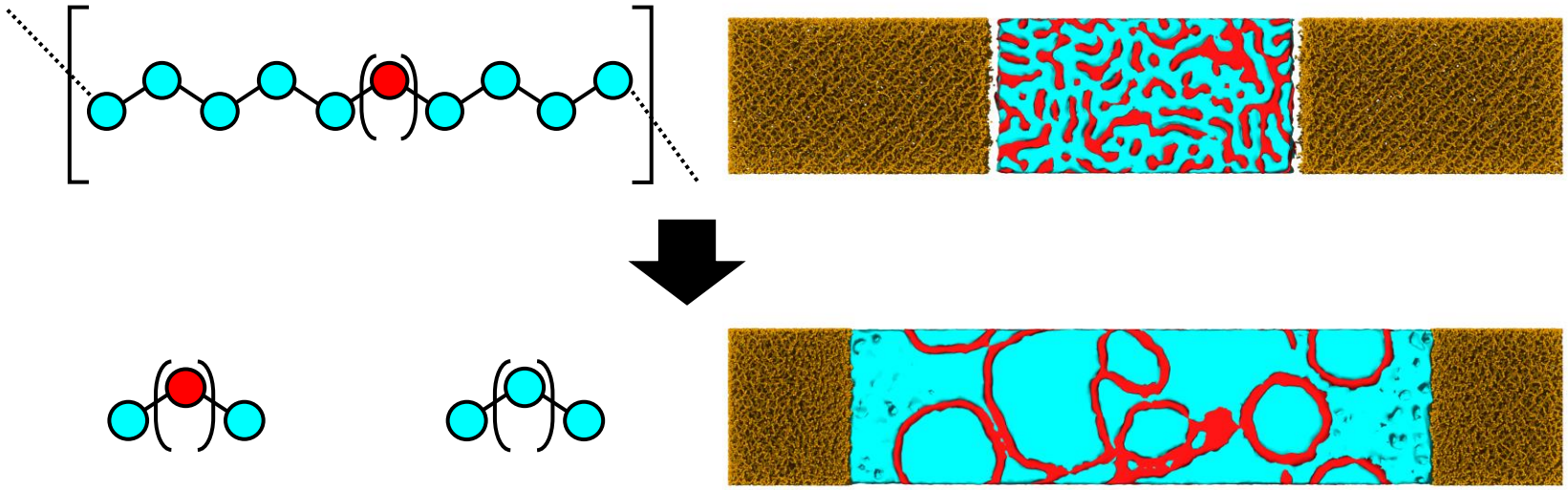
Degradation of Block Copolymer Films Confined in Elastic Media

Ryan Sayko[1], Zilu Wang[1], Matthew L. Becker[2], and Andrey V. Dobrynin[1]



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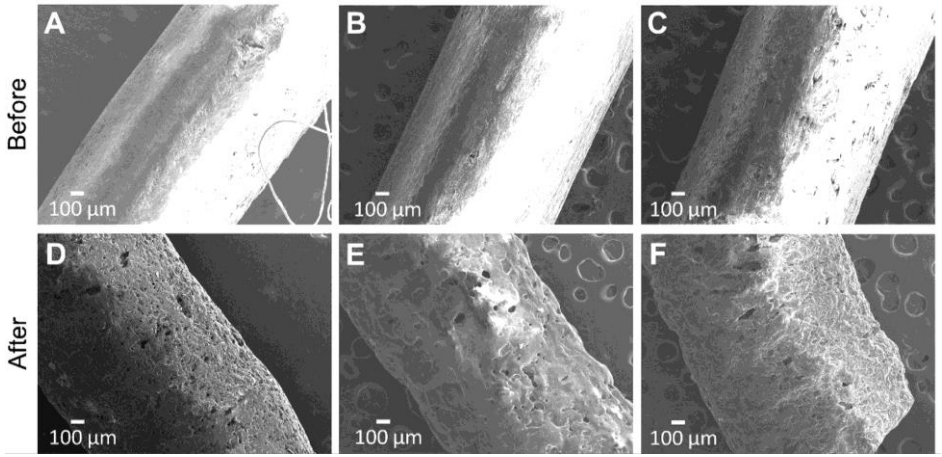
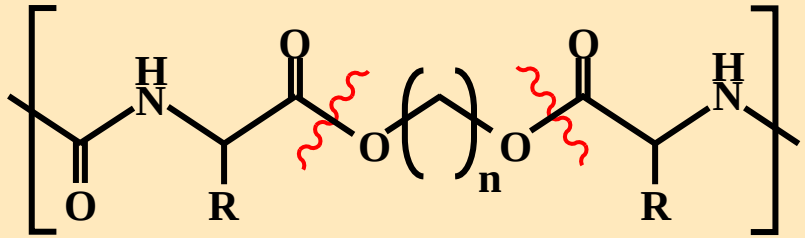
APS March Meeting – Thursday, March 18th, 2021

Motivation: Background



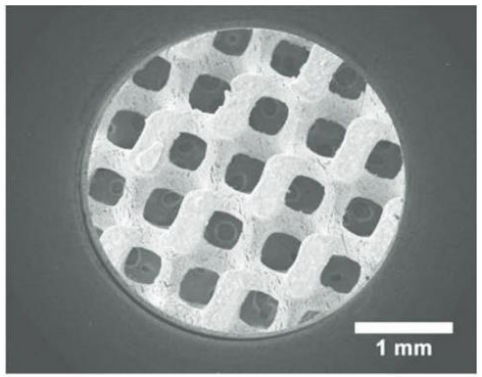
Abel, A. et al, *Biomacromolecules.* **2020**, 2, 946-954.

