Estimating Improved Reactivity Ratios

Comparative Study of Reactivity Ratio Estimation based on Composition Data at Various Conversion Levels in Binary and Ternary Polymerization Systems

Niousha Kazemi, Tom Duever, and Alex Penlidis

Institute for Polymer Research (IPR)
Department of Chemical Engineering
University of Waterloo

May 2011
A Glance at the Literature

- Large amount of literature since 1944.
- Reactivity ratios determined through inaccurate linear estimation methods.
- More than 80% of publications after 1985 used statistically incorrect estimation techniques.
- In recent publications, these methods are still used and inaccurate results are reported.
- Apparently, this practice has become routine.

What is the real drawback?
As stated in the literature:

“The paradox we are confronted with is that on one hand, an exceptionally useful amount of experimental data has been gathered so far. On the other hand, that huge amount of experimental data often gets misinterpreted which results in coming up with unreliable reactivity ratios”
Main Objective
  o How can these issues be improved with respect to accuracy and precision?

Background
  o Multicomponent polymerization models
  o Review of the estimation method: Error-in-Variables-Model (EVM)

First Question: Why should we use cumulative composition models?

Second Question: Why use binary reactivity ratios in ternary systems?

Concluding remarks

Future Steps
Background:

**Multicomponent Polymerization Models**

- **Copolymer Composition data**
  - Instantaneous model
    - Mayo-Lewis equation
  - Cumulative model
    - Meyer-Lowry equation
- **Terpolymer composition data**
  - Instantaneous model
    - Alfrey-Goldfinger equations
Copolymerization Models

- Copolymer Composition data
  - Instantaneous model
    - Mayo-Lewis equation
  - Cumulative model
    - Meyer-Lowry equation
    - Direct Numerical Integration

\[ F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \]
Copolymerization Models

Copolymer Composition data

Instantaneous model
Mayo-Lewis equation

Cumulative model
Meyer-Lowry equation
Direct Numerical Integration

\[ x = 1 - \left[ \frac{f_1}{f_{10}} \right]^{\alpha} \left[ \frac{f_2}{f_{20}} \right]^{\beta} \left[ \frac{f_{10} - \delta}{f_1 - \delta} \right]^\gamma \]

\[ \begin{align*}
\alpha &= \frac{r_2}{(1 - r_2)} \\
\beta &= \frac{r_1}{(1 - r_1)} \\
\delta &= \frac{(1 - r_2)}{(2 - r_1 - r_2)} \\
\gamma &= \frac{1 - r_1 r_2}{(1 - r_1)(1 - r_2)}
\end{align*} \]
Copolymerization Models

Copolymer Composition data

Instantaneous model
- Mayo-Lewis equation

Cumulative model
- Meyer-Lowry equation

Direct Numerical Integration

\[
\frac{df_1}{dx_n} = \frac{f_1 - F_1}{1 - x_n}
\]

\[
F_1 = \frac{f_{10} - f_1(1 - x_n)}{x_n}
\]
Error-in-Variables-Model (EVM)

- EVM takes into account the error in all variables

- EVM consists of two statements:
  - Equating the vector of measurements (e.g., $f_i$ and $F_i$) to the vector of true values (e.g., $f_i^*$ and $F_i^*$),
    \[
    \begin{align*}
    f_{ij} &= f_{ij}^*(1 + \epsilon_{f_i}) \\
    F_{ij} &= F_{ij}^*(1 + \epsilon_{F_i})
    \end{align*}
    \]
  - The true values of the parameters ($\theta^*$) and variables are related with the model (e.g., the Mayo-Lewis model):
    \[
    f_i(\xi_i^*, \theta^*) = F_i^* - \frac{r_1^* f_{1i}^* + f_{1i}^*(1 - f_{1i}^*)}{r_1^* f_{1i}^* + 2f_{1i}^*(1 - f_{1i}^*) + r_2^*(1 - f_{1i}^*)^2}
    \]
First Question
Why Cumulative Composition Data?

Avoiding the problems with the instantaneous composition model.

Increased information from the full conversion trajectory, not only very low conversions.
The precision of the estimation results is shown by their 95% joint confidence region (JCR).

The smaller the JCR, the higher the reliability of the point estimates.

Considerable overlap between JCRs, great agreement between the instantaneous and cumulative results.

