



Binary vs. ternary reactivity ratios: Appropriate estimation procedures with terpolymerization data

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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.

1. Introduction

Reactivity ratios are crucial to the study of the kinetics of multi-component 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 (Eq. (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). Eq. (1) relates instantaneous (not cumulative) terpolymer composition properties.

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

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

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

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 Eq. (1)). The recast version, presented in Eq. (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}).

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

$$+ f_2 \left(\frac{f_1}{r_{12}r_{31}} + \frac{f_2}{r_{21}r_{32}} + \frac{f_3}{r_{13}r_{32}} \right) \left(f_2 + \frac{f_1}{r_{21}} + \frac{f_3}{r_{23}} \right)$$

$$+ f_3 \left(\frac{f_1}{r_{13}r_{21}} + \frac{f_2}{r_{23}r_{12}} + \frac{f_3}{r_{13}r_{23}} \right) \left(f_3 + \frac{f_1}{r_{31}} + \frac{f_2}{r_{32}} \right) \quad (2a)$$

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

$$+ f_2 \left(\frac{f_1}{r_{12}r_{31}} + \frac{f_2}{r_{21}r_{32}} + \frac{f_3}{r_{13}r_{32}} \right) \left(f_2 + \frac{f_1}{r_{21}} + \frac{f_3}{r_{23}} \right)$$

$$+ f_3 \left(\frac{f_1}{r_{13}r_{21}} + \frac{f_2}{r_{23}r_{12}} + \frac{f_3}{r_{13}r_{23}} \right) \left(f_3 + \frac{f_1}{r_{31}} + \frac{f_2}{r_{32}} \right) \quad (2b)$$

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

$$+ f_2 \left(\frac{f_1}{r_{12}r_{31}} + \frac{f_2}{r_{21}r_{32}} + \frac{f_3}{r_{13}r_{32}} \right) \left(f_2 + \frac{f_1}{r_{21}} + \frac{f_3}{r_{23}} \right)$$

$$+ f_3 \left(\frac{f_1}{r_{13}r_{21}} + \frac{f_2}{r_{23}r_{12}} + \frac{f_3}{r_{13}r_{23}} \right) \left(f_3 + \frac{f_1}{r_{31}} + \frac{f_2}{r_{32}} \right) \quad (2c)$$

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 (Eq. (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).

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \quad (3)$$

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 \bar{F}_1 is the cumulative fraction of monomer 1 in the product copolymer.

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

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 Eq. (5).

$$\frac{df_1}{dX} = \frac{f_1 - F_1}{1-X} \quad (5)$$

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 Eqs. (4) and (5) are replaced with systems of equations (Eqs. (6) and (7), respectively). In theory, these systems of equations can be extended for the analysis of any multi-component polymerization.

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

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

⋮

⋮

$$\frac{df_1}{dX} = \frac{f_1 - F_1}{1-X} \quad (7a)$$

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