Model discrimination techniques with applications to polymerization reactions

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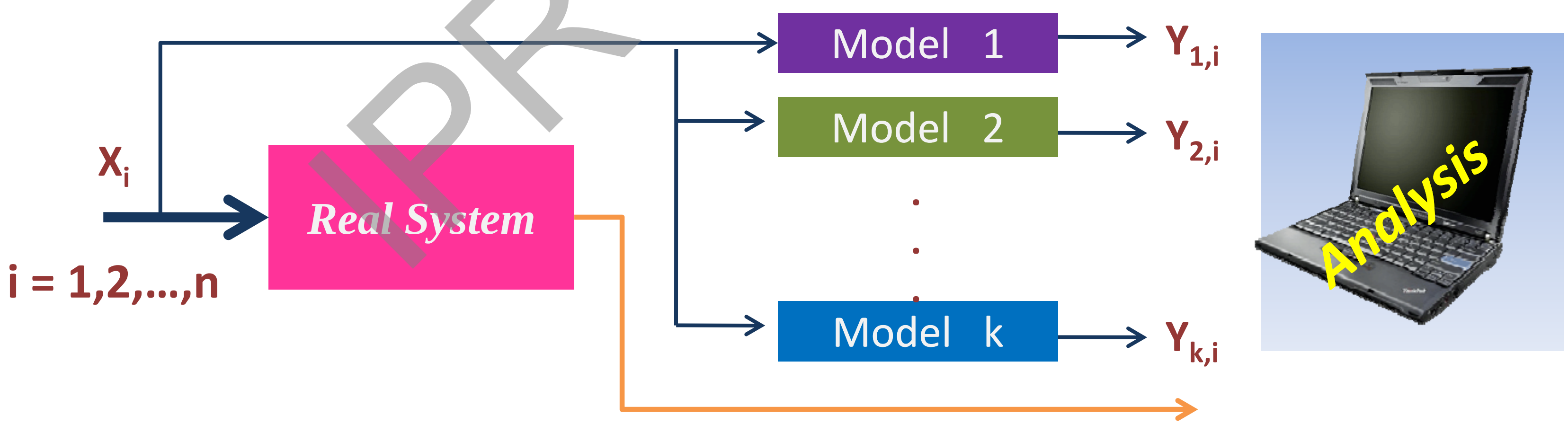
Outline

- What is Model discrimination
- Model discrimination and polymerization
- Previous works in our group
- Our motivation
- Complete Model Discrimination Procedure
- Hsiang-Reilly method
- Sequential Marginal Likelihood
- Case study
- Future work
- Conclusion

Model Discrimination

The problem of choosing the most appropriate model to describe the behavior of a real system in situations where more than one candidate model can be proposed to explain a process.



Model Discrimination

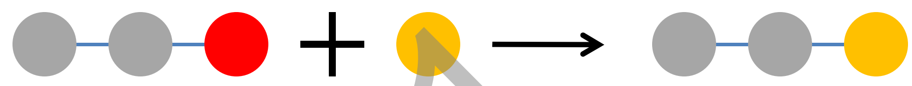
Two class of Models

Empirical models:
Predict the response (response surface problem)

Mechanistic models:
Physical mechanisms can be suggested

Copolymerization

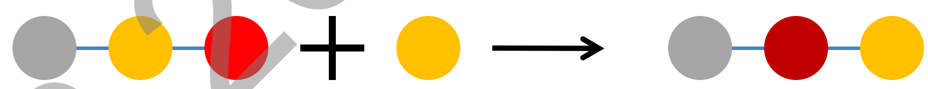
- Terminal



$$R_{n,i\cdot} + M_j \xrightarrow{k_{ij}} R_{n+1,j\cdot}$$

$$r_1 = \frac{k_{11}}{k_{12}}; \quad r_2 = \frac{k_{22}}{k_{21}}$$

- Penultimate



$$R_{n,ij\cdot} + M_k \xrightarrow{k_{ijk}} R_{n+1,jk\cdot}$$

$$r_{11} = \frac{k_{111}}{k_{112}}; \quad r_{21} = \frac{k_{211}}{k_{212}}$$

$$r_{22} = \frac{k_{222}}{k_{221}}; \quad r_{12} = \frac{k_{122}}{k_{121}}$$

$$s_1 = \frac{k_{211}}{k_{111}}; \quad s_2 = \frac{k_{122}}{k_{222}}$$

Nested models

$$\left\{ \begin{aligned} \hat{r}_{11} &= \hat{r}_{21} \\ \hat{r}_{22} &= \hat{r}_{12} \\ \hat{s}_1 = \hat{s}_2 &= 1 \end{aligned} \right.$$