The area of EVM JCR is smaller for cumulative model, demonstrating the advantage of employing cumulative models.

Both cumulative models provide comparable results.

Data set from Madruga and Fernandez-Garcia (1994)
Reactivity ratio estimates are in good agreement with low conversion data analysis.

Considerable increase in confidence in the point estimates.

Reactivity ratio estimates are of higher precision.

Data set from Madruga and Fernandez-Garcia(1994)
Useful data of high conversion polymerization are utilized to estimate reactivity ratios.

More information for the analysis: More reliable reactivity ratios.

In most cases, good agreement between the Direct Numerical Integration and the Meyer-Lowry model.

Direct Numerical Integration has always performed successfully (no convergence problem) over the full conversion trajectory.
Potential problems with Meyer-Lowry equation:

- Restrictive underlying assumptions.
- When $f_1$ is one of the measured variables.
- When $r_1$ or $r_2$ approach one.

Convergence issues for Meyer-Lowry model have been observed:

- Data sets with higher than moderate conversion levels.
- Significantly differing reactivity ratios.
- Considerable experimental error.
Remarks:

Direct Numerical Integration vs. Meyer-Lowry Model

Direct Numerical Integration:

- No convergence or other numerical issues.
- Uses all available information up to full conversion.

Direct and General

Straightforward

More Reliable

Data set from Madruga and Fernandez-Garcia (1994)
Further Remarks

Data set from McManus and Penlidis (1996)

- Reactivity ratio estimates, reference
- Reactivity ratio estimates, current work
- Experimental work

Often ignored conversion values “hide” a lot of information!
Reactivity ratios obtained from copolymerization experiments are commonly used in problems dealing with terpolymerization reactions.

The only justification seems to be the similarity of the kinetic mechanism used in derivation of both copolymerization and terpolymerization composition equation models.

There are several reasons why binary reactivity ratios should not be used for terpolymerizations:

- Conflicting reactivity ratio values for copolymerization systems in the literature.
- Inaccuracies in binary reactivity ratios can propagate in the terpolymerization composition equations.
- Between the existing sets of reactivity ratios... which set of values should be used?!
Terpolymerization Instantaneous Composition Model

- Instantaneous terpolymerization composition equations—Alfrey-Goldfinger model:

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

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

- Application of EVM on Alfrey-Goldfinger equations.

- How significantly can the quality of reactivity ratio estimates be improved?
EVM using Ternary Data

- Reactivity ratios are estimated using EVM.

- Variation in sizes of JCRs.

- Potential reasons:
  - Larger experimental error for some pairs
  - Poor experimental design (overall)

- The determination of reactivity ratios should be directly based on terpolymerization data, using adequate experimental information and appropriate experimental design.

Data set from Brar and Hekmatyar (1999)
● Binary reactivity ratios fall inside and outside of the 95% JCRs.
● Clear inconsistency between literature values for binary reactivity ratios.
● These results make us skeptical about using binary reactivity ratios for terpolymerization systems.
Further Remarks

Terpolymerization of acrylonitrile (AN, M₁) / styrene (Sty, M₂) / 2,3-dibromopropyl acrylate (DBPA, M₃)

<table>
<thead>
<tr>
<th></th>
<th>r₁₂</th>
<th>r₂₁</th>
<th>r₁₃</th>
<th>r₃₁</th>
<th>r₂₃</th>
<th>r₃₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binary reactivity ratios</td>
<td>0.100</td>
<td>0.440</td>
<td>0.900</td>
<td>0.860</td>
<td>0.430</td>
<td>0.140</td>
</tr>
<tr>
<td>Ternary reactivity ratios</td>
<td>0.077</td>
<td>0.419</td>
<td>0.390</td>
<td>0.460</td>
<td>0.411</td>
<td>0.191</td>
</tr>
</tbody>
</table>

- Using binary reactivity ratios: **No Azeotrope**.
- An azeotropic point is found, but **ONLY** after using reactivity ratio estimates based directly on terpolymerization data.
- System studied in literature and shown to exhibit azeotrope!
- A practical example of one of the consequences of using binary reactivity ratios instead of ternary ones.

Data set from Saric et al (1983)
Our main goal is to determine reliable reactivity ratios with the highest possible precision.

