Reactivity Ratio Estimation in Terpolymerizations with and without an Azeotrope

Niousha Kazemi, Thomas Duever, and Alexander Penlidis
Department of Chemical Engineering, University of Waterloo

INTRODUCTION

- Terpolymerization is a three monomer-based polymerization; the chain micro-structural composition can be predicted from the knowledge of monomer concentrations and the related reactivity ratios.
- Obtaining reactivity ratios from terpolymerization experimental data is a nonlinear multi-response parameter estimation problem.
- Due to the fact that the terpolymerization mechanism is considered to be analogous to that of copolymerization, **reactivity ratios obtained from copolymerization experiments are commonly used in problems dealing with terpolymerization reactions.**
- One of the common requirements during polymer production is to maintain homogeneous polymer composition.
- The 'ternary azeotropic point', similar to a binary azeotrope, corresponds to a feed composition at which the polymerization does not exhibit composition drift.
- Several groups have reported methods of evaluating azeotropic compositions given reactivity ratios. Some attempts have been made to calculate analytically conditions for ternary critical points. **Nonetheless, no general solutions/approaches have emerged from these efforts. Often, conflicting remarks are made, based on graphical approaches, with hardly any experimental verification.**

LITERATURE APPROACH

- For terpolymerization at low conversion, the compositions of the monomer and polymer phases can be obtained by the following equations, based on the Alfrey-Goldfinger model (ref.1):

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

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

f_i is the mole fraction of monomer i in the feed; F_i is the mole fraction of monomer i in the terpolymer; r_{ij} are binary reactivity ratios.

- Traditionally, the estimation methods for reactivity ratios vary from (incorrect) linear to non-linear parameter estimation techniques. In the literature, these reactivity ratios are commonly obtained from binary copolymer data and not based **directly** on terpolymer composition data.
- For azeotropic systems, literature is dominated by graphical solutions, which are only approximate.
- For many of the claimed azeotropic compositions, methods of derivation are vague and frequently the reported compositions can not satisfy the Alfrey-Goldfinger model.

OBJECTIVES

- **The first objective is to compare reactivity ratio estimates obtained directly from terpolymerization experimental data with those calculated from separate binary pairs and evaluate the potential improvement in the reactivity ratios estimates accordingly.**

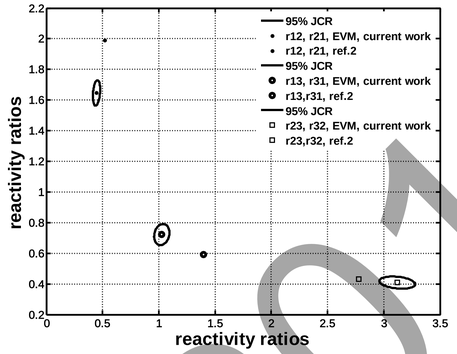

Figure 1. Joint confidence regions (JCR) for terpolymerization of Leucine-N-carboxyanhydride (L-NCA, M_1)/ β-Benzyl aspartate-N-carboxyanhydride (D-NCA, M_2)/ Valine-N-carboxyanhydride (V-NCA, M_3)

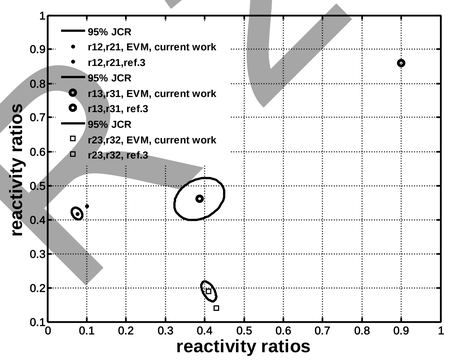

Figure 2. JCRs for terpolymerization of Acrylonitrile (AN, M_1)/Styrene (STY, M_2)/2,3 Dibromopropylacrylate (DBPA, M_3)

- **As another objective, the Alfrey-Goldfinger equations were solved (set of nonlinear algebraic equations) in order to arrive at a general direct numerical solution of the terpolymerization azeotropic composition.**

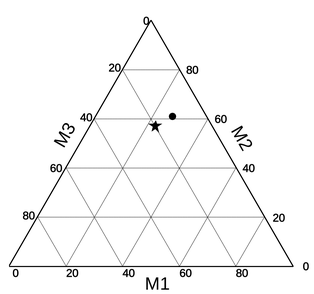

Figure 3. Ternary azeotropic composition for Acrylonitrile (AN, M_1)/ Styrene (STY, M_2)/2,3 Dibromopropylacrylate (DBPA, M_3) (*) current work, (•) ref.3

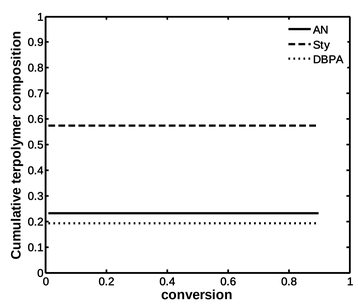

Figure 4. Compositional drift of Acrylonitrile (AN)/ Styrene (STY)/2,3 Dibromopropylacrylate (DBPA) terpolymerization

RESULTS

- **Our studies have confirmed that implementing a novel, more reliable parameter estimation technique, the error-in-variables-model (EVM) method (ref.4), on reactivity ratio estimation directly from terpolymerizations has a great potential to improve the results.**
- **Figures 1/2:**
  - The 95% joint confidence regions (JCR) in both figures demonstrate that literature values obtained from copolymerization pairs (ref.2 and ref.3), are not contained in 95% JCRs of EVM based on terpolymerization experimental data.
  - It can be suggested that use of binary reactivity ratios seems to be an oversimplification, not only with respect to the values themselves, but also with respect to not including measures (and hence effect) of their uncertainty.
  - It can clearly be seen that in Figure 1, 95% JCRs have very similar sizes confirming a proper information content in the experimental design/data. On the other hand, in Figure 2, the variation in the size of 95% JCRs is considerable, indicating a high level of uncertainty in the reactivity ratio estimation results.
  - Since the success of analysis is strongly dependent on the information contained in the data, data accuracy and experimental design are extremely important for parameter estimation and thus they can affect the conclusions drawn. Therefore, terpolymerization experiments with replicates and good experimental designs are preferable for parameter estimation.
- **Our general numerical approach is capable of locating the correct azeotropic composition for any ternary (or multicomponent) system, if such a point exists. Compared to all prior approaches for azeotropic composition calculation in the literature, our numerical approach can be considered as general, direct, reliable, and more straightforward.**
- **Figures 3/4:**
  - The reported azeotropic point in ref.3 could not be verified numerically. The main culprit here appears to be again the sensitivity of the solution to the reactivity ratio values.
  - In Figure 3, the reported and our azeotropic point seem relatively close, but **ONLY** after using reactivity ratio estimates based **directly** on terpolymerization data.
  - The above observations point to the benefits of (a) using a general numerical approach, and (b) employing correct reactivity ratio values.

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