



Institute for Polymer Research



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!

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

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 $\underline{\theta}$

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

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

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

Data File

Low Conversion Analysis of Copolymerization Systems

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

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

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

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

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

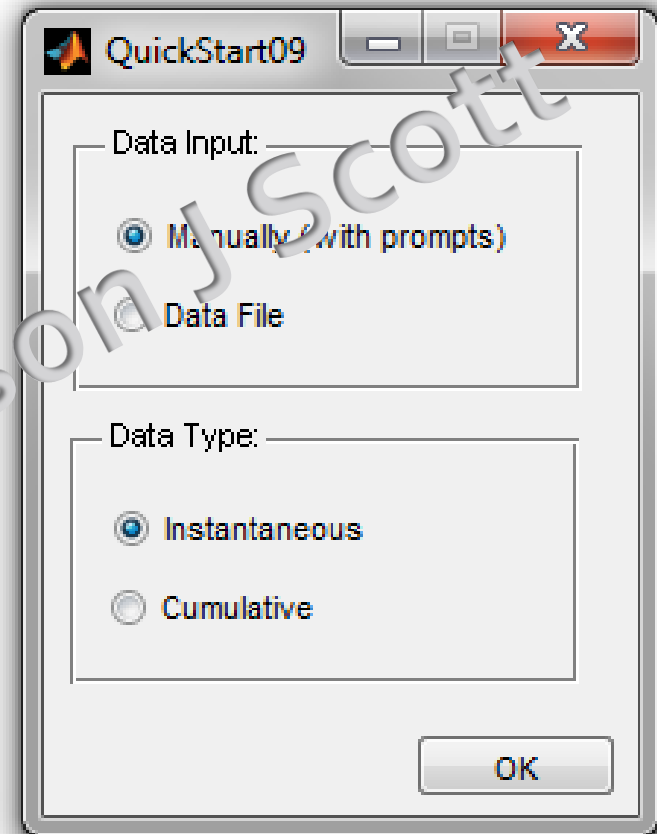
- Zip file contents:
 - Program instructions (“read me” file)
 - MATLAB program for RR estimation (for low conversion **OR** medium-high conversion data)
 - MATLAB program for plotting JCRs (optional)
 - Data files for several sample case studies



MATLAB®

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]

Preliminary Estimates

Enter preliminary estimate for r1:
0.717

Enter preliminary estimate for r2:
0.128

OK Cancel

Copolymerization Data

Enter f10 values (separated by semicolons):
[0.079; 0.079; 0.079; 0.079; 0.719; 0.719; 0.719; 0.719]

Enter F1 values (separated by semicolons):
[0.296; 0.308; 0.303; 0.286; 0.716; 0.736; 0.736; 0.732]

OK Cancel

Default Settings

Parameters
2

Equations
1

Variables
2

Error Type (0-additive, 1-multiplicative)
1

Error Tolerance
0.000001

Scaling Factor
1

Variance-Covariance
[0.000033; 0; 0; 0.000833]

