

Utilizing concepts of mechanics, transport, and assembly in Nature – towards responsive materials

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Distinguished Professor

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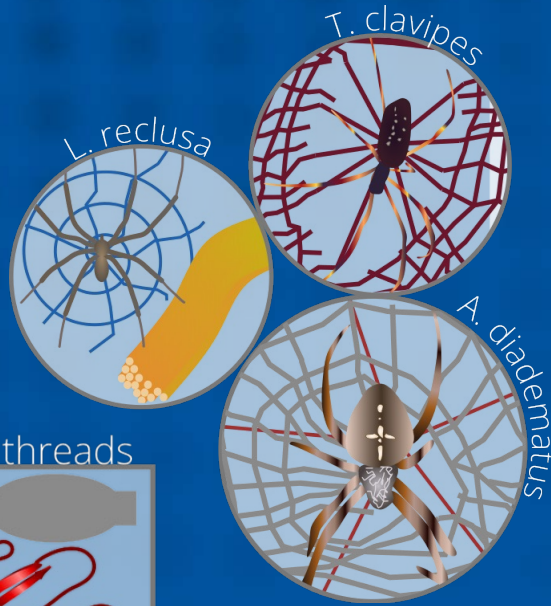
*Assoc. Director, Center for Research in Soft
Matter and Polymers (CRiSP)*

University of Delaware

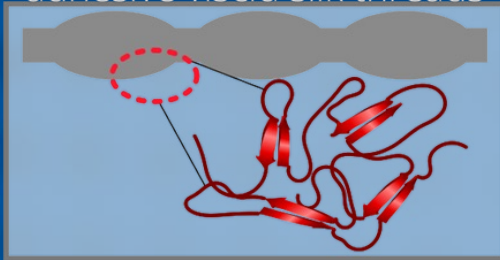
December 7, 2023

2023 NSF Nanoscale Science and Engineering Grantees Conference

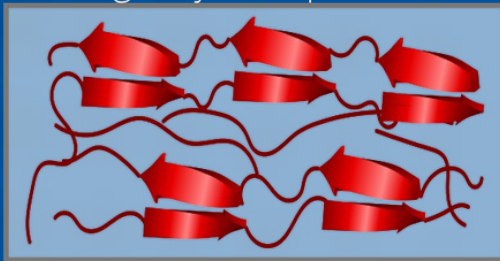
SPIDERS MANUFACTURE COMPLEX MATERIALS



adhesive viscid silk threads



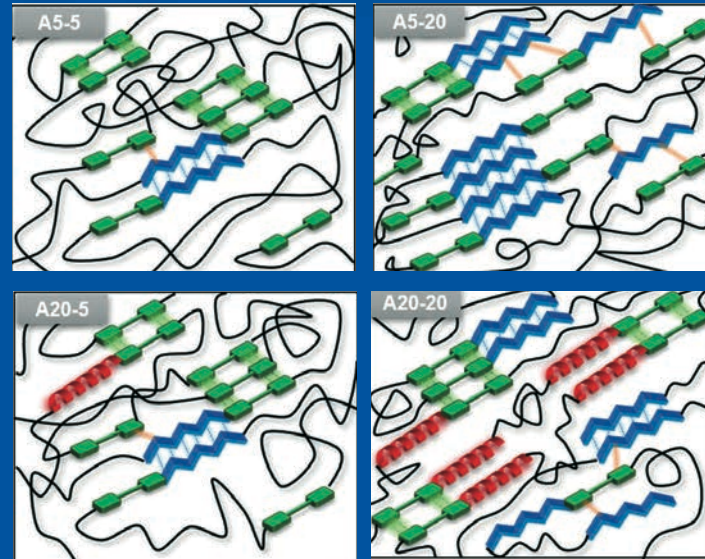
strong major ampullate silk



Key Features:

- *species variants for climate stability*
- *function variation in shape and strength*
- *multiscale ordering that develops structural diversity*

MATERIAL DESIGN ENABLES BUILT-IN FUNCTIONALITY



Korley et al. *Molec. Sys. Desig. Eng.* (2021)

Functional Peptides

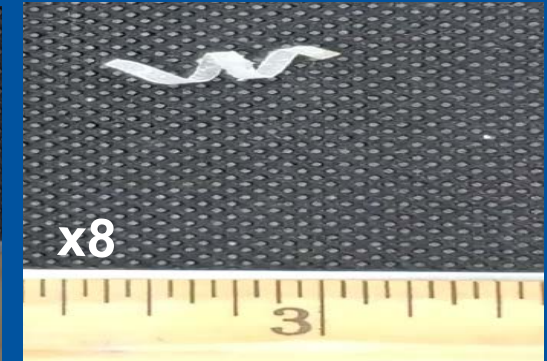
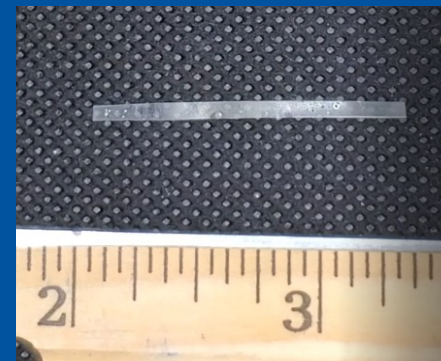
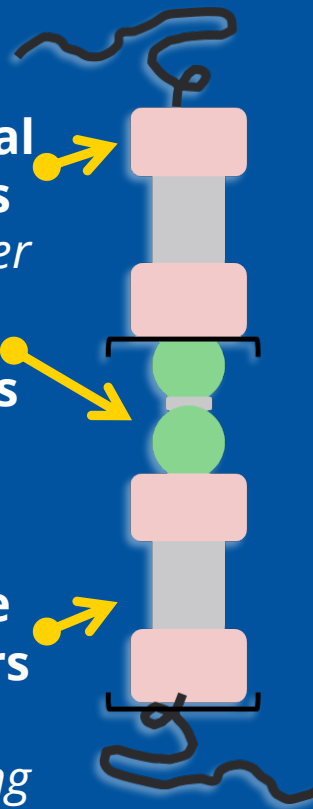
direct order

