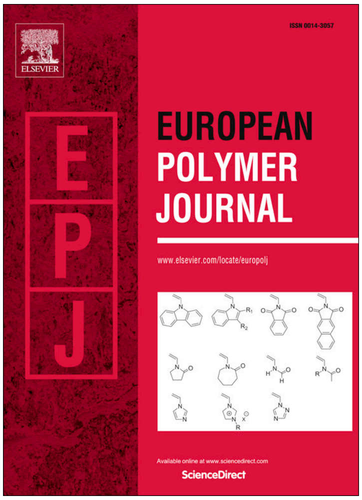

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Alison J. Scott, Alexander Penlidis

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Binary vs. Ternary Reactivity Ratios: Appropriate Estimation Procedures with Terpolymerization Data

*Alison J. Scott, Alexander Penlidis**

Institute for Polymer Research, Department of Chemical Engineering, University of Waterloo, 200 University Avenue West, Waterloo, Ontario, N2L 3G1, Canada;
E-mail: penlidis@uwaterloo.ca

Abstract: There is a widely accepted analogy between copolymerization and terpolymerization mechanisms that has allowed researchers to use reactivity ratios obtained for binary pairs (from copolymerization experiments) in models dealing with terpolymerizations. However, binary reactivity ratios are not always applicable to terpolymerization systems; using the binary-ternary analogy (even as an approximation) requires making considerable assumptions about the system. When binary reactivity ratios are used to describe ternary systems, the consequences may include substantial differences in reactivity ratio estimates, poor composition prediction performance, and incorrect determination of product (terpolymer) characteristics. Experimental results and reactivity ratio estimation (via the error-in-variables-model) for the terpolymerization of 2-acrylamido-2-methylpropane sulfonic acid (AMPS), acrylamide (AAm) and acrylic acid (AAc) (and associated copolymers) are compared, all other conditions being equal.

Keywords: copolymerization; design of experiments; error-in-variables-model (EVM); polymerization kinetics; reactivity ratio estimation; terpolymerization.

1. Introduction

Reactivity ratios are crucial to the study of the kinetics of multicomponent polymerization systems. Terpolymerization systems are frequently utilized in industry and academia, yet there is a considerable lack of reactivity ratio estimation studies for such systems. This is partially due to the structural complexity of the terpolymer composition model, the Alfrey-Goldfinger (A-G) model (Equation 1). F_i is the instantaneous mole fraction of monomer i incorporated (bound) in the terpolymer, r_{ij} are the monomer reactivity ratios relating radical i with monomer j, and f_i is the corresponding mole fraction of unreacted monomer i (often referred to as the feed mole fraction). Equation 1 relates instantaneous (not cumulative) terpolymer composition properties.

$$\frac{F_1}{F_2} = \left(\frac{f_1}{f_2}\right)\left(\frac{f_1/r_{31}r_{21} + f_2/r_{21}r_{32} + f_3/r_{31}r_{23}}{f_1/r_{12}r_{31} + f_2/r_{12}r_{32} + f_3/r_{32}r_{13}}\right)\left(\frac{f_1 + f_2/r_{12} + f_3/r_{13}}{f_2 + f_1/r_{21} + f_3/r_{23}}\right) \tag{1a}$$

$$\frac{F_1}{F_3} = \left(\frac{f_1}{f_3}\right)\left(\frac{f_1/r_{31}r_{21} + f_2/r_{21}r_{32} + f_3/r_{31}r_{23}}{f_1/r_{13}r_{21} + f_2/r_{23}r_{12} + f_3/r_{13}r_{23}}\right)\left(\frac{f_1 + f_2/r_{12} + f_3/r_{13}}{f_3 + f_1/r_{31} + f_2/r_{32}}\right) \tag{1b}$$

$$\frac{F_2}{F_3} = \left(\frac{f_2}{f_3}\right)\left(\frac{f_1/r_{12}r_{31}+f_2/r_{12}r_{32}+f_3/r_{32}r_{13}}{f_1/r_{13}r_{21}+f_2/r_{23}r_{12}+f_3/r_{13}r_{23}}\right)\left(\frac{f_2+f_1/r_{21}+f_3/r_{23}}{f_3+f_1/r_{31}+f_2/r_{32}}\right) \tag{1c}$$

The Alfrey-Goldfinger model provides ratios of the instantaneous terpolymer compositions (mole fractions), which means that the terpolymer mole fractions are not presented explicitly. In a recent study, Kazemi et al. [1] illustrated the advantages of using a recast version of the Alfrey-Goldfinger model, which provides direct relationships between the individually measured mole fractions (instead of the ratios shown in Equation 1). The recast version, presented in Equation 2, eliminates symmetry issues and ensures that the error structure of the measured responses is not distorted. This significantly improves the reliability of the parameter estimates (that is, the ternary reactivity ratios r_{ij}).

$$F_1 - \frac{f_1\left(\frac{f_1}{r_{21}r_{31}}+\frac{f_2}{r_{21}r_{32}}+\frac{f_3}{r_{31}r_{23}}\right)\left(f_1+\frac{f_2}{r_{12}}+\frac{f_3}{r_{13}}\right)}{f_1\left(\frac{f_1}{r_{21}r_{31}}+\frac{f_2}{r_{21}r_{32}}+\frac{f_3}{r_{31}r_{23}}\right)\left(f_1+\frac{f_2}{r_{12}}+\frac{f_3}{r_{13}}\right)+f_2\left(\frac{f_1}{r_{12}r_{31}}+\frac{f_2}{r_{21}r_{32}}+\frac{f_3}{r_{13}r_{32}}\right)\left(f_2+\frac{f_1}{r_{21}}+\frac{f_3}{r_{23}}\right)+f_3\left(\frac{f_1}{r_{13}r_{21}}+\frac{f_2}{r_{23}r_{12}}+\frac{f_3}{r_{13}r_{23}}\right)\left(f_3+\frac{f_1}{r_{31}}+\frac{f_2}{r_{32}}\right)} = 0 \tag{2a}$$

$$F_2 - \frac{f_2\left(\frac{f_1}{r_{12}r_{31}}+\frac{f_2}{r_{21}r_{32}}+\frac{f_3}{r_{13}r_{32}}\right)\left(f_2+\frac{f_1}{r_{21}}+\frac{f_3}{r_{23}}\right)}{f_1\left(\frac{f_1}{r_{21}r_{31}}+\frac{f_2}{r_{21}r_{32}}+\frac{f_3}{r_{31}r_{23}}\right)\left(f_1+\frac{f_2}{r_{12}}+\frac{f_3}{r_{13}}\right)+f_2\left(\frac{f_1}{r_{12}r_{31}}+\frac{f_2}{r_{21}r_{32}}+\frac{f_3}{r_{13}r_{32}}\right)\left(f_2+\frac{f_1}{r_{21}}+\frac{f_3}{r_{23}}\right)+f_3\left(\frac{f_1}{r_{13}r_{21}}+\frac{f_2}{r_{23}r_{12}}+\frac{f_3}{r_{13}r_{23}}\right)\left(f_3+\frac{f_1}{r_{31}}+\frac{f_2}{r_{32}}\right)} = 0 \tag{2b}$$

$$F_3 - \frac{f_3\left(\frac{f_1}{r_{13}r_{21}}+\frac{f_2}{r_{23}r_{12}}+\frac{f_3}{r_{13}r_{23}}\right)\left(f_3+\frac{f_1}{r_{31}}+\frac{f_2}{r_{32}}\right)}{f_1\left(\frac{f_1}{r_{21}r_{31}}+\frac{f_2}{r_{21}r_{32}}+\frac{f_3}{r_{31}r_{23}}\right)\left(f_1+\frac{f_2}{r_{12}}+\frac{f_3}{r_{13}}\right)+f_2\left(\frac{f_1}{r_{12}r_{31}}+\frac{f_2}{r_{21}r_{32}}+\frac{f_3}{r_{13}r_{32}}\right)\left(f_2+\frac{f_1}{r_{21}}+\frac{f_3}{r_{23}}\right)+f_3\left(\frac{f_1}{r_{13}r_{21}}+\frac{f_2}{r_{23}r_{12}}+\frac{f_3}{r_{13}r_{23}}\right)\left(f_3+\frac{f_1}{r_{31}}+\frac{f_2}{r_{32}}\right)} = 0 \tag{2c}$$