Application of Model Discrimination in Polymerization

- Burke, A.L., Duever, T.A. & Penlidis, A. 1994, "Model discrimination via designed experiments: discriminating between the terminal and penultimate models on the basis of composition data", *Macromolecules.*

•STY/MMA : Styrene methyl methacrylate •STY/AN : Styrene Acrylonitrile •STY/BA : Styrene butyl acrylate	Real system: •Terminal •Strong Penultimate •Small Penultimate
Initial Reactivity Ratio Estimates: •Poor •Neutral •Good	Error Level: •Low •Medium •High

Application of Model Discrimination in polymerization

- **Burke, A.L., Duever, T.A. & Penlidis, A. 1994, "Model Discrimination Via Designed Experiments - Discriminating between the Terminal and Penultimate Models Based on Triad Fraction Data", *Macromolecular theory and simulations*.**
- **Burke, A.L., Duever, T.A. & Penlidis, A. 1995, "Model discrimination via designed experiments: Discrimination between the terminal and penultimate models based on rate data", *Chemical Engineering Science*.**
- **Burke, A., Duever, T. & Penlidis, A. 1996, "An experimental verification of statistical discrimination between the terminal and penultimate copolymerization models", *Journal of Polymer Science Part A Polymer Chemistry*.**
- **Landry, R., Duever, T.A. & Penlidis, A. 1999, "Model Discrimination via Designed Experiments: Discriminating Between the Terminal and Penultimate Models on the Basis of Weight Average Chain Length", POLYMER REACTION ENGINEERING.**
- **Landry, R., Penlidis, A. & Duever, T.A. 2000, "A study of the influence of impurities when discriminating between the terminal and penultimate copolymerization models", Journal of Polymer Science Part A: Polymer Chemistry**

Motivation

- Hsiang and Reilly method works poorly

- New Markov Chain Monte Carlo (MCMC) Methods are available

Objective

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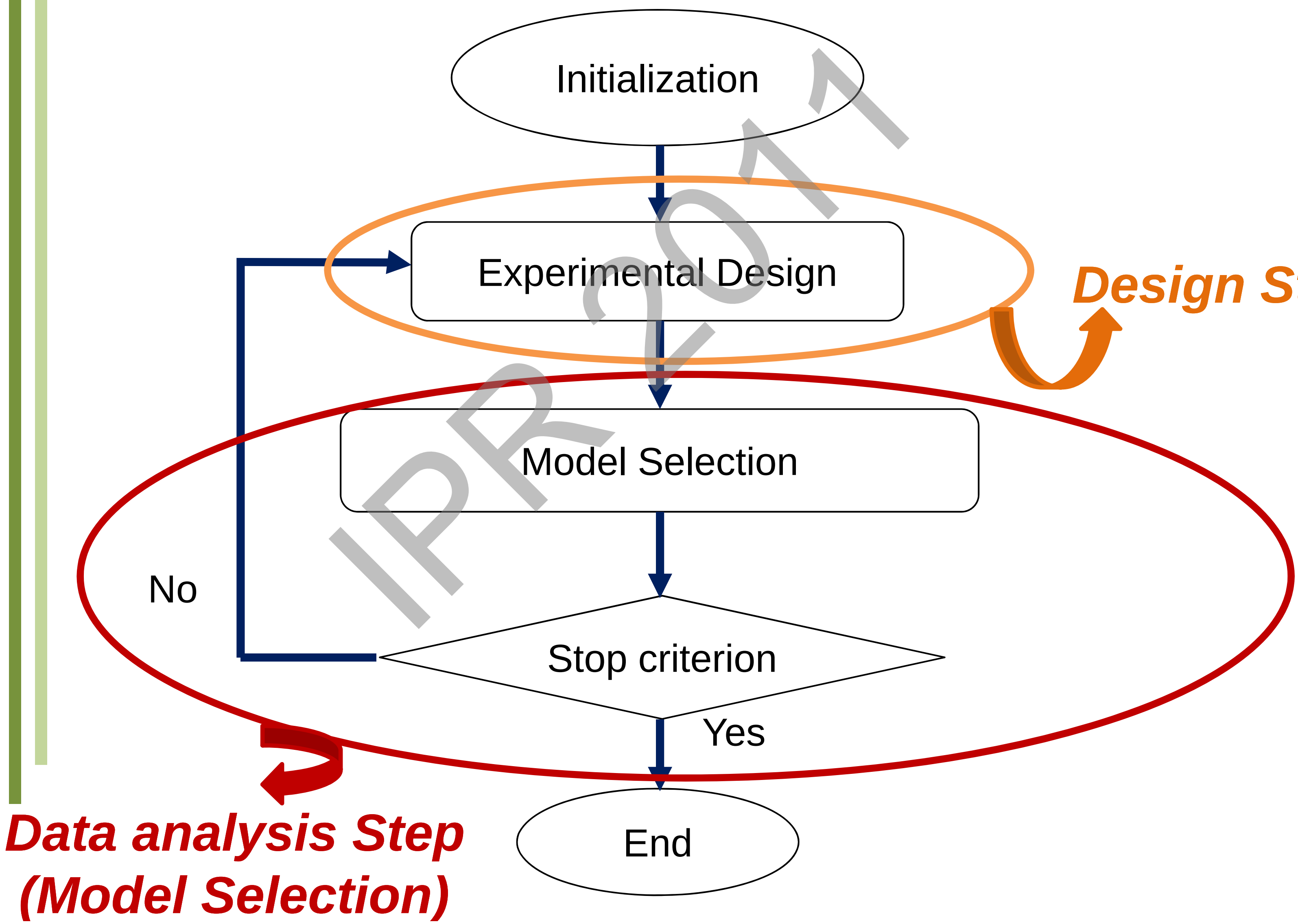
- Establishing a procedure for model discrimination between nonlinear models using an MCMC based approach

