Facilitating Reactivity Ratio Estimation with the Error-in-Variables-Model: 'prêt-à-porter' computational package.

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Introduction

- Reactivity ratios are a valuable piece of information in polymer synthesis, but reported values are often **inaccurate**
- Many researchers shy away from statistically correct techniques (excuses!)
  - Linear approximation is "close enough"
  - Non-linear parameter estimation is computationally intensive
- Solution: MATLAB-based computational package designed for the 'non-programming' polymer chemist or engineer

Overview

- Background Information
  - Reactivity Ratio Estimation
  - Error-in-Variables-Model (EVM)
  - Low Conversion & Medium-High Conversion Analyses
- EVM Program Details
- Case Studies: (more at poster in the evening)
  - #1: Low Conversion Data Analysis
    - Styrene (STY) & Ethyl Acrylate (EA)
  - #2: Medium-High Conversion Data Analysis
    - *n*-Butyl Methacrylate (BMA) & *n*-Butyl Acrylate (BA)

Reactivity Ratio Estimation

- Sources of error in parameter estimation:
  - Linear parameter estimation techniques
  - Experimental difficulties
  - Inappropriate kinetic models
  - Poorly designed experiments
- The copolymerization model is NOT LINEAR!

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

Error-in-Variables-Model (EVM)

Source of Error	EVM Solution
Linear estimation techniques	Non-linear parameter estimation technique
Experimental difficulties	Considers error in all variables (both independent & dependent)
Inappropriate kinetic models	Allows for medium-high conversion data (no conversion restrictions)
Poorly designed experiments	Uses sequential design of experiments (more information from fewer runs)

EVM for Parameter Estimation

EVM Driver: Minimize Φ

Outer Loop: Find $\underline{\theta}$

$$\underline{g}\left(\underline{\xi}_i, \underline{\theta}\right) = 0$$

Inner Loop: Find $\underline{\xi}$

$$\underline{x}_i = \underline{\xi}_i(1 + k\underline{\varepsilon}_i)$$

Data File

Low Conversion Analysis of Copolymerization Systems

- Simplest case: instantaneous Mayo-Lewis model
  - Assumes no composition drift
  - Conversion restricted below 5% - 10%

$$\underline{g}\left(\underline{\xi}_i, \underline{\theta}\right) = F_1 - \left(\frac{r_1 f_1^2 + f_1(1 - f_1)}{r_1 f_1^2 + 2f_1(1 - f_1) + r_2(1 - f_1)^2}\right)$$

Low Conversion Analysis of Copolymerization Systems

- Input data required:
  - Preliminary estimates for reactivity ratios (from literature or preliminary experiments)
  - Initial feed composition
  - Cumulative copolymer composition
  - No conversion data needed
    - This may require inaccurate assumptions
    - Low conversion data prone to error

Data File

Medium-High Conversion Analysis of Copolymerization Systems

- More complex case: cumulative model using direct numerical integration
  - Valid for full conversion range
  - Provides more data in fewer experimental runs
  - Higher degree of accuracy
  - Easily solved

$$\underline{g}\left(\underline{\xi}_i, \underline{\theta}\right) = \overline{F}_1 - \left(\frac{f_{1,0} - f_1(1 - X_n)}{X_n}\right)$$

Medium-High Conversion Analysis of Copolymerization Systems

- Input data required:
  - As before: preliminary estimates, initial feed composition & cumulative copolymer composition for each point
  - Conversion at each point
  - Molecular weight of each comonomer
- Potential to include variance/covariance matrix, if available

