methods, such as the Metropolis-Hastings method, should be used.

## Chapter 7

# Conclusions and Recommendations

The work conducted in this thesis was motivated by questions raised by previous researchers, focusing on the use of different data sources and models ability to accurately estimate reactivity ratios. Accurate reactivity ratio estimates are important due to the use of these values in both representing the copolymer system and discriminating between mechanistic models.

In Chapter 4, a literature update showed the abundant use of reactivity ratio estimates in current research publications, despite the fact that the estimates are obtained via statistically incorrect linear techniques. The first stage in this work was then to re-demonstrate that applying linear parameter estimation techniques to a nonlinear problem, do not provide accurate estimates for all systems and thus caution should be heeded before using these simple methods. Infact some nonlinear methods also have issues; namely model assumptions ignoring error in certain variables and an inability to transform the copolymerization equations into the desired model form. It is for this reason that the error in variables model was selected as the parameter estimation method for this work, as it is adaptable to nonlinear multiple response problems and it accounts for the measurement error in all variables.

The objectives of the case studies in Chapters 5 and 6 were then to determine: the potential improvement in reactivity ratio estimates using triad fractions data in place of and in addition to composition data for the instantaneous model; and the potential benefit in using cumulative models over the full conversion range. As a side project estimation of reactivity ratios from terpolymer composition data was also attempted. The conclusions drawn from analysis of the case studies can be seen in the following summarized points.

## 7.1 Concluding Remarks

Statements 1 – 4, 6 and 8 are summarized points made from Chapter 5, (Instantaneous Copolymer Data Case Studies). Statements 5 and 7 are concluding remarks from Chapter 4 (Literature Update and Case Studies). Where as, remarks 9 and 10 are resulting from analysis of Chapter 6, (Cumulative Copolymer Data Case Studies).

### 1) Improvement in reactivity ratio estimates from instantaneous triad fractions data

Improvement in reactivity ratio estimation using triad fractions data in place of composition data was seen in all case studies by a reduction in the size of the joint confidence region, regardless of error structure.

### 2) Agreement of reactivity ratio estimates from different data sources

Generally, reactivity ratio estimates from instantaneous triad fractions and composition data analysis agree when an additive error structure is imposed to the respective cases; but disagree when a multiplicative error structure is imposed. That is, the reactivity ratio estimates joint confidence regions (JCR) from triad fractions data and composition data analysis, imposing additive error structures to both cases, would overlap significantly; whilst the multiplicative cases would generally have JCR that were separate. In some cases all the contours overlapped, indicating an extremely well behaved system.

### 3) Error structure effect on location of point estimate

It is known that the imposed error structure affects the size of the joint confidence region and thus uncertainty in the parameter estimates; the multiplicative error structure giving the smaller confidence contour than the additive counterpart. However, when considering triad fractions data there was discrepancy in the estimates obtained from employing an additive or a multiplicative error structure. Therefore, it can be said that the selected error structure for triad fractions data significantly affects the location of the reactivity ratio point estimates and thus requires further attention. On the other hand, the error structure used for composition data does not significantly affect the location of the reactivity ratio point estimates; only the size of the joint confidence region.

### 4) No improvement in reactivity ratio estimates from combined instantaneous triad fractions and composition data

The combination of using triad fractions and composition data in the parameter estimation routine, did not offer any remarkable improvement in the reactivity ratio estimates over the single source data set result. Consequently, it is recommended that if triad fractions data is able to be obtained then it should be used to estimate reactivity ratios; provided that the error structure of the triad fractions variables are known.

### 5) Instantaneous copolymer composition curve

Reactivity ratio point estimates for a particular system, sampled from the EVM joint confidence region, can be used to create a 95% confidence band on the instantaneous copolymer composition curve. That is, at a particular feed composition one can be certain at the 95% confidence level that the corresponding copolymer composition measurement will fall within the band for that copolymer system. This is particularly useful as a quick reference guide for the anticipated copolymer composition in an industry that concentrates on select copolymer systems.

It has also been shown that visual inspection of the predicted instantaneous copolymer composition curves is not a valid model discrimination technique for the penultimate and terminal models. That is, visually comparing experimental copolymer composition data, at varying feeds, to predicted values from the different models, is not a statistically valid discrimination technique (particularly when no error bars are present). Unless the model predictions have a quantifiable deviation from the measured data which is beyond the extent of typical measurement errors, discrimination between the models is not possible. If model discrimination is desired, then careful experimental design is required and specific statistical techniques used. There are numerous articles detailing model discrimination techniques, one being by Burke (1994) who gives a detailed discussion of model discrimination techniques specifically for copolymerization studies.

### 6) Data accuracy and experiment design

Data accuracy and experiment design can greatly affect the parameter estimates obtained from copolymer composition data and subsequently the conclusions drawn from analyzing the estimates. It has been shown in a number of case studies, when multiple data sets are available for the same copolymerization system, that the data set used can significantly affect the location and size of the reactivity ratio estimate's joint confidence region. The data accuracy and experimental design can thus affect the conclusions drawn from reactivity ratio joint confidence regions. For example, the variation in the reactivity ratio joint confidence regions when using different solvents may be considered to be a possible solvent effect. However, the solvent effect can not be statistically proven unless the error levels are known, the experiment is optimally designed for parameter estimation and specific feed regions, which ensure that the precipitation of monomers (e.g. polyAN) will not affect the copolymerization, are used. All these factors affect the data set, which is used in the estimation of the reactivity ratios joint confidence region, which is in turn used to draw conclusions, such as a potential solvent effect. Therefore, copolymerization experiments with many replicates and good experimental design, as discussed in Burke (1994), are preferable for parameter estimation.

### 7) Parameter estimation methods

Linear and non linear least squares parameter estimates may agree with EVM estimates on occasion for particular copolymerization systems; however this is not always the case. Furthermore, even when the linear parameter estimates fall within the joint confidence contour obtained from EVM, they may not be representing the system very well. For example, in the NAS-DMA copolymerization system (refer to Section 4.3.5) case study the linear estimates provided by the research group calculated $r_{DMA}$ to be slightly greater than $r_{NAS}$, thus suggesting that the copolymer would have a lower mole fraction of NAS than the initial feed composition. However, from inspection of the raw data it was seen that the copolymer formed was slightly richer in NAS than the feed concentration. Consequently, the data suggested that $r_{NAS}$ should be slightly greater than $r_{DMA}$, which was in agreement with the EVM result. Thus despite the fact that both point estimates fell within the same contour, the EVM model was more accurately representing the copolymer situation. Furthermore, nonlinear least squares (NLLS) estimates published in the literature for triad fractions case studies generally did not agree with the EVM estimates obtained from analyzing the same data set, regardless of which error structure was imposed in EVM. The discrepancy between the two non linear estimates was attributed to the assumption in NLLS that the error in the feed composition measurement was insignificant and the small data sample size.

### 8) Estimating reactivity ratios from terpolymer composition data

Reactivity ratio estimation from terpolymer composition data proved to be unsuccessful with the original EVM estimation program as the routine was unable to converge. The program was sucessfuly updated by changing the optimization routine from a Newton search method to a more robust Simplex method.

### 9) Composition cumulative and instantaneous models for the full conversion range

At low conversion the instantaneous composition model reactivity ratio estimates agree with those obtained from the cumulative Meyer Lowry and the numerically integrated (ODECCC) models, as expected. While at moderate-high conversions the instantaneous model's estimates deviate from the cumulative models and in general the joint confidence regions do not overlap. However, the use of the cumulative models does not in general decrease the size of the joint confidence region and thus the uncertainty in the parameter estimates at low conversion. Consequently, the case studies showed that there is no improvement in the reactivity ratio estimates for cumulative models, unless composition drift is occurring. Thus at moderate-high conversion levels, the cumulative model should be used to account for the variation in the feed composition by including conversion as a random variable; while at low conversion any of the models can be used.

### 10) Triad fractions cumulative and instantaneous models for low conversion data

The triad fractions data case studies showed that at low conversion the instantaneous and cumulative numerically integrated (ODECCTF) models reactivity ratio estimates agree. In the first case study this was shown by the fact that the joint confidence regions obtained from the different models, overlapped considerably. However, the second case study did not show this same confidence contour overlap. Consequently, the estimates underwent diagnostic testing and from this it was evident that the reactivity ratio estimates from the instantaneous and cumulative models were in agreement, despite the fact that the confidence contours were separated. This result was understandable as the joint confidence regions can misrepresent the true nature of the parameter estimates, as discussed by Polic (2001). It was therefore recognized that when the parameter estimates are to be used for model comparison or discrimination, it is better to use the Markov Chain Monte Carlo methods, such as the Metropolis Hasting technique.

## 7.2 Recommendations for Future Work

### 1) Error structure study

An error structure study is required to determine the true error structure, either additive or multiplicative, of triad fractions/$C^{13}$-NMR normalized peak areas data. It is important because it can be seen in Chapter 5 that the error structure can influence the location and uncertainty in the parameter estimates in many systems, including 'well behaved' systems. Furthermore, if the true error structure of copolymerization data is infact additive, then the cumulative case studies analysis will need to be rerun using an additive error structure, as only the multiplicative error structure was considered. The error structure study of triad fractions is also required in order to determine whether there is correlation amongst the triads or with feed composition.

The error structure study would involve running an experiment containing many replicates, to place emphasis on the variance component analysis of measurement. The analysis would begin by imposing an additive structure in the EVM routine. Once the estimates of the 'true' variables were obtained from EVM, the variables residuals are then plotted against the variables estimated 'true' value. If a fan-like trend is present in the plot then this would indicate that the log of the variables is required and thus a multiplicative error structure is more appropriate; on the other hand if there is no trend present then an additive error structure is sufficient. The correlation amongst triads or with feed composition could also be determined by considering the residual plots of the variables.

### 2) Assume the errors to be normally distributed

In order to calculate the covarianve matrix, V in the error in variables model algorithm the variance of each variable was input. In order to input an assumed value of the variance of the variable a simple calculation was made based on the assumption that the variables were identically and uniformally distributed. Typically however it is a better method to calculate the variance assuming the variables are normally distributed. Yet for the purpose of this study the complexity to evaluate the variance given the variable has a normal distribution was too great and really should only be considered when the true error structure of the data is known. Consequently, after the error structure study is performed, the covariance matrix should be evaluated assuming a normally distributed error for the random variables.

### 3) Future updates for the MATLAB EVM code

The coding of the error in variables model and the subsequent joint confidence region calculation files in MATLAB for the different scenarios (i.e. composition data, triad fractions data, instantaneous model, cumulative model, etc.) could be improved by further work on the following areas:

- In cases where the JCEllipse file in MATLAB program could not be solved, due to the information G matrix being diagonal, the information was put into an Excel spreadsheet and the elliptical shaped joint confidence region was obtained through use of the equation for a contour that is approximate in shape and confidence level. Thus, work is required on developing the MATLAB code in the EVMDriver file to create an 'if statement' that suggests when the information matrix is diagonal that the appropriate form of the equation be used. Or rather than finding the joint confidence regions, the Markov Chain Monte Carlo methods should be implemented.
- Include the tacticity as a parameter in the study of $C^{13}$-NMR normalized peak areas. When using $C^{13}$-NMR normalized peak areas, there is a requirement to know the tacticity values for the system in order to translate the data into triad fractions form. However, these values are not necessarily constant and thus should be considered as parameters in the EVM MATLAB routine.
- In the cumulative models EVM routine for the ODECCC (cumulative composition) and ODECCTF (cumulative triad fractions) the feed composition and weight fraction conversion were assumed to be perfectly known. It would be preferred that these variables be included as random variables in the estimation routine. However, a detailed study of this is required as the variables are used as initial values in the solution of ordinary differential equations as well as being variables that are estimated in the iterative EVM scheme.

### 4) Simulate, or design experiment for moderate conversion triad fractions data

Moderate conversion triad fractions data is required via either simulation or experimental analysis, in order to see if there is a composition drift effect on the reactivity ratio estimates obtained from triad fractions data. That is, whether the cumulative triad fractions model should be used over the instantaneous model at high conversions, or when composition drift is believed to be occurring. This work should be conducted once a better understanding of the dynamics of the triad fractions system at low conversion is obtained through analysis of the error structure study.

### 5) Program the triad fractions data problem to use all response variables.

In order to deal with colinearity issues, which are caused by the normalization of the responses and can lead to singularities, two response variables are currently being eliminated. This can sometimes lead to problems, if done arbitrarily (as is the case in this work). A potentially more balanced and robust method of eliminating these singularities has been described in a paper by Box, in which all of the responses are retained in the analysis. Since the singularities are the result of linear equality constraints, they may also be dealt with the use of Langrange multipliers. While these approaches may be slightly more numerically intensive, they are also more elegant and complete.

### 6) Design and run experiment for terpolymer or multicomponent composition data

It was noticed that there was a lack of experimental data in the literature for multicomponent polymer composition data with the required minimum number of data points (i.e. minimum number of data points = number of parametes to be estimated, which is six in this case). Therefore, a well designed multicomponent polymer experiment is required with many replicates so as to be able to accurately test the current EVM procedure on this type of data/model. In 1993, Burke et al. revisited the design of experiments for copolymer reactivity ratio estimation and extended the Tidwell-Mortimer criteria for constrained designs. A similar study will be very timely and of practical use for a terpolymerization case: (i) Deriving optimal feed points for estimation of reactivity ratios, (ii) Minimum number of feed points needed for parameter identifiability, and (iii) Constraint design in view of limitations over certain feed ranges.

### 7) Design and run experiment for full conversion range, measuring feed composition and total molar conversion

By considering the ordinary differential equation (Equation 6.16) it can be seen that the variation of the feed composition can be monitored with respect to total molar conversion. The reason this equation is not used solely in the solution of cumulative problems is due to the fact that typically measurement of the final copolymer composition is recorded rather than directly measuring the final feed composition. That is using the Equation 6.16 solely as the solution to cumulative problems requires the measurement of initial and final feed composition and total molar conversion. As a result the reactivity ratio estimation over the full conversion range (the cumulative composition model) could be simplified to the solution of only one ordinary differential expression.

# References

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1. Aguilar,M., Gallardo,A., Fernandez,M., and Roman,J. (2002) In Situ Quantitative H NMR Monitoring of Monomer Consumption: A Simple and Fast Way of Estimating Reactivity Ratios. *Macromolecules* **35,** 2036-2041.

2. Ahmad,B., Bashir,S., Nisa,S., and Huglin,M. (2004) Chemically crosslinked N-vinyl-2-pyrrolidone/2-hydroxyethyl methacrylate (VP/HEMA) copolymer for the controlled release of cyclic oligopeptide. *Turkish Journal of Chemistry* **28,** 279-285.

3. Aitken,A. (1935) On least squares and linear combinations of observations. *Proceedings of the Royal Statistical Society* **55,** 42-48.

4. Ajzenberg,N. and Ricard,A. (2001) Kinetic study by differential scanning calorimetry of the bulk copolymerization of 2-hydroxyethyl methacrylate with ethylene glycol dimethacrylate. *Journal of Applied Polymer Science* **80,** 1220-1228.

5. Al-Arbash,A., Elsagheer,F., Ali,A., and Elsabee,M. (1999) Glass-Transition Temperature of Polydialkyl Fumarate Copolymers. *Journal of Polymer Science Part A: Polymer Chemistry* **37,** 1839-1845.

6. Alfrey,T. and Goldfinger,G. (1944) The Mechanism of Copolymerization. *The Journal of Chemical Physics* **12,** 205-209.

7. Ameduri,B. and Bauduin,G. (2003) Synthesis and Polmerization of Fluorinated Monomers Bearing a Reactive Lateral Group. XIV. Radical Copolymerization of Vinylidene Fluoride with Methyl 1,1-Dihydro-4,7-dioxaperfluoro-5,8-dimethyl Non-1-enoate. *Journal of Polymer Science Part A: Polymer Chemistry* **41,** 3109-3121.

8. Amosova,S., Antsiferova,L., Shaulina,L., Toryashinova,D., Golentovskaya,N., and Kustova,S. (2001) New polymeric sorbents based on N-(vinyloxyethyl)dithiocarbamoylethylcarbonitrile. *Russian Journal of Applied Chemistry* **74,** 39-43.

9. Anand,V. and Choudhary,V. (2001) Studies on the copolymerization of methyl methacrylate with N-(O/M/P-chlorophenyl) itaconimides. *Journal of Applied Polymer Science* **82,** 2078-2086.

10. Anand,V. and Choudhary,V. (2003) Copolymerization and thermal behavior of methyl methacrylate with N-(phenyl/p-tolyl) itaconimides. *Journal of Applied Polymer Science* **89,** 1195-1202.

11. Anand,V., Kumar,R., and Choudhary,V. (2004) Methyl methacrylate/N-(o-/m-/p-chlorophenyl) itaconimide copolymers: Microstructure determination by NMR spectroscopy. *Journal of Applied Polymer Science* **91,** 2016-2027.

12. Annenkov,V., Danilovtseva,E., Tenhu,H., Aseyev,V., Hirvonen,S., and Mikhaleva,A. (2004) Copolymers of 1-vinylimidazole and (meth)acrylic acid: Synthesis and polyelectrolyte properties. *European Polymer Journal* **40,** 1027-1032.

13. Appelt,M. and Schmidt-Naake,G. (2004) Stable free-radical copolymerization of styrene with acrylates using OH-TEMPO. *Macromolecular Chemistry and Physics* **205,** 637-644.

14. Arun,A. and Reddy,B. (2003) Photocurable and Thermally Stable Polymers Based on 1,4-Pentadien-3-one-1-p-hydroxyphenyl-5-p-phenyl Methacrylate: Copolymerizatio with Ethyl Acrylate. *Journal of Polymer Science Part A: Polymer Chemistry* **41,** 1632-1640.

15. Arun,A. and Reddy,B. (2004) Influence of the comonomers (styrene and methyl acrylate) on the rate of photocrosslinking of 4-{[-3-(4-hydroxybenzylidene)-2-oxocyclohexylidene]methyl}-phenyl acrylate. *Journal of Applied Polymer Science* **92,** 2494-2503.

16. Arun,A. and Reddy,B. (2004) Photocrosslinkable polymers based on 4-[5-(4-hydroxyphenyl)-3-oxopenta-1,4-dienyl]phenyl-2-methacrylate: photocrosslinking studies and reactivity ratios with vinylcyclohexane. *European Polymer Journal* **40,** 589-597.

17. Atta,A. and Arndt,K. (2001) Synthesis and characterization of polyelectrolyte hydrogels with controlled swelling behaviour. *Polymer International* **50,** 1360-1369.

18. Azab,M. (2004) Thermal behavior of pentachlorophenyl methacrylate-acrylonitrile copolymers. *Journal of Applied Polymer Science* **91,** 296-302.

19. Azimipour,B. and Reibel,L. (2002) Radical copolymerization of potassium 4-vinyl biphenyl-sulfonyl imide and oligo(oxyethylene) methacrylates. Thermal behavior and single-ion conductivity of the copolymer electrolytes formed. *Polymer Bulletin* **49,** 225-233.

20. Badawy,S. and Dessouki,A. (2002) Radiation polymerization of acrylonitrile in a viscous system with styrene. *Journal of Applied Polymer Science* **84,** 268-275.

21. Bajpai,R. and Srivastava,A. (2001) Copolymerization of methylmethacrylate with styrene using triphenylbismuthoniumylide as radical initiator. *Journal of Applied Polymer Science* **80,** 2774-2781.

22. Balaji,R., Sivakumar,N., Vijayanand,P., and Nanjundan,S. (2001) Copolymerization of 2-(n-phthalimido)-2-methylpropyl acrylate with methyl methacrylate. *Journal of Macromolecular Science, Pure and Applied Chemistry* **A38,** 159-171.

23. Balaji,R. and Nanjundan,S. (2002) Studies on photosensitive homopolymer and copolymers having a pendant photocrosslinkable functional group. *Journal of Applied Polymer Science* **86,** 1023-1037.

