SAND2022-16002C

# Glass Transition Behavior of Crosslinked Epoxy/Amine Resins with Prospective Self-Healability

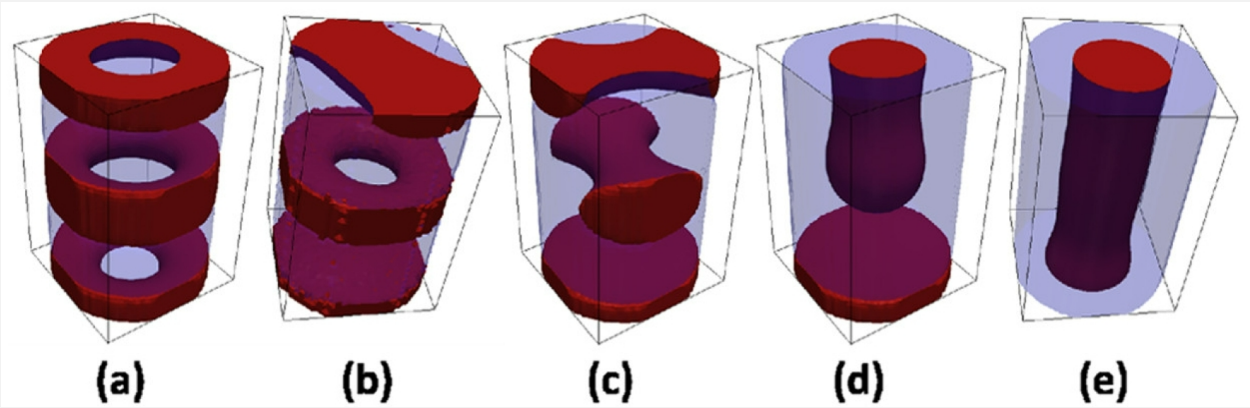
Cody Bezik and Amalie Frischknecht

11/14/2022 - 2022 AIChE Annual Meeting

Faculty Candidates in CoMSEF/Area 1a, Session 1

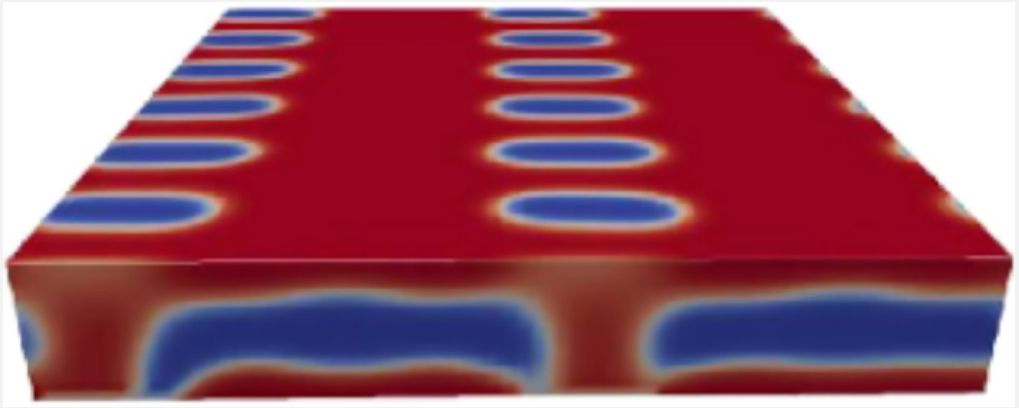
# Multiscale Simulations of Complex Polymer Systems

## Self-assembly In Cylindrical Hole Confinements



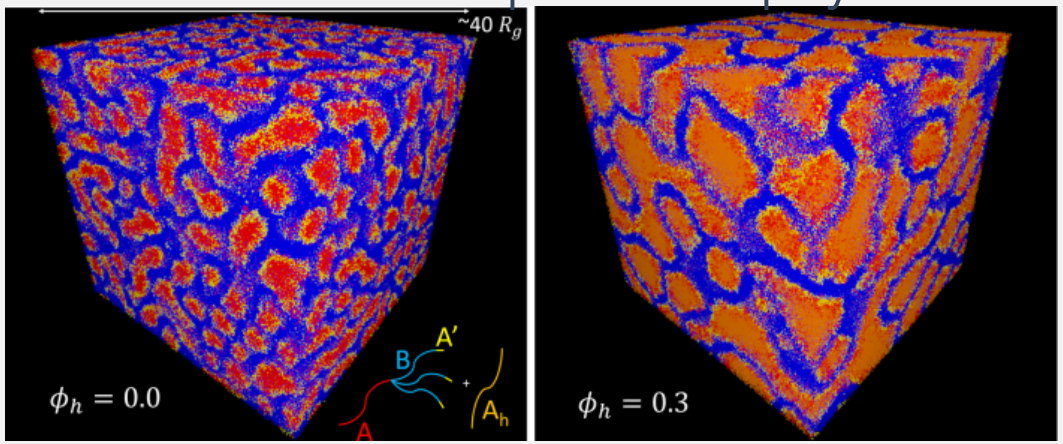

Bezik et al. (2018)

## Stitched Morphology In Block Copolymer Thin Films



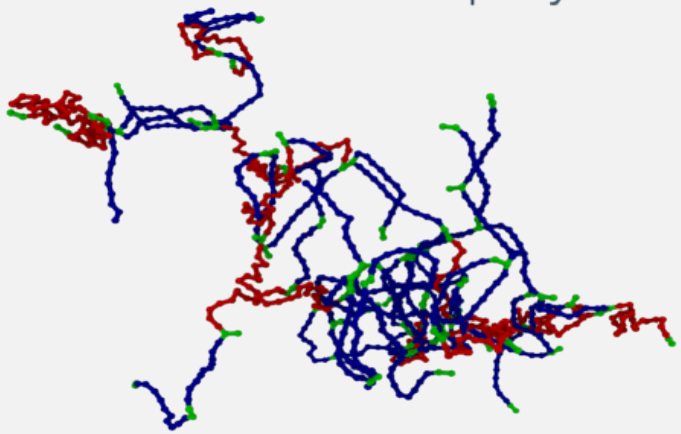
Bezik et al. (2020)

## "Bricks-and-Mortar" Mesophase In Copolymer Blends




Bezik et al. (2022)

