Outline

• Review of SIPN process

• Updates on kinetic modeling
  – “Decomposition” method and implementation
  – Model evaluation and heuristic experiment design
  – Application for optimization

• Future work discussion

• Conclusion
Fig 1. Seeded suspension polymerization reactor
SIPN Process Overview (2)

Fig 2. Stages of the simulation

I. Swelling
II. Polymerization
III. Crosslinking

Particle Growth model
Binary Polymer kinetic model

- Monomer
- Monomer / initiator
- Seed polymer
Semi-IPN Kinetic Model Development

• Complex Chemical Reaction

Propagation
\[ \text{C}_2\text{H}_4 + \text{R}^* \overset{k_p}{\longrightarrow} \text{R}^* + \text{C}_2\text{H}_2 \]

Termination by coupling
\[ \text{R}-\text{CH}_3^* + \text{R}^*-\text{CH}_3 \overset{k_t}{\longrightarrow} \text{R}-\text{CH}_2-\text{CH}_2-\text{R}^* \]

Termination by disproportionation
\[ \text{R}-\text{CH}_3^* + \text{R}''-\text{CH}_3-\text{CH}_2 \overset{k_d}{\longrightarrow} \rightarrow \text{RCH}_3 + \text{R}''-\text{CH}=\text{CH}_3 \]

Chain transfer with transfer agent
\[ \text{R}^* + \text{SA} \overset{k_s}{\longrightarrow} \text{RA} + \text{S}^- \]
\[ \overset{k_m}{\longrightarrow} \text{R}-\text{CH}_2-\text{CH}_2 + \text{C}_2\text{H}_5^- \]

Chain transfer with monomer
\[ \text{R}-\text{CH}_2-\text{CH}_2 \overset{k_m}{\longrightarrow} \text{R} = \text{CH}=\text{CH}_3 + \text{C}_2\text{H}_5^- \]

Intramolecular H-transfer
\[ \text{R}-\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2 \overset{k_0}{\longrightarrow} \text{R} = \text{CH}-\text{C}_2\text{H}_4 \]

Intermolecular H-transfer
\[ \text{R}^* + \text{R}^*-\text{CH}_2 \overset{k_l}{\longrightarrow} \text{RH} + \text{R}^*-\text{CH}-\text{R}'' \]
\[ \overset{k_p}{\longrightarrow} \text{R}^* + \text{CH}_2=\text{C}-\text{CH}_2-\text{R}^* \]

\[ \overset{k_p}{\longrightarrow} \text{R}^* + \text{CH}_2=\text{C}-\text{CH}_2-\text{R}^* \]

β-Scission
\[ \text{R}-\text{CH}_3-\text{C}-\text{CH}_2-R' \overset{k_p}{\longrightarrow} \text{R}'' + \text{CH}_3=\text{C}-\text{CH}_2-\text{R}'' \]

And more • • •
Polymer “Decomposition” strategy

Fig 3. Schematic representation of SIPN component “decomposition”

SIPN topology

Part 1: Component B
• Grafted chain
• Homo- polymer

Part 2: Component A
• Networking component
Previous Model Assumption

Fig 4. Decomposition as relatively independent components

SIPN topology

Part 1: Component B
• Grafted chain
• Homo- polymer

Part 2: Component A
• Networking component

Polymer A chain

Linear Polymer B

Grafted Polymer B

Grafting/ Crosslinking site

Relatively independent
Separation of Complexity

• Polymer B

The method of moment

The i-th moment of molecular weight $p(x,t)$ are defined by

$$p^{(i)}(t) = \sum_{1}^{\infty} x^i p(x,t) dx$$

Assumption 1:
Polymerized polymer B is intact during polymer A networking

• Polymer A

Fixed pivot technique

• The distribution is discretized at finite number of grids

The distribution are approximated by representative chain length

Assumption 2:
Polymer A undergoes random grafting and crosslinking
Comparison is made for a single polymer A crosslinking system

Fig 5. Simulation of polymer A gel fraction vs. measurement data in the literature

- Simulation results from crosslinking kinetic model shows consistent trend with the measurements provided in the literature
Inference About Optimization?

• Formulating optimization problem to reduce the processing time

\[
\begin{align*}
\text{min} & : & t_f \\
\text{s.t.} & : & Gel_f > Gel_{\text{target}} \\
& & \text{SIPN model}
\end{align*}
\]

• Decision variables reach their upper bounds

The higher the better?

