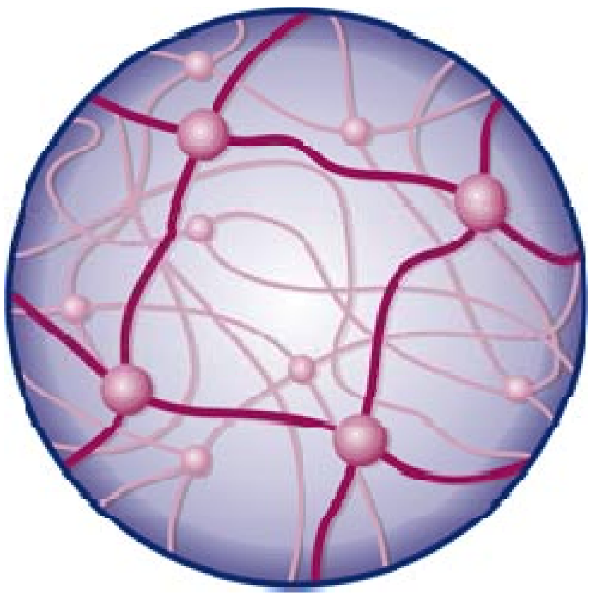
Kinetic Modeling for a Semi-Interpenetrating Polymer Network (SIPN) Process



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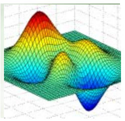
Outline

- 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


SIPN Process Overview (1)

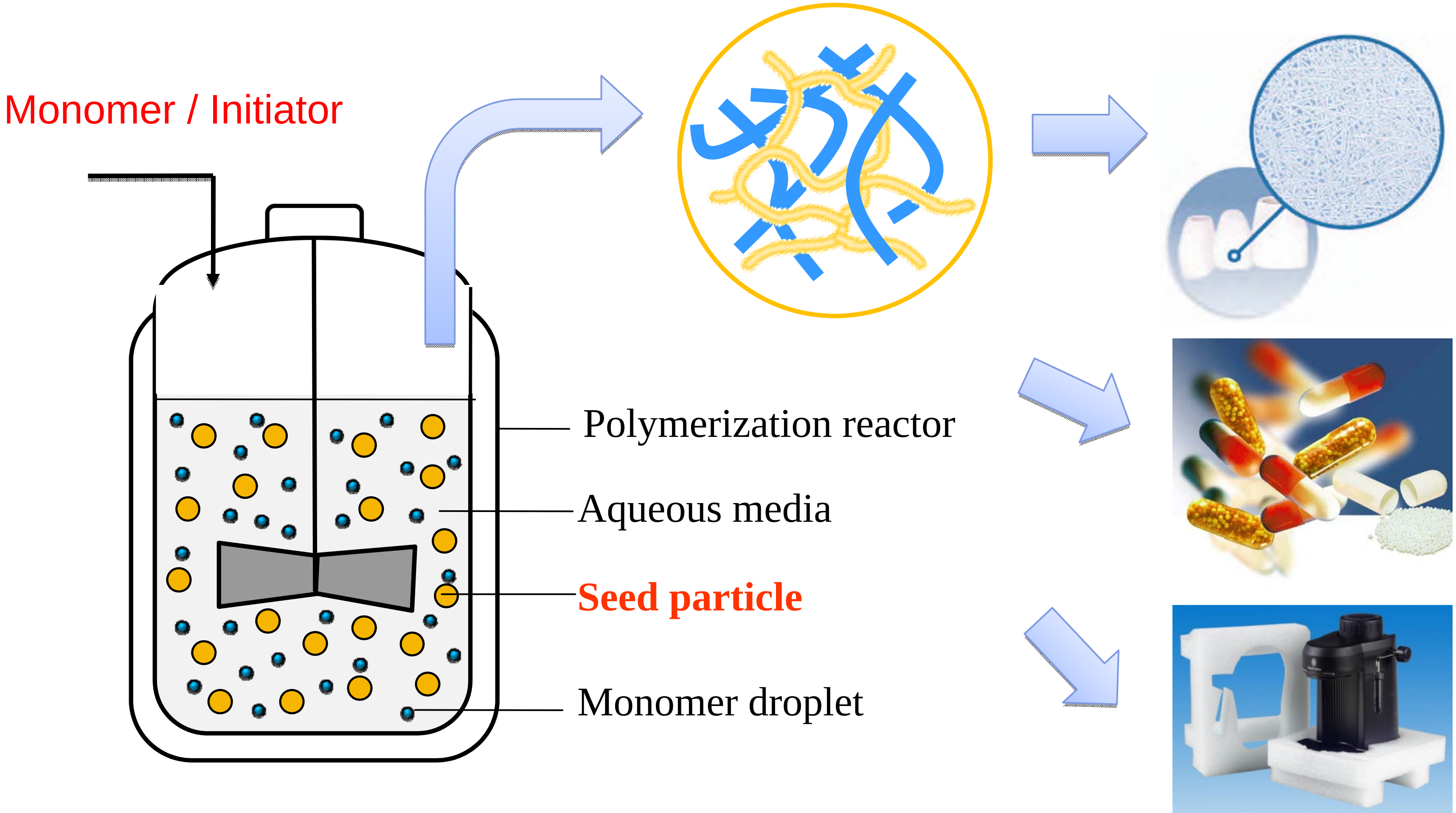
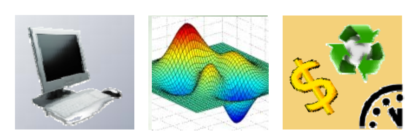