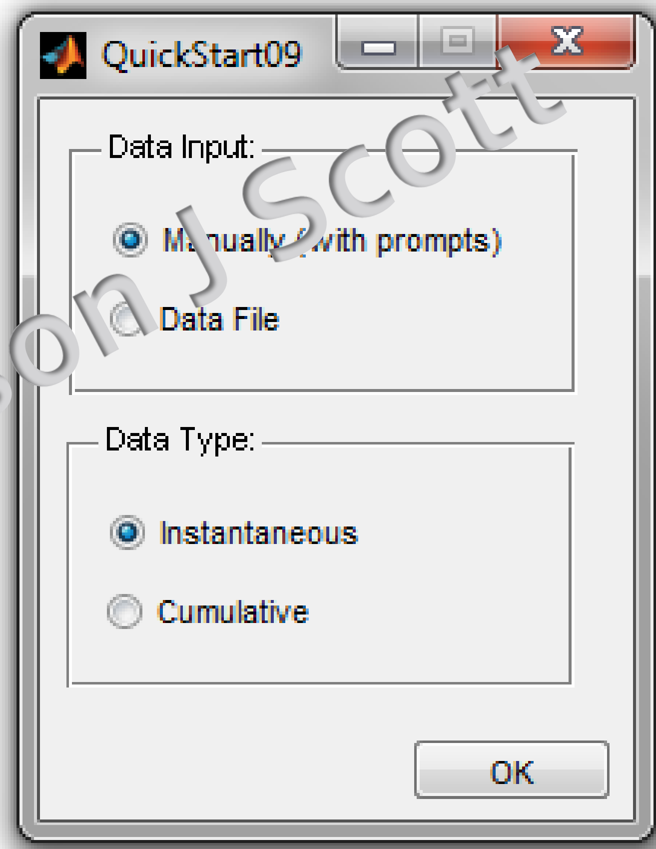
Data File

EVM Program Details

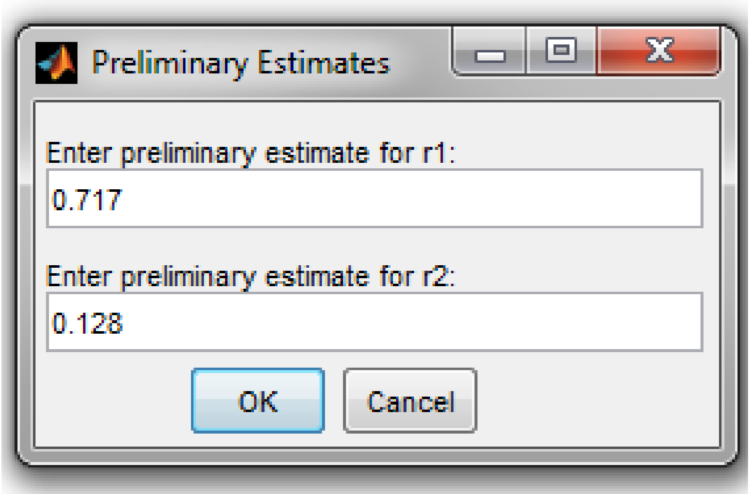
- Zip file contents:
  - Program instructions ("read me" file)
  - MATLAB program for RR estimation (for low conversion **OR** medium-high conversion data)
  - MATLAB program for plotting JCRs (optional)
  - Data files for several sample case studies

