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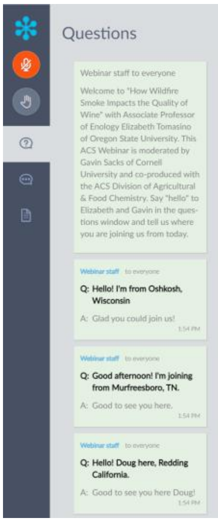

Webinar staff to everyone

Welcome to "How Wildfire Smoke Impacts the Quality of Wine" with Associate Professor of Enology Elizabeth Tomasino of Oregon State University. This ACS Webinar is moderated by Gavin Sacks of Cornell University and co-produced with the ACS Division of Agricultural & Food Chemistry. Say "hello" to Elizabeth and Gavin in the questions window and tell us where you are joining us from today.

Webinar staff to everyone

Q: Hello! I'm from Oshkosh, Wisconsin

A: Glad you could join us!

1:54 PM

Webinar staff to everyone

Q: Good afternoon! I'm joining from Murfreesboro, TN.

A: Good to see you here.

1:54 PM

Webinar staff to everyone

Q: Hello! Doug here, Redding California.

A: Good to see you here Doug!

1:54 PM

"Why am I muted?"

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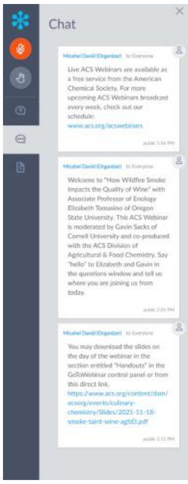

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https://www.acs.org/content/dam/acsorg/events/culinary-chemistry/Slides/2021-11-18-smoke-taint-wine-agfd3.pdf

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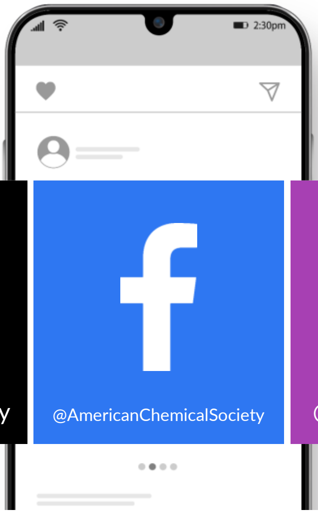

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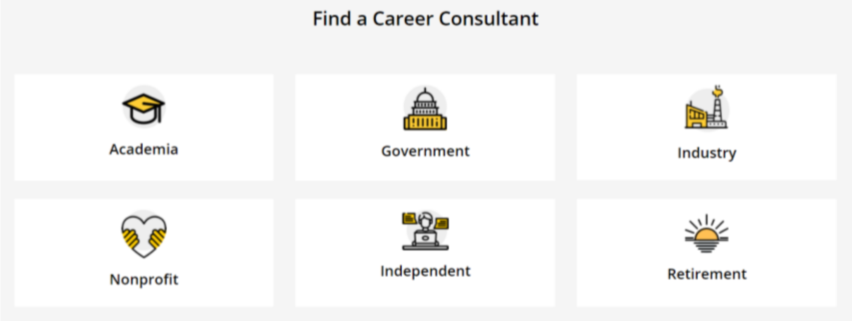

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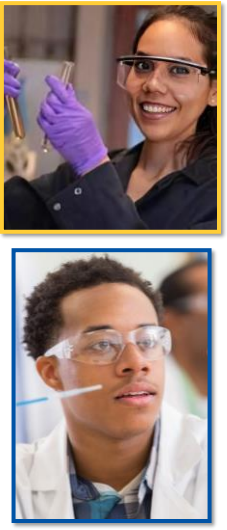

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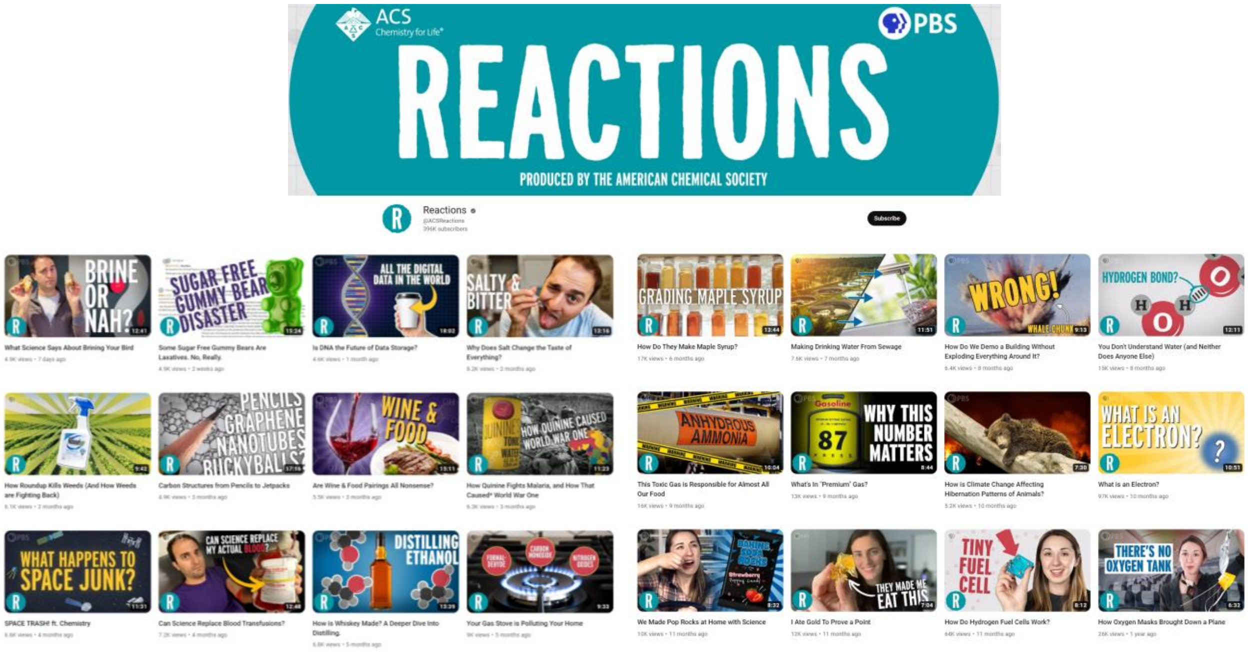

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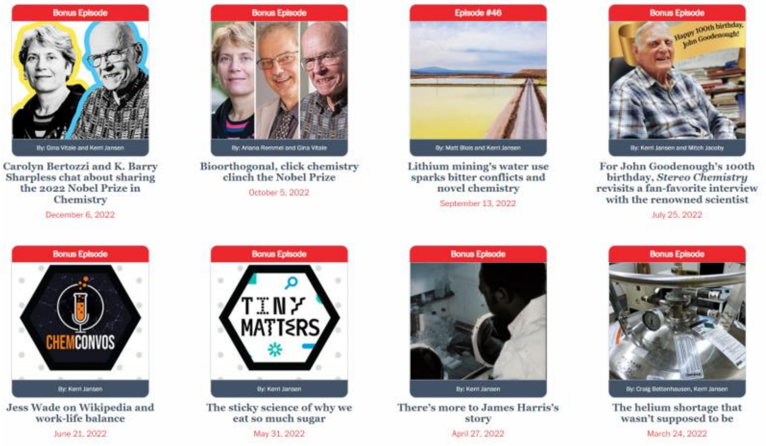

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By: Gina Vitale and Kerri Jansen
Carolyn Bertozzi and K. Barry Sharpless chat about sharing the 2022 Nobel Prize in Chemistry
December 6, 2022

Bonus Episode
By: Ariana Remmel and Gina Vitale
Bioorthogonal, click chemistry clinch the Nobel Prize
October 5, 2022

Episode #46
By: Matt Blois and Kerri Jansen
Lithium mining's water use sparks bitter conflicts and novel chemistry
September 13, 2022

Bonus Episode
Happy 100th birthday, John Goodenough!
By: Kerri Jansen and Mitch Jacoby
For John Goodenough's 100th birthday, *Stereo Chemistry* revisits a fan-favorite interview with the renowned scientist
July 25, 2022

Bonus Episode
CHEMCONVOS
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Jess Wade on Wikipedia and work-life balance
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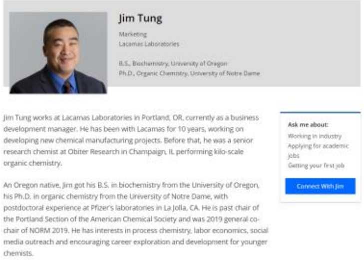

Jim Tung
Marketing
Lacamas Laboratories

B.S., Biochemistry, University of Oregon
Ph.D., Organic Chemistry, University of Notre Dame

Jim Tung works at Lacamas Laboratories in Portland, OR, currently as a business development manager. He has been with Lacamas for 10 years, working on developing new chemical manufacturing projects. Before that, he was a senior research chemist at Obiter Research in Champaign, IL performing kilo-scale organic chemistry.

An Oregon native, Jim got his B.S. in biochemistry from the University of Oregon, his Ph.D. in organic chemistry from the University of Notre Dame, with postdoctoral experience at Pfizer's laboratories in La Jolla, CA. He is past chair of the Portland Section of the American Chemical Society and was 2019 general co-chair of NORM 2019. He has interests in process chemistry, labor economics, social media outreach and encouraging career exploration and development for younger chemists.

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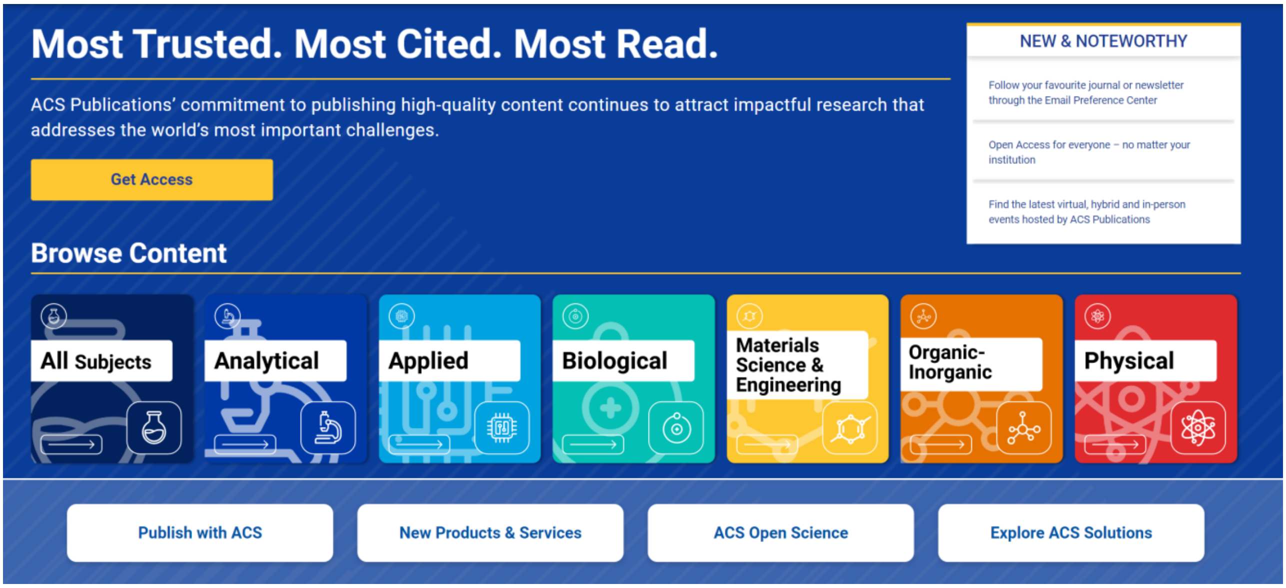

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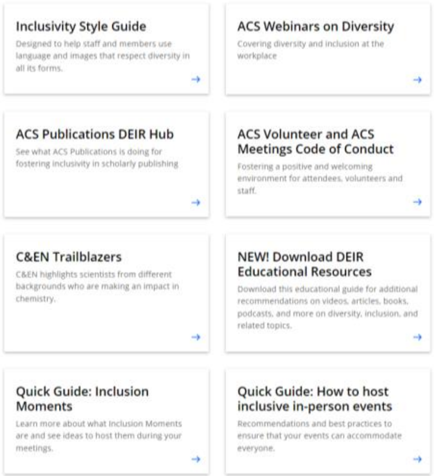

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Inclusion**
Builds a culture of belonging by actively inviting the contribution and participation of all people. Every person's voice adds value, and ACS strives to create balance in the face of power differences. In addition, no one person can or should be called upon to represent an entire community.

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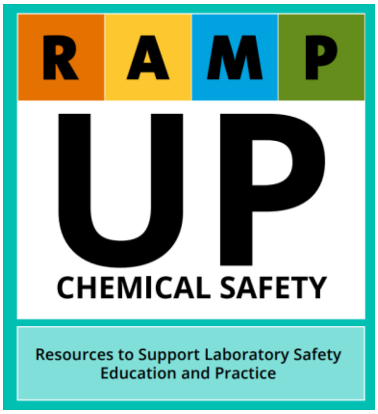

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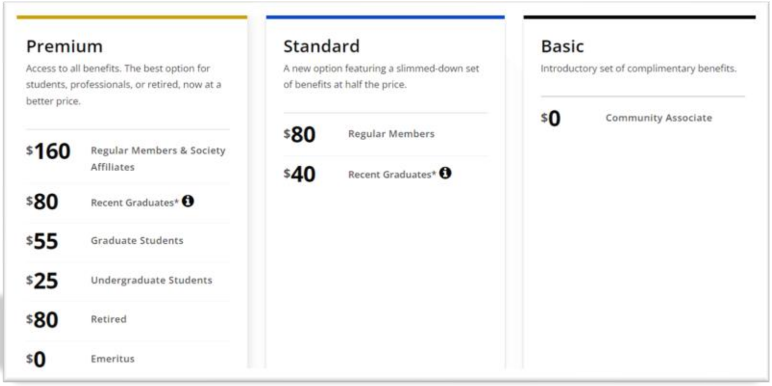

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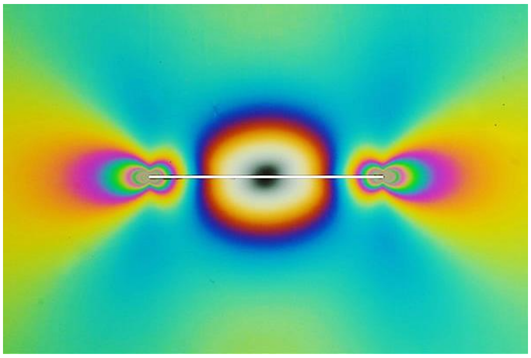

Breaking Down the Mechanics of Polymers: From Networks to Viscoelasticity

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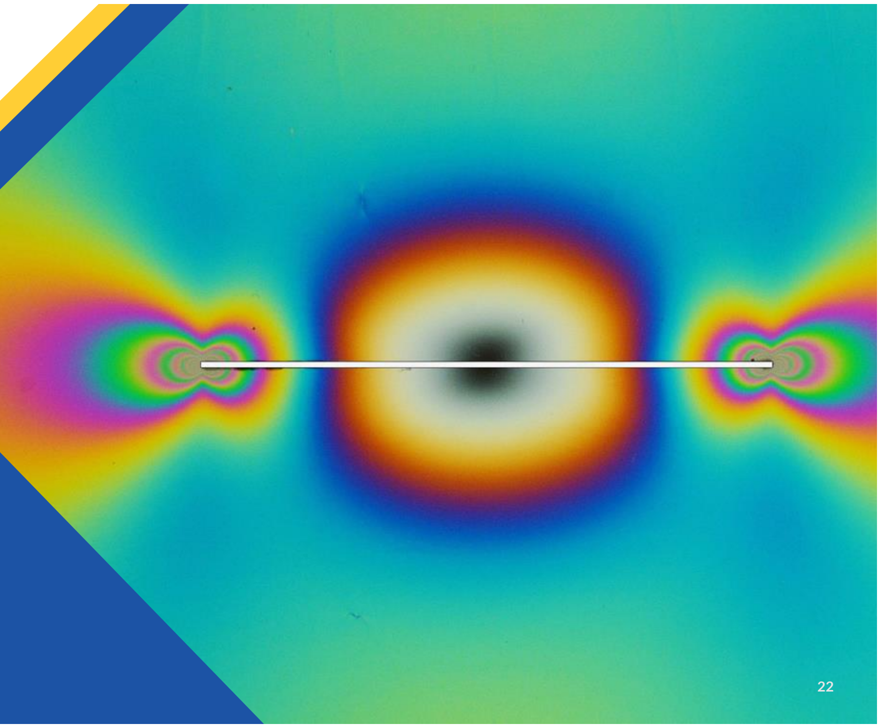