Poly(ester urea)

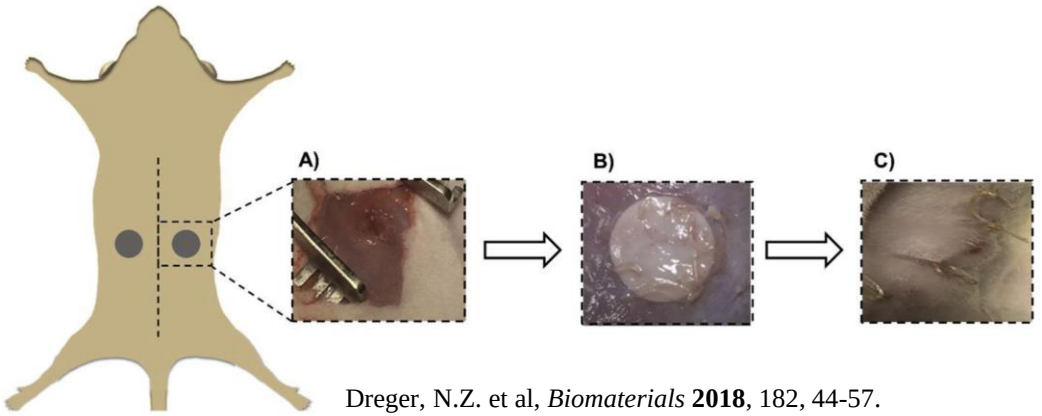


R: Amino Acid Group

- **Tunable mechanical properties**
- **Tunable drug release**
- **Adhesion**
- **Nontoxic degradation products**
- **Shape memory performance**



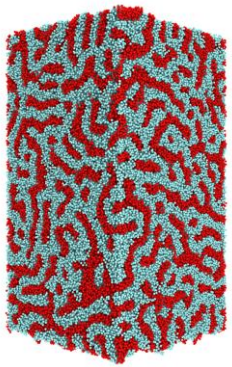
Nettleton, K. et al, *Adv. Healthcare Mater.* **2019**, 8, 1900646.



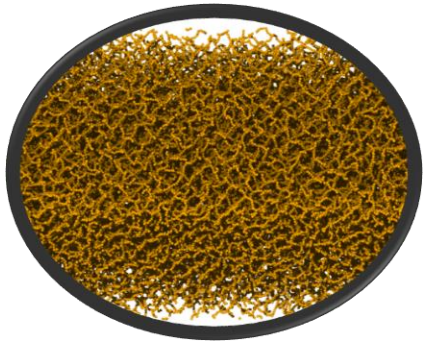
Dreger, N.Z. et al, *Biomaterials* **2018**, 182, 44-57.

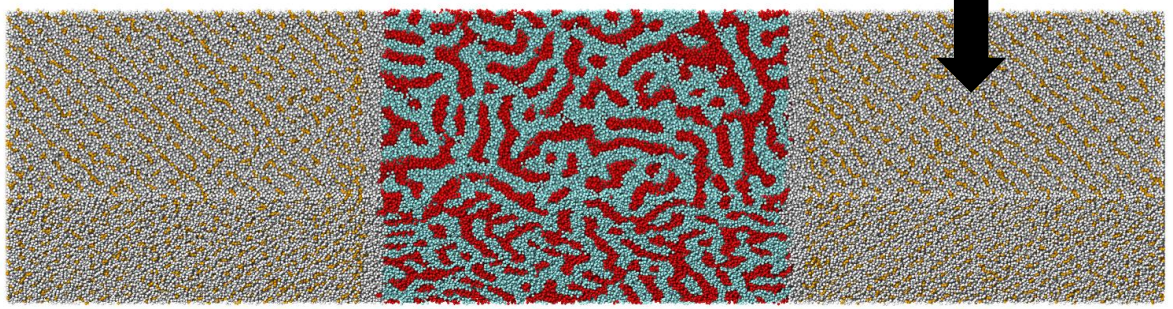
System Overview: Mapping Experiment to Simulation

Polymer Insertion



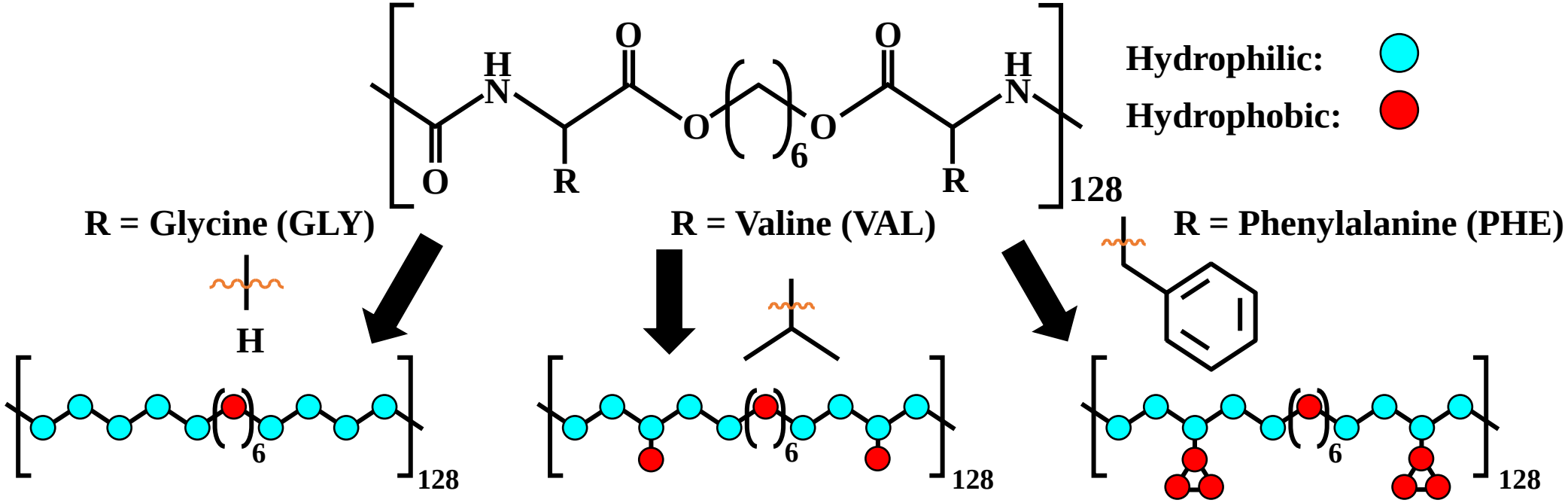
Copolymer Film





Dreger, N.Z. et al, *ACS Biomater. Sci. Eng.* **2018**, 4, 4, 1346-1356.