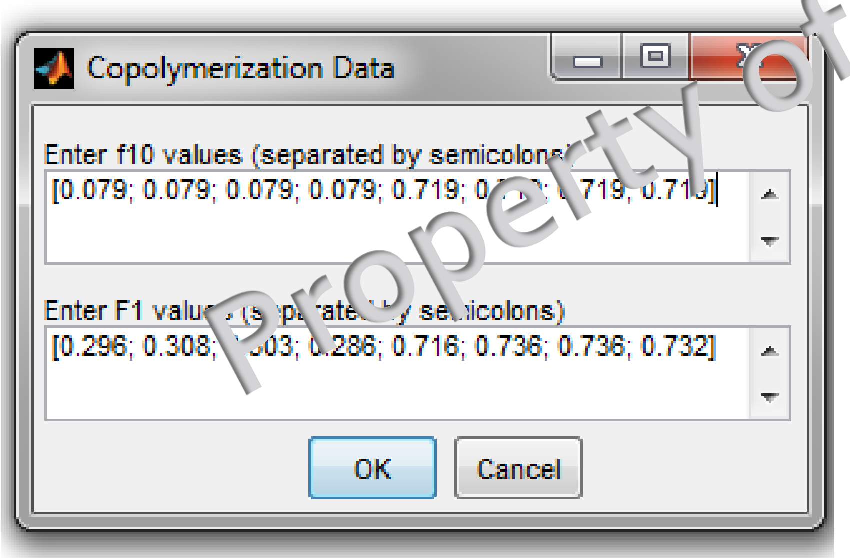
EVM Program Details

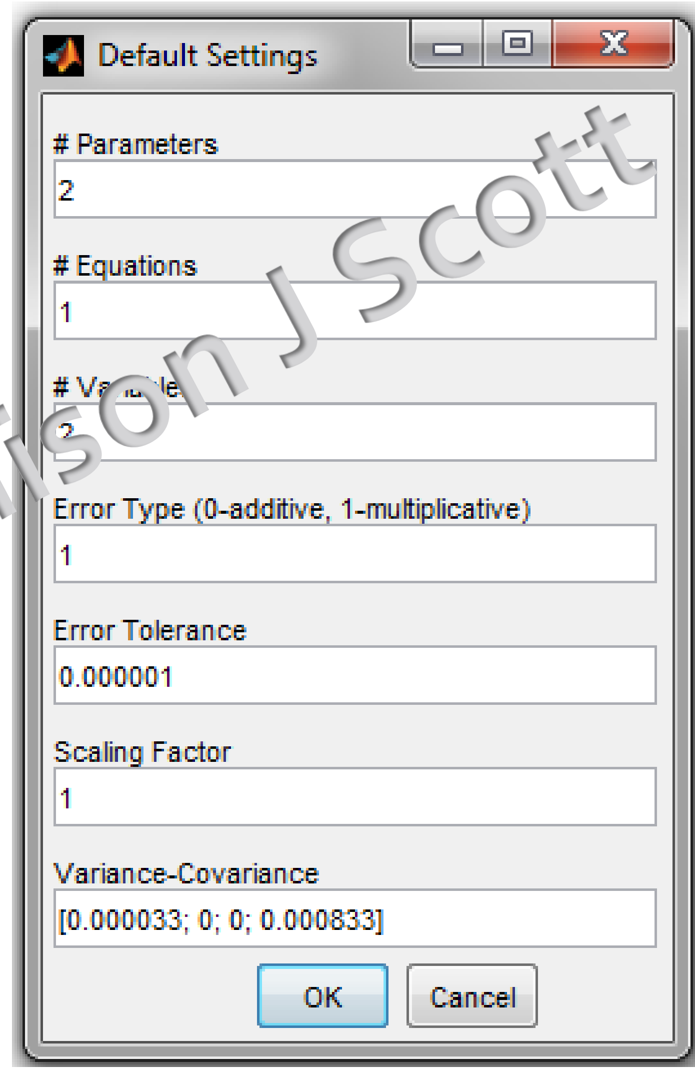
- Quick Start Menu
- Data Input:
  - Step-by-Step (for beginners)
  - Data File (for advanced users)
- Data Type:
  - Low Conversion Data
  - Medium-High Conversion Data



Case Study #1: Low Conversion Data for Styrene and Ethyl Acrylate [1]







Case Study #1: Low Conversion Data for Styrene and Ethyl Acrylate

Command Window

```
THETA =

    0.7187
    0.1286


XI =

    0.0790    0.2981
    0.0791    0.2982
    0.0790    0.2982
    0.0789    0.2980
    0.7186    0.7297
    0.7192    0.7301
    0.7192    0.7301
    0.7191    0.7300
```

- THETA (θ) = Best estimates for parameters (reactivity ratios)
- XI (ξ) = Best estimates for "true" values of variables