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Breaking Down the Mechanics of Polymers:
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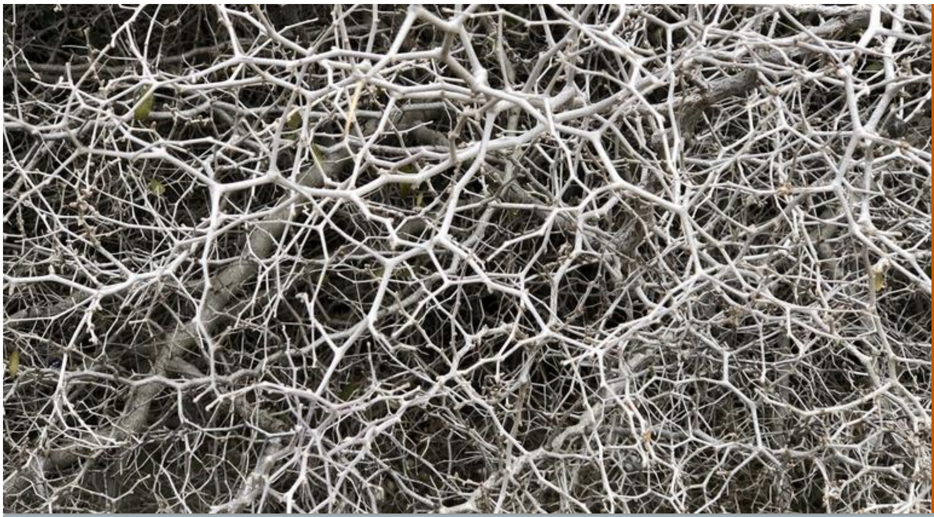


Adrianne Rosales

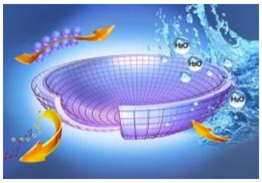
The University of Texas at Austin

December 13, 2023

Breaking Down the Viscoelasticity of Polymer Networks and Gels

Viscoelastic gels are important to many fields and applications

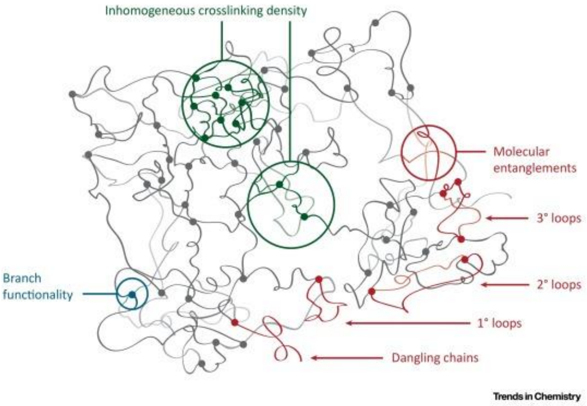
Consumer products



Devices & coatings

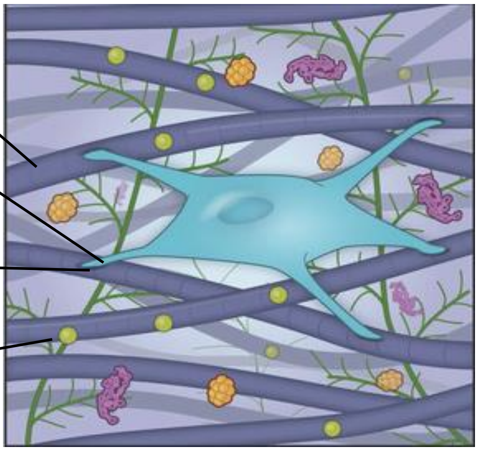
Construction materials

Peptide processing



Building blocks: small molecules, polymers, colloidal particles

Bioinspiration: reconfigurability of the extracellular matrix



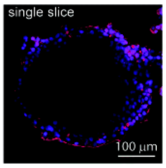
fibrous microstructure

cell adhesion and matrix remodeling

strain responsive

viscoelastic properties

Tissue Engineering Scaffolds

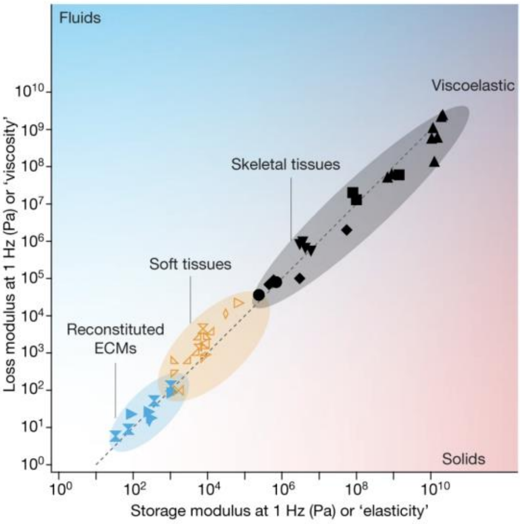


In Vitro Disease Models

Cell Delivery Vehicles

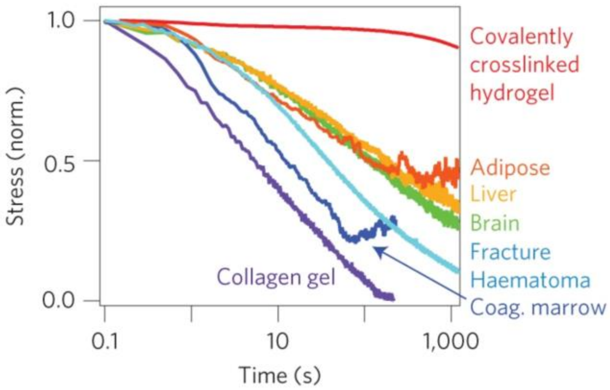
http://onlinelibrary.wiley.com/doi/10.1002/adma.201503918/full

Synthetic scaffolds do not replicate dynamic mechanics of ECM



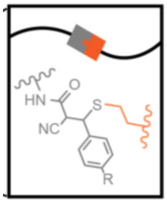
Chaudhuri, O., Cooper-White, J., Janmey, P.A. *et al*. *Nature* **2020**

How can we replicate this behavior in synthetic hydrogels?

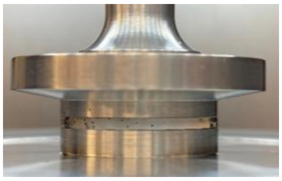


Chaudhuri and Mooney, et al. *Nat Mater.* **2016**

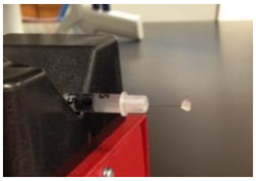
Breaking down the viscoelasticity of polymer networks and gels: Linking chemistry to mechanical response



I. Control of viscoelasticity with dynamic bonds



II. Measuring linear viscoelasticity with shear rheology

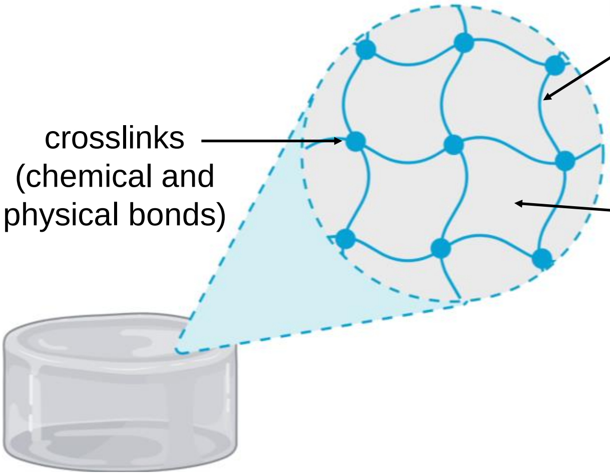


III. Nonlinear rheology

Mimicking the ECM with Hydrogels

Challenge

Recapitulating the dynamic complexity of native ECM

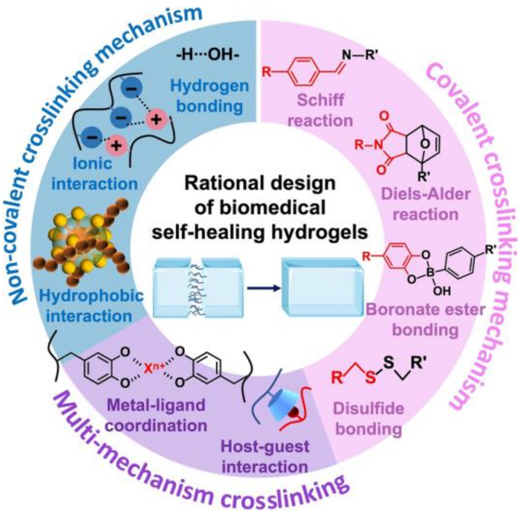


crosslinks (chemical and physical bonds)

Polymer chains (variety of backbones)

Water >90 vol%

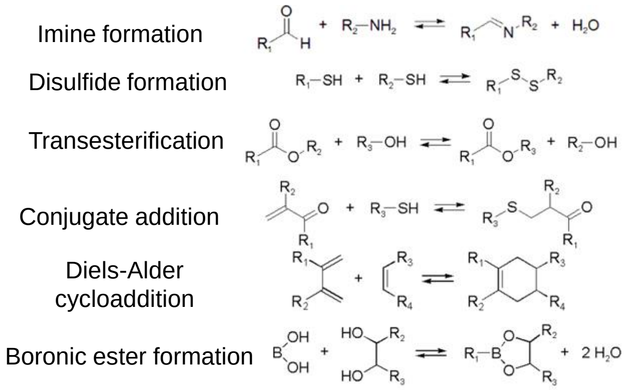
Dynamic chemistries for hydrogel crosslinks



- Various non-covalent and dynamic covalent mechanisms
- Most are explored in water
- Many more reactions and mechanisms beyond the ones shown!

Xu and Hsu. *J Biomed Sci.* **2023**

Dynamic covalent bonds in hydrogels



Imine formation

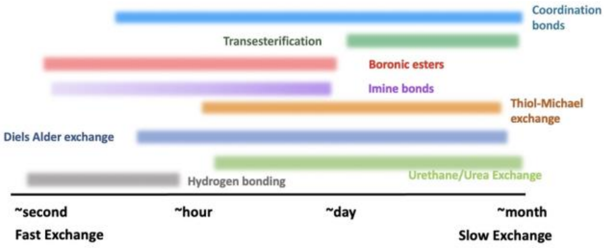
Disulfide formation

Transesterification

Conjugate addition

Diels-Alder cycloaddition

Boronic ester formation

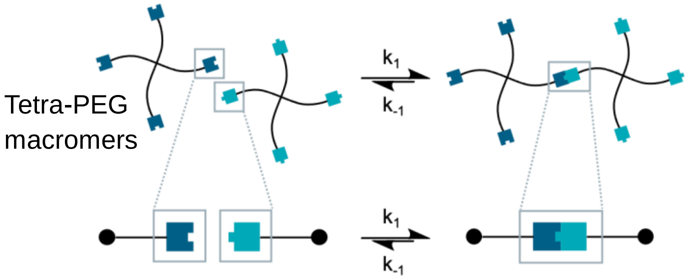


Konkolewicz, et al. *ACIE,* **2022**, 61(50).

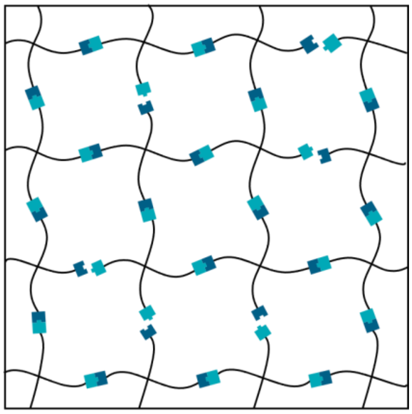
How do bond lifetimes affect dynamic behavior of cytocompatible hydrogels?

Tetra-PEG macromers with dynamic bond motifs

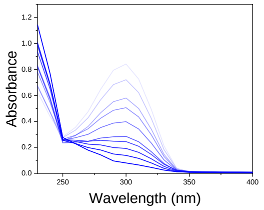
Bond exchange kinetics describe the rate at which crosslinks form and break.

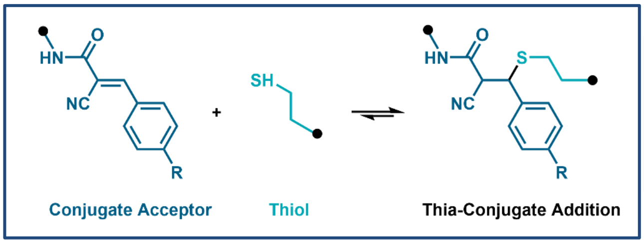


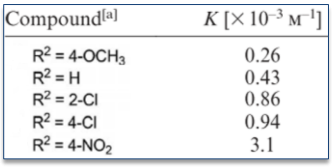
Parameter:	k_1	k_{-1}	$K_{eq} = \frac{k_1}{k_{-1}}$
Associated with:	Gelation	Relaxation	Plateau modulus



Reversible thiol-ene crosslinking reaction is highly tunable

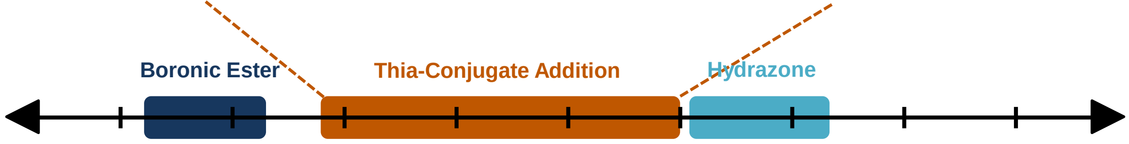






Compound[a]	K [$\times 10^{-3}$ M^{-1}]
R^2 = 4-OCH_3	0.26
R^2 = H	0.43
R^2 = 2-Cl	0.86
R^2 = 4-Cl	0.94
R^2 = 4-NO_2	3.1

Zhong, Anslyn, *Eur. J. Org. Chem*, **2013**,.



Boronic Ester **Thia-Conjugate Addition** **Hydrazone**

10^{-2} **10** **10^3** **10^5** **10^7**

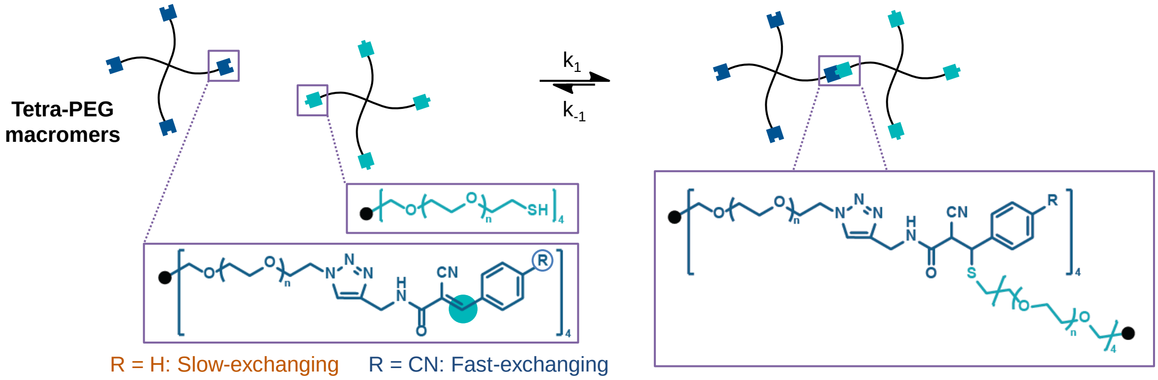
Fast
High k_{-1}
More viscous

Relaxation time (seconds)
(inversely proportional to k_{-1})

Slow
Low k_{-1}
More elastic

Adapted from Tang, Richardson, Anseth. *Progress in Materials Science*, **2021**.

Reversible thiol-ene crosslinking in model polymer networks

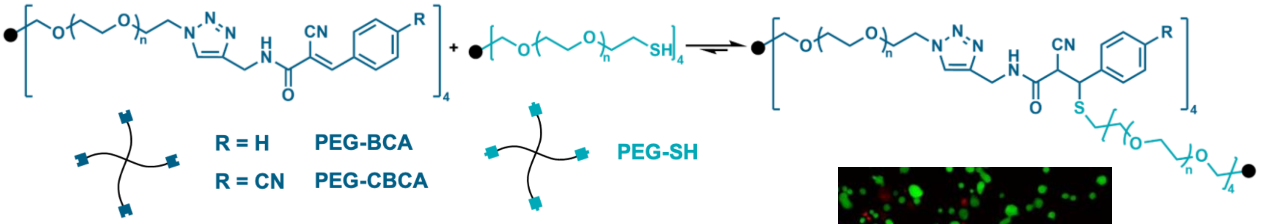


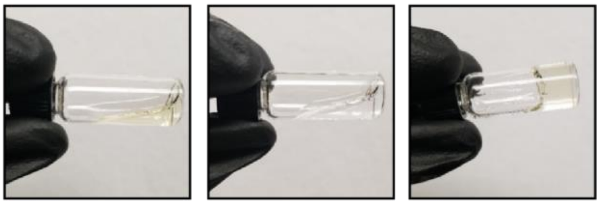
R = H: Slow-exchanging   R = CN: Fast-exchanging

	k_1 (M^{-1} s^{-1})	k_{-1} (s^{-1})	K_{eq} (M^{-1})
Fast-exchanging	500	0.11	4400 ± 400
Slow-exchanging	26	0.019	1300 ± 60

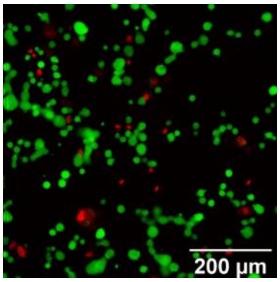
FitzSimons, Anslyn, Rosales, and coworkers. *Macromolecules*, **2020**, 53(10), 3738-3746.