The following points have been made:

- Cumulative copolymer composition models should be preferred over the use of instantaneous models.
- Direct Numerical Integration is a superior approach for estimating reactivity ratios.
- If ternary system data are available, then no need to use reactivity ratios from the corresponding binary pairs.
Determining the best reactivity ratios is not only about finding “the best calculation method”. Several factors such as analytical method and/or experimental design play significant roles.

- **Copolymerization studies:**
  - Studying cumulative triad fraction models/data
  - Considering penultimate models

- **Terpolymerization studies:**
  - D – optimal design in order to improve the quality of reactivity ratio estimates.
  - Studying full conversion range data
Questions?

Thank you!
Back-up Slides
References

## Reactivity Ratio Point Estimates for DBI/MMA

<table>
<thead>
<tr>
<th>Copolymerization model</th>
<th>Conversion level</th>
<th>$r_1$</th>
<th>$r_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Madruga and Fernandez-Garcia[17]</td>
<td>Mayo-Lewis</td>
<td>Low</td>
<td>0.717</td>
</tr>
<tr>
<td>Current work</td>
<td>Mayo-Lewis</td>
<td>Low</td>
<td>0.7098</td>
</tr>
<tr>
<td>Current work</td>
<td>Meyer-Lowry</td>
<td>Low</td>
<td>0.7129</td>
</tr>
<tr>
<td>Current work</td>
<td>Direct Numerical Integration</td>
<td>Low</td>
<td>0.7156</td>
</tr>
<tr>
<td>Current work</td>
<td>Meyer-Lowry</td>
<td>High</td>
<td>0.6794</td>
</tr>
<tr>
<td>Current work</td>
<td>Direct Numerical Integration</td>
<td>High</td>
<td>0.6798</td>
</tr>
</tbody>
</table>
Comparison between two cumulative copolymer composition model performances for Sty/MMA copolymerization based on simulated composition data of different error levels

<table>
<thead>
<tr>
<th>Error in $X_n$ and</th>
<th>Maximum conversion</th>
<th>Meyer-Lowry point estimates</th>
<th>Direct Numerical Integration point estimates</th>
</tr>
</thead>
<tbody>
<tr>
<td>In $X_n = 1%$</td>
<td>$X_n \leq 55%$</td>
<td>$r_1 = 0.4600$</td>
<td>$r_1 = 0.4572$</td>
</tr>
<tr>
<td>In $\bar{F}_1 = 5%$</td>
<td></td>
<td>$r_2 = 0.4317$</td>
<td>$r_2 = 0.4389$</td>
</tr>
<tr>
<td>In $X_n = 0.5%$</td>
<td>$X_n \leq 80%$</td>
<td>$r_1 = 0.4409$</td>
<td>$r_1 = 0.4408$</td>
</tr>
<tr>
<td>In $\bar{F}_1 = 2%$</td>
<td></td>
<td>$r_2 = 0.4345$</td>
<td>$r_2 = 0.4347$</td>
</tr>
<tr>
<td>In $X_n = 0.1%$</td>
<td>$X_n \leq 90%$</td>
<td>$r_1 = 0.4453$</td>
<td>$r_1 = 0.4452$</td>
</tr>
<tr>
<td>In $\bar{F}_1 = 0.5%$</td>
<td></td>
<td>$r_2 = 0.4313$</td>
<td>$r_2 = 0.4311$</td>
</tr>
<tr>
<td>In $X_n = 0%$</td>
<td>$X_n \leq 90%$</td>
<td>$r_1 = 0.4317$</td>
<td>$r_1 = 0.4317$</td>
</tr>
<tr>
<td>In $\bar{F}_1 = 0%$</td>
<td></td>
<td>$r_2 = 0.4218$</td>
<td>$r_2 = 0.4218$</td>
</tr>
</tbody>
</table>
**Importance of Information Content**

Styrene (STY, \(M_1\)) / Ethyl Acrylate (EA, \(M_2\))

Cumulative models would provide higher quality parameter estimates (smaller JCRs).