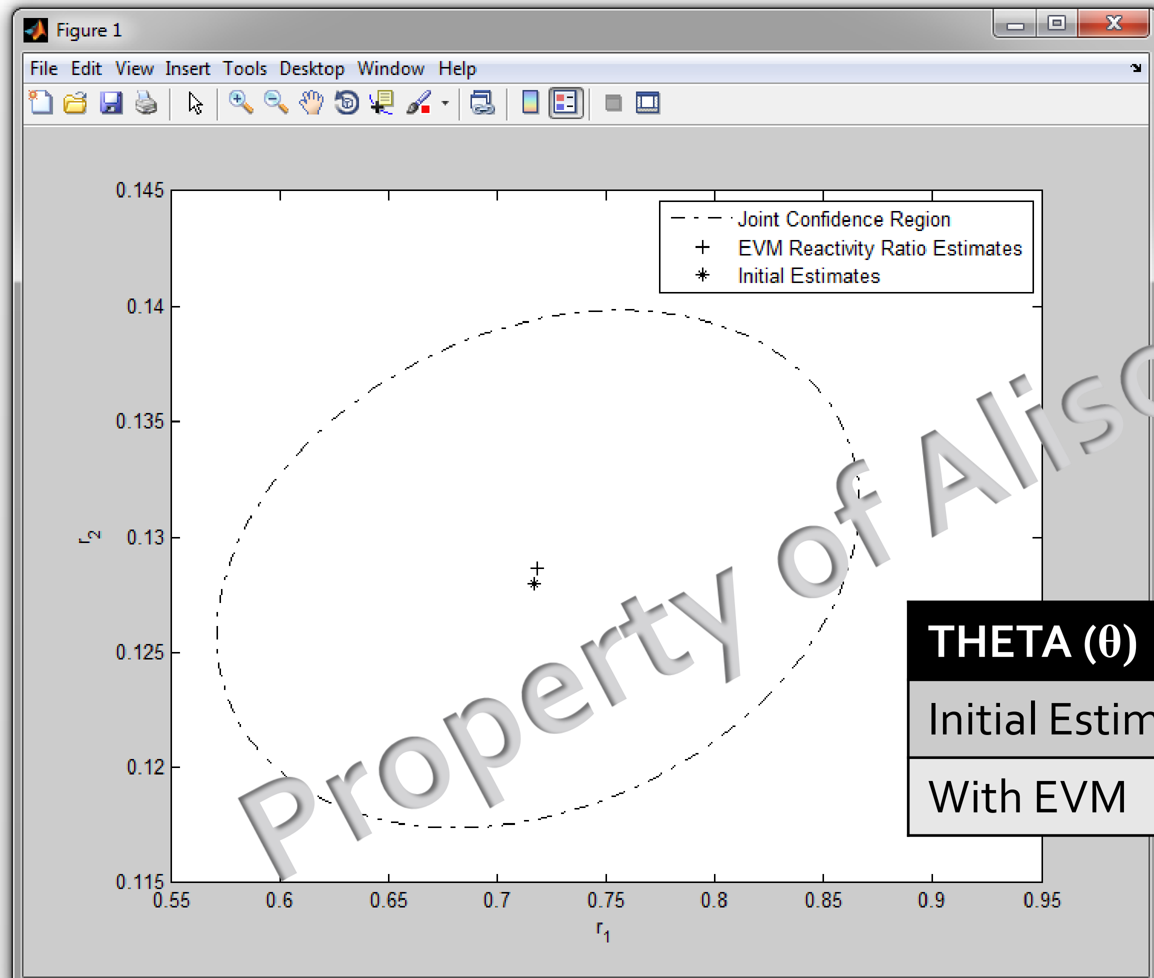
Case Study #1: Low Conversion Data for Styrene and Ethyl Acrylate

```
Command Window

Phi =

    2.1471


G =

  1.0e+004 *

    0.0295   -0.0998
   -0.0998    5.1008

All Calculations converged.
fx Do you wish to continue with Joint Confidence Calculations (Y/N):
```

- Phi (Φ) = Objective function
- $\underline{G}$ = Provides valuable information about the parameter estimates (related to the $\underline{V}$ matrix)

```
Do you wish to continue with Joint Confidence Calculations (Y/N): Y
```

Case Study #1: Low Conversion Data for Styrene and Ethyl Acrylate



- Program is in excellent agreement with results published previously.

THETA (θ)	r_1 (STY)	r_2 (EA)
Initial Estimates [1]	0.717	0.128
With EVM	0.7187	0.1286

Case Study #2: Medium-High Conversion Data for BMA and BA [2]

Table 2. Bulk BA/BMA copolymerization results for reactivity ratio estimation at 80 °C, [BPO] = 0.1 wt%.