24. Balaji,R., Grande,D., and Nanjundan,S. (2004) Photoresponsive polymers having pendant chlorocinnamoyl moieties: synthesis, reactivity ratios and photochemical properties. *Polymer* **45,** 1089-1099.

25. Baradie,B. and Shoichet,M. (2002) Synthesis of Fluorocarbon-Vinyl Acetate Copolymers in Supercritical Carbon Dioxide: Insight into Bulk Properties. *Macromolecules* **35,** 3569-3575.

26. Bard,Y. (1974) *Nonlinear parameter estimation.* Academic Press, New York.

27. Barner-Kowollik,C., Heuts,J., and Davis,T. (2001) Free-Radical Copolymerization of Styrene and Itaconic Acid Studied by 1H NMR Kinetic Experiments. *Journal of Polymer Science Part A: Polymer Chemistry* **39,** 656-664.

28. Bartsch,A. and Schmidt-Naake,G. (2004) N-oxyl-controlled radical copolymerization of styrene with ethyl a-cyanocinnamate. *Macromolecular Chemistry and Physics* **205,** 1519-1524.

29. Beal,S. and Sheiner,L. (1988) Heteroscedastic nonlinear regression. *Technometrics* **30,** 327-338.

30. Behnken,D. (1964) Estimation of Copolymer Reactivity Ratios: An Example of Nonlinear Estimation. *Journal of Polymer Science* **2,** 645-668.

31. Belleney,J., Helary,G., and Migonney,V. (2002) Terpolymerization of methyl methacrylate, poly(ethylene glycol) methyl ether methacrylate or poly(ethylene glycol) ethyl ether methacrylate with methacrylic acid and sodium styrene sulfonate: determination of the reactivity ratios . *European Polymer Journal* **38,** 439-444.

32. Bernhardt,S., Glockner,P., and Helmut,R. (2001) Cyclodextrins in polymer synthesis: Influence of methylated ß-cyclodextrin as host on the free radical copolymerization reactivity ratios of hydrophobic acrylates as guest monomers in aqueous medium . *Polymer Bulletin* **46,** 153-157.

33. Bevington,J., Huckerby,T., Hunt,B., and Jenkins,A. (2001) Further study of allyl ethers and related compounds as transfer agents in radical polymerization. *Journal of Macromolecular Science, Pure and Applied Chemistry* **A38,** 981-990.

34. Bhawal,S. and Devi,S. (2002) Recaclulation of the monomer reactivity and experimental differences in emulsion and microemulsion copolymerizations of partially water-soluble monomers. *Journal of Applied Polymer Science* **86,** 2802-2810.

35. Bisht,H., Ray,S., Pandey,D., Sharma,C., and Chatterjee,A. (2002) Copolymerization of Dodecyl-4-vinyl Benzoate and Dodecyl Acrylate by Conventional, Atom Transfer, and Nitroxide-Mediated Free-Radical Polymerization. *Journal of Polymer Science Part A: Polymer Chemistry* **40,** 1818-1830.

36. Bisht,H., Ray,S., and Chatterjee,A. (2003) Rapid Communicatio: Resonance, Polar, and Steric Effects of Substituent on Monomer Reactivity in Radical Polymerization of Alkyl 4-Vinylbenzoate and Butylacrylate. *Journal of Polymer Science Part A: Polymer Chemistry* **41,** 1864-1866.

37. Bisht,H., Ray,S., and Chatterjee,A. (2003) Conventional and atom transfer radical copolymerization of n-octyl acrylate-styrene: chemoselectivity and monomer sequence distribution by 1H NMR. *European Polymer Journal* **39,** 1413-1420.

38. Bokias,G. and Hourdet,D. (2001) Synthesis and characterization of positively charged amphiphilic water soluble polymers based on poly(N-isopropylacrylamide). *Polymer* **42,** 6329-6337.

39. Bouquey,M. and Soum,A. (2001) Anionic ring-opening copolymerization of cyclodisilazanes. *Macromolecular Chemistry and Physics* **202,** 1232-1238.

40. Bourdais,J. (1955) *Bulletin de la Société chimique de France* 485. In Shawki and Hamielec, see ref #451.

41. Bourgeat-Lami,E., Tissot,I., and Lefebvre,F. (2002) Synthesis and Characterization of SiOH-Functionalized Polymer Latexes Using Methacryloxy Propyl Trimethoxysilane in Emulsion Polymerization. *Macromolecules* **35,** 6185-6191.

42. Bouteiller,V., Garnault,A., Teyssie,D., Boileau,S., and Moller,M. (1999) Synthesis, thermal and surface charactyerization of fluorinated polystyrenes. *Polymer International* **48,** 765-772.

43. Box,G. and Draper,N. (1965) The Bayesian estimation of common parameters from several responses. *Biometrika* **52,** 355-365.

44. Brar,A., Jayaram,B., and Dutta,K. (1994) Microstructure determination of acrylonitrile-alkyl methacrylate copolymers by Monte Carlo simulations and NMR spectroscopy. *Journal of Polymer Materials* **11,** 171-179.

45. Brar,A. and Dutta,K. (1998) One- and Two-Dimensional Nuclear Magnetic Resonance Studies on the Compositional Sequence and the Microstructure of Acrylonitrile-Pentyl Methacrylate Copolymers. *Journal of Applied Polymer Science* **69,** 2507-2516.

46. Brar,A. and Dutta,K. (1998) Microstructure and Compositional Sequence Determination of Acrylonitrile/Acrylic Acid Copolymers by NMR Spectroscopy. *European Polymer Journal* **34,** 1585-1597.

47. Brar,A. and Thiyagarajan,M. (1998) Microstructure of trans-4-acryloyloxyazobenzene/methyl methacrylate copolymers by n.m.r spectroscopy. *Polymer* **39,** 5923-5927.

48. Brar,A. and Dutta,K. (1998) Reactivity ratios and sequence determination of acrylonitrile/hexyl methacrylate copolymers by one and two dimensional NMR spectroscopy . *Macromolecular Chemistry and Physics* **199,** 2005-2015.

49. Brar,A., Dutta,K., and Hekmatyar,S. (1998) Stereochemical and Compositional Assignment of Acrylonitrile/Methyl Methacrylate Copolymers by DEPT and Inverse HETCOR NMR Spectroscopy. *Journal of Polymer Science Part A: Polymer Chemistry* **36,** 1081-1092.

50. Brar,A. and Thiyagarajan,M. (1999) Sequencing of Trans-4-methacryloyloxyazobenzene/Vinylidene Chloride Copolymers by One- and Two-Dimensional NMR Spectroscopy. *Journal of Polymer Science Part A: Polymer Chemistry* **37,** 3179-3185.

51. Brar,A. and Dutta,K. (1999) Microstructural Characterization of Acrylonitril/Pentyl Acrylate Copolymers by One and 2-D NMR Spectroscopy. *Journal of Polymer Science Part A: Polymer Chemistry* **37,** 533-543.

52. Brar,A. and Hekmatyar,S. (1999) Investigation of Microstructure of the Acrylonitrile-Styrene Copolymers by 2-D NMR Spectroscopy. *Journal of Polymer Science Part A: Polymer Chemistry* **37,** 721-727.

53. Brar,A. and Hekmatyar,S. (1999) Microstructure determination of the acrylonitrile–styrene–methyl methacrylate terpolymers by NMR spectroscopy . *Journal of Applied Polymer Science* **74,** 3026-3032.

54. Brar,A. and Yadav,A. (2001) Microstructure of Glycidylmethacrylate/Vinyl Acetate Copolymers by Two-Dimensional Nuclear Magnetic Resonance Spectroscopy. *Journal of Polymer Science Part A: Polymer Chemistry* **39,** 4051-4060.

55. Brar,A. and Hekmatyar,S. (2001) Characterization of styrene/methacrylic acid copolymers by 2D-NMR spectroscopy. *Journal of Applied Polymer Science* **82,** 2444-2453.

56. Brar,A. and Pradhan,D. (2001) Complete assignment of 1H and 13C NMR spectra of methacrylonitrile/methyl methacrylate copolymers. *Polymer Journal* **33,** 602-609.

57. Brar,A. and Kumar,R. (2001) Sequence determination of N-vinyl-2-pyrrolidone/acrylonitrile copolymers by NMR spectroscopy. *European Polymer Journal* **37,** 1827-1835.

58. Brar,A. and Thiyagarajan,M. (2001) One- and two-dimensional NMR studies on the compositional sequence and the microstructure of trans-4-methacryloyloxyazobenzene/styrene copolymers. *European Polymer Journal* **37,** 507-514.

59. Brar,A. and Kumar,R. (2002) One- and Two-Dimensional NMR Characterization of N-Vinyl-2-pyrrolidone/Methyl Acrylate Copolymers. *Journal of Polymer Science Part A: Polymer Chemistry* **40,** 2225-2236.

60. Brar,A. and Kumar,R. (2002) Microstructure analysis of N-vinyl-2-pyrrolidone/vinyl acetate copolymers by NMR spectroscopy. *Polymer International* **51,** 519-529.

61. Brar,A. and Kumar,R. (2002) Microstructure determination of N-vinyl-2-pyrrolidone/butyl acrylate copolymers by NMR spectroscopy. *Journal of Molecular Structure* **616,** 37-47.

62. Brar,A. and Kumar,R. (2002) Investigation of microstructure of the N-vinyl-2-pyrrolidone/methyl methacrylate copolymers by NMR spectroscopy. *Journal of Applied Polymer Science* **85,** 1328-1336.

63. Brar,A. and Kaur,M. (2002) Complete spectral assignment of poly(N-vinylcarbazole-co methyl acrylate)s by NMR spectroscopy. *Polymer Journal* **34,** 325-331.

64. Brar,A., Yadav,A., and Hooda,S. (2002) Characterization of glycidyl methacrylate/styrene copolymers by one- and two-dimensional NMR spectroscopy. *European Polymer Journal* **38,** 1683-1690.

65. Brar,A. and Kumar,R. (2002) Sequencing of N-vinyl-2-pyrrolidone/glycidyl methacrylate copolymers by one-dimensional and two-dimensional nuclear magnetic resonance spectroscopy. *Journal of Applied Polymer Science* **84,** 50-60.

66. Brar,A. and Yadav,A. (2002) Characterization of glycidylmethacrylonitrile copolymers by NMR spectroscopy. *Journal of Molecular Structure* **602-603,** 29-39.

67. Brar,A. and Pradhan,D. (2003) Investigation of microstructure of the acrylonitrile-styrene-glycidyl methacrylate terpolymers by 1D and 2D NMR spectroscopy. *Journal of Applied Polymer Science* **89,** 1779-1790.

68. Brar,A., Kumar,R., and Kaur,M. (2003) N-vinyl-2-pyrrolidone and methacrylonitrile copolymers: nuclear magnetic resonance characterization. *Journal of Molecular Structure* **650,** 85-92.

69. Brar,A. and Kaur,M. (2003) Nuclear magnetic resonance studies of N-vinylcarbazole/methyl methacrylate copolymers. *Journal of Applied Polymer Science* **88,** 3005-3012.

70. Brar,A. and Pradhan,D. (2003) Complete spectral assignments of methacrylonitrile-styrene-methyl methacrylate terpolymers by 2D NMR spectroscopy. *Journal of Molecular Structure* **649,** 245-255.

71. Brar,A. and Kaur,M. (2003) 1D and 2D NMR studies of N-vinylcarbazole-butyl methacrylate copolymers. *European Polymer Journal* **39,** 705-713.

72. Brar,A. and Yadav,A. (2003) Glycidyl methacrylate and vinylidene chloride copolymers. Nuclear magnetic resonance characterization. *Polymer Journal* **35,** 37-43.

73. Brar,A., Pradhan,D., and Hooda,S. (2004) Reactivity ratios and sequence determination of methacrylonitrile/butyl acrylate copolymers by NMR spectroscopy. *Journal of Molecular Structure* **699,** 39-45.

74. Braun,D., Elsasser,H., and Hu,F. (2001) Free radical terpolymerization of three non-homopolymerizable monomers. Part III. *European Polymer Journal* **37,** 1779-1784.

75. Braun,D. and Hu,F. (2004) Free radical terpolymerization of three non-homopolymerizable monomers. Part IV. Terpolymerization of maleic anhydride, trans-anethole and vinyl-iso-butylether. *Polymer* **45,** 61-70.

76. Brown,D., Ramachandran,K., Carter,K., and Allen,C. (2001) Poly[(vinyloxy)cyclophosphazenes]. *Macromolecules* **34,** 2870-2875.

77. Brown,P. and Fujimori,K. (1994) A novel mechanistic study of the radical copolymerization of styrene with citraconic anhydride via 13C NMR spectroscopy. *Polymer* **35,** 2302-2306.

78. Buback,M., Wittkowski,L., Lehmann,S., and Mahling,F. (1999) High-pressure free radical copolymerization of ethene-methacrylic acid and of ethene-acrylic acid. Part 1. (Meth)acrylic acid reactivity ratios. *Macromolecular Chemistry and Physics* **200,** 1935-1941.

79. Buback,M. and Wittkowski,L. (2000) High-pressure free-radical copolymerization of ethene with methacrylic acid and ethene with acrylic acid, 2. Ethene reactivity ratios . *Macromolecular Chemistry and Physics* **201,** 419-426.

80. Buback,M., Feldermann,A., and Barner-Kowollik,C. (2001) Propagation Rate Coefficients of Acrylate-Methacrylate Free-Radical Bulk Copolymerizations. *Macromolecules* **34**, 5439-5448.

81. Buback,M. and Dietzsch,H. (2001) High-pressure free-radical copolymerization of ethene and methyl methacrylate. *Macromolecular Chemistry and Physics* **202**, 1173-1181.

82. Bulai,A., Alencar de Queiroz,A., Gallardo,A., and Roman,J. (1999) Microstructural analysis of p-acryloyloxy-acetanilide and N,N0 dimethylacrylamide copolymers of biomedical interest by NMR. *Polymer* **40**, 4953-4960.

83. Burke,A., Duever,T., and Penlidis,A. (1993) Revisiting the design of experiments for copolymer reactivity ratio estimation. *Journal of Polymer Science, Part A: Polymer Chemistry* **31**, 3065-3072.

84. Burke,A. (1994) Model Discrimination Techniques for the Modelling of Copolymerization Reactions. Ph.D University of Waterloo, Department of Chemical Engineering.

85. Burke,A., Duever,T., and Penlidis,A. (1994) Model discrimination via designed experiments: discriminating between the terminal and penultimate models based on triad fraction data. *Macromolecular Theory and Simulation* **3**, 1005-1031.

86. Burke,A., Duever,T., and Penlidis,A. (1996) An Experimental Verification of Statistical Discrimination between the Terminal and Penultimate Copolymerization Models. *Journal of Polymer Science Part A: Polymer Chemistry* **34**, 2665-2678.

87. Cabaness,W., Yen-Chin Lin,T., and Parkanyi,C. (1971) Effect of pH on the reactivity ratios in the copolymerization of acrylic acid and acrylamide. *Journal of Polymer Science Part A-1: Polymer Chemistry* **9**, 2155-2170.

88. Cao,L., Wu,Z., and Pittman,C. (1999) Relative Reactivities of Cyclic Ketene Acetals via Cationic 1,2-Vinyl Addition Copolymerization. *Journal of Polymer Science Part A: Polymer Chemistry* **37**, 2841-2852.

89. Carlotti,S., Menoret,S., Barabanova,A., Desbois,P., and Deffieux,A. (2004) Retarded anionic polymerization: copolymerization of butadiene and styrene in the presence of alkyllithium and n,s-dibutylmagnesium or triisobutylaluminium derivatives. *Macromolecular Chemistry and Physics* **205**, 656-663.

90. Catalgil-Giz,H. and Giz,A. (1994) Compensating the composition drift in reactivity ratio calculations for copolymerizations carried to high conversions. *Macromolecular Chemistry and Physics* **195**, 855-864.

91. Catalgil-Giz,H., Giz,A., Alb,A., Oncul Koc,A., and Reed,W. (2002) Online Monitoring of Composition, Sequence Length, and Molecular Weight Distributions during Free Radical Copolymerization, and Subsequent Determination of Reactivity Ratios. *Macromolecules* **35**, 6557-6571.

92. Cazalis,C., Heroguez,V., and Fontanille,M. (2002) Polymerizability of cycolalkenes in "living" ring-opening metathesis polymerization initiated by Schrock complexes. 3. Effect of monomer structure. *Macromolecular Symposia* **183**, 103-112.

93. Chambard,G., Klumperman,B., and German,A. (1999) Dependence of chemical composition of styrene/butyl acrylate copolymers on temperature and molecular weight . *Polymer* **40**, 4459-4463.

94. Chang,C., Sheu,Y., Hu,W., Wang,L., and hen,J. (1998) Synthesis and Properties of Copolymers from 2-Hydroxyethyl Methacrylate-Linked Nonsteroidal Antiinflammatory Agents with Methacrylic Acid. *Journal of Polymer Science Part A: Polymer Chemistry* **36**, 1481-1490.

95. Chen,Z., Pruess,J., Flechtner,U., and Warnecke,H. (2002) Modeling of emulsion copolymerization of 2-hydroxyethyl methacrylate and styrene. *Chemical Engineering and Technology* **25**, 1115-1119.

96. Cheong,S. and Penlidis,A. (2004) Modeling of the copolymerization, with depropagation, of a-methyl styrene and methyl methacrylate at an elevated temperature. *Journal of Applied Polymer Science* **93,** 261-270.

97. Chetham,P., Huckerby,T., and Tabner,B. (1994) A high-field 13C-NMR study of the aqueous copolymerizations of acrylonitrile and vinyl acetate. Determination of comonomer reactivity ratios. *European Polymer Journal* **30,** 581-587.

98. Chetham,P. and Tabner,B. (1994) A high-field 13C-NMR study of the aqueous copolymerization of acrylonitrile and vinyl acetate. Microstructure observations. *European Polymer Journal* **30,** 1367-1373.

99. Chiang,W. and Ding,F. (2000) Copolymerization of N-(-4-Carboxyphenyl)-maleimide with Acrylonitrile and the Properties of Its Membrane. *Journal of Polymer Research* **7,** 251-255.

100. Chiu,C., Lin,K., and Chou,H. (2003) Chain composition dependence of luminescence properties for copolymers of 2-methoxy-5-2'-ethyl-hexyloxy-1,4-phenylenevinylene and 2,3-diphenyl-5-octyl-1,4-phenylenevinylene. *Journal of Polymer Science Part A: Polymer Chemistry* **41,** 2180-2186.

101. Chojnowski,J., Cypryk,M., Fortuniak,W., Rozga-Wijas,K., and Scibiorek,M. (2002) Cntrolled synthesis of vinylmethylsiloxane-dimethylsiloxane gradient, block and alternate copolymers by anionic ROP of cyclotrisiloxanes. *Polymer* **43,** 1993-2001.

102. Choudhary,V., Rajya,S., and Singh,D. (2004) Studies on the copolymerization of N-isopropyl-acrylamide with glycidyl methacrylate. *Macromolecular Symposia* **210,** 49-57.

103. Chung,T. and Lu,H. (1998) Kinetic and Microstructure Studies of Poly(ethylene-co-p-methylstyrene) Copolymers Prepared by Metallocene Catalysts with Constrained Ligand Geometry. *Journal of Polymer Science Part A: Polymer Chemistry* **36,** 1017-1029.

104. Cianga,L. and Yagci,Y. (2002) Synthesis and Characterization of Thiophene-Substituted N-Phenyl Maleimide Polymers by Photoinduced Radical Polymerization. *Journal of Polymer Science Part A: Polymer Chemistry* **40,** 995-1004.

105. Coote,M., Zammit,M., and Davis,T. (1997) Copolymerization propagation kinetics of styrene/ methyl methacrylate- Revisted. 1. Pulsed laser polymerization study. *Macromolecules* **30,** 8182-8191.

106. Coote,M., Johnston,L., and Davis,T. (1997) Copolymerization propagation kinetics of styrene/ methyl methacrylate- Revisted. 2.Kinetic analysis. *Macromolecules* **30,** 8191-8205.

