Model-based experimental analysis for inter-polymer process

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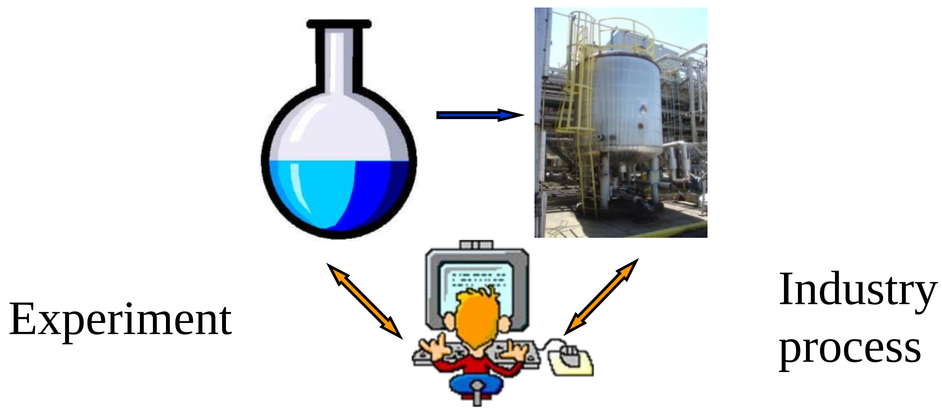
Outline

- Project overview
- Primitive model construction
- Model refinement and existing challenges
- Future work and conclusion

Model-based experimental analysis

- The link between experiment and industry process



- Kinetic modeling is a key technology
  - Design, control, operation of manufacturing process
  - Better understand of the micro-scale phenomena in chemical systems

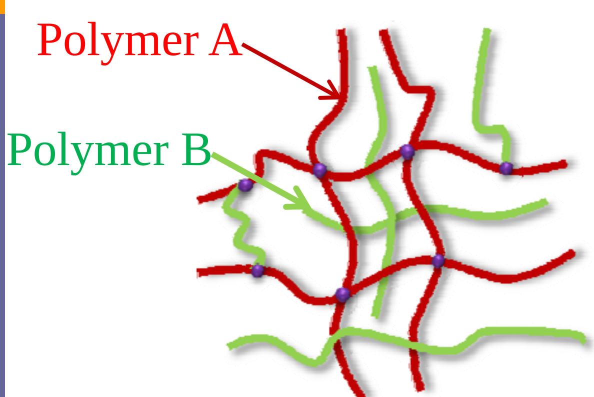
Inter-polymer process

ARCEL

Polystyrene (PS) + Polyethylene (PE)

TOUGH × **FLEXIBLE**

Advanced packaging material



Interpenetrating polymer network product processed in a sequential way

Model-based experimental analysis for inter-polymer process

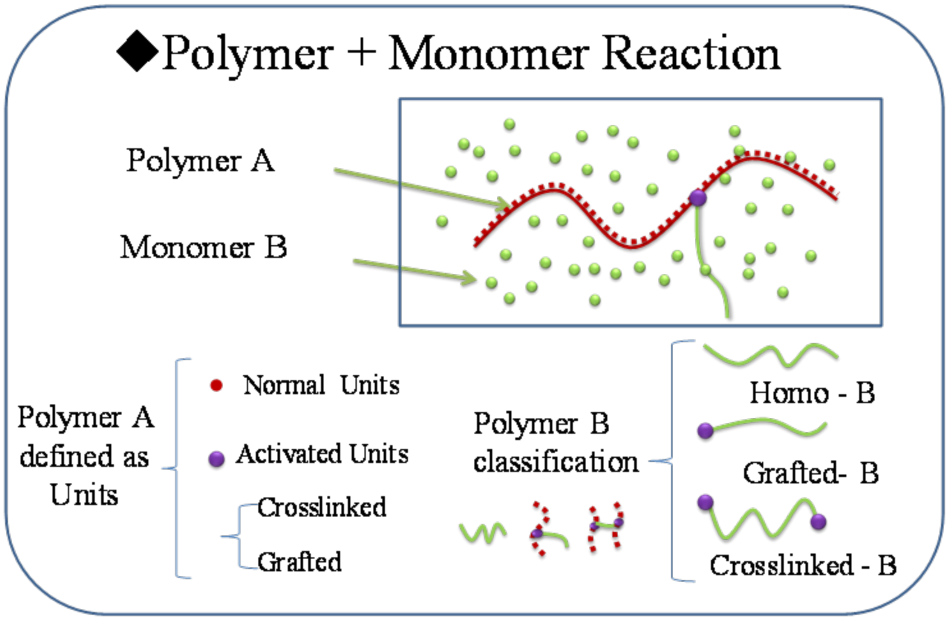
- Objective --- Model-Based experimental design
- Challenge --- Complex kinetic mechanism