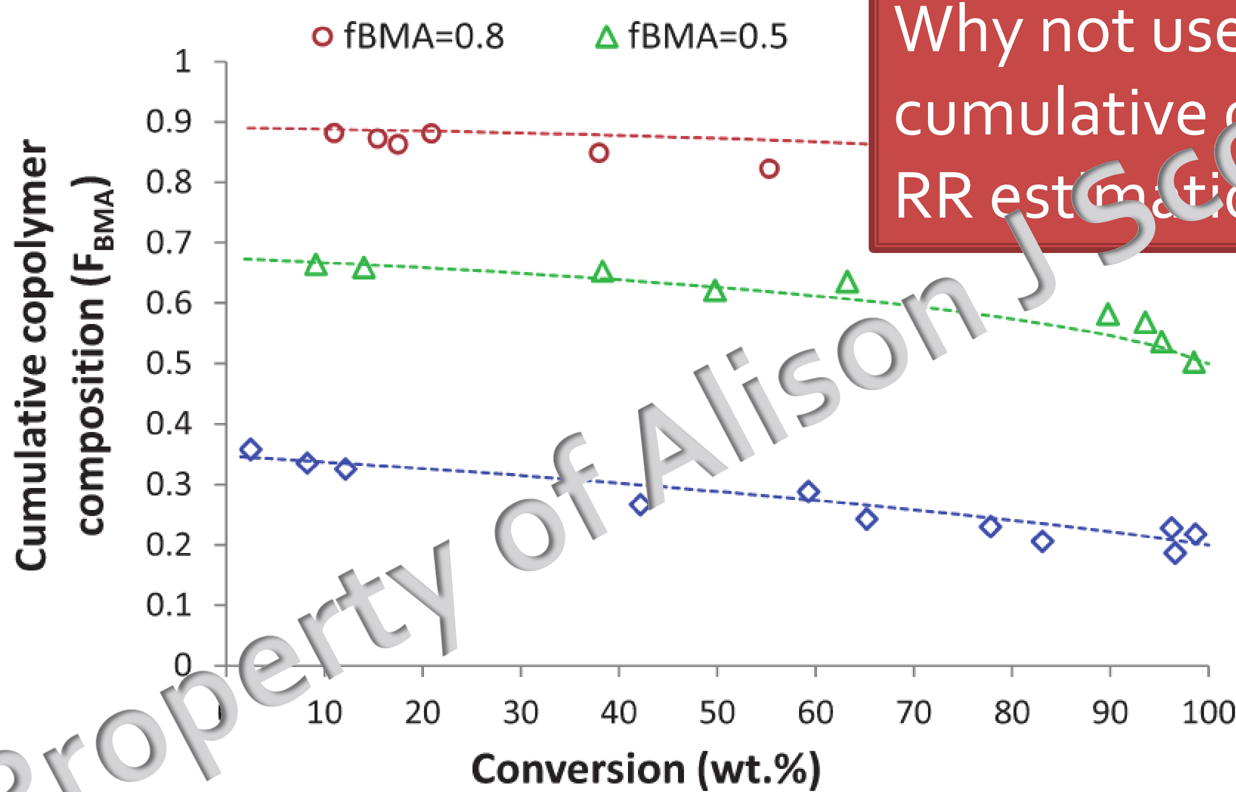
Sample	Feed composition f_{BMA} [mol fraction]	Copolymer composition F_{BMA} [mol fraction]	Time [min]	Conversion [wt%]
1	0.100	0.187	25	1.4
2	0.200	0.331	20	2.1
3	0.300	0.459	18	1.5
4	0.410	0.620	18	2.9
5	0.501	0.668	18	3.9
6	0.601	0.762	15	3.8
7	0.700	0.820	15	6.8
8	0.801	0.882	15	6.5
9	0.897	0.968	15	1.0

Case Study #2: Medium-High Conversion Data for BMA and BA [2]

Table 2. Bulk BA/BMA copolymerization results for reactivity ratio estimation at 80 °C, [BPO] = 0.1 wt%.

Sample	Feed composition f_{BMA} [mol fraction]	Copolymer composition F_{BMA} [mol fraction]	Time [min]	Conversion [wt%]
⋮	⋮	⋮	⋮	⋮
TM1-1	0.487	0.656	15	5.1
TM1-2	0.487	0.654	15	5.9
TM1-3	0.487	0.651	15	4.0
TM1-4	0.487	0.655	15	5.0
TM2-1	0.196	0.344	22	8.5
TM2-2	0.196	0.348	22	9.0
TM2-3	0.196	0.344	22	8.7
TM2-4	0.196	0.353	22	9.5

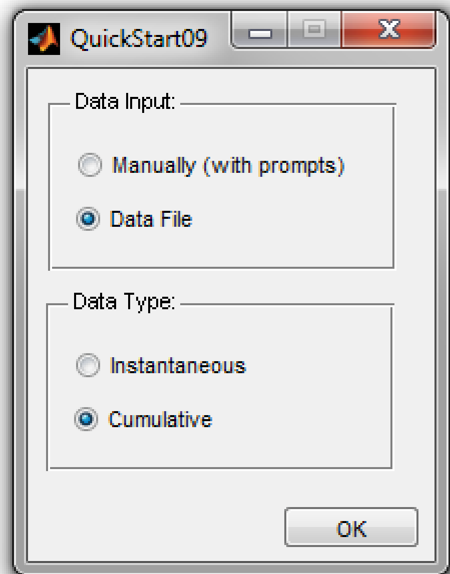
Case Study #2: Medium-High Conversion Data for BMA and BA [2]