Coarse-Grained Model of Poly(ester urea), Simulation Details



Truncated Shifted Lennard-Jones potential:

$$U_{\mathrm{LJ}}(r) = \begin{cases} 4\varepsilon_{\mathrm{LJ}}\left[(\sigma/r)^{12} - (\sigma/r)^{6} - (\sigma/r_{\mathrm{cut}})^{12} + (\sigma/r_{\mathrm{cut}})^{6}\right] & r \le r_{\mathrm{cut}} \\ 0 & r > r_{\mathrm{cut}} \end{cases}$$

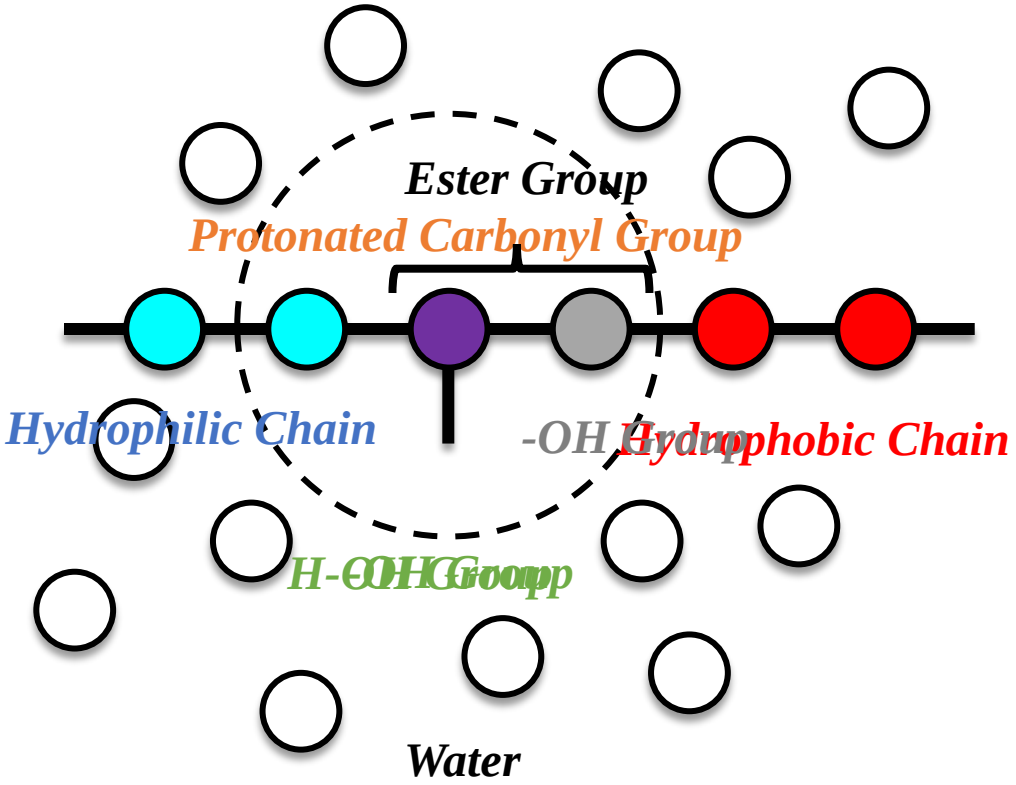
FENE Bond potential:

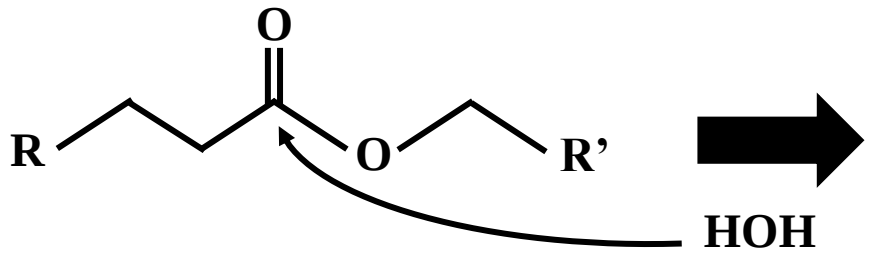
$$U_{FENE} = -0.5kR_{\max}^{2}\ln\left[1-(r/R_{\max})^{2}\right] + 4\varepsilon\left[(\sigma/r)^{12} - (\sigma/r)^{6}\right] + \varepsilon$$

Pair Interaction Type	Interaction
Hydrophilic-Water	Strongly Attractive
Same bead types Network-Water Hydrophilic-Network	Weakly Attractive
Hydrophobic-Water Hydrophobic-Hydrophilic Hydrophobic-Network	Repulsive

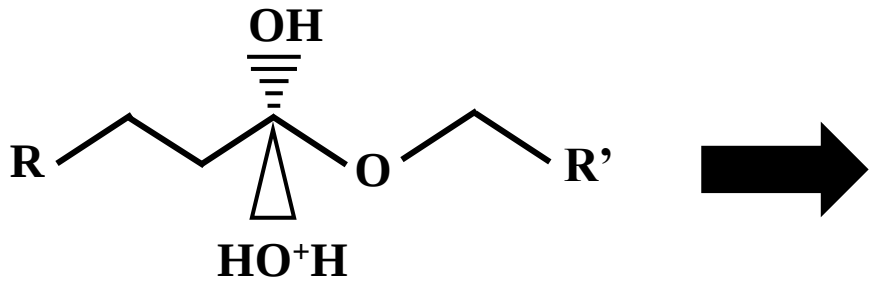
Sayko, R. et al, *Macromolecules* **2020**, 53, 1270.

