Estimating Improved Reactivity Ratios

Institute for Polymer Research
IPR
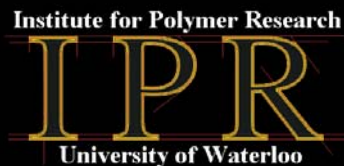University of Waterloo

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

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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.
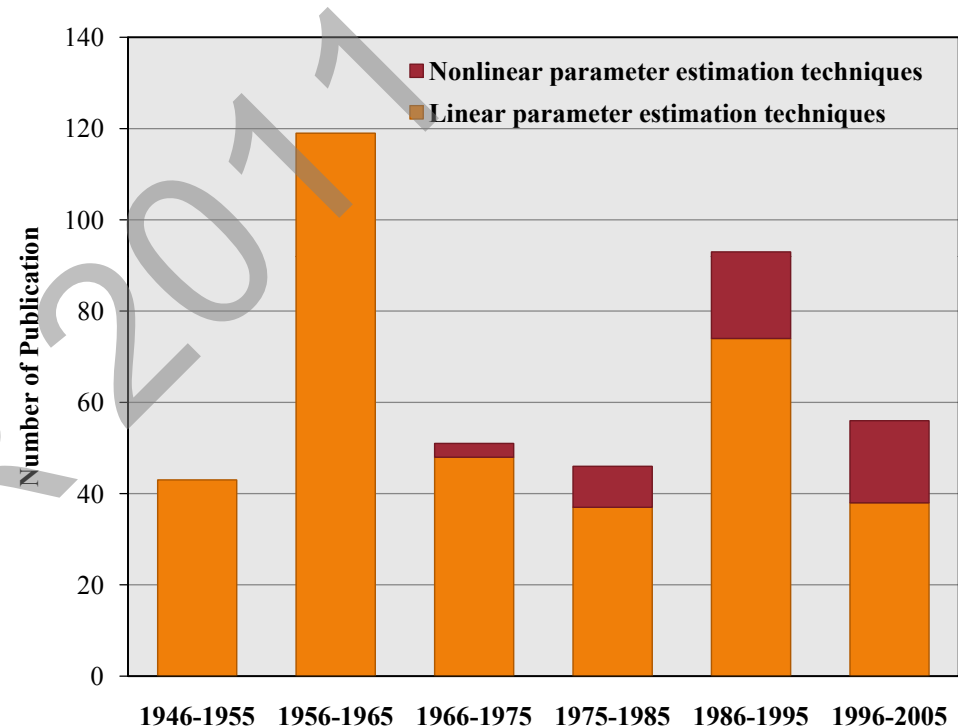
What is the real drawback ?

Styrene (STY) and Methyl Methacryalte (MMA) Copolymerization
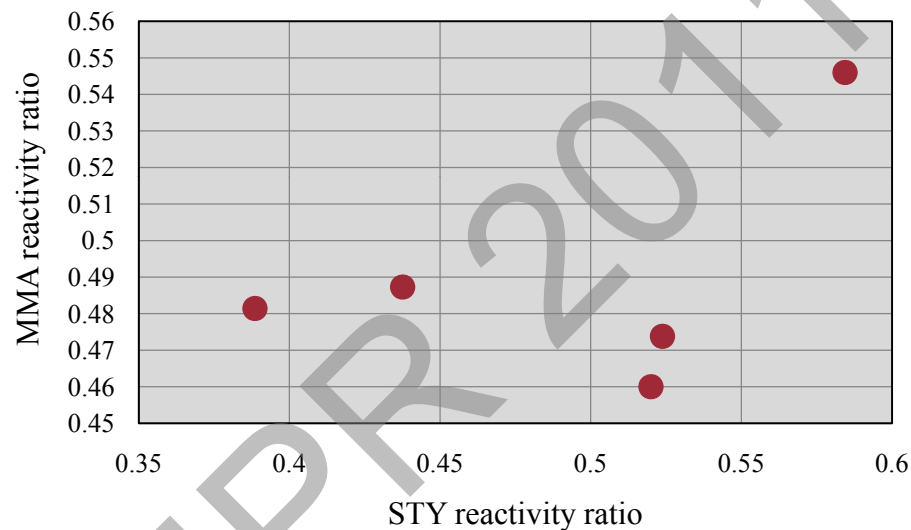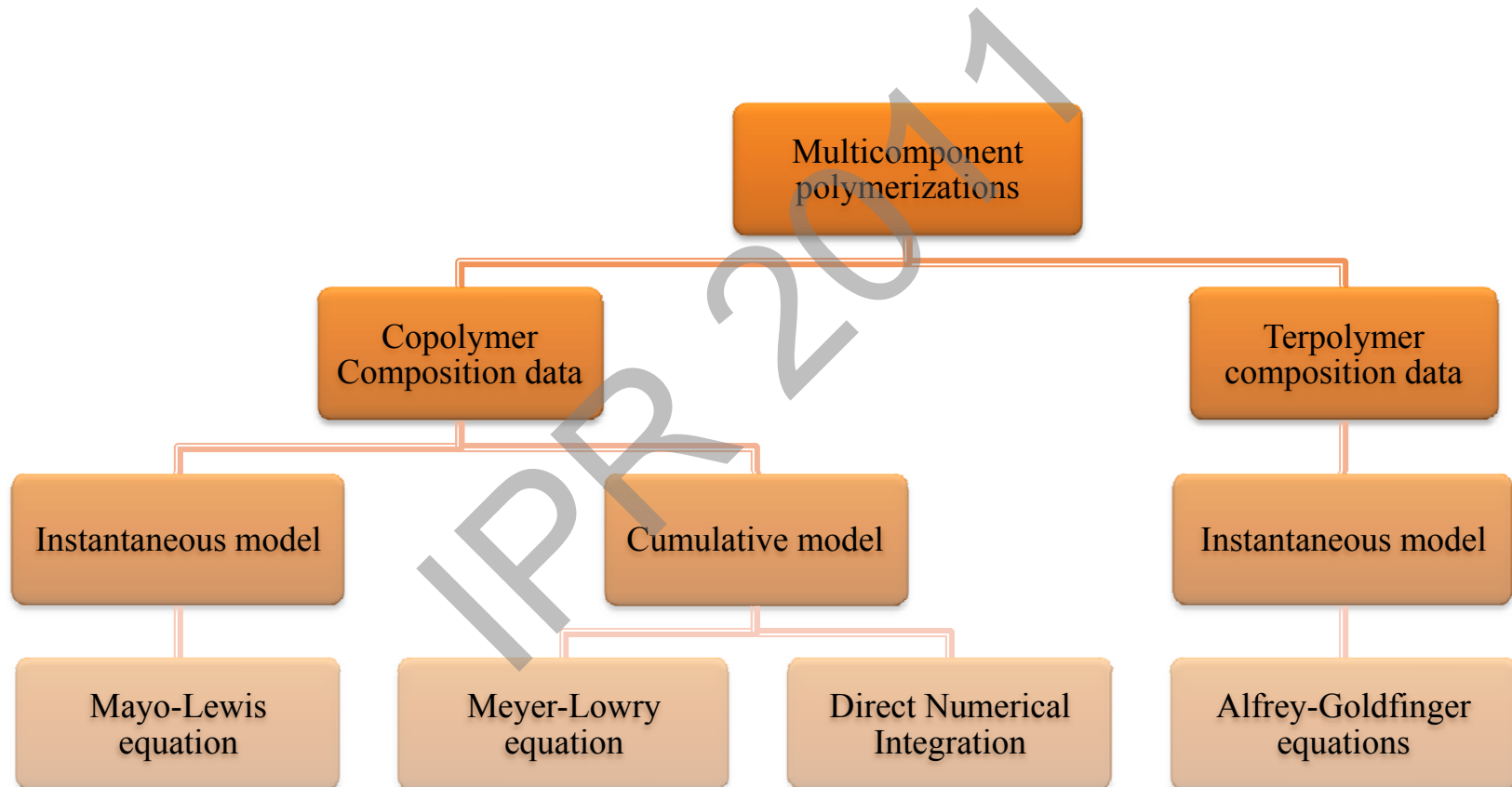