Stiff Polymers

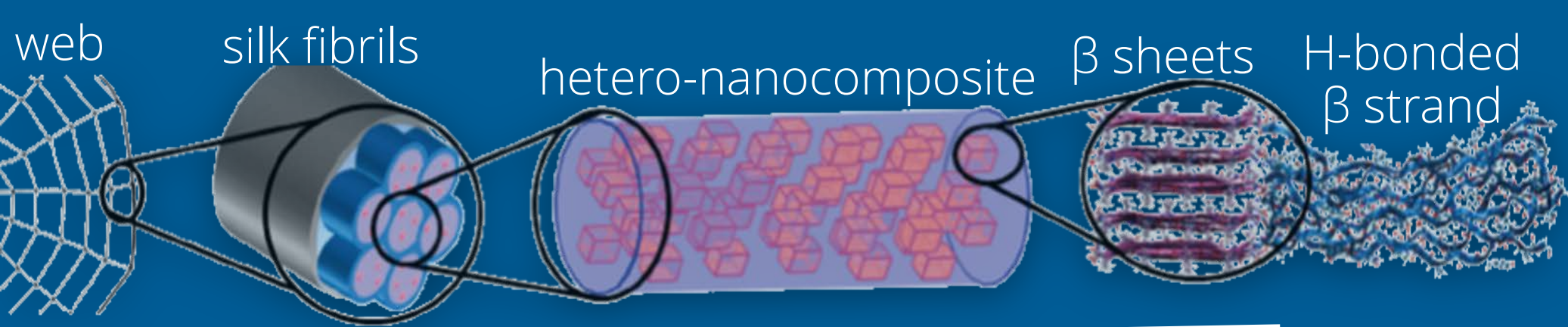
promote strength

Flexible Polymers

enable processing

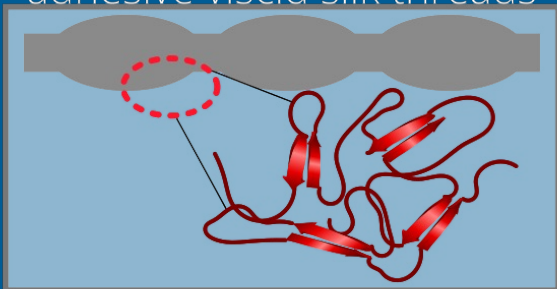


SMART MATERIALS FROM NATURE

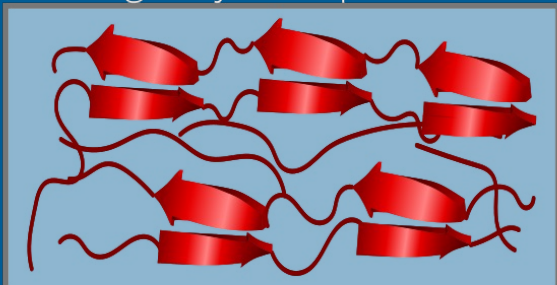


← architectural length scale

adhesive viscid silk threads

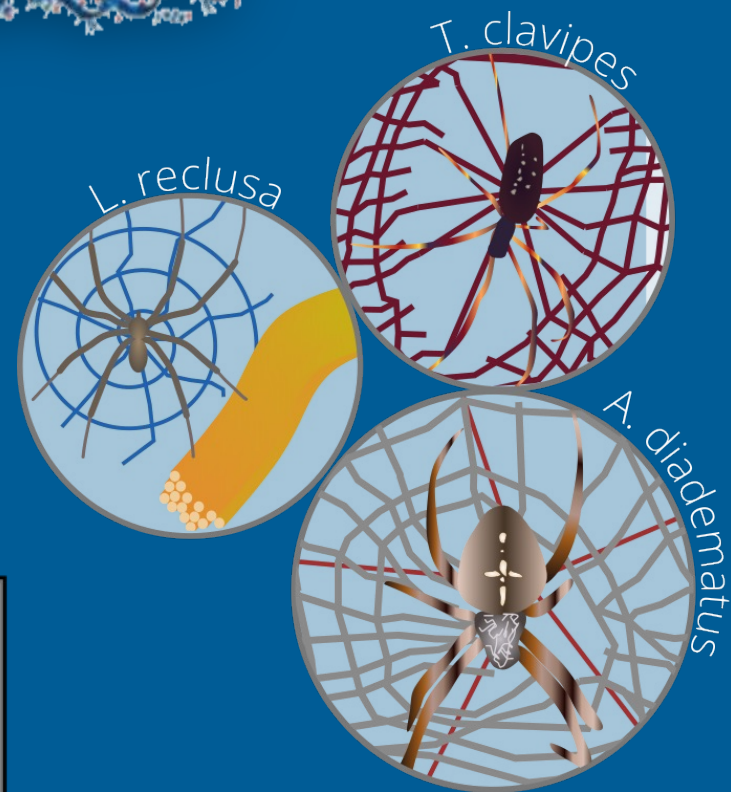
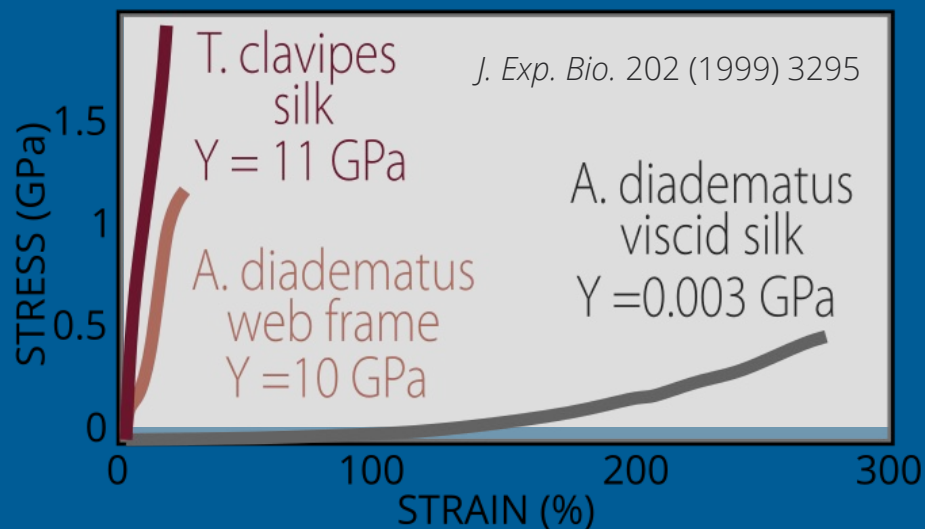


strong major ampullate silk



function

processability and performance



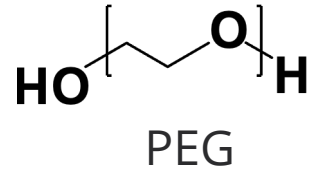
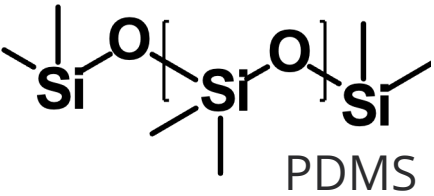
species

A Bio-inspired Platform for Self-Assembled Materials

FLEXIBLE POLYMER SEGMENT

promotes chain mobility, entanglement

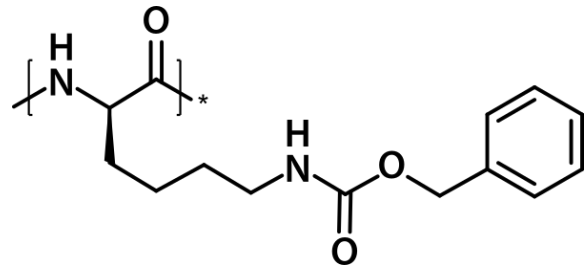
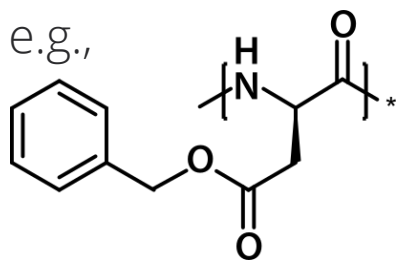
e.g.,



PEPTIDE SEGMENT

promotes self-assembled structure

e.g.,



CHAIN EXTENSION

HARD SEGMENTS

Phase Controlled Peptide-Urea

CHAIN EXTENSION

Thermoresponsive Peptide-Urea
Shape Memory Polymers

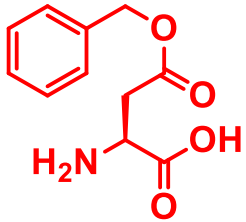
HYDRATION

Injectable, Thermally Robust Hydrogels

CROSSLINKERS

Highly Ordered Peptide-Urea Networks

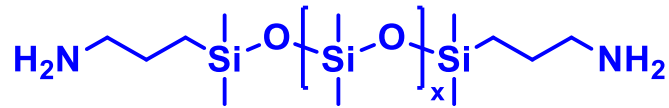
Natural-Synthetic Polymer Hybrids toward Hierarchical Materials



Poly(β -benzyl-L-aspartate)
(PBLA)

Peptide

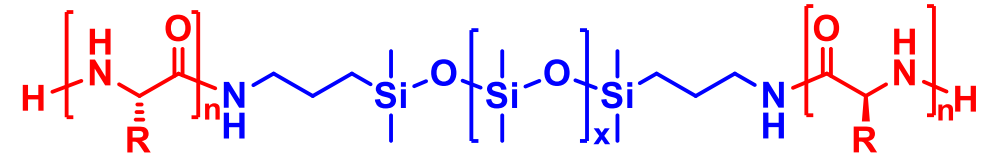
- common natural approach
- responsible for unique self-assembled structure
- chemically labile (e.g., pH-responsive)



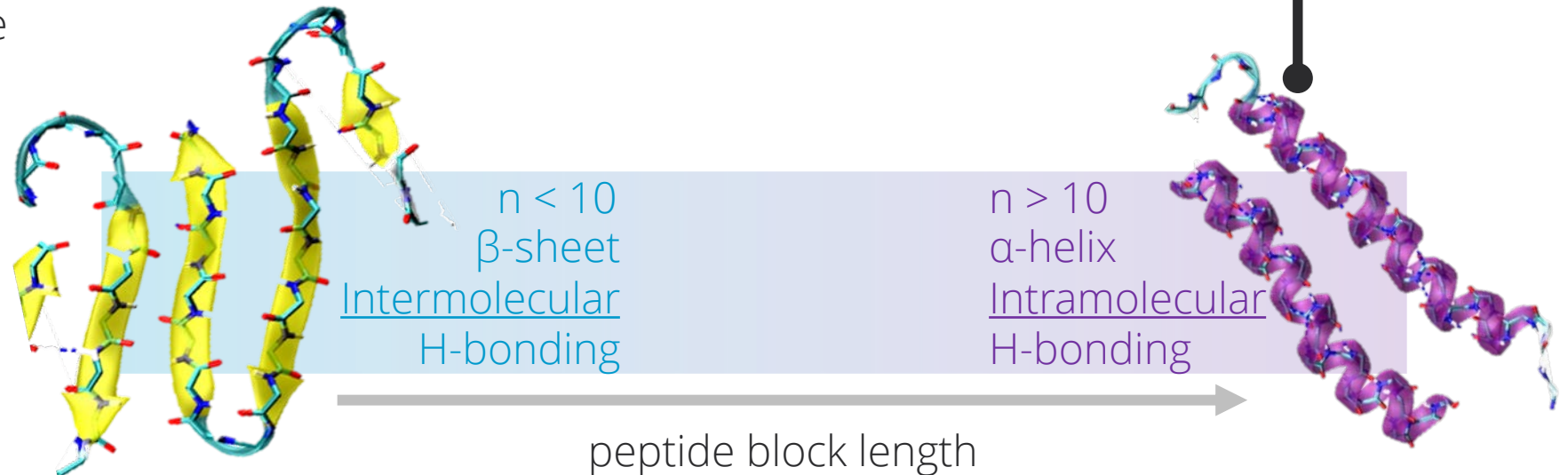
Poly(dimethyl siloxane)
(PDMS)