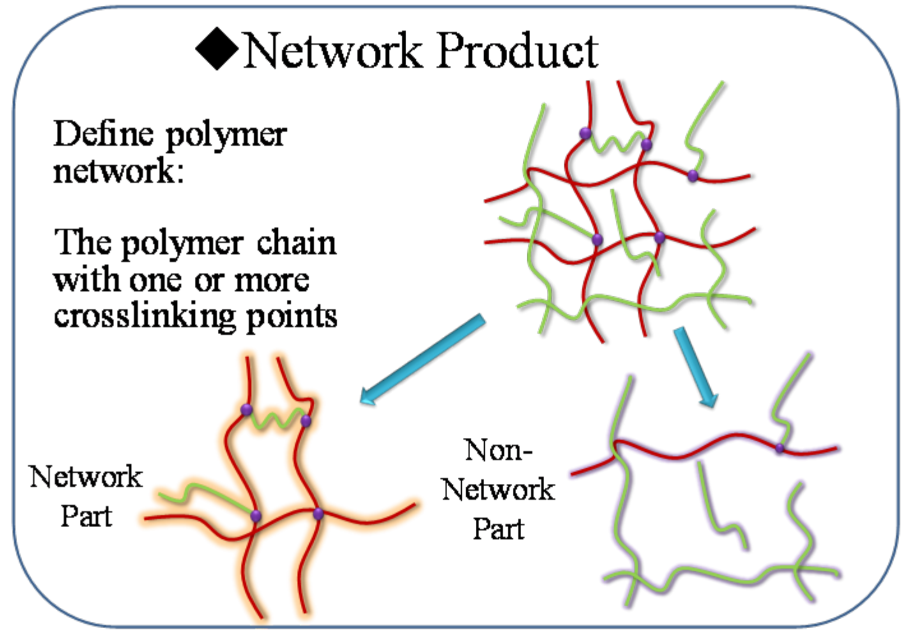
- Major questions were raised
  - How to build an initial model
  - How to solve the inverse problem
  - How to evaluate the model
  - How to implement the experimental design

Primitive model construction(1)