As stated in the literature:

"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"

Outline

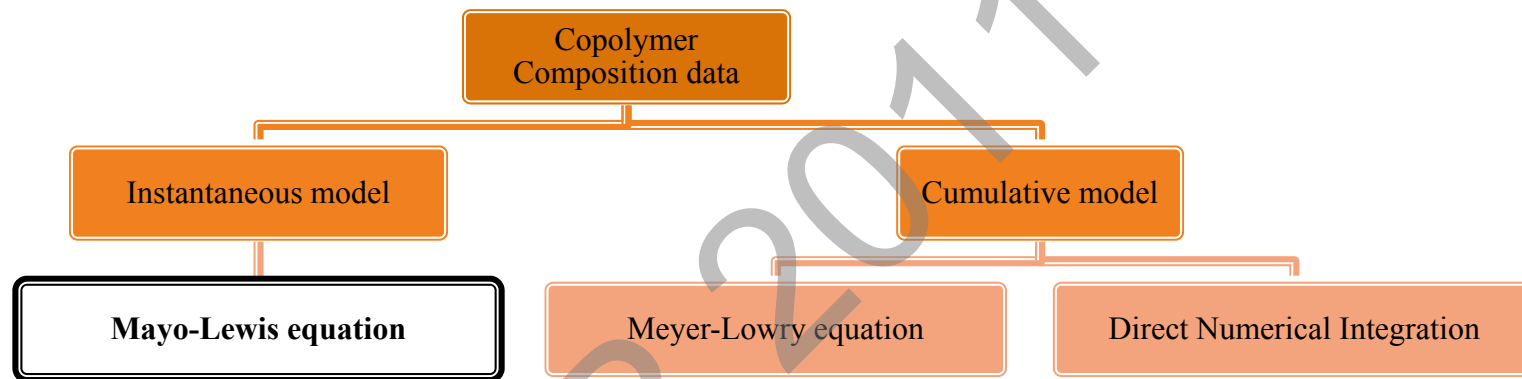- Main Objective

  - How can these issues be improved with respect to accuracy and precision?

- Background

  - Multicomponent polymerization models
  - 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

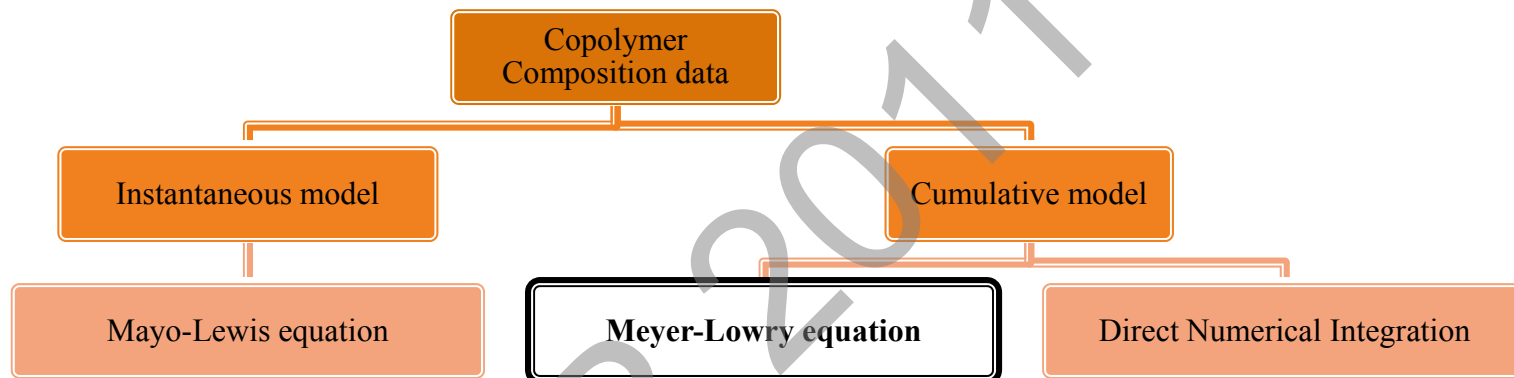- Future Steps

Background:

Multicomponent Polymerization Models

```
                    ┌──────────────────────┐
                    │    Multicomponent    │
                    │    polymerizations   │
                    └──────────────────────┘
           ┌────────────────┴────────────────────┐
  ┌──────────────────┐                  ┌──────────────────┐
  │    Copolymer     │                  │    Terpolymer    │
  │ Composition data │                  │ composition data │
  └──────────────────┘                  └──────────────────┘
    ┌──────┴────────┐                            │
┌─────────────┐  ┌─────────────┐         ┌─────────────┐
│Instantaneous│  │ Cumulative  │         │Instantaneous│
│    model    │  │    model    │         │    model    │
└─────────────┘  └─────────────┘         └─────────────┘
      │        ┌──────┴──────┐                  │
┌───────────┐ ┌───────────┐ ┌───────────┐ ┌───────────────┐
│Mayo-Lewis │ │Meyer-Lowry│ │  Direct   │ │Alfrey-Goldfinger│
│ equation  │ │ equation  │ │ Numerical │ │   equations    │
│           │ │           │ │Integration│ │                │
└───────────┘ └───────────┘ └───────────┘ └───────────────┘
```

Copolymerization Models

```
                    ┌─────────────────────┐
                    │     Copolymer       │
                    │  Composition data   │
                    └─────────────────────┘
              ┌───────────────┴───────────────┐
    ┌──────────────────┐          ┌──────────────────┐
    │ Instantaneous    │          │ Cumulative model │
    │     model        │          └──────────────────┘
    └──────────────────┘            ┌──────────┴──────────┐
┌──────────────────────┐  ┌──────────────────┐  ┌────────────────────────────┐
│  Mayo-Lewis equation │  │ Meyer-Lowry      │  │ Direct Numerical Integration│
│                      │  │   equation       │  │                            │
└──────────────────────┘  └──────────────────┘  └────────────────────────────┘
```

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

Copolymerization Models

```
                    ┌─────────────────────┐
                    │   Copolymer         │
                    │ Composition data    │
                    └─────────────────────┘
          ┌──────────────────┴──────────────────┐
┌─────────────────────┐              ┌─────────────────────┐
│ Instantaneous model │              │  Cumulative model   │
└─────────────────────┘              └─────────────────────┘
          │                    ┌───────────┴───────────┐
┌─────────────────────┐ ┌─────────────────────┐ ┌─────────────────────────────┐
│ Mayo-Lewis equation │ │ Meyer-Lowry equation│ │ Direct Numerical Integration│
└─────────────────────┘ └─────────────────────┘ └─────────────────────────────┘
```

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

$$\alpha = \frac{r_2}{(1 - r_2)} \quad \beta = \frac{r_1}{(1 - r_1)}$$

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

Copolymerization Models

```
┌─────────────────────┐
│     Copolymer       │
│ Composition data    │
└─────────────────────┘
```

Instantaneous model — **Cumulative model**

Mayo-Lewis equation | **Meyer-Lowry equation** | **Direct Numerical Integration**
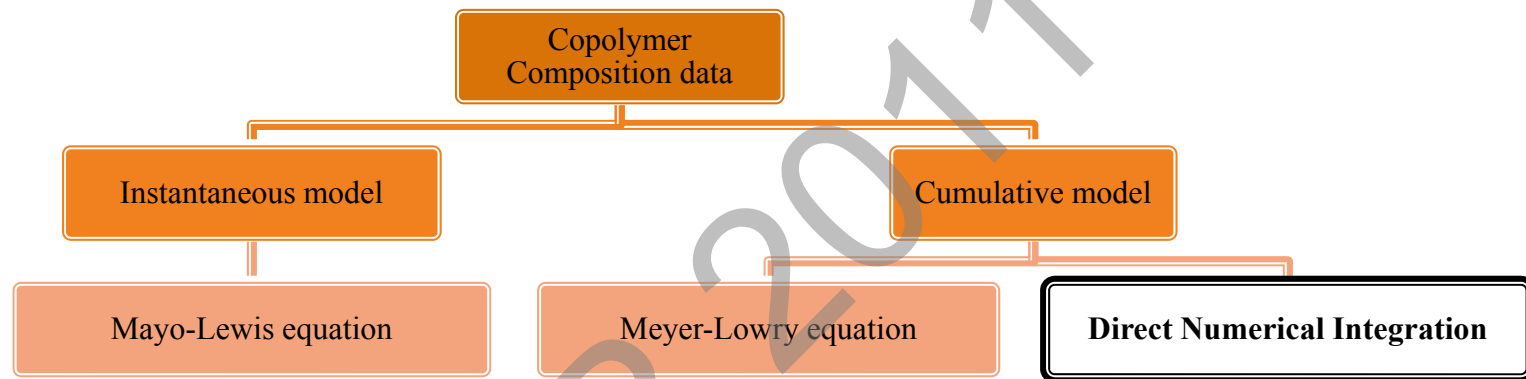
$$\frac{df_1}{dx_n} = \frac{f_1 - F_1}{1 - x_n}$$