Synthetic Polymer

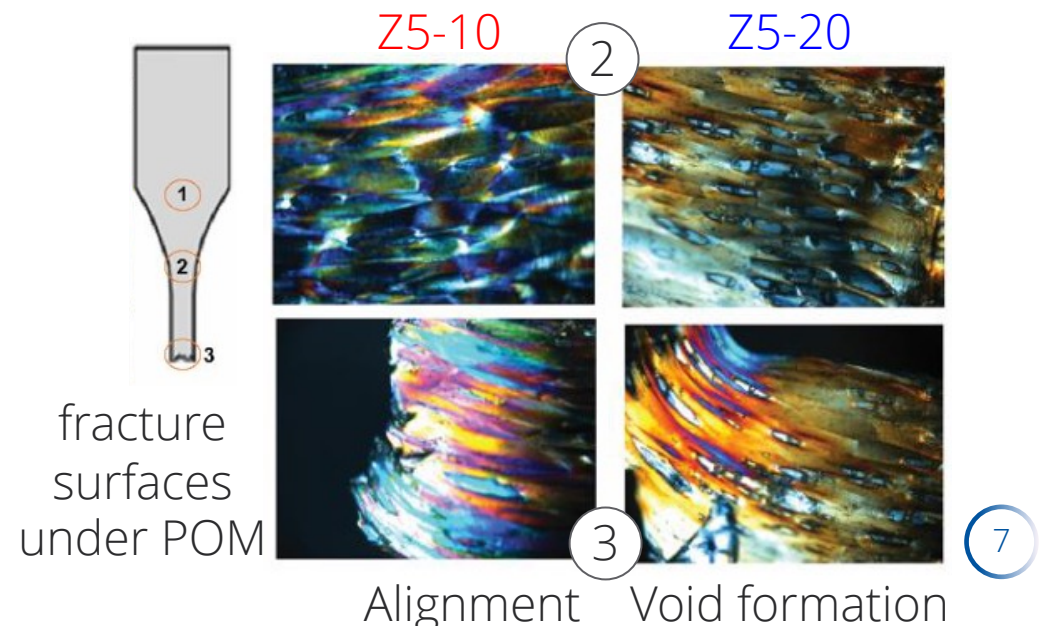
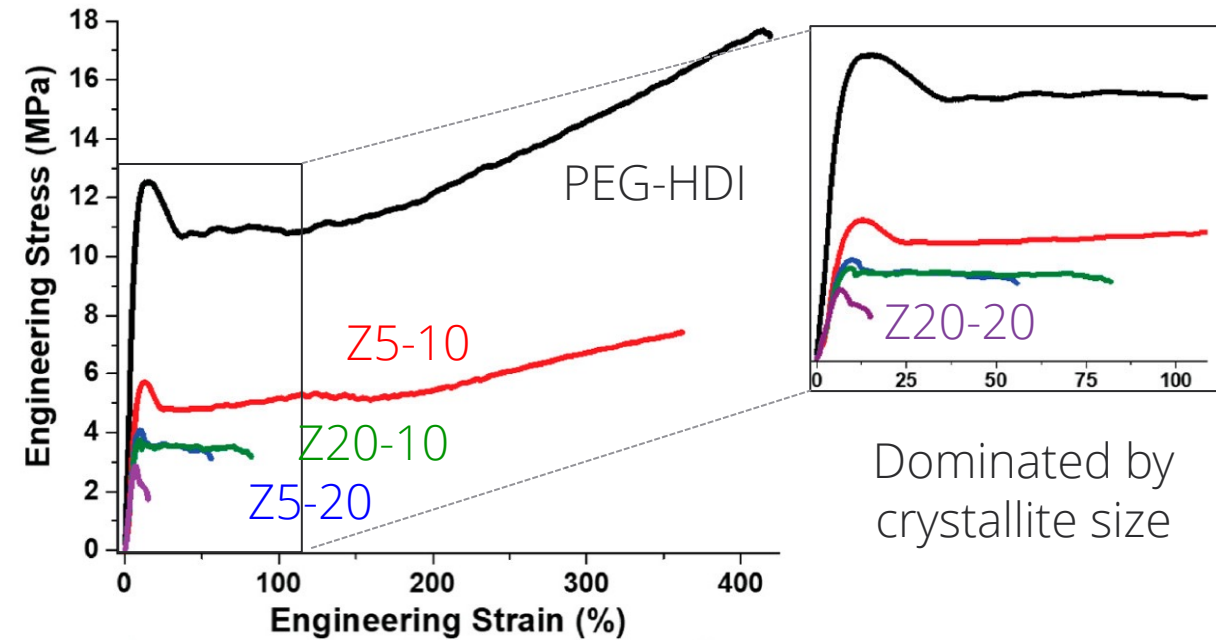
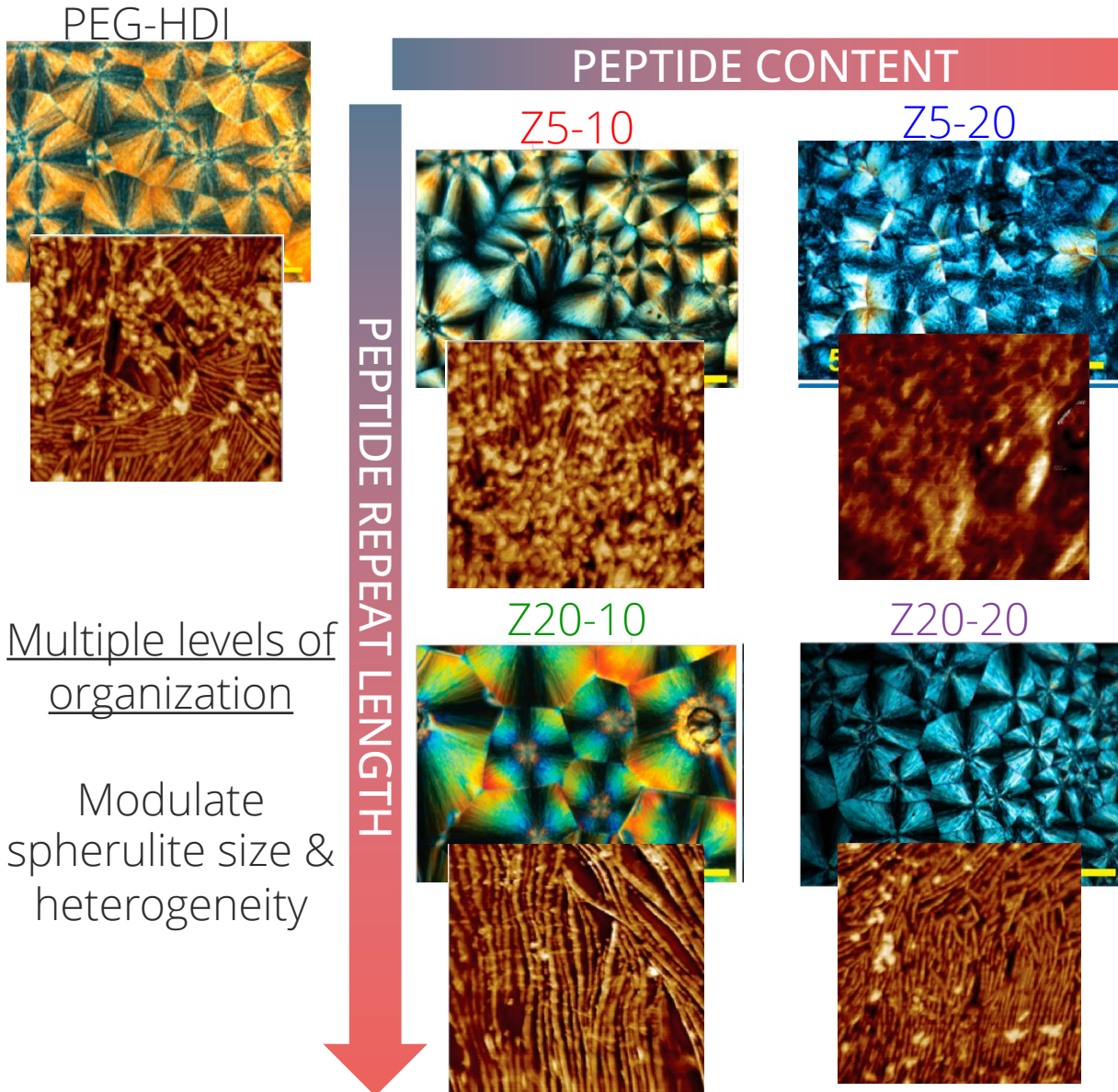
- easy to obtain in desirable M_w
- imparts desirable polymer characteristics (e.g., flexibility, crystallinity, entanglement)



Peptide-PDMS-Peptide

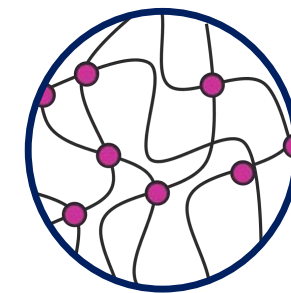
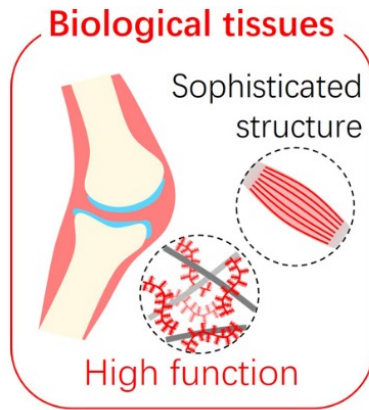
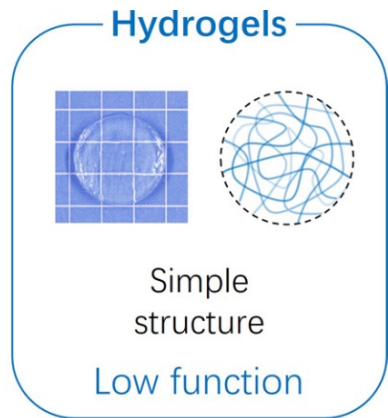


—Hybrids Possess Unique Crystalline Morphologies and Fracture Mechanics—

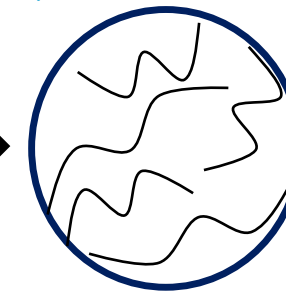
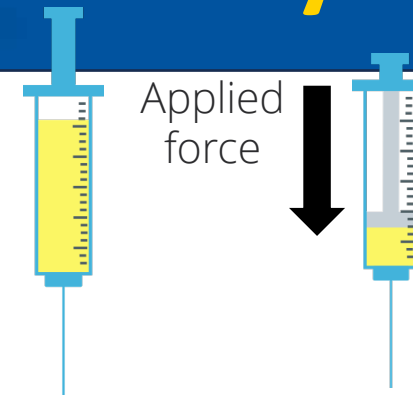


Designing dynamic hydrogels

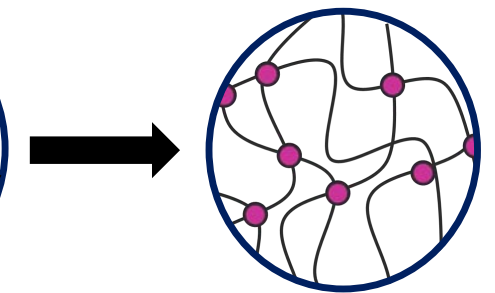
Desirable properties of dynamic networks: shear thinning, responsivity, self-healing
Challenge: mechanical strength



