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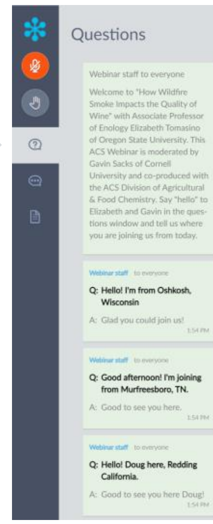

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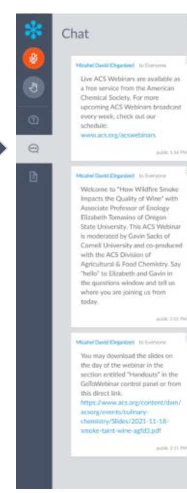

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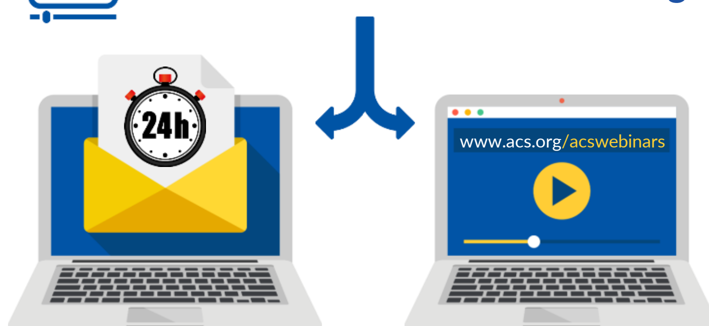

All Registrants

Watch the unedited recording linked in the **Thank You Email for 24 hours.**

ACS Members w/Premium Package

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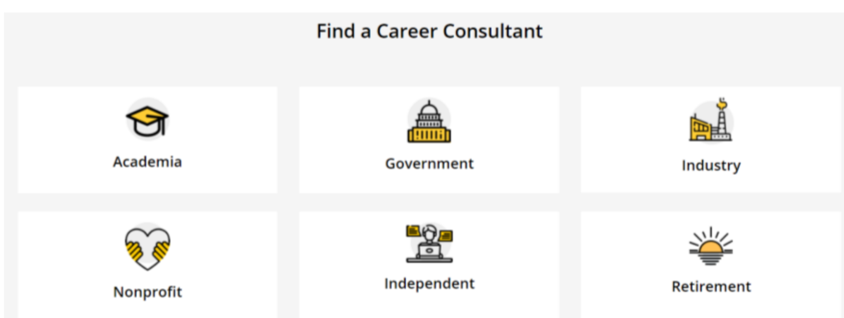
ChemIDP is an Individual Development Plan designed specifically for graduate students and postdoctoral scholars in the chemical sciences. Through immersive, self-paced activities, users explore potential careers, determine specific skills needed for success, and develop plans to achieve professional goals. **ChemIDP** tracks user progress and input, providing tips and strategies to complete goals and guide career exploration.

https://chemidp.acs.org

5

5

Career Consultant Directory



- ACS Member-exclusive program that allows you to arrange a one-on-one appointment with a certified ACS Career Consultant.
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6

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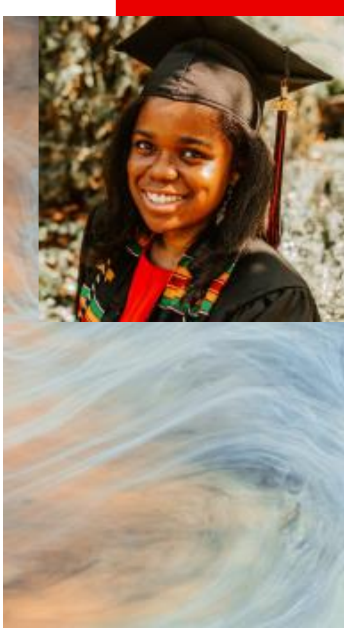

ACS Scholar Adunoluwa Obisesan

BS, Massachusetts Institute of Technology, June 2021
(Chemical-biological Engineering, Computer Science & Molecular Biology)