Dynamic crosslinking leads to spontaneous gelation





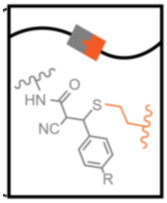
Rapid gelation upon mixing



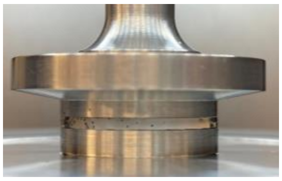
- ✓ Near ideal networks
- ✓ Biocompatible
- ✓ Defined functionality

FitzSimons, Anslyn, Rosales, and coworkers. *Macromolecules*, **2020**, 53(10), 3738-3746.

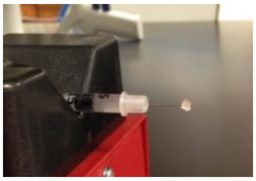
Breaking down the viscoelasticity of polymer networks and gels: Linking chemistry to mechanical response



I. Control of viscoelasticity with dynamic bonds



II. Measuring linear viscoelasticity with shear rheology



III. Nonlinear rheology

Bulk Rheometry to Examine Viscoelasticity

Measurements

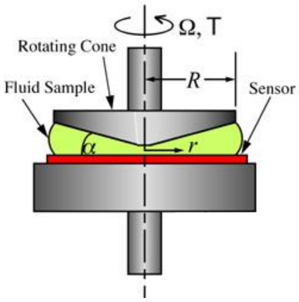
Load a sample between two surfaces.

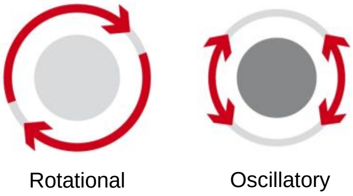
Rotate the top surface. → Measure the required **torque**.

Impose a certain **torque**. → Measure the resulting **rotation**.

Calculations

- Convert from **rotational measurements** and **torque** to material properties.
- Calculations depend on measurement type.



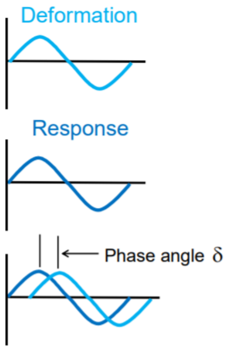


Soft Matter, School of Engineering and Applied Sciences, Harvard University; Basics of Rheology, Anton Paar.

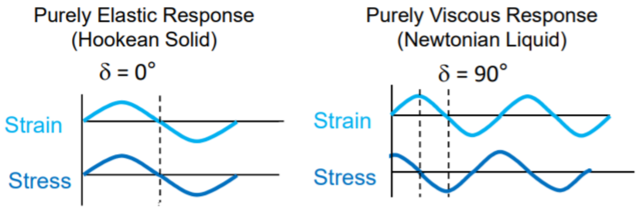
Phase Angle

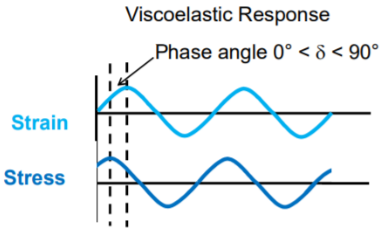
Experiment

- Impose a deformation.
- Measure a response.



Possible Results





$$G = \frac{\text{stress}}{\text{strain}}$$

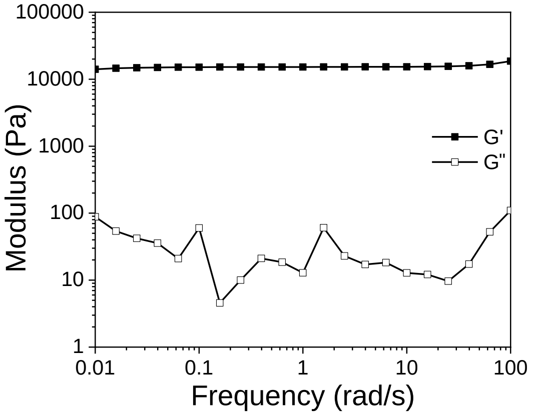
$$G' = \frac{\text{stress}}{\text{strain}} * \cos(\delta)$$

$$G'' = \frac{\text{stress}}{\text{strain}} * \sin(\delta)$$

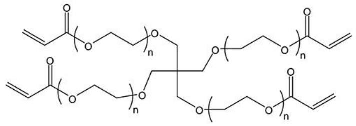
TA | TAINSTRUMENTS.COM

Rheology: Theory and Applications. TA Instruments (2019).

Elastic thiol-ene gels have frequency independent moduli

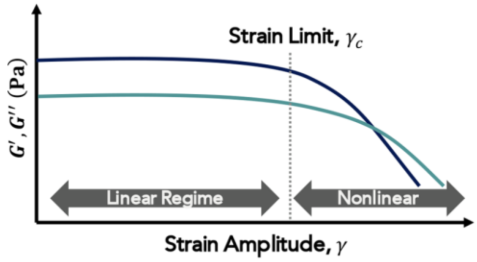


Rheology measurement taken at 1% strain



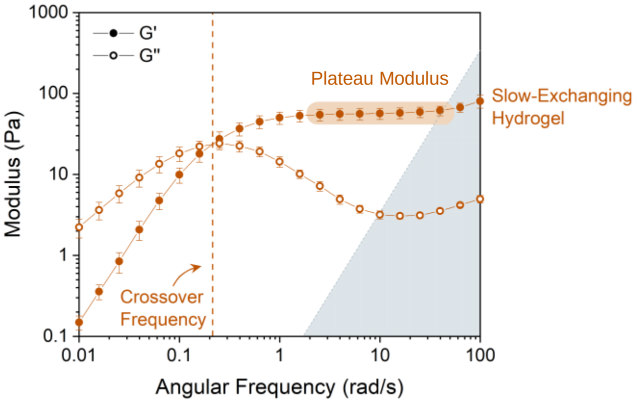
4-arm PEG-Acrylate

Amplitude sweep indicates linear viscoelastic regime:



FitzSimons, Anslyn, Rosales, and coworkers. *Macromolecules*, **2020**, 53(10), 3738-3746.

Reversible thiol-ene gels have frequency dependent moduli



Audience Survey Question

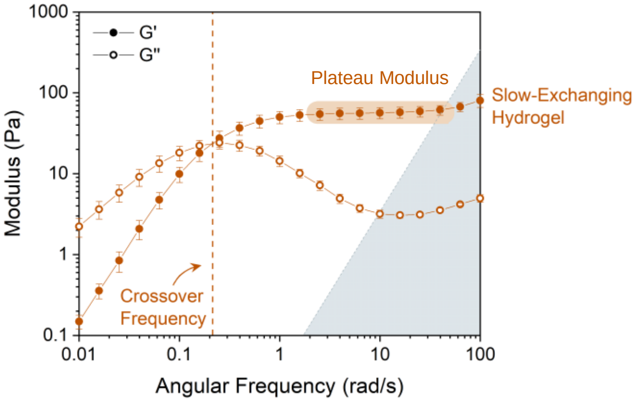
ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT

In general, how should the plateau modulus change if the dynamic bond equilibrium constant is higher?

a) Plateau modulus will increase
b) Plateau modulus will decrease
c) Plateau modulus will stay the same

FitzSimons, Anslyn, Rosales, and coworkers. *Macromolecules*, **2020**, 53(10), 3738-3746.
Crowell, FitzSimons, Anslyn, Schultz, Rosales. *Macromolecules,* **2023**.

Reversible thiol-ene gels have frequency dependent moduli



Audience Survey Question

ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT

In general, how should the crossover frequency change if the dynamic bond exchange kinetics are faster?

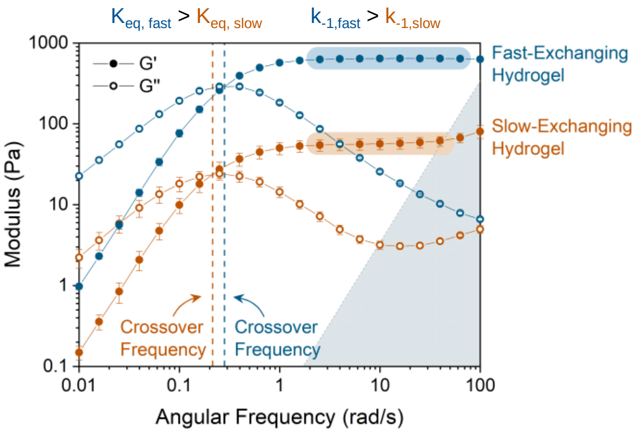
a) Crossover frequency will increase
b) Crossover frequency will decrease
c) Crossover frequency will stay the same

The University of Texas at Austin
McKetta Department of Chemical Engineering
Cockrell School of Engineering

FitzSimons, Anslyn, Rosales, and coworkers. *Macromolecules*, **2020**, 53(10), 3738-3746.
Crowell, FitzSimons, Anslyn, Schultz, Rosales. *Macromolecules,* **2023**.

ROSALES RESEARCH GROUP
at The University of Texas at Austin

Reversible thiol-ene gels have frequency dependent moduli



Frequency Dependence

- Indicates viscoelastic behavior

Plateau Storage Modulus, G'_∞

- G'_{fast} > G'_{slow}
- Tied to K_{eq}

Crossover Frequency, ω_{CO}

- $\omega_{CO,\ fast}$ > $\omega_{CO,\ slow}$
- Tied to stress relaxation and k_{-1}

The University of Texas at Austin
McKetta Department of Chemical Engineering
Cockrell School of Engineering

FitzSimons, Anslyn, Rosales, and coworkers. *Macromolecules*, **2020**, 53(10), 3738-3746.
Crowell, FitzSimons, Anslyn, Schultz, Rosales. *Macromolecules,* **2023**.

ROSALES RESEARCH GROUP
at The University of Texas at Austin

Simple constitutive models of linear viscoelasticity

Hooke's Law: $\sigma = G\gamma$

σ = stress
G = shear modulus
γ = strain

Newton's Law: $\sigma = \eta \frac{d\gamma}{dt} = \eta\dot{\gamma}$

σ = stress
η = viscosity
$\dot{\gamma}$ = strain rate (shear rate)

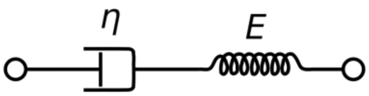
Interesting rheological properties arise when G and η are dependent on time and strain.

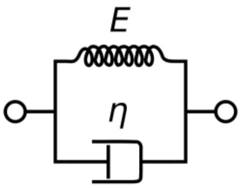
Simple constitutive models of linear viscoelasticity

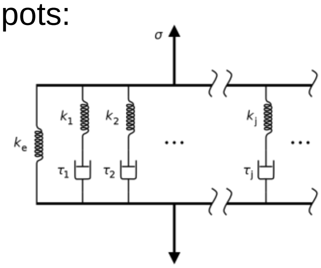
Spring (elastic component)

Dashpot (viscous component)

Models consist of linear combinations of springs and dashpots:

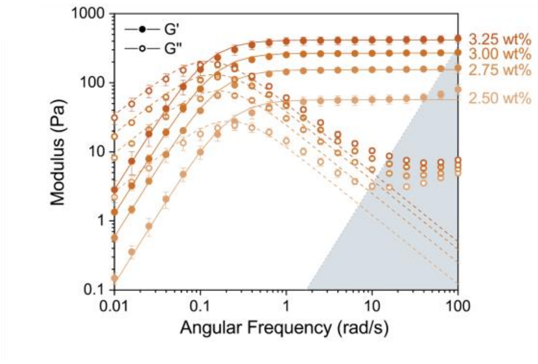




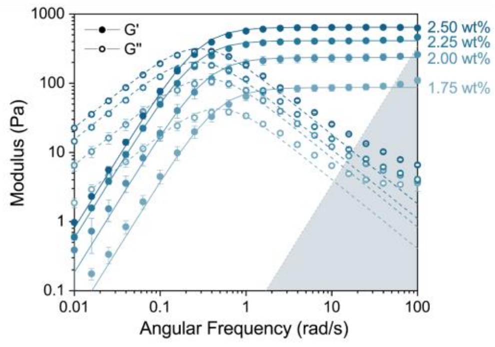


Frequency sweeps fit by single-mode Maxwell model

Slow-Exchanging Gel



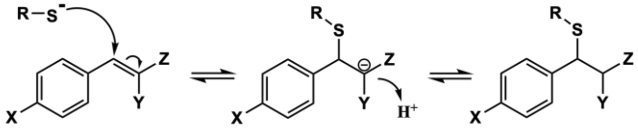
Fast-Exchanging Gel

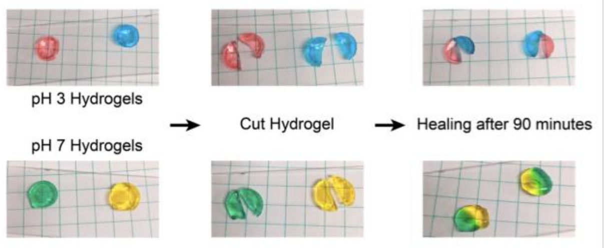


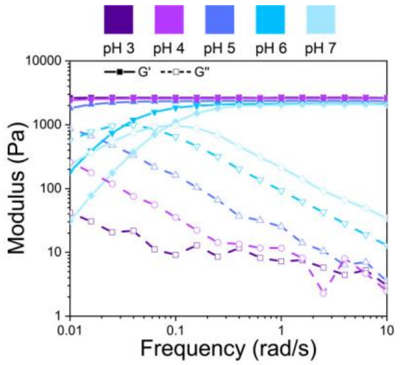
Indicates one type of relaxation process

FitzSimons, Anslyn, Rosales, and coworkers. *Macromolecules*, **2020**, 53(10), 3738-3746.
Crowell, FitzSimons, Anslyn, Schultz, Rosales. *Macromolecules,* **2023**.

Kinetics can be tuned via pH and temperature



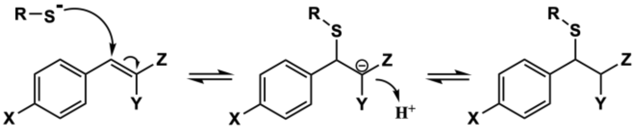


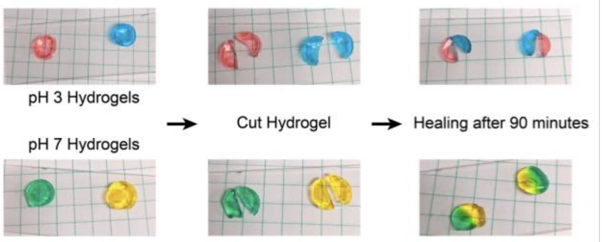


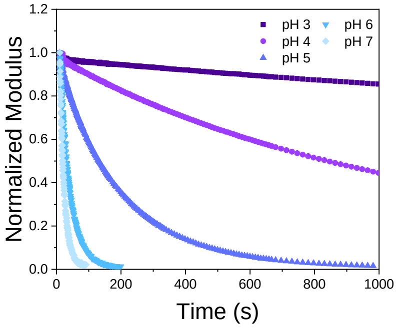
- Reverse reaction rate increases faster with pH
- Relaxation time is tunable over multiple orders of magnitude

FitzSimons, Anslyn, Rosales. *ACS Polymers Au,* **2021,** 2(2), 129-136.

Kinetics can be tuned via pH and temperature





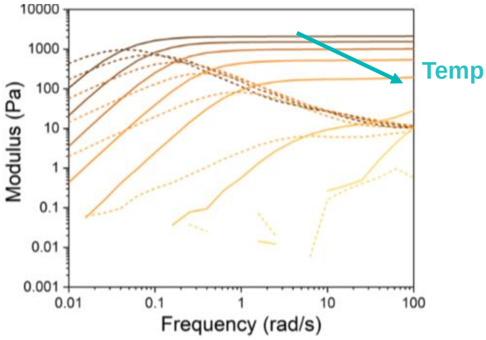


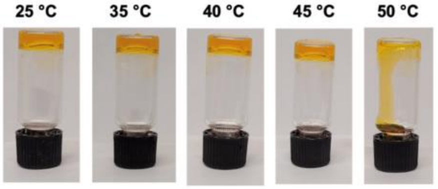
- Reverse reaction rate increases faster with pH
- Relaxation time is tunable over multiple orders of magnitude

FitzSimons, Anslyn, Rosales. *ACS Polymers Au,* **2021,** 2(2), 129-136.