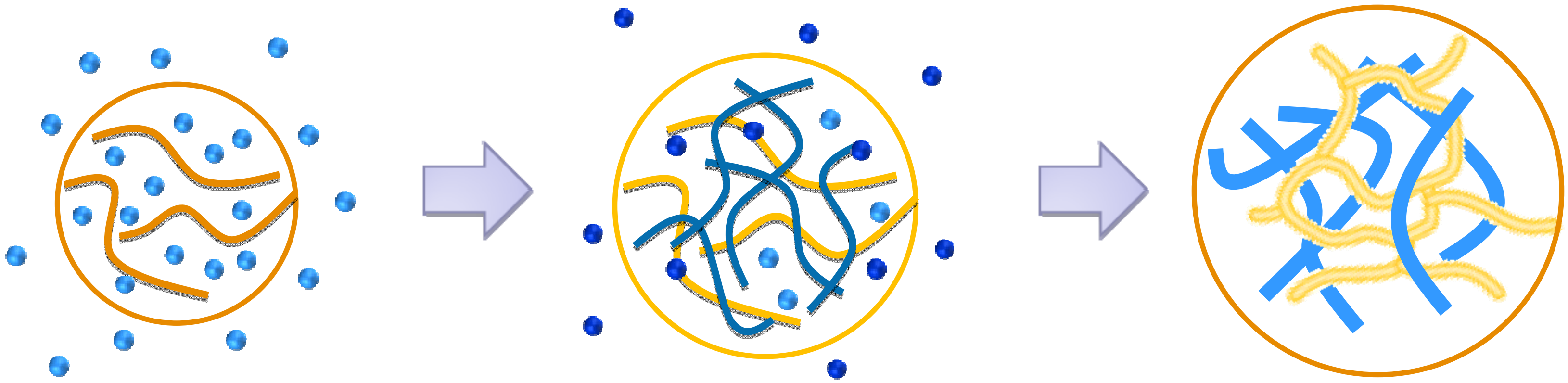
Fig 1. Seeded suspension polymerization reactor



SIPN Process Overview (2)

Fig 2. Stages of the simulation

I. Swelling | **II. Polymerization** | **III. Crosslinking**



- Monomer
- Monomer / initiator
- Seed polymer

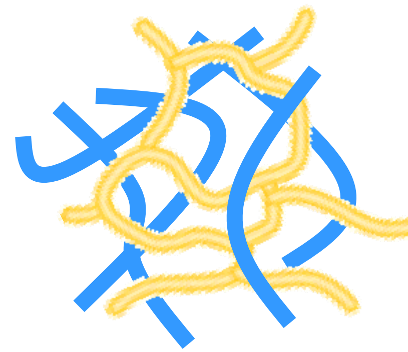
Particle Growth model

Binary Polymer kinetic model

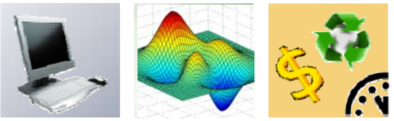
Semi-IPN Kinetic Model Development

- ## Complex Chemical Reaction

Propagation	$C_2H_4 + R\cdot_n \xrightarrow{k_p} R\cdot_{n+1}$,
Termination by coupling	$R{-}CH_2\cdot + R'{-}CH_2\cdot \xrightarrow{k_t} R{-}CH_2{-}CH_2{-}R'$.
Termination by disproportionation	$R{-}CH_2\cdot + R''{-}CH_2{-}CH_2\cdot \xrightarrow{k_{t'}} \rightarrow RCH_3 + R''{-}CH{=}CH_2$
Chain transfer with transfer agent	$R\cdot + SA \xrightarrow{k_s} RA + S\cdot$,
Chain transfer with monomer	$R{-}CH_2{-}CH_2\cdot + C_2H_4 \xrightarrow{k_m} R{-}CH_2{-}CH_3 + C_2H_3\cdot$; $R{-}CH_2{-}CH_2\cdot + C_2H_4 \xrightarrow{k_{m'}} R{-}CH{=}CH_2 + C_2H_5\cdot$,
Intramolecular H-transfer	$R{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2\cdot \xrightarrow{k_b} R{-}\dot{C}H{-}C_4H_9$,
Intermolecular H-transfer	$R\cdot + R'{-}CH_2{-}R'' \xrightarrow{k_l} RH + R'{-}\dot{C}H{-}R''$,
β-Scission	$R{-}CH_2{-}\dot{C}(R''){-}CH_2{-}R' \xrightarrow{k_\beta} R\cdot + CH_2{=}C(R''){-}CH_2{-}R'$; $R{-}CH_2{-}\dot{C}(R''){-}CH_2{-}R' \xrightarrow{k_\beta} R'\cdot + CH_2{=}C(R''){-}CH_2{-}R$,