$$\overline{F}_1 = \frac{f_{10} - f_1(1 - x_n)}{x_n}$$

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_1 and F_1) to the vector of true values (e.g., f_1^* and F_1^*),

$$\begin{cases} f_{1j} = f_{1j}^*(1 + \varepsilon_{f_1}) \\ F_{1j} = F_{1j}^*(1 + \varepsilon_{F_1}) \end{cases}$$

  ○ The true values of the parameters ($\theta*$) and variables are related with the model (e.g., the Mayo-Lewis model):

$$f_i(\xi_i^*, \theta^*) = F_1^* - \frac{r_1^* f_{1i}^{*2} + f_{1i}^*(1 - f_{1i}^*)}{r_1^* f_{1i}^{*2} + 2f_{1i}^*(1 - f_{1i}^*) + r_2^*(1 - f_{1i}^*)^2}$$

First Question

Why Cumulative Composition Data?

Instantaneous model

- Mayo-Lewis equation

- EVM

Cumulative model

- Meyer-Lowry equation

- Direct Numerical Integration

- Implementing EVM

Evaluation

- Obtaining the best possible estimates of the parameters

- Taking into account all information available

- Reasonably easy to use
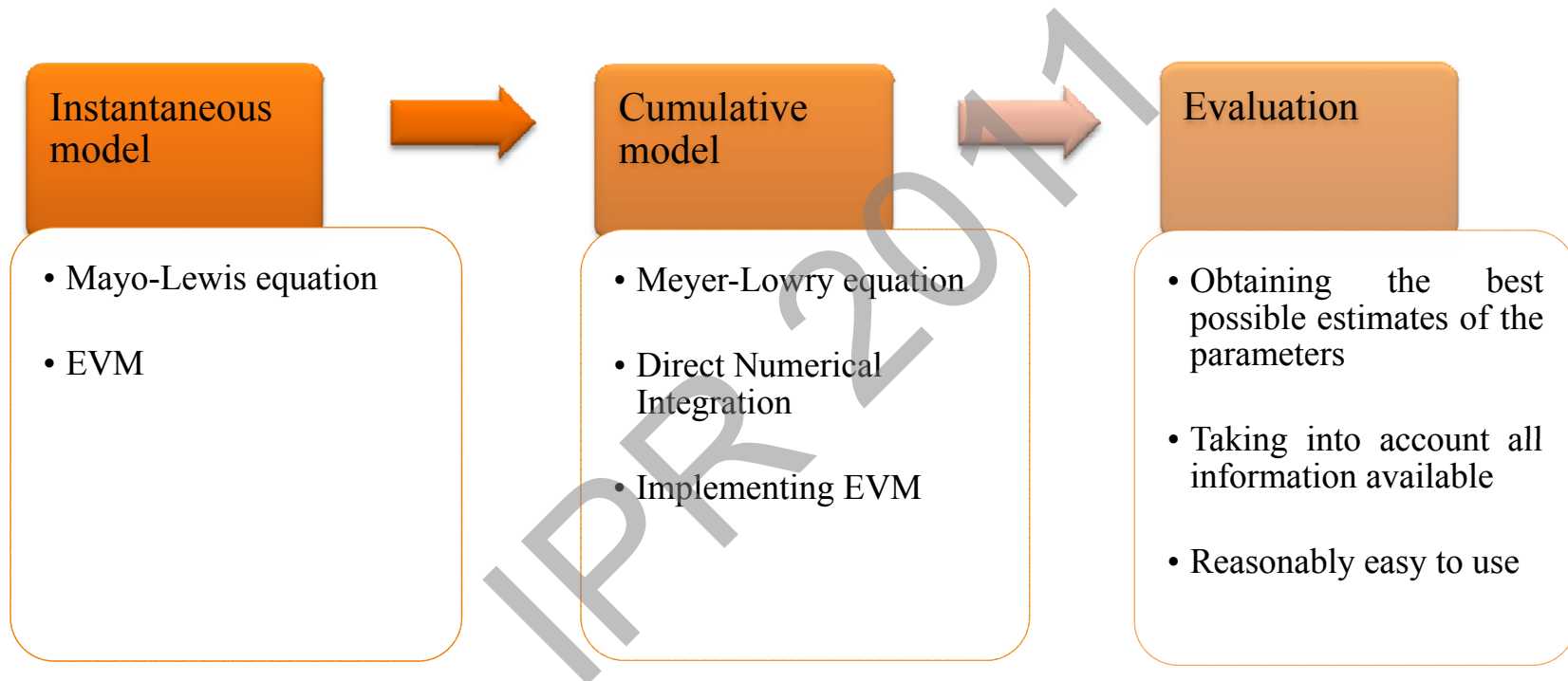
Avoiding the problems with the instantaneous composition model.

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.

Legend:
- Direct Numerical Integration JCR
- Meyer-Lowry model JCR
- □ Reactivity ratio estimates, reference
- ▲ Reactivity ratio estimates, Meyer-Lowry model
- ● Reactivity ratio estimates, Direct Numerical Integration
- Mayo-Lewis JCR
- ◆ Reactivity ratio estimates, Mayo-Lewis model

Di-n-Butyl Itaconate (DBI, M_1)
Methyl Methacrylate (MMA, M_2)

Axis: $r2$ (vertical), $r1$ (horizontal)
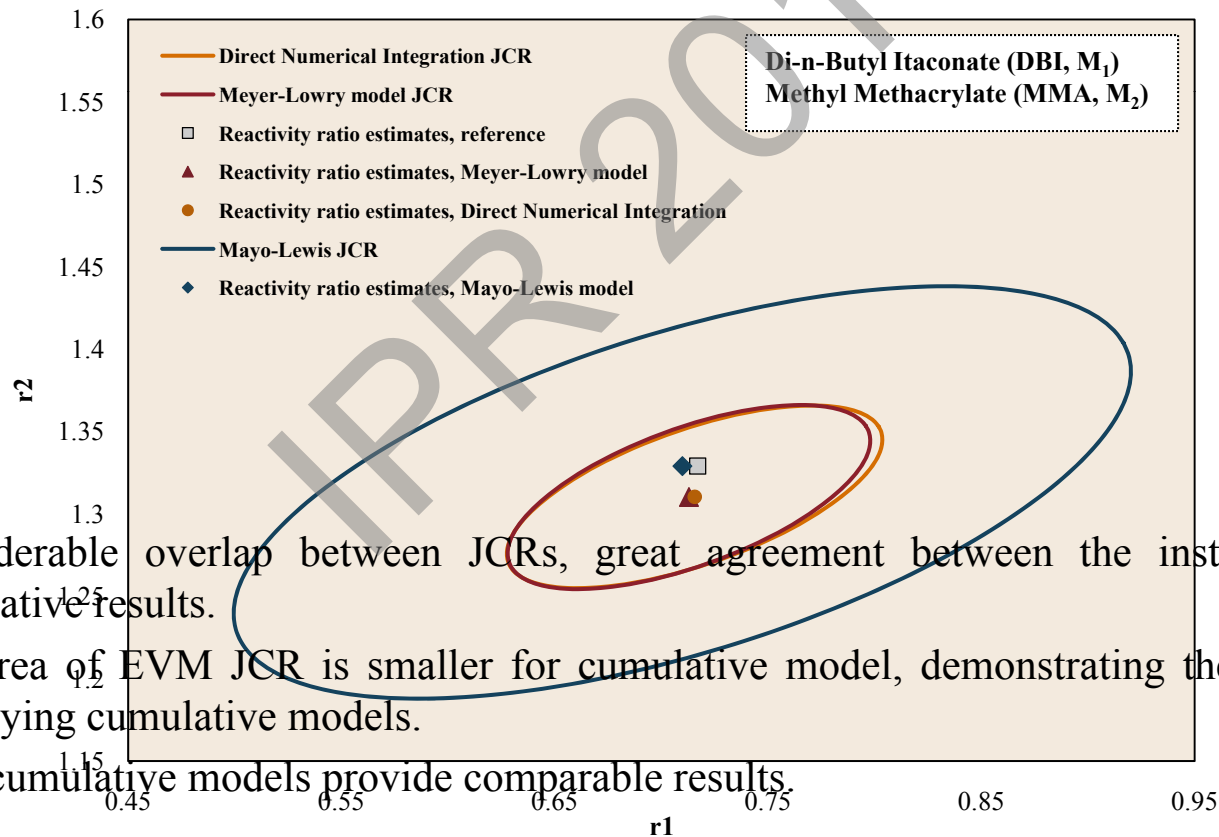
- Considerable overlap between JCRs, great agreement between the instantaneous and cumulative results.
- The area of EVM JCR is smaller for cumulative model, demonstrating the advantage of employing cumulative models.
- Both cumulative models provide comparable results.