Reduce the complexity of the Inter-polymer system

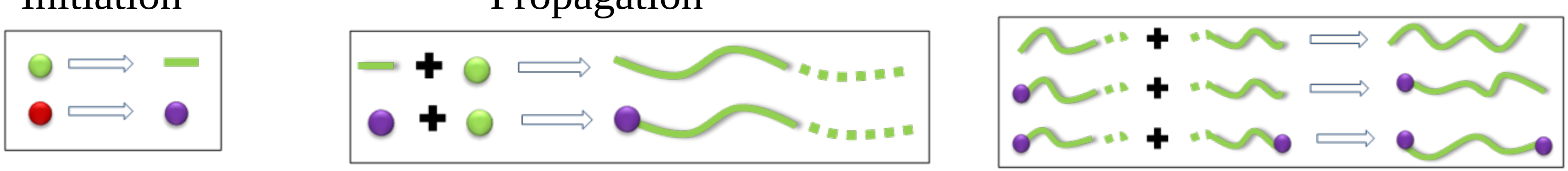
Active unit concept





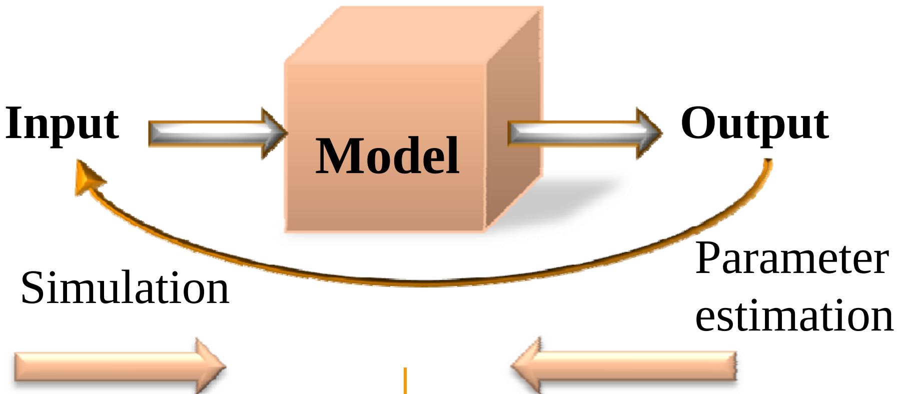
Compact kinetic model scheme (Free radical Polymerization)

Initiation　　Propagation　　Termination



Primitive model construction(2)

Inverse approach for parameter estimation



$$f(\frac{dx}{dt}, x, y, t) = 0$$

$$f(\frac{dx}{dt}|_{t=0}, x(0), y(0), 0) = 0$$

$$x \in R^n, y \in R^m$$

$$Min \;\; Tr(V^{-1}M(\theta)) = \sum_u \sum_j e_u^T V^{-1} e_u$$

S.t. $f(\frac{dx}{dt}, x, y, t) = 0$

$$f(\frac{dx}{dt}|_{t=0}, x(0), y(0), 0) = 0,$$

$$x_L \le x \le x_U, y_L \le y \le y_U$$

~~Arrhenius equation $K = Ae^{-E_a/RT}$~~

Apparent kinetic reaction rates

- Gel effect
- Glass effect
- Cage effect

Parameter-estimation-assisted

$K(t_1), K(t_2), K(t_3), \; K(t_4) \;\; \cdots$

$\Rightarrow K(time) \Rightarrow K(X)$

Primitive model construction(2)

Inverse approach for parameter estimation (Cont.)

Compute implementation

Convergence and robustness problems of the nonlinear estimation algorithms

$$Min.\ \sum_u \sum_j e_{ju}^2$$

S.t. $f(\frac{dx}{dt}, x, y, t) = 0$

$$x_L \le x \le x_U$$

$$y_L \le y \le y_U$$

$$f(\frac{dx}{dt}|_{t=0}, x(0), y(0), 0) = 0,$$

Simultaneous approach

Discretize all the variable in time at Radau collocation points

$$y(t) = y_{i-1} + h_i \sum_{q=1}^{NC} \Omega_q (\frac{t - t_{i-1}}{h_i}) \frac{dy}{dt_{i,q}}$$