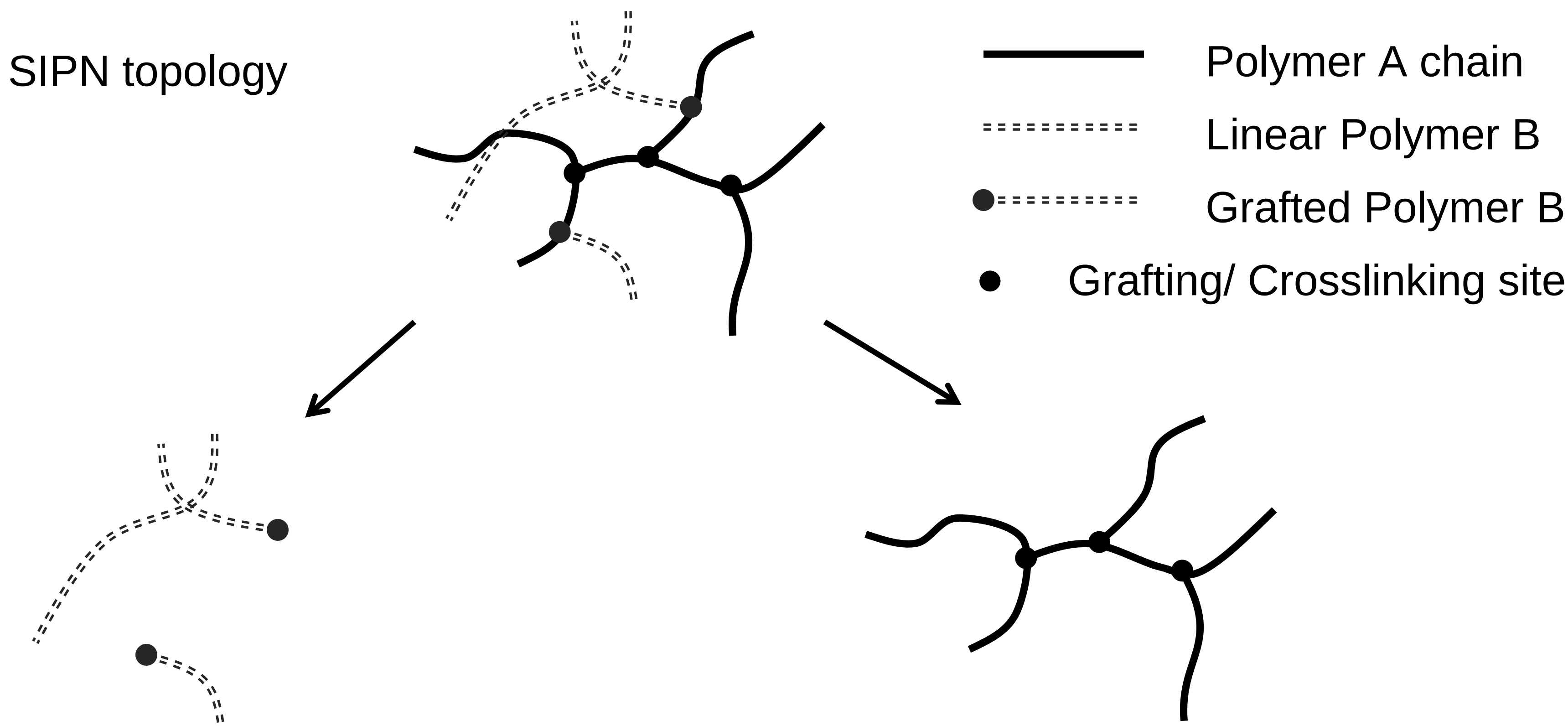


And more • • •



Polymer “Decomposition” strategy

Fig 3. Schematic representation of SIPN component “decomposition”