107. Coskun,F., Erol,I., Demirelli,K., and Coskun,M. (2002) A study of copolymerization with 4-bromobenzyl methacrylate and ethyl methacrylate. *Journal of Macromolecular Science, Pure and Applied Chemistry* **A39,** 889-900.

108. Coskun,M. and Ilter,Z. (2002) Copolymerization of (2-Phenyl-1,3-dioxolane-4-yl)methyl Methacrylate with Alkyl Methacrylates: Reactivity Ratios and Copolymer Characterization. *Journal of Polymer Science Part A: Polymer Chemistry* **40,** 1184-1191.

109. Coskun,M., Demirelli,K., Guzel,D., and Coskun,M. (2002) Free-Radical Copolymerization of 3-Phthalimido-2-hydroxypropyl Methacrylate with Styrene: The Determination of Monomer Reactivity Ratios and Thermal Analysis Studies. *Journal of Polymer Science Part A: Polymer Chemistry* **40,** 650-658.

110. Couvreur,L., Charleux,B., Guerret,O., and Magnet,S. (2003) Direct synthesis of controlled poly(styrene-co-acrylic acid)s of various compositions by nitroxide-mediated random copolymerization. *Macromolecular Chemistry and Physics* **204,** 2055-2063.

111. Covolan,V., Ruggeri,G., and Chiellini,E. (2000) Synthesis and Characterization of Styrene/Boc-p-Amino Styrene Copolymers. *Journal of Polymer Science Part A: Polymer Chemistry* **38,** 2910-2918.

112. Cuervo-Rodriguez,R., Fernandez-Monreal,C., and Madruga,E. (2002) Kinetic Study of the Stable Free-Radical Copolymerization of Styrene with Butyl Methacrylate. *Journal of Polymer Science Part A: Polymer Chemistry* **40,** 2750-2758.

113. Czerwinski,W. (1998) Copolymerization at moderate to high conversion levels:2. Estimation of relative reactivity ratios in terms of the penultimate model for systems $r_{2=0}$. *Polymer* **39,** 189-192.

114. Czerwinski,W. (1998) Copolymerization at moderate to high conversion levels: 1. New evaluation procedure of the relative reactivity ratios in terms of the terminal model . *Polymer* **39,** 183-187.

115. D'Agosto,F., Charreyre,M., Veron,L., Llauro,M., and Pichot,C. (2001) Kinetic study of free-radical solution copolymerization of N-acryloylmorpholine with activated ester-type monomer, N-acryloxysuccinimide. *Macromolecular Chemistry and Physics* **202,** 1689-1699.

116. Dalvi,A. Chemical Engineering Department, University of Waterloo. 2004.
Ref Type: Personal Communication

117. Daniel,N. and Srivastava,A. (2001) p-Acetylbenzylidene triphenylarsonium ylide (p-ABTAY) initiated radical copolymerization of methyl methacrylate with styrene. *Journal of Macromolecular Science, Pure and Applied Chemistry* **A38,** 1059-1074.

118. Daniel,N. and Srivastava,A. (2002) Free radical copolymerization of styrene with vinyl acetate using p-acetylbenzylidene triphenylarsonium ylide as an initiator. *Advances in Polymer Technology* **21,** 108-115.

119. Davidenko,N., Peniche,C., Sastre,R., and Roman,J. (1998) Photoinitiated copolymerisation of furfuryl methacrylate and N,N-dimethyl acrylamide. *Polymer* **39,** 917-921.

120. Davis,T. (2001) The mechanism of propagation in free-radical copolymerization. *Journal of Polymer Science Part A: Polymer Chemistry* **39,** 597-603.

121. de la Fuente,J., Fernandez-Garcia,M., Fernandez-Sanz,M., and Madruga,E. (2001) Sequence Distribution and Stereoregularity of Methyl Methacrylate and Butyl Acrylate Statistical Copolymers Synthesized by Atom Transfer Radical Polymerization. *Macromolecules* **34,** 5833-5837.

122. De,P. and Sathyanarayana,D. (2002) High-Pressure Kinetics of Oxidative Copolymerization of Styrene with *a*-Methylstyrene . *Macromolecular Chemistry and Physics* **203,** 2218-2224.

123. De,P. and Sathyanarayana,D. (2002) Determination of the reactivity ratios for the oxidative copolymerization of idene with methyl, ethyl and butyl acrylates. *Macromolecular Chemistry and Physics* **203,** 573-579.

124. De,P., Sathyanarayana,D., Sadasivamurthy,P., and Sridhar,S. (2002) Reactivity ratios for the oxidative copolymerizations of indene with methyl methacrylate and methacrylonitrile. *European Polymer Journal* **38,** 847-855.

125. De,P. and Sathyanarayana,D. (2002) Oxidative copolymerization of indene with p-tert-butylstyrene: synthesis, characterization, thermal analysis, and reactivity ratios. *Journal of Polymer Science Part A: Polymer Chemistry* **40,** 9-18.

126. De,P. and Sathyanarayana,D. (2002) Synthesis and characterization of copolyperoxides of indene with styrene, a-methylstyrene, and a-phenylstyrene. *Journal of Polymer Science Part B: Polymer Physics* **40,** 2004-2017.

127. De,P. and Sathyanarayana,D. (2002) Free radical oxidative copolymerization of indene with vinyl acetate and isopropenyl acetate: synthesis and characterization. *Journal of Applied Polymer Science* **86,** 639-646.

128. De,P. and Sathyanarayana,D. (2002) Reactivity ratios for the terpolymerization of methyl methacrylate, vinyl acetate, and molecular oxygen. *Journal of Polymer Science Part A: Polymer Chemistry* **40,** 564-572.

129. Debling,J. and Teymour,F. (2002) A new arithmetic for linear free radical copolymerization. *Macromolecular Symposia* **182,** 195-207.

130. Deming,E. (1943) *Statistical Adjustment of Data.* Wiley, New York.

131. Demirelli,K., Coskun,M., and Dilsiz,N. (1999) 2-(3-Phenyl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate and acrylonitrile copolymers: Synthesis, characterization, determination of monomer reactivity ratios, and investigation of their antifungal effects. *Polymer International* **48,** 382-386.

132. Demirelli,K., Coskun,M., and Erol,I. (2000) Copolymerization and monomer reactivity ratios of 2-(3-mesityl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate and acrylonitrile. *European Polymer Journal* **36,** 83-88.

133. Demirelli,K., Kaya,I., and Coskun,M. (2001) 3,4-Dichlorobenzyl methacrylate and ethyl methacrylate system: monomer reactivity ratios and determination of thermodynamic properties at infinite dilution by using inverse gas chromatography. *Polymer* **42,** 5181-5188.

134. Dettmer,C., Gray,M., Torkelson,J., and Nguyen,S. (2004) Synthesis and Functionalization of ROMP-Based Gradient Copolymers of 5-Substituted Norbornenes. *Macromolecules* **37,** 5504-5512.

135. Devasia,R., Reghunadhan,N., and Ninan,K. (2002) Solvent and kinetic penultimate unit effects in the copolymerization of acrylonitrile with itaconic acid. *European Polymer Journal* **38,** 2003-2010.

136. Devasia,R., Nair,C., Reghunadhan,N., and Ninan,K. (2002) Polyacrylonitrile precursors for carbon fiber with imidocarboxylic acid units: copolymerization of acrylonitrile with maleimidobenzoic acid. *Journal of Macromolecular Science, Pure and Applied Chemistry* **A39,** 693-708.

137. Devasia,R., Reghunadhan,N., and Ninan,K. (2003) Copolymerization of acrylonitrile with itaconic acid in dimethylformamide: effect of triethylamine. *European Polymer Journal* **39,** 537-544.

138. Dincer,S., Koseli,V., Kesim,H., Rzaev,Z., and Piskin,E. (2002) Radical copolymerization of N-isopropylacrylamide with anhydrides of maleic and citrconic acids. *European Polymer Journal* **38,** 2143-2152.

139. Dube,M., Sanayei,R., Penlidis,A., O'Driscoll,K., and Reilly,P. (1991) A microcomputer program for estimation of copolymerization reactivity ratios. *Journal of Polymer Science, Part A: Polymer Chemistry* **29,** 703-708.

140. Duc,S. and Petit,A. (1999) Copolymerization of phenylacetylene and 1-hexyne using Ziegler-Natta and metathesis catalyst systems: copolymer compositions and reactivity ratios by H n.m.r spectroscopy. *Polymer* **40,** 589-597.

141. Dudmun,M. (2001) Quantifying and controlling the composition and 'randomness' distributions of random copolymers. *Macromolecular Theory and Simulations* **10,** 795-801.

142. Duever,T., O'Driscoll,K., and Reilly,P. (1983) The Use of the Error-in-Variables Model in Terpolymerization. *Journal of Polymer Science, Polymer Chemistry Edition* **21,** 2003-2010.

143. El-Ghaffar,M., Youssef,E., and El-Halawany,N. (2002) Preparation and characterization of some acrylic acid chelating copolymers by emulsion techniques. *Journal of Macromolecular Science, Pure and Applied Chemistry* **A39,** 1037-1059.

144. El-Nagger,A., Zohdy,M., Sahar,S., and Allam,E. (2001) Reactivity ratios during radiation-induced grafting of comonomer mixtures onto polyester fabrics. *Polymer International* **50,** 1082-1088.

145. Elvira,C., Gallardo,A., and Roman,J. (1999) Free radical copolymerization of methyl methacrylate with methacrylic monomers derived from salicylic acid. Microstructural analysis, chaini flexibility and hydration behaviour of the prepared copolymers. *Polymer* **40,** 6911-6924.

146. Elvira,C., Gallardo,A., Zunszain,P., and Roman,J. (2000) Vinyl pyrrolidone-methacrylic monomers bearing salicylic acid derivative moieties: copolymerization parameters and microstructure analysis. *Polymer* **41,** 7303-7309.

147. Elvira,C., Gallardo,A., Lacroix,N., Schacht,E., and San Roman,J. (2001) Incorporation of salicylic acid derivatives to hydrophilic copolymer systems with biomedical applications. *Journal of Materials Science: Materials in Medicine* **12,** 535-542.

148. Endo,K. and Matsuda,Y. (1999) Copolymerization of Styrene and Butadiene with Ni(acac)$_{2\text{-Methylaluminoxane Catalyst}}$. *Journal of Polymer Science Part A: Polymer Chemistry* **37,** 3838-3844.

149. Erbil,C., Ozdemir,S., and Uyanik,N. (2000) Determination of the monomer reactivity ratios for copolymerization of itaconic acid and acrylamide by conductometric titration method. *Polymer* **41,** 1391-1394.

150. Erceg,A., Vukovic,R., Bogdanic,G., Srica,V., and Fles,D. (2001) Copolymerization of N-acryl-N, N'-dicyclohexylurea and N-methacryl-N,N'-dicyclohexylurea with styrene. *Journal of Macromolecular Science, Pure and Applied Chemistry* **A38,** 839-850.

151. Erol,I., Soykan,C., and Ahmedzade,M. (2002) Monomer Reactivity Ratios of the 2-(3-Mesityl-3-methylcyclobutyl)-2-hydroxyethyl Methacrylate and Styrene System from HNMR. *Journal of Polymer Science Part A: Polymer Chemistry* **40,** 1756-1763.

152. Erol,I. and Soykan,C. (2002) Copolymerization of methyl methacrylate with 2-methylbenzyl methacrylate and 4-methylbenzyl methacrylate: synthesis, characterization, and monomer reactivity ratios. *Journal of Macromolecular Science, Pure and Applied Chemistry* **A39,** 953-968.

153. Erol,I., Yavuz,F., and Durgun,M. (2004) Synethsis and characterization of [2-oxo-2-(4-methyl)phenylamino]ethylene methacrylate-styrene copolymers and determination of monomer reactivity ratios. *Polymer Journal* **36,** 303-309.

154. Escher,F. and Galland,G. (2004) Carbon nuclear magnetic resonance of ethylene-propylene-1-hexene terpolymers. *Journal of Polymer Science Part A: Polymer Chemistry* **42,** 2474-2482.

155. Fan,Z., Yasin,T., and Feng,L. (2000) Copolymerization of Propylene with 1-Octene Catalyzed by rac-Me$_{2\text{Si(2,4,6-Me3-Ind)2ZrCl2/Methyl Aluminoxane}}$. *Journal of Polymer Science Part A: Polymer Chemistry* **38,** 4299-4307.

156. Faragalla,M., Hill,D., and Whittaker,A. (2002) The copolymerization of N-vinyl-2-pyrrolidone with 2-hydroxyethyl methacrylate. *Polymer Bulletin* **47,** 421-427.

157. Feldermann,A., Toy,A., Phan,H., Stenzel,M., Davis,T., and Barner-Kowollik,C. (2004) Reversible addition fragmentation chain transfer copolymerization: influence of the RAFT process on the copolymer composition. *Polymer* **45,** 3997-4007.

158. Ferando,A. and Longo,A. (1997) Determination of reactivity ratios from 13C NMR analysis of triad fractions for styrene-acrylontrile copolymerization as a function of temperature. *Polymer Preprints* **38,** 798-799.

159. Ferbitz,J. and Mormann,W. (2002) Copolymerization of maleic anhydride with electron-acceptor monomers. *Macromolecular Symposia* **181,** 63-71.

160. Ferbitz,J. and Mormann,W. (2003) Copolymers from tert-butyl methacrylate with trimethylsilyl methacrylate or methacrylic acid: Models for resist polymers. *Macromolecular Chemistry and Physics* **204,** 577-583.

161. Ferbitz,J. and Mormann,W. (2003) Copolymers from tert-butyl methacrylate and 2-propenyl isocyanate-polymers for photoresist application. *Polymer* **44,** 527-533.

162. Fernandez-Garcia,M., Fernandez-Sanz,M., Madruga,E., Cuervo-Rodriguez,R., Hernandez-Gordo,V., and Fernandez-Monreal,M. (2000) Solvent Effects on the Free-Radical Copolymerization of Styrene with Butyl Acrylate. I. Monomer Reactivity Ratios. *Journal of Polymer Science Part A: Polymer Chemistry* **38,** 60-67.

163. Fernandez-Garcia,M., de la Fuente,J., Fernandez-Sanz,M., and Madruga,E. (2001) An analysis of the solvent effects on the monomer reactivity ratios using the copolymer glass transition temperatures. *Macromolecular Rapid Communications* **22,** 451-455.

164. Fernandez-Monreal,C., Sanchez-Chaves,M., Martinez,G., and Madruga,E. (1999) High-resolution H-NMR spectroscopy of 2-HEMA/styrene copolymers. *Acta Polymerica* **50,** 408-412.

165. Fernandez-Monreal,C., Martinez,G., Sanchez-Chaves,M., and Madruga,E. (2000) Inter and intramolecular structure predictions in 2-hydroxyethyl methacrylate-tert-butyl acrylate copolymers obtained at high conversion. *Polymer* **41,** 8155-8159.

166. Fernandez-Monreal,C., Martinez,G., Sanchez-Chaves,M., and Madruga,E. (2001) Solvent effect on the Free-Radical Copolymerization of 2-Hydroxyethyl Methacrylate with t-Butyl Acrylate. *Journal of Polymer Science Part A: Polymer Chemistry* **39,** 2043-2048.

167. Fernia,M., Torrado,M., Martinez,G., Sanchez-Chaves,M., and Madruga,E. (2000) Free radical copolymerization of 2-hydroxyethyl methacrylate with butyl methacrylate: determination of monomer reactivity ratios and glass transition temperatures . *Polymer* **41,** 8001-8008.

168. Filley,J., McKinnon,J., Wu,D., and Ko,J. (2002) Theoretical Study of Ethylene-Vinyl Acetate Free-Radical Copolymerization: Reactivity Ratios, Penultimate Effects, and Relative Rates of Chain Transfer to Polymer. *Macromolecules* **35,** 3731-3738.

169. Fineman,M. and Ross,S. (1950) Linear method for determining monomer reactivity ratios in copolymerization. *Journal of Polymer Science* **5,** 259-262.

170. Fujiwara,H., Narita,T., and Hamana,H. (2001) Monomer reactivity ratios and Q,e-values of trialkylsilyl acrylates and methacrylates. *Polymer Journal* **33,** 102-103.

171. Fujiwara,T., Makal,U., and Wynne,K. (2003) Synthesis and characterization of novel amphiphilic telechelic polyoxetanes. *Macromolecules* **36,** 9383-9389.

172. Fukuda,T., Ma,Y., and Inagaki,H. (1985) 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* **18,** 17-26.

173. Fukuda,T., Kubo,K., Ma,Y., and Inagaki,H. (1987) Free-Radical Copolymerization V. Rate Constants of Propagation and Termination for a Styrene/Methyl Methacrylate/Toluene System. *Polymer Journal* **19,** 523-530.

174. Galimberti,M., Piemontesi,F., Fusco,O., Camurati,I., and Destro,M. (1998) Ethene/Propene Copolymerization with High Product of Reactivity Ratios from a Single Center, Metallocene-Based Catalytic System. *Macromolecules* **31,** 3409-3416.

175. Galimberti,M., Piemontesi,F., Mascellani,N., Camurati,I., Fusco,O., and Destro,M. (1999) Metallocene for Ethene/Propene Copolymerizations with High Product of Reactivity Ratios. *Macromolecules* **32,** 7968-7976.

176. Galimberti,M., Piemontesi,F., Baruzzi,G., Mascellani,N., Camurati,I., and Fusco,O. (2001) Ethene/propene copolymerizations from metallocene-based catalytic systems: the role of comonomer concentrations. *Macromolecular Chemistry and Physics* **202,** 2029-2037.

177. Gallardo,A., Rodriguez,G., Aguilar,M., Fernandez,M., and San Roman,J. (2003) A Kinetic Model To Explain the Zero-Order Release of Drugs from Ionic Polymeric Drug Conjugates: Application to AMPS-Triflusal-Derived Polymeric Drugs. *Macromolecules* **36,** 8876-8880.

178. Garcia-Rubio,L. (1981) An experimental investigation on the free-radical synthesis and characterization of styrene acrylonitrile copolymers. Ph.D McMaster University.

179. Garcia-Rubio,L., Lord,M., MacGregor,J., and Hamielec,A. (1985) Bulk copolymerization of styrene and acrylonitrile: Experimental kinetics and mathematical modelling. *Polymer* **26,** 2001-2013.

180. Gatica,N., Gargallo,L., and Radic,D. (1998) 2-Vinylpyridine-co-N-vinyl-2-pyrrolidone and 4-Vinylpyridine-co-N-vinyl-2-pyrrolidone Copolymers: Synthesis and reactivity Ratios. *Polymer International* **45,** 285-290.

181. Gatica,N., Gargallo,L., and Radic,D. (2002) Synthesis and monomer reactivity ratios of (vinylcyclohexane-co-N-vinyl-2-pyrrolidone) copolymer. *European Polymer Journal* **38,** 1371-1375.

182. Gatica,N., Fernandez,N., Opazo,A., Alegria,S., Gargallo,L., and Radic,D. (2003) Synthesis and characterization of functionalized vinyl copolymers. Electronegativity and comonomer reactivity in radical copolymerization. *Polymer International* **52,** 1280-1286.

183. Gatica,N., Gargallo,L., and Radic,D. (2004) Monomer Reactivity in Functionalized Vinyl Copolymers: A Theoretical Approach. *Journal of Macromolecular Science, Pure and Applied Chemistry* **A41,** 181-188.

184. Gauthier,M., Carozzella,T., and Penlidis,A. (2002) Sulfobetaine zwitterionomers based on n-butyl acrylate and 2-ethoxyethyl acrylate: monomer synthesis and copolymerization behavior. *Journal of Polymer Science Part A: Polymer Chemistry* **40,** 511-523.