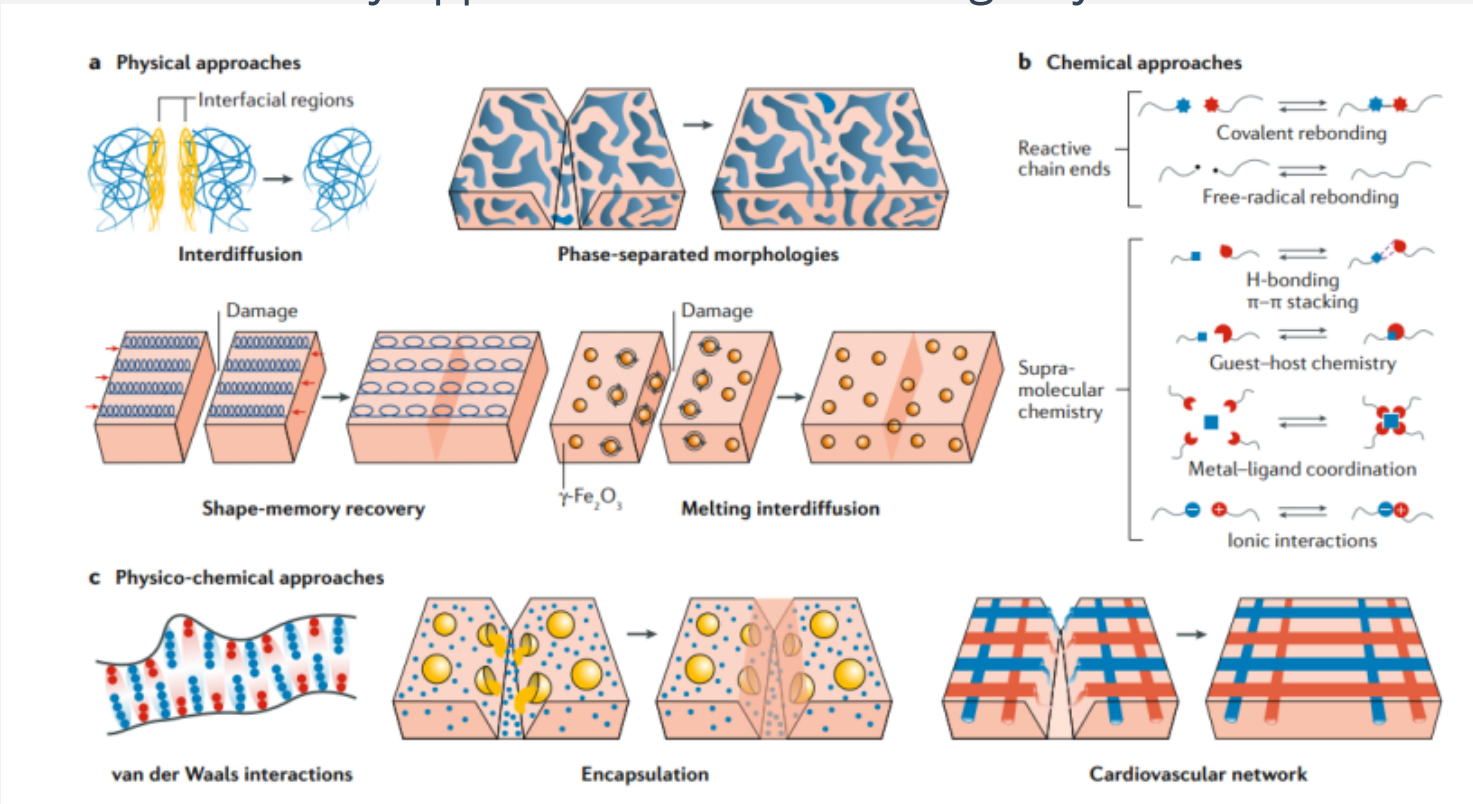
## $T_g$ Behavior of Crosslinked Epoxy/Amine Resins



Bezik et al. (in prep)

# Self-Healing Polymers Represent Cost-Saving, Sustainability

## Many Approaches To Self-Healing Polymers

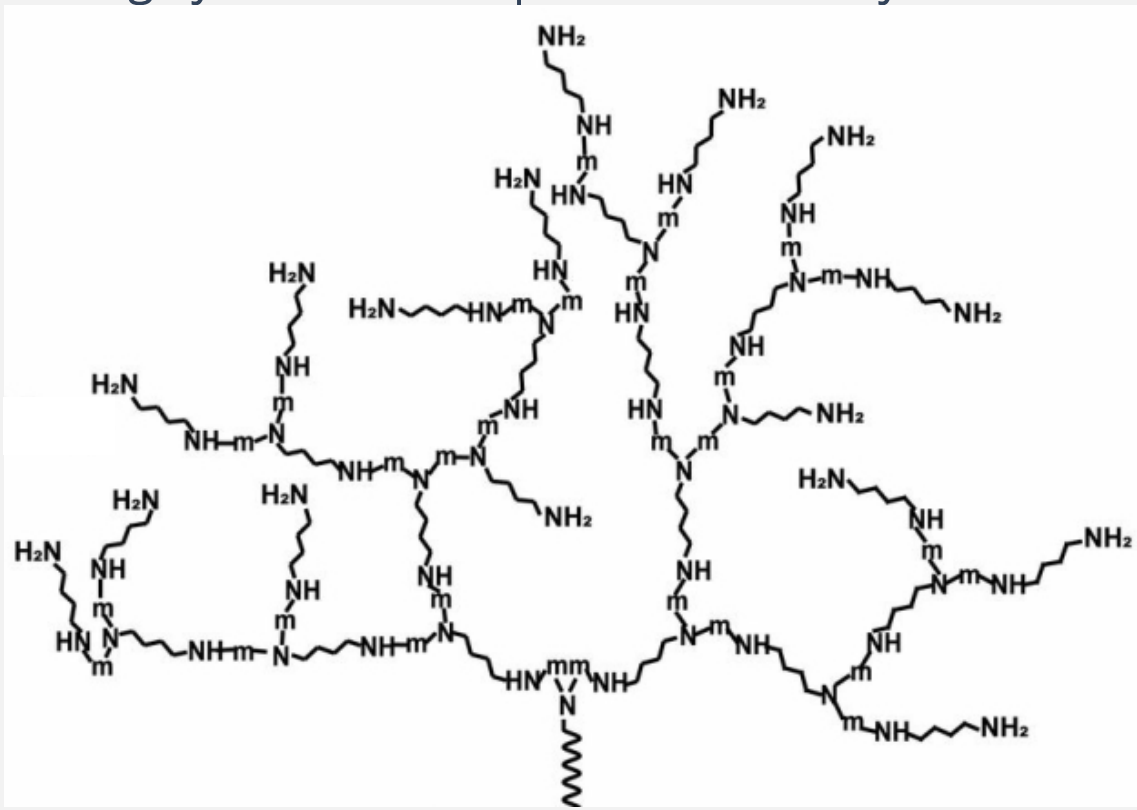



- Supramolecular interactions represent a path to **autonomous, repeatable** self-healing
- How can the other (thermomechanical) properties of the material be designed *in tandem* with self-healability?