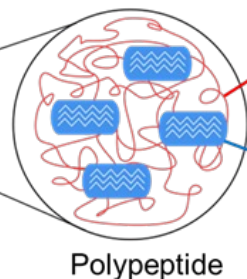
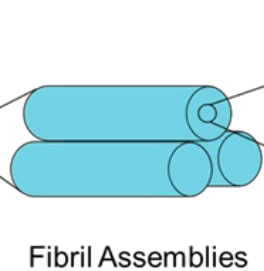
Solid-like properties



Yield to flow



Network Recovery

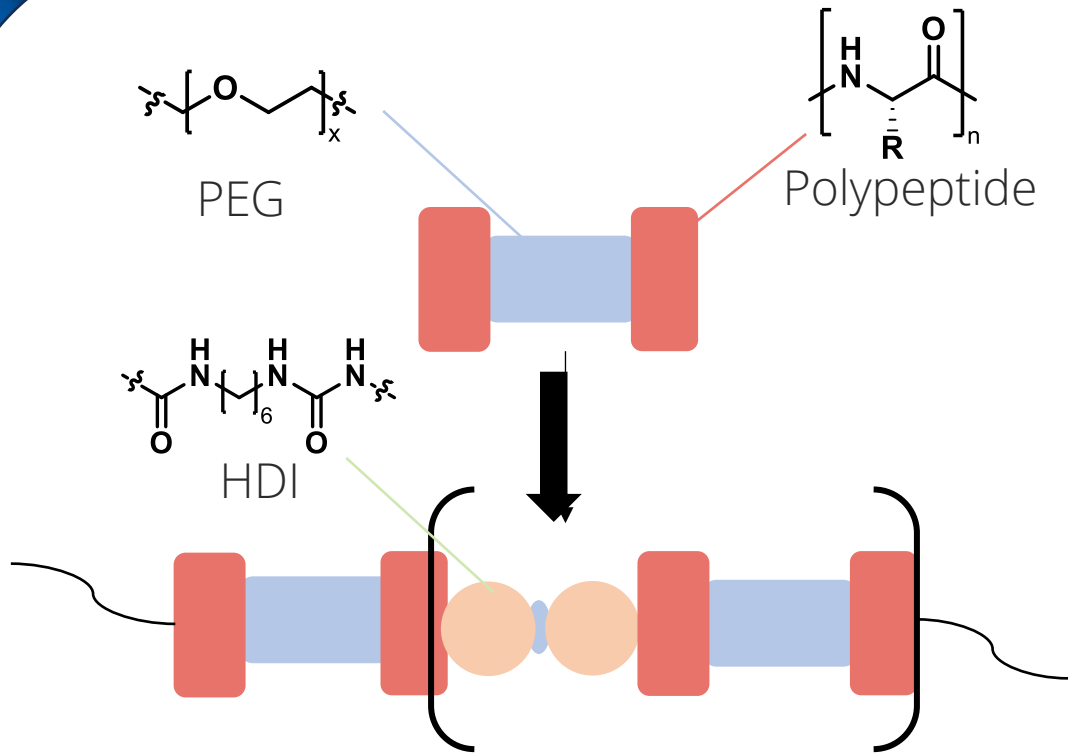


Amorphous domains,
intramolecular bonding →
elasticity

β -sheet crystalline domains,
intermolecular bonding →
mechanical reinforcement

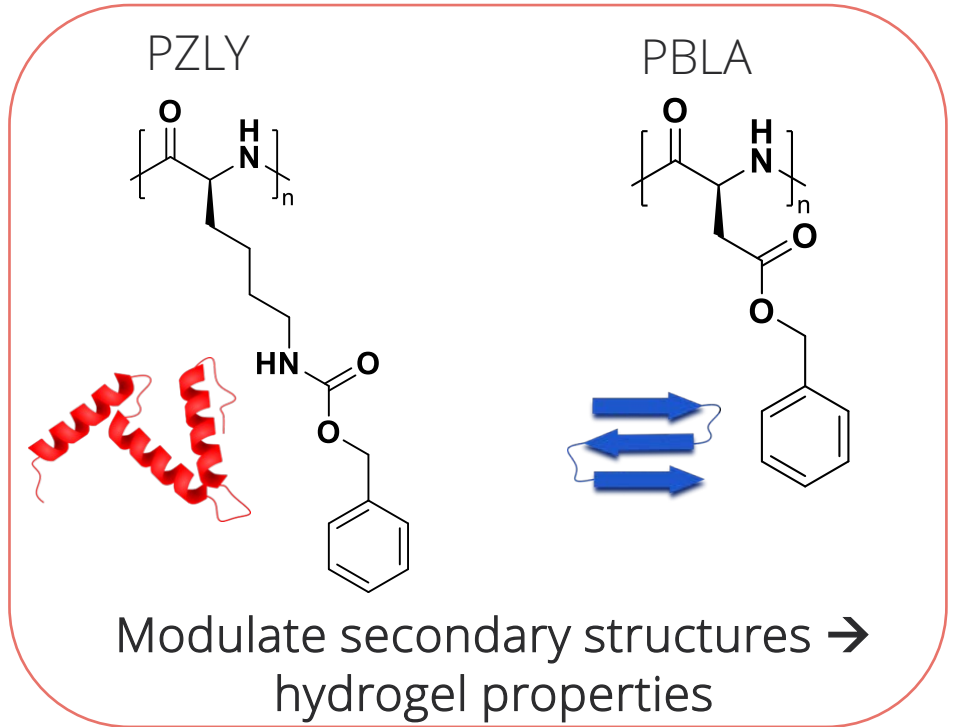
Build complex, reversible interactions into polymer systems

Bio-inspired assemblies for dynamic hydrogels

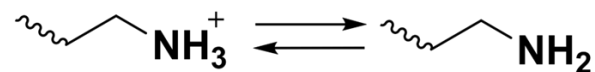


Deprotection of side chain residues: added
responsivity & reinforcement opportunities

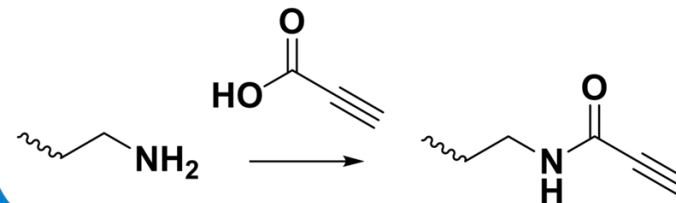
Peptide Blocks



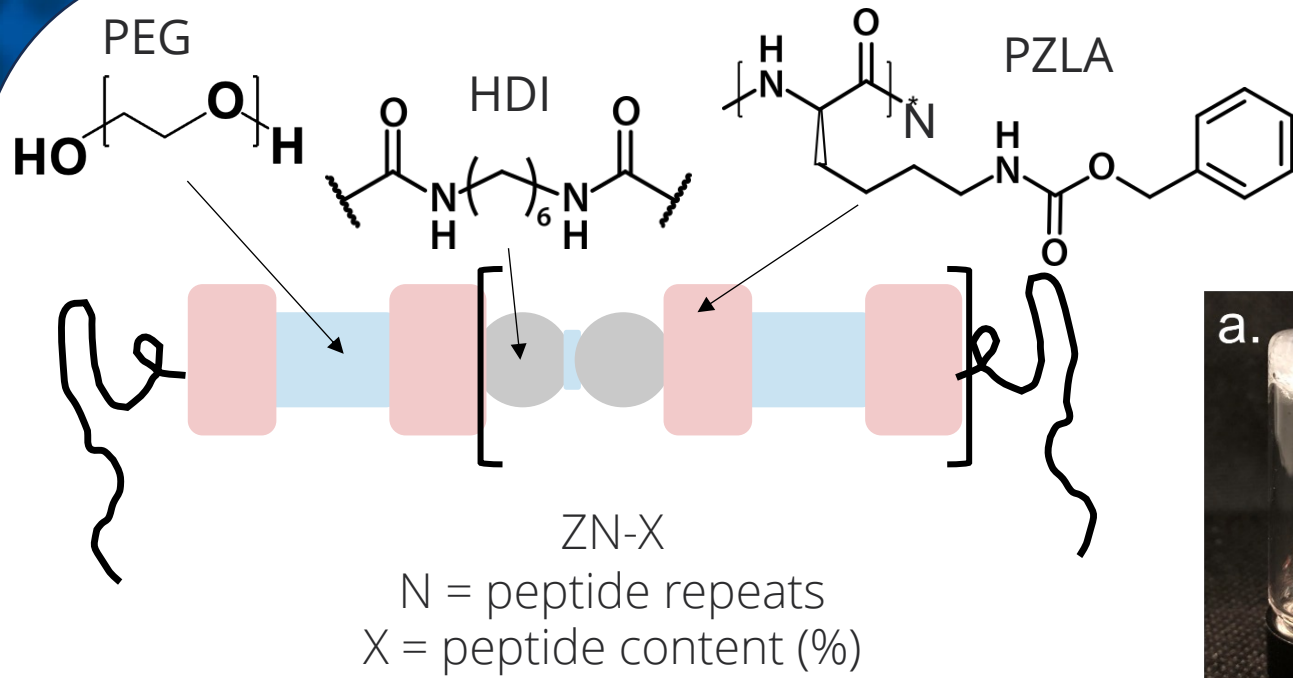
pH Response



Chemical Modification



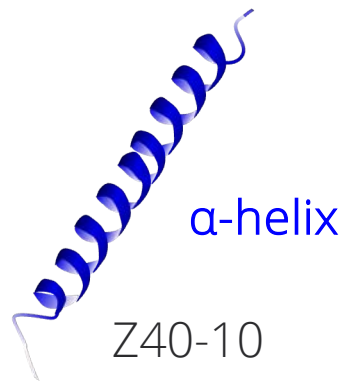
Peptide-polyurea hybrids as physical hydrogels