OK Cancel

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

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

```
Command Window

Phi =

    2.1471

G =

    1.0e+004 *

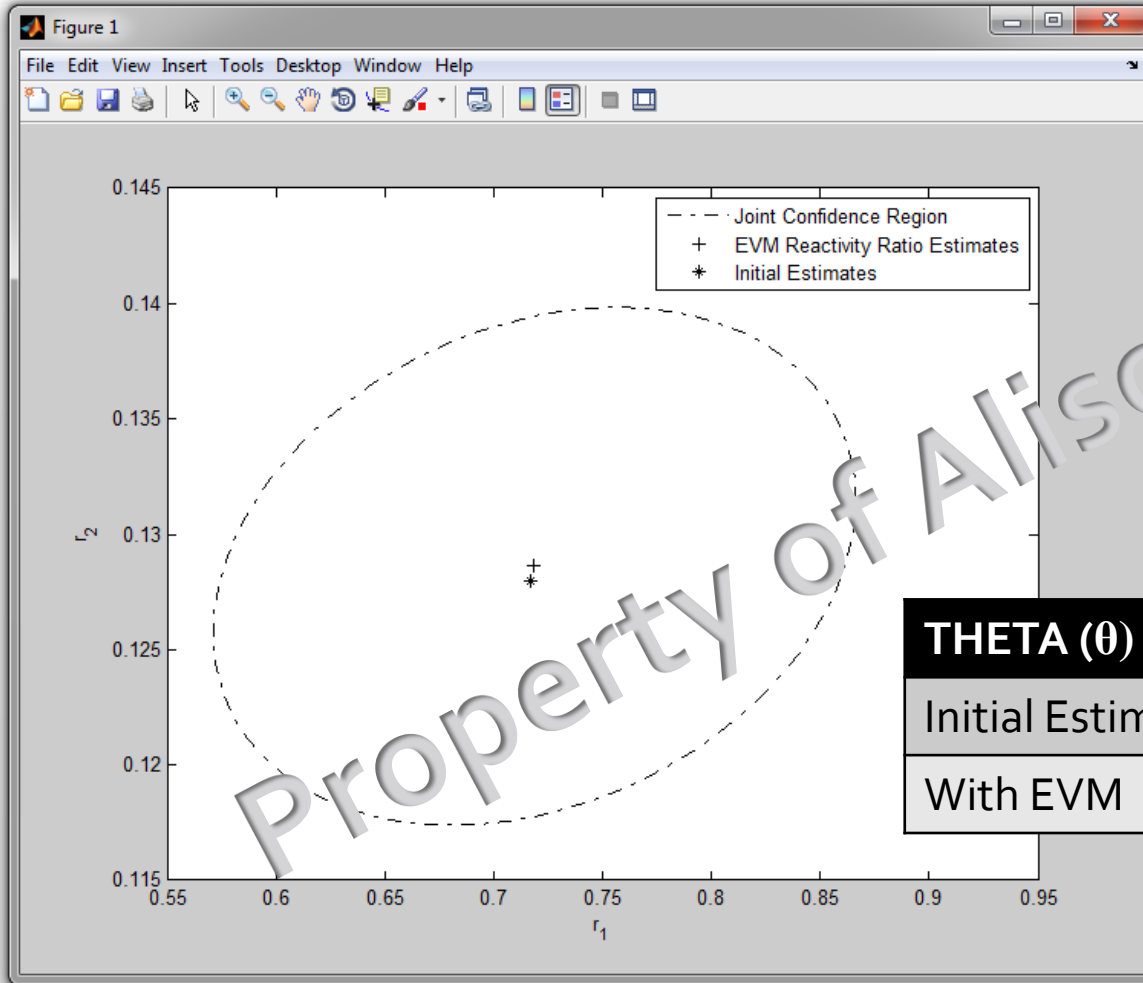
    0.0295    -0.0998
   -0.0998     5.1008

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

- 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]

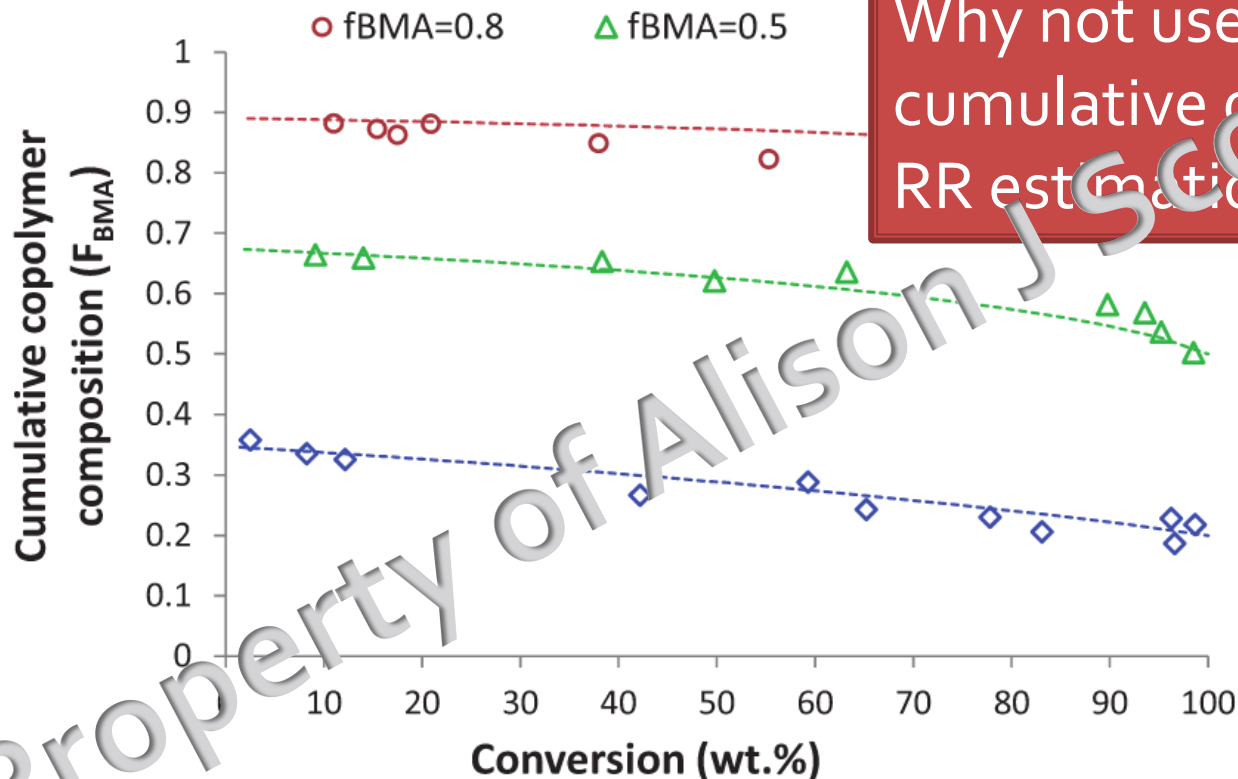
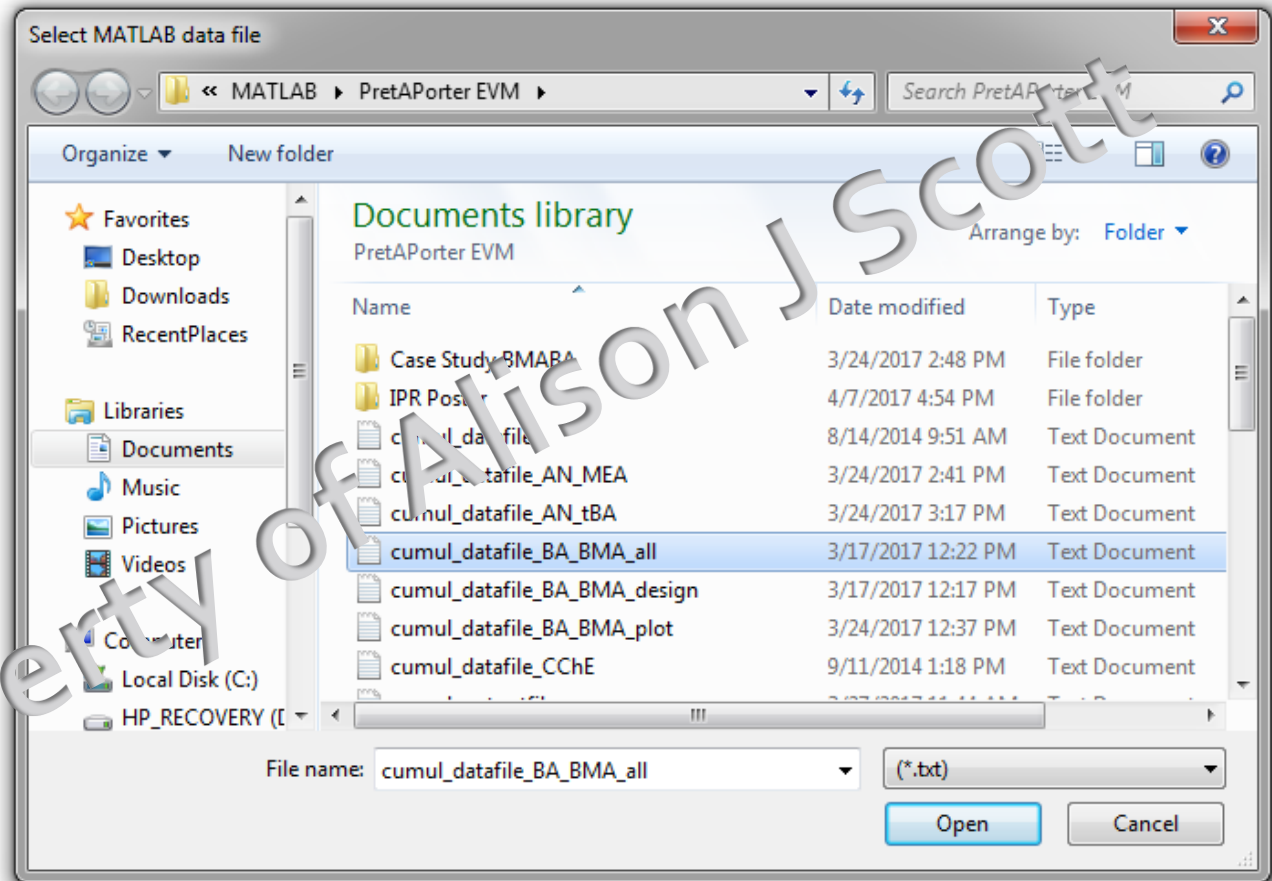
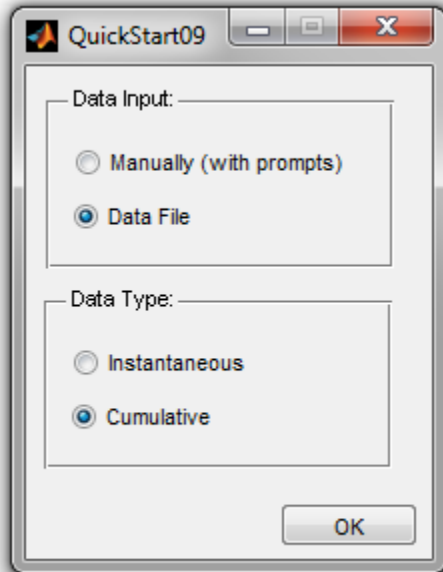


Figure 5. Cumulative copolymer composition versus conversion for BA/BMA bulk copolymerization at various f_{BMA} . Dashed lines are integrated Mayo-Lewis model predictions.

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



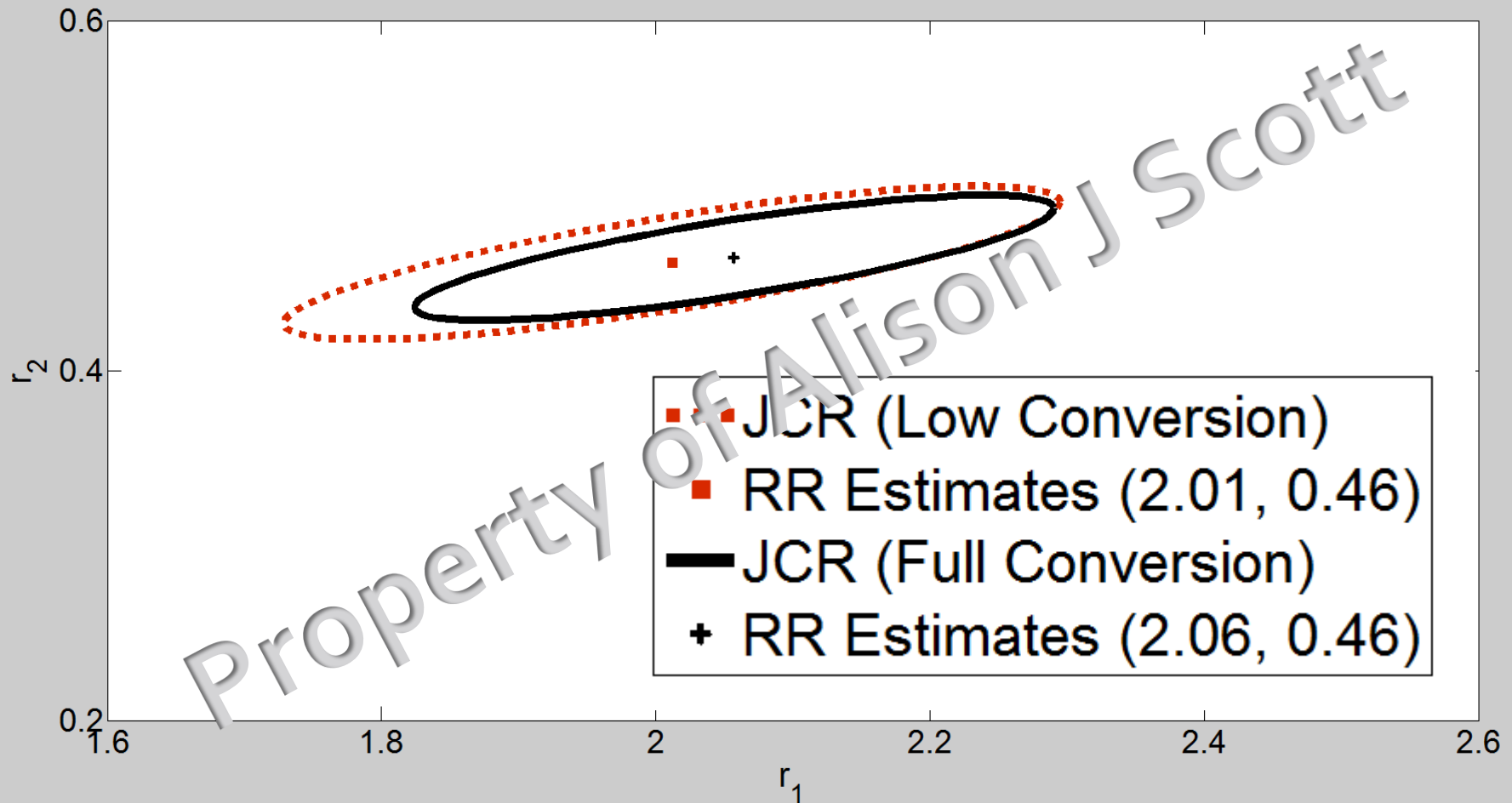
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Case Study #2: Medium-High Conversion Data for BMA and BA

Row	Contents		
1	Default Parameters		
2	Preliminary RRE		
3	Monomer MWs		
4	<u>V</u> Matrix (Default)		
5+	Data		
:	X_W	1.0	\bar{F}_1

File	Edit	Format	View	Help
2	1	1	1	0.000001
2.100	0.489			
142.2	138.2			
0.000				
0.019	0.100	0.187		
0.021	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

"EVM-on-a-Chip":
Investigating Kinetic Behaviour of Copolymerization