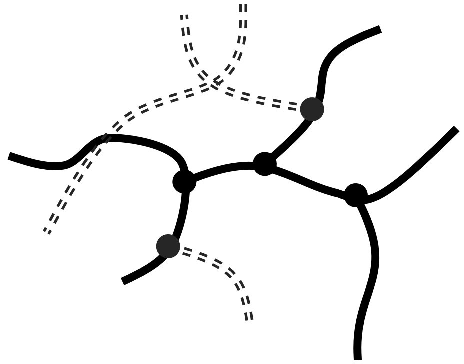
Part 1: Component B
- Grafted chain
- Homo- polymer

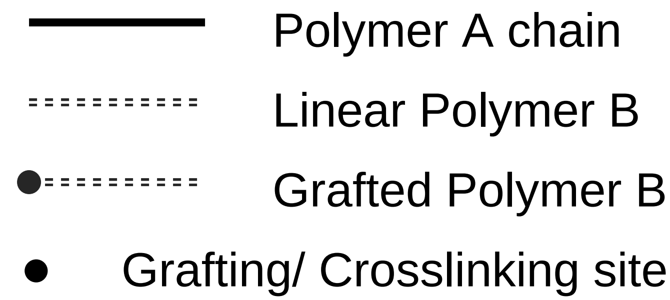
Part 2: Component A
- Networking component

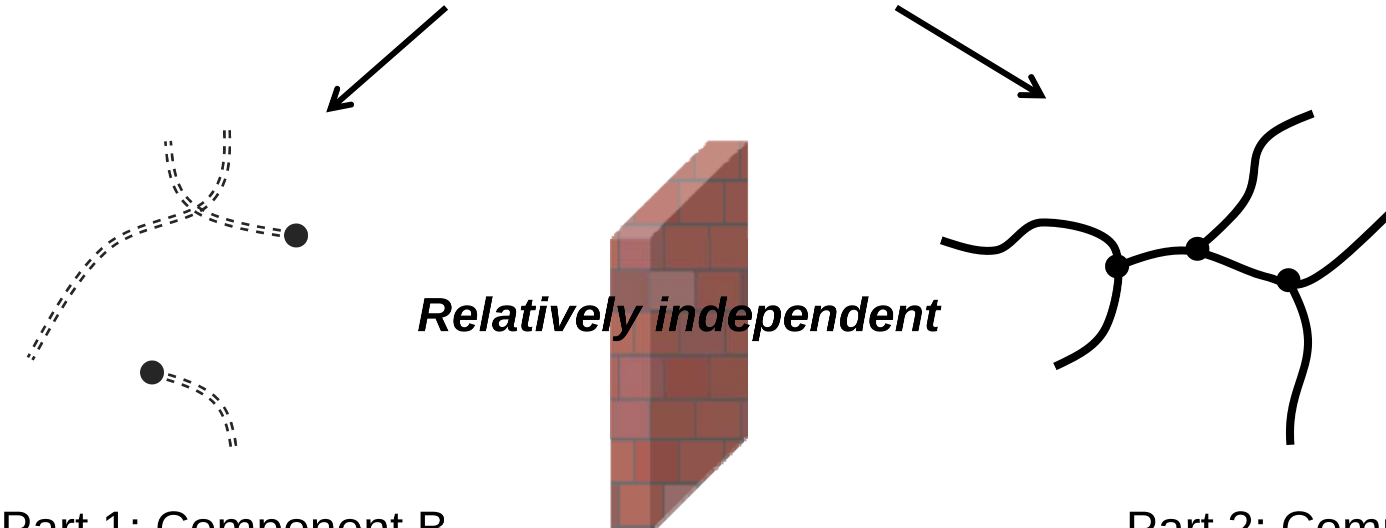
Previous Model Assumption

Fig 4. Decomposition as relatively independent components

SIPN topology







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

Part 2: Component A
- Networking component

Separation of Complexity

- Polymer B

The method of moment

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

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

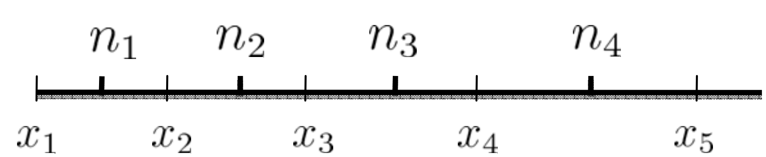
Assumption 1:
Polymerized polymer B is intact during polymer A networking