Wang and Urban (2020)
Wang et al. (2020)

# Network Polymers with Hydrogen Bonds Could Enable Self-Healing Below $T_g$

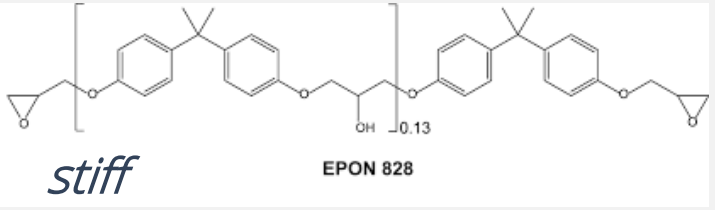
Highly-branched, Supramolecular Polymers



- The strong, glassy core enables high $T_g$, while supramolecular interactions at the termini enable self-healing
- Understanding the **glass transition temperature** of these systems represents a key first step toward designing them

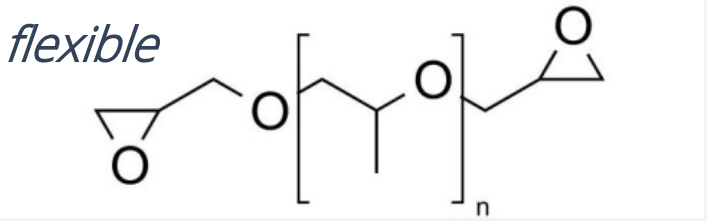
Wang and Urban (2020)
Wang et al. (2020)

# Experimental $T_g$ Shows A Maximum For Blended Networks



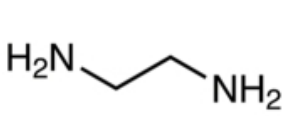

*stiff*

MW = 366 (g/mol)