Data set from Madruga and Fernandez-Garcia(1994)

What Happens Over the Full Conversion?

- 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.

Legend:
- Direct Numerical Integration JCR
- Meyer-Lowry model JCR
- □ Reactivity ratio estimates, reference
- ▲ Reactivity ratio estimates, Meyer-Lowry model
- ● Reactivity ratio estimates, Direct Numerical Integration
- Mayo-Lewis JCR
- ◆ Reactivity ratio estimates, Mayo-Lewis model

Di-n-Butyl Itaconate (DBI, M_1)
Methyl Methacrylate (MMA, M_2)

Data set from Madruga and Fernandez-Garcia(1994)

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Full Conversion Composition Data

- ✓ 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.

Problems with Meyer-Lowry Model

o 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.

o Convergence issues for Meyer-Lowry model have been observed:

  ➢ Data sets with higher than moderate conversion levels.

  ➢ Significantly differing reactivity ratios.

  ➢ Considerable experimental error.

Direct Numerical Integration:

➢ No convergence or other numerical issues.

➢ Uses all available information up to full conversion.

Direct and General

Straightforward

More Reliable

Legend:
- Direct Numerical Integration JCR
- Meyer-Lowry model JCR
- ■ Reactivity ratio estimates, reference
- ▲ Reactivity ratio estimates, Meyer-Lowry model
- ● Reactivity ratio estimates, Direct Numerical Integration

Di-n-Butyl Itaconate (DBI, M_1)
Methyl Methacrylate (MMA, M_2)

Axes: $r2$ (vertical), $r1$ (horizontal)

Data set from Madruga and Fernandez-Garcia (1994)

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Data set from McManus and Penlidis (1996)
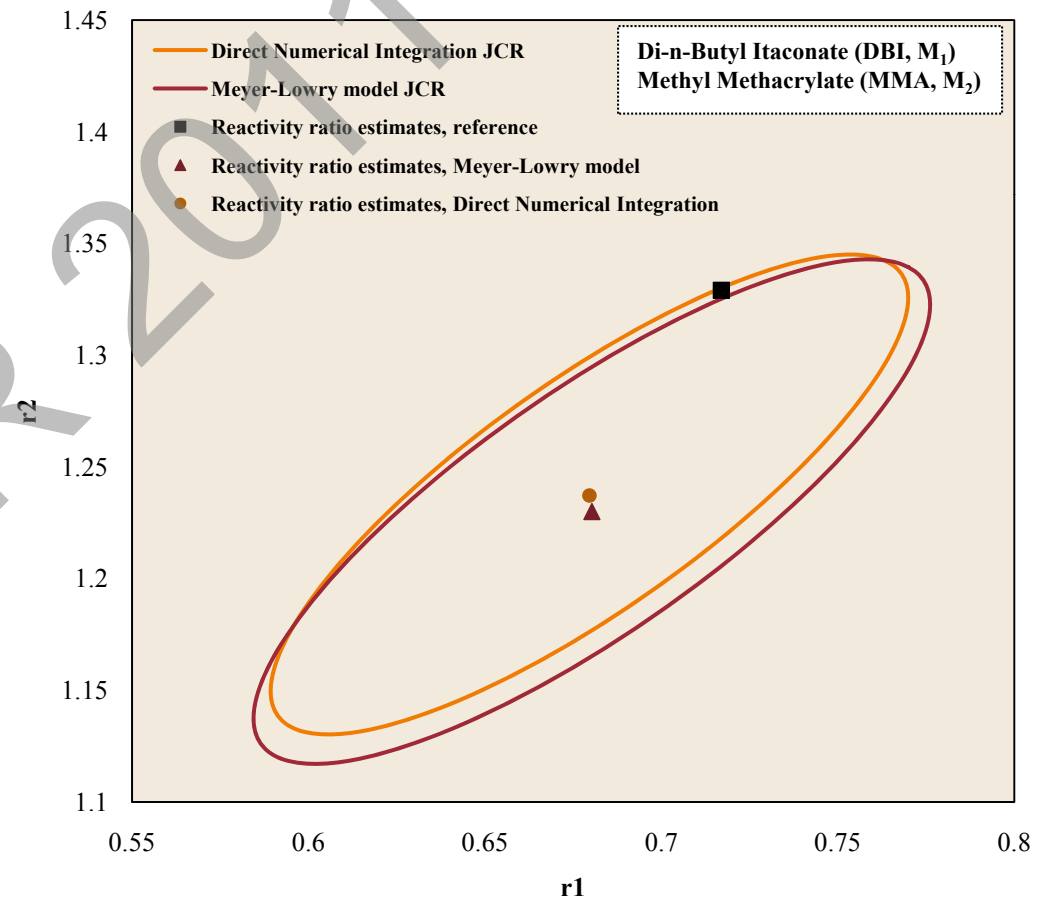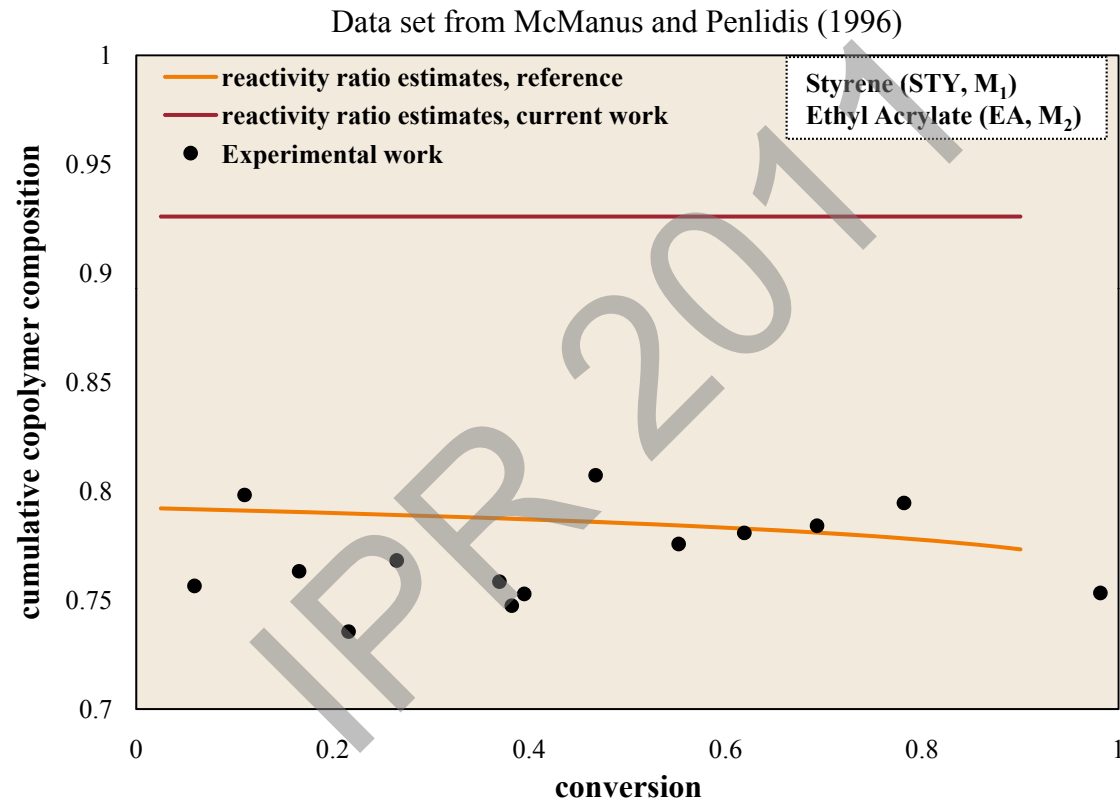
Often ignored conversion values "hide" a lot of information!