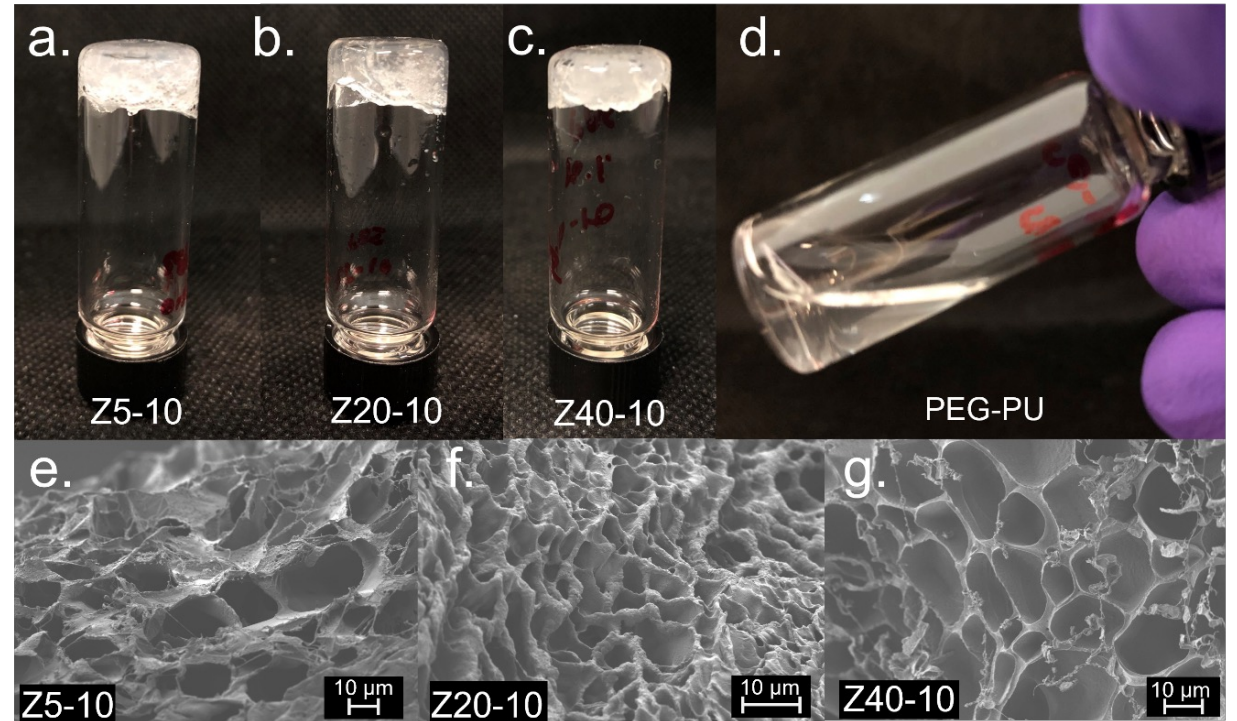
Z5-10



Z20-10

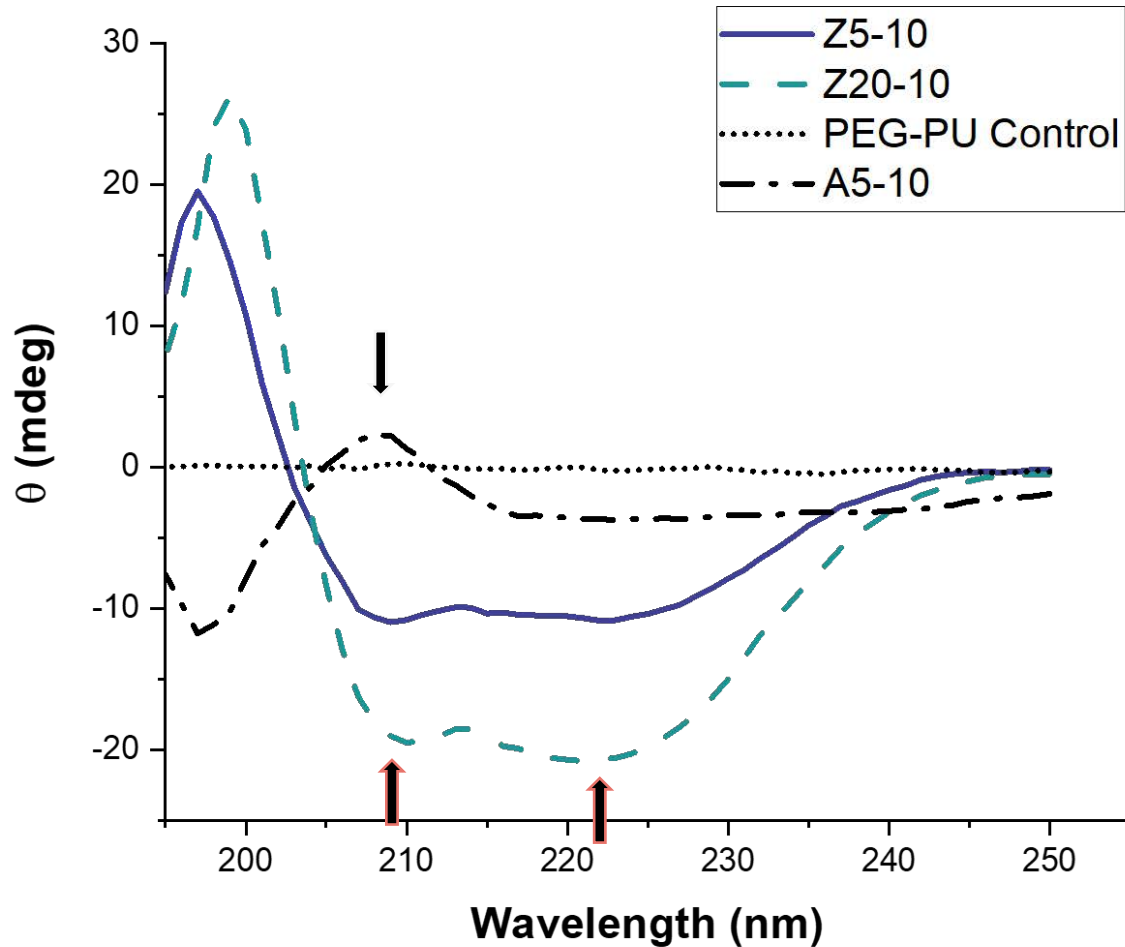


Z40-10

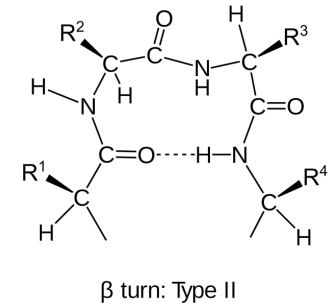


Secondary structure drives gelation

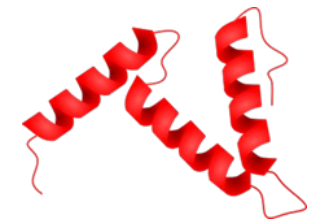
Circular dichroism (CD) Spectroscopy reveals dominant α - helical behavior in gel-forming hybrids