- Polymer A

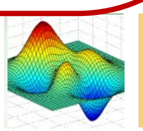
Fixed pivot technique

- The distribution is discretized at *finite* number of grids

The distribution are approximated by representative chain length



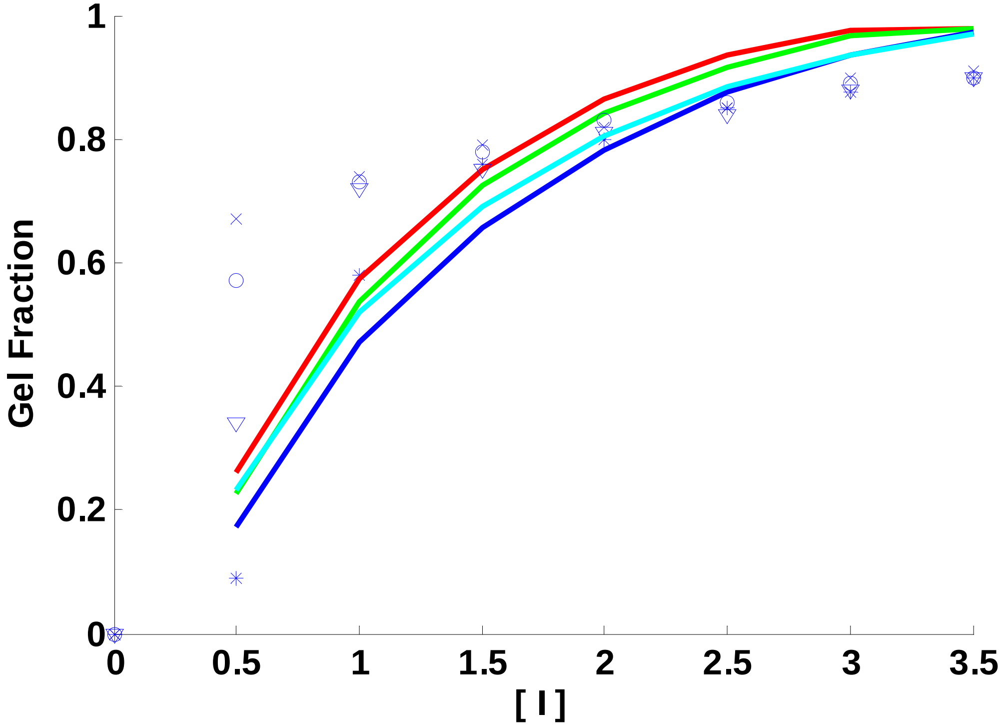
Assumption 2:
Polymer A undergoes random grafting and crosslinking


Study of Polymer A 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 ?

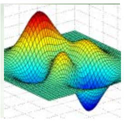
- Formulating optimization problem to reduce the processing time

$$
\begin{aligned}
\min: \quad & t_f \\
s.t. \quad & Gel_f > Gel_{target} \\
& \text{SIPN model}
\end{aligned}
$$

- Decision variables reach their upper bounds

  The higher the better ?

  – process temperature
  – initiator concentration
  – monomer conversion


Missed Facts and Raised Challenges

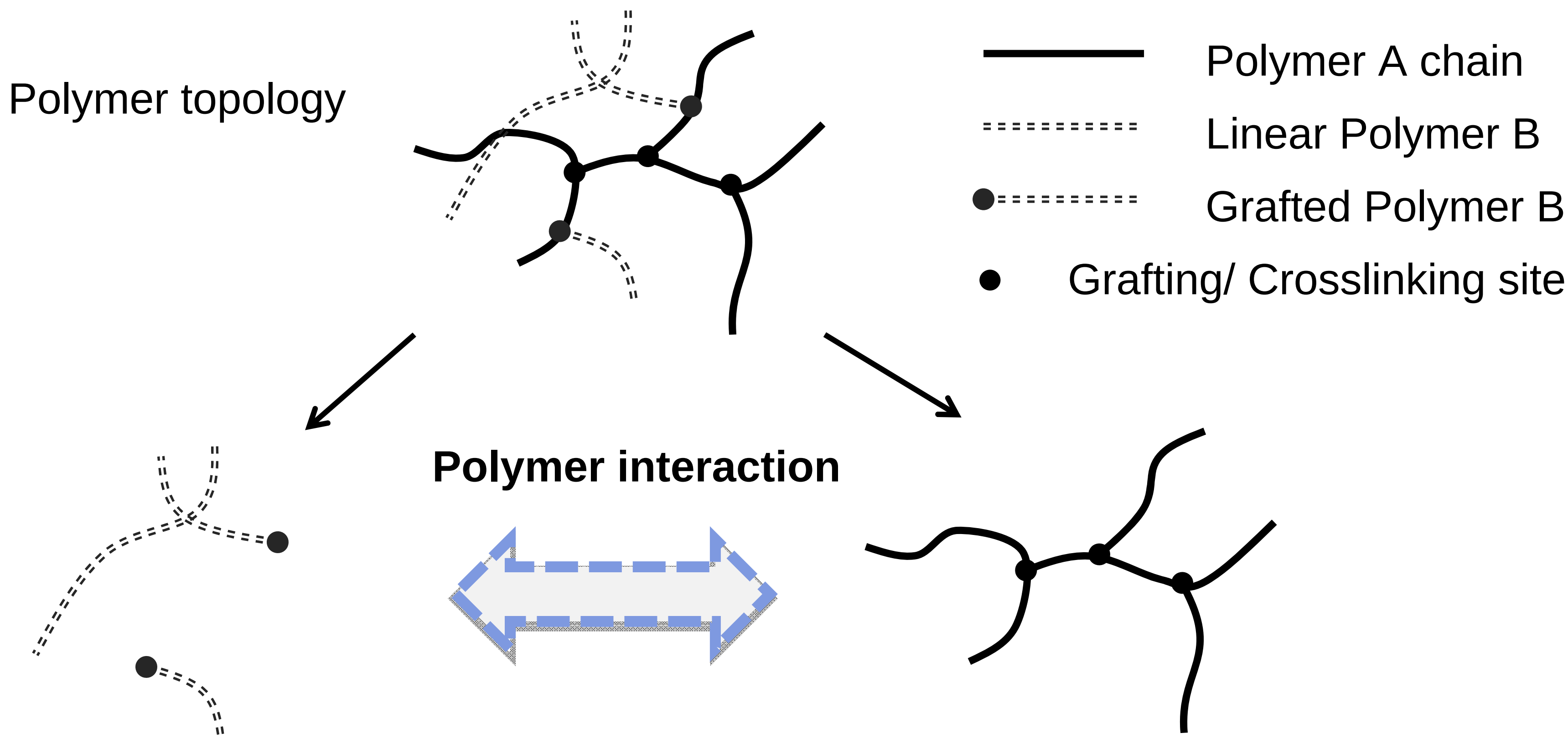
- Possible side reactions
  - Initiation of polymer B
  - Polymer B degradation
  - Interaction between two polymers