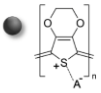
Viscoelasticity as a function of temperature

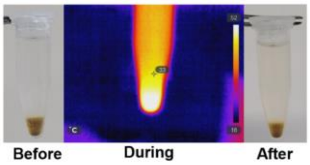
Gel-sol transition

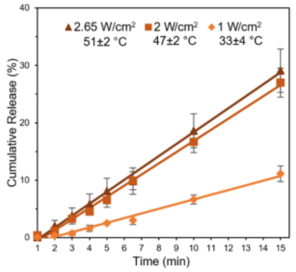




Photothermal response upon addition of PEDOT NPs





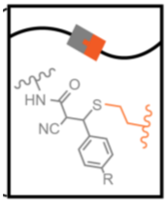


- More viscoelastic at elevated temperature
- Additional handle for therapeutic cargo release

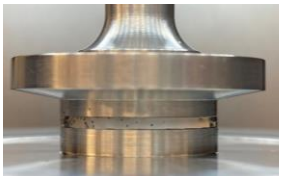
Tania Betancourt
Texas State University

Thapa, Rosales, Betancourt, et al. *Submitted,* **2023.**

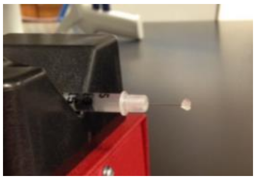
Breaking down the viscoelasticity of polymer networks and gels: Linking chemistry to mechanical response



I. Control of viscoelasticity with dynamic bonds



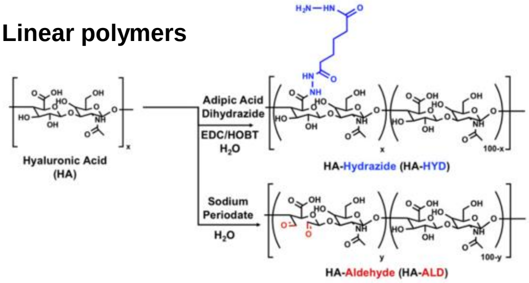
II. Measuring linear viscoelasticity with shear rheology

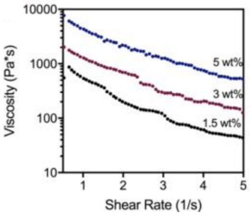


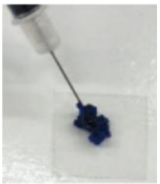
III. Nonlinear rheology

Dynamic covalent bonding enables injectability

Linear polymers

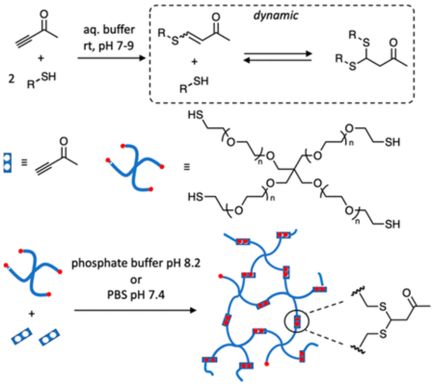






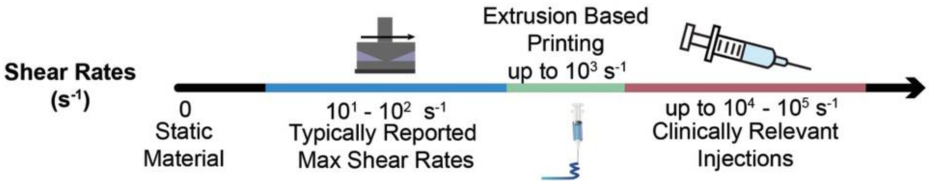
Wang, et al. *JBMR.* **2018**, 106(4).

Multi-arm polymers



ACS Macro Lett. **2020**, 9(6), 776–780.

Material properties at various shear rates



Shear Rates (s^{-1})

0
Static
Material

10^1 - 10^2 s^{-1}
Typically Reported
Max Shear Rates

Extrusion Based
Printing
up to 10^3 s^{-1}

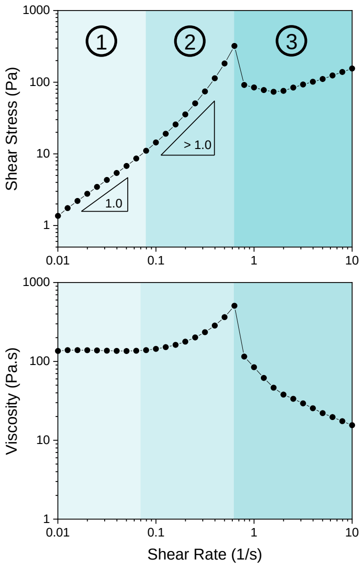
up to 10^4 - 10^5 s^{-1}
Clinically Relevant
Injections

Experimental Design

- Use hydrogels with different bond exchange kinetics and concentrations to access a range of material properties.
- Characterize material properties at shear rates relevant to 3D printing and injection.

Lopez Hernandez, H. et al. (2020) *Macromol. Biosci.*

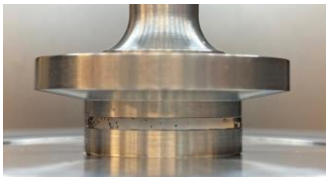
Rheological properties under steady shear



The rheological properties of the hydrogels depend on the shear rate.

1) Newtonian →

2) Shear thickening

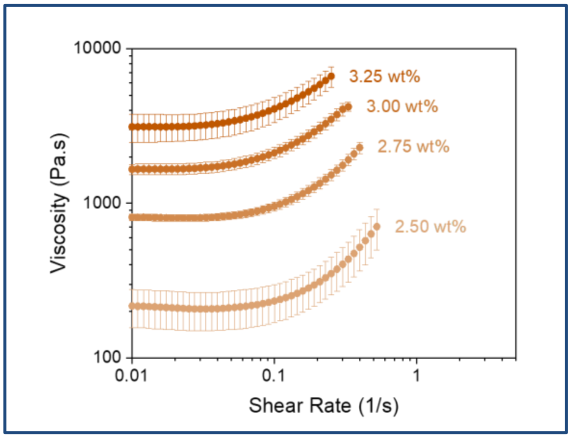


3) Flow instability and material expulsion ↓

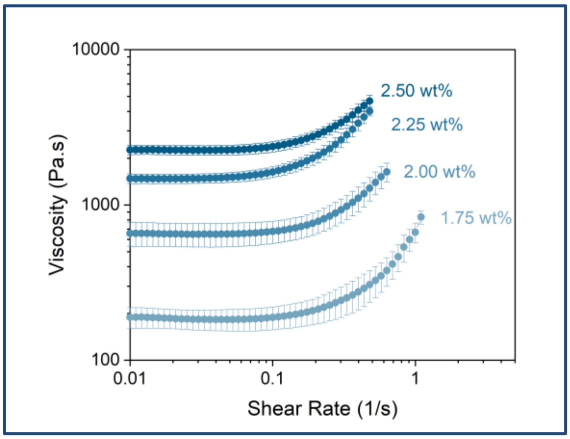
Crowell, FitzSimons, Anslyn, Schultz, Rosales. *Macromolecules,* **2023**.

Reversible thiol-ene gels below c* are shear-thickening

Slow-Exchanging Gel



Fast-Exchanging Gel

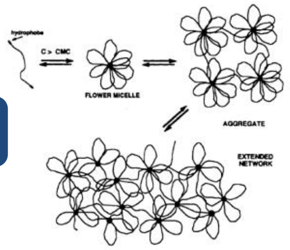


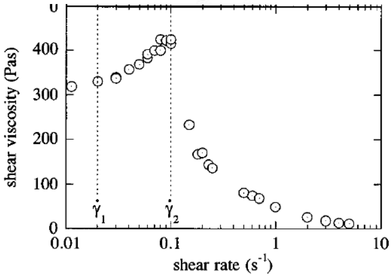
Shear thickening behavior is observed at experimentally accessible shear rates.

Crowell, FitzSimons, Anslyn, Schultz, Rosales. *Macromolecules,* **2023**.

Shear thickening in other systems

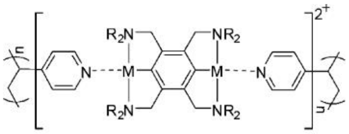
Telechelic polymers





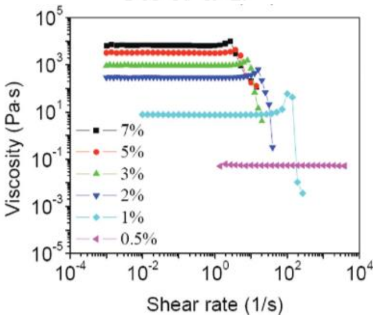
Xu, Craig, et al. *Macromolecules* **2010**

Linear associative polymers



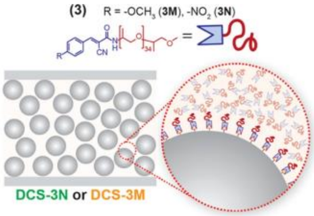
1 M= Pd R= Me

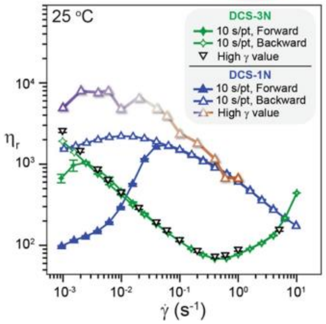
2 M= Pd R= Et



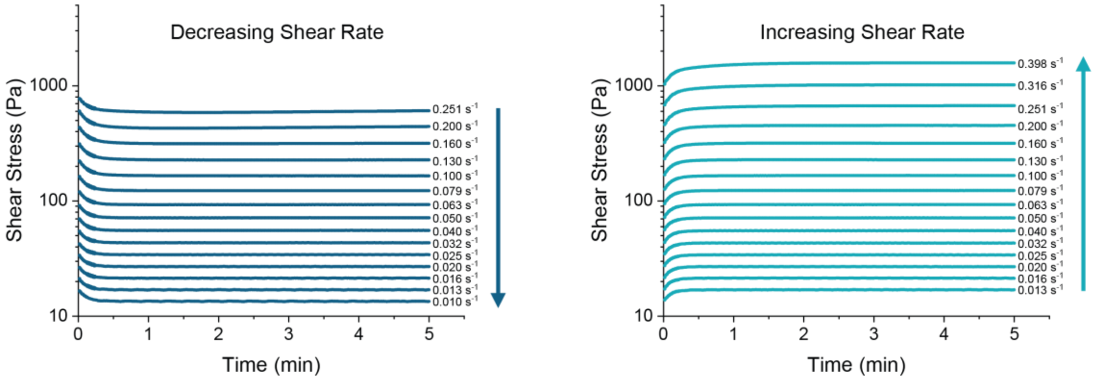
Jaeger, et al. *Macromolecules* **2022**

Dense suspensions





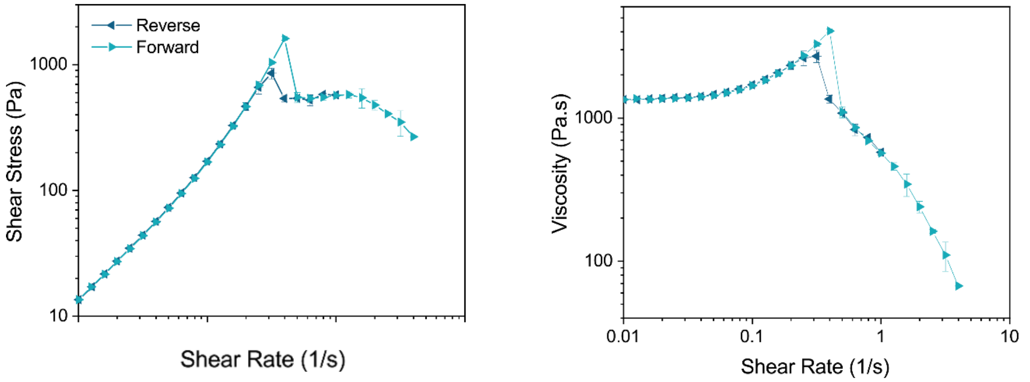
Transient shear data shows thickening is reversible



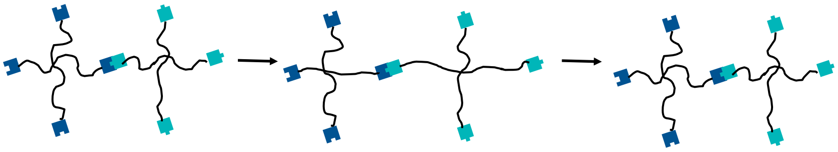
- Measured shear stress as a function of time at different shear rates
- Ensured each measurement reached steady state

Crowell, FitzSimons, Anslyn, Schultz, Rosales. *Macromolecules,* **2023**.

Transient shear data shows thickening is reversible

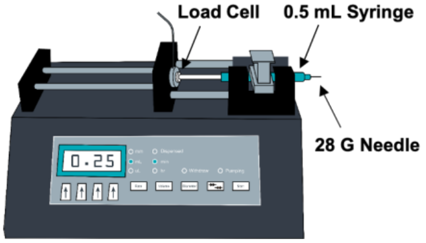


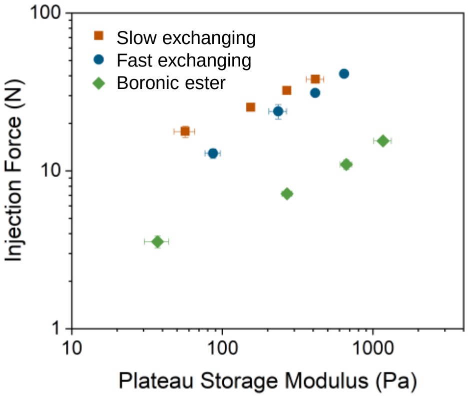
Suggests that chain stretching plays a key role

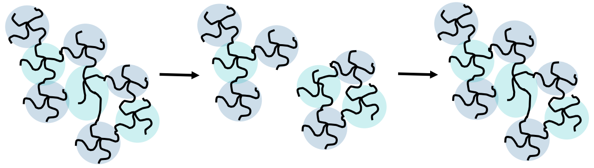


Crowell, FitzSimons, Anslyn, Schultz, Rosales. *Macromolecules,* **2023**.

What does this imply for injectability?



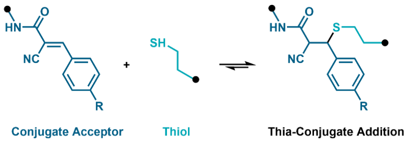


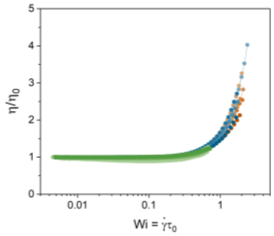


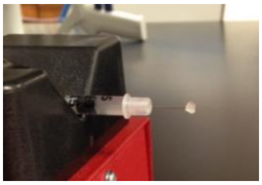
Clinically-relevant injection forces are typically < 50 N

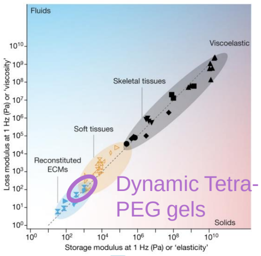
Crowell, FitzSimons, Anslyn, Schultz, Rosales. *Macromolecules,* **2023**.