Even with an improved model for terpolymer composition, the bigger issue associated with ternary systems is a widely accepted analogy between copolymerization and terpolymerization mechanisms. Many researchers [2-13] have used binary reactivity ratios (obtained from copolymerization experiments) in models dealing with terpolymerizations. Although this approximation has been successfully used in some instances (see, for example, [6-8, 13]), it is not always accurate [2-4, 10]. Using binary reactivity ratios to describe ternary systems effectively ignores the presence of the third comonomer, which will inevitably change the reaction conditions (and may ultimately affect the polymerization kinetics). The effect of the third comonomer ultimately depends on its chemical identity and the overall polymerization ‘recipe’ to which it is being added. At the very least, monomer concentration may vary, potentially affecting rate of polymerization and molecular weight averages. For recipes similar to the case study presented in Sections 3 and 4, there can also be a significant electrostatic effect (consider how an additional charged monomer can change the ionic strength of the system). Incorporation (propagation) of a particular monomer may have occurred quickly and easily in an associated copolymer system, but the introduction of a third monomer may result in competitive monomer addition. Thus, using this type of binary analogy for ternary systems calls into question the accuracy of the reactivity ratios, which in turn affects model prediction performance of terpolymer product characteristics.

Previously, it has been suggested that ternary reactivity ratios should be estimated directly from terpolymer composition data, as opposed to using the related binary copolymer reactivity ratios [1]. However, direct comparison between binary and ternary systems has never been possible; differences in reactivity ratios may have been due to numerous other factors including reaction conditions and parameter estimation methods. Now, experimental binary and ternary data are directly compared for the 2-acrylamido-2-methylpropane sulfonic acid (AMPS)/acrylamide (AAm)/acrylic acid (AAc) system, based on recent copolymerization studies by Riahinezhad et al. [14] and Scott et al. [15], and an associated terpolymerization study [16]. To our knowledge, this is the first time that binary and ternary reactivity ratios have been compared directly, for the same system, with all other variables kept constant; to the extent possible, only the number of comonomers (two or three) and the feed composition were varied. Therefore, a direct comparison of binary and ternary reactivity ratios is finally possible.

2. Reactivity Ratio Estimation

Problems associated with reactivity ratio estimation and design of experiments for copolymer and terpolymer systems have largely been resolved using the error-in-variables-model (EVM), which was discussed in detail by Kazemi et al. [17], and will be reviewed briefly in the current paper.

The EVM technique is one of the most powerful non-linear regression approaches, as it considers all sources of experimental error (both in the independent and dependent variables) [18-20]. In using EVM, the experimenter is required to consider all sources of error, and the program provides estimates of the true values of the independent variables involved in the model along with the parameter estimates. An additional advantage of EVM is the ability to use the cumulative composition model for medium-high conversion data in terpolymer systems [1]. This alternative presents several benefits over the standard instantaneous model (for low conversion data). Namely, we can eliminate the assumption that composition drift is negligible (a requirement for implementing the instantaneous model) and we are able to retain more information content (that is, more data points over the conversion trajectory) from a single experiment [21]. Thus, EVM is by far the most statistically correct and comprehensive approach for reactivity ratio estimation.

2.1 Reactivity Ratio Estimation in Copolymerization

One of the most common models is the instantaneous copolymer composition model, or the Mayo-Lewis model (Equation 3). This model is only applicable to low conversion data, as it assumes that composition drift in the free monomer fraction is negligible (which may be true below 10% conversion).

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \tag{3}$$

In this investigation, medium-high conversion level data are used for parameter estimation, which requires a slightly more complex analysis [22]. Reactivity ratios are therefore estimated by applying the cumulative composition model (using direct numerical integration (DNI)) to the data through EVM (see Equation 4, often referred to as the Skeist equation). Here $f_{1,0}$ is the initial mole fraction of monomer 1 in the pre-polymerization feed, and $\overline{F}_1$ is the cumulative fraction of monomer 1 in the product copolymer.

$$\overline{F}_1 = \frac{f_{1,0} - f_1(1-X)}{X} \tag{4}$$

As expected, conversion (X) varies with time as the polymerization proceeds. Thus, the instantaneous composition of the unreacted (unbound) monomer (f_i) can be evaluated using the differential copolymer composition equation shown in Equation 5.

$$\frac{df_1}{dX} = \frac{f_1 - F_1}{1 - X} \tag{5}$$

Solving these equations simultaneously makes it possible to minimize the sum of squares between the measured and the predicted values (for both the independent variables and the parameter estimates), which is the main objective of EVM.

2.2 Reactivity Ratio Estimation in Terpolymerization

The EVM algorithm can also be applied directly to terpolymerization data, which eliminates the need to use binary reactivity ratios for ternary systems. Details have been presented previously by Kazemi et al. [1], so only a brief overview is provided herein. As for binary reactivity ratios, DNI can be applied to the ternary cumulative composition model, which makes it possible to use data up to medium-high conversion levels. For the terpolymerization case, the Skeist equation and the differential copolymer composition equation described previously (recall Equations 4 and 5) are replaced with systems of equations (Equations 6 and 7, respectively). In theory, these systems of equations can be extended for the analysis of any multi-component polymerization.

$$\overline{F}_1 = \frac{f_{1,0} - f_1(1-X)}{X} \tag{6a}$$

$$\overline{F}_2 = \frac{f_{2,0} - f_2(1-X)}{X} \tag{6b}$$

$$\vdots$$

$$\vdots$$

$$\frac{df_1}{dX} = \frac{f_1 - F_1}{1-X} \tag{7a}$$

$$\frac{df_2}{dX} = \frac{f_2 - F_2}{1-X} \tag{7b}$$

$$\vdots$$

$$\vdots$$

Again, DNI makes it possible to determine the terpolymer composition over the course of conversion, which can then be used to estimate ternary reactivity ratios using EVM.

2.3 Case Study: Terpolymerization of AN/Sty/MA

Estimating accurate reactivity ratios for multi-component systems is an important aspect of polymer reaction engineering, as the reactivity ratios are used to predict composition and sequence length properties of the polymer product. Hence, it is important to check the reliability of the model by evaluating, for instance, agreement between experimentally determined composition data and predicted terpolymer compositions. Many of the research groups who have used binary reactivity ratios to describe ternary systems have observed serious deviations between their experimental data and model predictions, which has led them to question the credibility of the Alfrey-Goldfinger terpolymerization model (see, for example, [2,4,10], with a more detailed discussion in [1]). In reality, it is the accuracy of the reactivity ratios (as parameter estimates used within the model) that should be questioned.

As an example (first exhibited by Kazemi [23] and re-evaluated for the current work), the terpolymerization of acrylonitrile (AN, M_1), styrene (Sty, M_2) and maleic anhydride (MA, M_3) was studied by Kressler et al. [4]. In the original investigation, the corresponding binary reactivity ratios (for each of the possible copolymer systems) were obtained from the literature (see Table 1), and were used to predict terpolymerization composition. As shown in Figure 1(a), there was a significant disagreement between the experimental data and the model predictions when binary reactivity ratios were used.

By applying the EVM methodology to their (instantaneous) terpolymerization data, it is possible to estimate ternary reactivity ratios for the system (see again Table 1). Figure 1(b) shows that using these ternary reactivity ratios significantly improves the prediction performance of the A-G model. These excellent results can be attributed to (1) choosing to include the third comonomer in the estimation process and (2) using the EVM methodology for reactivity ratio estimation.