- Chain length dependent reactions rates
  - Chain scission, chain transfer …

Modeling two interacting distributions ?

Improved Model Assumption

Fig 6. Considering polymer-polymer interaction



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

Part 2: Component A
•Networking component

Efficient Computational Method

- Polymer B

Polymer interactions

- Polymer A

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

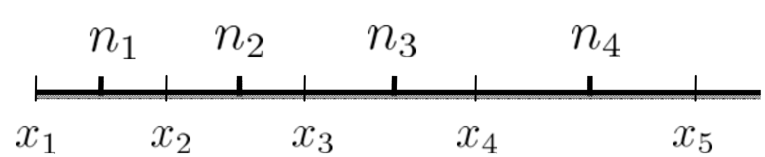
$$p^{(i)}(t) = \int_0^\infty x^i p(x,t)dx$$

- ☐ Polymerization
- ☐ Grafting
- ☐ Degradation

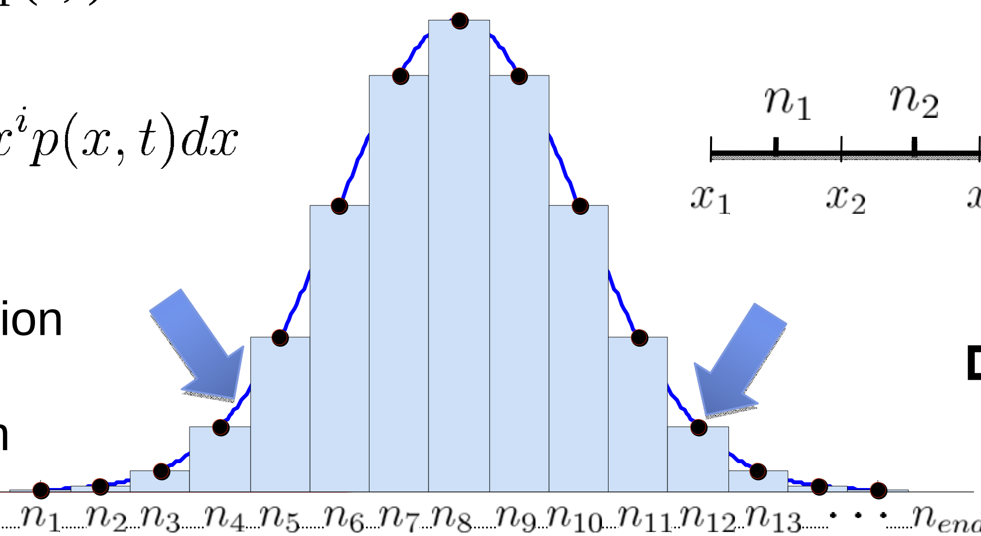
Fixed pivot technique

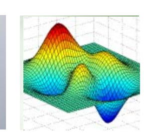
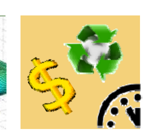
- The distribution is discretized at *finite* number of grids