Summary: viscoelasticity depends on dynamic chemistry









Nanoscale ***Macroscale***

- Dynamic chemistry allows for molecular rearrangement under stress → viscoelastic materials!
- Linear viscoelasticity: applicable for small deformations
- Nonlinear viscoelasticity: larger deformations
- Biological tissues are viscoelastic

Acknowledgements

Group
Thomas FitzSimons, PhD
Logan Morton
Anne Crowell
Darren Loh
Katie Halwachs
Carolyn Watkins
Sam West
Aldaly Pineda-Hernandez
David Castilla Casadiego, PhD
Nate Conrad, PhD

Collaborators
Eric Anslyn
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Nate Lynd
Janet Zoldan
Keith Keitz
Kelly Schultz, Lehigh

Lilly
NSF
3M

BURROUGHS WELLCOME FUND
NIH NIGMS
CDCM Center for Dynamics and Control of Materials: an NSF MRSEC

The University of Texas at Austin
McKetta Department of Chemical Engineering
Cockrell School of Engineering

ROSALES RESEARCH GROUP
at The University of Texas at Austin

59

THE UNIVERSITY *of* NORTH CAROLINA *at* CHAPEL HILL

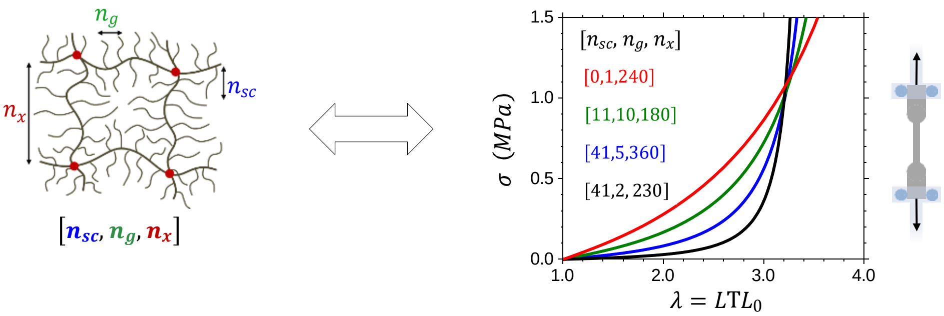
ACS Webinars

NSF

Encoding network mechanics by architecture

Sergei S. Sheiko

University of North Carolina at Chapel Hill



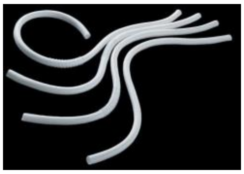
60

Motivation: Materials with tissue-mimetic mechanical properties

Medical

Wound closure

Vascular



Reconstructive

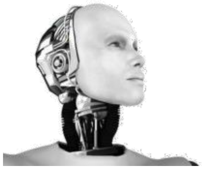
Orthopedics

Non-medical

Impact absorbers

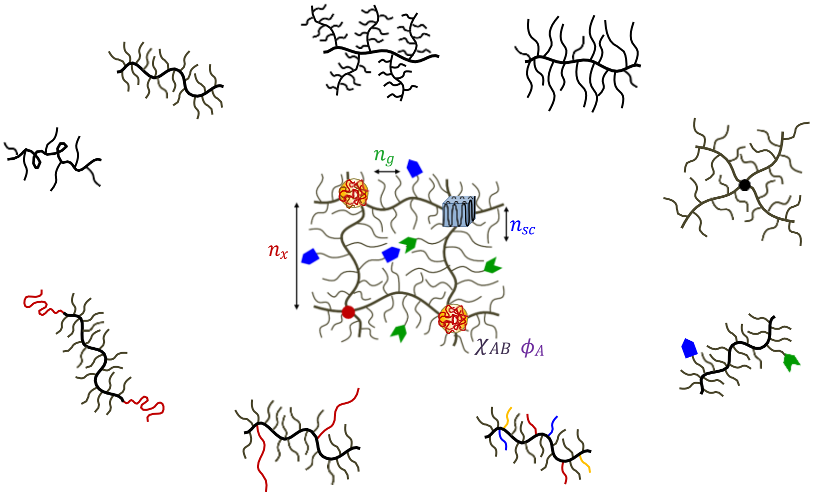
Adhesives

Soft Robotics



Waterproof sealants

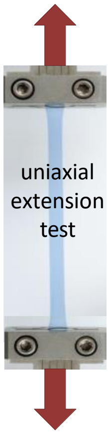
Our Approach: Design-by-Architecture

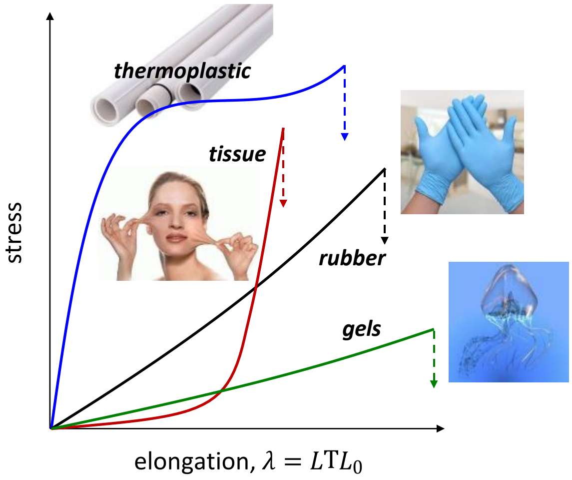


architectural code: $[n_{sc}, n_g, n_{bb}, \phi_A, N_A, \chi_{AB}, \ldots]$

Challenge: Controlling properties at constant chemical composition

Mimicking tissue mechanics is challenging





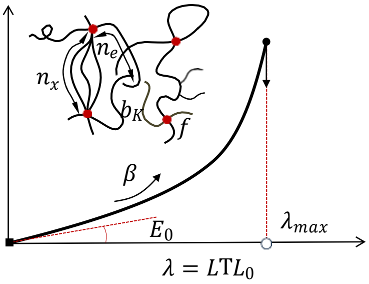
Tissues combine very distinct mechanical properties:

soft-yet-firm and elastic-yet-damping

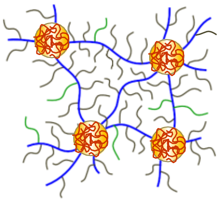
Outline

1. Mechanical properties
   - Definitions
   - Equilibrium vs apparent
   - Equation of state
   - Data analysis
   - Forensics of polymer networks

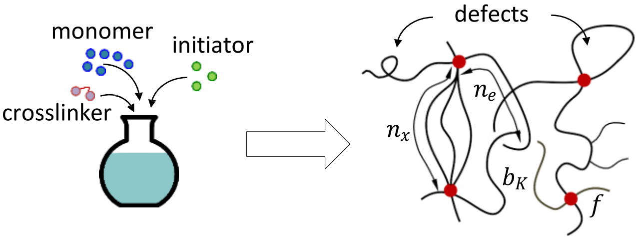
$$\frac{\sigma(\lambda)}{\lambda^2-\lambda^{-1}} == \frac{G}{3}\left[1+2\left(1-\frac{\beta I_1(\lambda)}{3}\right)^{-2}\right]$$



2. Encoding mechanical properties in architecture
   - Disentanglement
   - Architectural code
   - Super-soft elastomers
   - Decoupling modulus, elongation-at-break, and swelling ratio



Synthesis of a polymer network



n_x - degree of polymerization of network strand

n_e - degree of polymerization of entanglement strand

b_K - Kuhn length (strand flexibility)

f - crosslink functionality

Q1: What do we know about the structure of a synthesized network? (select all that apply)

- a) We know n_x
- b) We know f
- c) We know b_K
- d) We know n_e
- e) We know fraction of defects

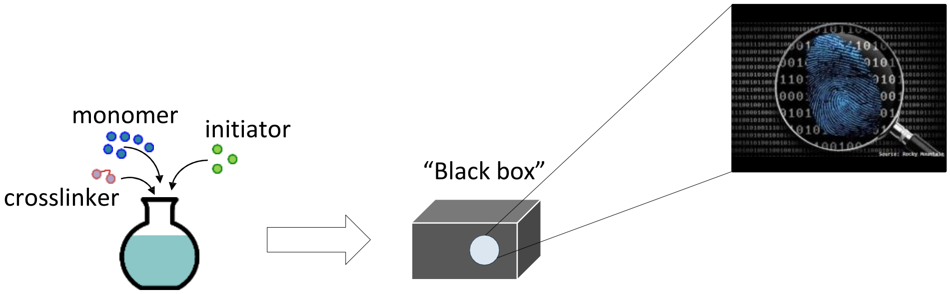
Audience Survey Question

ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT

A1: We know nothing.

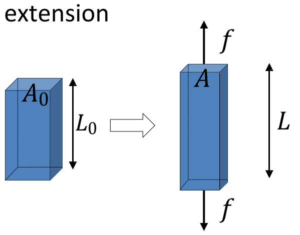
Polymer networks are a black box sealed by a stochastic crosslinking process.

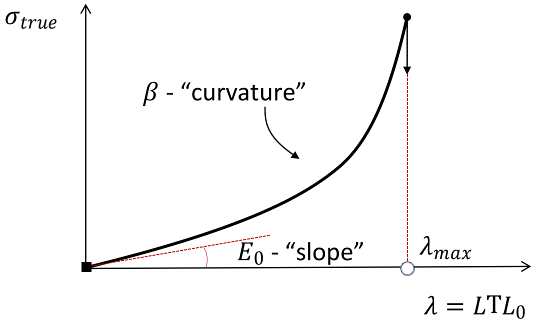
Forensics of polymer networks?



Mechanical properties: Definitions

Uniaxial extension





Strain: $\varepsilon = \frac{L - L_0}{L_0} = \frac{L}{L_0} - 1$

Elongation: $\lambda = \frac{L}{L_0} = 1 + \varepsilon$

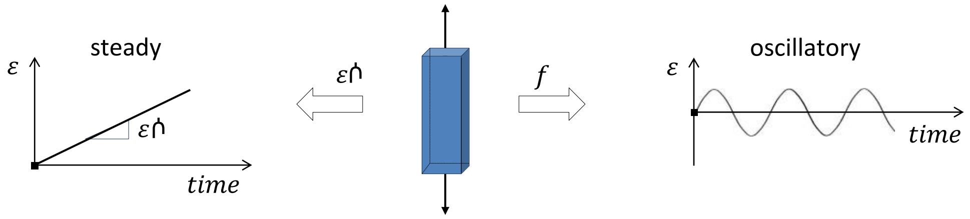
True stress: $\sigma_{true} = \frac{f}{A}$

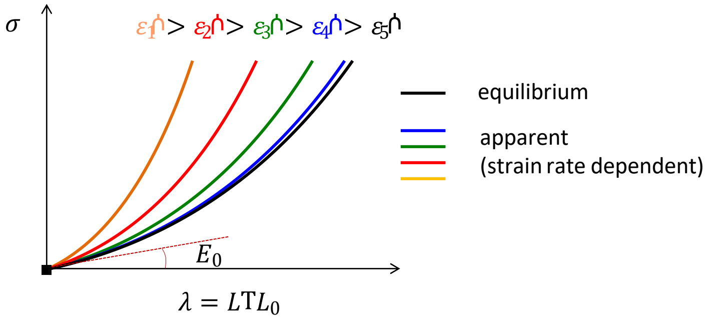
Engineering stress: $\sigma_{eng} = \frac{f}{A_0}$

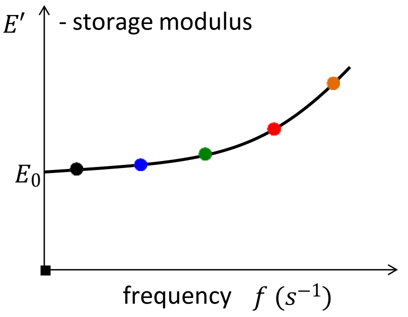
$E_0 = \frac{\partial\sigma}{\partial\lambda}\Big|_{\lambda\to1}$ - Young's modulus

β - strain-stiffening or firmness parameter

Mechanical properties: Equilibrium vs. apparent

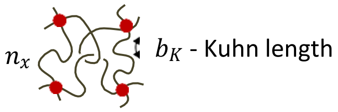




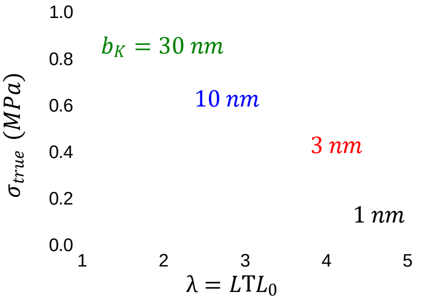


We will talk about equilibrium properties first.

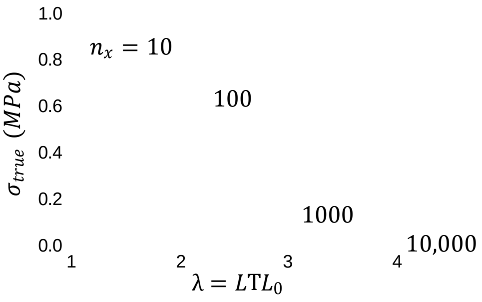
Effect of network structure on elastic response



effect of Kuhn length @ $n_x = 500$



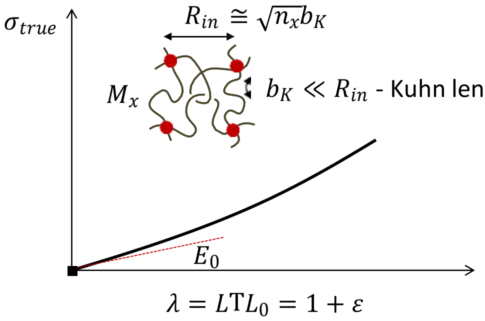
effect of crosslink density @ $b_K = 1\ nm$



Q2: Can we get n_x and b_K from a stress-strain curve?

A2: It should be possible. But how to extract this information from a stress-strain curve? The answer to this question is hidden in the equation of state.

Equation of state: Flexible chains



R_{in} - end-to-end distance before stretching (initial)

$M_x = M_0 n_x$ - molar mass of network strand

n_x - degree of polymerization of network strand

Approximation for flexible chains ($R_{in} \gg b_K$):

$$\sigma_{true}(\lambda) = G(\lambda^2 - \lambda^{-1}) \xrightarrow{\varepsilon \ll 1} \sigma(\varepsilon) = 3G\varepsilon$$

shear modulus:

$$G \cong \frac{\rho RT}{M_x} = \frac{RT}{V_x} = \frac{RT}{N_{av} v_x} = \frac{k_B T}{v_x} = \rho_x k_B T$$

ρ_x - number of strands per unit volume

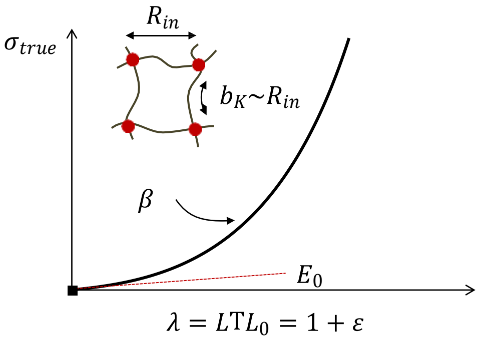
Young's modulus

$$E_0 = 2(1+v)G \xrightarrow{v \cong 0.5} E_0 \cong 3G$$

$$v = -\frac{d\varepsilon_\perp}{d\varepsilon_\parallel}$$ - Poisson ration

$$\sigma(\varepsilon) = 3G\varepsilon \xrightarrow{v \cong 0.5} \sigma(\varepsilon) \cong E_0\varepsilon$$

Equation of state: Semiflexible chains



$$\langle R_{in}^2 \rangle = l_p R_{max} - 2 l_p^2 \left(1 - e^{-\frac{R_{max}}{l_p}}\right)$$

$l_p = \frac{b_K}{2}$ - persistence length of a strand

$R_{max} = n_x l$ - contour length of a strand

A. V. Dobrynin et al., *Macromolecules* 44, 140 (**2011**)

Full equation including semiflexible chains ($R_{in} \sim b_K$):

$$\sigma_{true}(\lambda) = \frac{G}{3}(\lambda^2 - \lambda^{-1})\left[1 + 2\left(1 - \frac{\beta I_1(\lambda)}{3}\right)^{-2}\right]$$

$I_1(\lambda) = \lambda^2 + 2\mathrm{T}\lambda$ - first invariant

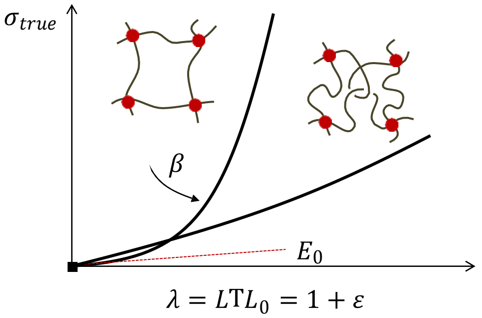
Mechanical characteristics:

$G \cong \frac{\rho RT}{M_x}$ - structural modulus

$\beta = \frac{R_{in}^2}{R_{max}^2} \cong \frac{b_K}{R_{max}}$ - strain-stiffening (firmness)

$E_0 = G\left(1 + \frac{2}{(1-\beta)^2}\right)$ - Young's modulus at $\lambda \to 1$

Equation of state: Transition from semiflexible to flexible



Young's modulus depends on chain flexibility (b_K) as

$$E_0 = G\left(1 + \frac{2}{(1-\beta)^2}\right)$$

For flexible chains, E_0 is defined by crosslink density

$$E_0 \cong 3G$$

Full equation including semiflexible chains ($R_{in} \sim b_K$):

$$\sigma_{true}(\lambda) = \frac{G}{3}(\lambda^2 - \lambda^{-1})\left[1 + 2\left(1 - \frac{\beta I_1(\lambda)}{3}\right)^{-2}\right]$$

$$E_0 = G\left(1 + \frac{2}{(1-\beta)^2}\right)$$

flexible strands ($R_{in} \gg b_K$):

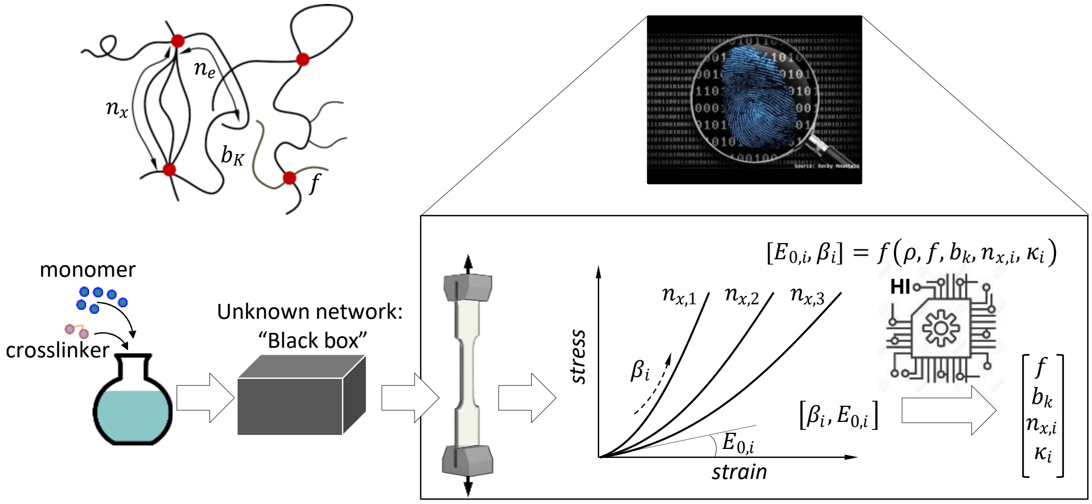
$$\beta \cong \frac{b_K}{R_{max}} \to 0$$