Table 1. Comparison of Binary and Ternary Reactivity Ratio Estimates AN(M_1)/Sty(M_2)/MA(M_3)

Reactivity Ratios	$\mathbf{r_{12}}$	$\mathbf{r_{21}}$	$\mathbf{r_{13}}$	$\mathbf{r_{31}}$	$\mathbf{r_{23}}$	$\mathbf{r_{32}}$
Binary	0.04	0.41	6.00	10^{-4}	0.04	10^{-4}
Ternary	0.14	0.58	0.40	2.40	0.05	0.07

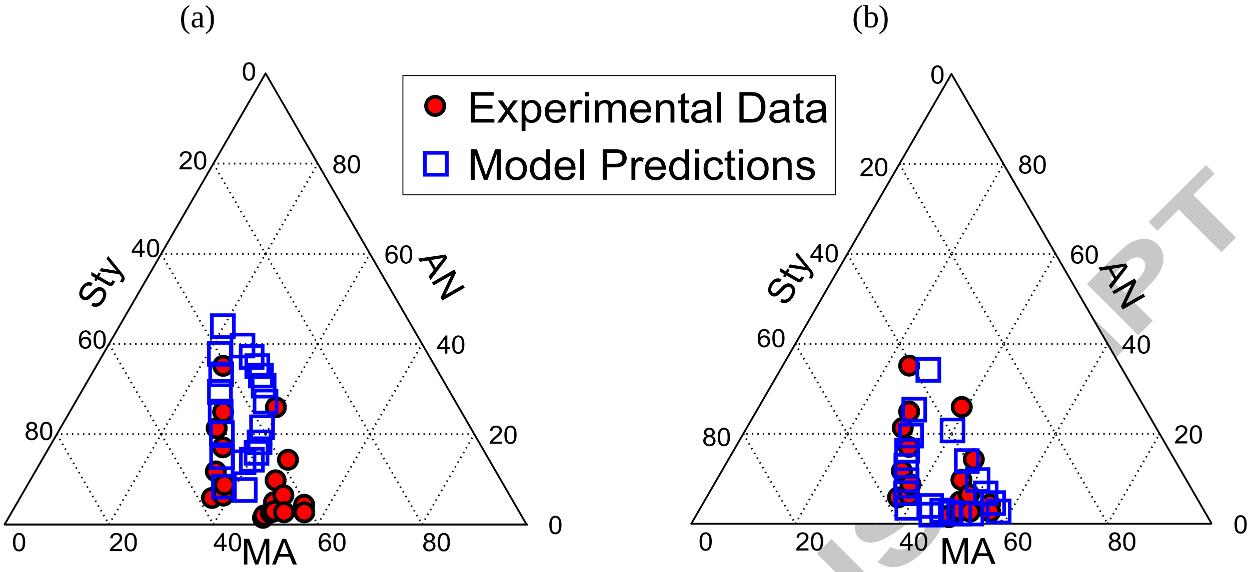

Figure 1. Experimental [4] and predicted terpolymer composition for the AN/Sty/MA terpolymer, using (a) binary and (b) ternary reactivity ratio estimates for prediction (inspired by [23]).

These results confirm the hypothesis that binary and ternary reactivity ratios can differ significantly for a given system, and therefore should not be used interchangeably. However, since the binary reactivity ratios used for the original analysis were taken from literature (and would have been estimated using various techniques), the accuracy of the binary values was rather questionable. For a direct and fair comparison of binary and ternary reactivity ratio estimates, it is necessary to collect dependable experimental data from both terpolymerization experiments and (the so-called analogous) copolymerization experiments. This ensures experimental consistency as well as statistically sound parameter estimation (using EVM) for both the binary and ternary systems. Thus, in what follows, the terpolymer of 2-acrylamido-2-methylpropane sulfonic acid/ acrylamide/acrylic acid will be compared to the associated copolymers, based on recent studies by Riahinezhad et al. [14] and Scott et al. [15].

3. Experimental

The terpolymer of 2-acrylamido-2-methylpropane sulfonic acid (AMPS), acrylamide (AAm) and acrylic acid (AAc) has the potential to be used in enhanced oil recovery (EOR). The copolymer of AAm/AAc is often used as a viscosity modifier (for polymer flooding), but tends to degrade at the high temperatures and pressures characteristic of EOR. It has been suggested that by adding AMPS to the polymerization recipe, the steric hindrance from the sulfonic acid group will increase main-chain stability and control potential degradation of AAm [24,25].

Synthesizing the AMPS/AAm/AAc terpolymer and the associated copolymers will not only offer a direct comparison of binary and ternary reactivity ratio estimates, but it will also provide kinetic information about the polymerization. The complexity of this system also adds another unique element to the analysis; research has shown the significant effects of solution properties (including feed composition, ionic strength, pH, and monomer concentration) on the polymerization kinetics (see, for example, [14, 26-29]). Accurate reactivity ratios (obtained directly from experimental data) will make it possible to generate terpolymers with specific custom properties that meet (or exceed) the application requirements for EOR.

3.1 Reagent Purification

Monomers 2-acrylamido-2-methylpropane sulfonic acid (AMPS; 99%), acrylamide (AAm; electrophoresis grade, 99%), and acrylic acid (AAc; 99%) were purchased from Sigma-Aldrich (Oakville, ON, Canada). AAc was purified via vacuum distillation at 30°C, while AAm and AMPS were used as received. Initiator (4,4′-azo-bis-(4-cyanovaleric acid), ACVA), inhibitor (hydroquinone) and sodium hydroxide were also purchased from Sigma-Aldrich. Sodium chloride from EMD Millipore (Etobicoke, ON, Canada) was used as received. In terms of solvents, water was Millipore quality (18 MΩ·cm); acetone (99%) and methanol (99.8%) were used as received. Nitrogen gas (4.8 grade) used for degassing solutions was purchased from Praxair (Mississauga, ON, Canada).

3.2 Polymer Synthesis

In general, the experimental techniques described by Riahinezhad et al. [30] were adopted for these copolymer and terpolymer systems. Pre-polymerization solutions with 0.004 M initiator (ACVA) and a total monomer concentration of 1 M were prepared; comonomer ratios for each run were selected according to the EVM design of experiments (see Kazemi et al. [31] for details). Two optimal feed compositions were required for each of the copolymerization experiments (AAm/AAc, AMPS/AAm and AMPS/AAc), and these are described in recent publications by Riahinezhad et al. [14] and Scott et al. [15].

For the terpolymer system, three optimally designed feed compositions (within the optimal design regions) can generate enough data to obtain accurate reactivity ratio estimates [16]. As per the EVM design of experiments procedure for terpolymerizations [17], each feed composition is rich in one comonomer ($f_{\mathrm{AMPS},0}/f_{\mathrm{AAm},0}/f_{\mathrm{AAc},0}$ = 0.8/0.1/0.1, 0.1/0.8/0.1, 0.1/0.2/0.7). Non-optimal recipes were also used for additional terpolymer synthesis (the reason for which is made clear in Section 4.2). As an aside, this design of experiments stage highlights an additional advantage of using terpolymerization data for ternary reactivity ratio estimation: only three optimally designed runs are required to estimate reactivity ratios (compared to the six optimal runs that are required for three binary pairs, considered separately).

As demonstrated previously by Riahinezhad et al. [14,27], constant pH and ionic strength (IS) are extremely important in copolymer and terpolymer synthesis. Thus, all monomer solutions (for both copolymerizations and terpolymerizations) were titrated with sodium hydroxide to adjust the pH to approximately 7 (±0.5), whereas sodium chloride was added to adjust IS among the experiments. Prior to polymerization, all solutions were purged with 200 mL/min nitrogen for 2h.

After degassing, aliquots of ~20 mL of solution were transferred to sealed vials using the cannula transfer method. Free-radical solution (aqueous phase) polymerizations were run in a temperature controlled shaker-bath (OLS200; Grant Instruments, Cambridge, UK) at 40°C and 100 rpm. Vials were removed at selected time intervals, placed in ice and further injected with approximately 1 mL of 0.2 M hydroquinone solution to stop the polymerization. Polymer samples were isolated by precipitating the products in acetone or methanol, filtered (paper filter grade number 41, Whatman; Sigma-Aldrich, Oakville, ON, Canada) and vacuum dried for 1 week at 50°C. All polymerizations were independently replicated.