Enforce continuity at each finite element

$$y(z) = y_{i-1} + h_i \sum_{q=1}^{NC} \Omega_q (1) \frac{dy}{dz_{i,q}}$$

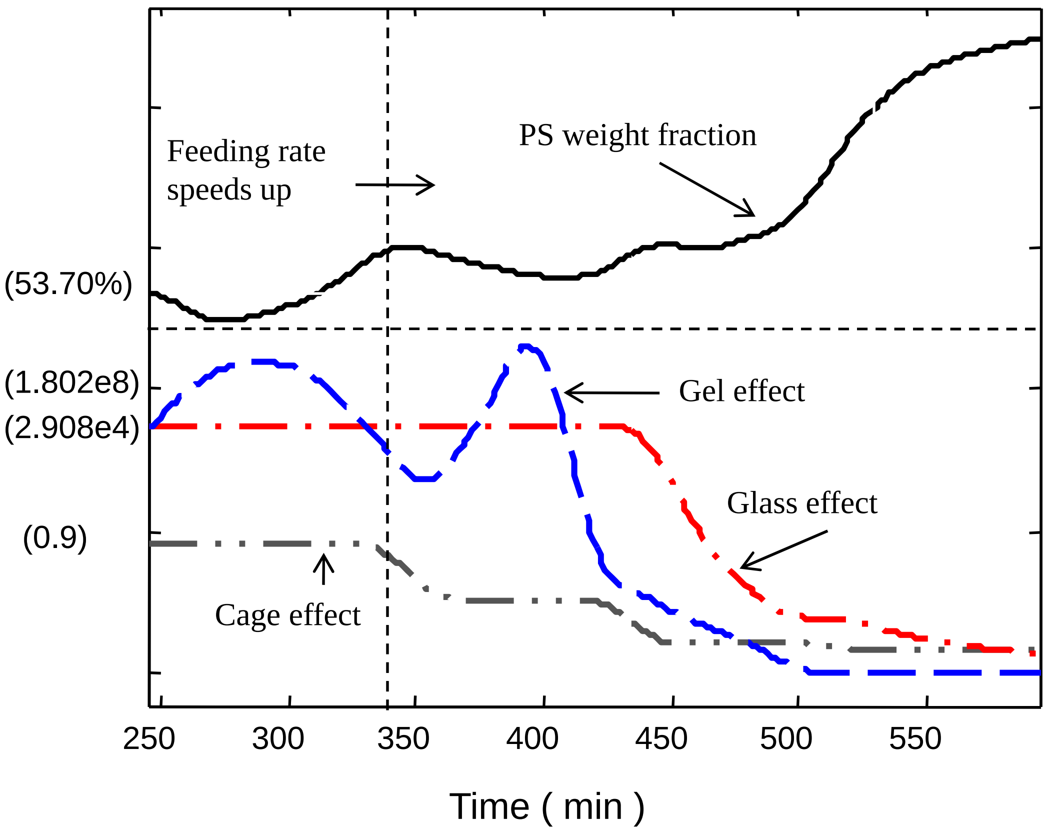
Solved as large scale nonlinear optimization problem (IPOPT)

$\text{var.} \ge 3,000$ In each sub-model

Primitive model construction (2)
Inverse approach for parameter estimation (Cont.)