  - sequential marginal likelihood

  - modified Hsiang and Reilly approach in which MCMC methods will be used

- Applying this method to polymerization case studies

Model Discrimination



Hsiang - Reilly

Hsiang and Reilly (1971)

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Set Prior for models

Set Prior for parameters

Design and Perform experiment

Update Parameter Probabilities

Rescale parameter tables and update probabilities

Calculate model probabilities and check adequacy

Models probability :

$P_1 = 0.5$ 0.8

$P_2 = 0.5$ 0.2

Model 1 : *Parameter 1 :*

Parameter 2 :	1.5	1.85	2.15	2.5
100	0.01	0.07	0.02	0.02
110	0.02	0.05	0.06	0.01
120	0.01	0.12	0.20	0.03
130	0.02	0.14	0.032	0.01
140	0.015	0.08	0.01	0.003

Model 2 : *Parameter 1 :*

Parameter 2 :	10	20
1e5	0.1	0.11
2e5	0.08	0.08
3e5	0.12	0.13
4e5	0.1	0.08
5e5	0.02	0.08
6e5	0.01	0.09

Hsiang - Reilly

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Experimental Design:

$$C(x_n) = \sum_{i=1}^{K} \sum_{j=i+1}^{K} |\hat{y}_i - \hat{y}_j| [pr(M_j|y) + pr(M_i|y)]$$

$$\hat{y}_i = \sum_{\tilde{\theta}_i} f_i(x_n, \tilde{\theta}_i) pr(\tilde{\theta}_i | M_i, y)$$

Sequential Marginal Likelihood

The posterior probability of a hypothesis is proportional to the product of the likelihood and the prior probability.

$$\underbrace{P(M_i|\mathbf{y})}_{\text{Posterior}} = \underbrace{L(M_i|\mathbf{y})}_{\text{Likelihood}} \times \underbrace{\pi(M_i)}_{\text{Prior}}$$

Following Bayes theorem, the marginal likelihood:

$$L(M_i|\mathbf{y}) = \int l_i(\theta|\mathbf{y}, M_i)\, \pi_i(\theta, M_i)\, d\theta$$

Design Step

Methods Based on Maximum Divergence:

Conditions where the difference between the predicted values of the rival models is maximized

$$\max \sum_{i=1}^{K-1} \sum_{j=i+1}^{K} (\hat{y}_i - \hat{y}_j)^2$$

$$\max \sum_{i=1}^{K-1} \sum_{j=i+1}^{K} \frac{(\hat{y}_i\ (x) - \hat{y}_j\ (x))^2}{var(\hat{y}_i\ (x) - \hat{y}_j\ (x))}$$

Roth (1965) weighted average of the total separation between the models where weights are the Bayesian posterior probabilities

$$Z(\xi) = \sum_{i=1}^{K} \left[p(i, n-1) \prod_{\substack{j=1 \\ j \neq i}}^{K} \left| \hat{y}_{(j)}(\xi) - \hat{y}_{(i)}(\xi) \right| \right]$$