3.3 Polymer Characterization

Conversion of the polymer samples was determined using gravimetry. The mass of the sodium ions was also considered in conversion calculations, as per the recommendation of Riahinezhad et al. [14]. Copolymer composition was measured using elemental analysis (CHNS, Vario Micro Cube, Elementar). Calculation of composition did not include H content, as residual water has been known to affect the determined H content [30]. Select samples were independently replicated.

4. Results and Discussion

In what follows, the error-in-variables-model (EVM) is used to estimate reactivity ratios for the copolymerizations and the terpolymerization associated with the AMPS/AAm/AAc system. Data sets containing monomer feed composition, conversion and cumulative copolymer compositions are fed to a MATLAB-based EVM program to obtain the best possible reactivity ratio estimates (and associated joint confidence regions, JCRs) [1,19]. However, the goal here is to investigate more than just the reactivity ratios themselves. For the first time (to our knowledge), we can do a direct comparison of binary and ternary systems, all else (polymerization conditions, reactivity ratio estimation techniques, etc.) being equal.

Thus, in Section 4.1, there will be a comparison of point estimates and the estimated degree of precision associated with the reactivity ratio estimates (JCRs) for binary and ternary systems. To complement these results, Section 4.2 will provide an in-depth look at composition prediction performance (using binary and ternary reactivity ratio estimates to predict cumulative terpolymer composition).

4.1 Comparison of Reactivity Ratio Estimates

Experimental information and data used for reactivity ratio estimation have been presented previously by Riahinezhad et al. [14] and Scott et al. [15,16]. Now, we are finally able to show a direct comparison of the binary reactivity ratios (for three distinct copolymerizations) and the ternary reactivity ratios (for the AMPS/AAm/AAc terpolymer). A numerical comparison is provided in Table 2, and joint confidence regions for each comonomer pair are presented in Figures 2 through 4.

It is important for the reader to note that three distinct data sets were used to estimate the binary reactivity ratios (one for each comonomer pair). In contrast, all six ternary reactivity ratio estimates were obtained from a single data set (experimental terpolymerization data). However, the JCRs have been split into comonomer pairs (in Figures 2 through 4) for straightforward comparison. The main focus of this investigation is to compare copolymerization and terpolymerization data for ternary reactivity ratio estimation, but a second (more practical) observation cannot be ignored: using copolymerization data to describe a ternary system requires double the experimental work (2 optimal copolymer feed compositions × 3 comonomer combinations (6 polymerizations in total) vs. 3 optimal terpolymer feed compositions (3 polymerizations in total)). This advantage becomes even more significant when we consider replication and/or evaluation of model prediction performance: the binary reactivity ratios would need a minimum of four additional runs (each of the 3 comonomer pairs plus 1 terpolymerization). Conversely, 1 terpolymerization run would provide enough data to confirm the ternary reactivity ratio estimates and demonstrate the accuracy of the terpolymerization model prediction.

Table 2. Comparison of Binary and Ternary Reactivity Ratio Estimates AMPS/AAm/AAc

Reactivity Ratios	$\mathbf{r_{AMPS/AAm}}$	$\mathbf{r_{AAm/AMPS}}$	$\mathbf{r_{AMPS/AAc}}$	$\mathbf{r_{AAc/AMPS}}$	$\mathbf{r_{AAm/AAc}}$	$\mathbf{r_{AAc/AAm}}$
Binary	0.18	0.85	0.19	0.86	1.06	0.22
Ternary	0.66	0.82	0.82	0.61	1.61	0.25

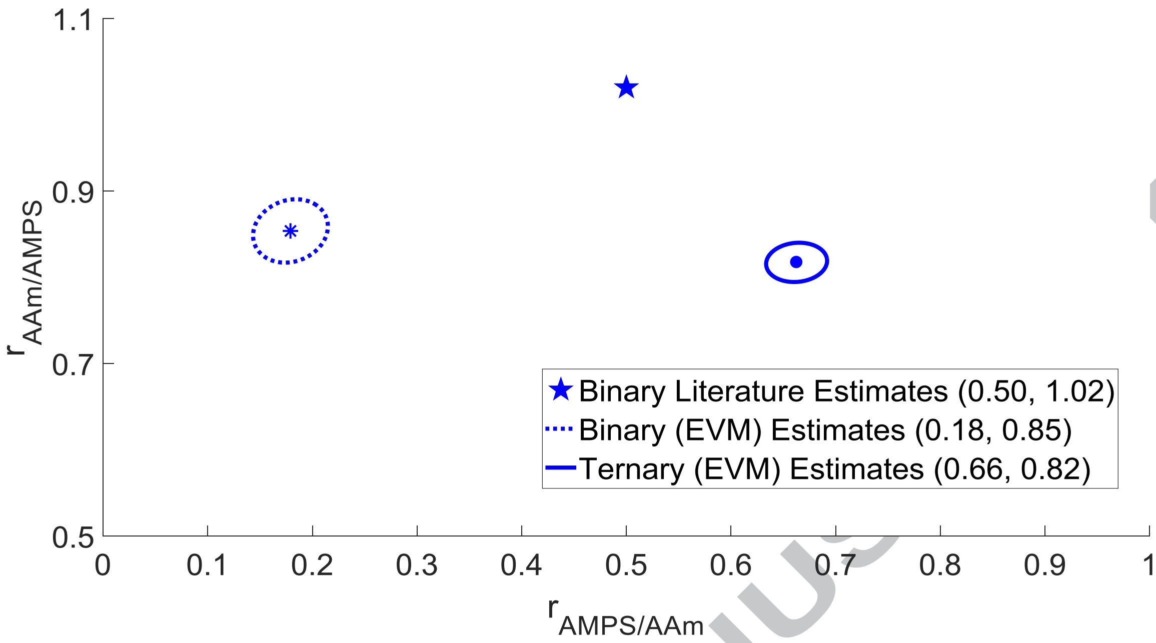

Figure 2. Comparison of reactivity ratio estimates for comonomers AMPS/AAm using copolymerization data (binary estimates) and terpolymerization data (ternary estimates).

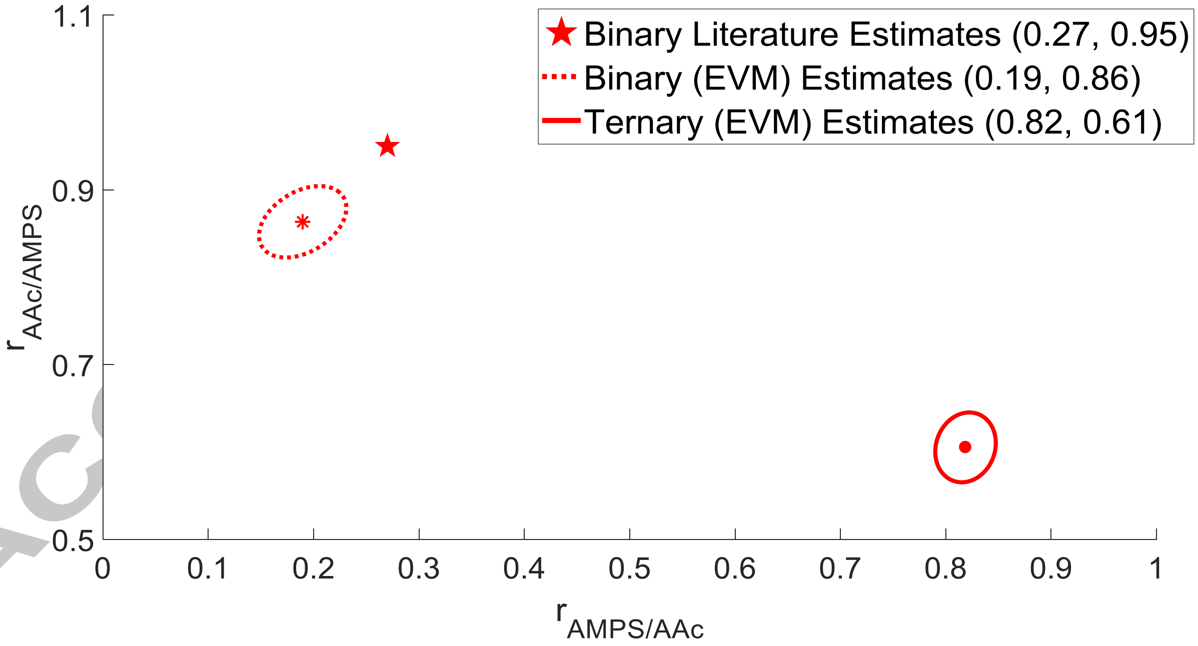

Figure 3. Comparison of reactivity ratio estimates for comonomers AMPS/AAc using copolymerization data (binary estimates) and terpolymerization data (ternary estimates).

