Enforcing the formation of cycles in the random graph modelling of polymerising HDDA

Tamika van ’t Hoff  
*University of Amsterdam, the Netherlands*, t.e.vanthoff@uva.nl

Piet Iedema  
*University of Amsterdam*

Ivan Kryven  
*University Utrecht*

Follow this and additional works at: https://dc.engconfintl.org/prexi

**Recommended Citation**

Tamika van ’t Hoff, Piet Iedema, and Ivan Kryven, "Enforcing the formation of cycles in the random graph modelling of polymerising HDDA" in "Polymer Reaction Engineering XI", Timothy McKenna, Université de Lyon, France; Claudia Sayer, Federal University of Santa Catarina, Brazil; Joe Schork, Georgia Tech, USA; John Tsavalas, University of New Hampshire, USA; Jay Reimers, Exxonmobil Chemicals, USA; Jose Ramon Leiza, University of the Basque Country, Spain; Robin Hutchinson, Queen's University, Canada; Brian Greenhalgh, Exxonmobil Chemicals, USA; Markus Busch, TU Darmstadt, Germany Eds, ECI Symposium Series, (2022). https://dc.engconfintl.org/prexi/33

This Abstract and Presentation is brought to you for free and open access by the Proceedings at ECI Digital Archives. It has been accepted for inclusion in Polymer Reaction Engineering XI by an authorized administrator of ECI Digital Archives. For more information, please contact franco@bepress.com.
Enforcing the Formation of Cycles in the Random Graph Modelling of Polymerising HDDA

Tamika van ‘t Hoff
December 13th 2022
Polymerisation of Acrylates

• 1,6-hexanediol diacrylate (HDDA)

• 2 functional vinyl groups

• Formation up to 4 crosslinks
Polymerisation of Acrylates

**Assumption**
- Unreacted vinyl group
- Radical containing site
- No longer reactive

\[
\#v, \#r, \#cl = [2, 0, 0]
\]

**Propagation**
- \([1, 1, 0]\) + \([2, 0, 0]\) → \([1, 0, 1]\)

**Termination Disproportionation**
- \([1, 1, 0]\) + \([1, 1, 0]\) → \([1, 0, 0]\) + \([1, 0, 0]\)

**Termination Recombination**
- \([1, 1, 0]\) + \([1, 1, 0]\) → \([1, 0, 1]\)

Unreacted vinyl group
- Radical containing site
- No longer reactive
Polymerisation of Acrylates

- 1st Order reaction
- Size of cycle dependent on the distance between reactive sites

Goal: introduce cycles in a Random Graph Model
Random Graph Modelling

- Input: probability degree distribution $u_t(k)$ for given time $t$
- Infinite system of nodes with half-edges

\[ P\{d = 0\} = u_t(0) \quad P\{d = 1\} = u_t(1) \quad P\{d = 2\} = u_t(2) \quad P\{d = 3\} = u_t(3) \]

- Any pair of half-edges has the same probability to connect
Random Graph Modelling

Graphs are formed according to $u_t(i)$ in a tree-like structure
Application: Polymerising Acrylates

• How to model a chemical system as graph?
  • Monomers as nodes
  • Crosslinks as edges

• PB model generates $u(k)$ through time

• How does the graph relate to chemistry?
  • Oligomers correspond to finite connected components
  • Polymers correspond to the giant component

Global properties describing the graph, describe the polymer
Application: Polymerising Acrylates

\[ t_{gel} = 3 \text{ ms} \]
Challenges with Cyclization

1. Random Graphs are assembled in a tree-like structure

2. Sequential information is not included in Random Graphs
Enforcing cycles in a Random Graph

How to create cycles in a randomly constructed graph?

Introduce asymmetric, or directed edges in the graph

Undirected edge

Directed edge
Enforcing cycles in a Random Graph

1. Find cycles in a given graph
2. Introduce an imaginary node with only directed in-edges
3. Replace undirected edges with directed out-edges
4. Create a new probability distribution with the additional information
Enforcing cycles in a Random Graph

• So far: cycles with a size of 3

• Optimal cycle size varies per system
  • Steric hindrens
  • Number of radicals in system

A similar approach works for other cycle sizes
Application: Polymerising Acrylates

\[
\begin{align*}
    k_1 &= 584 \text{ s}^{-1} \\
    k_2 &= 397 \text{ s}^{-1} \\
    k_3 &= 529 \text{ s}^{-1} \\
    k_4 &= 733 \text{ s}^{-1} \\
    &\vdots \\
    k_{11} &= 248 \text{ s}^{-1} \\
    k_{12} &= 248 \text{ s}^{-1} \\
    k_{13} &= 187 \text{ s}^{-1} \\
    k_{14} &= 149 \text{ s}^{-1}
\end{align*}
\]

\[
\begin{align*}
    \frac{dA(t)}{dt} &= -k_1 A(t)B(t) \\
    \frac{dB(t)}{dt} &= -k_1 A(t)B(t) \\
    &\vdots \\
    \frac{dY(t)}{dt} &= k_n X(t)W(t) \\
    \frac{dZ(t)}{dt} &= k_n X(t)W(t)
\end{align*}
\]
MD based: Preliminary Results

$bc = 0.3201$
MD based: Preliminary Results
Cycle PB model

\[ M_{[1,0,1]} + M_{[1,0,2]} + M_{[1,1,1]} \rightarrow M_{[0,1,2]} + M_{[1,0,2]} + M_{[1,0,2]} \]

\[ M_{[1,0,1,0,0]} + M_{[1,0,2,0,0]} + M_{[1,1,1,0,0]} \rightarrow M_{[0,1,2,0,0]} + M_{[1,0,2,0,0]} + M_{[1,0,2,0,0]} \]

\[ M_{[1,0,1,0,0]} + M_{[1,0,2,0,0]} + M_{[1,1,1,0,0]} \rightarrow M_{[0,1,0,1,0]} + M_{[1,0,0,1,0]} + M_{[1,0,0,1,0]} + M_{[0,0,0,3]} \]
Cycle PB model

- The inclusion of directionality increases complexity
  - No cyclization: $F_{max} = 4$  
    -> 5 possible nodes
  - Cyclization: $F_{max} = [4, x, 14]$  
    -> $4 \times 14 \times x$ possible nodes

- Larger cycles: cyclization can occur more than once
Summary

• Method to incorporate cycles in a Random Graph

• Influence of cycle enforcing visible with low concentrations

• Work in progress: Construct PRE model with full range of cyclization reactions

• Next: Influence of cycle size/abundance on $t_{gel}$
Acknowledgements

• Prof. Dr. P.D. Iedema
• Dr. D. Dubbeldam
• Dr. I. Kryven (UU)

• Computational Chemistry Group
  HIMS/University of Amsterdam

CHARM: This project has received funding from the ECSEL Joint Undertaking (JU) under grant agreement No 876362. The JU receives support from the European Union’s Horizon 2020 research and innovation programme and Austria, Belgium, Czech Republic, Finland, Germany, Italy, Latvia, Netherlands, Poland, and Switzerland