- ❖ 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:

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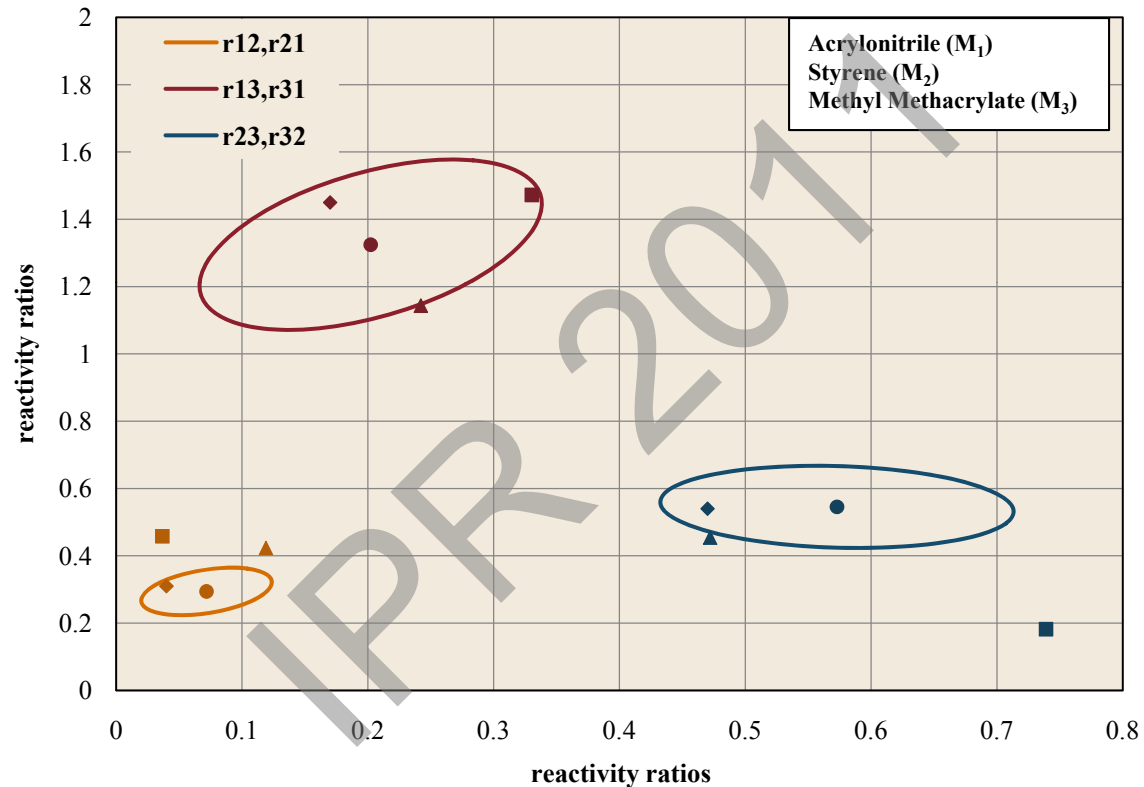rac{f_2}{r_{12}} + \dfrac{f_3}{r_{13}}\right)}{f_2\left(\dfrac{f_1}{r_{12}r_{31}} + \dfrac{f_2}{r_{12}r_{32}} + \dfrac{f_3}{r_{13}r_{32}}\right)\left(f_2 + \dfrac{f_1}{r_{21}} + \dfrac{f_3}{r_{23}}\right)}$$

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

- 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.


Acrylonitrile (M_1) / Styrene (M_2) / Methyl Methacrylate (M_3)

Legend: r12,r21; r13,r31; r23,r32

Data set from Brar and Hekmatyar (1999)

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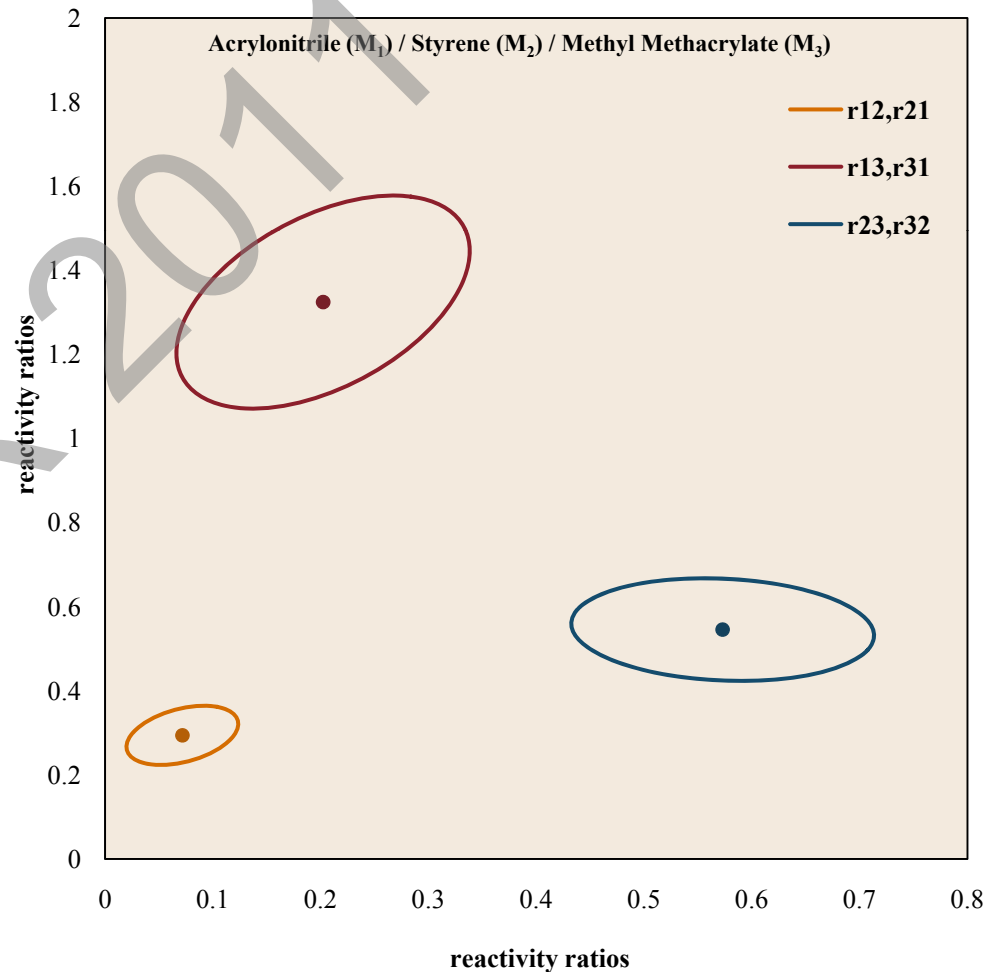
How to choose … ?

- 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.