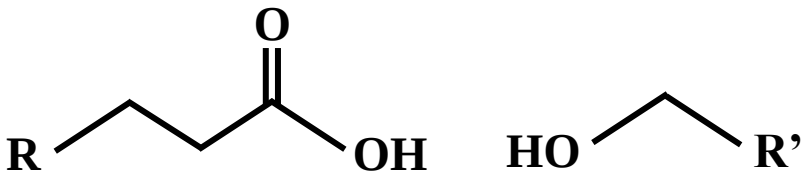
Degradation Algorithm



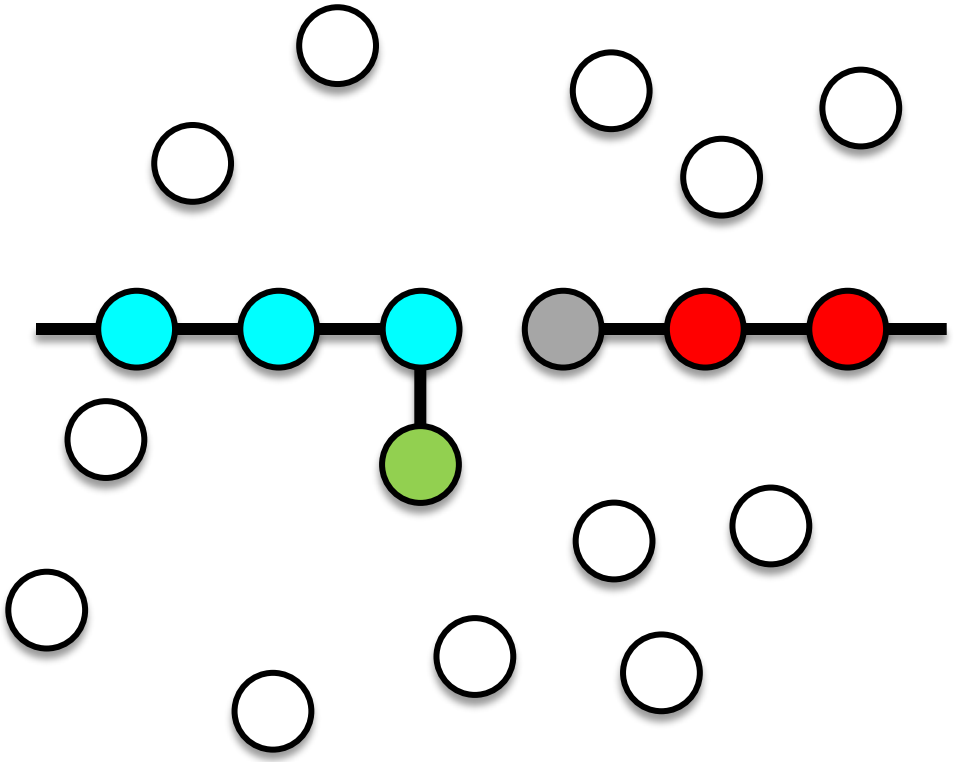


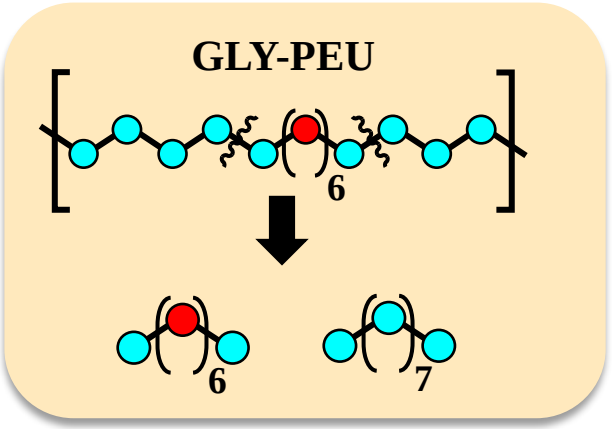
Transition State

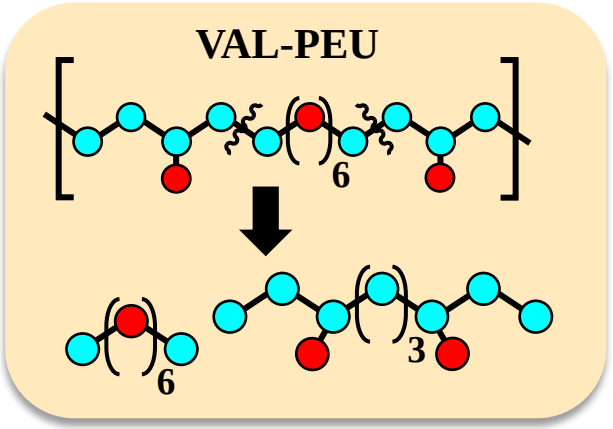


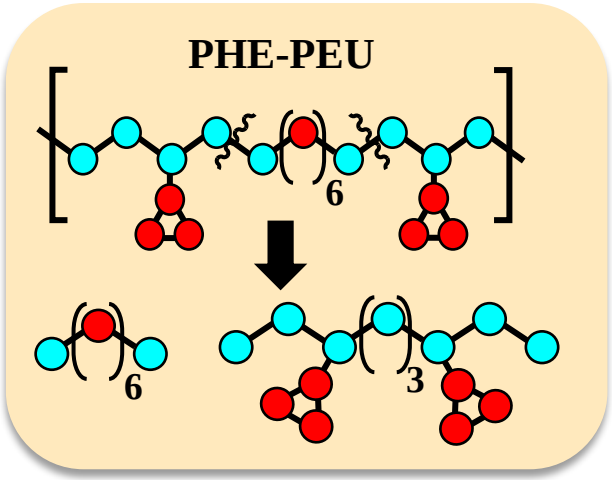


Degradation Algorithm









Degradation Rate:

$$\lambda = P_{form} P_{break} \alpha$$

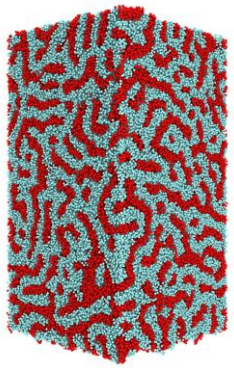
$$P_{form} = 0.01$$

$$P_{break} = 1.0$$

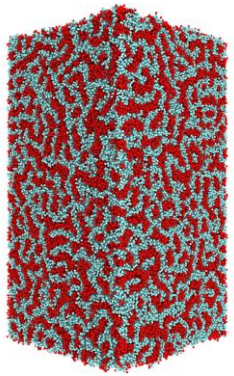
$$\alpha = 0.2\tau_{LJ}^{-1}$$

The bond-forming process is the rate-limiting step of degradation

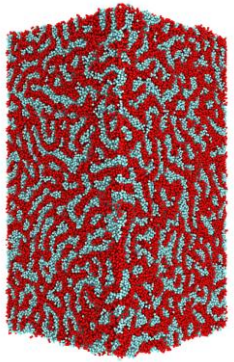
System Overview



GLY-PEU Film

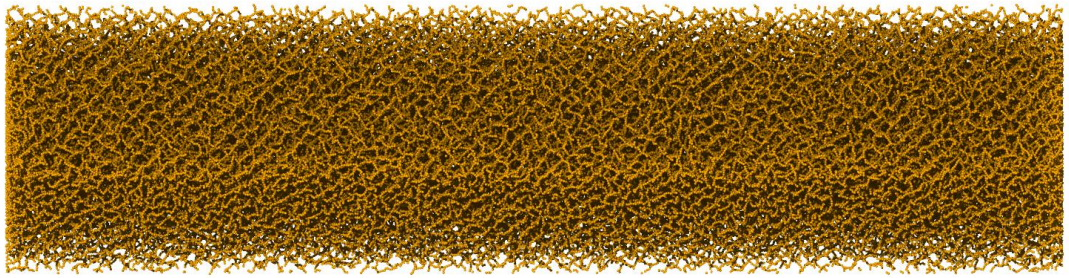


VAL-PEU Film