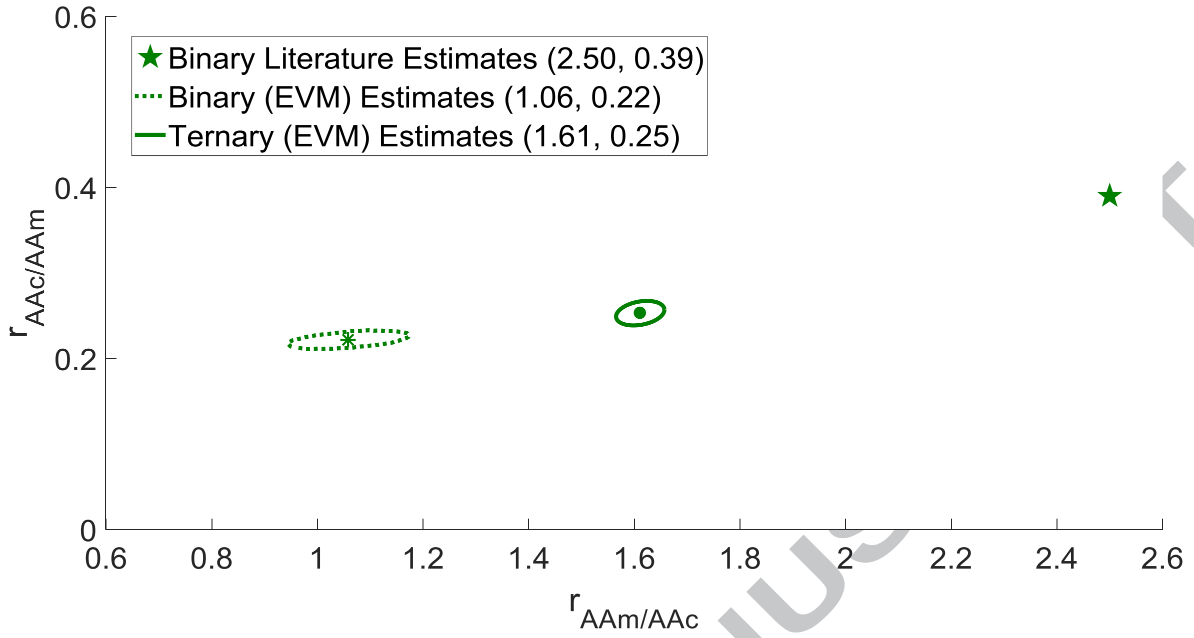

Figure 4. Comparison of reactivity ratio estimates for comonomers AAm/AAc using copolymerization data (binary estimates) and terpolymerization data (ternary estimates).

The most important observation from Figures 2 through 4 is the following: binary and ternary reactivity ratios for a given comonomer pair differ significantly, even under the same reaction conditions. For all three comonomer pairs, no overlap of JCRs is observed. Although individual reactivity ratio estimate values are similar (between binary and ternary systems) for $r_{AAm/AMPS}$ and $r_{AAc/AAm}$, they should not be evaluated without their corresponding counterparts (that is, we cannot make statements about r_{ij} without also considering r_{ji}). Thus, point estimates are statistically different when we compare the binary and ternary estimates.

In Figure 2 and Figure 3, the size and orientation of the binary and ternary JCRs are similar, which indicates that we can have a similar degree of confidence in both the binary reactivity ratio estimates and ternary reactivity ratio estimates. Since JCRs are fairly round (and not inclined), we have confirmed that there is little correlation between the parameter estimates. This is largely due to the fact that EVM-based design of experiments was used to select feed compositions for both the copolymerization and terpolymerization studies. In Figure 4, the uncertainty in $r_{AAm/AAc}$ seems to be much larger than the uncertainty in $r_{AAc/AAm}$ (notice how the JCR is somewhat "stretched" horizontally). However, this is partially due to the relative values of $r_{AAm/AAc}$ and

$r_{AAc/AAm}$. Since $r_{AAm/AAc}$ is almost 6 times larger than $r_{AAc/AAm}$, the absolute error is necessarily larger in the horizontal direction; this phenomenon has also been addressed by Scott and Penlidis [21]. This behavior is visible for the copolymer because the analysis is evaluating the AAm/AAc relationship in isolation. When the full terpolymerization data set is used for analysis, additional information content helps to improve the precision of all reactivity ratio estimates.

We can also evaluate the data by looking at the three comonomer "pairs" herein, as they are divided into Figures 2 through 4. One might expect that if $r_{ij} > r_{ji}$ for the binary system, the same would be true for the ternary system. However, this is not always the case! As shown in the case study of Section 2.3 (with data from Kressler et al. [4]), relationships between comonomers may change between the binary and ternary systems; see again Table 1.

In the current study, only two of the three comonomer pairs have consistent trends between the binary and ternary reactivity ratio estimates (see again Table 2). In looking at the combination of AMPS and AAm, $r_{AAm/AMPS} > r_{AMPS/AAm}$ for both co- and terpolymerization. The trend is also consistent for AAm/AAc. Thus, it is reasonable to conclude that acrylamide is more reactive than the other comonomers (under these experimental conditions), regardless of whether a copolymer or a terpolymer is being synthesized.

When we look at the AMPS/AAc comonomer pair, the relationship between reactivity ratios is not so predictable. While $r_{AAc/AMPS} > r_{AMPS/AAc}$ for the binary system, the opposite is true for the ternary system. The reactivity ratio estimates are also (numerically) closer together for the terpolymerization than they are for the copolymerization. We would postulate that this is due to the presence of acrylamide in the recipe; a non-ionized monomer in the presence of two ionized monomers would influence electrochemical interactions (and reduce repulsion) between AMPS and AAc.

More generally, it is also important to recognize the increase in AMPS reactivity for the terpolymerization. Table 2 indicates that $r_{AMPS/i}$ is noticeably larger for the ternary system than for the binary system, where *i* can be either AAm or AAc. This would suggest that the low reactivity of AMPS in the binary systems is not due to steric hindrance, but rather due to charge effects.

Direct comparison of binary and ternary reactivity ratios for the AMPS/AAm/AAc system has shown significant numerical differences, as well as some shifts in behavior. However, point estimates are only one part of the story. It is equally important to evaluate the prediction performance when binary and ternary reactivity ratio estimates are used in the terpolymerization model.

4.2 Comparison of Composition Predictions

As mentioned previously, binary reactivity ratios are often used to predict terpolymer composition using the Alfrey-Goldfinger (A-G) model. However, for more accurate results, the recast A-G model (Equation 2) can be used in combination with recently determined ternary reactivity ratios [1]. In what follows, the recast A-G model is used to predict terpolymer composition using both the binary and ternary reactivity ratio estimates of Table 2. Experimentally determined composition measurements (obtained using elemental analysis; see Section 3.3) are also included for evaluation of the model.