PBLA-PEG PUs: Random coil (Beta turn) – positive band at 210 nm

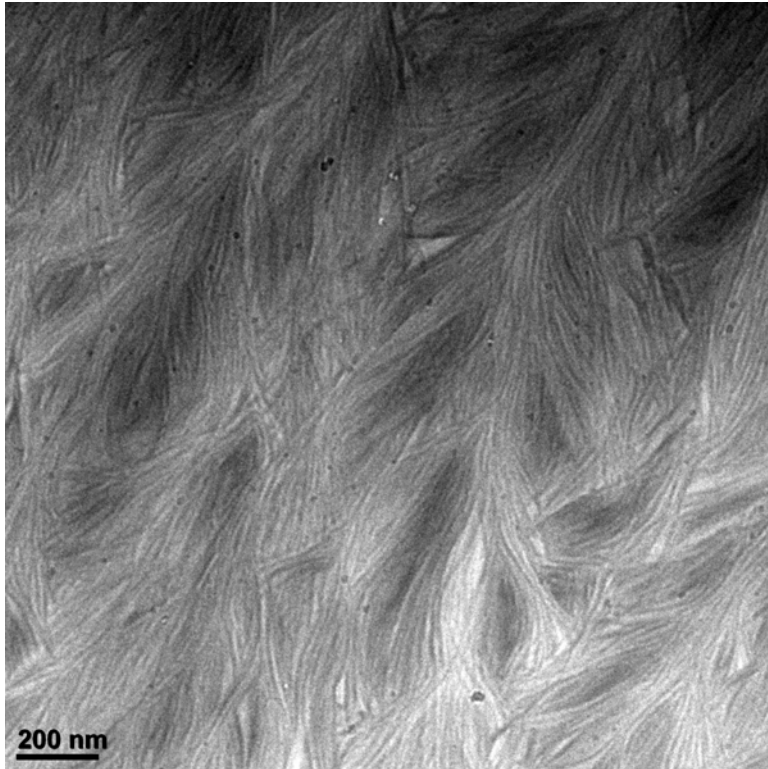


PZLY-PEG PUs: α - helical structures- negative bands at 209, 222 nm

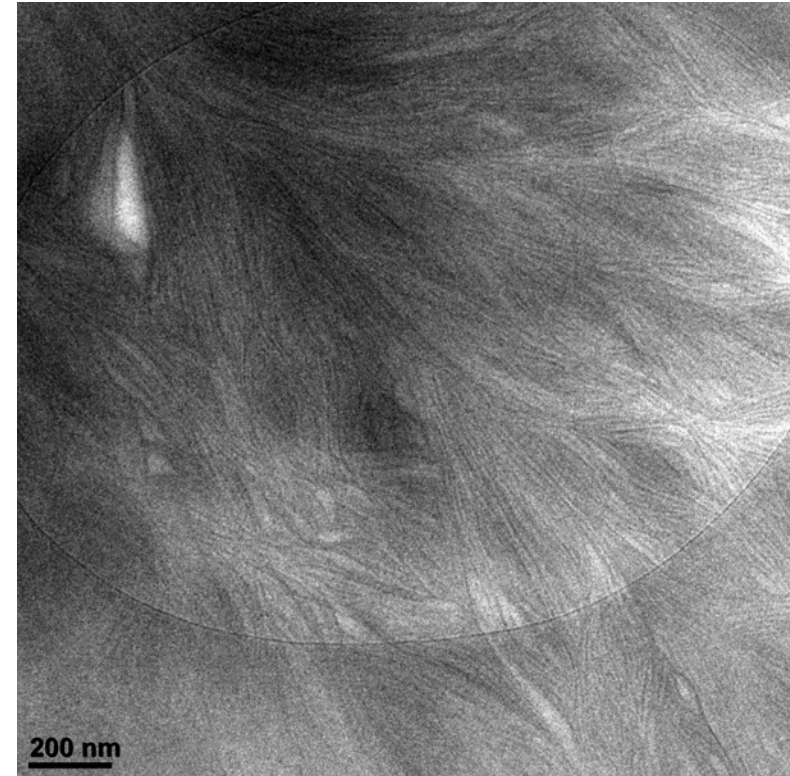


Gelation mechanism tied to peptide secondary structure

Visualizing higher-order assemblies



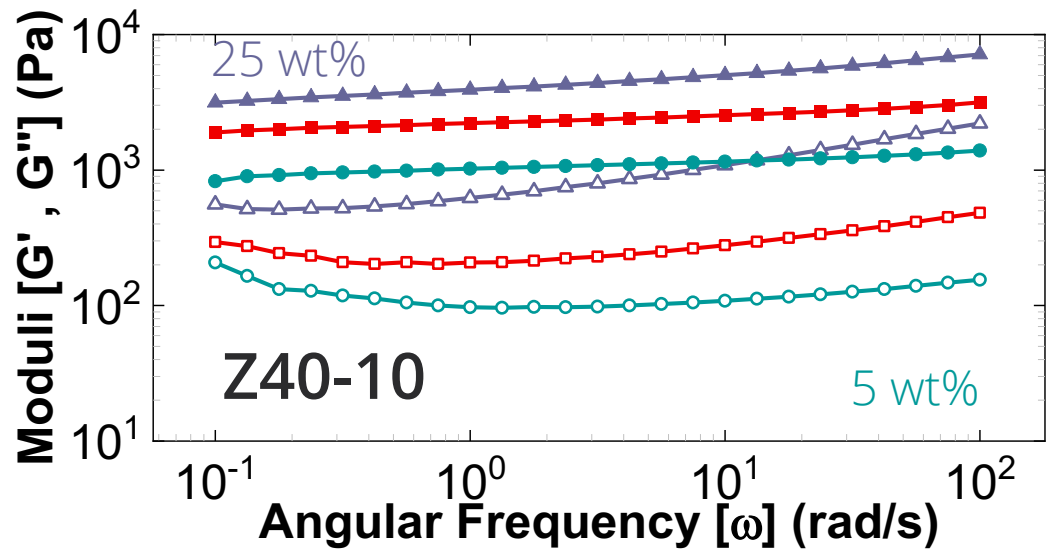
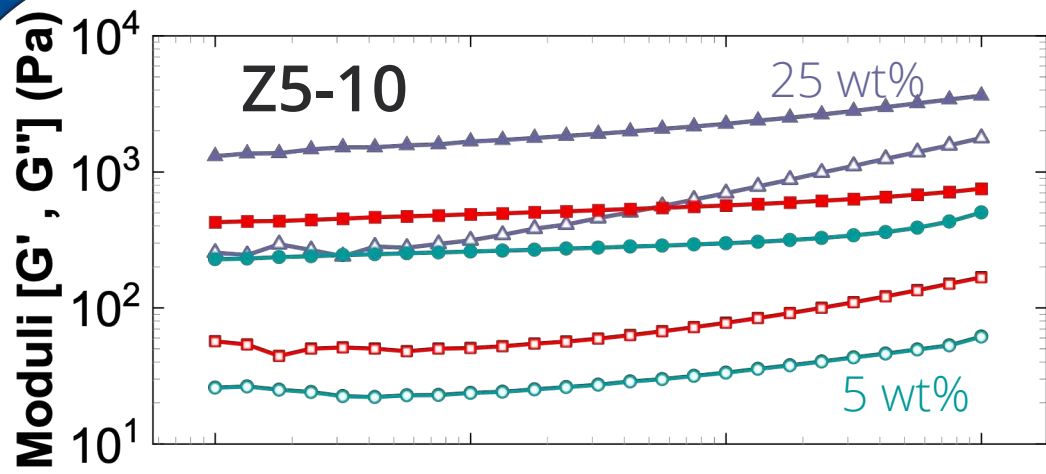
Z5-10, 10 wt%



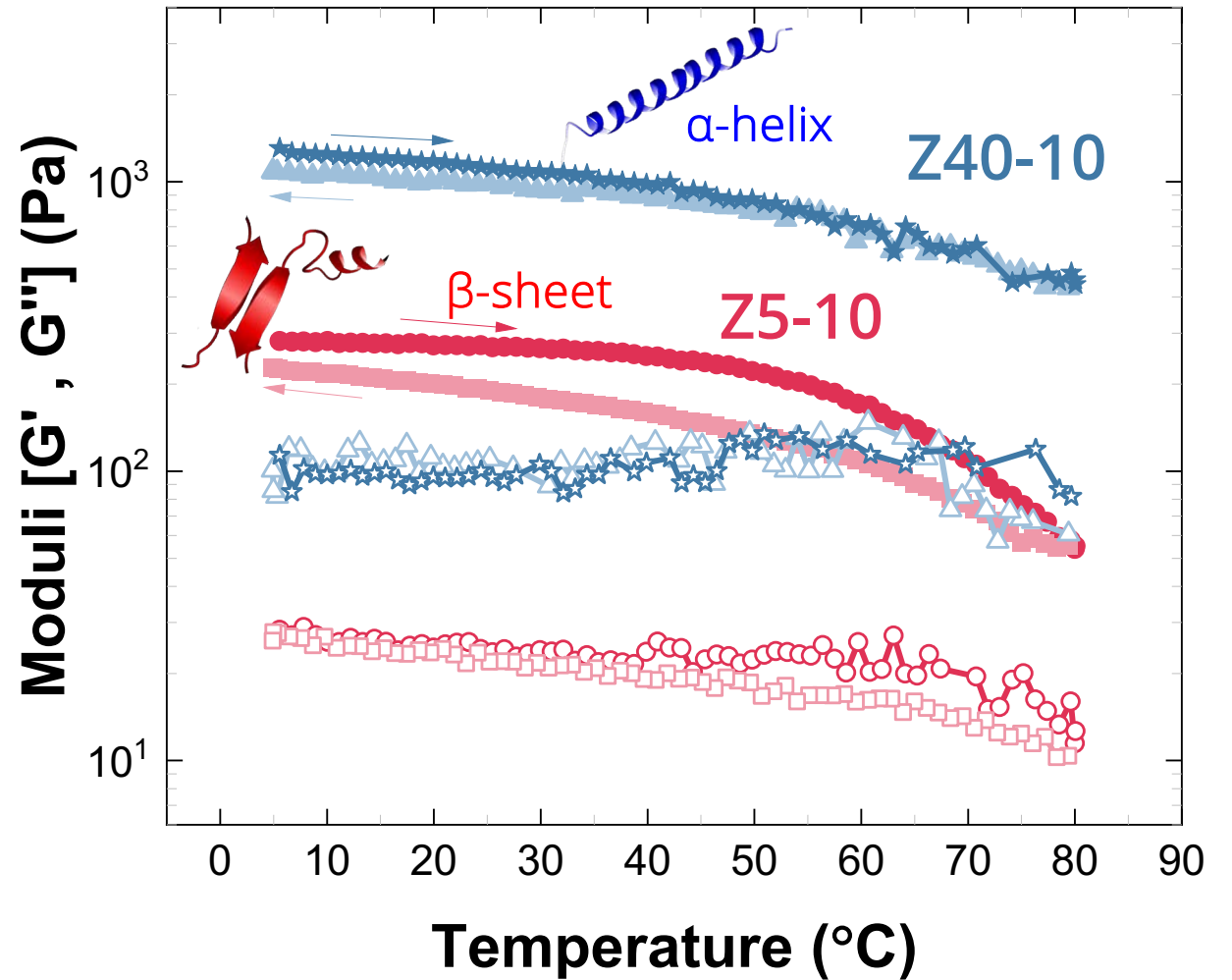
Z20-10, 10 wt%

Cryo-TEM images reveal dense fibrous networks present in α -helical polyurea hybrid hydrogels