185. German,A. and Heikens,D. (1971) *Journal of Polymer Science, Part A: Polymer Chemistry* **9,** 2225-2232.

186. Ghi,P., Hill,D., and Whittaker,A. (1999) A Study of the Copolymerization of Hydroxyethyl Methacrylate and Tetrahydrofurfuryl Methacrylate. *Journal of Polymer Science Part A: Polymer Chemistry* **37,** 3730-3737.

187. Ghim,H., Kim,J., and Lyoo,W. (2003) Thermodynamics of copolymerization of vinyl acetate and vinyl pivalate. *Polymer* **44,** 895-900.

188. Giz,A. (1998) An error-in-variables method for use when the reactivity ratios in copolymerization are close to one. *Macromolecular Theory and Simulations* **7,** 391-398.

189. Glockner,P. and Ritter,H. (1999) Cyclodextrins in polymer chemistry. Influence of methylated b-cyclodextrin as host on the free radical copolymerization reactivity ratios of isobornyl acrylate and butyl acrylate as guest monomers in aqueous medium. *Macromolecular Rapid Communications* **20,** 602-605.

190. Godwin,G., Jone Selvamalar,C., Penlidis,A., and Nanjundan,S. (2004) Homopolymer of 4-propanoylphenyl methacrylate and its copolymers with glycidyl methacrylate: Synthesis, characterization, reactivity ratios and application as adhesives. *Reactive and Functional Polymers* **59,** 197-209.

191. Goiti,E., Huglin,M., and Rego,J. (2001) Some observations on the copolymerization of styrene with furfuryl methacrylate. *Polymer* **42,** 10187-10193.

192. Goksel,C., Hacioglu,B., and Akbulut,U. (1997) Spontaneous Copolymerization of Maleic Anhydride and N-Vinylimidazole in 1,4-Dioxane. I. Charge Transfer Complexation and Kinetics of teh Copolymerization. *Journal of Polymer Science Part A: Polymer Chemistry* **35,** 3735-3743.

193. Gonzalez,N., Elvira,C., and Roman,J. (2002) Hydrophilic and Hydrophobic Copolymer Systems Based on Acrylic Derivatives of Pyrrolidone and Pyrrolidine. *Journal of Polymer Science Part A: Polymer Chemistry* **41,** 395-407.

194. Grishin,D., Semyonycheva,L., Illichev,I., and Artemov,A. (2001) Tricarbonylchromium complexes of styrene in radical copolymerization. *Applied Organometallic Chemistry* **15,** 169-177.

195. Grunden,B. and Sung,C. (2003) Cure Characterization of Unsaturated Polyester Resin by Near-IR and Mid-IR Spectroscopy. *Macromolecules* **36,** 3166-3173.

196. Guay,M. and McLean,D. (1995) Optimization and Sensitivity analysis for multiresponse parameter estimation in systems of ordinary differential equations. *Computers chemical engineering* **19,** 1271-1285.

197. Guiot,J., Ameduri,B., and Boutevin,B. (2002) Synthesis and Polmerization of Fluorinated Monomers Bearing a Reactive Lateral Group. XII. Copolymerization of Vinylidene Fluoride with 2,3,3-Trifluoroprop-2-enol. *Journal of Polymer Science Part A: Polymer Chemistry* **40,** 3634-3643.

198. Guiot,J., Ameduri,B., Boutevin,B., and Lannuzel,T. (2003) Synthesis and polymerization of fluorinated monomers bearing a reactive lateral group. 13. Copolymerization vinylidene fluoride with 2-benzoyloxypentafluoropropene. *European Polymer Journal* **39,** 887-896.

199. Guo,X., Li,Z., Du,Q., Yang,Y., and Lin,M. (2002) Free radical copolymerization of tert-butyl 3-isopropenylcumylperoxide with styrene and grafting of methyl methacrylate onto the copolymers. *Journal of Applied Polymer Science* **84,** 2318-2326.

200. Guo,Z., Yang,G., Wan,D., and Huang,J. (2001) Controllable radical copolymerization of styrene and methyl methacrylate using 1,1,2,2-teraphenyl-1,2-bis(trimetylsilyloxy) ethane as initiator. *Journal of Applied Polymer Science* **82,** 1474-1482.

201. Gupta,K. and Sahoo,S. (2001) Graft Copolymerization of Acrylonitrile and Ethyl Methacrylate Comonomers on Cellulose Using Ceric Ions. *Biomacromolecules* **2,** 239-247.

202. Gupta,K. and Khandekar,K. (2002) Graft copolymerization of acrylamide-methyl acrylate comonomers onto cellulose using ceric ammonium nitrate. *Journal of Applied Polymer Science* **86,** 2631-2642.

203. Gupta,K. and Khandekar,K. (2003) Acrylamide-methyl methacrylate graft copolymerization onto cellulose using ceric ammonium nitrate. *Journal of Macromolecular Science, Pure and Applied Chemistry* **A40,** 155-179.

204. Ha,N. (1998) A new method for evaluating the applicability of the five copolymerization models to the experimental data of composition and triad fractions of styrene-co-citraconic anhydride-polymers. *Computational and Theoretical Polymer Science* **7,** 121-129.

205. Ha,T., Fujimori,K., Tucker,D., and Henry,P. (1999) Non-linear least squares curve fitiing of copolymerization models to the alternating triad fraction of copolymers of styrene and citraconic anhydride, and copolymers of styrene and maleic anhydride prepared in N,N-dimethylformamide. *Journal of Macromolecular Science, Pure and Applied Chemistry* **A36,** 893-900.

206. Habibi,A., Vasheghani-Farahani,E., Semsarzadeh,M., and Sadaghiani,K. (2003) Monomer reactivity ratios for lauryl methacrylate-isobutyl methacrylate in bulk free radical copolymerization. *Polymer International* **52,** 1434-1443.

207. Habibi,A., Vasheghani-Farahani,E., Semsarzadeh,M., and Sadaghiani,K. (2003) A Generalized Least Square Model for the Determination of Monomer Reactivity Ratios in Free Radical Copolymerization Systems . *Macromolecular Theory and Simulations* **12,** 184-195.

208. Habibi,A., Vasheghani-Farahani,E., Semsarzadeh,M., and Sadaghiani,K. (2004) Estimation of Monomer Reactivity Ratios in Free-Radical Solution Copolymerization of Lauryl Methacrylate-Isobutyl Methacrylate. *Journal of Polymer Science Part A: Polymer Chemistry* **42,** 112-129.

209. Haddleton,D., Crossman,M., Hunt,K., Topping,C., Waterson,C., and Suddaby,K. (1997) Identifying the Nature of the Active Species in the Polymerization of Methacrylates: Inhibition of Methyl Methacrylate Homopolymerizations and Reactivity Ratios for Copolymerization of Methyl Methacrylate/n-Butyl Methacrylate in Classical Anionic, Alkyllithium/Trialkylaluminum-Initiated, Group Transfer Polymerization, Atom Transfer Radical Polymerization, Catalytic Chain Transfer, and Classical Free Radical Polymerization. *Macromolecules* **30,** 3992-3998.

210. Hagiopol,C. and Frangu,O. (2003) Strategies in improving the accuracy of reactivity ratios estimation. *Journal of Macromolecular Science, Pure and Applied Chemistry* **A40,** 571-584.

211. Hakim,M., Verhoeven,V., McManus,N., Dube,M., and Penlidis,A. (2000) High-temperature solution polymerization of butyl acrylate/methyl methacrylate: Reactivity ratio estimation . *Journal of Applied Polymer Science* **77,** 602-609.

212. Hamielec,A., MacGregor,J., and Penlidis,A. (1989) Copolymerization. Pergamon Press.

213. Harrison,S., Davis,T., Evans,R., and Rizzardo,E. (2001) Copolymerization Behavior of 7-Methylene-2-methyl-1,5-dithiacyclooctane: Reversible Cross-Propagation. *Macromolecules* **34,** 3869-3876.

214. Harrison,S., Davis,T., Evans,R., and Rizzardo,E. (2002) Pulsed laser copolymerization of ring-opening cyclic allylic sulfide monomers with methyl methacrylate and styrene. *Macromolecules* **35,** 2474-2480.

215. Hasegawa,M., Kimata,M., and Kobayashi,S. (2002) Mechanochemical copolymerization of methyl methacrylate and styrene initiated by the grinding of quartz. *Journal of Applied Polymer Science* **84,** 2011-2017.

216. Hatada,K., Kitayama,T., Nishiura,T., and Shibuya,W. (2002) Relation between reactivities of vinyl monomers and their NMR spectra. *Current Organic Chemistry* **6,** 121-153.

217. Hautus,F., Linssen,H., and German,A. (1984) Dependence of computed copolymer reactivity ratios on the calculation method. II: Effects of experimental design and error structure. *Journal of Polymer Science, Polymer Chemistry* **22,** 3661-3671.

218. Hautus,F. and German,A. (1985) On Numerical Problems When Reactivity Ratios Are Computer Using the Integrated Copolymer Equation. *Journal of Polymer Science: Polymer Letters Edition* **23,** 311-315.

219. Hill,D., Lang,A., O'Donnell,J., and O'Sullivan,P. (1989) Determination of Reactivity Ratios from Analysis of Triad Fractions- Analysis of the Copolymerization of Styrene and Acrylonitrile as Evidence for the Penultimate Model. *European Polymer Journal* **25,** 911-915.

220. Hill,D., Lang,A., Munro,P., and O'Donnell,J. (1992) The Effect of Solvent on the Styrene-Acrylonitrile Copolymerization. *European Polymer Journal* **28,** 391-398.

221. Hocking,M. and Klimchuk,K. (1996) A refinement of the terpolymer equation and its simple extension to two- and four-component systems. *Journal of Polymer Science, Part A: Polymer Chemistry* **34,** 2481-2497.

222. Hong,S., Jia,S., Teodorescu,M., Kowalewski,T., Matyjaszewski,K., Gottfried,A., and Brookhart,M. (2002) Polyolefin graft copolymers via living polymerization techniques: preparation of poly(n-butyl acrylate)-graft-polyethylene through the combination of Pd-mediated living olefin polymerization and atom transfer radicl polymerization. *Journal of Polymer Science Part A: Polymer Chemistry* **40,** 2736-2749.

223. Hong,S., Lutz,J., Inoue,Y., Strissel,C., Nuyken,O., and Matyjaszewski,K. (2003) Use of an Immobilized/Soluble Hybrid ATRP Catalyst System for the Preparation of Block Copolymers, Random Copolymers, and Polymers with High Degree of Chain End Functionality. *Macromolecules* **36,** 1075-1082.

224. Hongo,T., Yoshida,S., Yamada,T., and Tanaka,H. (1999) Radical copolymerization of methyl a-acryloxyacrylates with some vinyl monomers. *Polymer International* **48,** 505-508.

225. Hooda,S. and Brar,A. (2001) Compositional sequence determination of 4-vinylpyridine/ethyl methacrylate copolymers by one- and two-dimensional NMR spectroscopy. *Polymer Journal* **33,** 390-398.

226. Hooda,S. and Brar,A. (2003) Investigation of microstructure of 4-vinyl pyridine-methacrylonitrile copolymers by NMR spectroscopy. *Journal of Applied Polymer Science* **88,** 3232-3238.

227. Hou,C., Wang,C., Cai,H., and Zhang,W. (2003) Determination of the reactivity ratios for acrylonitrile/N-vinylpyrrolidone copolymerization systems. *Journal of Applied Polymer Science* **89,** 422-425.

228. Hsu,S., Chiu,W., Lee,C., and Chang,H. (2001) Composition control of copolymer in semibatch emulsion copolymerization I. Methyl methacrylate/styrene two-component system. *Polymer Journal* **33,** 27.

229. Huafang,N. and Hunkeler,D. (1997) Prediction of copolymer composition drift using artificial neural networks: copolymerization of acrylamide with quaternary ammonium cationic monomers . *Polymer* **38,** 667-675.

230. Huang,C., Wang,S., Kuo,S., Huang,W., and Chang,F. (2004) Homopolymerization and copolymerization of tert-butyl methacrylate and norbornene with nickel-based methylaluminoxane catalysts. *Journal of Applied Polymer Science* **92,** 1824-1833.

231. Huang,W., Chang,F., and Chu,P. (2000) Copolymerization of Norbornene with Ethylene: a High-resolution Liquid NMR, DSC and Solid State NMR Study. *Journal of Polymer Research* **7,** 51-56.

232. Hull,D. and Kennedy,J. (2001) Synthesis, Characterization, and Crosslinking of Novel Stars Comprising Eight Poly(isobutylene-azeotropic-styrene) Copolymer Arms with Allyl or Hydroxyl Termini. I. Living Azeotropic Copolymerization of Isobutylene and Styrene. *Journal of Polymer Science Part A: Polymer Chemistry* **39,** 1515-1524.

233. Hung,J., Cole,A., and Waymouth,R. (2003) Control of Sequence Distribution of Ethylene Copolymers: Influence of Comonomer Sequence on the Melting Behavior of Ethylene Copolymers. *Macromolecules* **36,** 2454-2463.

234. Ilter,Z., Coskun,M., and Erol,I. (2001) Copolymers of (2-Cyclohexylidene-1,3-dioxolane-4-yl) Methyl Methacrylate with Acrylonitrile and Styrene: Synthesis, Characterization, and Monomer Reactivity Ratios. *Journal of Polymer Science Part A: Polymer Chemistry* **39,** 2326-2331.

235. Ilter,Z., Soykan,C., and Koca,M. (2003) Synthesis and Spectral and Thermal Properties of Copolymers of (2-Cyclopentylidene-1,3-dioxolane-4-yl)-methyl Methacrylate with Styrene and Acrylonitrile and the Determination of the Monomer Reactivity Ratios. *Journal of Polymer Science Part A: Polymer Chemistry* **41,** 2996-3005.

236. Ishizu,K., Mori,A., and Shibuya,T. (2001) Synthesis of alternating hyperbranched copolymers using photofunctional inimer via living radical mechanism. *Polymer* **42,** 7911-7914.

237. Ishizu,K., Takashimizu,C., Shibuya,T., and Uchida,S. (2003) Synthesis and solution properties of alternating maleimide/styrene hyperbranched copolymers via controlled radical mechanism. *Polymer International* **52,** 1010-1015.

238. Ishizu,K., Park,J., Ohta,Y., and Shibuya,T. (2003) Synthesis and characterization of methyl methacrylate/styrene hyperbranched copolymers via living radical mechanism. *Journal of Applied Polymer Science* **89,** 2490-2495.

239. Ishizu,K., Shibuya,T., Park,J., and Uchida,S. (2004) Novel synthesis and solution properties of hyperbranched poly(ethyl methacrylate)s by quasi-living radical copolymerization using photofunctional inimer. *Polymer International* **53,** 259-265.

240. Isusi,M., Rodriguez,M., Garay,T., Vilas,J., and Leon,L. (2002) Thermal properties of copolymers of N-vinylcarbazole with acrylic acid and methacrylic monomers. *Journal of Macromolecular Science, Physics* **B41,** 241-253.

241. Ito,H., Dalby,C., Pomerantz,A., Sherwood,M., Sato,R., Sooriyakumaran,R., Guy,K., and Breyta,G. (2000) Monomer Reactivities and Kinetics in Radical Copolymerization of Hydroxystyrene Derivatives and *tert*-Butyl (Meth)acrylate. *Macromolecules* **33,** 5080-5089.

242. Ito,H., Okazaki,M., and Miller,D. (2004) Radical Copolymerization of 2-Trifluoromethylacrylic Monomers. III. Kinetics and Monomer Reactivities in the Copolymerization of t-Butyl 2-Trifluoromethylacrylate and Methacrylate with Styrene Bearing Hexafluoroisopropanol. *Journal of Polymer Science Part A: Polymer Chemistry* **42,** 1506-1527.

243. Ito,H., Okazaki,M., and Miller,D. (2004) Radical Copolymerization of 2-Trifluoromethylacrylic Monomers. II. Kinetics, Monomer Reactivities, and Penultimate Effect in Their Copolymerization with Norbornenes and Vinyl Ethers. *Journal of Polymer Science Part A: Polymer Chemistry* **42,** 1478-1505.

244. Ito,T. and Otsu,T. (1969) Solvent Effect in Radical Copolymerization of Methyl Methacrylate with Styrene. *Journal of Macromolecular Science, Pure and Applied Chemistry* **A3,** 197-203.

245. Jaimes,C., Collet,A., Giani-Beaune,O., Schue,F., Amass,W., and Amass,A. (1998) Ring-Opening Homo- and Copolymerization of Lactones Part 1. Homo- and Copolymerization of Racemic b-Butyrolactone with e-Caprolactone and d-Valerolactone by Tetraisobutyldialuminoxane (TIBAO) Catalyst. *Polymer International* **45,** 5-13.

246. Jansen,J., Houben,E., Tummers,P., Wienke,D., and Hoffmann,J. (2004) Real-time infared determination of photoinitiated copolymerization reactivity ratios: Application of the Hilbert transform and critical evaluation of data analysis techniques. *Macromolecules* **37,** 2275-2286.

247. Janus,L., Carbonnier,B., Morcellet,M., Richart,G., Crini,G., and Deratani,A. (2003) Mass spectrometric characterization of a new 2-hydroxypropyl-b-cyclodextrin derivative bearing methacrylic moieties and its copolymerization with 1-vinyl-2-pyrrolidone. *Macromolecular Bioscience* **3,** 198-209.

248. Jenkins,A. and Jenkins,J. (2001) The prediction of reactivity in radical polymerization. *Macromolecular Symposia* **174,** 187-195.

249. Jia,X., Pang,Y., and Huang,J. (1998) Copolymerization of Ethyl a-(Hydroxymethyl) acrylate with Maleimide and Characterization of the Resulting Copolymer. *Journal of Polymer Science Part A: Polymer Chemistry* **36,** 1291-1299.

250. Jiang,X., Xia,P., Liu,W., and Yan,D. (2000) Atom Transfer Radical Copolymerization of Styrene and N-Cyclohexylmaleimide. *Journal of Polymer Science Part A: Polymer Chemistry* **38,** 1203-1209.

251. Jiang,X., Yan,D., Zhong,Y., Liu,W., and Chen,Q. (2000) Atom transfer radical copolymerization of methyl methacrylate with N-cyclohexylmaleimide. *Polymer International* **49,** 893-897.

252. Jitjareonchai and J . Chemical Engineering Department, University of Waterloo. 2005.
Ref Type: Personal Communication

253. Johnson,D., Clarke,N., and Rasmussen,P. (2001) The copolymerization of 1-alkylvinazenes with styrene. *Journal of Macromolecular Science, Pure and Applied Chemistry* **A38,** 773-783.

254. Jone Selvamalar,C., Penlidis,A., and Nanjundan,S. (2003) Copolymers of 4-benzyloxycarbonylphenyl methacrylate with methyl methacrylate: synthesis, characterization and reactivity ratios. *Journal of Macromolecular Science, Pure and Applied Chemistry* **A40,** 1019-1033.

255. Jone Selvamalar,C., Krithiga,T., Penlidis,A., and Nanjundan,S. (2003) Copolymerization of 4-benzyloxycarbonylphenyl methacrylate with glycidyl methacrylate: synthesis, characterization, reactivity ratios and application as adhesives. *Reactive and Functional Polymers* **56,** 89-101.

256. Jone Selvamalar,C., Vijayanand,P., Penlidis,A., and Nanjundan,S. (2004) Homopolymer and copolymers of 4-benzyloxycarbonylphenyl acrylate with glycidyl methacrylate: Synthesis, characterization, reactivity ratios, and application as adhesive for leather. *Journal of Applied Polymer Science* **91,** 3604-3612.

257. Kaim,A. and Oracz,P. (1998) True reactivity ratios for styrene-methyl methacrylate copolymerization in bulk . *Macromolecular Theory and Simulations* **7,** 97-103.

258. Kaim,A. and Oracz,P. (1998) Terminal and penultimate models of copolymerization in the styrene-acrylonitrile system in bulk according to UNIFAC . *Polymer* **39,** 3901-3904.

259. Kaim,A. (1998) Terminal and penultimate reactivity ratios in the STY/AN free-radical copolymerization in bulk. *Journal of Macromolecular Science, Pure and Applied Chemistry* **A35,** 577-588.