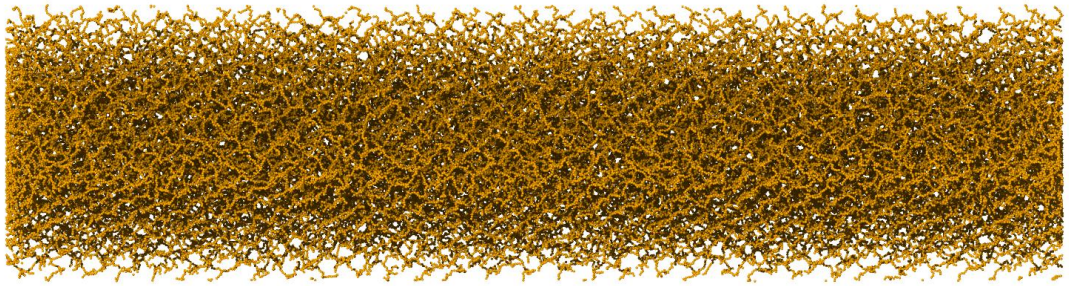


PHE-PEU Film

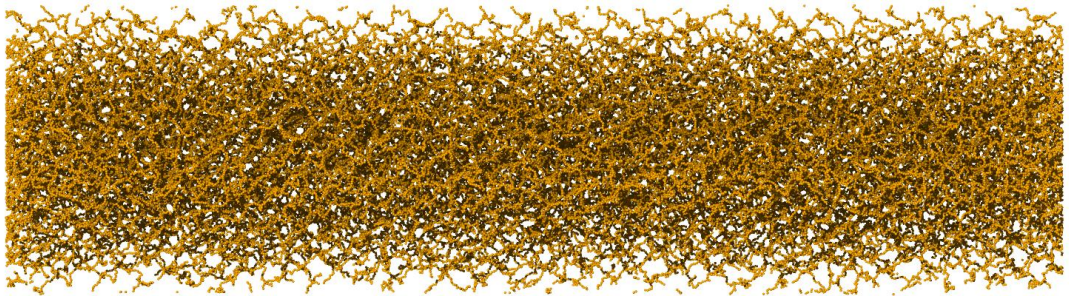
***N* = 6**



***N* = 10**



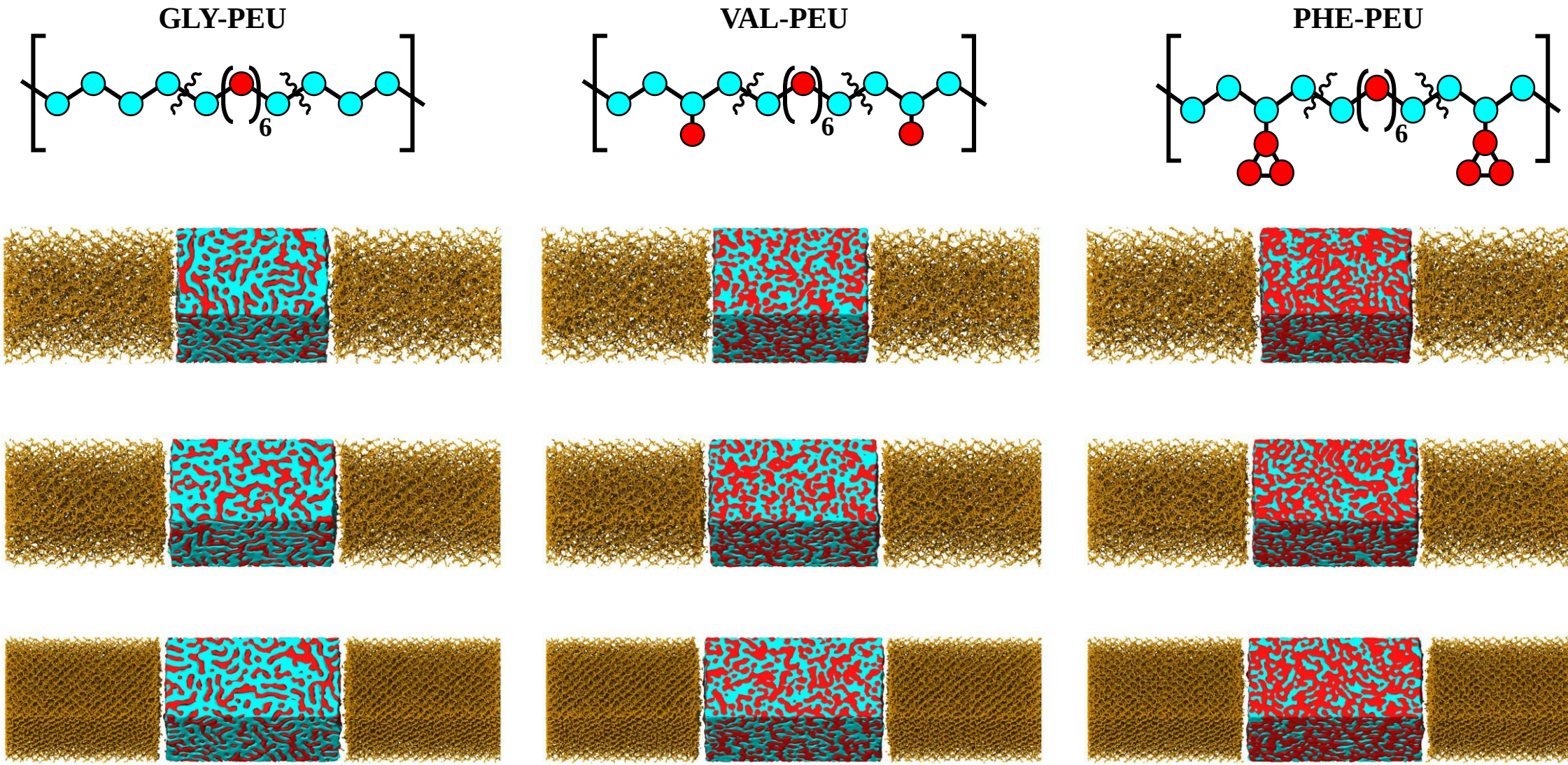
***N* = 14**



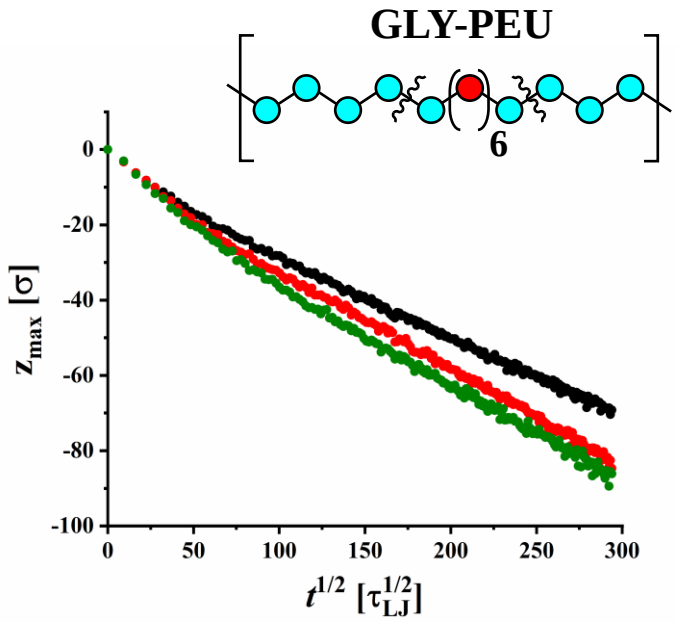
***N*: Degree of Polymerization of network strands**

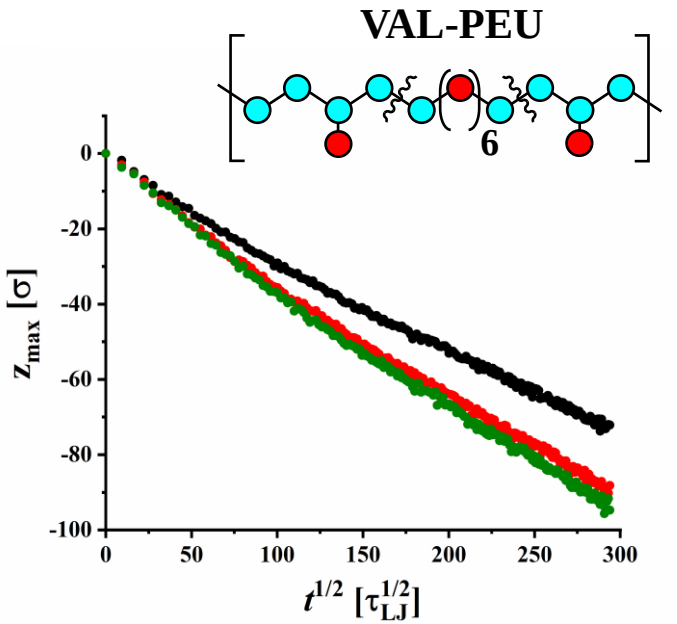
Angle potential: $U_{angle} = 1.5 k_B T \left[1 - \cos\left(\theta - \theta_0 \right) \right]$