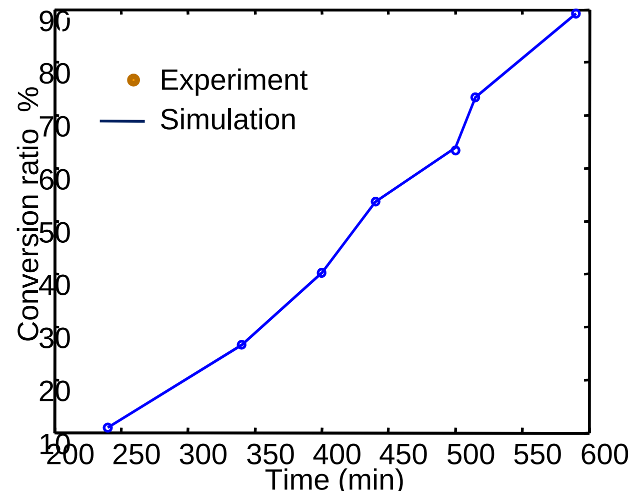
Based on the first set of data

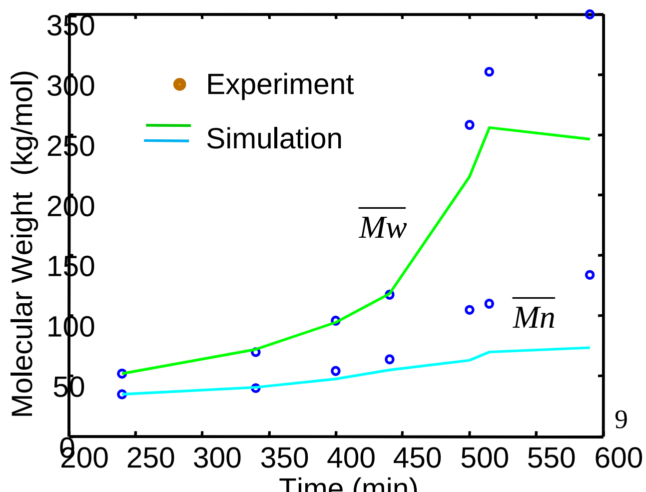
Simulation results



(Result for Polymerization Stage)

Comparisons

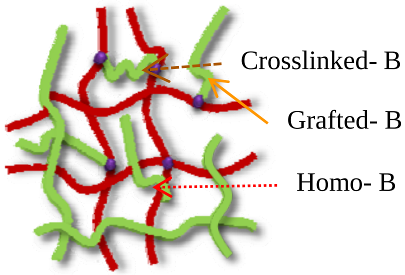




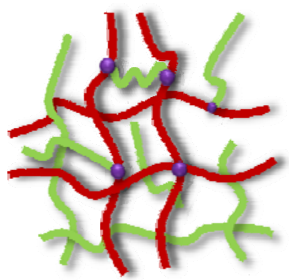
Primitive model construction (3)
Hybrid methods for property simulation

Molecular weight distribution / Network fraction

Step 1



Step 2



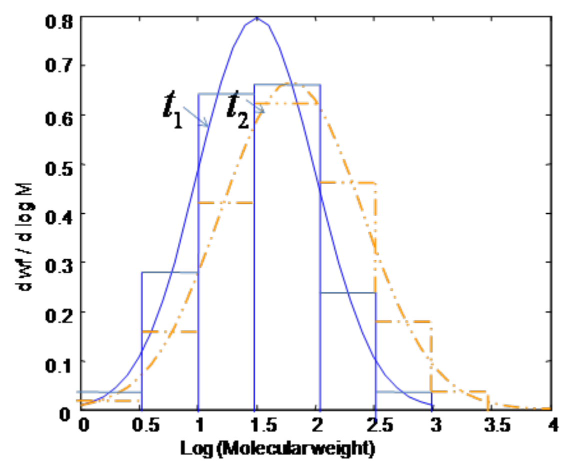
Step 3

Step 1: Separated Molecular weight distribution

The method of finite molecular weight moments

$$f_{(m,n)} = \frac{\sum_{i=m}^{n} iD_i}{\sum_{i=2}^{\infty} iD_i} = \frac{\textit{weight of polymer with chain length from m to n}}{\textit{total weight of polymer}}$$

$$\frac{df_{(m,n)}}{dt} = \frac{1}{\lambda_1}\sum_{i=m}^{n} i\frac{dD_i}{dt} - \frac{f_{(m,n)}}{\lambda_1}\frac{d\lambda_1}{dt}$$



Quasi-steady-state assumption to live polymer

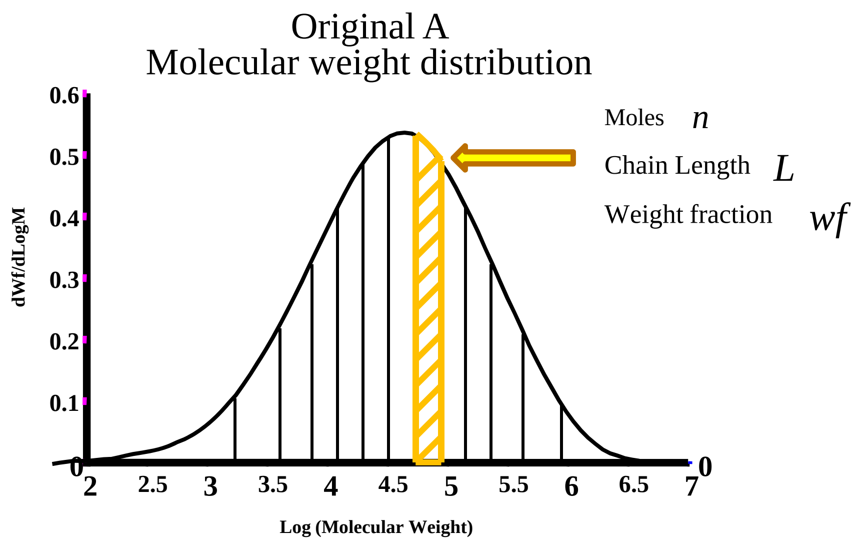
$$L_i = (1-\alpha)L\alpha^{i-1} \qquad \frac{dD_i}{dt} = \frac{1-\alpha}{\alpha}k_p D L_i$$