260. Kaim,A. and Oracz,P. (1999) Solvent effects on true terminal reactivity ratios for styrene-methyl methacrylate copolymerization system. *Polymer* **40,** 6925-6932.

261. Kaim,A. (2000) Application of the Monomer Reactivity Ratios to the Kinetic-Model Discrimination and the Solvent-Effect Determination for the Styrene/Acrylonitrile Monomer System. *Journal of Polymer Science Part A: Polymer Chemistry* **38,** 846-854.

262. Kaita,S., Otaki,T., Kobayashi,E., Aoshima,S., and Furukawa,J. (1997) Copolymerization of Vinyl Monomers with Gd(OCOCCl$_{3)3\text{-(i-Bu)3Al-Et2AlCl}}$. *Journal of Polymer Science Part A: Polymer Chemistry* **35,** 2591-2597.

263. Karanikolopoulos,G., Batis,C., Pitsikalis,M., and Hadjichristidis,N. (2004) Zirconocene-catalyzed copolymerization of methyl methacrylate with other methacrylate monomers. *Journal of Polymer Science Part A: Polymer Chemistry* **42,** 3761-3774.

264. Kavousian,A., Ziaee,F., Nekoomanesh,M., Leamen,M., and Penlidis,A. (2004) Determination of Monomer Reactivity Ratios in Styrene/2-Ethylhexylacrylate Copolymer. *Journal of Applied Polymer Science* **92,** 3368-3370.

265. Keeler,S. (1989) The error-in-variables model applied to parameter estimation when the error covariamce matrix is unknown and to the design of experiments. Ph.D. University of Waterloo, Department of Chemical Engineering.

266. Keeler,S. and Reilly,P. (1991) The error in variables model applied to parameter estimation when the error covariance matrix is unknown. *The Canadian Journal of Chemical Engineering* **69,** 27-34.

267. Kelen,T. and Tudos,F. (1975) Analysis of the Linear Methods for Determining Copolymerization Reactivity Rations. I. A New Imporved Linear Graphic Method. *Journal of Macromolecular Science - Chem.* **A9,** 1-27.

268. Kim,W., Byun,K., Lee,D., Min,K., Park,L., Seo,K., Kang,I., and Park,S. (2003) Synthesis of photocrosslinkable polymers using abietic acid and their characterization. *Polymer Journal* **35,** 450-454.

269. Kim,Y. and Harwood,H. (2002) Analysis of sequnce distribution in methyl methacrylate-methyl acrylate copolymers by 13C-NMR spectroscopy. *Polymer* **43,** 3229-3237.

270. Kim,Y., Priddy,D., and Harwood,H. (2003) Polymerization and copolymerization of dimethyl(1-ethoxycarbonyl)vinyl phosphate. *Polymer* **44,** 4165-4170.

271. Klumperman,B. and Kraeger,I. (1994) Effect of Solvent on the Copolymerization of Styrene and Acrylonitrile. Application of the Bootstrap Effect to the Penultimate Unit Model. *Macromolecules* **27,** 1529-1534.

272. Kobayashi,E., Hayashi,N., Aoshima,S., and Furukawa,J. (1998) Copolymerization of Dienes with Neodymium Tricarboxylate-Based Catalysts and Cis-Polymerization Mechanism of Dienes. *Journal of Polymer Science Part A: Polymer Chemistry* **36,** 1707-1716.

273. Koch,U. and Yaacoub,E. (2003) Batch Emulsion Copolymerization of 3-O-Methacryloyl-1,2:5,6-di-O-isopropylidene-a-D-glucofuranose and Butyl Acrylate: Synthesis and Properties of the Sugar Latices. *Journal of Polymer Science Part A: Polymer Chemistry* **41,** 788-803.

274. Koenig,J. (1980) *Chemical microstructure of polymer chains.* John Wiley & Sons Ltd, New York.

275. Kostov,G., Ameduri,B., Boutevin,B., Bauduin,G., and Stankova,M. (2004) Synethsis and Characterization of Original Functional Polymers of Tetrafluoroethylene and 4,5,5-Trifluoro-4-ene Pentyl Acetate. *Journal of Polymer Science Part A: Polymer Chemistry* **42,** 1693-1706.

276. Kothandaraman,H. and Sangeetha,D. (2001) Effect of the catalyst on the copolymers of styrene with methyl methacrylate by Ziegler-Natta polymerization. *Polymer Journal* **37,** 485-495.

277. Kramer,I., Pasch,H., Handel,H., and Albert,K. (1999) Chemical heterogeneity analysis of high-conversion poly[styrene-co-(ethyl acrylate)]s by NMR and on-line coupled SEC-NMR`. *Macromolecules Chemistry and Physics* **200,** 1734-1744.

278. Kucharski,M. and Renata,L. (1997) Copolymerization of hydroxyalkyl methacrylates with acrylamide and methacrylamide I. Determination of reactivity ratios . *Journal of Applied Polymer Science* **64,** 1259-1265.

279. Kumar,R., Gao,W., and Gross,R. (2002) Functionalized Polylactides: Preperation and Charaterization of [L]-Lactide-co-Pentofuranose. *Macromolecules* **35,** 6835-6844.

280. Kunisada,H., Ito,T., Takagi,K., and Yuki,Y. (2001) Synthesis and polymerization of isopropenyl-1,3,5-triazines carrying a long alkyl chain with oxyethylene spacer and the side chains crystallization of obtained comb-like polymers. *Journal of Macromolecular Science, Pure and Applied Chemistry* **A38,** 417-427.

281. Kuzmic,A., Vukovic,R., Podolski,S., and Fles,D. (2001) Polymerization of N-(p-phenoxy-phenyl)acrylamide and copolymers with styrene. *Journal of Macromolecular Science, Pure and Applied Chemistry* **A38,** 1075-1086.

282. Lad,J., Harrisson,S., Mantovani,G., and Haddleton,D. (2003) Copper mediated living radical polymerization: interactions between monomer and catalyst. *Dalton Transactions* 4175-7180.

283. Larraz,E., Elvira,C., and Roman,J. (2003) Novel Acrylic Macromoner with Amphiphilic Character Derived from Triton X-100: Radical Copolymerization with Methyl Methacrylate and Thermal Properties. *Journal of Polymer Science Part A: Polymer Chemistry* **41,** 1641-1649.

284. Lebedeva,O., Shaglaeva,N., Pirogova,G., Fedorov,S., and Khaliullin,A. (2001) Copolymerization of vinyl chloride with 1-vinyl-1,2,4-triazole. *Russian Journal of Applied Chemistry* **74,** 1413-1414.

285. Lee,S., Russel,A., and Matyjaszewski,K. (2003) ATRP synthesis of amphiphilic random, gradient, and block copolymers of 2-(dimethylamino)ethyl methacrylate and n-butyl methacrylate in aqueous media. *Biomacromolecules* **4,** 1386-1393.

286. Lee,Y., Onimura,K., Tsutsumi,H., and Oishi,T. (2000) Synthesis and Polymerization of Chiral Methacrylates Bearing a Cholesteryl or Menthyl Group. *Journal of Polymer Science Part A: Polymer Chemistry* **38,** 4315-4325.

287. Lee,Y., Onimura,K., Tsutsumi,H., and Oishi,T. (2001) Synthesis of novel chiral polymethacrylate bearing urethane and 1,1'-binaphthlene moieties and its chiral recognition ability. *Polymer Journal* **33,** 411-418.

288. Lee,Y., Yamashita,K., Eto,M., Onimura,K., Tsutsumi,H., and Oishi,T. (2002) Synthesis of novel chiral poly(methacrylate)s bearing urethane and cinchona alkaloid moieties in side chain and their chiral recognition abilities. *Polymer* **43,** 7539-7547.

289. Lee,Y., Hisamitsu,N., Onimura,K., Tsutsumi,H., and Oishi,T. (2002) Synthesis of novel chiral poly(methacrylate)s having urea moieties and (S)-methylbenzyl or L-phenylalanine methyl ester groups and their chiral recognition abilities. *Polymer Journal* **34,** 9-17.

290. Lee,Y., Nakashima,Y., Onimura,K., Tsutsumi,H., and Oishi,T. (2003) Synthesis of novel polymethacrylate bearing an (S)-(+)-1-cyclohexylethyl urea group in the side chain and its chiral recognition ability. *Journal of Applied Polymer Science* **90,** 1018-1025.

291. Lee,Y., Nakashima,Y., Onimura,K., Tsutsumi,H., and Oishi,T. (2003) Free-Radical Polymerization of (R)-(-)-1-(1-Naphthyl)ethyl(2-methacryloyloxyethyl)urea and Chiral Recognition Ability. *Macromolecules* **36,** 4735-4742.

292. Li,A., Zhang,W., Liang,H., and Lu,J. (2004) Living cationic random copolymerization of b-pinene and isobutylene with 1-phenylethyl. *Polymer* **45,** 6533-6537.

293. Li,M., Zhuo,R., and Qu,F. (2002) Synthesis and Characterization of Novel Biodegradable Poly(ester amide) with Ether Linkage in the Backbone Chain. *Journal of Polymer Science Part A: Polymer Chemistry* **40,** 4550-4555.

294. Li,X. and Berner,B. (1997) Copolymers of (±) 2-Ethylhexyl Acrylate and 3-[3,3,3-Trimethyl-1,1-bis (trimethylsiloxy) disiloxanyl] propyl Methacrylate. *Journal of Polymer Science Part A: Polymer Chemistry* **35,** 3571-3574.

295. Li,Z., Du,Q., Yang,Y., and Lin,M. (2001) Copolymerization of tert-butyl 3-isopropenylcumyl peroxide with butyl acrylate and grafting of styrene onto the copolymers. *Macromolecular Chemistry and Physics* **202,** 2314-2320.

296. Liaw,D. and Sang,H. (1999) Radical Polymerization of New Functional Monomers Derived from Methacrloyl Isocyanate and Urea. *Journal of Polymer Science Part A: Polymer Chemistry* **37,** 1789-1796.

297. Liaw,D. and Liaw,B. (2000) Radical Polymerization of New Functional Monomer: Methacryloyl Isocyanate Containing 4-Chloro-1-phenol. *Journal of Polymer Science Part A: Polymer Chemistry* **38,** 469-473.

298. Liaw,D., Huang,C., Sang,H., and Wu,P. (2000) microstructure, reactivity ratio and viscometric studies of water-soluble cationic and/or zwitterionic copolymers. *Polymer* **41,** 6123-6131.

299. Lin,W., Hsieh,Y., Warganich,D., Zhou,W., Kurth,M., and Krochta,M. (1998) Solution copolymerization of D-lactose-O-(p-vinylbenzyl)-hydroxime with acrylonitrile. *Polymer* **39,** 4911-4914.

300. Lin,Z., Huang,Z., Shi,L., and Huang,J. (2000) Synthesis of a New Monomer N'-(b-methacryloyloxyethyl)-2-pyrimidyl-(p-benzyloxycarbonyl)aminobenzenesulfonamide and Its Copolymerization with N-Phenyl Maleimide. *Journal of Polymer Science Part A: Polymer Chemistry* **38,** 2548-2554.

301. Ling,J. and Shen,Z. (2002) Lanthanum tris(2,6-di-tert-butyl-4-methylphenolate) as a novel, versatile initiator for homo- and copolymerization of cyclic carbonates and lactones. *Macromolecular Chemistry and Physics* **203,** 735-738.

302. Litvinenko,G., Simon,P., and Mueller,A. (2001) Molecular Parameters of Hyperbranched Copolymers Obtained by Self-Condensing Vinyl Copolymerization,2. Non-Equal Rate Constants. *Macromolecules* **34,** 2418-2426.

303. Liu,G., Zhang,Y., Qu,X., and Zhang,L. (2003) Kinetic model of mechanism of alternating radical copolymerization and its quantitative treatment method. *Polymer International* **52,** 987-992.

304. Liu,H. and Wilen,C. (2001) Hyperbranched polymers with maleic functional groups as radical crosslinkers. *Journal of Polymer Science Part A: Polymer Chemistry* **39,** 964-972.

305. Liu,Z. and Rimmer,S. (2002) Synthesis and release of 5-fluorouracil from poly(N-vinylpyrrolinone) bearing 5-fluorouracil derivatives. *Journal of Controlled Release* **81,** 91-99.

306. Longo,P., Siani,E., Pragliola,S., and Monaco,G. (2002) Copolymerization of ethene and propene in the presence of Cs symmetric group 4 metallocenes and methylaluminoxane. *Journal of Polymer Science Part A: Polymer Chemistry* **40,** 3249-3255.

307. Loos,R., Kobayashi,S., and Mayr,H. (2003) Ambident reactivity of the thiocyanate anion revisited: can the product ratio be explained by the hard soft acid base principle? *Journal of the American Chemical Society* **125,** 14126-14132.

308. Lousenberg,R. and Shoichet,M. (2000) Radical Copolymerization of Novel Trifluorovinyl Ethers with Ethyl Vinyl Ether and Vinyl Acetate: Estimating Reactivity Ratios and Understanding Reactivity Behavior of the Propagating Radical. *Journal of Polymer Science Part A: Polymer Chemistry* **38,** 1344-1354.

309. Lovell,L., Stansbury,J., Syrpes,D., and Bowman,C. (1999) Effects of composition and reactivity on the reaction kinetics of dimethacrylate/dimethacrylate copolymerizations. *Macromolecules* **32,** 3913-3921.

310. Madruga,E. (2002) From classical to living/controlled statistical free-radical copolymerization. *Progress in Polymer Science* **27,** 1879-1924.

311. Mahrholz,T., Klein,J., and Klein,T. (2002) New poly(sodium carboxylate)s based on saccharides, 1: Synthesis and characterization of ionic allyl glycoside polymers. *Macromolecular Chemistry and Physics* **203,** 2640-2649.

312. Mao,R. and Huglin,M. (1992) A new linear method to calculate monomer reactivity ratios by using high conversion copolymerization data: terminal model. *Polymer* **34,** 1709-1715.

313. Marcu,I., Daniels,E., Dimonie,V., Hagiopol,C., Roberts,J., and El-Aasser,M. (2003) Incorporation of Alkoxysilanes into Model Latex Systems: Vinyl Copolymerization of Vinyltriethoxysilane and n-Butyl Acrylate. *Macromolecules* **36,** 328-332.

314. Martin-Gomis,L., Cuervo-Rodriguez,R., Fernandez-Monreal,M., Madruga,E., and Fernandez-Garcia,M. (2003) Monomer Reactivity Ratios and Glass-Transition Temperatures of Copolymers Based on Dimethyl Amino Ethyl Methacrylate and Two Structural Hydroxy-Functional Acrylate Isomers. *Journal of Polymer Science Part A: Polymer Chemistry* **41,** 2659-2666.

315. Martinez-Pina,F., Gargallo,L., and Radic,D. (1998) N-Vinylimidazole-N-vinyl-2-pyrrolidone Copolymers. Part I. Reactivity Ratios, Solubility and Viscosimetric Study. *Polymer International* **47,** 340-344.

316. Martinez,G., Sanchez-Chaves,M., Madruga,E., and Fernandez-Monreal,C. (2000) Monomer reactivity ratios and microstructural analysis of 2-hydroxyethyl methacrylate–*t*-butyl acrylate copolymers. *Polymer* **41,** 6021-6026.

317. Martinez,G., Sanchez-Chaves,M., and Madruga,E. (2002) Preparation of Amphiphilic Statistical Copolymers of 2-Hydroxyethyl Methacrylate with 2-Diethylaminoethyl Methacrylate, Precursors of Water-Soluble Copolymers. *Journal of Polymer Science Part A: Polymer Chemistry* **40,** 2427-2434.

318. Masuda,S., Miyahara,T., Minagawa,K., and Tanaka,M. (1999) Polymerization and Complexation of Methacryloylglycine. *Journal of Polymer Science Part A: Polymer Chemistry* **37,** 1303-1309.

319. Masuda,S., Minagawa,K., Okamura,H., and Tanaka,M. (2002) Copolymerization of methyl 2-acetamidoacrylate and styrene in the presence of stannic chloride. *European Polymer Journal* **38,** 327-331.

320. Mathakiya,I., Vangani,V., and Rakshit,A. (1998) Terpolymerization of Acrylamide, Acrylic Acid, and Acrylonitrile: Synthesis and Properties. *Journal of Applied Polymer Science* **69,** 217-228.

321. Mathakiya,I., Rakshit,A., and Rao,P. (2003) Synthesis, Characterization, and Solution Properties of Acrylic Ester Polymers. *International Journal of Polymer Analysis and Characterization* **8,** 339-358.

322. Mathias,L., Jensen,J., Thigpen,K., McGowen,J., McCormick,D., and Somlai,L. (2001) Copolymers of 4-adamantylphenyl methacrylate derivatives with methyl methacrylate and styrene. *Polymer* **42,** 6527-6537.

323. Matsumoto,A. and Mohri,Y. (1999) Effects of Solvent as an Electron-Pair Acceptor on Propagation Reactions During Radical Polymerization and Copolymerization of Polar Vinyl Monomers. *Journal of Polymer Science Part A: Polymer Chemistry* **37,** 2803-2814.

324. Matsumoto,A., Ichiryu,Y., Aota,H., Shiraki,K., and Iwata,T. (2002) Free-radical crosslinking copolymerization of 2,2'-Azobis[N-(2-propenyl)-2-methylpropionamide] with vinyl benzoate resulting in polymeric azo initiators. *Journal of Polymer Science Part A: Polymer Chemistry* **40,** 317-325.

325. Matyjaszewski,K. (2002) Factors Affecting Rates of Comonomer Consumption in Copolymerization Processes with Intermittent Activation. *Macromolecules* **35,** 6773-6781.

326. Mav,I. and Zigon,M. (2001) HNMR Study of the Kinetics of Substituted Aniline Polymerization. II. Copolymerization of 2-Methoxyaniline and 3-Aminobenzenesulfonic Acid. *Journal of Polymer Science Part A: Polymer Chemistry* **39,** 2482-2493.

327. Mav,I. and Zigon,M. (2002) A kinetic study of the copolymerization of substituted anilines by H NMR. *Polymer International* **51,** 1072-1078.

328. Maxwell,I., Aerdts,A., and German,A. (1993) Free Radical Copolymerization: An NMR Investigation of Current Kinetic Models. *Macromolecules* **26,** 1956-1964.

329. Mayo,F. and Lewis,F. (1944) Copolymerization I. Abasis for comparing the behaviour of monomer in copolymerization; the copolymerization of styrene and methyl methacrylate. *Journal of American Chemical Society* **66,** 1594-1601.

330. McManus,N., Kim,J., and Penlidis,A. (1998) Observations on styrene-hydroxyethyl acrylate and styrene-hydroxyethyl acrylate-ethyl acrylate polymerizations . *Polymer Bulletin* **41,** 661-668.

331. McManus,N., Penlidis,A., and Rempel,G. (1998) A kinetic investigation of the copolymerization of acrylonitrile and vinyl acetate in bulk. *Chemical Engineering Mineral Procesing* **6,** 153-170.

332. McManus,N., Dube,M., and Penlidis,A. (1999) High temperature bulk copolymerization of butyl acrylate/methyl methacrylate: Reactivity ratio estimation. *Polymer Reaction Engineering* **7,** 131-145.

333. McManus,N., Lona,L., and Penlidis,A. (2002) Comparative trends of copolmerization involving alpha methyl styrene at elevated temperatures. *Polymer Reaction Engineering* **10,** 285-309.

334. McManus,N., Penlidis,A., and Dube,M. (2002) Copolymerization of alpha-methyl styrene with butyl acrylate in bulk . *Polymer* **43,** 1607-1614.

335. Metheo,A., Pantoja,M., and Venancio,E. (2004) Effect of monomer ratio in the electrochemical synthesis of poly(aniline-co-o-methoxyaniline). *Solid State Ionics* **171,** 91-98.