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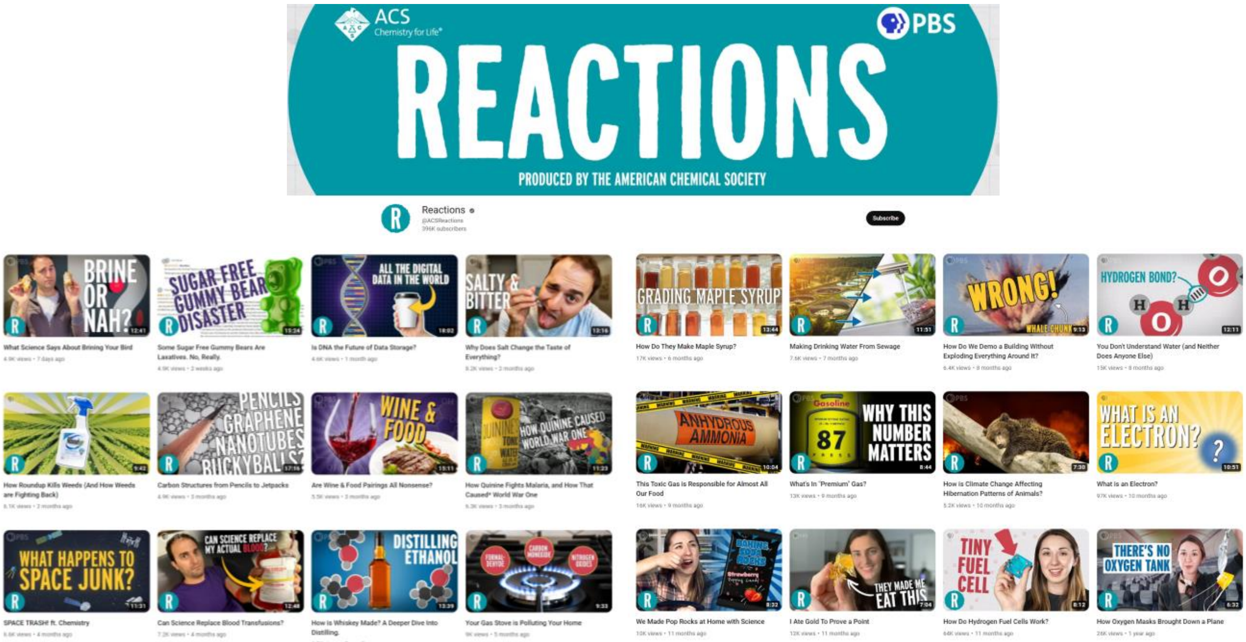

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Sam Jones, PhD
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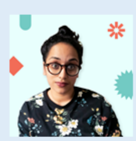

Deboki Chakravarti, PhD
Science Writer & Co-Host

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10

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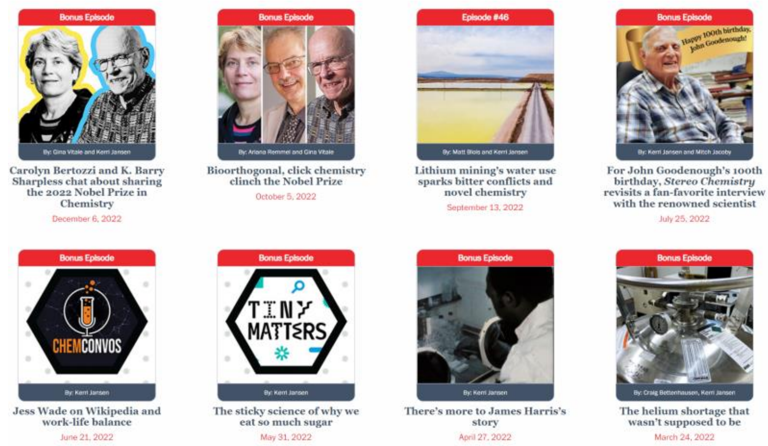

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13

ACS Career Resources

ACS Chemistry for Life®

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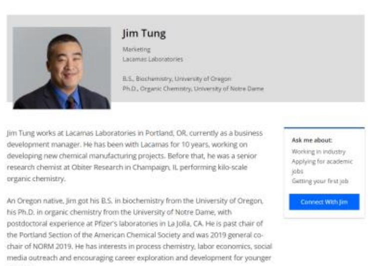
Personal Career Consultations



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.