Thermally-stable hydrogels with structure-controlled assembly



PEG ZN-X
N = peptide repeats
X = peptide content (%)
T = 37°C

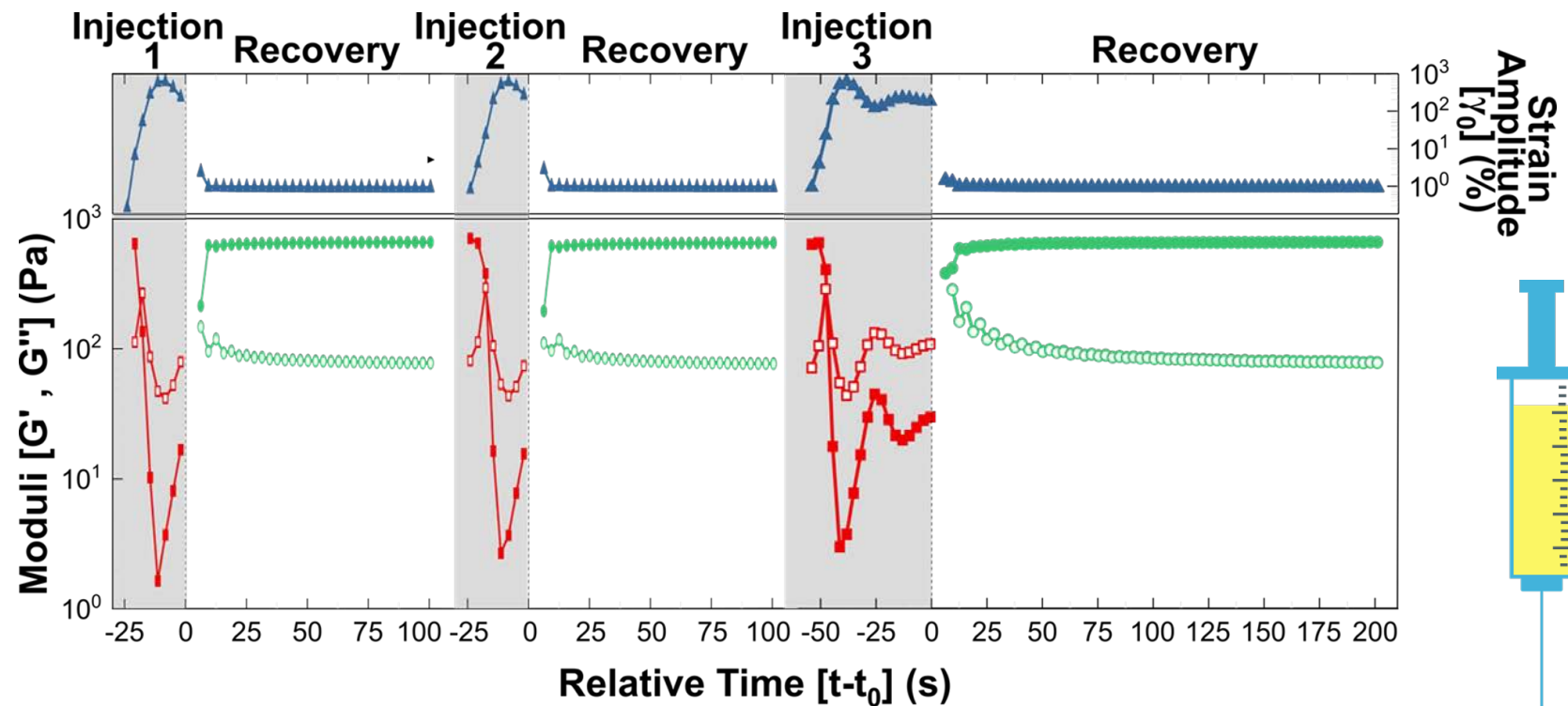


temperature cycling reveals complex thermo-rheological response

Network recovery achieved

Design Considerations for Applicability:

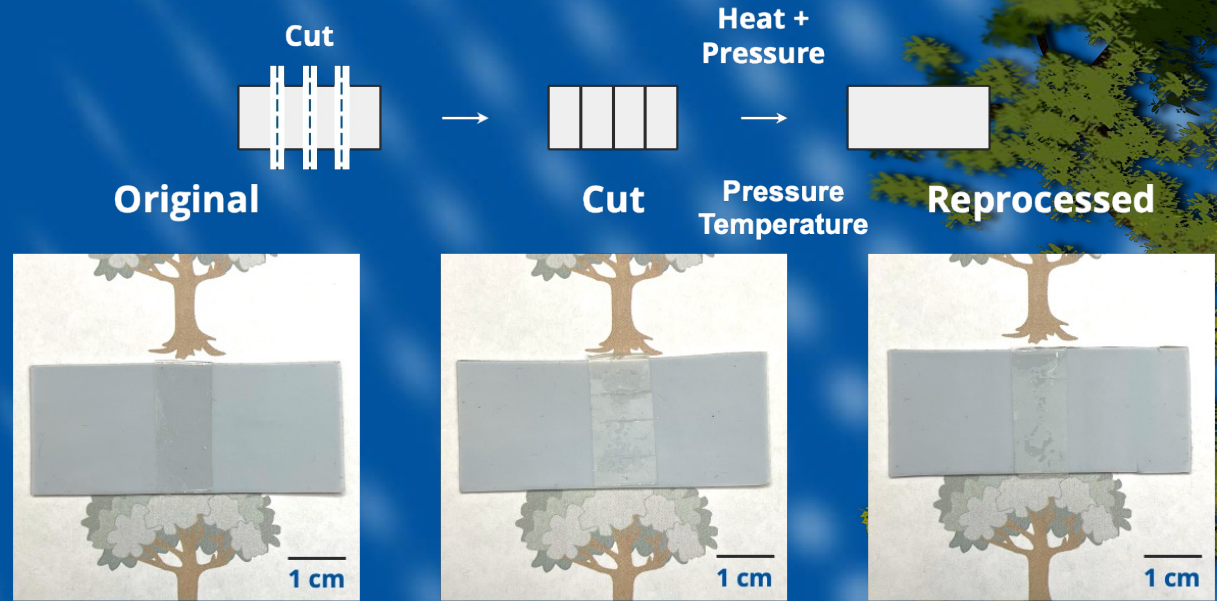
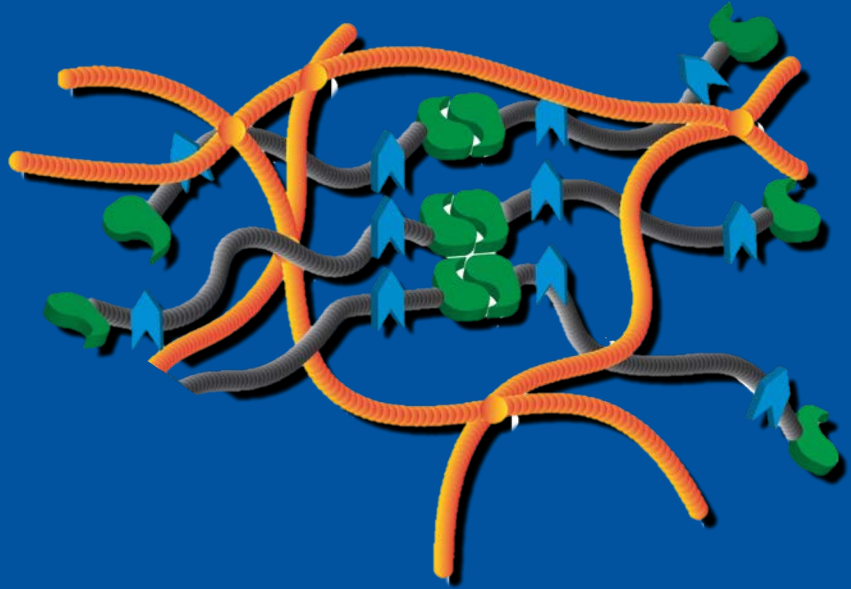
- More solid-like behavior, shear thinning
- Ability to recover from applied force
- Sufficient mechanical strength



PZLY-PEG PU hydrogels display network recovery from shear

MIMICKING NATURAL ARCHITECTURES

Korley et al. *Euro. Poly. J.* (2019)



Korley et al. *Unpublished*

TOPOLOGICALLY DISTINCT, MULTI-NETWORK POLYMERS

Permanent + Exchangeable Polymer Networks

- enables stiffness gradients (inspired by Nereis jaw)
- self-healing abilities

REINVENTING POLYMERS FROM NATURAL BUILDING BLOCKS

Renewable Materials

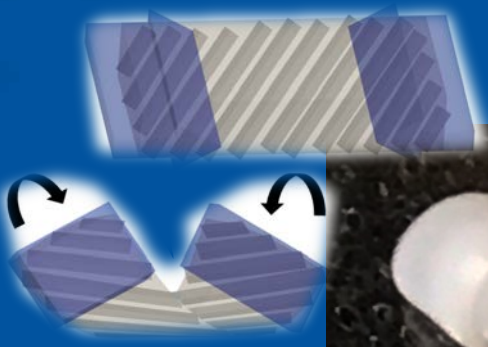
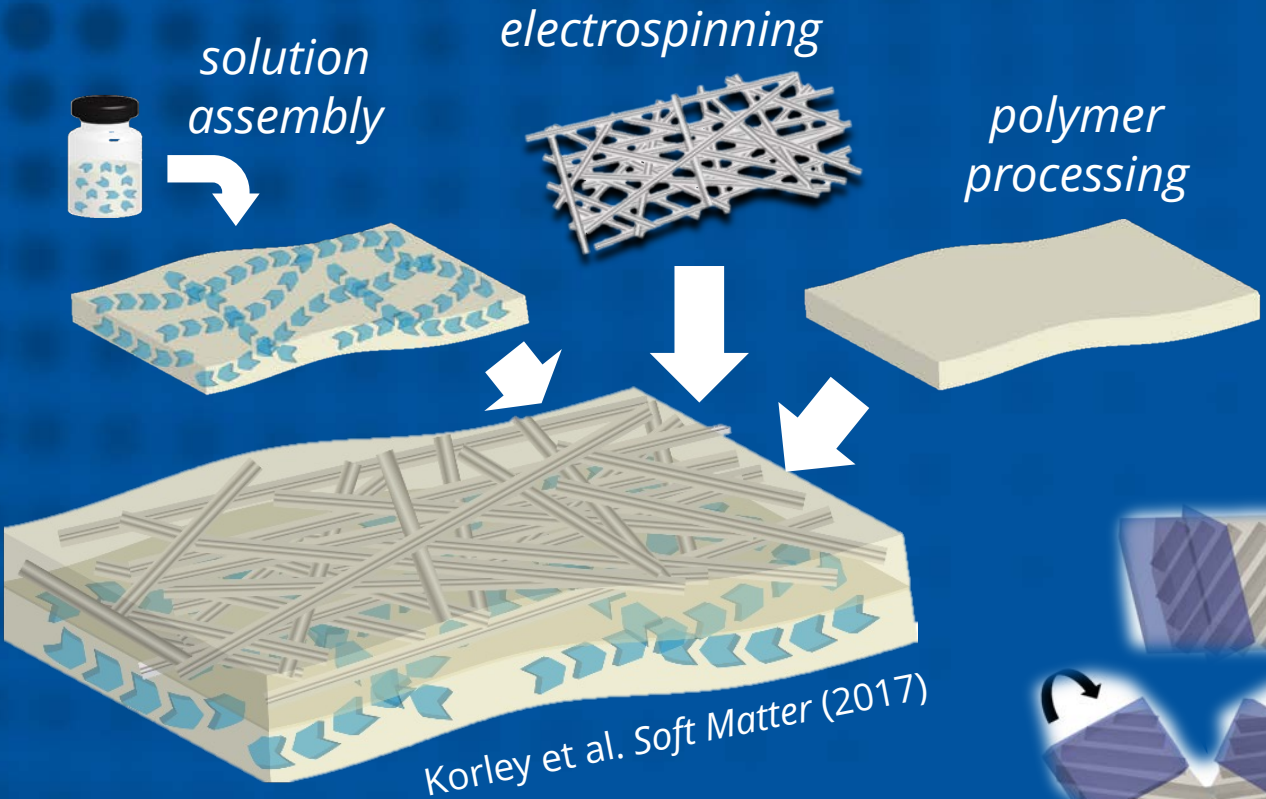
- derivable from renewable sources (e.g., wood wastes)
- enables re-processability and long-term stability