*flexible*

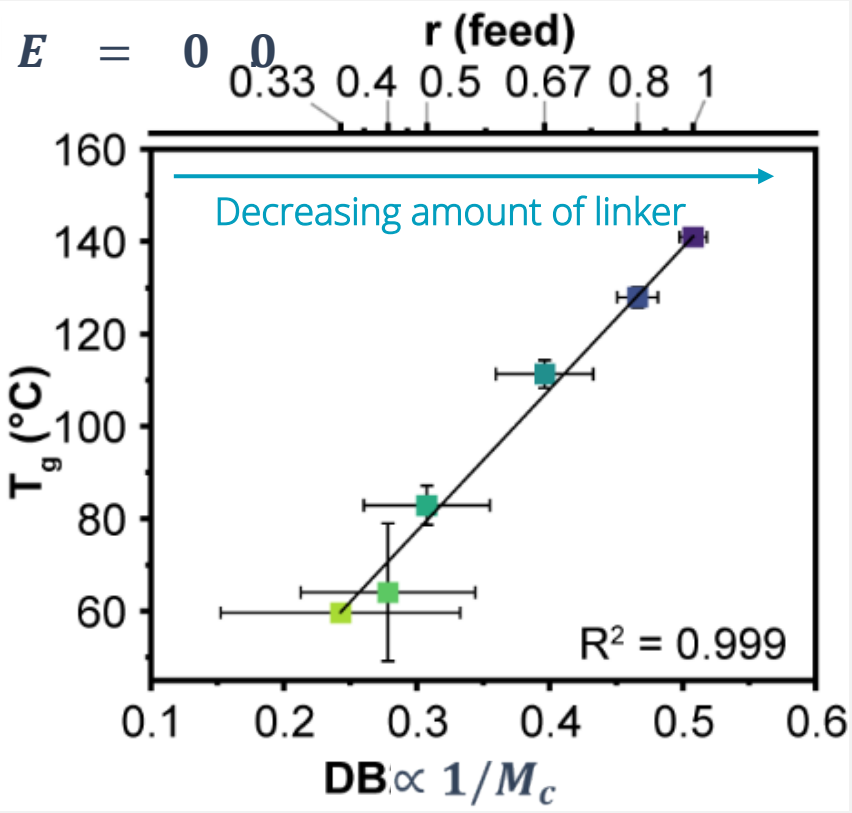
MW = 640 *(g/mol)*



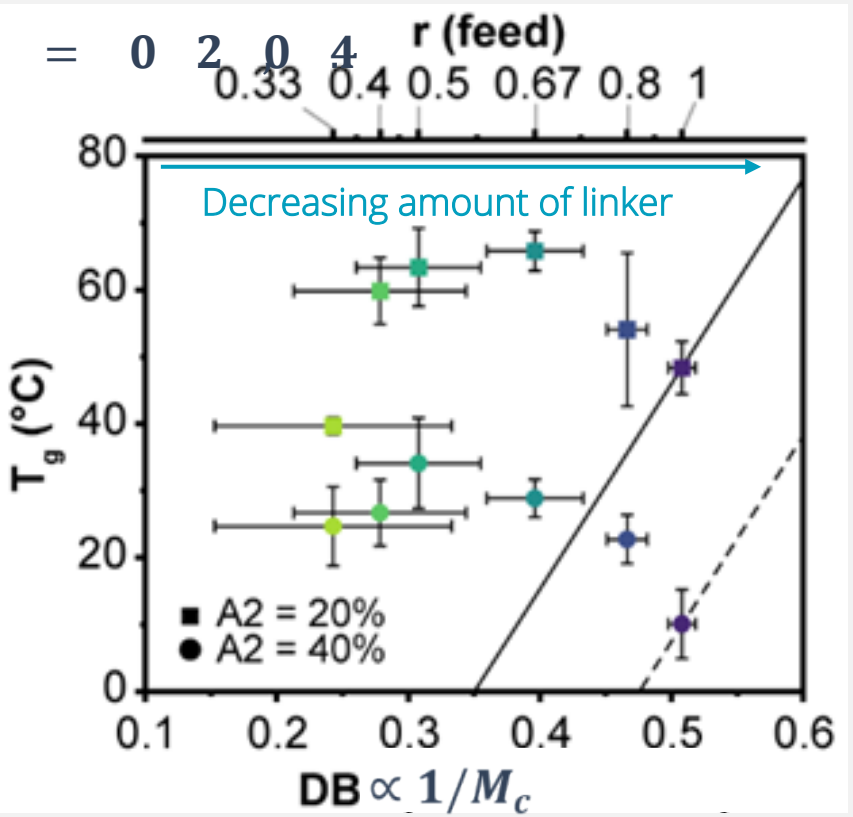

*linker*

MW = 60.1 *(g/mol)*

Purely stiff networks




Blended flexible/stiff networks

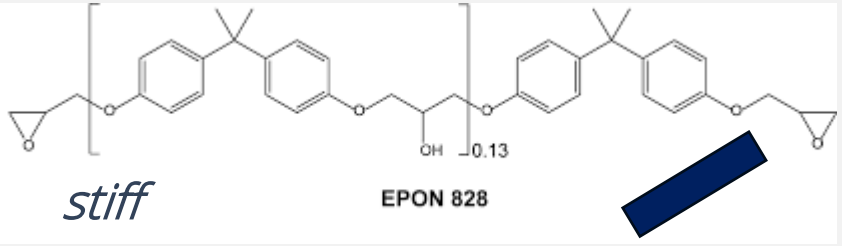



- $E = \frac{flexible}{stiff+flexible}$
- $r = \frac{stiff+flexible}{2 \times linker}$
- $DB = \frac{D}{D+L}$
  - $D = dendritic\ junctions$
  - $L = linear\ junctions$
- Flory-Fox equation for crosslinked networks:
  - $T_g = T_{g,\infty} + \frac{K}{M_c}$

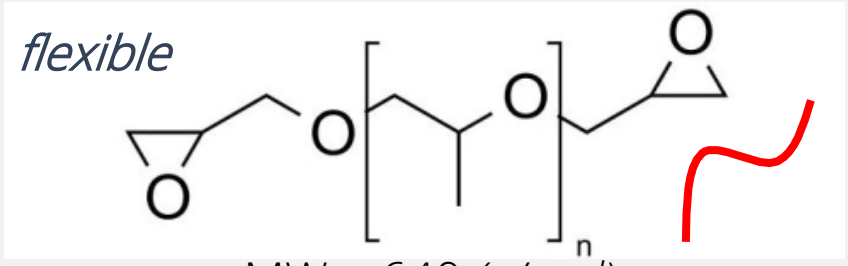
1. *What is the role of blending on $T_g$?*
2. *What is the role of hydrogen bonds on $T_g$?*

Foster et al. (2022, in review)

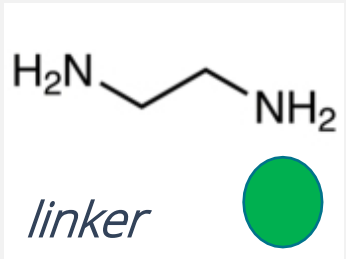
# Methods – Lennard-Jones Polymer Model



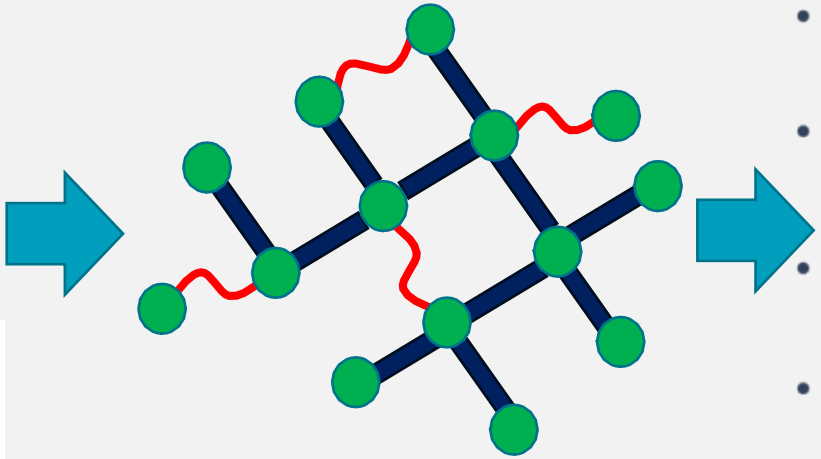

MW = 366 (g/mol)




MW = 640 *(g/mol)*

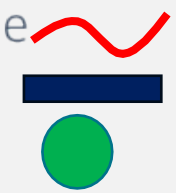


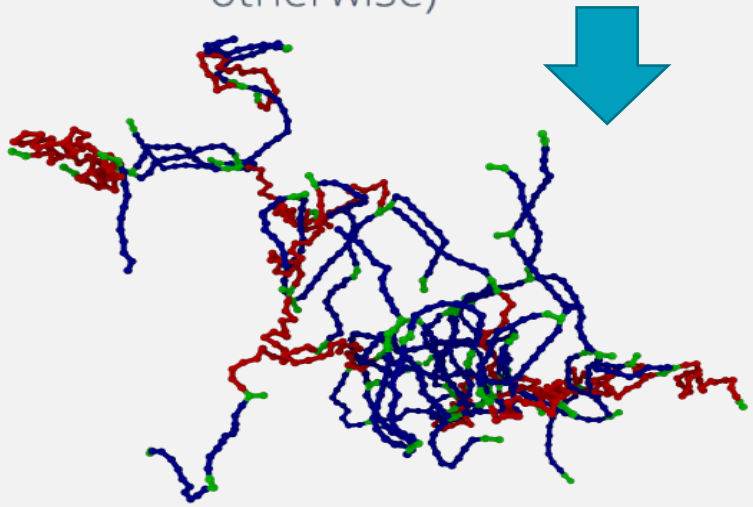

MW = 60.1 *(g/mol)*



- Kremer-Grest polymer model, implemented in LAMMPS:
- Lennard-Jones interactions
  - $\sigma = 1, \epsilon = 1, r_{cut} = 2 \times 2^{\frac{1}{6}}\sigma$
- FENE bonds, cosine angles
  - $U_{angle} = k(1 - \cos\theta)\ ;\ k_{stiff} = 2.5$
- Attractive hydrogen bonding sites attached at amine termini
  - $\sigma_{sticky} = 0.35$, $\epsilon_{sticky} = 3$ (repulsive otherwise)