Sequential Marginal Likelihood SML

- *Using Roth method to pick the next experiment*
- *Calculating the posterior probability of the models*

Case study

(Order of a chemical reaction)

- **Box and Hill (1967)**

$$B \rightarrow C$$

$$f_1(t, T, A_1, E_1) = \exp[-A_1 t\, exp(-E_1/T)]$$

$$f_2(t, T, A_1, E_1) = [1 + A_2 t\, exp(-E_1/T)]^{-1}$$

$$f_3(t, T, A_1, E_1) = [1 + 2A_3 t\, exp(-E_1/T)]^{-1/2}$$

$$f_4(t, T, A_1, E_1) = [1 + 3A_4 t\, exp(-E_1/T)]^{-1/3}$$

Case study *(Order of a chemical reaction)*

$$M_j: ln v_i = \ln f_i(t_i, T_i, A_j, E_j) + \epsilon_i \qquad \begin{array}{c} i = 1,2,3,\ldots,N \\ j = 1,2,3,4 \end{array}$$

ϵ_i is the measurement error which is assumed normally distributed with mean zero and known standard deviation $\ln(1.25)$. So, errors on $\ln(v_i)$ are normally distributed.

Case study *(Order of a chemical reaction)*

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Time: $0 < t_i \leq 150$ minutes

Temperature: $450 \leq T_i \leq 600$ Kelvin

Experimental results are simulated by assuming that the reaction is of second order, where

$$A_2 = 5000000\,,\ E_2 = 10000$$

$$0 < E_j < 25000\,,\ 10^5 \leq A_j \leq 49.6 \times 10^6$$

HR Method (Case study)

Experiment				Probability			
Iteration	t_i	T_i	υ_i	π_1	π_2	π_3	π_4
1	149.519	599.954	-3.18818	0.388303	0.0860234	0.270728	0.254945
2	123.252	537.307	-1.67623	3.82878e-009	0.120238	0.794711	0.0850514
3	29.3985	564.197	-1.28813	4.62886e-023	0.267502	0.732215	0.000282809
4	27.6406	560.686	-1.07611	1.19216e-040	0.567527	0.432473	1.16335e-007
5	127.683	561.647	-2.6718	7.97811e-074	0.777846	0.222154	1.60512e-008
6	120.359	571.032	-2.5703	8.12498e-117	0.999065	0.000934847	7.06358e-009

SML Method (Case study)

Experiment				Probability			
Iteration	t_i	T_i	υ_i	π_1	π_2	π_3	π_4
1	123.202	561.702	-2.45356	1.15159e-022	0.386645	0.613355	1.97201e-022
2	106.392	499.147	-0.772253	2.98121e-024	0.608582	0.391418	7.28182e-024
3	123.138	578.132	-3.177	3.13135e-028	0.991917	0.00808252	8.82541e-029

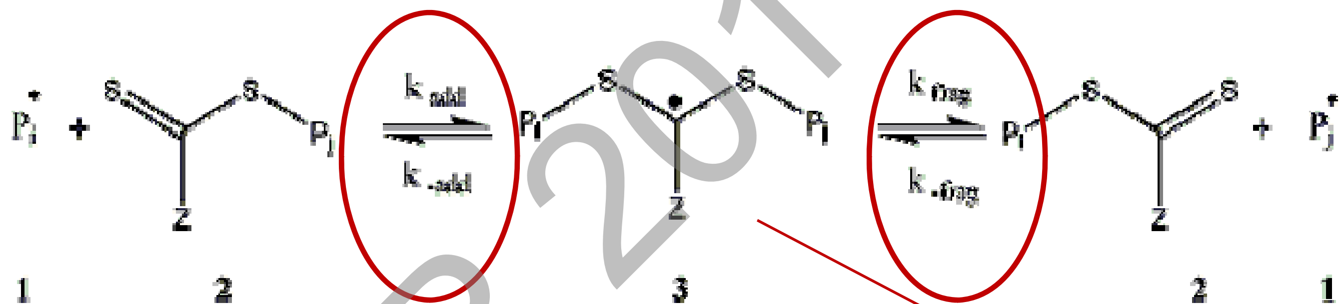
Future Works

- Modifying and finalizing of the SML procedure

- Appling the SML method in more case studies

RAFT

The RAFT process was introduced in 1998 as a controlled/living radical polymerization method (CLRP).



✓The irreversible termination method

Termination with other radical species, cross termination, or even self-termination

✓The slow fragmentation mechanism

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