We can start by looking at ternary composition diagrams for the AMPS/AAm/AAc terpolymer (Figure 5). The three optimal feed compositions used for reactivity ratio estimation (established using EVM design of experiments) are close to the corners of the triangle, since each is rich in one comonomer. The initial feed compositions, along with the measured and predicted terpolymer compositions, are shown in Figure 5 for both the binary and ternary reactivity ratio estimates. One should note that these compositions have been measured over the full conversion range, so scatter is due to composition changes (as a function of conversion), and should not be taken as poor reproducibility.

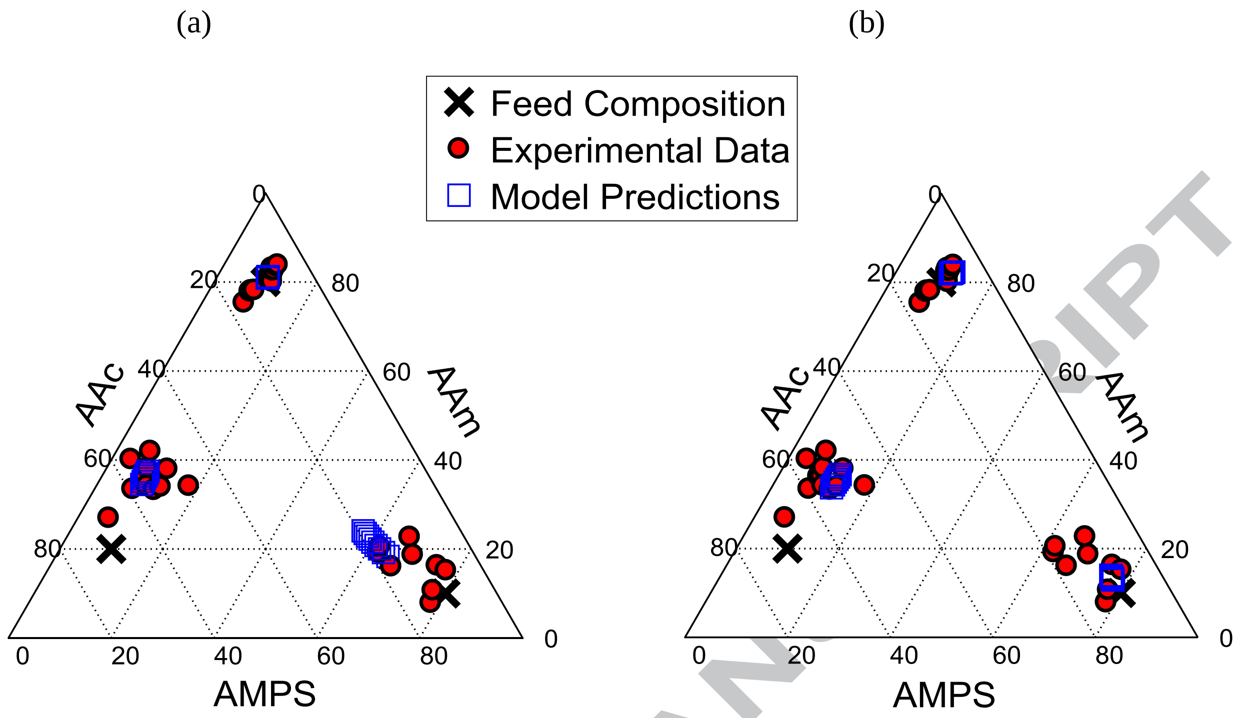

Figure 5. Experimental [16] and predicted terpolymer composition for the AMPS/AAm/AAc terpolymer, using (a) binary and (b) ternary reactivity ratio estimates for prediction.

The ternary composition diagrams show fairly good agreement between the predicted and measured cumulative terpolymer compositions. However, when we look closely at the prediction performance of the binary reactivity ratio estimates, the AMPS-rich terpolymer composition is not well predicted (especially compared to the prediction performance of the ternary reactivity ratio estimates for the same recipe).

Thus, we are motivated to look at this AMPS-rich system in more detail. In Figure 6, the cumulative terpolymer compositions for all three comonomers (AMPS, AAm and AAc) are plotted against conversion, and the stark contrast between binary and ternary predictions is clearly visible. The experimental data are in much better agreement with the ternary-based model. This is to be expected (as per previous discussion), and confirms the importance of using ternary reactivity ratios to describe/model terpolymer systems.

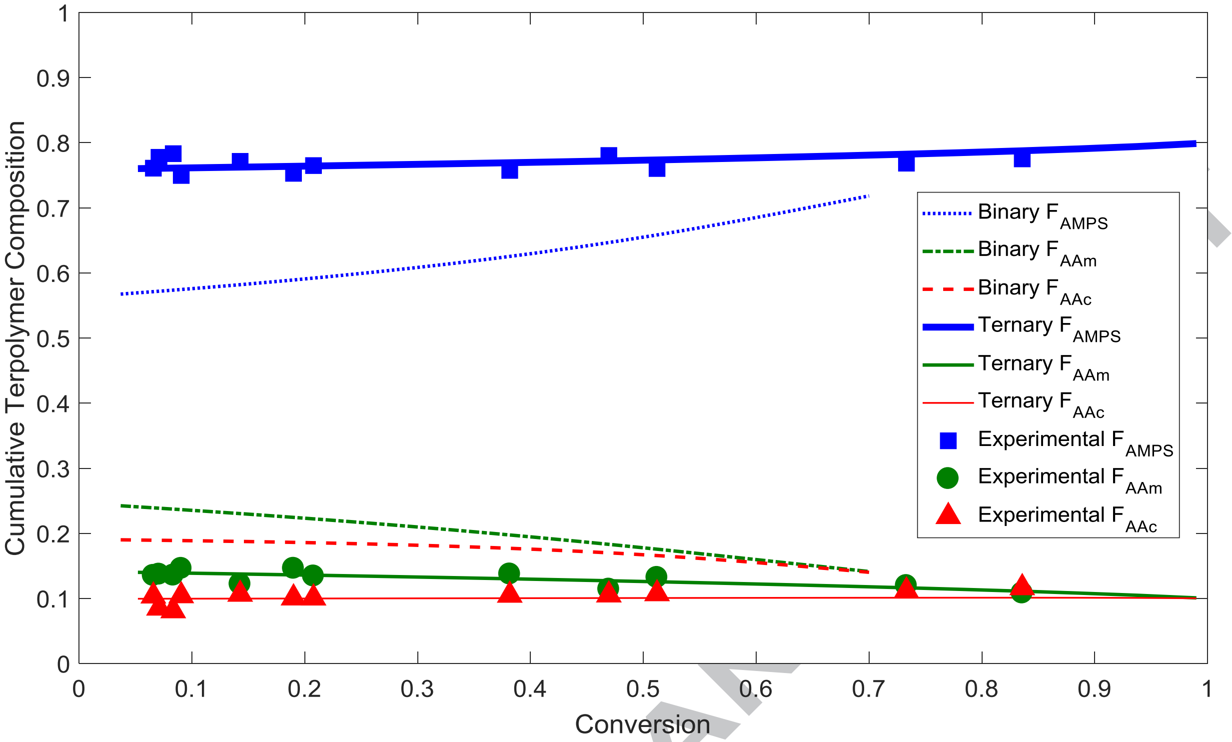

Figure 6. Experimental [16] and predicted terpolymer composition for the AMPS-rich terpolymer ($f_{AMPS,0}/f_{AAm,0}/f_{AAc,0}$ = 0.8/0.1/0.1).

It is always good to confirm that model predictions (after parameter estimation) agree with experimental data. However, we typically evaluate the model using the same experimental data that were used for parameter estimation [16]. It is important, then, to confirm that the model still holds when the behavior of new recipes (that is, feed compositions not included in the design data) is being predicted. As mentioned previously, three optimal recipes were chosen for reactivity ratio estimation using EVM design of experiments; these are described in Section 3.2 and in previous work by Scott et al. [16]. Due to the nature of the design, all three points are near the corners of the composition triangle; they are rich in one comonomer and have low quantities of the other two comonomers. It is interesting to evaluate whether the model obtained from these three points still holds when the operating conditions are closer to the “middle” of the triangle. That is, do the reactivity ratio estimates discussed in Section 4.1 apply to the entire composition range?