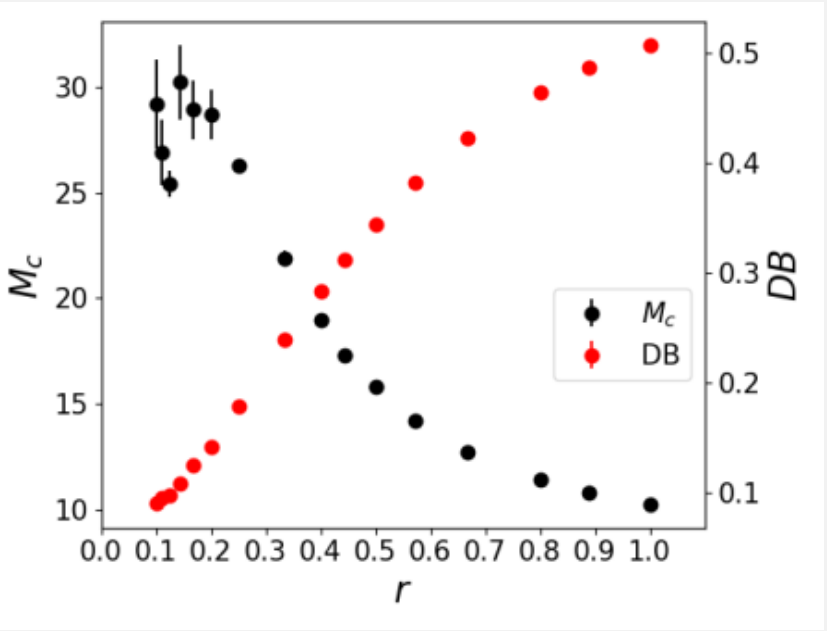
N = 20 beads, flexible
N = 10 beads, stiff
N = 2 beads

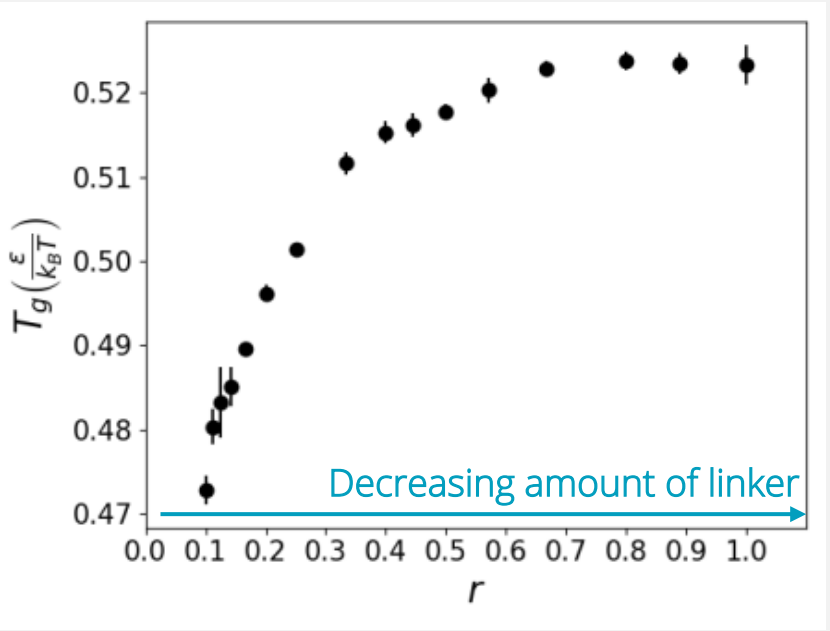


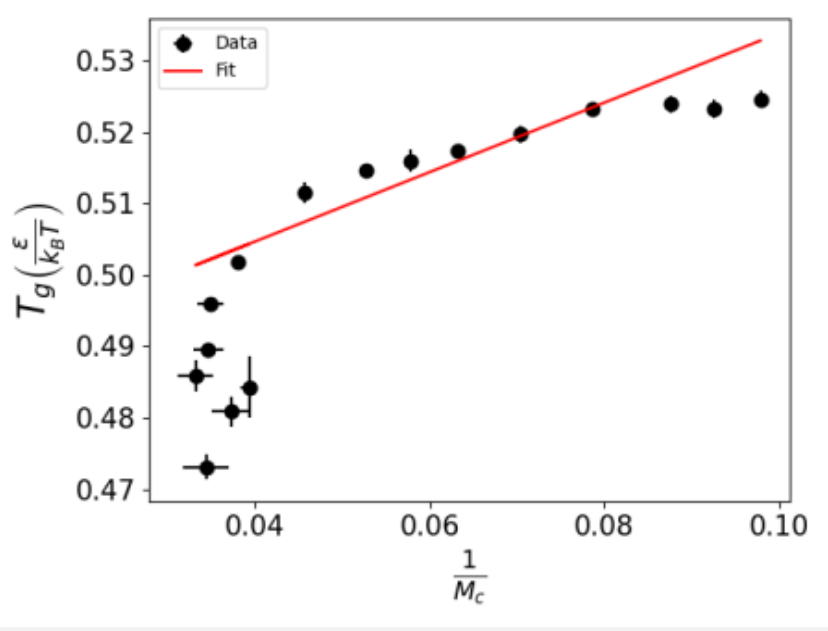


# $T_g$ at $E = 0.0$ – Crosslinked Region Follows the Flory-Fox Equation

No hydrogen bonding sites included ($T_g$ as a function of network properties)