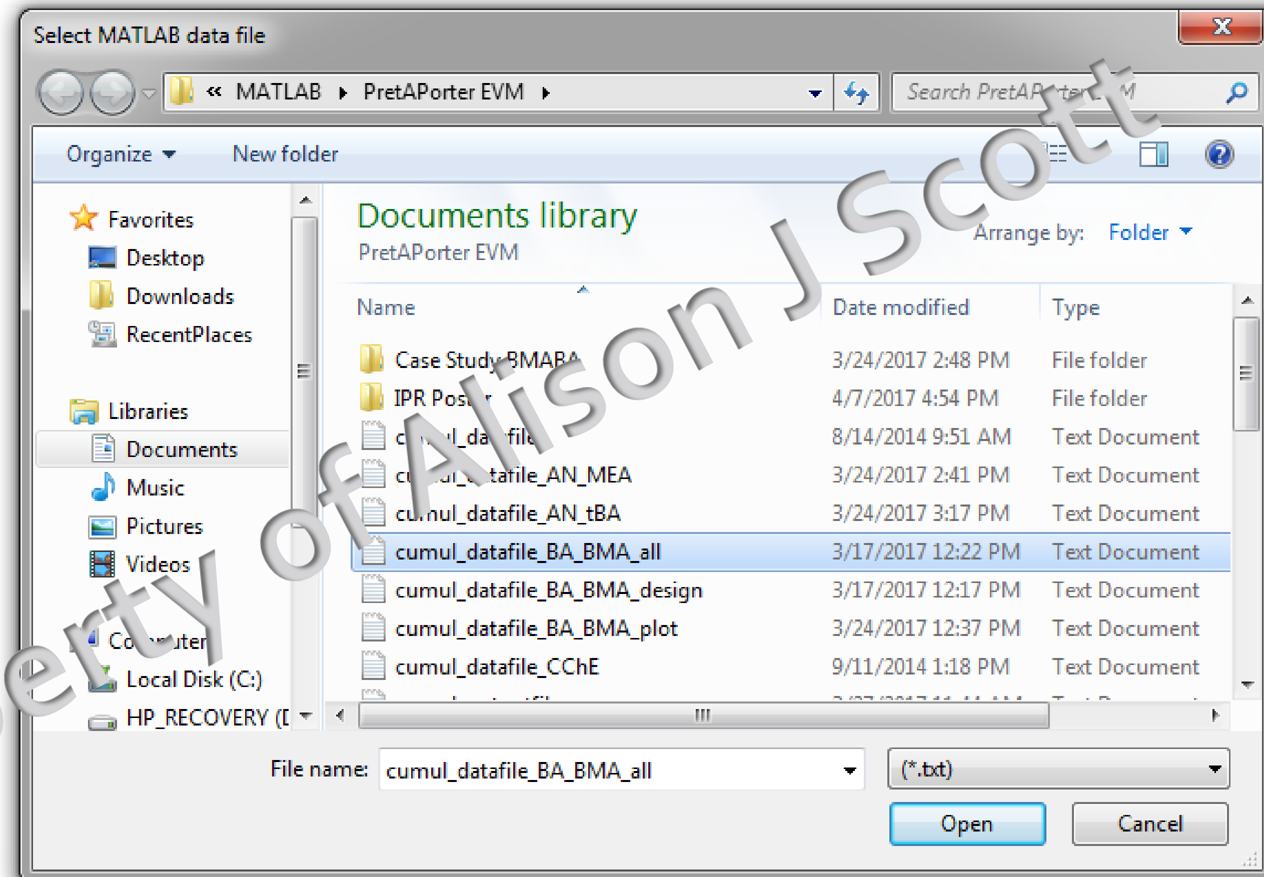


Why not use cumulative data for RR estimation?

Figure 5. Cumulative copolymer composition versus conversion for BA/BMA bulk copolymerization at various f_{BMA}. Dashed lines are integrated Mayo–Lewis model predictions.