336. Meyer,V. and Lowry,G. (1965) Integral and Differential Binary Copolymerization Equations. *Journal of Polymer Science: Part A: Polymer Chemistry* **3,** 2843-2851.

337. Mi,X., Ma,Z., Wang,L., Ke,Y., and Hu,Y. (2003) Homo- and copolymerization of norbornene and styrene with Pd- and Ni-based novel bridged dinuclear diimine complexes and MAO. *Macromolecular Chemistry and Physics* **204,** 868-876.

338. Mignard,E., Leblanc,T., Bertin,D., Guerret,O., and Reed,W. (2004) Online Monitoring of Controlled Radical Polymerization: Nitroxide-Mediated Gradient Copolymerization. *Macromolecules* **37,** 966-975.

339. Miyagawa,T., Sandu,F., and Endo,T. (2001) Radical copolymerization behavior of 2,2-dimethyl-5-methylene-1,3-dioxolan-4-one with common monomers. *Macromolecular Chemistry and Physics* **202,** 1602-1605.

340. Mohammed,S., Daniels,E., Klein,A., and El-Aasser,M. (1998) Bulk copolymerization of dimethyl meta-isopropenyl benzyl isocyanate (TMI): Determination of reactivity ratios . *Journal of Applied Polymer Science* **67,** 559-568.

341. Mokhtar,S., Sabaa,M., Elkholy,S., and Elsabee,M. (2000) Radical Polymerization and Copolymerization Behavior of 1-Cyanoethanoyl-4-acryloyl-thiosemicarbzide. *Journal of Polymer Research* **7,** 229-235.

342. Mokhtar,S., Youssef,E., and El-Ghaffar,M. (2001) Characterization and electrical properties of itaconic acid/butyl acrylate copolymers and their metal complexes. *Journal of Macromolecular Science, Pure and Applied Chemistry* **A38,** 19-32.

343. Monett,D., Mendez,J., Abraham,G., Gallardo,A., and San Roman,J. (2002) An Evolutionary Approach to the Estimation of Reactivity Ratios . *Macromolecular Theory and Simulations* **11,** 525-532.

344. Mormann,W. and Ferbitz,J. (2002) Copolymers from methacrylic acid and trimethylsilyl methacrylate - synthesis, reactivity ratios and thermal properties. *Macromolecular Chemistry and Physics* **203,** 2616-2623.

345. Mormann,W. and Ferbitz,J. (2003) Copolymers from tert-butyl methacrylate and itaconic anhydride-reactivity ratios and polymer analogous reactions. *European Polymer Journal* **39,** 489-496.

346. Mukherjee,M., Chatterjee,S., and Brar,A. (1999) One- and Two-Dimensional Nuclear Magnetic Resonance Studies on the Compositional Sequence and the Microstructure of Acrylamide/Acrylonitrile Copolymers. *Journal of Applied Polymer Science* **73,** 55-67.

347. Naguib,H., Mokhtar,S., Ali,R., and Elsabee,M. (2003) Terpolymerization of Ethyl Methacrylate, N-Phenylmaleimide, and Itaconic Acid. *Journal of Polymer Science Part A: Polymer Chemistry* **41,** 3180-3187.

348. Naguib,H., Saad,G., and Elsabee,M. (2003) Copolymerization of bromophenylmaleimide with ethyl or butyl methacrylate. *Polymer International* **52,** 1217-1221.

349. Naguib,H., Aly,R., Sabaa,M., and Mokhtar,S. (2003) Gamma radiation induced graft copolymerization of vinylimidazole-acrylic acid onto polypropylene films. *Polymer Testing* **22,** 825-830.

350. Nair,C., Chaumont,P., and Chamot,D. (1999) Addition-Fragmentation Behavior of a Capto-Dative Group-Substituted Acrylic Ester in Free-Radical Polymerization and Reactivity of the Derived Macromonomers. *Journal of Polymer Science Part A: Polymer Chemistry* **37,** 2511-2524.

351. Nath,D., Shiono,T., and Ikeda,T. (2002) Copolymerization of 1,3-Butadiene and Isoprene with Cobalt Dichloride/Methylaluminoxane in the Presence of Triphenylphosphine. *Journal of Polymer Science Part A: Polymer Chemistry* **40,** 3086-3092.

352. Neugebauer,D. and Matyjaszewski,K. (2003) Copolymerization of N,N-Dimethylacrylamide with n-Butyl Acrylate via Atom Transfer Radical Polymerization. *Macromolecules* **36,** 2598-2603.

353. Nguyen,L., Koerner,H., and Lederer,K. (2003) Free radical co- and terpolymerization of styrene, hydrogenated cardanyl acrylate, and cardanyl acetate. *Journal of Applied Polymer Science* **88,** 1399-1409.

354. Nguyen,T. (1997) A novel method to evaluate the copolymerization models based on the non linear least squares curve fitting of the theoretical equation to the experimental data of copolymer composition and triad fractions applied for the styrene-co-maleic anhydride-polymers. *Tap Chi Hoa Hoc* **35,** 88-92.

355. Nishida,S., Nishida,H., and Endo,T. (2002) Radical Copolymerization Behavior of a Highly Fluorinated Cyclic Olefin with Vinyl Ether. *Journal of Polymer Science Part A: Polymer Chemistry* **40,** 1151-1156.

356. Nishida,S., Nishida,H., and Endo,T. (2003) Radical Copolymerization of a Highly Fluorinated Cyclic Olefin Octafluorocyclopentene with Alkyl Vinyl Ethers. *Polymer Bulletin* **51,** 1-8.

357. Nomura,K., Oya,K., and Imanishi,Y. (2001) Ethylene/ a-olefin copolymerization by various nonbridged (cyclopentadienyl)(acryloxy)titanium (IV) complexes -MAO catalyst system. *Journal of Molecular Catalysis A: Chemical* **174,** 127-140.

358. Nurkeeva,Z., Mun,G., Koblanov,S., Yermukhambetova,B., Abdykalykova,R., and Khutoryanskiy,V. (2002) Radiation synthesis of novel cationic flocculants based on copolymers of vinyl ethers of monoethanolamine ethyleneglycol. *Radiation Physics and Chemistry* **64,** 9-12.

359. O'Driscoll,K. (1980) Computation of reactivity ratios from sequence distribution information. *Journal of Polymer Science: Polymer Chemistry Edition* **18,** 2747-2749.

360. O'Driscoll,K. and Kale,L. (1984) Applicability of the Mayo-Lewis Equation to High-Conversion Copolymerization of Styrene and Methylmethacrylate. *Journal of Polymer Science: Polymer Chemistry Edition* **22,** 2777-2788.

361. O'Driscoll,K. and Kale,L. (1984) Applicability of the Mayo-Lewis Equation to High-Conversion Copolymerization of Styrene and Methylmethacrylate. *Journal of Polymer Science: Polymer Chemisrty Edition* **22,** 2777-2788.

362. O'Driscoll,K. and Reilly,P. (1987) Determination of reactivity ratios in copolymerization. *Makromol.Chem., Makroml.Symp.* **10/11,** 355-371.

363. O'Leary,K. and Paul,D. (2004) Copolymers of poly(n-alkyl acrylates): synthesis, characterization, and monomer reactivity ratios. *Polymer* **45,** 6575-6585.

364. Ochiai,B., Tomita,I., and Endo,T. (2001) Radical polymerization behavior of 4-monosubstituted and 2,4-disubstituted enyne. *Macromolecular Chemistry and Physics* **202,** 3099-3105.

365. Odian,G. (1933) *Principles of Polymerization.* McGraw-Hill, New York.

366. Oliva,L., Longo,P., Izzo,L., and Di Serio,M. (1997) Zirconocene-based catalysts for the ethylene-styrene copolymerization: reactivity ratios and reaction mechanism. *Macromolecules* **30,** 5616-5619.

367. Oracz,P. and Kaim,A. (2001) Use of the maximum likelihood method for composition data analysis in the radical copolymerization terminal model. *Macromolecular Theory and Simulations* **10,** 374-380.

368. Ortiz,C., Vazquez,B., and Roman,J. (1998) Synthesis, characterization and properties of polyacrylic systems derived from vitamin E. *Polymer* **39,** 4107-4114.

369. Oxby,P., Duever,T., and Reilly,P. (2003) Multivariate Weighted Least Squares as an Alternative to the Determinant Criterion for Multiresponse Parameter Estimation. In *Dynamic Model Development: Methods, Theory and Applications.* (Edited by Asprey,A. and Machietto,S.) Elsevier.

370. Pack,J., Kim,S., Cho,I., Park,S., and Kim,Y. (2002) Microstructure analysis and thermal property of copolymers made of glycolide and e-caprolactone by stannous octoate. *Journal of Polymer Science Part A: Polymer Chemistry* **40,** 544-554.

371. Palacios,O., Aliev,R., and Burillo,G. (2003) Radiation Graft Copolymerization of Acrylic Acid and N-Isopropylacrylamide from binary mixtures onto Polytetrafluoroethylene. *Polymer Bulletin* **51,** 191-197.

372. Palmer,D., McManus,N., and Penlidis,A. (2000) Copolymerization with Depropagation: A Study of a-Methyl Styrene/Methyl Methacrylate in Bulk at Elevated Temperatures. *Journal of Polymer Science Part A: Polymer Chemistry* **38,** 1981-1990.

373. Palmer,D., McManus,N., and Penlidis,A. (2001) Copolymerization with Depropagation: A study of a-Methyl Styrene/Methyl Methacrylate in Solution at Elevated Temperatures. *Journal of Polymer Science Part A: Polymer Chemistry* **39,** 1753-1763.

374. Pandey,D. and Srivastava,A. (2033) Mechanistic and kinetic studies of the copolymerization of citronellol and acrylonitrile initiated by benzoylperoxide. *Designed Monomers and Polymers* **6,** 197-209.

375. Pandey,P. and Srivastava,A. (2002) Benzoyl Peroxide-Initiated Copolymerization of Citronellol and Vinyl Acetate. *Journal of Polymer Science Part A: Polymer Chemistry* **40,** 1243-1252.

376. Pandey,P. and Srivastava,A. (2002) Synthesis and characterization of optically active and functional terpolymer of citronellol, styrene, and methyl methacrylate: a kinetic study. *Advances in Polymer Technology* **21,** 59-64.

377. Pang,X., Sun,H., and Shen,Q. (2004) Copolymerizations of 2-(dimethylamino)ethyl methacrylate with (methyl)acrylates initiated by a neutral Pd(II)-based complex. *Polymer* **45,** 4029-4035.

378. Pasquale,A. and Long,T. (2004) Determination of monomer reactivity ratios using in situ FTIR spectroscopy for maleic anhydride/norbornene-free-radical copolymerization. *Journal of Applied Polymer Science* **92,** 3240-3246.

379. Patel,M., Patel,D., Ray,A., and Patel,R. (2003) Microbial screening of copolymers of 2,4-dichlorophenyl methacrylate with N-vinylpyrrolidone: synthesis and characterization. *Polymer International* **52,** 367-372.

380. Patel,M., Patel,S., Ray,A., and Patel,R. (2003) Synthesis, characterization, and antimicrobial activity of acrylic copolymers. *Journal of Applied Polymer Science* **89,** 895-900.

381. Patel,P., Shah,B., Ray,A., and Patel,R. (2004) Acrylic Homo- and Co-polymers Based on 2,4-dichlorophenyl Methacrylate and 8-quinolinyl Methacrylate. *Journal of Polymer Research* **11,** 65-73.

382. Patino-Leal,H. (1979) Advances in the Theory of the Error-in-Variables Model with Applications in Chemical Engineering. Ph.D University of Waterloo, Department of Chemical Engineering.

383. Patino-Leal,H., Reilly,P., and O'Driscoll,K. (1980) On the Estimation of Reactivity Ratios. *Journal of Polymer Science: Polymer Letters Edition* **18,** 219-227.

384. Pazhanisamy,P., Ariff,M., and Anwaruddin,Q. (1997) Copolymers of a-methylstyrene with N-cyclohexylacrylamide: synthesis, monomer reactivity ratios, and mean sequence length. *Journal of Macromolecular Science, Pure and Applied Chemistry* **A34,** 1045-1054.

385. Pekel,N., Sahiner,N., Guven,O., and Rzaev,Z. (2001) Synthesis and characterization of N-vinylimidazole-ethyl methacrylate copolymers and determination of monomer reactivity ratios. *European Polymer Journal* **37,** 2443-2451.

386. Pekel,N., Rzaev,Z., and Gueven,O. (2004) Synthesis and characterization of poly(N-vinylimidazole-co-acrylonitrile) and determination of monomer reactivity ratios. *Macromolecular Chemistry and Physics* **205,** 1088-1095.

387. Penlidis,A. Personal Communication. 2005.

388. Perry,M., Volpert,V., Lewis,L., Nichols,H., and Pojman,J. (2003) Free-radical frontal copolymerization: The dependence of the front velocity on the monomer feed composition and reactivity ratios. *Macromolecular Theory and Simulations* **12,** 276-286.

389. Pierik,S. and Van Herk,A. (2003) Catalytic chain transfer copolymerization of methyl methacrylate and butyl acrylate. *Macromolecular Chemistry and Physics* **204,** 1406-1418.

390. Pittman,C. and Lee,H. (2003) Radical-Initiated Polymerization of b-Methyl-a-methylene-g-butyrolactone. *Journal of Polymer Science Part A: Polymer Chemistry* **41,** 1759-1777.

391. Plaumann,H. and Branston,R. (1989) On Estimating Reactivity Ratios Using the Integrated Mayo-Lewis Equation. *Journal of Polymer Science: Part A: Polymer Chemistry* **27,** 2819-2822.

392. Polic,A., Duever,T., and Penlidis,A. (1998) Case studies and Literature Review on the Estimation of Copolymerization Reactivity Ratios. *Journal of Polymer Science, Part A: Polymer Chemistry* **36,** 813-822.

393. Polic,A. (2001) A Protocol for the Estimation of Parameters in Process Models. Ph.D University of Waterloo, Chemical Engineering Department.

394. Prevost,V., Petit,A., and Pla,F. (1999) Studies on chemical oxidative copolymerization of aniline and *o*-alkoxysulfonated anilines II. Mechanistic approach and monomer reactivity ratios . *European Polymer Journal* **35,** 1229-1236.

395. Pritchard,E., Downie,T., and Bacon,D. (1977) Further consideration of heteroscedasticity in fitting kinetic-models. *Technometrics* **19,** 227-236.

396. Rachkov,A., Minoura,N., and Shimizu,T. (2003) Photoisomerization study of p-phenylazoacrylanilide and its homo- and copolymers. *Optical Materials* **21,** 307-314.

397. Rainaldi,I., Cristallini,C., Ciardelli,G., and Giusti,P. (2000) Copolymerization of acrylic acid and 2-hydroxyethyl methacrylate onto poly(N-vinylpyrrolidone): template influence on comonomer reactivity. *Macromolecular Chemistry and Physics* **201,** 2424-2431.

398. Reddy,B. and Balasubramanian,S. (2002) Novel activated acrylates: synthesis, characterization and the reactivity ratios of 4-acetamidophenyl acrylate copolymers with methyl methacrylate and glycidyl methacrylate. *European Polymer Journal* **38,** 803-813.

399. Reddy,J., Naidu,V., and Reddy,R. (2003) Synthesis and characterization of poly(N-phenyl methacrylamide-co-methyl methacrylate) and reactivity ratios determination. *Journal of Applied Polymer Science* **90,** 2179-2186.

400. Reddy,R., Ranganathan,R., Sivakumar,S., and Sriram,R. (2002) Emulsion copolymerization of methyl acrylate with methyl methacrylate and with acrylonitrile. *Designed Monomers and Polymers* **5,** 97-114.

401. Reddy,R., Babu,Y., and Reddy,S. (2002) Microemulsion and conventional emulsion copolymerization of methyl methacrylate with acrylonitrile. *Journal of Applied Polymer Science* **85,** 1503-1510.

402. Reilly,P. and Blau,G. (1978) A method for linear or nonlinear parameter estimation when the error variance depends on the magnitude of the quantity being measured., Czechoslovakia.

403. Reilly,P. and Patino-Leal,H. (1981) Bayesian study of the error-in-variables model. *Technometrics* **23,** 221-231.

404. Reilly,P., Keeler,S., and Reilly,H. (1993) Algorithm AS 286: Parameter Estimation in the Error-in-Variable Model. *Applied Statistics* **42,** 693-702.

405. Restrepo,A., Pinzon,N., and Ju,L. (2004) Synthesis of pH-Sensitive Surfactants by the Terpolymerization of Methacrylic Acid, Methoxy Poly(ethylene glycol) Methacrylate, and Lauryl Methacrylate: Initiator Effect and Reactivity Ratio Study. *Journal of Polymer Science Part A: Polymer Chemistry* **42,** 2950-2959.

406. Rodriguez,G., Gallardo,A., Fernandez,M., Rebuelta,M., Bujan,J., Bellon,J., Honduvilla,N., Escudero,C., and San Roman,J. (2004) Hydrophillic polymer drug from derivative of salicylic acid: Synthesis, controlled release studies and biological behavior. *Macromolecular Bioscience* **4,** 579-586.

407. Roos,S., Mueller,A., and Matyjaszewski,K. (1999) Copolymerization of n-Butyl Acrylate with Methyl Methacrylate and PMMA Macromonomers: Comparison of Reactivity Ratios in Conventional and Atom Transfer Radical Copolymerization. *Macromolecules* **32,** 8331-8335.

408. Rossignoli,P. (1993) Estimation and design considerations for obtaining reactivity ratios. M.A.Sc University of Waterloo, Department of Chemical Engineering.

409. Rossignoli,P. and Duever,T. (1995) The Estimation of Copolymer Reactivity Ratios: A Review and Case Studies Using the Error-In-Variables Model and Nonlinear Least Squares. *Polymer Reaction Engineering* **3,** 361-395.

410. Rudin,A., O'Driscoll,K., and Rumack,M. (1981) Use of NMR data to calculate copolymer reactivity ratios. *Polymer* **22,** 740-747.

411. Rutkaite,R., Buika,G., and Grazulevicius,J. (2001) Synthesis and characterization of copolymers of carbazoylalkyl(meth)acrylates and methacrylic acid. *Polymer Bulletin* **46,** 59-66.

412. Ryttel,A. (1999) Copolymerization of ethyl methacrylate with N-(3- or 4-halophenyl)maleimides: The monomer reactivity ratios. *Journal of Applied Polymer Science* **74,** 2924-2930.

413. Rzaev,Z. (1998) Tin Effect in Formation and Photocross-linking Reactions of Tri-n-Butylstannyl Methacrylate-Allyl Chloroacetate Copolymer. *Journal of Polymer Science Part A: Polymer Chemistry* **36,** 2339-2345.

414. Rzaev,Z., Guner,A., Kibare,G., Kaplan Can,H., and Asici,A. (2002) Terpolymerization of maleic anhydride, trans-stilbene and acrylic monomers. *European Polymer Journal* **38,** 1245-1254.

415. Sahloul,N. and Penlidis,A. (2004) High temperature copolymerization of styrene/ethyl acrylate: Reactivity ratio estimation in bulk and solution. *Advances in Polymer Technology* **23,** 186-195.

416. Saidi,S., Guittard,F., and Geribaldi,S. (2002) Monomers reactivity ratios of fluorinated acrylates-styrene copolymers. *Polymer International* **51,** 1058-1062.

417. Sakai,H., Kodani,T., Takayama,A., and Nomura,M. (2002) Film-formation property of vinylidene chloride-methyl methacrylate copolymer latex. Part I. Effect of emulsion-polymerization process. *Journal of Polymer Science Part B: Polymer Physics* **40,** 939-947.

418. Sanchez-Chaves,M., Martinez,G., and Madruga,E. (1999) Low- and High-Conversion Studies of the Free Radical Copolymerization of 2-Hydroxyethyl Methacrylate with Styrene in N,N'-Dimethylformamide Solution. *Journal of Polymer Science Part A: Polymer Chemistry* **37,** 2941-2948.