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Institute for Polymer Research
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Research Motivation

- To demonstrate the advantages of the error-in-variables-model (EVM) and to make the statistically correct parameter estimation technique more accessible for researchers.
- To provide a user-friendly way to apply EVM for reactivity ratio estimation by creating a simple, ready-to-use computational package.

Background

- Reactivity Ratios (RRs): Describe the tendency of incorporation of monomers in the polymer, can be estimated with experimental data and a copolymerization model.
- Copolymerization Kinetics:
 - Instantaneous Model^[1]: The Mayo-Lewis model is the most popular copolymerization model, but only applies to low conversion compositions ($< 5\%$), where the monomer deficit is minor.

$$\frac{dM_1}{dt} = -k_p \frac{M_1}{M_1 + M_2} \left(\frac{r_1 M_1 + M_2}{M_1 + M_2} \right) M_1$$

- Can solve using Numerical Integration (NDI) using ordinary differential equation to evaluate copolymer composition up to medium-high conversion levels.

$$M_1 = \frac{f_1 - x_1}{1 - x_1} \quad f_1 = \frac{r_1 x_1 - f_1(1 - x_1)}{x_1}$$

- Error-in-Variables-Model (EVM)^[2]: considers all sources of error, not non-linear parameter estimation.

What are the Advantages?

Medium-High Conversion Data Sets?

- Copolymerization of n-Butyl Methacrylate^[3] / n-Butyl Acrylate^[3]
- Original investigation: 9 low conversion experiments at 3 full conversion runs.
- Utilized cumulative analysis (i.e. full) conversion experiments
- Optimized using the cumulative
- Similar estimates and JCR areas indicate that 3 full conversion experiments have the same information content as 9 low conversion runs.
- Employing cumulative analysis (medium-high conversion data) can significantly decrease the number of experiments required.

Well-Conditioned Systems?

- Copolymerization of Maleic Anhydride^[4] / Methyl Methacrylate^[4]
- Original investigation: 5 low conversion experiments with varying feed compositions; RR estimation using (linear) graphical Mayo-Lewis method.
- EVM: Original data reanalyzed using the instantaneous model.
- When 10% error is considered, the JCR includes negative values. This is a physical impossibility!
- It is important to carefully consider experimental steps and kinetic models, even the most statistically correct technique cannot compensate for bad data or an incorrect model!