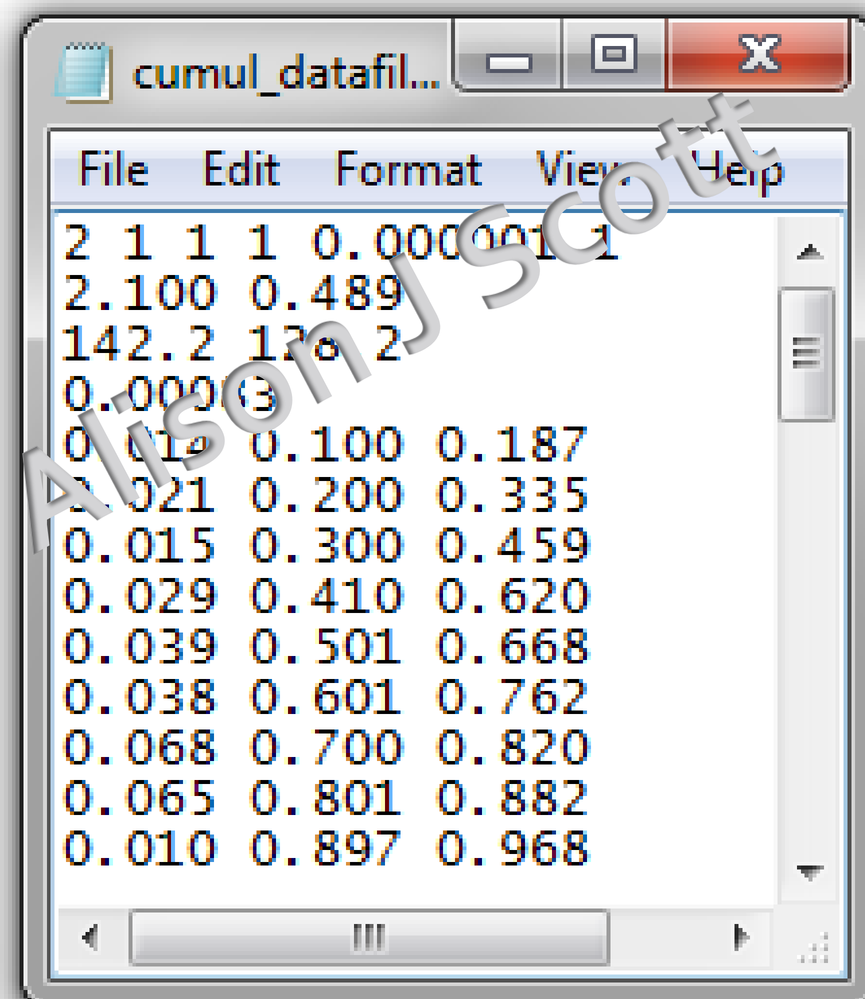
Case Study #2: Medium-High Conversion Data for BMA and BA





Case Study #2: Medium-High Conversion Data for BMA and BA

Row	Contents		
1	Default Parameters		
2	Preliminary RRE		
3	Monomer MWs		
4	<u>V</u> Matrix (Default)		
5+	Data		
⋮	X_W	f_{10}	$\overline{F}_1$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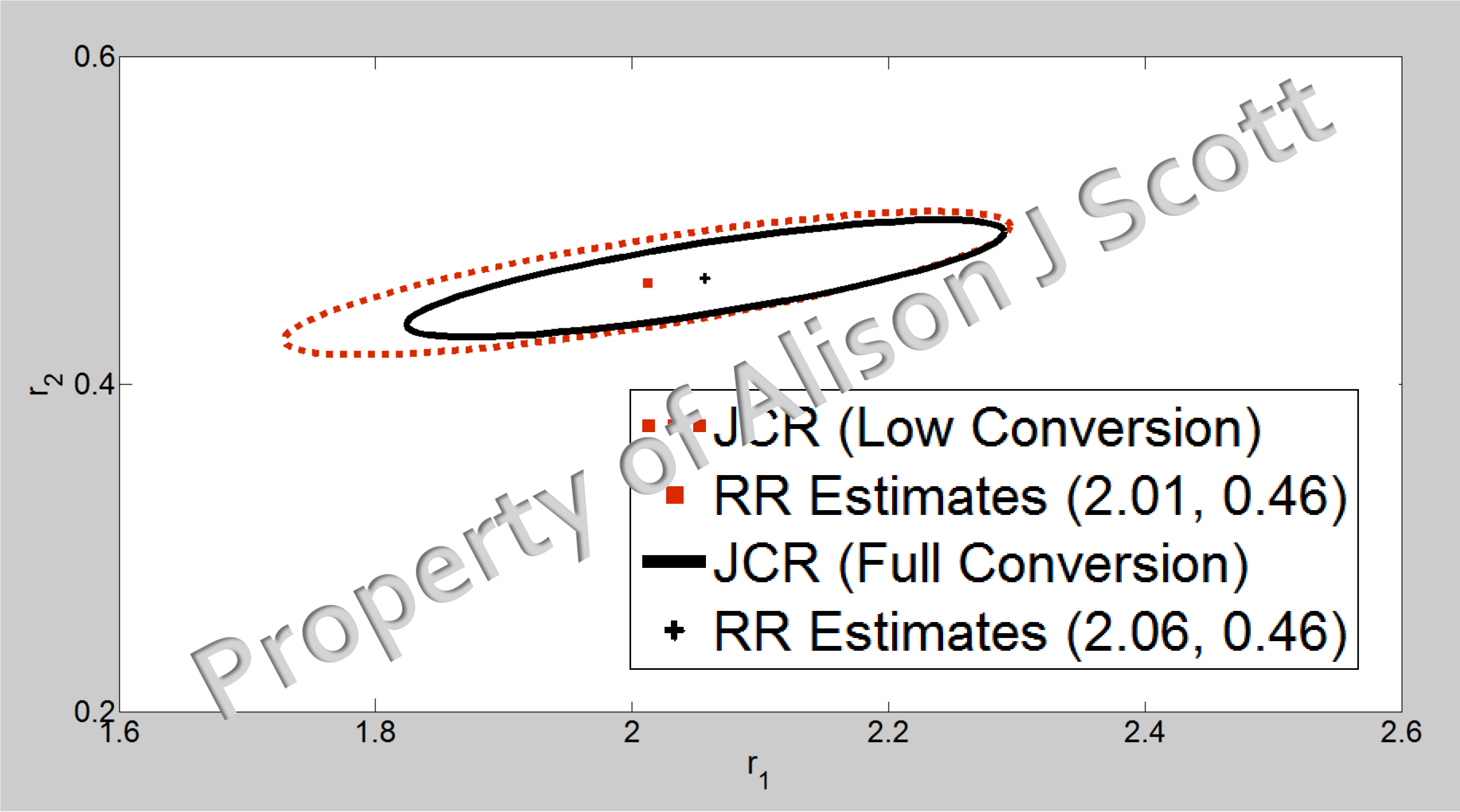
2.100 0.489
142.2 12[illegible] 2
0.000[illegible]3
0.01[illegible] 0.100 0.187
[illegible].021 0.200 0.335
0.015 0.300 0.459
0.029 0.410 0.620
0.039 0.501 0.668
0.038 0.601 0.762
0.068 0.700 0.820
0.065 0.801 0.882
0.010 0.897 0.968