Ask me about:
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14

14

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15

15

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Advancing ACS' Core Value of Diversity, Equity, Inclusion and Respect

Resources

Inclusivity Style Guide
Designed to help staff and members use language and images that respect diversity in all its forms.

ACS Webinars on Diversity
Covering diversity and inclusion at the workplace

ACS Publications DEIR Hub
See what ACS Publications is doing for fostering inclusivity in scholarly publishing

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Recommendations and best practices to ensure that your events can accommodate everyone.

Diversity, Equity, Inclusion, and Respect

**Adapted from definitions from the Ford Foundation Center for Social Justice:

Equity**
Seeks to ensure fair treatment, equality of opportunity, and fairness in access to information and resources for all. We believe this is only possible in an environment built on respect and dignity. Equity requires the identification and elimination of barriers that have prevented the full participation of some groups.

Diversity**
The representation of varied identities and differences (race, ethnicity, gender, disability, sexual orientation, gender identity, national origin, tribe, caste, socio-economic status, thinking and communication styles, etc.), collectively and as individuals. ACS seeks to proactively engage, understand, and draw on a variety of perspectives.

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.

Respect
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https://www.acs.org/diversity

16

16

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The impact and results of **ACS member advocacy** outreach and efforts by the numbers!

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Members participated In Act4Chemistry	ACS Advocacy Workshops participants or enrollees	Years of Public Policy Fellows	Letters sent to Congress
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American Chemical Society https://www.acs.org/policy 17

17

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Wednesday, November 22, 2023 | 2-3pm ET

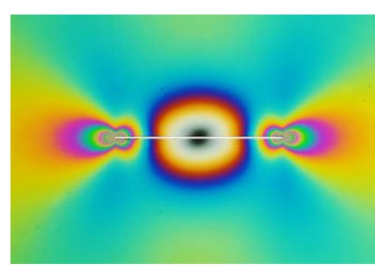
Desafíos y Soluciones a través de la Ecofarmacovigilancia

Co-produced with the Sociedad Química de México

Wednesday, December 6, 2023 | 2-3pm ET

Chemistry and the Economy: Looking forward to 2024?

Co-produced with the ACS Industry Member Programs and ACS Division of Business Development and Management



Wednesday, December 13, 2023 | 2-3:30pm ET

Breaking Down the Mechanics of Polymers From Networks to Viscoelasticity

Co-produced with the ACS Division of Polymeric Materials: Science & Engineering

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18

18

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A complete listing of ACS Safety Programs and Resources

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19

19

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ACS Award in Colloid Chemistry
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ACS Award in Polymer Chemistry
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Lam Research Corp.


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20

20

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21

21

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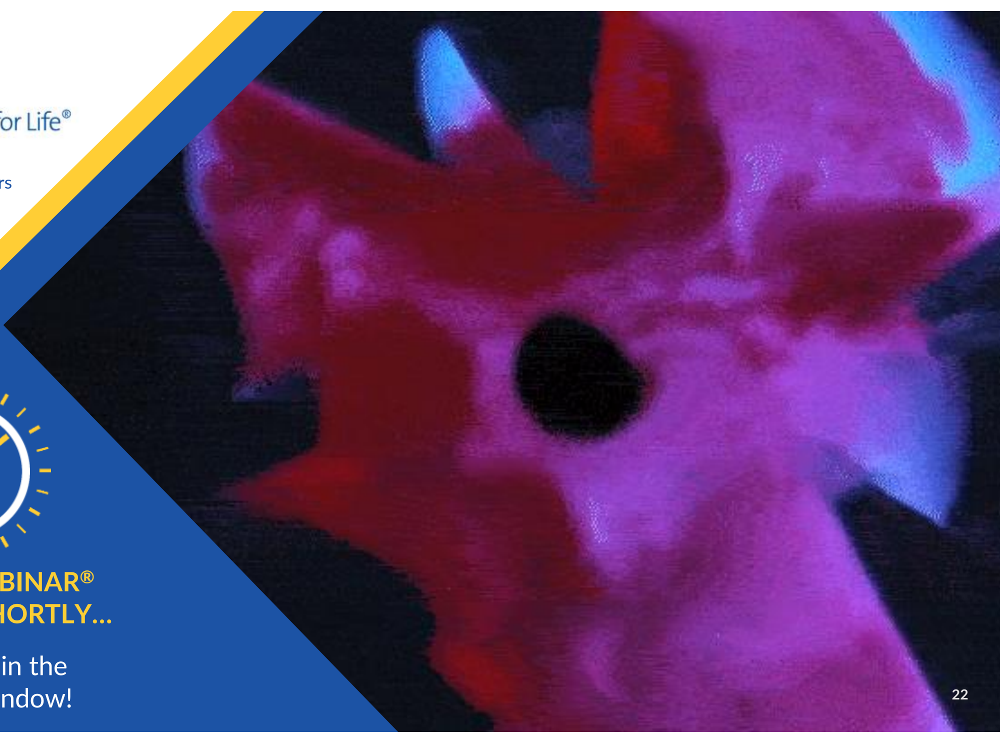