Instantaneous growing probability functions

$$\alpha = \frac{K_p M_s}{K_p M_s + K_t \mu_R^0 + E_r + \mu_E^0 + K_{fs} M_s + K_{fb} E_0}$$

Primitive model construction (3)
Hybrid methods for simulation (Cont.)

Step 2: Network fraction



1. Total activated units. N Moles
2. Soluble fraction for Chain Length L

$$Sf = \frac{C_{n\cdot N_A + N\cdot wf\cdot N_A - 2}^{n\cdot N_A - 2}}{C_{n\cdot N_A + N\cdot wf\cdot N_A - 1}^{n\cdot N_A - 1}} \approx \frac{n}{n + N\cdot wf}$$

Step 3:   Combined distribution

1. Total Network

   (A/ A-g-B) network + Crosslinked B

2. Combined Molecular weight

   A / B Non-Network

   Grafting probability $P_g = \frac{n_{grafted-units}}{n_{total-units}}$

   Combined Molecular Weight

   $$L\cdot[M_A + P_g\cdot EX(M_{g-B})]$$

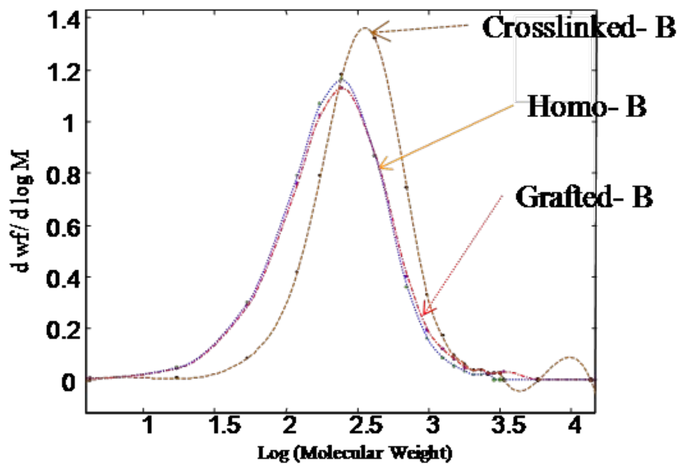
   Combined Mass

   $$[W_A\cdot wf + n\cdot L\cdot P_g\cdot EX(M_{g-B})]\cdot Sf$$

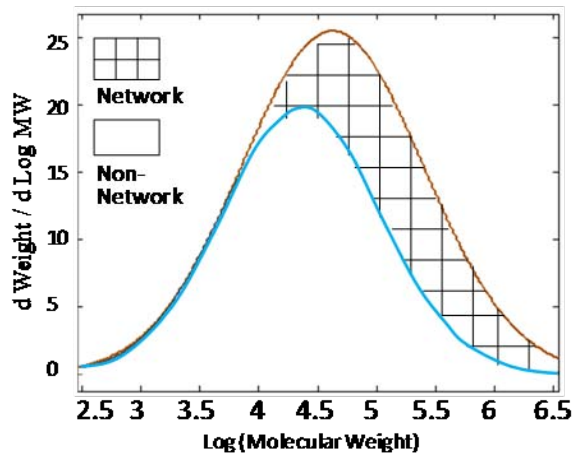
   + Homo-B

Primitive model construction (3)
Hybrid methods for simulation (Cont.)