Data set from Brar and Hekmatyar (1999)

Further Remarks

Terpolymerization of acrylonitrile (AN, M_1) / styrene (Sty, M_2) /2,3-dibromopropyl acrylate (DBPA, M_3)

	r_{12}	r_{21}	r_{13}	r_{31}	r_{23}	r_{32}
Binary reactivity ratios	0.100	0.440	0.900	0.860	0.430	0.140
Ternary reactivity ratios	0.077	0.419	0.390	0.460	0.411	0.191

- 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.
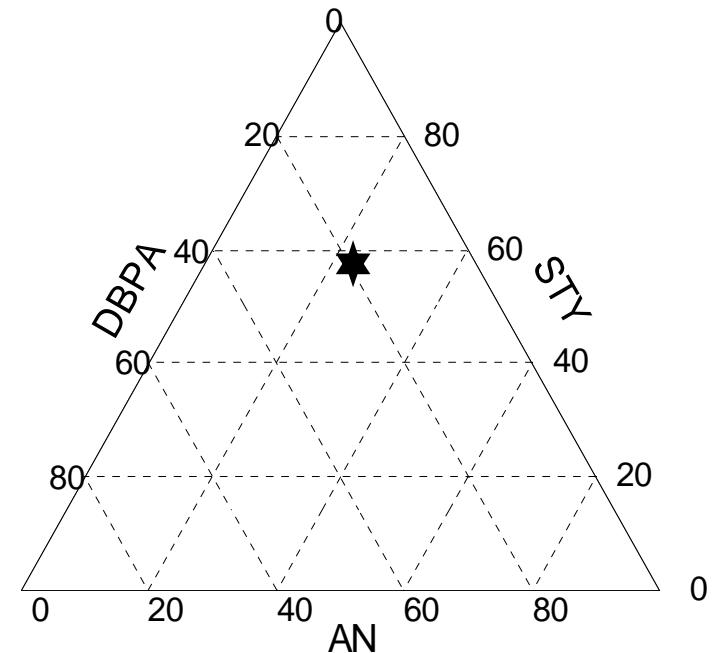
Data set from Saric et al (1983)

Concluding Remarks

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.

Future Steps

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

1. Alfrey, T. and Goldfinger, G., *J. of Chem. Phys., 12, 322 (1944).*

2. Brar, A. and Hekmatyar S*., J. of Appl. Polym. Sci., 74, 3026–3032 (1999).*

3. Duever, T. A., O' Driscoll, K. F. and Reilly, P. M., *J. of Polym. Sci. Part A: Polym. Chem., 21, 2003-2010 (1983).*

4. Hagiopol, C. *"Copolymerization, Towards Systematic Approach", Kluwer Academic/Plenum Publishers, New York (1999).*

5. Madruga, E. and Fernandez-Garcia, M*., Eur. Polym. J., 31, 1103-1107 (1995).*

6. Mayo, F. R. and Lewis, F. M., *J. of Amer. Chem. Soc., 66, 1594-1601 (1944).*

7. McManus, N. T. and Penlidis, A., *J. Polym. Sci. Part A: Polym. Chem.,* 34, 237 (1996).

8. Patino-Leal, H., Reilly, P. M. and O' Driscoll, K. F*., J. of Polym. Sci.: Polym. Letters Ed., 18, 219-227 (1980).*

9. Polic, A. L., Duever, T. A. and Penlidis, A., *J. of Polym. Sci. Part A: Polym. Chem., 36, 813-822 (1998).*

10. Reilly, P. M. and Patino-Leal, H*., Technometrics, 23, 221-232 (1981).*

Low conversion data, Maximum of conversion: 1.46%

High conversion data, Maximum of conversion: 96.15%

Reactivity ratio estimates for DBI/MMA

	Copolymerization model	Conversion level	r_1	r_2
Madruga and Fernandez-Garcia[17]	Mayo-Lewis	Low	0.717	1.329
Current work	Mayo-Lewis	Low	0.7098	1.313
Current work	Meyer-Lowry	Low	0.7129	1.310
Current work	Direct Numerical Integration	Low	0.7156	1.310
Current work	Meyer-Lowry	High	0.6794	1.229
Current work	Direct Numerical Integration	High	0.6798	1.238

Meyer-Lowry Model Convergence Issue

Comparison between two cumulative copolymer composition model performances for Sty/MMA copolymerization based on simulated composition data of different error levels

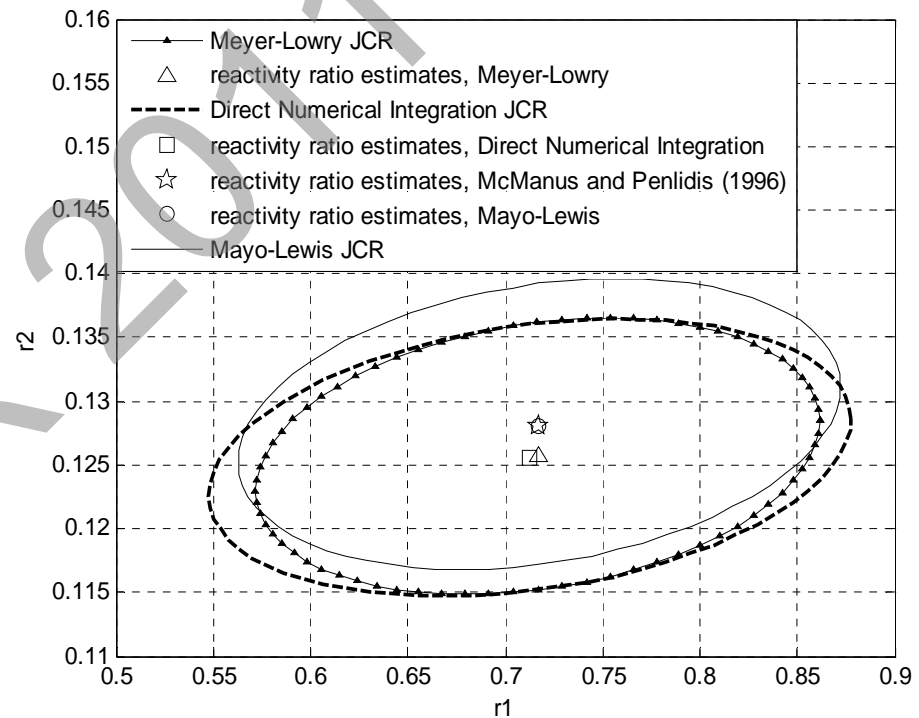| Error in X_w and	Maximum conversion	Meyer-Lowry point estimates	Direct Numerical Integration point estimates
In X_w= 1% In $\overline{F_1}$ = 5%	$X_w \leq 55\%$	r_1= 0.4600 r_2= 0.4317	r_1= 0.4572 r_2= 0.4389
In X_w= 0.5% In $\overline{F_1}$ = 2%	$X_w \leq 80\%$	r_1= 0.4409 r_2= 0.4345	r_1= 0.4408 r_2= 0.4347
In X_w= 0.1% In $\overline{F_1}$ = 0.5%	$X_w \leq 90\%$	r_1= 0.4453 r_2= 0.4313	r_1= 0.4452 r_2= 0.4311
In X_w= 0% In $\overline{F_1}$ = 0%	$X_w \leq 90\%$	r_1= 0.4317 r_2= 0.4218	r_1= 0.4317 r_2= 0.4218

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

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

Feed composition	Copolymer composition	Conversion (wt%)
$(f_o)_{Sty}$	F_{Sty}	X_w
0.0788	0.296	1.2
0.0788	0.308	1.27
0.0788	0.303	1.16
0.0788	0.286	1.04
0.7193	0.716	1.49
0.7193	0.736	1.48
0.7193	0.736	1.40
0.7193	0.732	1.46

Not much information !