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22

22


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Unbreakable Design: The Polymer Mechanochemistry of Self-Healing Materials
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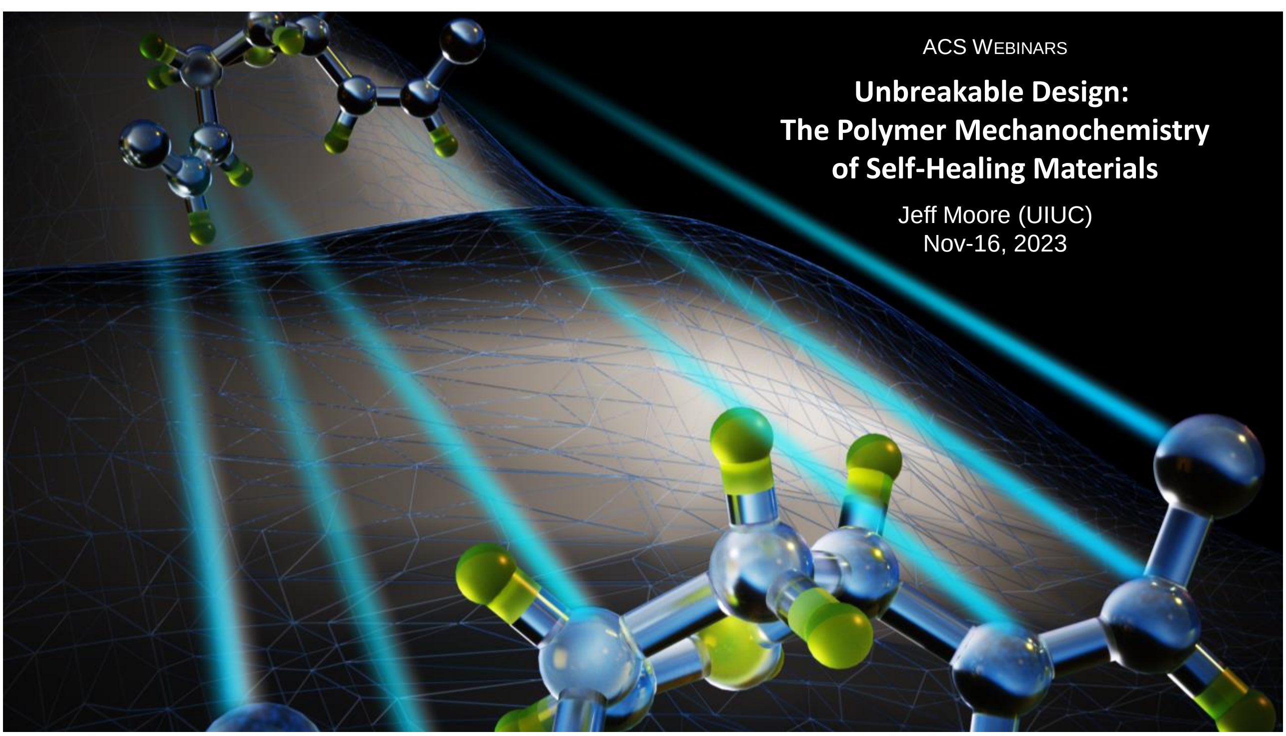
23

23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Jeff Moore (UIUC)
Nov-16, 2023