Approximation for flexible chains ($R_{in} \gg b_K$):

$$\sigma_{true}(\lambda) = G(\lambda^2 - \lambda^{-1})$$

$$E_0 \cong 3G$$

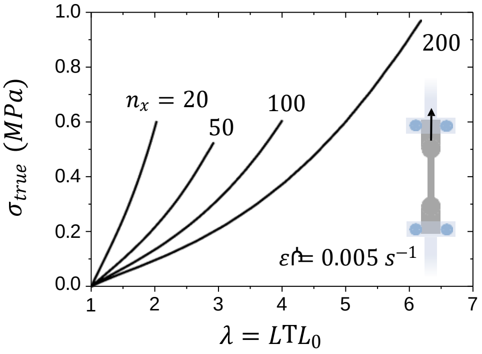
Forensics of polymer networks

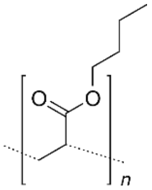


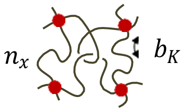
Extracting network structure from the non-linear response to deformation

Nature Materials 22, 1394 (**2023**)

Pol(*n*-butyl acrylate) networks with different crosslink densities







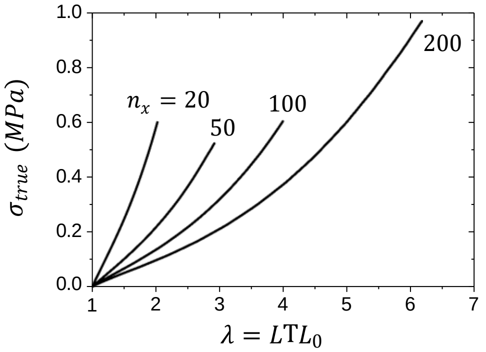
Targeted n_x

n_x
20
50
100
200

Two issues:

- actual n_x is unknown (Note: the indicated n_x values are targeted ones)
- Kuhn length (b_K) is unknown

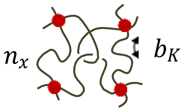
Fitting analysis



Fitting with the equation of state (red dashed lines)

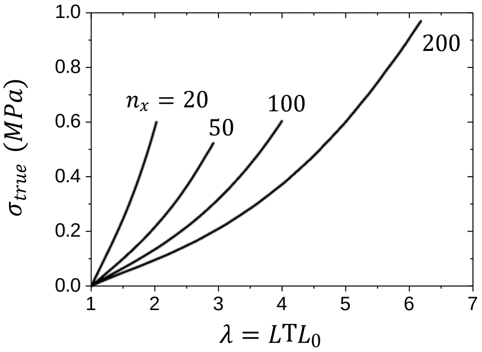
$$\sigma_{true}(\lambda) = (\lambda^2 - \lambda^{-1})\left(\frac{G_e}{\lambda} + \frac{G}{3}\left(1 + 2\left(1 - \frac{\beta(\lambda^2 + 2\lambda^{-1})}{3}\right)^{-2}\right)\right)$$

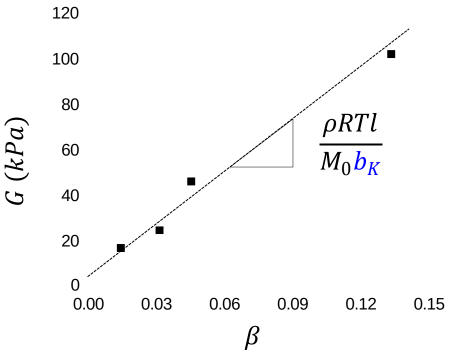
$$E_0 = \frac{G}{3}\left(1 + \frac{3G_e}{G} + 2(1-\beta)^{-2}\right)$$



n_x	$G\ (kPa)$	$G_e\ (kPa)$	β	$E_0\ (kPa)$
20	102.4	36.3	0.133	483.8
50	46.5	20.2	0.045	209.1
100	25.1	23.5	0.031	149.1
200	17.3	18.3	0.014	107.8

Pol(*n*-butyl acrylate) networks with different crosslink densities





$$G \cong \frac{\rho RT}{M_x} \cong \frac{\rho RT}{M_0 n_x}$$

$$\beta = \frac{R_{in}^2}{R_{max}^2} \cong \frac{b_K}{R_{max}} \cong \frac{b_K}{n_x l}$$

$$G \cong \frac{\rho RTl}{M_0 b_K}\beta$$

PBA:

$M_0 = 128\ gTmol$

$\rho = 1.08\ gTcm^3$

$l = 0.25\ nm$

$R = 8.31\ JTmol \cdot K$

$T = 298\ K$

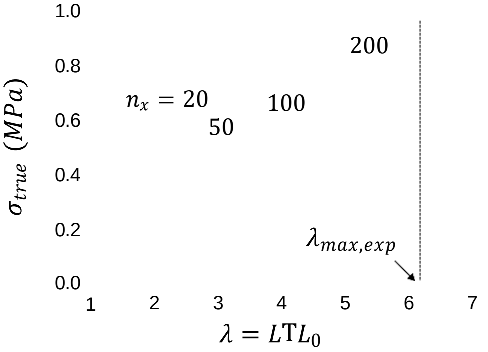
$b_K = 1.8 \pm 0.1\ nm$

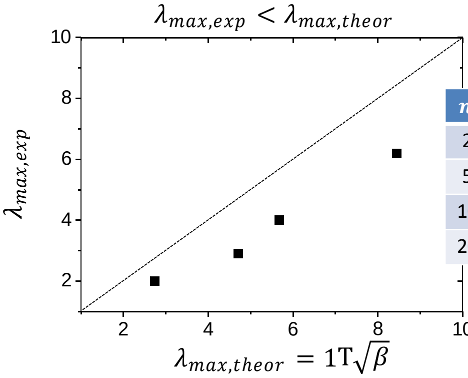
$$n_x \cong \frac{b_K}{\beta l}$$

$n_{x.targ}$	$n_{x.act}$
20	54
50	160
100	232
200	514

Two measured properties (G and β) give two network parameters (n_x and b_K)

Elongation-at-break: expected vs. measured





n_x	λ_{theor}	λ_{max}
20	2.7	2.0
50	4.7	2.9
100	5.7	4.0
200	8.5	6.2

strain-stiffening parameter:

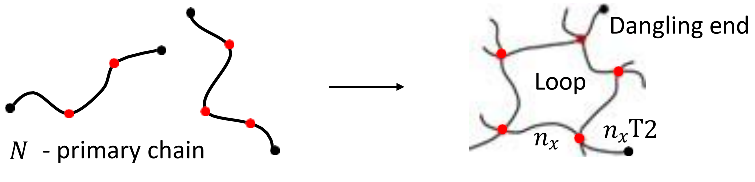
$$\beta \equiv \frac{R_{in}^2}{R_{max}^2}$$

strand elongation:

$$\lambda_{max,theor} \cong \frac{R_{max}}{R_{in}} \cong \frac{1}{\sqrt{\beta}}$$

Experimental elongation-at-break is always lower than the theoretical one due to molecular and macroscopic defects.

Real networks have defects

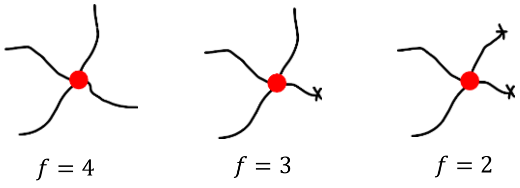


The dangling ends not only influence the density of the stress-supporting strands but also decrease the effective crosslink functionality.

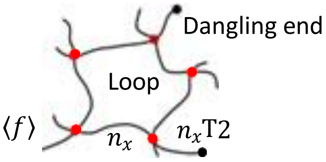
tetrafunctional crosslinks:

$$\langle f \rangle = 4 - \frac{2(N_c + 2)}{N_c^2 - 2N_c + 4}$$

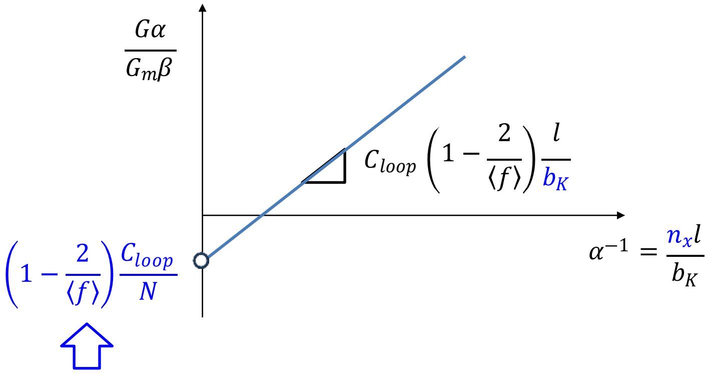
$$N_c = N/n_x$$



Forensics or real networks



$$\frac{G\alpha}{G_m\beta} = \left(1-\frac{2}{\langle f\rangle}\right) C_{loop}\left(\frac{l}{b_K}\alpha - \frac{1}{N}\right)$$



f, N, C_{loop} are difficult to decouple without additional information

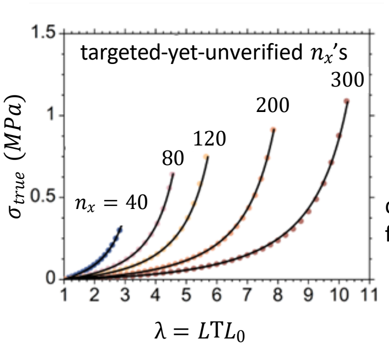
Nature Materials 22, 1394 (**2023**)

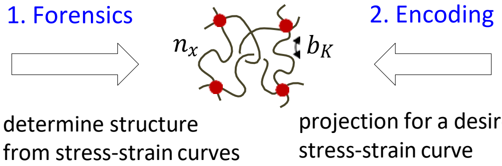
What we have learnt so far

Equation of state:

$$\sigma_{true}(\lambda) = (\lambda^2-\lambda^{-1})\left(\frac{G_e}{\lambda}+\frac{G}{3}\left(1+2\left(1-\frac{\beta(\lambda^2+2\lambda^{-1})}{3}\right)^{-2}\right)\right)$$

Two uses of the equation:



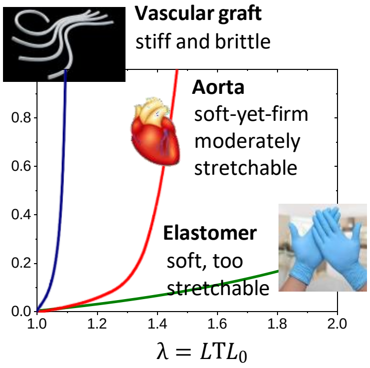


1. Forensics

determine structure from stress-strain curves

2. Encoding

projection for a desired stress-strain curve

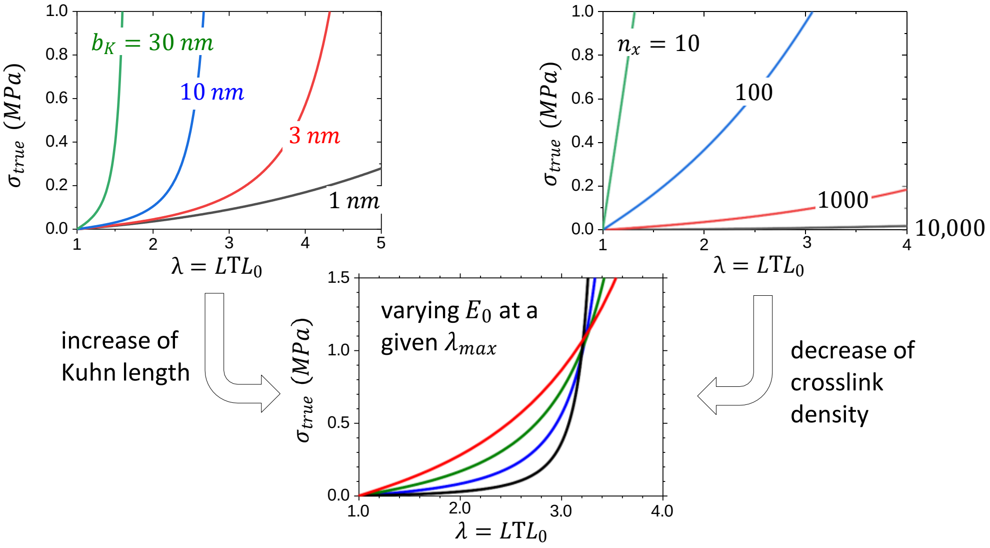


Vascular graft
stiff and brittle

Aorta
soft-yet-firm
moderately
stretchable

Elastomer
soft, too
stretchable

Network elasticity is controlled by two parameters: b_K and n_x



increase of Kuhn length

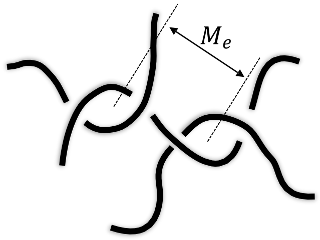
decrease of crosslink density

Two problems:

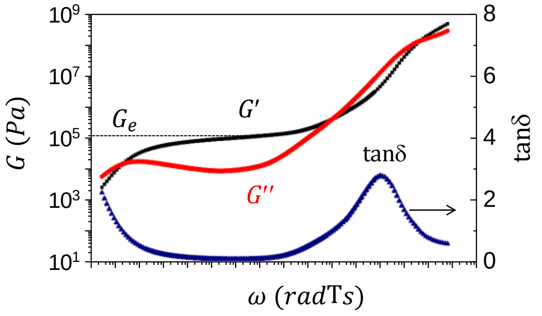
- low crosslink density is impeded by chain entanglements
- b_K variation requires change of chemical composition

Entanglement plateau modulus

Chain entanglements



Linear pBA melt (M_n=1.2·10^6)

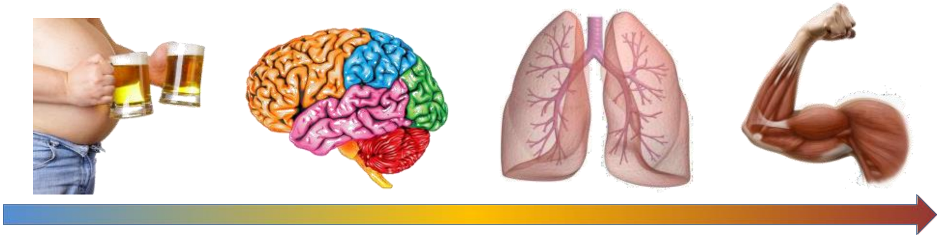


It is challenging to make materials softer than the entanglement modulus:

$$G_e \cong \frac{\rho RT}{M_e} \cong 10^5\ Pa \qquad M_e \cong 10^4\ gTmol$$

Soft tissues are much softer than the entanglement modulus

$$\boldsymbol{E = 10\,Pa - 1\,MPa}$$



Fat 0.02 kPa
Gland 0.1 kPa

Brain 0.3 kPa
Liver 0.5 kPa

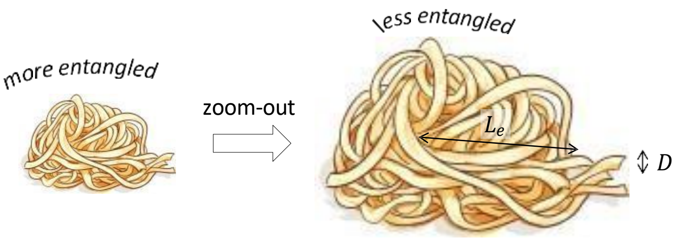
Kidney 2 kPa
Lung 5 kPa

Muscle 10-100 kPa
Tendon 300 kPa
Cartilage 1000 kPa

Q: How to disentangle chains?

Making molecules fatter…

Entanglement modulus: $G_e \cong \dfrac{\rho RT}{M_e} \cong \dfrac{RT}{V_e} \cong \dfrac{RT}{DL_e}$



Is the problem solved? Not quite… because $D \uparrow$ results in $b_K \uparrow$

Audience Survey Question

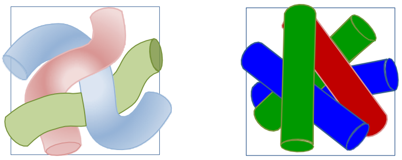
ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT

Q: What is more entangled: flexible or rod-like molecules?

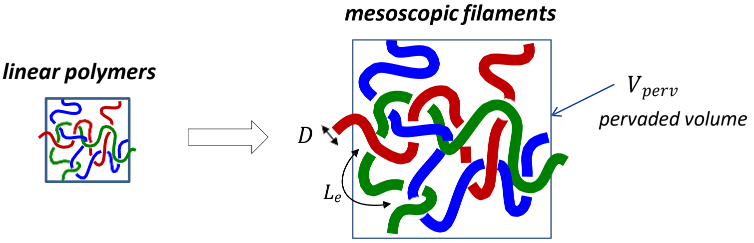
a) Flexible molecules

b) Rod-like molecules

c) They are equally entangled



Fat molecules: dilution vs. rigidity



Plateau modulus

$$G_e \cong \frac{\rho RT}{M_e} \cong \frac{k_B T}{V_e} \cong \frac{k_B T}{L_e D}$$

Kavassalis-Noolandi conjecture

$$P_e \cong \frac{V_{perv}}{V_e} \cong \frac{(L_e b)^{3T2}}{L_e D^2} \cong 20$$

$$G_e \cong \frac{k_B T}{L_e D^2} \sim \frac{b^3}{P_e^2 D^6} \sim \frac{b^3}{D^6}$$

rigidity (Kuhn length)

dilution (monomer size)

"dilution" is not enough… rigidity matters!