419. Sanchez-Chaves,M., Martinez,G., Madruga,E., and Fernandez-Monreal,C. (2002) Synthesis of Statistical Glycidyl Methacrylate-N-vinyl Pyrrolidone Copolymers and Their Reaction with Naproxen. *Journal of Polymer Science Part A: Polymer Chemistry* **40,** 1192-1199.

420. Sanghvi,P., Patel,A., Gopalkrishnan,K., and Devi,S. (2000) Reactivity ratios and sequence distribution of styrene–acrylonitrile copolymers synthesized in microemulsion medium . *European Polymer Journal* **36,** 2275-2283.

421. Sanghvi,P., Pokhriyal,N., and Devi,S. (2002) Effect of partitioning of monomer on the reactivities of monomers in microemulsion. *Journal of Applied Polymer Science* **84,** 1832-1837.

422. Sannigrahi,B., Wadgaonkar,P., Sehra,J., and Sivaram,S. (1997) Copolymerization of Methyl Methacrylate with Lauryl Methacrylate Using Group Transfer Polymerization. *Journal of Polymer Science Part A: Polymer Chemistry* **35,** 1999-2007.

423. Santhosh,P., Gopalan,A., and Vasudevan,T. (2003) In situ UV-visible spectroelectrochemical studies on the copolymerization of diphenylamine with ortho-methoxy aniline. *Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy* **59A,** 1427-1439.

424. Santhosh,P., Sankarasubramanian,M., Thanneermalai,M., Gopalan,A., and Vasudevan,T. (2004) Electrochemical, spectroelectrochemical and spectroscopic evidences for copolymer formation between diphenylmine and m-toluidine. *Materials Chemistry and Physics* **85,** 316-328.

425. Sarmah,D. and Baruah,S. (2003) Synthesis, characterization, and thermal properties of copolymers of behenyl acrylate and behenyl fumarate. *Journal of Applied Polymer Science* **90,** 2721-2726.

426. Sarzotti,D., Soares,J., and Penlidis,A. (2002) Ethylene/1-Hexene Copolymers Synthesized with a Single-Site Catalyst: Crystallization Analysis Fractionation,Modeling, and Reactivity Ratio Estimation. *Journal of Polymer Science Part B: Polymer Physics* **40,** 2595-2611.

427. Sato,T., Shimooka,S., and Seno,M. (1998) Radical Polymerization of Ortho-(1,3-Dioxolan-2-yl)phenyl Ethyl Fumarate Involving Intramolecular Hydrogen Abstraction and ring Opening of Cyclic Acetal. *Journal of Polymer Science Part A: Polymer Chemistry* **36,** 563-572.

428. Sato,T., Kitajima,T., Seno,M., and Hayashi,Y. (1998) Kinetic and ESR Studies on Radical Copolymerization of p-tert-Butoxystyrene and Di-n-butyl Maleate in Benzene. *Journal of Polymer Science Part A: Polymer Chemistry* **36,** 1449-1455.

429. Sato,T., Maeda,Y., Seno,M., and Hirano,T. (2001) Radical Heterogeneous Polymerization Behavior of N-Methyl-a-Fluoroacrylamide in Benzene. *Journal of Polymer Science Part A: Polymer Chemistry* **39,** 2196-2205.

430. Sayyah,S., El-Shafiey,Z., El-Sockary,M., and Kandil,U. (2002) Copolymerization of benzylidene malononitrile with methyl methacrylate and spectroscopic studies before and after irradiation with gamma rays of the obtained copolymer. *International Journal of Polymeric Materials* **51,** 225-242.

431. Schaverien,C., Ernst,R., Schut,P., and Dall'Occo,T. (2001) Ethylene Bis(2-indenyl) Zirconocenes: A New Class of Disastereomeric Metallocenes for the (Co)Polymerization of a-Olefins. *Organometallics* **20,** 3436-3452.

432. Schue,F., Jaimes,C., Dobreva-Schue,R., Giani-Beaune,O., Amass,W., and Amass,A. (2000) Synthesis and degradation of polyesters. *Polymer International* **49,** 965-974.

433. Scorah,M., Hua,H., and Dube,M. (2001) Bulk and solution copolymerization of methyl methacrylate and vinyl acetate . *Journal of Applied Polymer Science* **82,** 1238-1255.

434. Se,K. and Aoyama,K. (2004) Preparation and characterization of graft copolymers of methyl methacrylate and poly(n-hexyl isocyanate) macromolecules. *Polymer* **45,** 79-85.

435. Seber,G. and Wild,C. (1989) *Nonlinear Regression*. John Wiley & Sons Ltd, Toronto.

436. Selvam,P., Babu,K., Penlidis,A., and Nanjundan,S. (2004) Copolymers of 4-(3',4'-Dimethoxycinnamoyl)phenyl Acrylate and MMA: Synethsis, Characterization, Photocrosslinking Properties, and Monomer Reactivity Ratios. *Journal of Macromolecular Science, Pure and Applied Chemistry* **A41,** 791-809.

437. Selvamalar,C., Krithiga,T., Penlidis,A., and Nanjundan,S. (2003) Copolymerization of 4-benzyloxycarbonylphenyl methacrylate with glycidyl methacrylate: synthesis, characterization, reactivity ratios and application as adhesives. *Reactive and Functional Polymers* **56,** 89-101.

438. Selvamalar,C., Vijayanand,P., Penlidis,A., and Nanjundan,S. (2004) Homopolymer and copolymers of 4-benzyloxycarbonylphenyl acrylate with glycidyl methacrylate: Synthesis, characterization, reactivity ratios, and application as adhesive for leather. *Journal of Applied Polymer Science* **91,** 3604-3612.

439. Senel,S., Rzaev,Z., and Piskin,E. (2003) Copolymerization of N-phenylmaleimide with 2-hydroxyethyl and ethyl methacrylates. *Polymer International* **52,** 713-721.

440. Seno,A., Uno,T., Kubo,M., and Itoh,T. (2003) Synthesis and Polymerization of Novel Quinone Methide Ketals. *Polymer Bulletin* **50,** 1-8.

441. Senthilkumar,U., Balaji,R., and Nanjundan,S. (2001) Copolymerization of 2-(N-phthalimido)ethyl methacrylate with glycidyl methacrylate: synthesis, characterization, and monomer reactivity ratios. *Journal of Applied Polymer Science* **81,** 96-103.

442. Senthilkumar,U., Balaji,R., Prasath,R., and Nanjundan,S. (2001) Synthesis and characterization of hom- and copolymer of 2-(N-phthalimido)ethyl methacrylate and styrene. *Journal of Macromolecular Science, Pure and Applied Chemistry* **A38,** 67-78.

443. Senthilkumar,U., Ganesan,K., and Reddy,B. (2003) Synthesis, Characterization and Reactivity Ratios of Phenylethyl Acrylate/Methacrylate Copolymers. *Journal of Polymer Research* **10,** 21-29.

444. Shah,B., Patel,M., and Patel,R. (2004) Copolymers of 2,4-dichlorophenyl methacrylate with butyl methacrylate and their application as biocides. *International Journal of Polymeric Materials* **53,** 609-620.

445. Shaikh,S., Puskas,J., and Kaszaz,G. (2004) A new high throughput approach to measure copolymerization reactivity ratios using real time FTIR monitoring. *Journal of Polymer Science Part A: Polymer Chemistry* **42,** 4084-4100.

446. Shan,G., Weng,Z., Huang,Z., and Pan,Z. (2000) Reactivity ratios for copolymerization with the participation of a charge-transfer complex. *Chinese Journal of Polymer Science* **18,** 423-430.

447. Sharma,C. and Srivastava,A. (2003) Radical copolymerization of limonene with acrylonitrile: kinetics and mechanism. *Polymer-Plastics Technology and Engineering* **42,** 485-502.

448. Sharma,C. and Srivastava,A. (2003) Alternating copolymers of limonene with methyl methacrylate: Kinetics and mechanism. *Journal of Macromolecular Science, Pure and Applied Chemistry* **A40,** 593-603.

449. Sharma,S. and Srivastava,A. (2004) Synthesis and characterization of copolymers of limonene with styrene initiated by azobisisobutyronitrile. *European Polymer Journal* **40,** 2235-2240.

450. Sharma,S. and Srivastava,A. (2004) Synthesis and characterization of a terpolymer of limonene, styrene, and methyl methacrylate via a free-radical route. *Journal of Applied Polymer Science* **91,** 2343-2347.

451. Shawki,S. and Hamielec,A. (1979) Estimation of the Reactivity Ratios in the Copolymerization of Acrylic Acid and Acrylamide from Composition-Conversion Measurements by an Improved Nonlinear Least-Squares Method. *Journal of Applied Polymer Science* **23,** 3155-3166.

452. Shi,L., Wan,D., and Huang,J. (2000) Controllability of a Radical Copolymerization of a Maleimide and Ethyl a-(n-Propyl)acrylate Using 1,1,2,2-Tetraphenyl-1,2-bis(trimethylsilyloxy) Ethane as Initiator. *Journal of Polymer Science Part A: Polymer Chemistry* **38,** 2872-2878.

453. Shiho,H. and Desimone,J. (2000) Radical Polymerizations of a Silicone-Containing Acrylic Monomer in Supercritical Carbon Dioxide. *Journal of Polymer Science Part A: Polymer Chemistry* **38,** 3100-3105.

454. Shiho,H. and Desimone,J. (2000) Preparation of Silicone-Graft Copolymers by Homogeneous Radical Copolymerization in Supercritical Carbon Dioxide. *Journal of Polymer Science Part A: Polymer Chemistry* **38,** 1139-1145.

455. Shinoda,H., Miller,P., and Matyjaszewski,K. (2001) Improving the Structural Control of Graft Copolymers by Combining ATRP with the Macromonomer Method. *Macromolecules* **34,** 3186-3194.

456. Shu,W., Perng,L., Chin,W., and Hsu,C. (2003) Synthesis and properties of poly(styrene-co-phosphonate-containing maleimide). *Journal of Macromolecular Science, Pure and Applied Chemistry* **A40,** 897-913.

457. Shukla,A. and Srivastava,A. (2002) Terpolymerization of linalool, styrene, and methyl methacrylate: synthesis, characterization, and a kinetic study. *Polymer-Plastics Technology and Engineering* **41,** 777-793.

458. Shukla,A. and Srivastava,A. (2003) Free radical copolymerization of acrylamide and linalool with functional group as pendant. *High Performance Polymers* **15,** 243-257.

459. Shukla,A. and Srivastava,A. (2003) Kinetics and mechanism of copolymerization of linalool with acrylonitrile. *Journal of Macromolecular Science, Pure and Applied Chemistry* **A40,** 61-80.

460. Shukla,A. and Srivastava,A. (2004) Synthesis and characterization of functional copolymer of Linalool and vinyl acetate: a kinetic study. *Journal of Applied Polymer Science* **92,** 1134-1143.

461. Shukla,P. and Srivastava,A. (1994) Synthesis, characterization and kinetic studies of styrene-methylmethacrylate-acrylonitrile terpolymer initiated by styrene-arsenic sulfide complex. *Macromolecular Reports* **A31 (SUPPLS. 3&4),** 315-325.

462. Sideridou-Krayannidou,I. and Seretoudi,G. (1999) Synthesis and characterization of copolymers of N-vinylcarbazole and N,N-dimethylaminoethyl acrylate. *Polymer* **40,** 4915-4922.

463. Smith,B. and Klier,J. (1998) Determination of monomer reactivity ratios for copolymerizations of methacrylic acid with poly(ethylene glycol) monomethacrylate. *Journal of Applied Polymer Science* **68,** 1019-1025.

464. Song,Z., Li,H., and Zhu,X. (2003) Synthesis and thermal properties of a new cholic acid-containing copolymer. *Chinese Journal of Polymer Science* **21,** 521-526.

465. Souzy,R., Guiot,J., Ameduri,B., Boutevin,B., and Paleta,O. (2003) Unexpected Alternating Copolymerization of Vinylidene Fluoride Incorporating Methyl Trifluoroacrylate. *Macromolecules* **36,** 9390-9395.

466. Souzy,R., Ameduri,B., and Boutevin,B. (2004) Radical copolymerization of a-trifluoromethylacrylic acid with vinylidene fluoride and vinylidene fluoride/hexafluoropropene. *Macromolecular Chemistry and Physics* **205,** 476-485.

467. Soykan,C., Coskun,M., and Ahmedzade,M. (2000) Synthesis and characterization of phenacyl methacrylate-acrylonitrile copolymers and determination of monomer reactivity ratios. *Polymer International* **49,** 479-484.

468. Soykan,C. and Erol,I. (2003) Free-radical copolymerization of [(4-isopropyl phenyl) oxycarbonyl] methyl methacrylate with acrylonitrile and methyl methacrylate . *Journal of Applied Polymer Science* **88,** 2331-2338.

469. Soykan,C. and Erol,I. (2003) Synthesis, spectral and thermal properties of hom- and copolymers of 2-[(5-methylisoxazol-3-yl)amino]-2-oxo-ethyl methacrylate with styrene and methyl methacrylate and determination of monomer reactivity ratios. *European Polymer Journal* **39,** 2261-2270.

470. Soykan,C. and Erol,I. (2004) Copolymerization of 2-(4-tert-butylphenoxy)-2-oxo-ethyl Methacrylate with Metyl Methacrylate and Styrene: Synthesis, Characterization, and Monomer Reactivity Ratios. *Journal of Polymer Research* **11,** 53-63.

471. Soykan,C. and Erol,I. (2004) Radical copolymerization of N-(4-acetylphenyl)-maleimide and styrene: Monomer reactivity ratios and thermal properties. *Journal of Applied Polymer Science* **91,** 964-970.

472. Srivastava,A. and Pandey,P. (2001) Benzoyl peroxide-p-acetylbenzylidenetriphenyl arsoniumylide initiated copolymerization of citronellol and styrene. *Polymer International* **50,** 937-945.

473. Srivastava,A., Kamal,M., Kaur,M., Pandey,S., Daniel,N., Chaurasia,A., and Pandey,P. (2002) Terpolymerization: A Review. *Journal of Polymer Research* **9,** 213-220.

474. Stancu,I., Filmon,R., Cincu,C., Marculescu,B., Zaharia,C., Tourmen,Y., Basle,M., and Chappard,D. (2004) Synthesis of methacryloyloxyethyl phosphate copolymers and in vitro calcification capacity. *Biomaterials* **25,** 205-213.

475. Stanek,L., Heilmann,S., and Gleason,W. (2003) Synthesis and Monomer Reactivity Ratios of Methyl Methacrylate and 2-Vinyl-4,4'-dimethylazlactone Copolymers. *Journal of Polymer Science Part A: Polymer Chemistry* **41,** 3027-3037.

476. Stergiou,G., Dousikos,P., and Pitsikalis,M. (2002) Radical copolymerization of styrene and alkyl methacrylates: monomer reactivity ratios and thermal properties. *European Polymer Journal* **38,** 1963-1970.

477. Stewart,W., Caracotsios,M., and Sorensen,J. (1992) Parameter estimation from multiresponse data. *AIChE Journal* **38,** 641-650.

478. Subramanian,K. and Reddy,A. (2002) Synthesis and characterization of photosensitive copolymers of 4-(4'-nitrocinnamoyl)phenyl acrylate and glycidyl methacrylate. *Journal of Applied Polymer Science* **86,** 3264-3270.

479. Sun,L., Zhuo,R., and Liu,Z. (2003) Synthesis and Enzymatic Degradation of 2-Methylene-1,3-dioxepane and Methyl Acrylate Copolymers. *Journal of Polymer Science Part A: Polymer Chemistry* **41,** 2898-2904.

480. Sundarrajan,S., Ganesh,K., and Srinivasan,K. (2003) Synthesis, characterization, and reactivity ratio studies on new sulfide copolymers containing ethylbenzene units. *Polymer* **44,** 61-71.

481. Sünbül,D., Catalgil-Giz,H., Giz,A., and Reed,W. (2004) An Error-in-Variables Method for Determining Reactivity Ratios by On-Line Monitoring of Copolymerization Reactions . *Macromolecular Theory and Simulations* **13,** 162-168.

482. Szczubialka,K., Loska,R., and Nowakowska,M. (2001) Temperature-Induced Aggregation of the Copolymers of N-Isopropylacrylamide and Sodium 2-Acrylamido-2-methyl-1-propanesulphonate in Aqueous Solutions. *Journal of Polymer Science Part A: Polymer Chemistry* **39,** 2784-2792.

483. Taden,A., Tait,A., and Kraft,A. (2002) Synthesis and polymerization of 5-(methacrylamido)tetrazole, a water-soluble acidic monomer. *Journal of Polymer Science Part A: Polymer Chemistry* **40,** 4333-4343.

484. Talpur,M., Oracz,P., and Kaim,A. (1996) Study of methyl methacrylate-acrylamide copolymerization system in cyclohexanone in the absence of conventional radical initiator. *Polymer* **37,** 4149-4154.

485. Tanaka,H., Takeichi,T., and Hongo,T. (1997) Radical Homo- and Copolymerization of Methyl a-Trifluoroactoxyacrylate. *Journal of Polymer Science Part A: Polymer Chemistry* **35,** 3537-3541.

486. Thamizharasi,S., Gnanasundaram,P., and Reddy,B. (1997) Copolymerization of 4-acetylphenyl acrylate with methyl methacrylate and butyl methacrylate: synthesis, characterization and reactivity ratios. *European Polymer Journal* **33,** 1487-1494.

487. Thamizharasi,S., Gnanasundaram,P., and Reddy,B. (1997) Copolymerization of 4-nitrophenyl acrylate with glycidyl methacrylate: synthesis, characterization, and reactivity ratios. *Journal of Applied Polymer Science* **65,** 1285-1291.

488. Thamizharasi,S., Gnanasundaram,P., and Balasubramanian,S. (1999) Copolymerization of 4-nitrophenyl acrylate (NPA) with methyl methacrylate (MMA): synthesis, characterization and reactivity ratios. *Journal of Macromolecular Science, Pure and Applied Chemistry* **A36,** 1949-1966.

489. Thamizharasi,S., Srinivas,G., Sulochana,N., and Reddy,B. (1999) Copolymerization of 4-chlorophenyl acrylate with methyl acrylate: synthesis, characterization, reactivity ratios, and their applications in the leather industry. *Journal of Applied Polymer Science* **73,** 1153-1160.

490. Thamizharasi,S. and Reddy,B. (2001) Copolymerization of N-substituted maleimide with alkyl acrylate and its industrial applications. *Journal of Applied Polymer Science* **80,** 1870-1879.

491. Thamizharasi,S., Gnanasundaram,P., and Balasubramanian,S. (2003) Synthesis, characterization, and reactivity ratios of copolymers derived from 4-nitrophenyl acrylate and n-butyl methacrylate. *Journal of Applied Polymer Science* **88,** 1817-1824.

492. Tidwell,P. and Mortimer,G. (1965) An improved method of calculating copolymer reactivity ratios. *Journal of Polymer Science, Polymer Chemistry* **3,** 369-387.

493. Tritto,I., Boggioni,L., Jansen,J., Thorshaug,K., Sacchi,M., and Ferro,D. (2002) Ethylene-Norbornene Copolymers from Metallocene-Based Catalysts: Microstructure at Tetrad Level and Reactivity Ratios. *Macromolecules* **35,** 616-623.

494. Tronc,F., Li,M., Lu,J., Winnik,M., Kaul,B., and Graciet,J. (2003) Fluorescent polymer particles by emulsion and miniemulsion polymerization. *Journal of Polymer Science Part A: Polymer Chemistry* **41,** 766-778.

495. Valdebenito,N., Diaz,F., Tagle,L., Gargallo,L., and Radic,D. (2001) Functionalized copolymers. Methyl methacrylate-(4-hexyloxy-1-phenyloxycarbonyl)-1,4-phenylene ethylene copolymers: synthesis, monomer reactivity ratios, thermal stability and solubility. *European Polymer Journal* **37,** 1753-1758.