– process temperature
– initiator concentration
– monomer conversion
Missed Facts and Raised Challenges

• Possible side reactions
  – Initiation of polymer B
  – Polymer B degradation
  – Interaction between two polymers

• Chain length dependent reactions rates
  – Chain scission, chain transfer …

Modeling two interacting distributions?
Improved Model Assumption

Fig 6. Considering polymer-polymer interaction

Polymer topology

Polymer interaction

Part 1: Component B
- Grafted chain
- Homo- polymer

Part 2: Component A
- Networking component
- Grafted chain
- Linear Polymer B
- Grafted Polymer B
- Grafting/ Crosslinking site
Efficient Computational Method

- Polymer B
  **Continuous variable approximation**
  - The chain length $x$ is treated as a *continuous* variable

The $i$-th moment of molecular weight moment $p(x,t)$ are defined by

$$p^{(i)}(t) = \int_0^\infty x^i p(x,t) \, dx$$

- Polymer A
  **Fixed pivot technique**
  - The distribution is discretized at *finite* number of grids

The distribution are approximated by representative chain length

- Polymerization
- Grafting
- Degradation

- Crosslinking

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$n_1, n_2, n_3, n_4, n_5, n_6, n_7, n_8, n_9, n_{10}, n_{11}, n_{12}, n_{13}, \ldots \cdot n_{\text{end}}$
Simulation Results (1)

Fig 7. Impact on Polymer B average Molecular weight

- Mw of polymer B continues to change after monomer is used up
- Different effects are possible for grafted-B and homo-B
Simulation Results (2)

Fig 8. Impact on Gel fraction

- Polymer interaction also changes the gel behavior
- Side reaction does not necessary decrease the gel fraction
Model vs. Experiment (1)

- Which parameter can be estimated from the available data
  - Parameter identification problem

- Which experimental data is required for estimating a certain parameter $\theta$
  - Experiment design
Model vs. Experiment (2)

• Relationship with sensitivity analysis

\[ \text{cov}(\hat{\theta}) \geq (\text{FIM})^{-1} \] (Fisher information matrix)

\[ \text{FIM} = S^T \Sigma^{-1} S \]

Where \( S(\theta, v, W; x_0) = \frac{\partial y(\theta)}{\partial \theta} \)

Assume observations are uncorrelated and identical

\[ \Sigma = \sigma_y^2 I, \quad S' = \frac{1}{\sigma_y} \frac{\partial y}{\partial \theta}, \quad F = S'^T S' \]

A measure of variance

\[ \text{var} \hat{\theta} \geq \text{trace}(\text{FIM})^{-1} \]
Value of the Measurement

- **Inverse question:**
  - If measurement $y$ is available, how many more parameters are estimable

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Table 1. An analysis example on crosslinking model
Sensitivity Based Heuristic Approach

• Optimization oriented heuristics
  – Prescreen parameters which are sensitive for optimization problem
  – Test estimability based on sensitivity analysis

• Effective experiments
  – Independent parameters
    Separate runs for polymer A, polymer B
  – Linking parameters
    (Joint) Molecular weight distribution
Multi Scenario Optimization Problem

\( \theta_j \in \Theta, j \in J, \) estimated parameters

\( \theta_k \in \tilde{\Theta}, j \notin J, \) parameters which are not observable from data

Generate multi-scenario for \( \Theta \); apply literature value for \( \tilde{\Theta} \)

Multi-scenario optimization formulation

\[
\min_{\Delta t, T(t), x_{s0}} \sum_i w_i \Vert x_i(t_f) - \bar{x}(t_f) \Vert_{\Theta}^2
\]

\[
s.t. \quad \dot{x}_i = f_i(x_i, \theta_i, T)
\]

\[
x_i(t_0) = x_{s0}
\]

\[
t_f = t_0 + \Delta t
\]

\[
g(x_0, \Delta t_3, T) \leq 0
\]

**Objective function:**

- Find a process condition which best satisfies the product specification under parameter uncertainty
Continuous Work

- Kinetic parameter estimation and model validation
- Product specification
- Incorporation with energy consumption (economic related objective function)
- Connection of stage models for simultaneous optimization
Conclusion

- A comprehensive kinetic model is developed for SIPN process
- Decomposition strategy and efficient algorithms are applied in model simulation
- Sensitivity based heuristic approach is proposed for experimental design
- Multi-scenario optimization is planned for model with uncertainty