24

OUTLINE

Concepts for Polymer Lifecycle Control

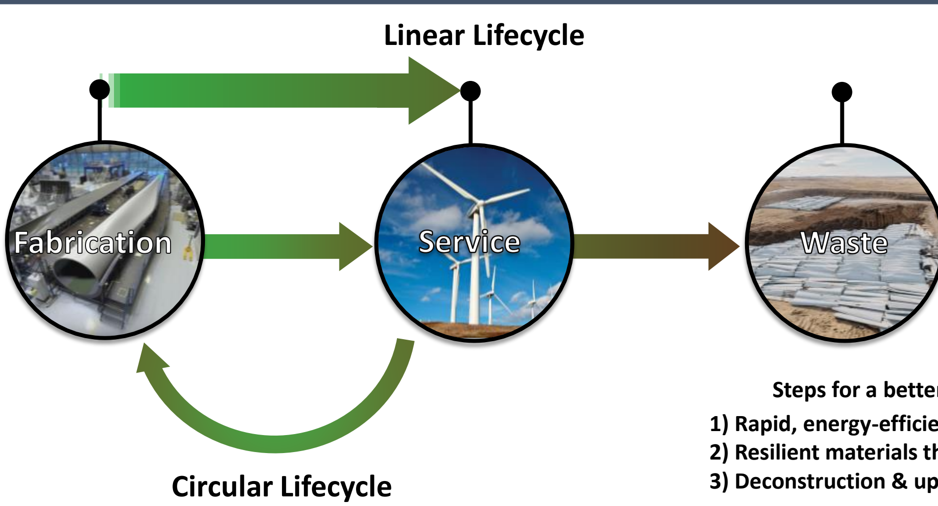
Mechanophore Phenomenology

- Statics
- Dynamics

AMS

25

The Thermoset Lifecycle



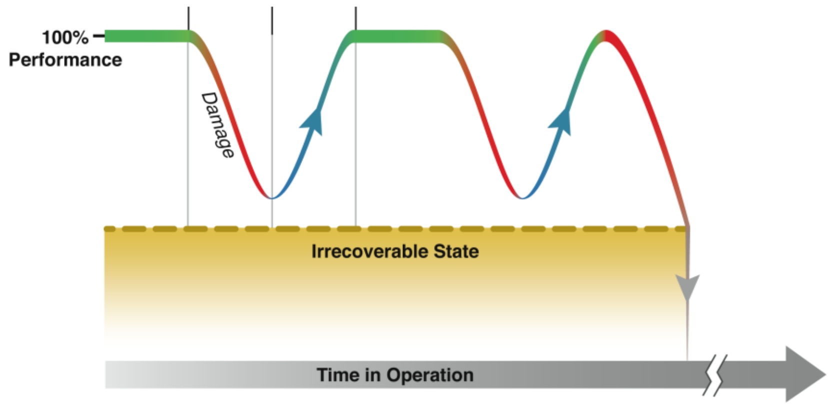
Steps for a better lifecycle

1) Rapid, energy-efficient manufacturing
2) Resilient materials that last longer
3) Deconstruction & upcycling/recycling

26

26

Lifecycle Control in Polymeric Materials



Patrick, Robb, Sottos, Moore, White, "Polymers with Autonomous Life-cycle Control", *Nature*, **2016**, *540*, 363-370.

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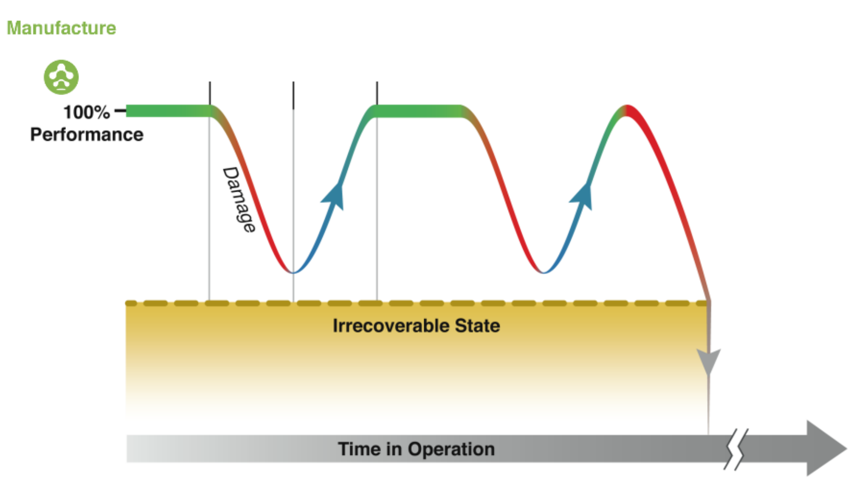

Patrick, Robb, Sottos, Moore, White, "Polymers with Autonomous Life-cycle Control", *Nature*, **2016**, *540*, 363-370.