The distribution are approximated by representative chain length



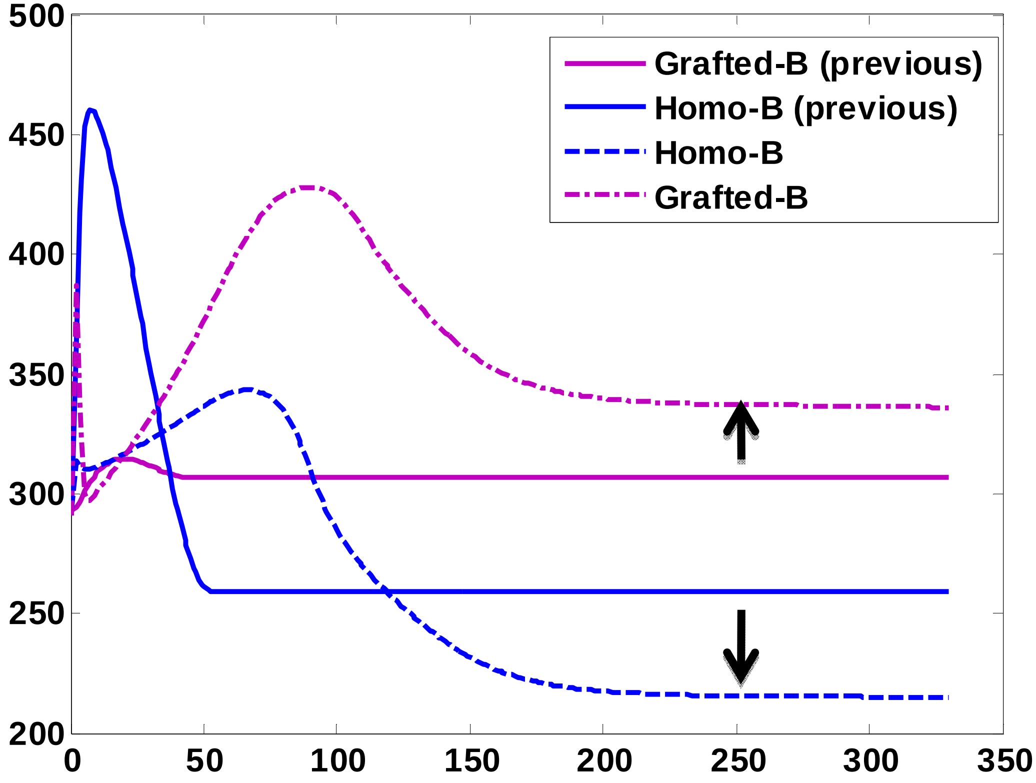
- ☐ Crosslinking



Simulation Results (1)

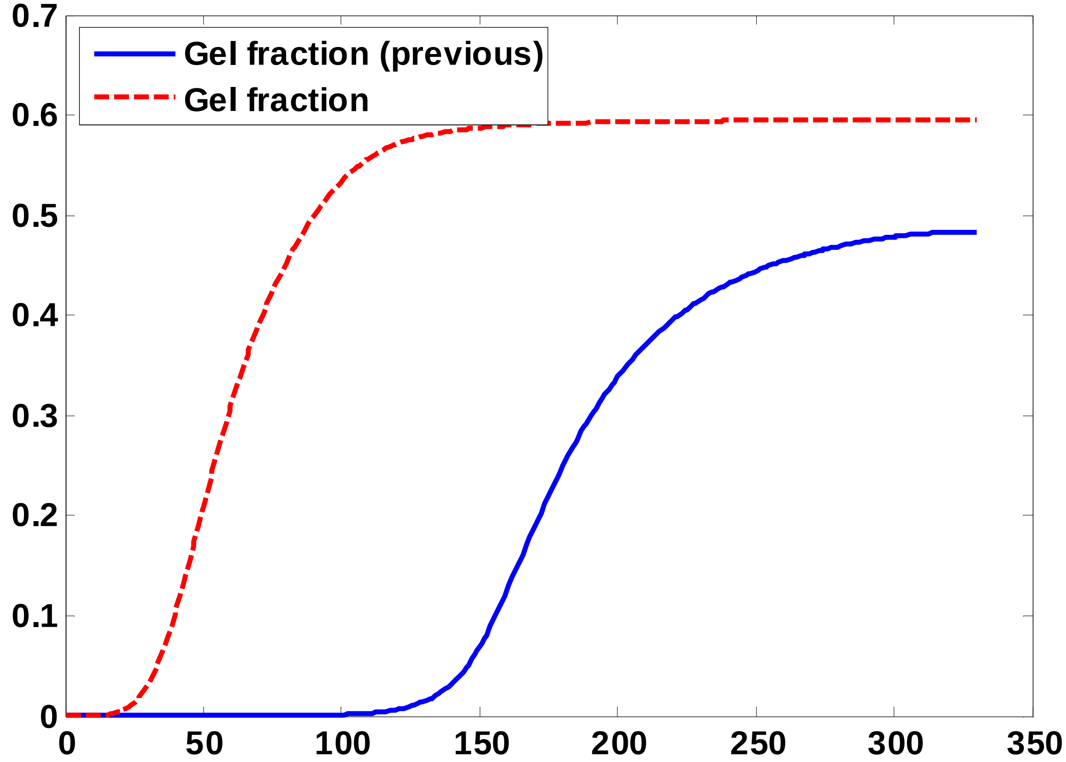
Fig 7. Impact on Polymer B average Molecular weight