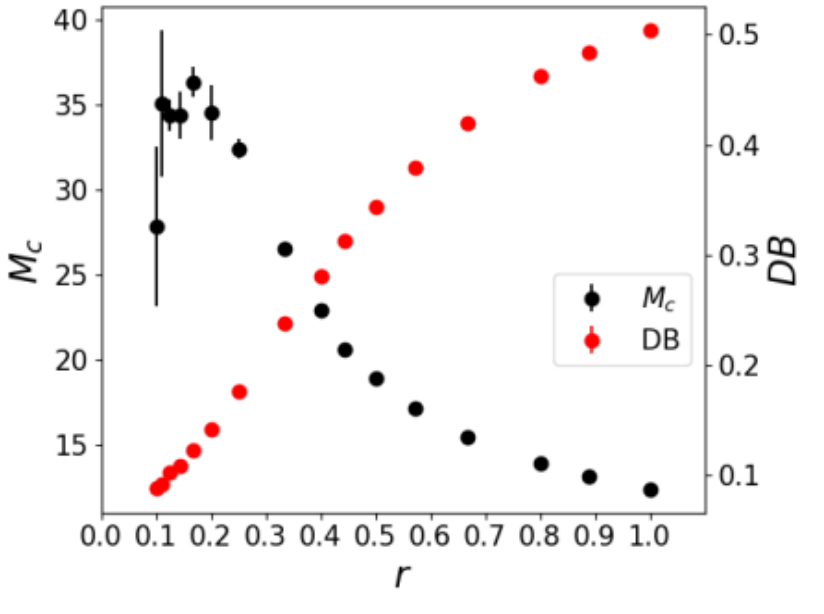



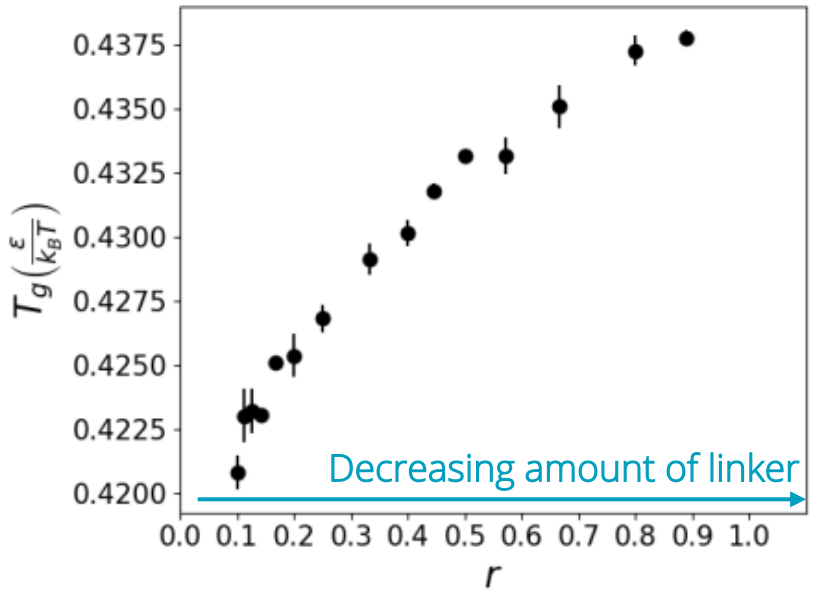

- Degree of branching and molecular weight between crosslinks follow an inverse relationship
- $T_g$ obtained from long, slow cooling runs and finding the inflection point of the volumetric coefficient of thermal expansion versus $T$
- Once networks are sufficiently crosslinked, $T_g$ fits a linear trend with $\frac{1}{M_c}$ reasonably well

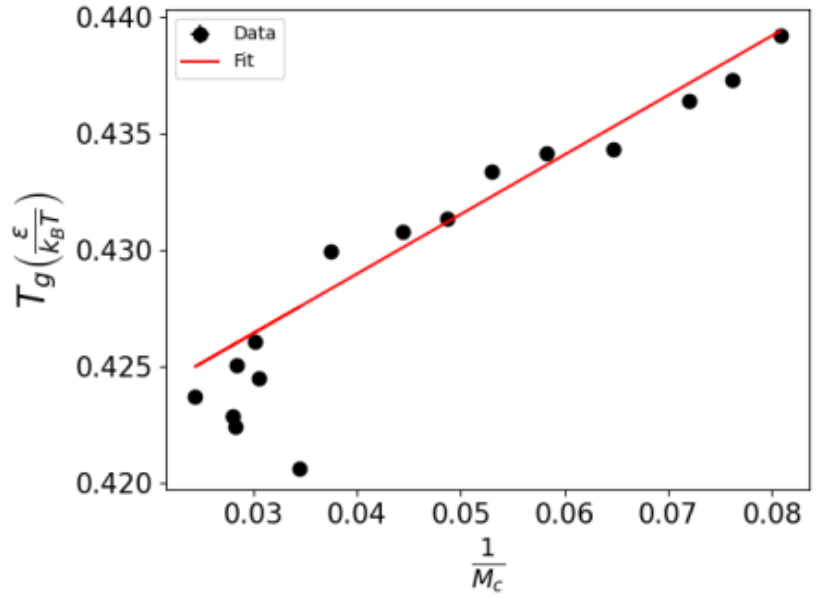
- $E = \frac{flexible}{flexible+stiff}$
- $r = \frac{flexible+stiff}{2 \times linker}$
- $DB = \frac{D}{D+L}$
- $T_g = T_{g,\infty} + \frac{K}{M_c}$

# $T_g$ at $E = 0.2$ – Blending Alone Does Not Lead to $T_g$ Maximum

No hydrogen bonding sites included ($T_g$ as a function of network properties)