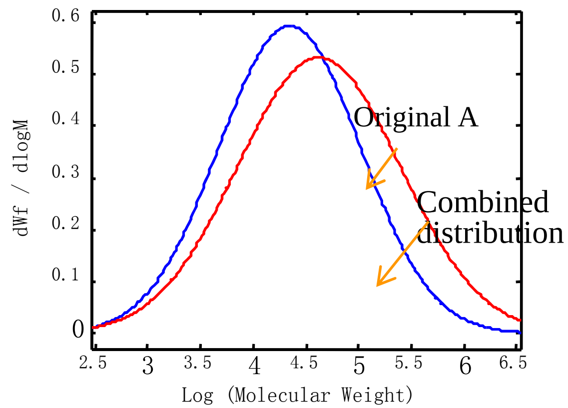
Separated molecular weight distribution
Result form step (1)



Network fraction
Result form step (2)



Combined molecular weight distribution Simulation (Step 3)

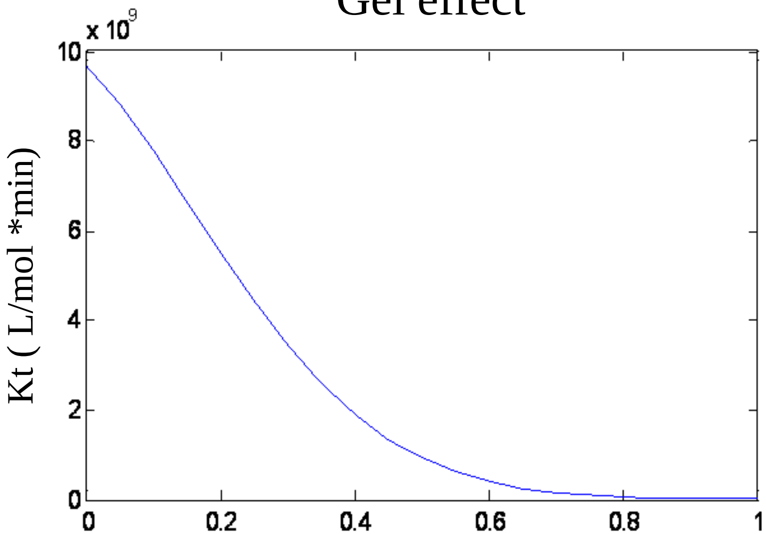


Model refinement and existing challenges
Coefficients sub model

Update the parameter estimation with new experimental data for a good fit

Simulation results

Gel effect

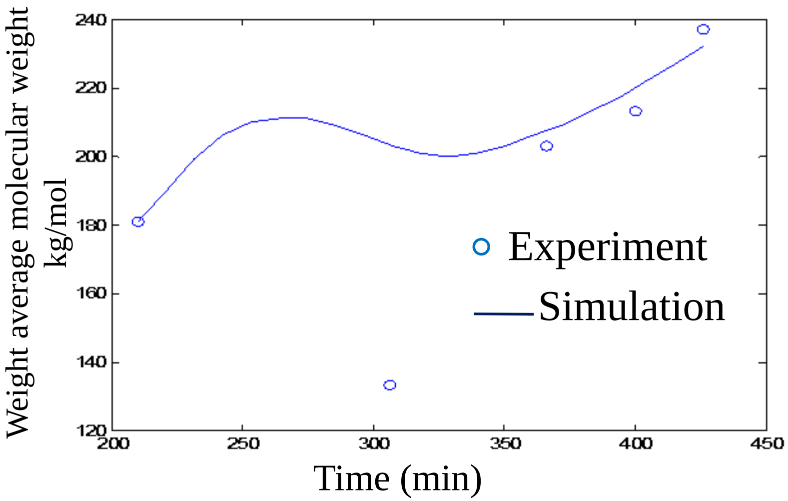


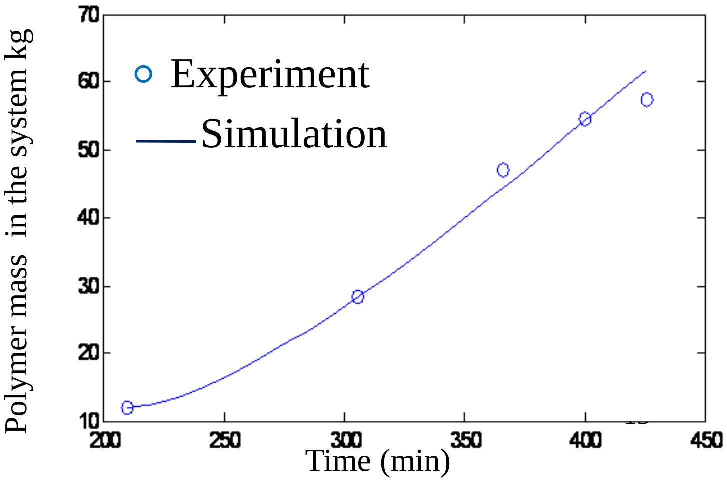
Polymer weight fraction

(Result for Polymerization Stage)

Comparisons

Average molecular weight development



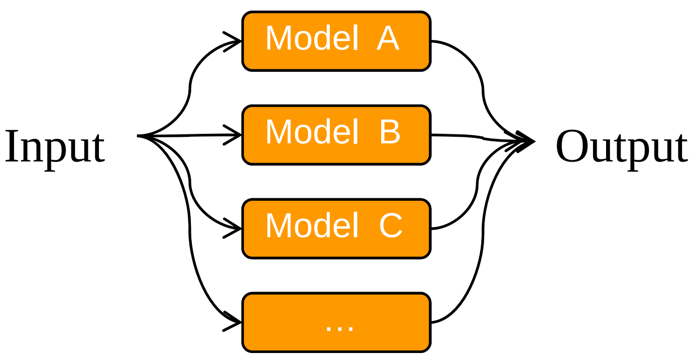


Model refinement and existing problems
Model discrimination

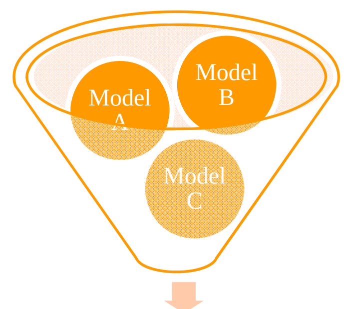
Better fit ≠ Better model

- Inversed problem for kinetic coefficients
  - Coefficients model discrimination

A lot of alternatives



Which is best?



"Best" Model ?

- Whether the parameter is identifiable
- Define the evaluation criteria

Model refinement and existing problems
Model discrimination (Cont)

- Alternative models
  - Polymer molecular theory
  - Empirical formula
  - Black-box model
- Discrimination Criteria
  - Physical acceptability
  - Compatibility with data diagnostic plot
  - Cp plot (Mallows,1964)
  - AIC score (Akaike, 1974)
  - The determinant of the parameter estimation equation (Bilardello, 1993)
  - Posterior probability (Stewart, etal. 1998)

Model refinement and existing problems
Incremental Model Development

- More things are worth to be considered
- Multi-phase system
  - Phase behavior model
    - Thermodynamic model for phase equilibrium
    - Molecular simulation (Coarse-grained model)
- Multi-Component Diffusion in polymeric liquids
  - Flux model
    - Macroscopic continuum thermodynamics and classical transport phenomena
    - Mesoscopic or coarse-grained level for complex fluids dynamics

Future work

- Develop a systematic model search approach for the model identification

- Goodness of fit test for the sub-model and structured model

- Model-based experimental design

Conclusion

- Kinetic model-based experimental design is one of the key technologies for chemical manufacturing process
- A primitive kinetic model is built for inter-polymer process
- Model refinement and discrimination is being developed with updating experimental data
- A systematic approach is needed for developing the integrated model structure