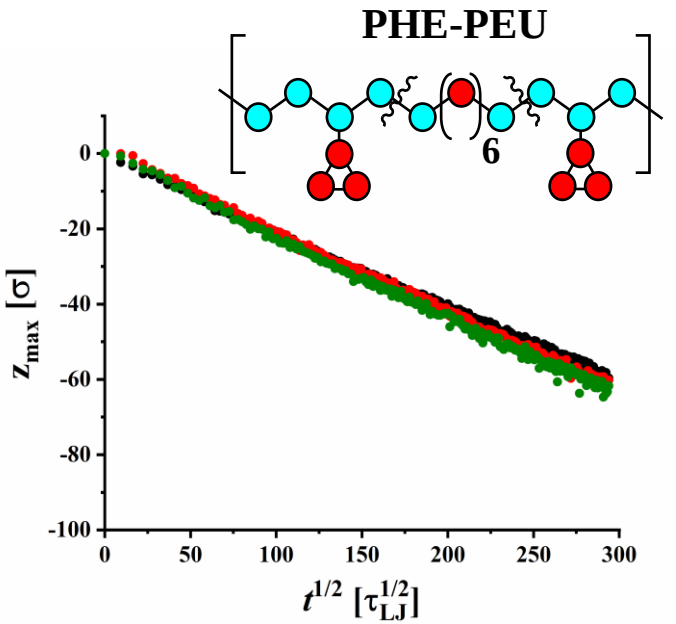
Polymer Swelling and Degradation



Copolymer–Network Interface Dynamics



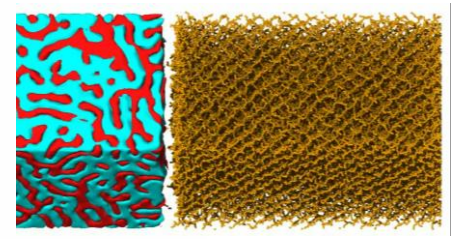


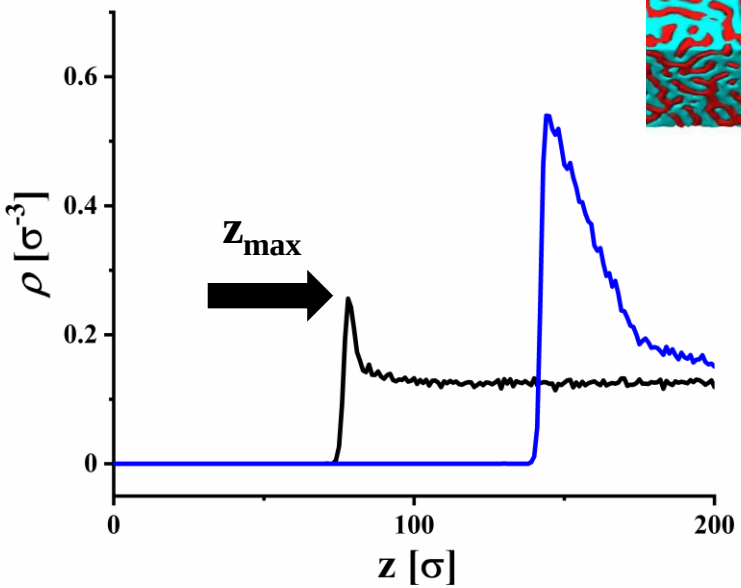


$N = 6$:
$N = 10$:
$N = 14$:

$z_{max} < 0$ ➡ **Network Compression**

The degradation of the copolymer films is a result of interplay between solvent diffusion into the film accompanied by film swelling and degradation along with the diffusion of degradation products into the network.





$t = 10^5 \tau_{LJ}$
$t = 0$

Film Degradation Kinetics: Conversion and Dispersity

$$p = \frac{N_{bb}}{N_{b0}}$$

N_{bb}: Number of broken bonds

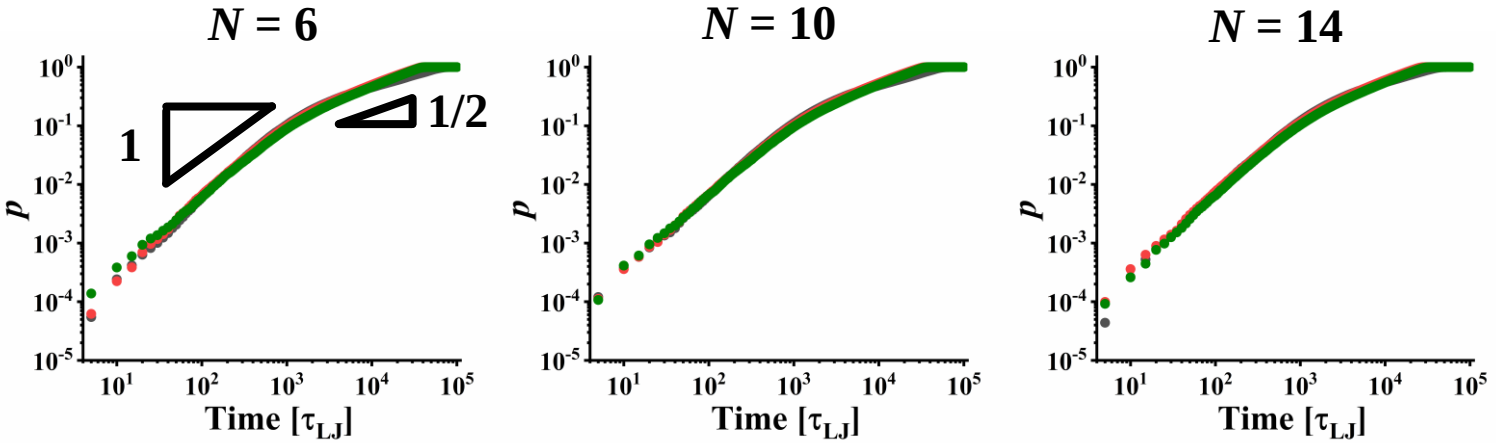
N_{b0}: Number of original bonds

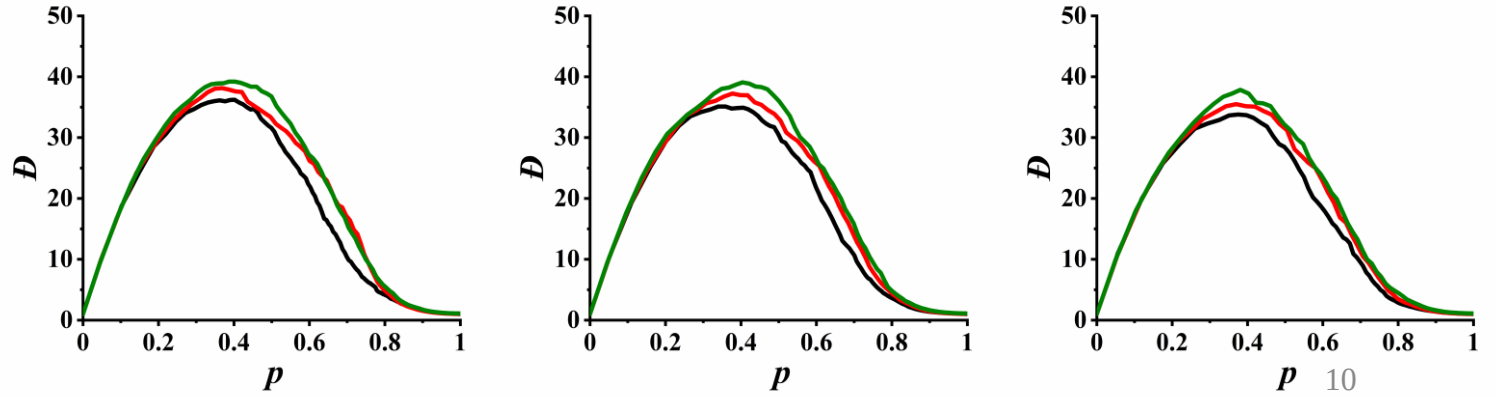
3 characteristic time regimes:

1) Initial degradation and swelling: $p \sim t$
2) Weaker dependence: $p \sim t^{1/2}$
3) Saturation: $p = 1$ (complete)

The small variation in the values of dispersity is due to the differences in degradation products.