To establish whether the reactivity ratio estimates (and subsequent terpolymer composition predictions) hold for all compositions, three sub-optimal terpolymerization recipes were evaluated. The same synthesis and characterization procedures were used as described previously (see Section 3 and previous work by Scott et al. [16]), but the results were not used for reactivity ratio estimation. Therefore, the reactivity ratio estimates are entirely independent of this sub-optimal region of experimental data. Figure 7 compares the experimentally measured terpolymer compositions and associated predicted (cumulative) terpolymer compositions for three additional recipes ($f_{\mathrm{AMPS},0}/f_{\mathrm{AAm},0}/f_{\mathrm{AAc},0}$ = 0.5/0.1/0.4; 0.2/0.4/0.4; 0.3/0.5/0.2).

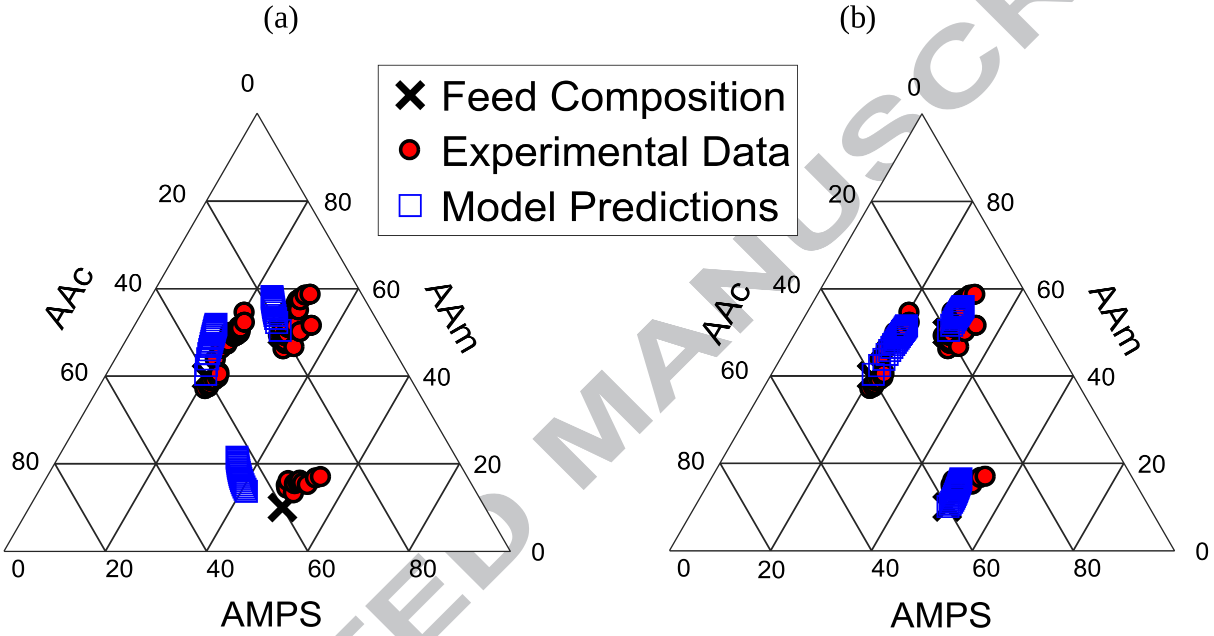

Figure 7. Experimental and predicted terpolymer composition for sub-optimal AMPS/AAm/AAc terpolymerizations, using (a) binary and (b) ternary reactivity ratio estimates for prediction.

For comparison (and to return to the main goal of the current study), we can again look at the prediction performance of both the binary and ternary reactivity ratio estimates. The binary estimates were lacking for the optimally designed experiments (recall Figure 5), but they are even worse for the sub-optimal experiments. In Figure 7(a), the biggest prediction discrepancy is for $f_{\mathrm{AMPS},0}/f_{\mathrm{AAm},0}/f_{\mathrm{AAc},0}$ = 0.5/0.1/0.4 (which is graphically the lowest feed composition in the triangle). The other two predictions (both containing more AAm) are in the right general region, but the direction of the prediction (that is, the slope of the predicted composition) does not agree with the experimental data.

We can contrast these results with the model prediction using ternary reactivity ratio estimates, as shown in Figure 7(b). The ternary prediction performance is much better than the binary prediction performance, which again highlights the importance of using ternary reactivity ratio estimates to describe/model/predict terpolymerization behavior. From these results, we can also confirm/conclude that ternary reactivity ratios obtained from optimally designed experiments [17] apply to the whole composition range; the recast A-G model holds for any initial feed composition.

Though the ternary model has excellent prediction performance for all three feed compositions, the trend is not entirely correct for $f_{\mathrm{AMPS,0}}/f_{\mathrm{AAm,0}}/f_{\mathrm{AAc,0}}$ = 0.5/0.1/0.4. The experimental data points seem to vary horizontally (physically, this indicates that $\overline{F}_{\mathrm{AAm}}$ shows very little drift). However, the model shows a different trend, suggesting that $\overline{F}_{\mathrm{AMPS}}$ is the comonomer fraction that remains approximately constant. For the sake of completeness, we can also look back to the binary prediction; because it varies in the opposite direction, it is predicting that $\overline{F}_{\mathrm{AAc}}$ will exhibit the least drift. Obviously, any one of these comonomer fractions are related to the other two ($\sum \overline{F}_i = 1$), but the model predictions and the experimental data seem to be in disagreement. Thus, we can examine the cumulative terpolymer composition as a function of conversion (Figure 8).

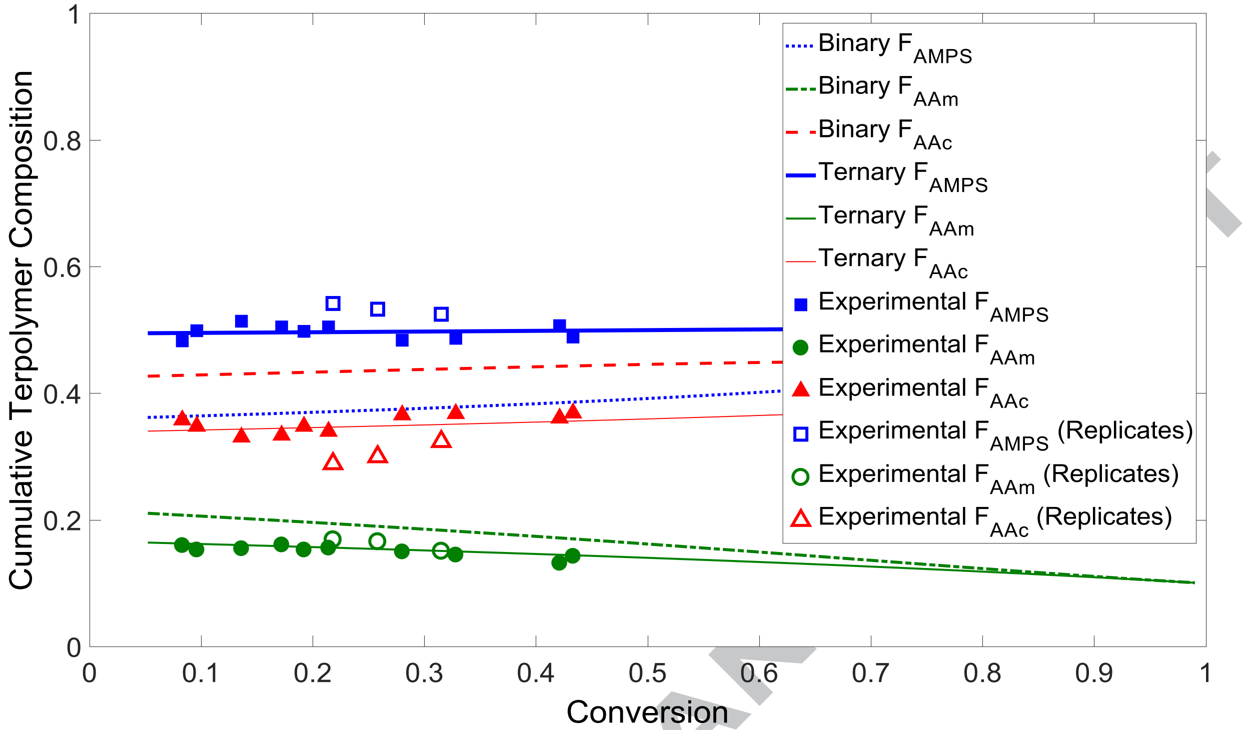

Figure 8. Experimental and predicted terpolymer composition for the sub-optimal terpolymer ($f_{AMPS,0}/f_{AAm,0}/f_{AAc,0}$ = 0.5/0.1/0.4).