Replicated Experiments?

- Copolymerization of n-Butyl Methacrylate^[5] / n-Butyl Acrylate^[5]
- Original investigation: 2 feed compositions (selected using design of experiments) with 4 measurements/data points each.
- EVM: Subsets of the original data analyzed to determine the importance of replication and symmetry.
- RR estimates are similar, regardless of how many replicates are used. However, JCRs became much smaller (and better defined) with additional (appropriate) replicates.

Sequentially Designed Experiments?

- Copolymerization of n-Butyl Acrylate^[6] / Methyl Methacrylate^[6]
- Original investigation: 2 feed compositions (selected using design of experiments) with 4 measurements/data points each, both feeds rich in monomer 1 ($f_{1,0} = 0.543$ and 0.798).
- EVM: Reanalysis of original data shows uncertainty in r_2 need more data from a run that is rich in monomer 2 ($f_{1,0} > f_{1,0}$).
- Using sequential design of experiments, the next feed composition for analysis should be $f_{1,0} = 0.1$ (rich in monomer 2).
- Re-estimating RR's significantly improves results, JCR is almost circular!

EVM Driver: Minimize Φ (Objective Function)

Outer Loop: Find θ $g(\hat{y}_i, \theta) = 0$
(Reactivity Ratio Estimates)

Inner Loop: Find \hat{y}_i (True Values of Variables)
 $\hat{y}_i = \hat{y}_i(1 + k_{\theta})$

MATLAB-Based EVM Program:	
Inputs	Outputs
$[f_{1,0}]$: Preliminary RR Estimates	\hat{r}_1 : RR Estimates
$[f_{2,0}]$: Feed Composition	\hat{r}_2 : Estimates of "True" Exp. Data
$[F_0]$: Copolymer Composition	$\hat{\Phi}$: Objective Function (minimized)
$[X_c]$: Conversion Level	\hat{M} : Expected Information Matrix (Cumulative Analysis Only)
$[k]$: Known Variance (σ^2) Matrix	\hat{C} : Joint Confidence Region (JCR)

Concluding Remarks

- The user-friendly EVM computer program can handle a variety of data sets for statistically correct reactivity ratio estimation.
- Medium-high conversion data sets, replicated experiments, and sequentially designed experiments provide valuable information to improve RR estimates.
- Experimental steps and kinetic models must be carefully evaluated prior to using EVM. EVM cannot compensate for insufficient data models.

References

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References

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- [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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