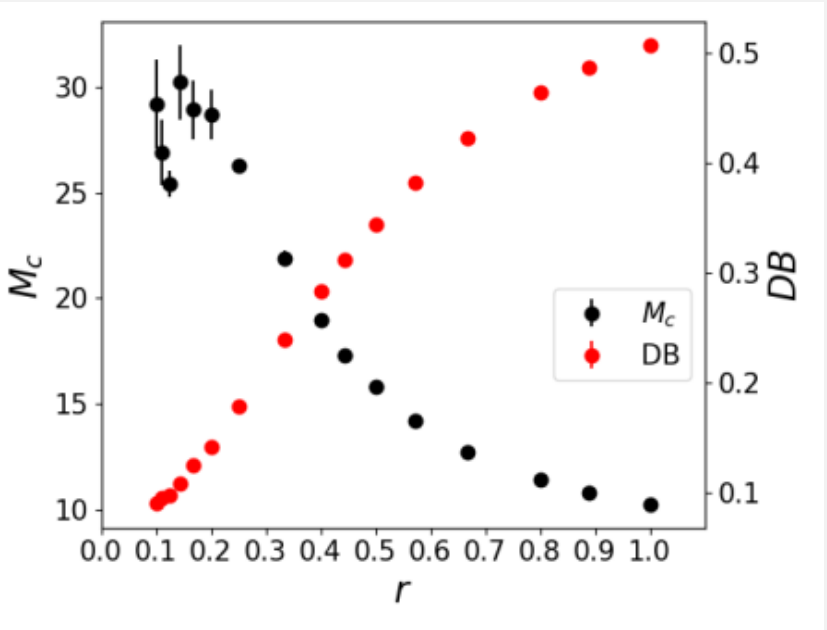



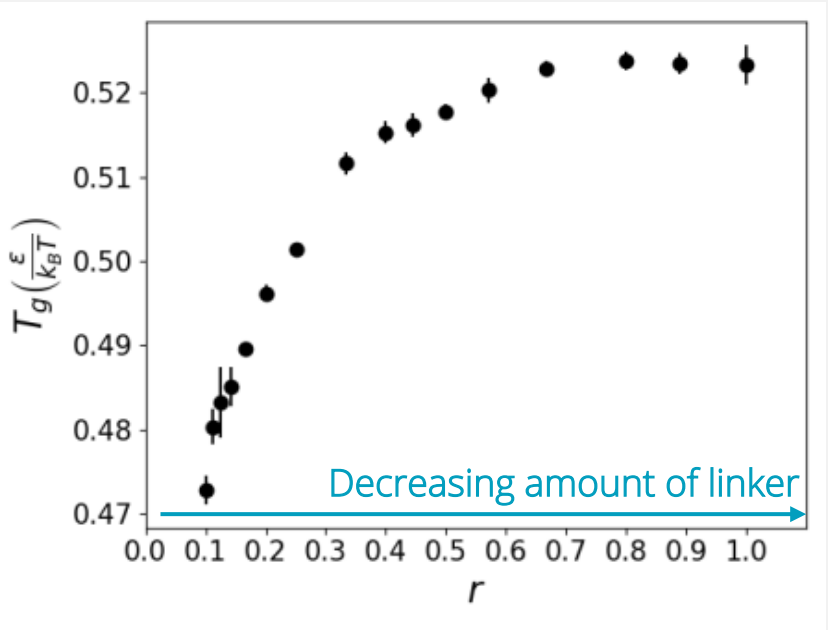

- Again, degree of branching and molecular weight between crosslinks follow an inverse relationship
- $T_g$ shows no maximum as a function of $r$
- The fit to the Flory-Fox equation is even better at this condition
- These blends are simulated assuming no difference in reaction kinetics and no phase separation

- $E = \frac{flexible}{flexible+stiff}$
- $r = \frac{flexible+stiff}{2 \times linker}$
- $DB = \frac{D}{D+L}$
- $T_g = T_{g,\infty} + \frac{K}{M_c}$

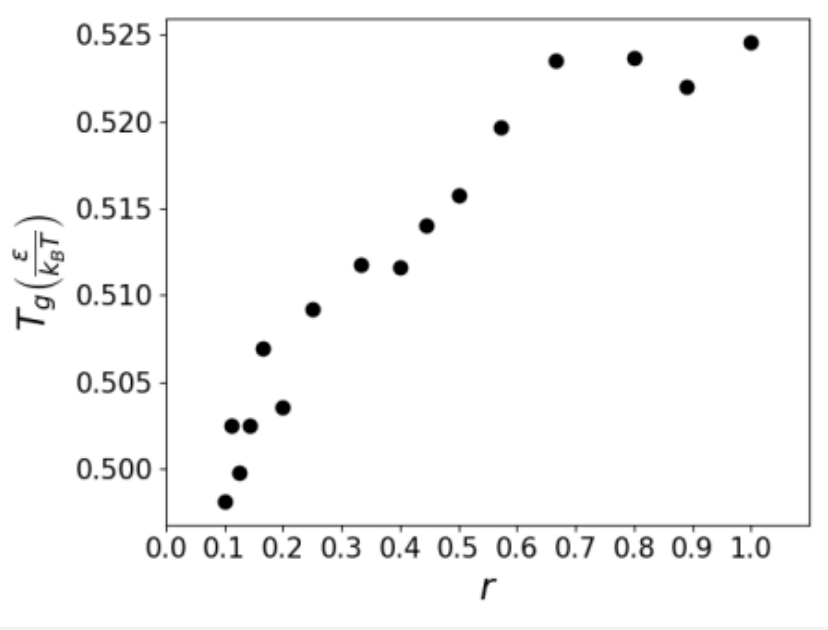
# $E = 0.0$ - Hydrogen Bonding Enhances $T_g$ For Lightly Crosslinked Systems

No hydrogen bonding sites included




Hydrogen bonding sites included ($\epsilon_{sticky} = 3$)