Film	N = 6	N = 10	N = 14
GLY-PEU	85,230 τ_{LJ}	77,750 τ_{LJ}	59,240 τ_{LJ}
VAL-PEU	46,010 τ_{LJ}	42,225 τ_{LJ}	33,370 τ_{LJ}
PHE-PEU	46,630 τ_{LJ}	42,730 τ_{LJ}	38,155 τ_{LJ}





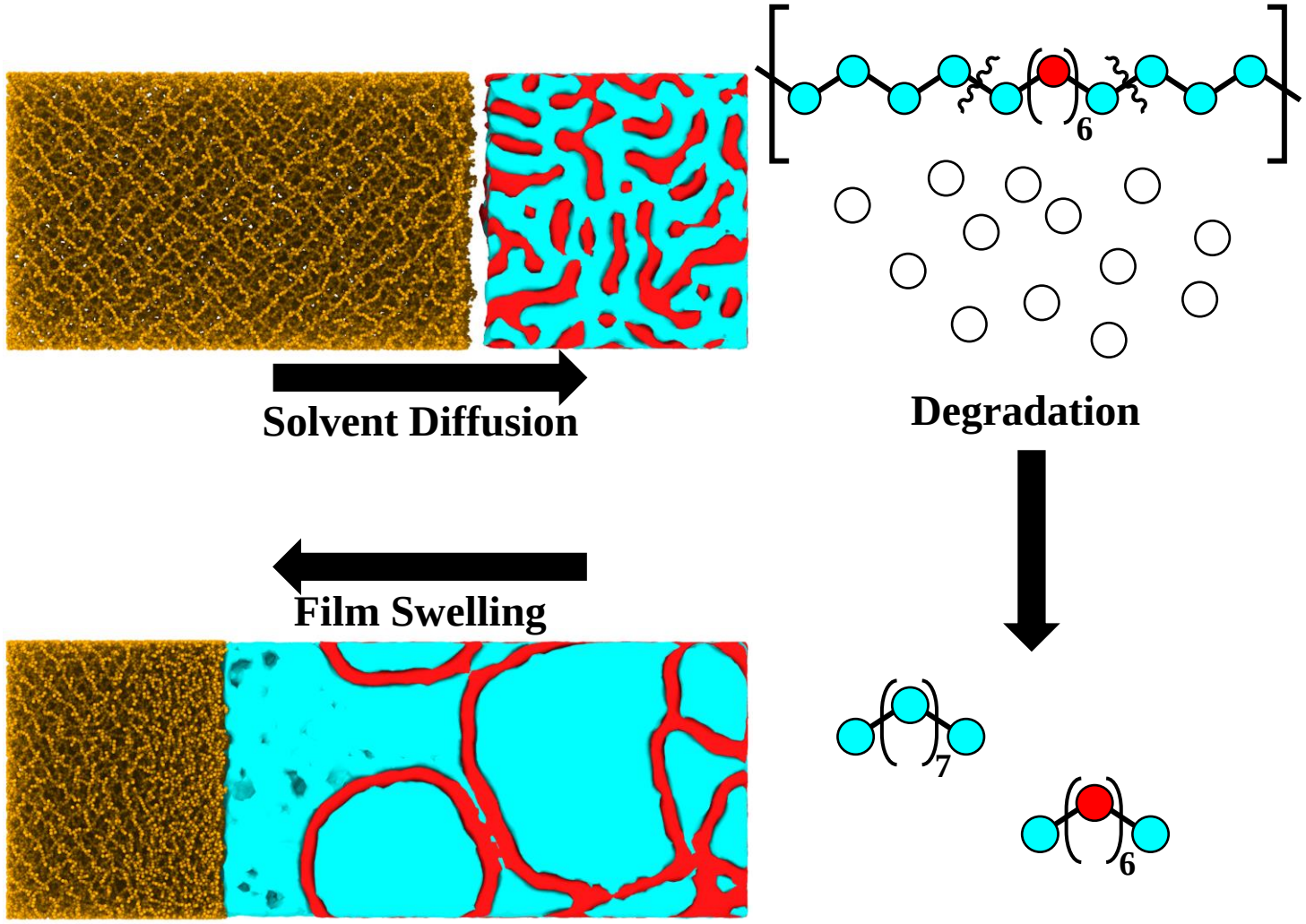
Summary

The network confinement slows the copolymer film degradation with decreasing degree of polymerization of network strands.

The network response to the copolymer film degradation is a result of interplay between the polymer degradation and solvent/polymer fragment exchange dynamics in the network.

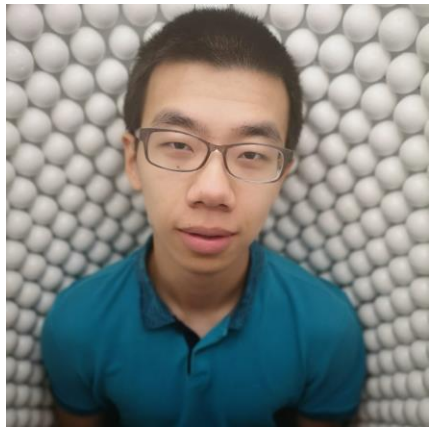
The dispersity of the PEU films vs the bond-breaking conversion shows a universality that may be related to experimental measurements of degradation of polymers.

Sayko, R. et al, *Macromolecules* **2020**, 53, 4, 1270-1280.
Sayko, R. et al, *Macromolecules* **2020**, 53, 21, 9460-9469.



Acknowledgements

Dr. Zilu Wang



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Thank you!

Questions?