As mentioned earlier (in the discussion surrounding Figure 7(b)), the ternary plot indicated that there may be some discrepancies between the experimentally observed trends and trends predicted by the model (specifically for $f_{AMPS,0}/f_{AAm,0}/f_{AAc,0}$ = 0.5/0.1/0.4). One might think that this variation is a result of composition drift changing with conversion, but it is actually due to slight differences between runs. Figure 8 confirms that any concerns about prediction performance are unfounded; the experimentally determined cumulative terpolymer composition and the ternary model prediction are in very good agreement. The inconsistency observed in Figure 7b was not a result of bad prediction performance. Rather, a replicate run was "biased high" (in terms of $\overline{F}_{AMPS}$ measurements) and created a false impression. This variability between runs is not a cause for concern; the replicate run was performed entirely independently (from stock solution preparation to synthesis to characterization), so some experimental error is perfectly normal.

Another important take-away from Figure 8 is the terrible prediction performance when binary reactivity ratios are used in the model. It has already been noted that the incorporation of AMPS changes considerably when the system changes from a copolymerization to a terpolymerization. This has been observed both in the change of reactivity ratio estimates (recall Table 1) and prediction performance for the optimally designed feed compositions (especially $f_{\mathrm{AMPS},0}/f_{\mathrm{AAm},0}/f_{\mathrm{AAc},0}$ = 0.8/0.1/0.1; see Figure 6). Previously, in Figure 6, we saw that using binary reactivity ratios in the recast Alfrey-Goldfinger model severely underestimated $\overline{F}_{\mathrm{AMPS}}$, which in turn affected the prediction performance for the other comonomer fractions. Now, for a sub-optimal recipe, we see that this problem is amplified.

The initial feed composition, again, is $f_{\mathrm{AMPS},0}/f_{\mathrm{AAm},0}/f_{\mathrm{AAc},0}$ = 0.5/0.1/0.4. It is important to restate this here, because the fractions of AMPS and AAc in the recipe are close, but $f_{\mathrm{AMPS},0} > f_{\mathrm{AAc},0}$. In the product terpolymer, the cumulative fraction of AMPS remains greater than that of AAc; $\overline{F}_{\mathrm{AMPS}} > \overline{F}_{\mathrm{AAc}}$ is measured throughout the polymerization (at least up to ~50% conversion). When the ternary reactivity ratio estimates are used in the recast A-G model, the model prediction supports these experimental observations, as it should. In contrast, when binary reactivity ratio estimates are used in the model, $\overline{F}_{\mathrm{AAc}} > \overline{F}_{\mathrm{AMPS}}$ for up to about 85% conversion. This inconsistency is a major disadvantage of using binary reactivity ratio estimates to describe a ternary system. Imagine trying to synthesize an AAc-rich terpolymer (given inappropriate binary data), and finding that the end product is actually AMPS-rich! This would only result in frustration and wasted resources. It is therefore preferable, when possible, to use ternary reactivity ratios to obtain information about terpolymerization systems.

5. Concluding Remarks

Terpolymerization kinetics are complex. Historically, binary reactivity ratios have been used to predict terpolymerization behavior (with some success), but the current work shows that this binary-ternary analogy is not always applicable. These results suggest that terpolymerization kinetics should not be oversimplified by applying binary reactivity ratios to ternary systems. When researchers use copolymerization data to describe a terpolymerization, they are essentially ignoring the presence of the third comonomer (and any possible interactions with the other two comonomers) and doubling the amount of experimental work required for reactivity ratio estimation.

In directly comparing the binary and ternary reactivity ratios for the AMPS/AAm/AAc system, we found significant differences in reactivity ratio estimates (numerically speaking) and in related trends. This ultimately affects model prediction performance; binary reactivity ratios applied to the (recast A-G) terpolymerization model did not agree with experimentally measured composition data. In contrast, ternary reactivity ratios gave very good predictions.

We have shown that three optimally designed feed compositions (selected using EVM-based design of experiments) provide enough information to accurately estimate ternary reactivity ratios. Not only do these three experiments provide better ternary reactivity ratio estimates (and subsequent prediction performance) than their so-called analogous binary estimates, but they also give equally good prediction performance for independent sub-optimal feed compositions.

Thus, whenever possible, researchers should be motivated to use terpolymerization data to estimate ternary reactivity ratios. Design of experiments and the error-in-variables-model make data collection and parameter estimation straightforward and (perhaps more importantly) kinetically and statistically accurate.

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Declarations of interest: none.

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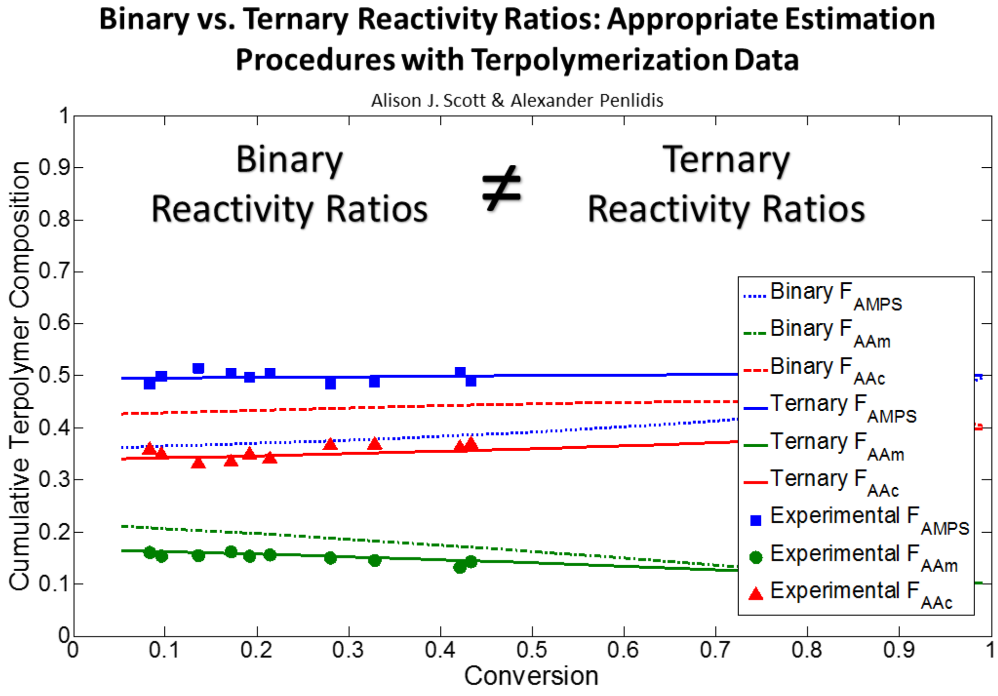
Highlights

- Significant differences observed between binary and ternary reactivity ratios.
- Binary reactivity ratios not the most appropriate to describe terpolymerizations.
- Ternary reactivity ratios improve model predictions in terpolymerizations.
- Proposed design of experiments reduces experimental workload for terpolymerization.
- Results from optimally designed experiments apply to the entire composition range.

Graphical abstarct:



Binary vs. Ternary Reactivity Ratios: Appropriate Estimation Procedures with Terpolymerization Data

Alison J. Scott & Alexander Penlidis