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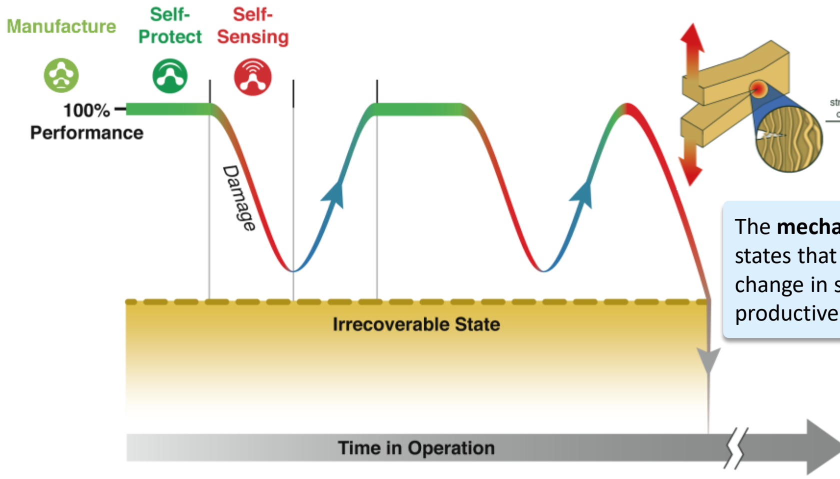
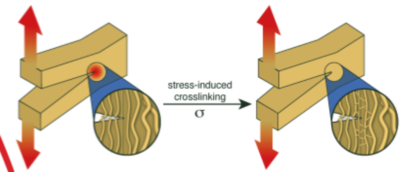
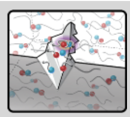




The **mechanophore hypothesis** states that force drives chemical change in selective and productive ways.

Toolbox of concepts



Mechanophore

Patrick, Robb, Sottos, Moore, White, "Polymers with Autonomous Life-cycle Control", *Nature*, **2016**, *540*, 363-370.

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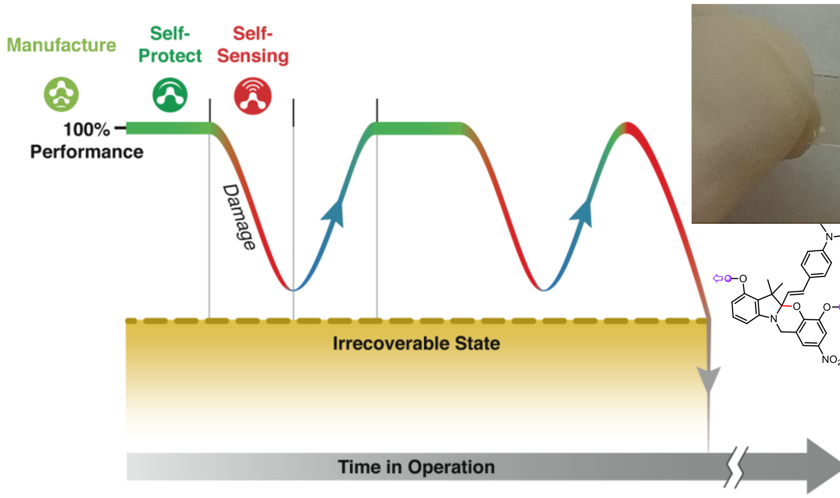
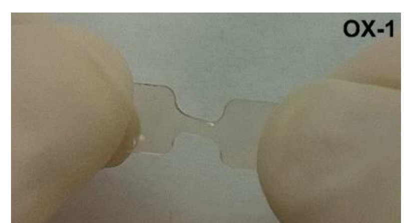
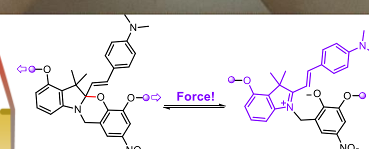
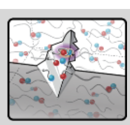