Legend:
- Meyer-Lowry JCR
- △ reactivity ratio estimates, Meyer-Lowry
- Direct Numerical Integration JCR
- □ reactivity ratio estimates, Direct Numerical Integration
- ☆ reactivity ratio estimates, McManus and Penlidis (1996)
- ○ reactivity ratio estimates, Mayo-Lewis
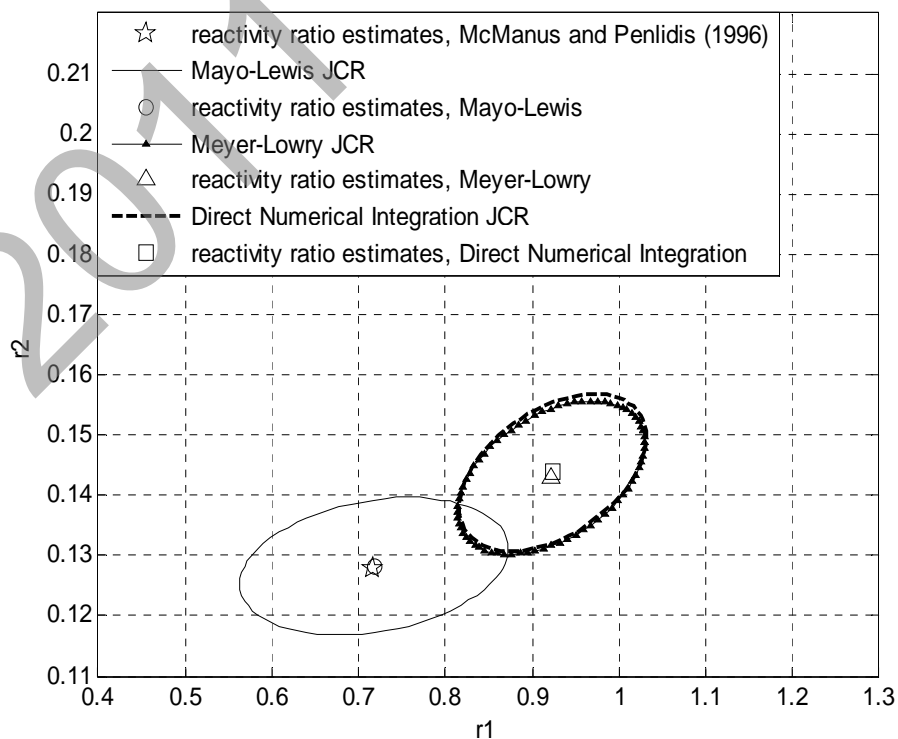- Mayo-Lewis JCR

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)

Low conversion data, Maximum of conversion: 4.75%

High conversion data, Maximum of conversion: 71.4%

Copolymerization model	Conversion level	r_1	r_2
McManus and Penlidis[15] — Mayo-Lewis	Low	0.717	0.128
Current work — Mayo-Lewis	Low	0.717	0.1282
Current work — Meyer-Lowry	Low	0.7166	0.1257
Current work — Direct Numerical Integration	Low	0.7127	0.1256
Current work — Meyer-Lowry	$X_w \leq 60\%$	0.9215	0.1429
Current work — Direct Numerical Integration	$X_w \leq 60\%$	0.9238	0.1438
Current work — Direct Numerical Integration	High	0.9318	0.1403

- ☆ reactivity ratio estimates, McManus and Penlidis (1996)
- —— Mayo-Lewis JCR
- ○ reactivity ratio estimates, Mayo-Lewis
- —▲— Meyer-Lowry JCR
- △ reactivity ratio estimates, Meyer-Lowry
- - - - Direct Numerical Integration JCR
- □ reactivity ratio estimates, Direct Numerical Integration

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 !

Data set from McManus and Penlidis (1996)

Enhanced Information Content
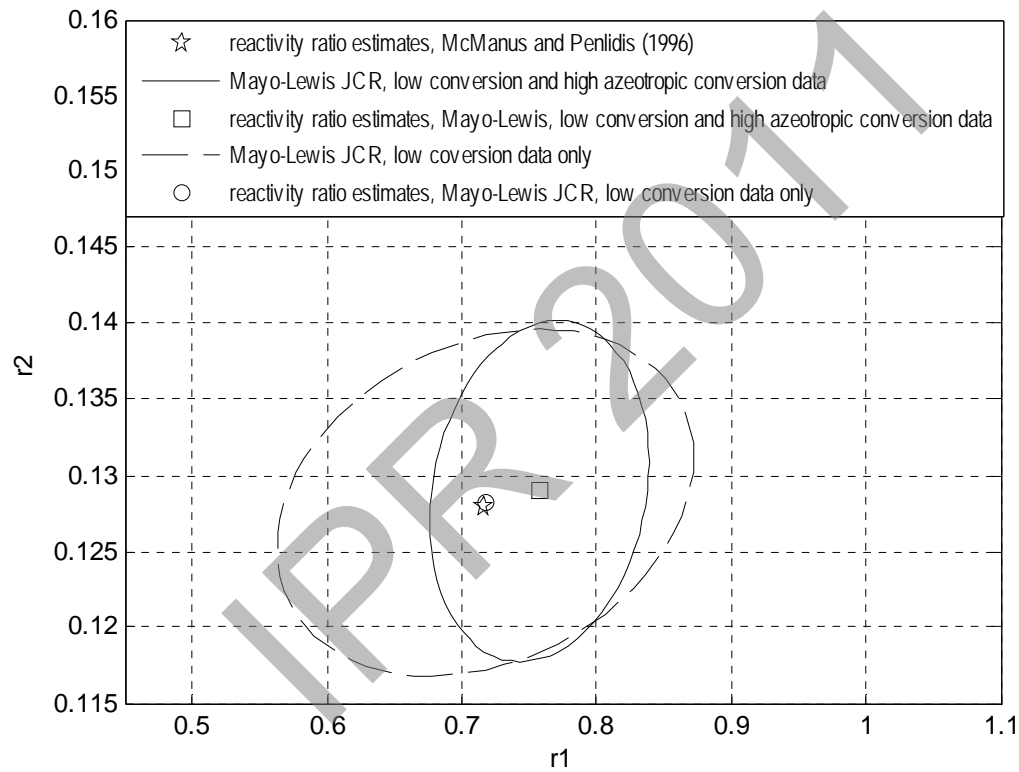
A demonstration of the fact that combining high conversion information at azeotropic conditions with low conversion data is much preferable, as it will increase the reliability/quality of the reactivity ratio estimates.

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.

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

Data set from McManus and Penlidis (1996)

- - - A111-Mayo-Lewis model

——— A111-Direct Numerical Integration model

- - - A211112-Mayo-Lewis model

——— A211112-Direct Numerical Integration model

- - - A212-Mayo-Lewis model

——— A212-Direct Numerical Integration model

Y-axis: Triad fractions; X-axis: f1
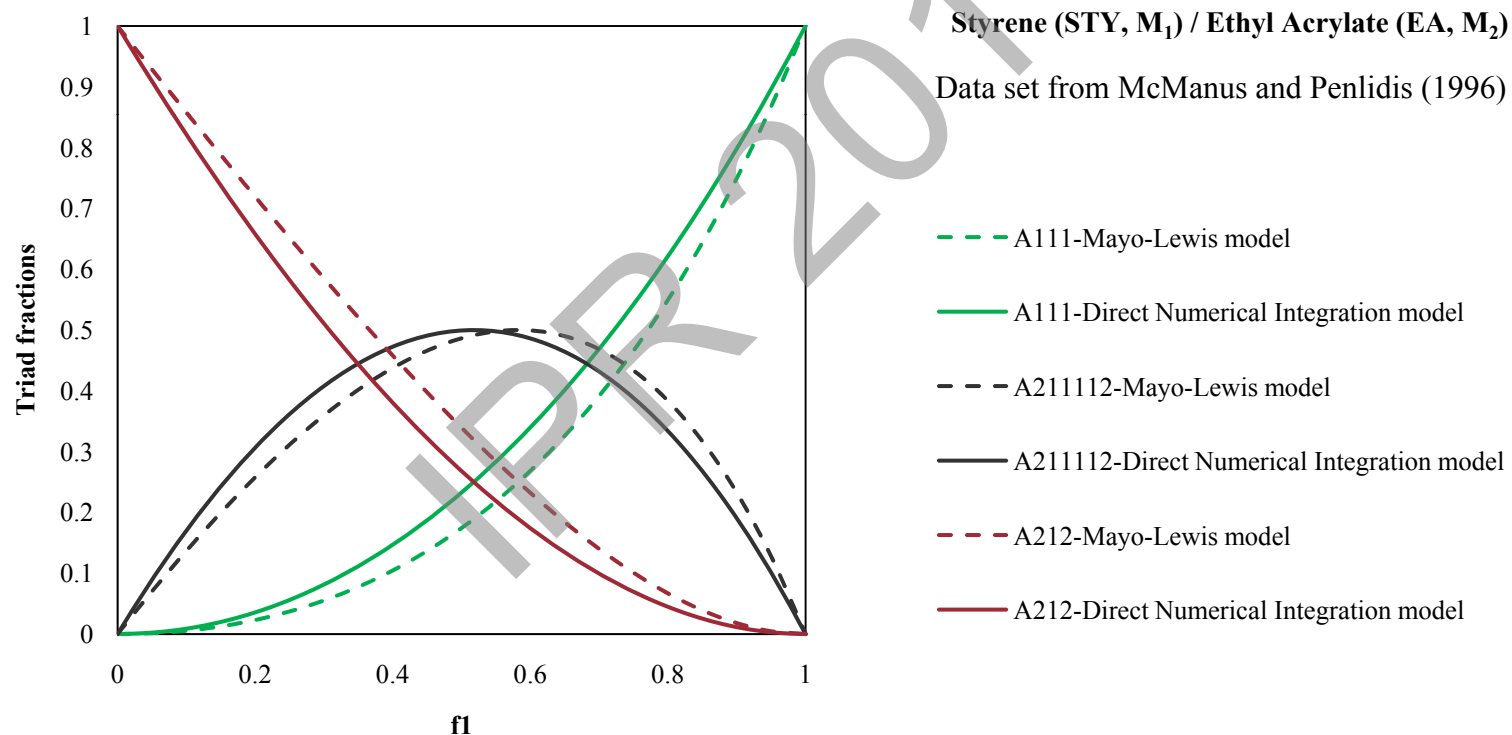
The difference between the performance of these two models shows the effect high conversion values can have on the outcome of the analysis.