496. Van Den Brink,M., Van Herk,A., and German,A. (1999) Nonlinear regression by visualization of the sum of residual space applied to the integrated copolymerization equation with errors in all variables. I. Introduction of the model, simulations and design of experiments . *Journal of Polymer Science Part A: Polymer Chemistry* **37,** 3793-3803.

497. Van Den Brink,M., Smulders,W., Van Herk,A., and German,A. (1999) Nonlinear regression by visualization of the sum of residual space applied to the integrated copolymerization equation with errors in all variables. II. Application to the system methyl methacrylate-a-methylene-a-butyrolactone using on-line Raman spectroscopy . *Journal of Polymer Science Part A: Polymer Chemistry* **37,** 3804-3816.

498. Van Der Meer,R., Linssen,H., and German,A. (1978) Improved methods of estimating monomer reactivity ratios in copolymerization by considering experimental errors in both variables. *Journal of Polymer Science, Polymer Chemistry Edition* **16,** 2915-2930.

499. Vazquez,B., Gurruchaga,M., Goni,I., and Roman,J. (1997) Non-ionizable Polyacrylic Hydrogels Sensitive to pH for Biomedical Applications. *Polymer International* **43,** 182-186.

500. Venkatesh,R., Harrison,S., Haddleton,D., and Klumperman,B. (2004) Olefin Copolymerization via Controlled Radical Polymerization: Copolymerization of Acrylate and 1-Octene. *Macromolecules* **37,** 4406-4416.

501. Veron,L., Ganee,A., Charreyre,M., Pichot,C., and Delair,T. (2004) New hydrolyzable pH-responsive cationic polymers for gene delivery: A preliminary study. *Macromolecular Bioscience* **4,** 431-444.

502. Vijayanand,P., Arunprasath,R., Balaji,R., and Nanjundan,S. (2002) Synthesis, spectral properties, and thermal properties of homo- and copolymers of 3,5-dimethylphenyl acrylate with glycidyl methacrylate and determination of reactivity ratios. *Journal of Applied Polymer Science* **85,** 2261-2270.

503. Vijayanand,P., Penlidis,A., Radhakrishnan,S., and Nanjundan,S. (2002) Copolymers of 3,5-dimethylphenyl methacrylate and methyl methacrylate: Synthesis, characterization, and determination of reactivity ratios. *Journal of Macromolecular Science, Pure and Applied Chemistry* **A39,** 591-608.

504. Vijayanand,P., Radhakrishnan,S., Prasath,R., and Nanjundan,S. (2002) Synthesis and characterization of homopolymer of 3,5-dimethylphenyl methacrylate and its copolymers with glycidyl methacrylate. *European Polymer Journal* **38,** 1319-1326.

505. Vijayanand,P., Selvamalar,C., Penlidis,A., and Nanjundan,S. (2003) Copolymers of 3,5-dimethylphenyl acrylate and methyl methacrylate: synthesis, characterization and determination of monomer reactivity ratios. *Polymer International* **52,** 1856-1862.

506. Vijayanand,P., Penlidis,A., and Nanjundan,S. (2003) Copolymerization of 4-benzyloxycarbonylphenyl acrylate with methyl methacrylate: Synthesis, characterization, and determination of reactivity ratios. *Journal of Macromolecular Science, Pure and Applied Chemistry* **A40,** 125-140.

507. Vijayaraghavan,P. and Reddy,B. (1996) Copolymerization of 4-methyl- and 4-methoxyphenyl acrylates with glycidyl methacrylate: synthesis, characterization, reactivity ratios, and applications as adhesives for the leather industry. *Journal of Applied Polymer Science* **61,** 935-943.

508. Vijayaraghavan,P. and Reddy,B. (1999) 4-chlorophenyl acrylate and glycidyl methacrylate copolymers: Synethsis, characterization, reactivity ratios and application. *Journal of Macromolecular Science, Pure and Applied Chemistry* **A36,** 1181-1196.

509. Vijayaraghavan,R., Surianarayanan,M., and Raghavan,K. (2003) Studies on synthesis and characterization of charge transfer polymerization of styrene and alkyl methacrylates. *Journal of Macromolecular Science, Pure and Applied Chemistry* **A40,** 1057-1080.

510. Virtanen,J. and Tenhu,H. (2001) Studies on Copolymerization of N-Isopropylacrylamide and Glycidyl Methacrylate. *Journal of Polymer Science Part A: Polymer Chemistry* **39,** 3716-3725.

511. Vosloo,J., Tonge,M., Fellows,C., D'Agosto,F., Sanderson,R., and Gilbert,R. (2004) Synthesis of Comblike Poly(butyl methacrylate) Using Reverisble Addition-Fragmentation Chain Transfer and an Activated Ester. *Macromolecules* **37,** 2371-2382.

512. Walling,C. and Briggs,E. (1945) Copolymerization. III. Systems Containing More than Two Monomers. *Journal of American Chemical Society* **67,** 1774-1778.

513. Wamsley,A., Jasti,B., Phiasivongsa,P., and Li,X. (2004) Synethsis of Random Terpolymers and Determination of Reactivity Ratios of N-Carboxyanhydrides of Leucine, b-Benzyl Aspartate, and Valine. *Journal of Polymer Science Part A: Polymer Chemistry* **42,** 317-325.

514. Wan,D., Shi,L., and Huang,J. (1998) Spontaneous Alternating Copolymerization of N-Phenylmaleimide with Ethyl a-Phenylacrylate. *Journal of Polymer Science Part A: Polymer Chemistry* **36,** 2927-2931.

515. Wan,D. and Huang,J. (1999) Transformation of Copolymerization Mechanism of N-phenyl Maleimide and Ethyl Phenylacrylate in the Mixture of Dioxane and Pyridine. *Journal of Polymer Science Part A: Polymer Chemistry* **37,** 2755-2761.

516. Wang,T., Leamen,M., McManus,N., and Penlidis,A. (2004) Copolymerization of alpha-methyl styrene with butyl acrylate: Parameter estimation considerations. *Journal of Macromolecular Science, Pure and Applied Chemistry* **A41**.

517. Wang,W., Kolodka,E., Zhu,S., and Hamielec,A. (1999) Continuous Solution Copolymerization of Ethylene and Octene-1 with Constrained Geometry Metallocene Catalyst. *Journal of Polymer Science Part A: Polymer Chemistry* **37,** 2949-2957.

518. Wang,X., Zhuo,R., and Liu,L. (2001) Synthesis and characterization of novel biodegradable poly(carbonate-co-phosphate)s. *Polymer International* **50,** 1175-1179.

519. Wen,J. and Zhuo,R. (1998) Preparation and Characterization of Poly(D,L-lactide-co-ethylene methyl phosphate). *Polymer International* **47,** 503-509.

520. Wharry,S. (2004) Randomness in Ziegler-Natta olefin copolymerizations as determined by 13C-NMR spectroscopy-the influence of chain heterogeneity. *Polymer* **45,** 2985-2989.

521. Wickel,H. and Agarwal,S. (2003) Synthesis and Characterization of Copolymers of 5,6-Benzo-2-methylene-1,3-dioxepane and Styrene. *Macromolecules* **36,** 6152-6159.

522. Wickel,H., Agarwal,S., and Greiner,A. (2003) Homopolymers and Random Copolymers of 5,6-Benzo-2-methylene-1,3-dioxepane and Methyl Methacrylate: Structural Characterization Using 1D and 2D NMR. *Macromolecules* **36,** 2397-2403.

523. Wiles,K., Bhanu,V., Pasquale,A., Long,T., and McGrath,J. (2004) Monomer Reactivity Ratios for Acrylonitrile-Methyl Acrylate Free-Radical Copolymerization. *Journal of Polymer Science Part A: Polymer Chemistry* **42,** 2994-3001.

524. Williamson,D., Buchanan,T., Elkins,C., and Long,T. (2004) Synethsis of Block Copolymers Based on the Alternating Anionic Copolymerization of Styrene and 1,3-Cyclohexadiene. *Macromolecules* **37,** 4505-4511.

525. Wu,L. and Sheares,V. (2001) Polar, Functionalized Diene-Based Materials. V. Free-Radical Polymerization of 2-[(N-Benzyl-N-metylamino)methyl]-1,3-butadiene and Copolymerization with Styrene. *Journal of Polymer Science Part A: Polymer Chemistry* **39,** 3227-3238.

526. Wu,Z., Cao,L., and Pittman,C. (1998) Cationic Copolymerization of Cyclic Ketene Acetals: The Effect of Substituents on Reactivity. *Journal of Polymer Science Part A: Polymer Chemistry* **36,** 861-871.

527. Xie,H., Guo,J., Yu,G., and Zu,J. (2001) Ring-opening polymerization of epichlorohydrin and its copolymerization with other alkylene oxides by quaternanry catalyst system. *Journal of Applied Polymer Science* **80,** 2446-2454.

528. Xu,G. and Cheng,D. (2001) Hom- and Copolymerization of 4-Methyl-1-pentene and Ethylene with Group 4 ansa-Cyclopentadienylamido Complexes. *Macromolecules* **34,** 2040-2047.

529. Xu,J., Zhu,Y., Fan,Z., and Feng,L. (2001) Copolymerization of Propylene with Various Higher a-Olefins Using Silica-Supported rac-Me$_{\mathrm{2Si(Ind)2ZrCl2}}$. *Journal of Polymer Science Part A: Polymer Chemistry* **39,** 3294-3303.

530. Xu,X., Goh,H., Siow,K., and Gan,L. (2001) Synthesis of Polymerizable Anionic Surfactants and Their Emulsion Copolymerization with Styrene. *Langmuir* **17,** 6077-6085.

531. Xue,W., Champ,S., and Huglin,M. (2000) Observations on some copolymerizations involving N-isopropylacrylamide. *Polymer* **41,** 7575-7581.

532. Yadav,S. and Srivastava,A. (2002) Kinetics and Mechanism of Copolymerization of alpha-terpineol with Methylmethacrylate in Presence of Azobisisobutyronitrile as an Initiator. *Journal of Polymer Research* **9,** 265-270.

533. Yadav,S. and Srivastava,A. (2003) Copolymerization of a-Terpineol with Styrene: Synthesis and Characterization. *Journal of Polymer Science Part A: Polymer Chemistry* **41,** 1700-1707.

534. Yaegashi,T., Takeshita,H., Takenaka,K., and Shiomi,T. (2003) Polymerization of 1,3-dienes with functional groups. II. Free-radical polymerization of N-(2-methylene-3-butenoyl)piperidine. *Journal of Polymer Science Part A: Polymer Chemistry* **41,** 1545-1552.

535. Yaegashi,T., Yodoya,S., Nakamura,M., Takeshita,H., Takenaka,K., and Shiomi,T. (2004) Polymerization of 1,3-Dienes with Functional Groups. III. Free-Radical Polymerization of N,N-Diethyl-2-methylene-3-butenamide. *Journal of Polymer Science Part A: Polymer Chemistry* **42,** 999-1007.

536. Yamada,B., Hirano,T., and Kobatake,S. (2003) Copolymerization of methyl a-(chloromethyl)acrylate with styrene accompanied by addition-fragmentation chain transfer. *Polymer Bulletin* **49,** 305-312.

537. Yamada,K., Nakano,T., and Okamoto,Y. (2000) Free-Radical Copolymerization of Vinyl Esters Using Fluoroalcohols as Solvents: The Solvent Effect on the Monomer Reactivity Ratio. *Journal of Polymer Science Part A: Polymer Chemistry* **38,** 220-228.

538. Yamada,K., Minoda,M., Fukuda,T., and Miyamoto,T. (2001) Amphiphilic Block and Statistical Copolymers with Pendant Glucose Residues: Controlled Synthesis by Living Cationic Polymerization and the Effect of Copolymer Architecture on Their Properties. *Journal of Polymer Science Part A: Polymer Chemistry* **39,** 459-467.

539. Yamamoto,K., Serizawa,T., Muraoka,Y., and Akashi,M. (2000) Synthesis and Functionalities of Poly(N-vinylalkylamide). XII. Syntheiss and Thermosensitive Property of Poly(vinylamine) Copolymer Prepared from Poly(N-vinylformamide-co-N-vinylisobutyramide). *Journal of Polymer Science Part A: Polymer Chemistry* **38,** 3674-3681.

540. Yamamoto,K., Serizawa,T., and Akashi,M. (2003) Synthesis and functionalities of poly(N-vinylalkylamide).XIV. Synthesis and thermosensitive properties of poly[(N-vinylamide)-co-(vinyl acetate)]s and their hydrogels. *Macromolecular Chemistry and Physics* **204,** 1027-1033.

541. Yan-Ming,G., Ting,W., Yin-Fang,Z., and Cai-Yuan,P. (2001) Atom transfer radical copolymerization of styrene and poly(THF) macromer. *Polymer* **42,** 6385-6391.

542. Yan,Z., Deng,Y., Zhang,D., and Yang,C. (2001) Synthesis and Characterization of Cationic Copolymers of Butylacrylate and [3-(Methacryloylamino)-propyl]trimethylammonium Chloride. *Journal of Polymer Science Part A: Polymer Chemistry* **39,** 1031-1039.

543. Yang,J., Yu,J., Li,M., Gu,Z., and Feng,X. (2002) Copolymerization and determination of monomer reactivity ratios of DL-lactide with 3-benzyloxymethyl-1,4-dioxane-2,5-dione. *Chinese Journal of Polymer Science* **20,** 413-417.

544. Yang,L., Liu,Y., Li,Y., Gao,J., Zhang,L., and Jin,R. (2004) Free-radical copolymerization and kinetic treatment of methyl methacrylate with N-p-tolymaleimide. *Journal of Applied Polymer Science* **91,** 867-870.

545. Ydens,I., Degree,P., Dubois,P., Libiszowski,J., Duda,A., and Penczek,S. (2003) Combining ATRP of methacrylates and ROP of L,L-dilactide and e-caprolactone. *Macromolecular Chemistry and Physics* **204,** 171-179.

546. Yoon,W., Lyoo,W., Ghim,H., Lee,J., Kim,J., and Kim,S. (2003) Effect of the copolycondensation temperature on the reactivities of bis(3-hydroxypropyl)terephthalate and bis(2-hydroxyethyl)terephthalate. *Journal of Applied Polymer Science* **89,** 1890-1895.

547. Zaldivar,C., del Sol,O., and Iglesias,G. (1997) On the preparation of acrylic acid/vinyl acetate copolymers with constant composition-1. Copolymerization reactivity ratios. *Polymer* **39,** 245-246.

548. Zerroukhi,A., Cincu,C., and Montheard,J. (1999) Substituted styrenes-maleic anhydride copolymers- Measurements of the reactivity ratios with high conversions and relations between molecular masses and viscosity. *Journal of Applied Polymer Science* **71,** 1447-1454.

549. Zetterlund,P., Tagashira,S., Izumi,K., Nagano,Y., Azukizawa,M., Yamazoe,H., Kumagai,M., and Yamada,B. (2002) Penultimate Unit Effects in Free Radical Copolymerization Studies Using the Individual Propagating Radical Concentrations from Electron Spin Resonance Spectroscopy. *Macromolecules* **35,** 8209-8215.

550. Zhang,C. and Easteal,A. (2003) Study of free-radical copolymerization of N-isopropylacrylamide with 2-acrylamido-2-methyl-1-propanesulphonic acid. *Journal of Applied Polymer Science* **88,** 2563-2569.

551. Zhang,H., Hong,K., Jablonsky,M., and Mays,J. (2003) Statistical radical copolymerization of styrene and methyl methacrylate in a room temperature ionic liquid. *Chemical Communications* 1356-1357.

552. Zhang,Q., Ni,X., Zhang,Y., and Shen,Z. (2001) Homopolymerization and copolymerization of isoprene and styrene with a neodymium catalyst using an alkylmagnesium cocatalyst. *Macromolecular Rapid Communications* **22,** 1493-1496.

553. Zhang,Q., Ni,X., and Shen,Z. (2002) Copolymerization of butadiene with styrene using a rare-earth metal compound- dialkylmagnesium- halohydrocarbon catalytic system. *Polymer International* **51,** 208-212.

554. Zhang,Z., Ying,S., Zhang,Q., and Xu,X. (2001) Well-Controlled Radical Copolymerization of Styrene with 2-[(Perfluorononenyl)oxy] Ethyl Methacrylate and Characterization of its Copolymers. *Journal of Polymer Science Part A: Polymer Chemistry* **39,** 2670-2676.

555. Zhao,Y., Jiang,J., Liu,H., Chen,C., and Xi,F. (2001) Atom Transfer Radical Copolymerization of N-Phenylmaleimide and Styrene Initiated with Dendritic Polyarylether 2-Bromoisobutyrate. *Journal of Polymer Science Part A: Polymer Chemistry* **39,** 3960-3966.

556. Zhao,Y., Liu,P., Liu,H., Jiang,J., Chen,C., and Xi,F. (2001) Quantitative determination of the contribution of charge-transfer complex in the microemulsion copolymerization of N-butyl maleimide and styrene. *Macromolecular Rapid Communications* **22,** 633-637.

557. Zhao,Y., Zhang,J., Jiang,J., Chen,C., and Xi,F. (2002) Atom Transfer Radical Copolymerization of N-Hexylmaleimide and Styrene in an Ionic Liquid. *Journal of Polymer Science Part A: Polymer Chemistry* **40,** 3360-3366.

558. Zhao,Y., Li,H., Liu,P., Liu,H., Jiang,J., and Xi,F. (2002) Reactivity ratios of free monomers and their charge-transfer complex in the copolymerization of N-butyl maleimide and styrene. *Journal of Applied Polymer Science* **83,** 3007-3012.

559. Zhao,Y., Jiang,J., Liu,H., Chen,C., and Xi,F. (2002) "Living"/controlled radical copolymerization of N-phenylmaleimide and styrene using Frechet-type dendritic initiators. *Science in China, Series B: Chemistry* **45,** 135-142.

560. Zhou,W., Kurth,M., Hsieh,Y., and Krochta,J. (1999) Synthesis and Thernal Properties of a Novel Lactose Containing Poly(N-isopropylacrylamide-co-acrylamidolactamine) Hydrogel. *Journal of Polymer Science Part A: Polymer Chemistry* **37,** 1393-1402.

561. Zhu,F., Yang,Y., Huang,Y., and Lin,S. (2001) Copolymerization of ethylene and butylene with monotitanocene/methyl aluminoxane as catalyst. *Macromolecular Chemistry and Physics* **202,** 1935-1940.

562. Ziaee,F. and Nekoomanesh,M. (1998) Monomer reactivity ratios of styrene-butyl acryalte copolymers at low and high conversions. *Polymer* **39,** 203-207.

563. Ziegler,M. and Matyjaszewski,K. (2001) Atom transfer radical copolymerization of methyl methacrylate and n-butyl acrylate. *Macromolecules* **34,** 415-424.

# Appendix A

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# MATLAB Program Guide for Copolymer Reactivity Ratio Estimation

The programs used to estimate the reactivity ratios using an error in all variables model for copolymer systems using either instantaneous triad fractions and/or copolymer composition data sets. The parameter estimation work conducted in this thesis was carried out in MATLAB Version 6.5 Release 13. MATLAB is available from the following address:

**The MathWorks Inc.**
3 Apple Hill Drive
Natick, MA 01760-2098
Web: www.mathworks.com
Phone: (508) 647 7000
Fax: (508) 647 7001

The parameter estimation MATLAB files estimate, using EVM, the copolymer reactivity ratios for copolymer composition data or triad fractions/normalized NMR peak area data with either the instantaneous or the cumulative copolymer models.

The programs are in separate MATLAB folders depending on whether the analysis uses an additive or multiplicative error structure and the data set used (composition and/or triad fractions). However, in order for the program files to run correctly, the following files need to be present in the same folder for the reactivity ratio estimation using EVM;

Datafile.txt
BFCalc.m
ZCalc.m
INNER.m
EVM.m
EVMDriver.m
JCExact.m
JCEllipse.m

The MATLAB program can be obtained on CD from either Prof T. A. Duever or Prof. A. Penlidis at the following address:

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