ENABLING RESPONSE VIA MANUFACTURING

COMBINED PROCESSES FOR PROGRAMMABLE MATERIALS

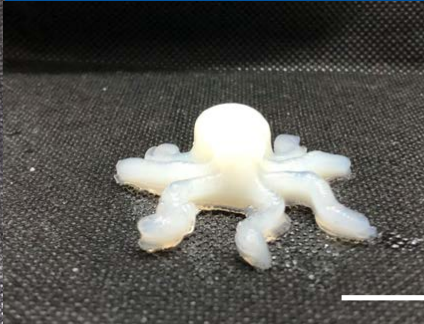
Polymeric Matrices + Nanofibers
shape programmability for pre-designed folding upon exposure to moisture



Korley et al. *Soft Matter* (2017)

SMART MANUFACTURING via 3D PRINTING

spatial control of motion enables robotics applications

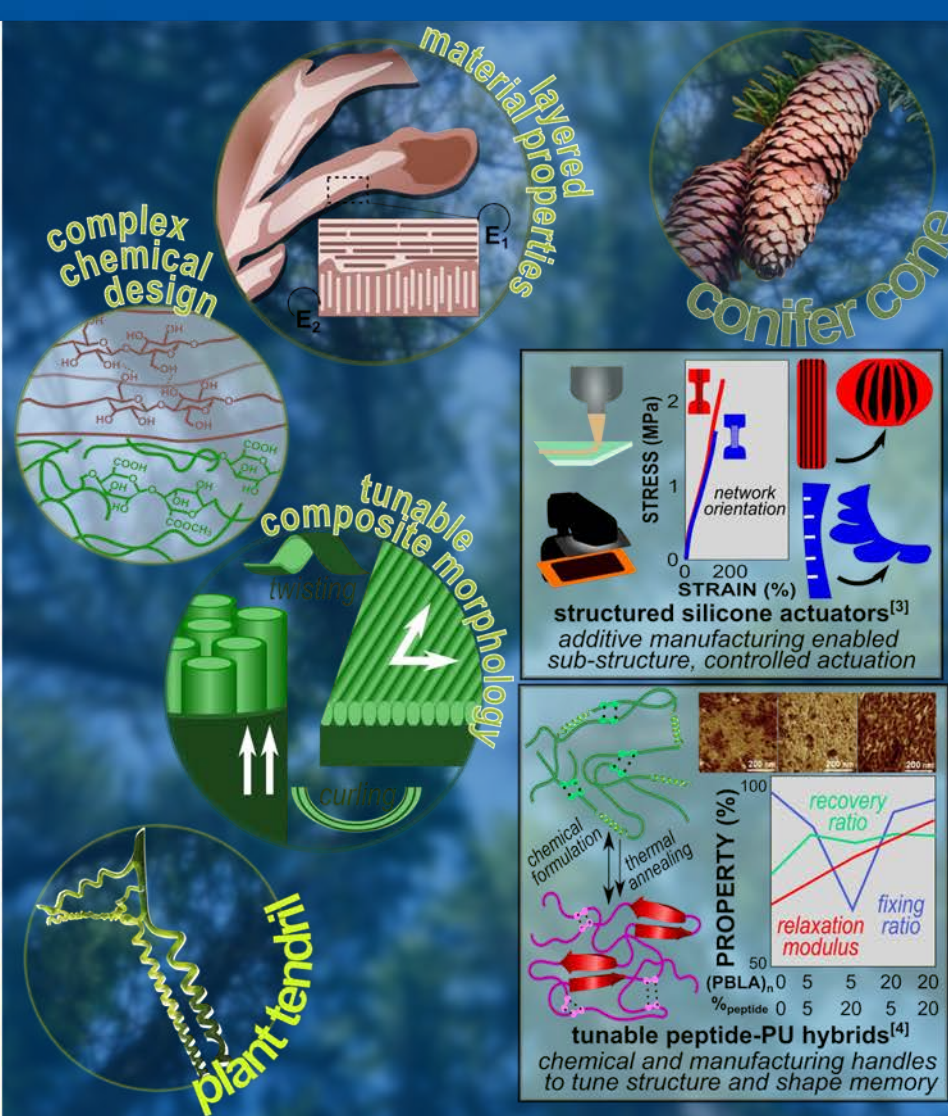
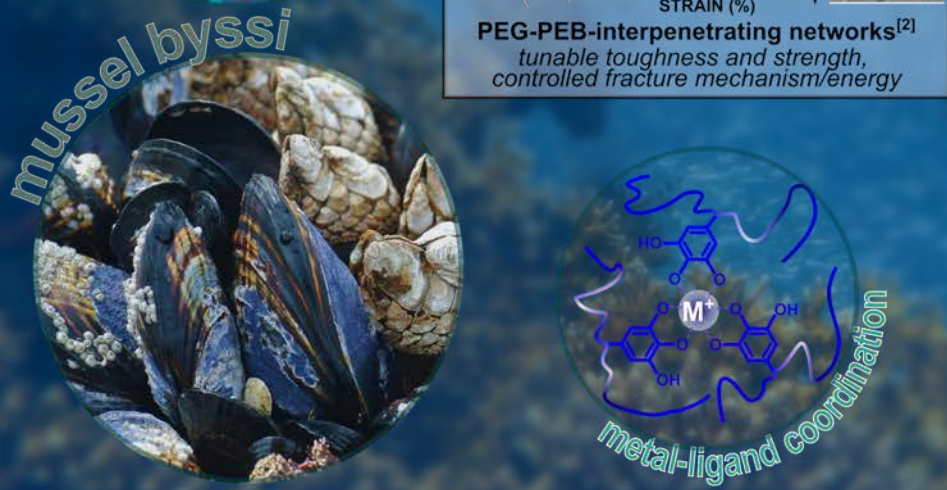
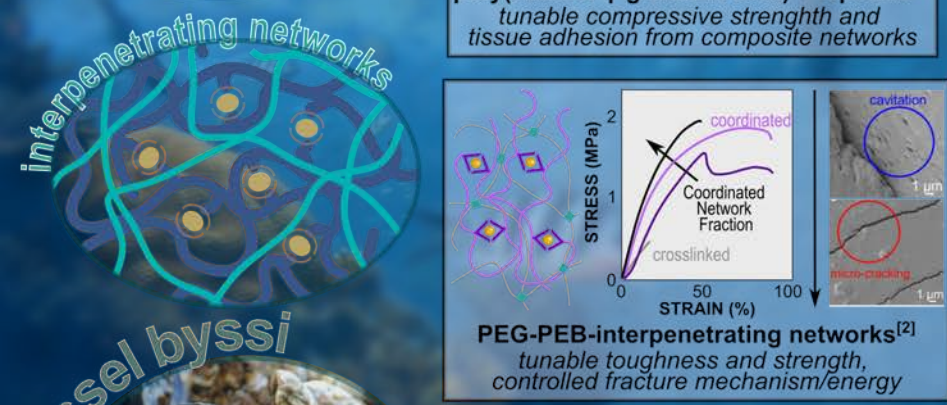
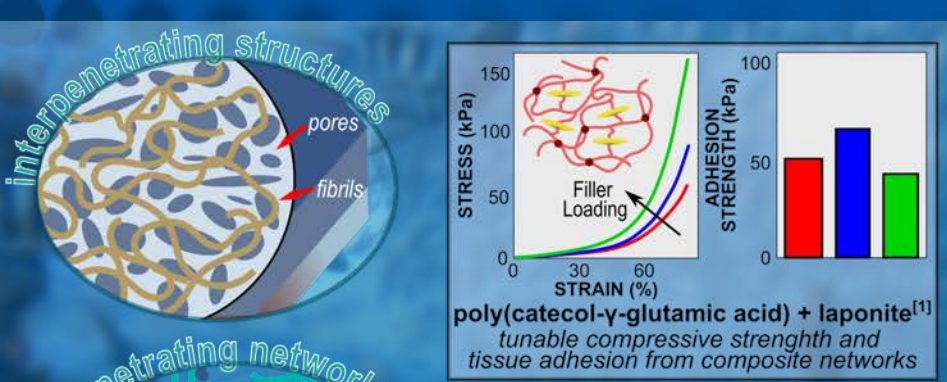


BUILDING A SUSTAINABLE BIOECONOMY

Architecture

Efficiency

Modularity



[1] Acta Biomater. 123 (2021) 254 [2] Euro. Poly. J. 116 (2019) 201 [3] Nature Comm. 9 (2018) 878 [4] Mol. Syst. Des. Eng. (2021)10.1039/d1me00043h

Environment

On-demand nanomanufacturing

Nanotemplating

Researchers

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NSF OISE - 1743475

PIRE: Bio-inspired Materials and Systems

NSF GCR Plastic Lifecycle Management
NSF DMR 2004682



NSF DMR-2011824

UD MRSEC Center for Hybrid, Active, and
Responsive Materials

NSF DMR 1608441