Case Study #2: Medium-High Conversion Data for BMA and BA

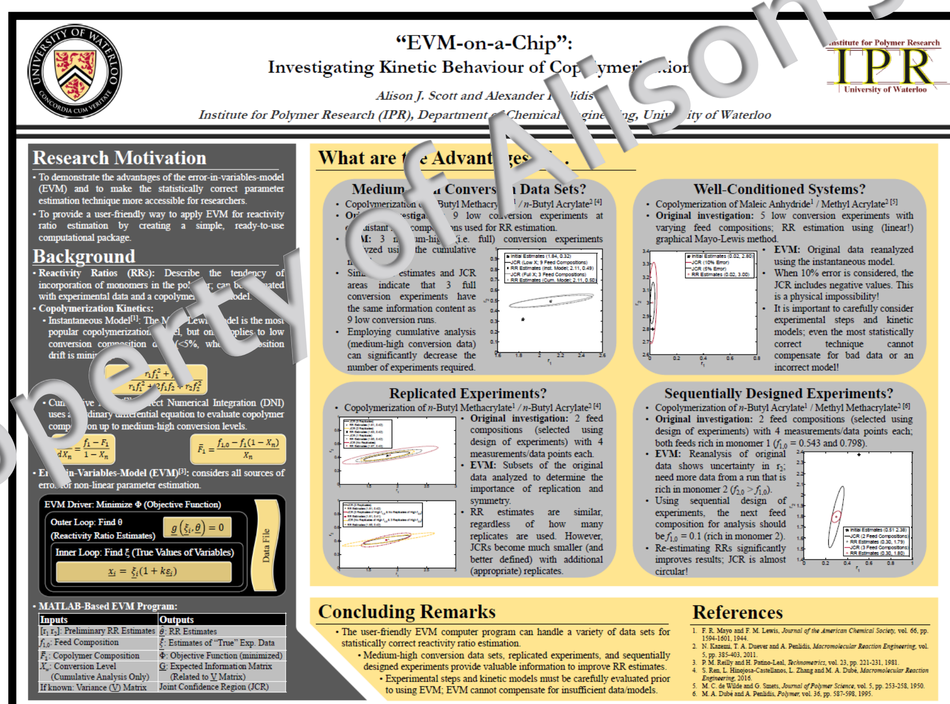


Concluding Remarks

- The error-in-variables-model (EVM) should be used for reactivity ratio estimation
  - Non-linear parameter estimation technique
  - Applicable to low and medium/high conversion data
- Additional advantages of cumulative model
  - Fewer assumptions
  - Increased information content
- MATLAB-based EVM program is user-friendly
  - No excuses - statistically correct & easy to use!

Concluding Remarks

- Poster Session: "EVM-on-a-Chip"
  - Additional examples & special cases
  - EVM program demonstration



References

[1] N. McManus and A. Penlidis, J. Polym. Sci. Part A: Polym. Chem., vol. 34, no. 2, pp. 237-248, 1996.

[2] S. Ren, L. Hinojosa-Castellanos, L. Zhang and M. A. Dubé, Macromol. React. Eng., 2016. doi:10.1002/mren.201600050

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