<table>
<thead>
<tr>
<th>Feed composition</th>
<th>Copolymer composition</th>
<th>Conversion (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((f_0)_{Sty})</td>
<td>(F_{Sty})</td>
<td>(X_w)</td>
</tr>
<tr>
<td>0.0788</td>
<td>0.296</td>
<td>1.2</td>
</tr>
<tr>
<td>0.0788</td>
<td>0.308</td>
<td>1.27</td>
</tr>
<tr>
<td>0.0788</td>
<td>0.303</td>
<td>1.16</td>
</tr>
<tr>
<td>0.0788</td>
<td>0.286</td>
<td>1.04</td>
</tr>
<tr>
<td>0.7193</td>
<td>0.716</td>
<td>1.49</td>
</tr>
<tr>
<td>0.7193</td>
<td>0.736</td>
<td>1.48</td>
</tr>
<tr>
<td>0.7193</td>
<td>0.736</td>
<td>1.40</td>
</tr>
<tr>
<td>0.7193</td>
<td>0.732</td>
<td>1.46</td>
</tr>
</tbody>
</table>

Since changes in the values of conversion are minimal, the information content of the cumulative models is not more than what the instantaneous model knows!

Data set from McManus and Penlidis (1996)
Reactivity ratio estimation results for Sty/EA

Low conversion data, Maximum of conversion: 4.75%
High conversion data, Maximum of conversion: 71.4%

<table>
<thead>
<tr>
<th>Copolymerization model</th>
<th>Conversion level</th>
<th>( r_1 )</th>
<th>( r_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>McManus and Penlidis[15]</td>
<td>Mayo-Lewis</td>
<td>Low</td>
<td>0.717</td>
</tr>
<tr>
<td>Current work</td>
<td>Mayo-Lewis</td>
<td>Low</td>
<td>0.717</td>
</tr>
<tr>
<td>Current work</td>
<td>Meyer-Lowry</td>
<td>Low</td>
<td>0.7166</td>
</tr>
<tr>
<td>Current work</td>
<td>Direct Numerical Integration</td>
<td>Low</td>
<td>0.7127</td>
</tr>
<tr>
<td>Current work</td>
<td>Meyer-Lowry</td>
<td>( X_w \leq 60% )</td>
<td>0.9215</td>
</tr>
<tr>
<td>Current work</td>
<td>Direct Numerical Integration</td>
<td>( X_w \leq 60% )</td>
<td>0.9238</td>
</tr>
<tr>
<td>Current work</td>
<td>Direct Numerical Integration</td>
<td>High</td>
<td>0.9318</td>
</tr>
</tbody>
</table>

Point estimates for the Meyer-Lowry model and direct numerical integration with moderate conversion data shifted considerably comparing to the Mayo-Lewis model point estimates with low conversion data!
A demonstration of the fact that combining high conversion information at azeotropc conditions with low conversion data is much preferable, as it will increase the reliability/quality of the reactivity ratio estimates.

Data set from McManus and Penlidis (1996)
The reactivity ratios obtained from Mayo-Lewis model (low conversion data) and the Direct Numerical Integration model (high conversion data) were used to simulate instantaneous triad fractions.

The difference between the performance of these two models shows the effect high conversion values can have on the outcome of the analysis.
Reactivity ratios obtained from copolymerization experiments are commonly used in problems dealing with terpolymerization reactions.

The only justification seems to be the similarity of the kinetic terminal unit mechanism used in derivation of both copolymerization and terpolymerization composition equation models.

There are several reasons why binary reactivity ratios should not be used for terpolymerizations:

- Conflicting reactivity ratio values for copolymerization systems in the literature.
- Inaccuracies in binary reactivity ratios can propagate in the terpolymerization composition equations.
- Between the existing sets of reactivity ratios... *which set of values should be used?*
- The underlying assumption resulting in the analogy between ternary and binary systems might not be always true.
- The presence of the third monomer has been completely ignored.
Comparison between Ternary and Binary Reactivity Ratios

Terpolymerization of Acrylonitrile (M₁) / Styrene (M₂) / Methyl Methacrylate (M₃)

Cumulative terpolymer composition versus conversion using binary and ternary reactivity ratios with initial feed composition 0.42/0.36/0.22

Clear difference between the cumulative composition trajectories!
Azeotropic point is a feed composition at which the polymerization does not exhibit composition drift

\[
\frac{d[m_1]}{[m_1]} dt = \frac{d[m_2]}{[m_2]} dt = \ldots
\]

Arrive at a general numerical solution of the multicomponent composition model

the Alfrey-Goldfinger equations were solved numerically at azeotropic conditions (solving a set of nonlinear algebraic equations using Matlab)

During the numerical testing phase with literature reports, we observed that literature results and those found by our program did not agree in most of the cases.