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

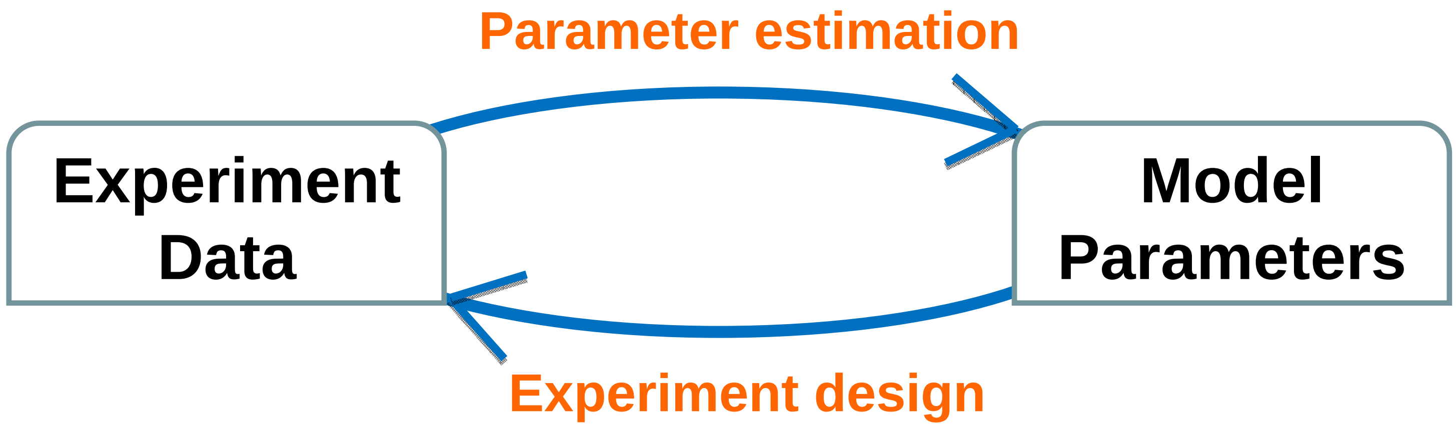
Simulation Results (2)

Fig 8. Impact on Gel fraction

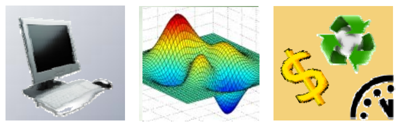


- Polymer interaction also changes the gel behavior
- Side reaction does not necessary decrease the gel fraction

Model vs. Experiment (1)



- Which parameter can be estimated from the available data
  - Parameter identification problem
- Which experimental data is required for estimate a certain parameter θ
  - Experiment design



Model vs. Experiment (2)

- Relationship with sensitivity analysis

$$cov(\hat{\theta}) \geq (\mathbf{FIM})^{-1}$$ (Fisher information matrix)

$$\mathbf{FIM} = S^T \Sigma^{-1} S$$

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

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

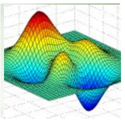
$$var\hat{\theta} \geq trace(\mathbf{FIM})^{-1}$$

Value of the Measurement

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

Table 1. An analysis example on crosslinking model

Measurement	Parameters	Measurement	Parameters
1 data set G_f^{end}	f	28 data set G_f^{end}	f (0.2) k_{tca} k_2 k_{tda} k_β (6.4) ↓

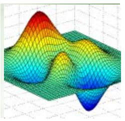

Sensitivity Based Heuristic Approach

- 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

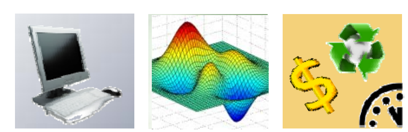
Generate multi-scenario for Θ ; apply literature value for $\tilde{\Theta}$

Multi-scenario optimization formulation

$$\begin{aligned}
\min_{\Delta t, T(t), x_{s0}} \sum_i w_i \| x_i(t_f) - \bar{x}(t_f) \|^2_{\Theta} \\
s.t. \quad \dot{x}_i &= f_i(x_i, \theta_i, T) \\
x_i(t_0) &= x_{s0} \\
t_f &= t_0 + \Delta t \\
g(x_0, \Delta t_3, T) &\leq 0
\end{aligned}$$

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