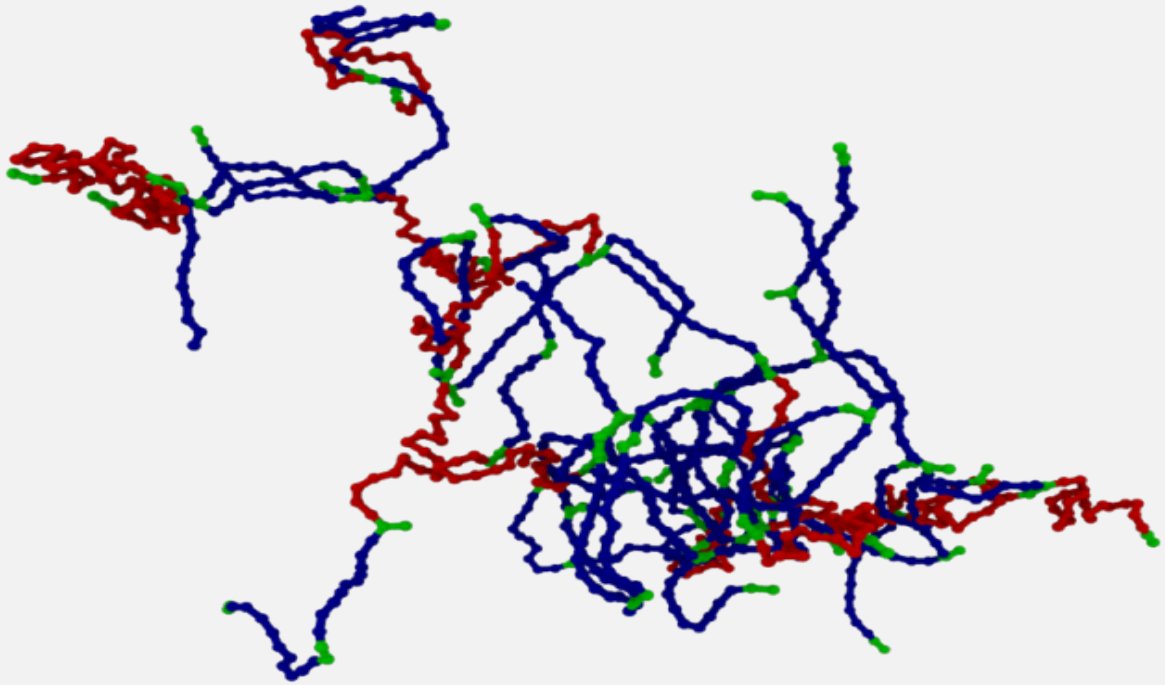



- Lightly crosslinked systems ($r < 0.5$) experience an enhancement of $T_g$ as a result of hydrogen bonding
  - This effect may ultimately lead to a $T_g$ maximum for blends
- Simulations demonstrate anomalous $T_g$ behavior in blends does not emerge purely as a result of blending, but may emerge as a result of hydrogen bonding
- Future research will focus on reaction kinetics, possible phase separation in the blends, and long-term on inverse design of polymer networks

- $E = \frac{flexible}{flexible+stiff}$
- $r = \frac{flexible+stiff}{2 \times linker}$
- $DB = \frac{D}{D+L}$
- $T_g = T_{g,\infty} + \frac{K}{M_c}$

# Summary & Acknowledgements


- Dr. Amalie Frischknecht, Dr. Jeff Foster, Dr. Erica Redline
  - Laboratory Directed Research & Development Project ID 222352

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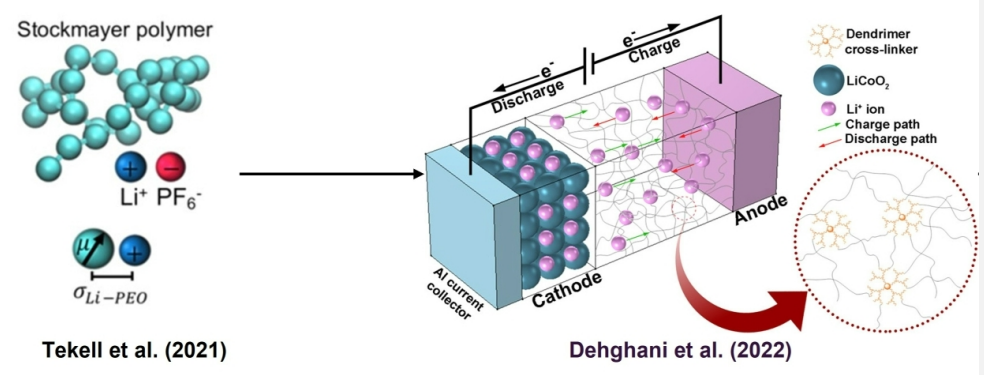
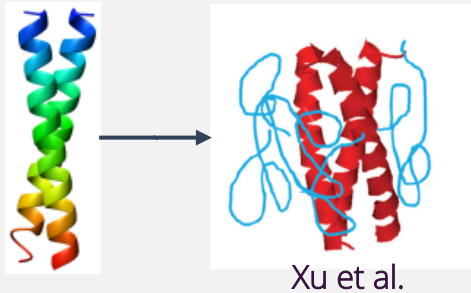
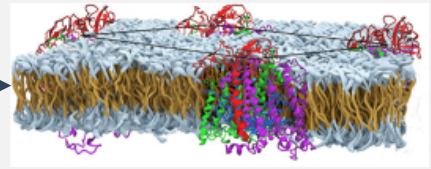
RESEARCH & DEVELOPMENT

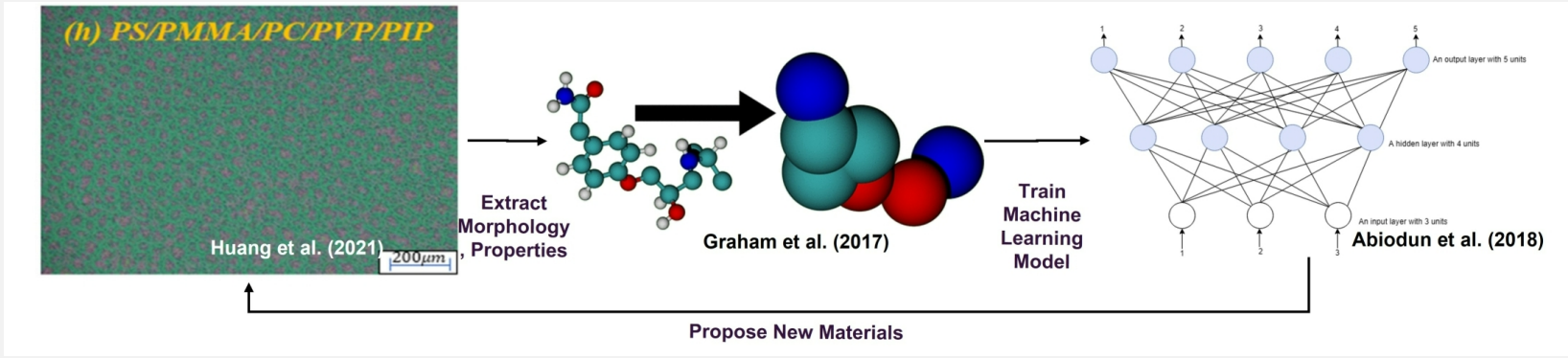
# Future Research Aims

- Experience gained in this project serves as a foundation for my future research aims in coarse-grained modeling of crosslinked gel polymer electrolytes (and conductive polymer hydrogels)
  - Past research experience serves as a foundation for other research aims in biomimetic block copolymer templating and high-entropy polymer blends



# BACKUP SLIDES

# $T_g$ Fitting Procedure