Why Use Binary Reactivity Ratios for Ternary Systems?

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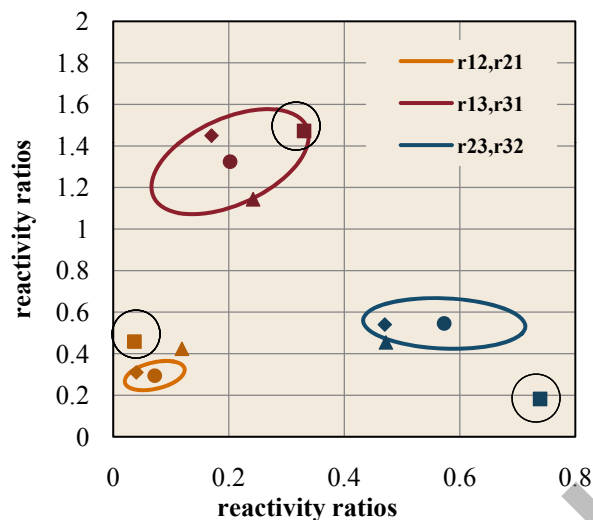
There are several reasons why binary reactivity ratios should not be used for terpolymerizations:

- ▪ 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.

Terpolymerization of Acrylonitrile (M_1) / Styrene (M_2) / Methyl Methacrylate (M_3)

ternary vs. **binary** reactivity ratios

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 !

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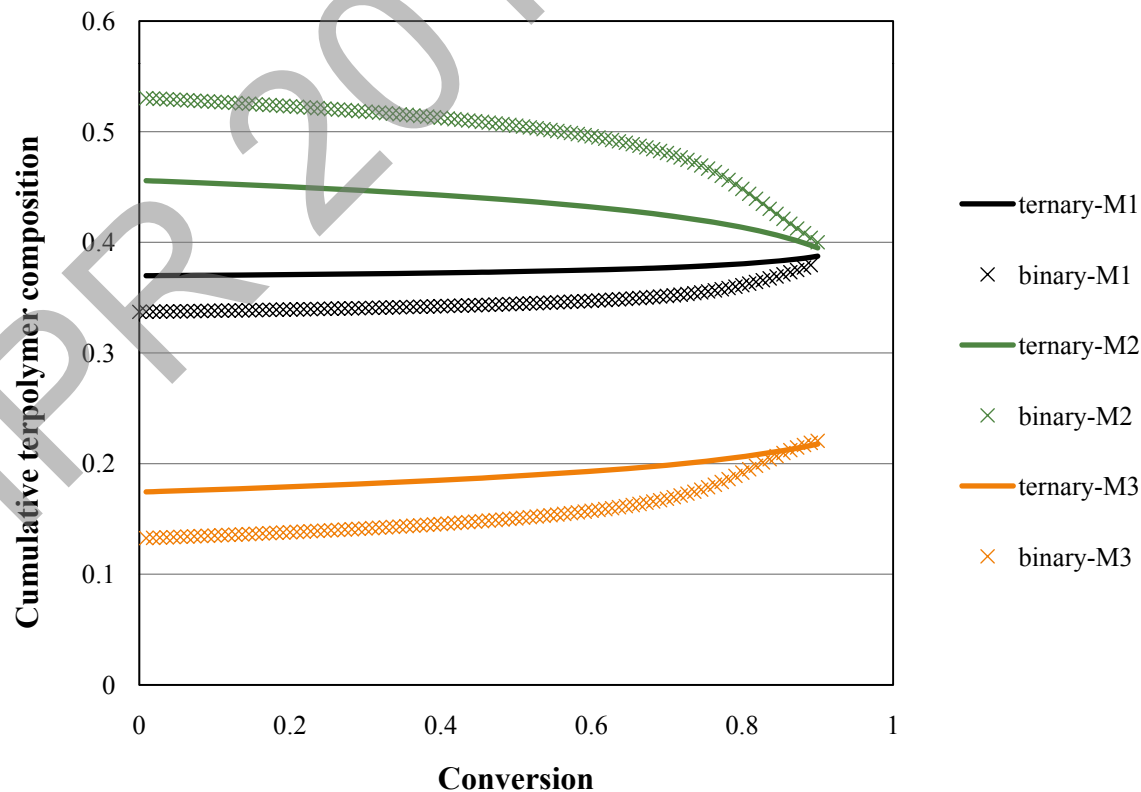
Azeotropy in Multicomponent Polymerization

- Azeotropic point is a feed composition at which the polymerization does not exhibit composition drift

$$\frac{d[m_1]}{[m_1]}dt = \frac{d[m_2]}{[m_2]}dt = \cdots$$

- 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.

Methyl acrylate (MA)
Di(tri-n-butyltin) itaconate (TBTI)
Acrylonitrile (AN)
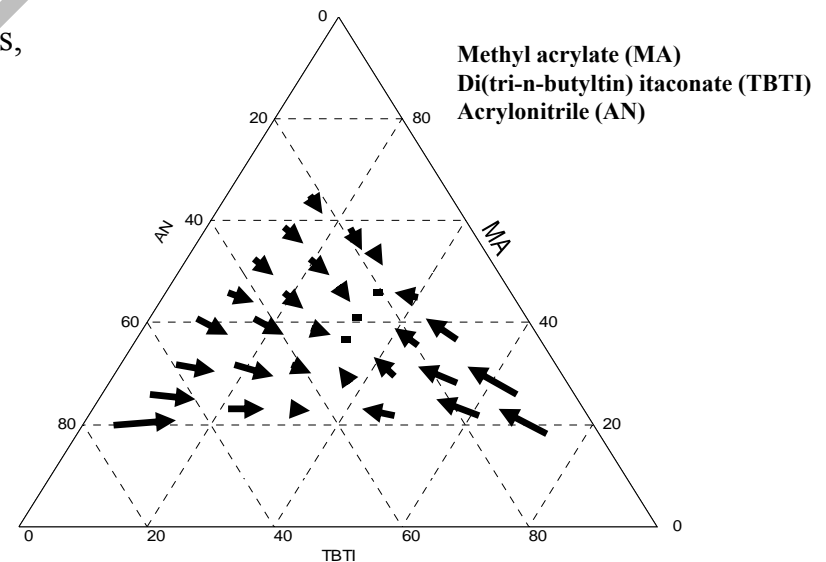
Instantaneous terpolymer composition as a function of monomer composition