Rigidity of filaments

Filament diameter

$D \sim M_L^{\ 1T2}$

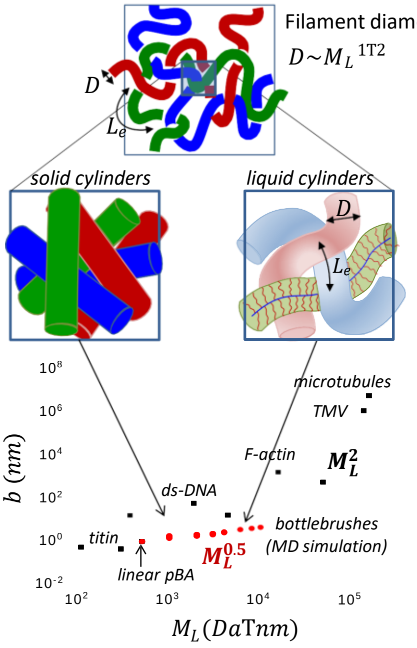
Energetic rigidity

Kuhn length

$b \cong D^4$

$G_e \sim \frac{b^3}{D^6} \sim D^6$

rigid filaments are more entangled



Entropic flexibility

Kuhn length

$b \cong D$

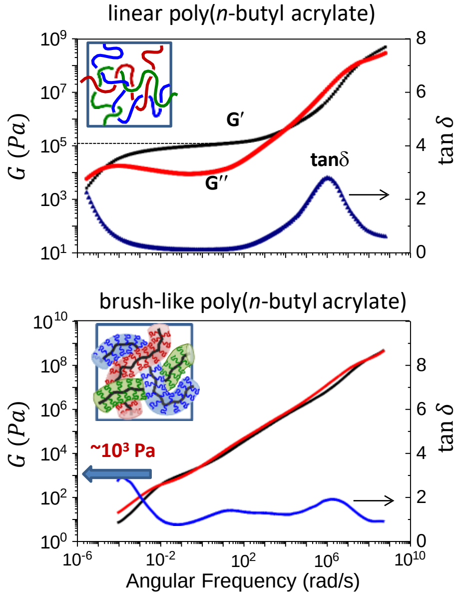
$G_e \sim \frac{b^3}{D^6} \sim D^{-3}$

$D \sim \sqrt{n_{sc}}$

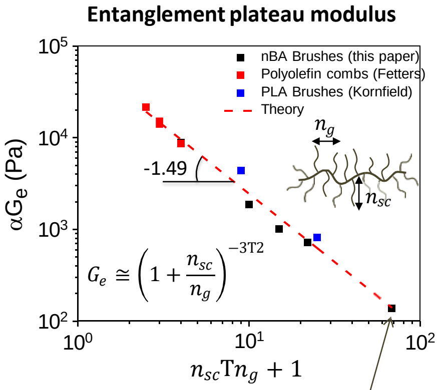
Bottlebrushes

$G_e \sim n_{sc}^{\ -3T2}$

Architecturally disentangled polymer melts


linear poly(*n*-butyl acrylate)

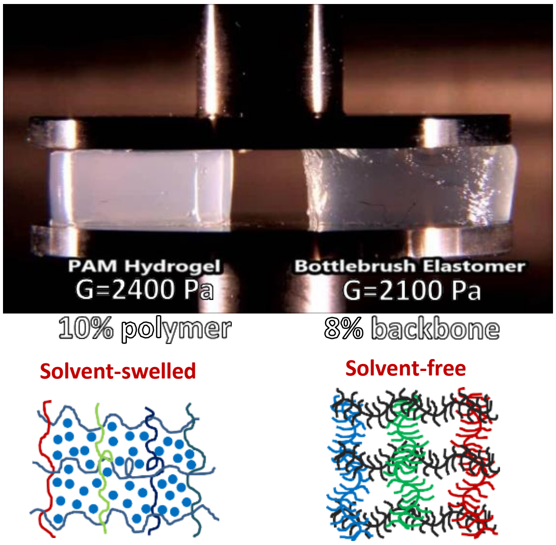
brush-like poly(*n*-butyl acrylate)


Entanglement plateau modulus

The entanglement modulus is dropped down to 100 Pa (the modulus of fat tissue)!

Nature Mater. **2016**, *15*, 183

Fat and Flexible Macromolecules Give Ultra-Soft, Super-Elastic Solvent-free Materials



Nature Mater. 15, 183 (**2016**)

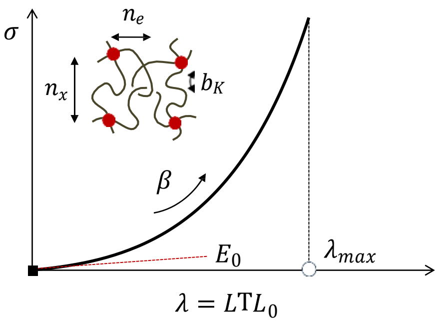
Controlling properties by architecture

Chemical code: $[l, v, b, \tau_0]$
- monomer length: l
- monomer volume: v
- chain flexibility: b
- monomer relaxation time: τ_0

Architectural code: $[n_x]$

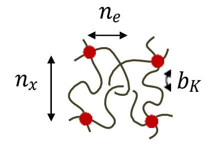
single parameter!

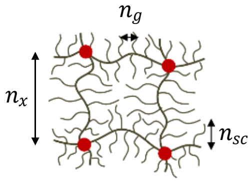
Kuhn length	$b_K = b \sim 1\ nm$
Entanglement DP	$n_e \cong P_e^2 \frac{v^2}{(bl)^3} \sim 100$
Modulus	$E_0 \cong 3G \cong \frac{k_B T}{v n_x}$
Strain-stiffening and elongation-at-break	$\beta \cong \frac{1}{\lambda_{max}^2} = \frac{b}{n_x l}$
Rouse time	$\tau_R \cong \tau_0 n_x^2$



All properties of linear polymer networks are coupled: They cannot be varied independently of one another without changing chemistry

Controlling properties by architecture





Architectural code:

$[n_{sc}, n_g, n_x]$

multiple parameters

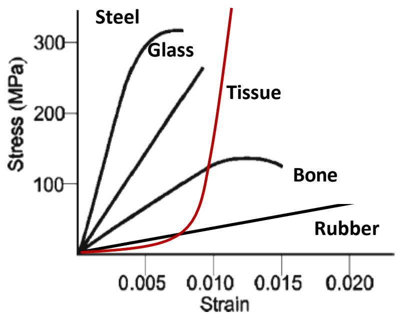
Kuhn length	$b_K = b \sim 1\ nm$	$b_K = \frac{v}{l^{3T2} b^{1T2}} \frac{1 + n_{sc} T n_g}{n_{sc}^{1T2}} \sim 10\ nm$
Entanglement DP	$n_e \cong P_e^2 \frac{v^2}{(bl)^3} \sim 100$	$n_e \cong \left(\frac{b}{b_K}\right)^3 \left(1 + \frac{n_{sc}}{n_g}\right)^2 n_{e,lin} \sim 1000$
Modulus	$E_0 \cong 3G \cong \frac{k_B T}{v n_x}$	$G \cong \frac{k_B T}{v n_x (1 + n_{sc} T n_g)}$
Strain-stiffening and elongation-at-break	$\beta \cong \frac{1}{\lambda_{max}^2} = \frac{b}{n_x l}$	$\beta \cong \frac{v}{l^{5T2} b^{1T2}} \frac{1 + n_{sc} T n_g}{n_x n_{sc}^{1T2}}$
Rouse time	$\tau_R \cong \tau_0 n_x^2$	$\tau_R \cong \tau_0 \frac{n_{sc}}{n_g^2} n_x^2$

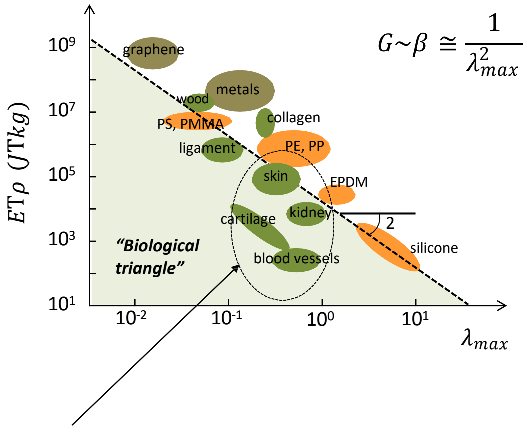
All properties are coupled through n_x

decoupled: can be varied independently of one another for a given chemistry

"Golden" rule: Stiffer materials are less flexible

From a textbook:

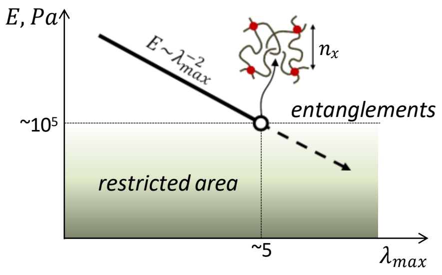


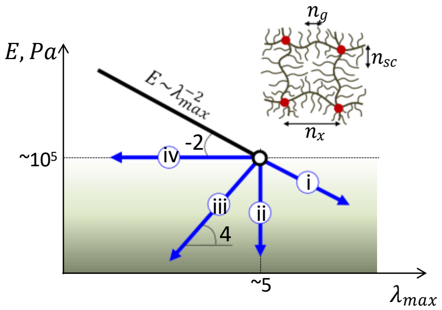


$$G \sim \beta \cong \frac{1}{\lambda_{max}^2} = \frac{b}{n_x l}$$

Biological tissues do no follow the rule: Independently varying stiffness and extensibility

Breaking the “Golden rule”





Linear-chain elastomers:

$$G \cong \frac{\rho RT}{m_o n_x} \sim \frac{1}{n_x}$$

$$\lambda_{max} \cong \frac{R_{max}}{R_0} \sim \sqrt{n_x}$$

$$G \sim \frac{1}{\lambda_{max}^2}$$

λ_{max} ↓ with G

“golden rule”

Bottlebrush elastomers:

$$G \sim \frac{n_g}{n_x n_{sc}}$$

$$\lambda_{max} \cong \frac{n_g^{1T4}}{n_{sc}^{1T4}} n_x^{1T2}$$

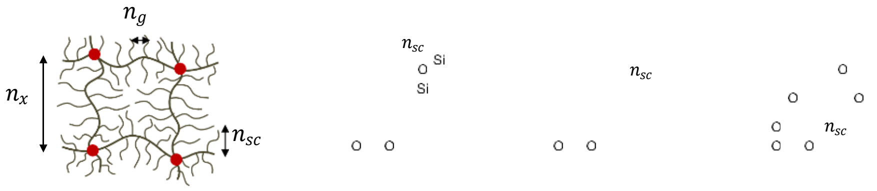
$$G \sim \lambda_{max}^4$$

λ_{max} ↑ with G

G and λ_{max} are coupled

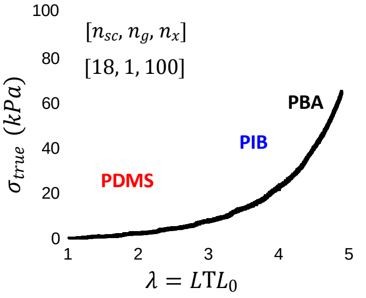
G and λ_{max} are decoupled

Architecture-Chemistry Superposition



$[n_{sc}, n_g, n_x]$ PDMS (T_g=-125°C) PIB (T_g=-75°C) PBA (T_g=-54°C)

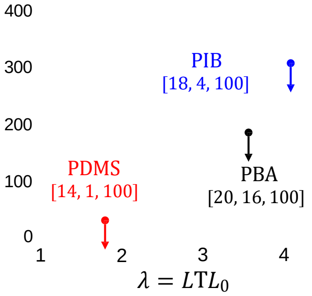
Same architecture - different elasticity



$$G \cong \frac{k_B T}{v n_x \left(1 + n_{sc} T n_g\right)}$$

$$\beta \cong \frac{v}{l^{5T2} b^{1T2}} \frac{1 + n_{sc} T n_g}{n_x n_{sc}^{1T2}}$$

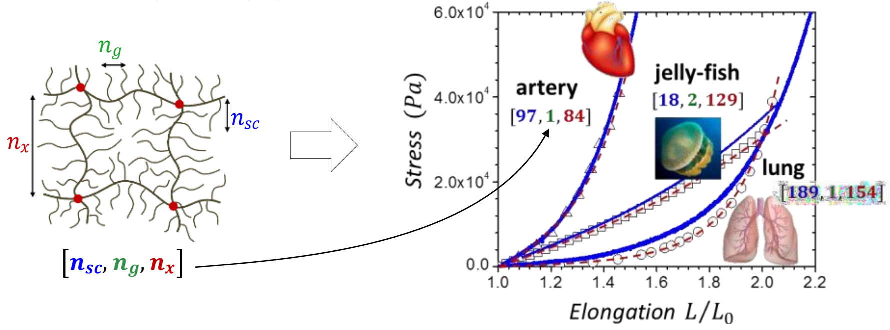
Matching elasticity by architecture



Encoding tissue mechanics by architecture

Architectural code

Mechanical phenotype



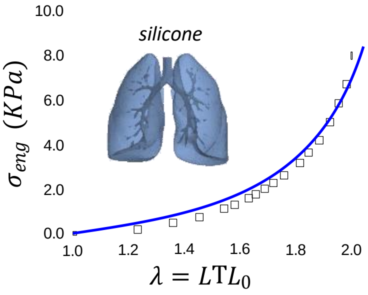
- *Sci. Adv*. 8, eabm2469 (**2022**)
- *Nat. Comm.* 12, 1-11 (**2021**)
- *Adv. Mater.* 32, 2005314 (**2020**)
- *Science Robotics* 3, eaat7175 (**2018**)
- *Science* 359, 1509 (**2018**)
- *Nature* 549, 497 (**2017**)
- *Advanced Mater.* 29, 1604209 (**2017**)
- *Nature Mater.* 15, 183 (**2016**)
- US Patent 10640649 Architectural programming of tissue mechanics

□ △ ○ : **Real tissues**

— **PDMS replicas of living tissues**

“Reverse tissue engineering”

1) Measurement (real tissue)



2) Fitting analysis

$$\sigma_{eng}(\lambda) = \frac{G}{3}(\lambda - \lambda^{-2})\left[1 + 2\left(1 - \frac{\beta I_1(\lambda)}{3}\right)^{-2}\right]$$

$$\beta = \frac{R_{in}^2}{R_{max}^2} = \frac{1}{\lambda_{max}^2}$$

$$I_1(\lambda) = \lambda^2 + 2\mathrm{T}\lambda$$

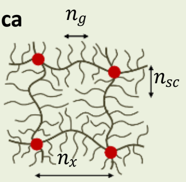
3) Molecular model

$$G \sim \frac{n_g}{n_{sc}} n_x^{-1} \qquad \beta \cong \sqrt{\frac{n_{sc}}{n_g}}\, n_x^{-1}$$

4) Architectural code

$$[n_{sc}, n_g, n_x]$$

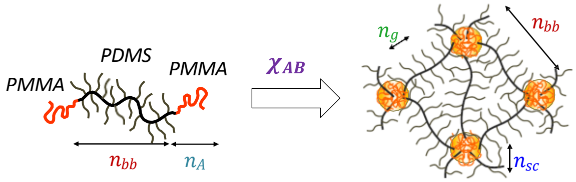
5) Synthetic replica



Nature 549, 549 (**2017**)

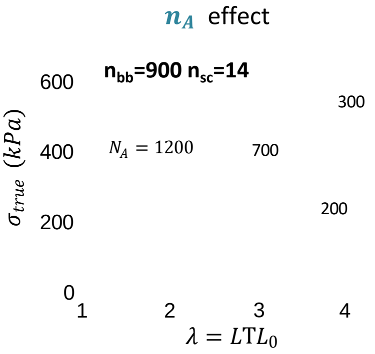
Enhancing firmness

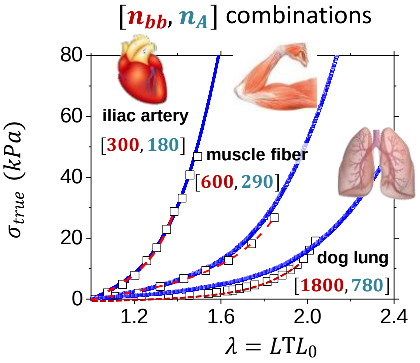
Self-assembled, moldable, reversible thermoplastic elastomers



advanced code:

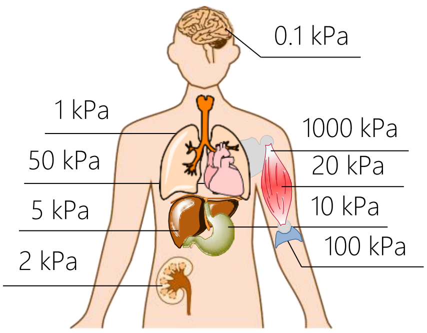
$[n_{sc}, n_g, n_{bb}, n_A, \chi_{AB}]$





Science 359, 1509 (**2018**)

Biological gels: Independent mechanics and swellability



70% water

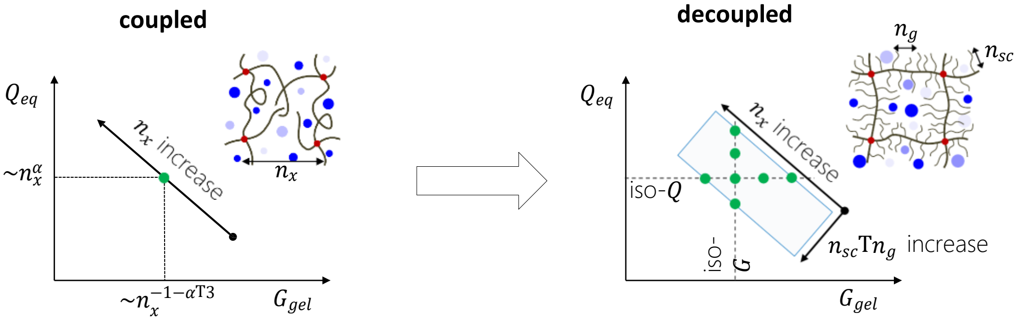
Can we design gels with the modulus ranging from 0.1 to 100 kPa at a constant solvent fraction?

Synthetic gels: Stiffness and swellability are coupled

Equilibrium swelling ratio (Flory-Rehner for θ-solvent):

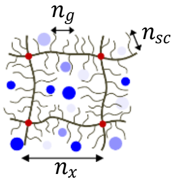
$$Q_{eq} = \frac{V_{gel}}{V_{dry}} \sim G^{-3T8} \sim n_x^{3T8}$$ - Q and G are directly coupled through n_x

coupled **decoupled**



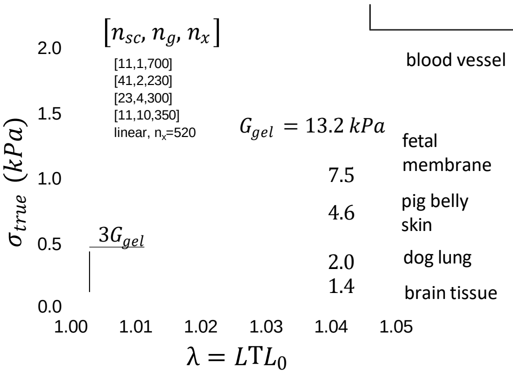
modulus and equilibrium swelling ratio are coupled

independently varying gel modulus and equilibrium swelling ratio

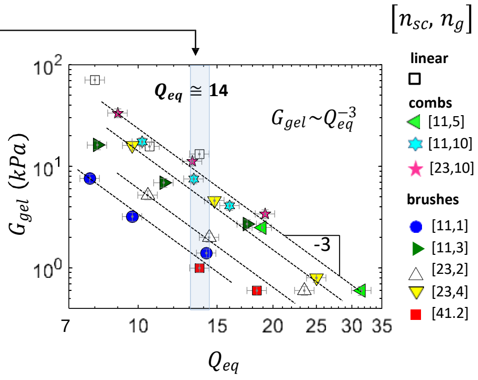


Different stiffness' at equal solvent content

Different G's at the same $Q_{eq} \cong 14$

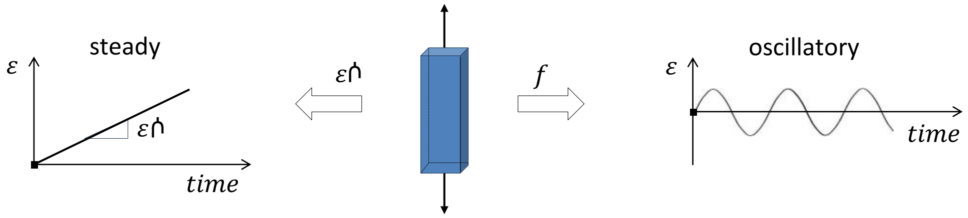


Modulus vs swelling ratio

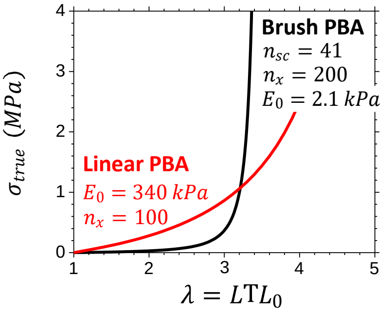


ACS Central Sci. 8, 845 (**2022**)

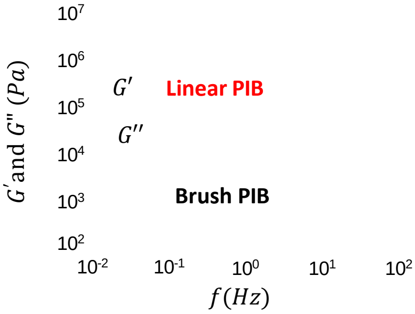
Outlook: Architectural control of dynamic properties

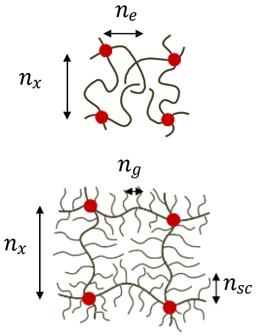


elastic: soft-yet-firm



dynamic: extended relaxation





Architecturally tuning polymer relaxation

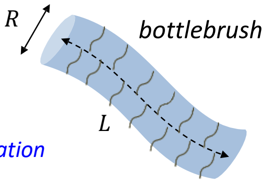
$$\tau_R \cong \frac{R^2}{D}$$ - Rouse time

$$D = \frac{k_BT}{\xi} \cong \frac{k_BT}{\xi_0}\frac{v^{2/3}}{R^2}$$

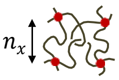
$$R^2 \cong \frac{V}{R_{sc}} \cong \frac{n_x n_{sc}^{1/2}}{n_g}$$

$$\tau_{R,bb} \cong \tau_0 \frac{n_{sc}}{n_g^2} n_x^2$$

assuming no interpenetration of side chains



Single parameter: limited control

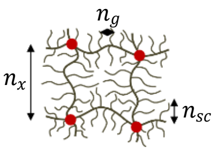


$$\boxed{\tau_{R,lin} \cong \tau_0 n_x^2}$$

entangled

$n_x < n_{e,lin} \cong 100$

Multiple parameters: wider range



$$\boxed{\tau_{R,bb} \cong \tau_0 \frac{n_{sc}}{n_g^2} n_x^2}$$

disentangled

$$n_x < n_{e,lin}\left(\frac{n_{sc}}{n_g}\right)^{1/2} \cong 1000$$

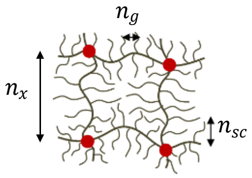
Effect of architecture on viscoelasticity and adhesion

Chemistry: PIB

o

o

n_{sc}



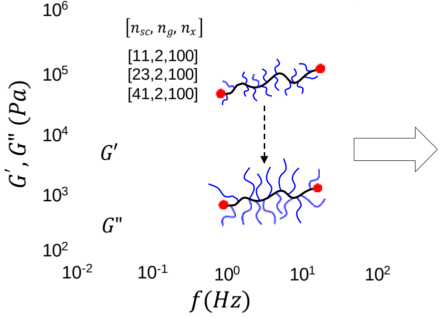
Architecture: $[n_x, n_g, n_{sc}]$

$n_x = 100 - 1000$

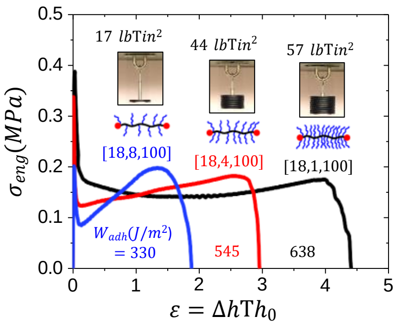
$n_g = 1 - 16$

$n_{sc} = 10 - 100$

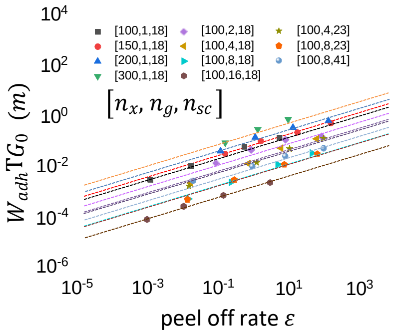
Viscoelasticity: $\tau_{R,bb} \cong \tau_0 \frac{n_{sc}}{n_g^2} n_x^2$



Adhesive stress



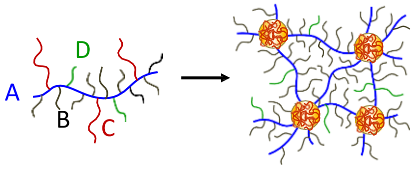
Work of adhesion



ACS Central Sci. 9, 197 (**2023**)

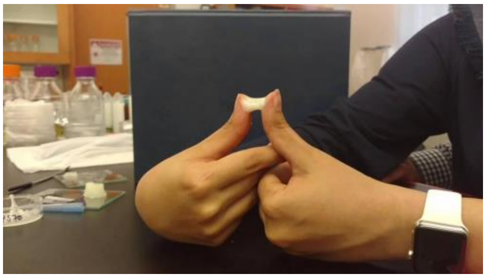
The All-in-One Adhesives

Integrating multiple functions in one molecule without using additives



- tackiness
- water sorption
- elasticity

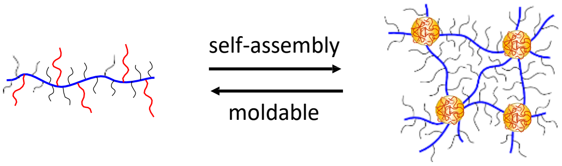
Elastic and tacky

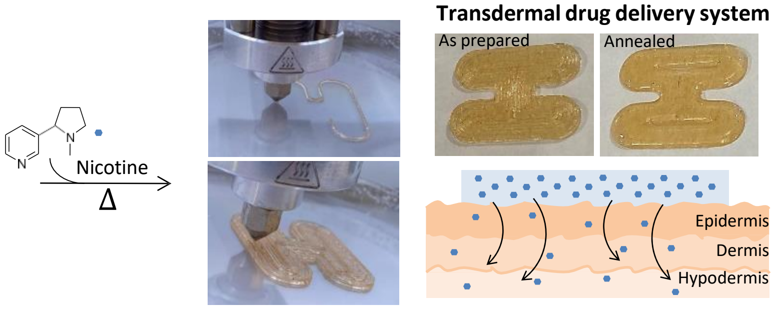


Distinct benefits

- No residues on skin (no leaching)
- Flexing with skin
- Sweat resistant
- Tunable adhesion for specific applications
- Adaptable for molding, film casting, and 3D printing

Moldable elastomers: Integrating tissue mechanics and adhesion into a biomedical device

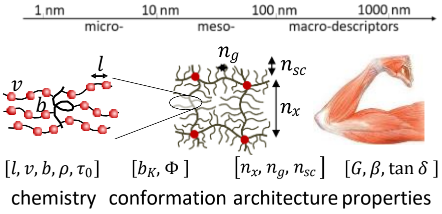


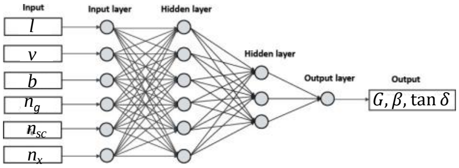


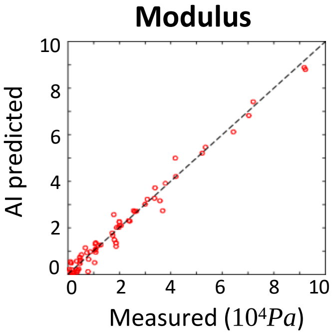
Transdermal drug delivery system

ACS Appl. Mater. Interf. 15 (35) 41870 (**2023**)

Conclusion and Outlook: Artificial Intelligence in Soft Materials Design







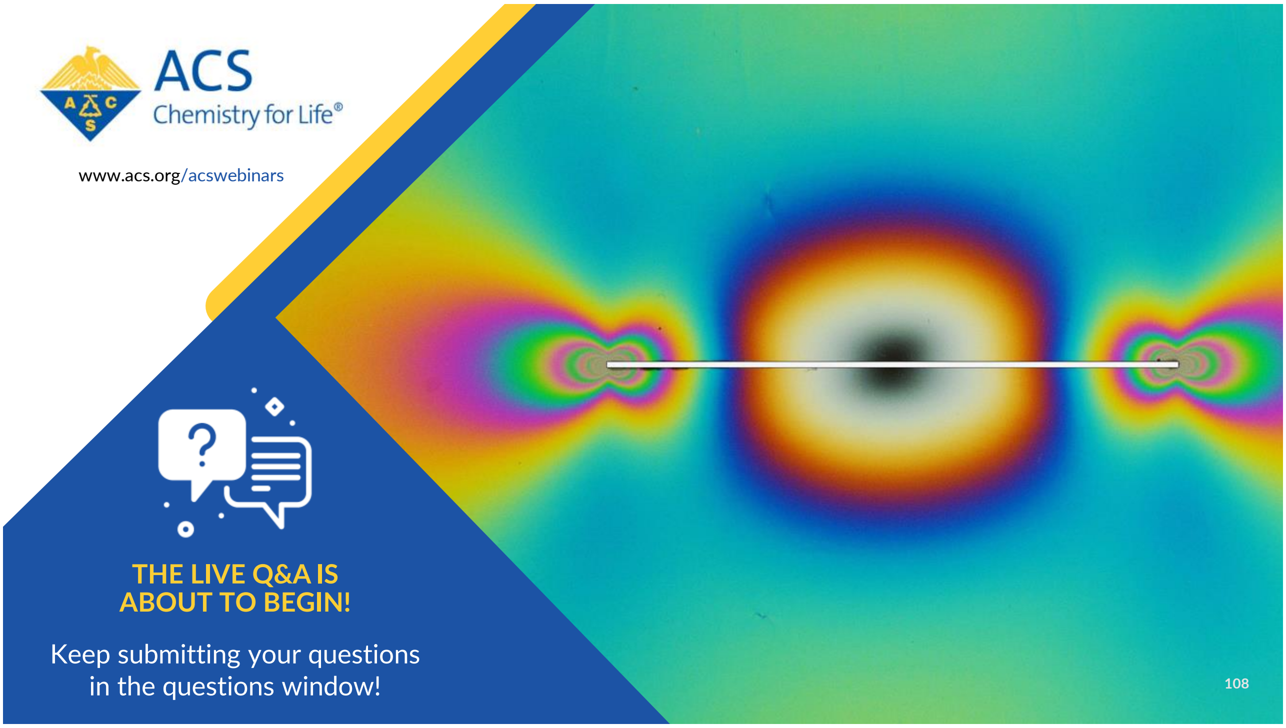
ACS Macro Lett. 12, 1510 (**2023**)

Thank you!

Students and postdocs
Mohammad Vatankhah
Foad Vashahi
Erfan Dashtimoghadam
Farah Fahimipour
Mitchel Maw
Benjamin Morgan
Andrew Keith
Daixuan Zhang
Joseph Collins
Jessica Garcia
Jing-Jing Wang

Cooperation
Krzysztof Matyjaszewski (CMU)
Andrey Dobrynin (UNC)
Dimitri Ivanov (CNRS, Mulhouse)
Michael Rubinstein (Duke)
Frank Leibfarth (UNC)
Wei You (UNC)
Harm-Anton Klok (EPFL)
Ekaterina Zhulina (St. Petersburg)
Oleg Borisov (UPau)

Funding:
NSF
Mitsui Chemicals
lululemon
TOTAL
EASTMAN
xona MICROFLUIDICS



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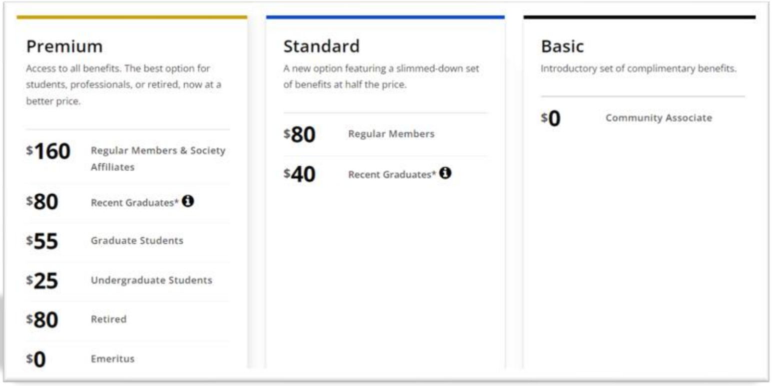

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