Toolbox of concepts



Mechanophore

Qian, Purwanto, Ivanoff, Halmes, Sottos, Moore, "Fast, Reversible Mechanochromism of Regioisomeric Oxazine Mechanophores: Developing in situ Responsive Force Probes for Polymeric Materials" Chem, **2021**, *7*, 1080 - 1091

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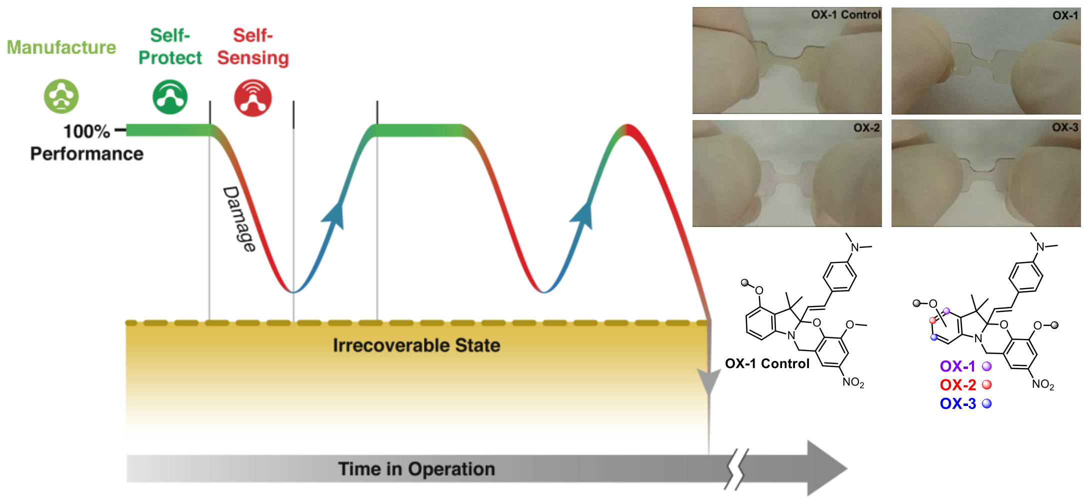
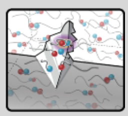


Toolbox of concepts



Mechanophore

Qian, Purwanto, Ivanoff, Halmes, Sottos, Moore, "Fast, Reversible Mechanochromism of Regioisomeric Oxazine Mechanophores: Developing in situ Responsive Force Probes for Polymeric Materials" Chem, **2021**, *7*, 1080 - 1091

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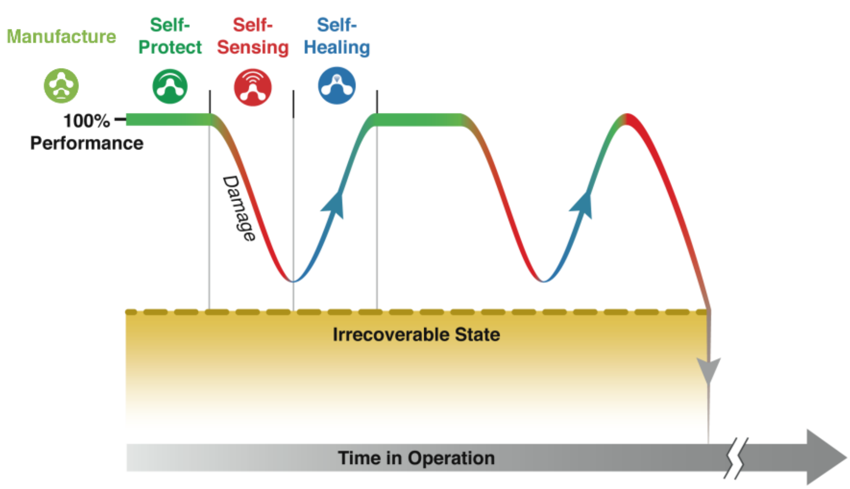
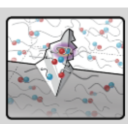
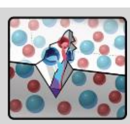


Toolbox of concepts



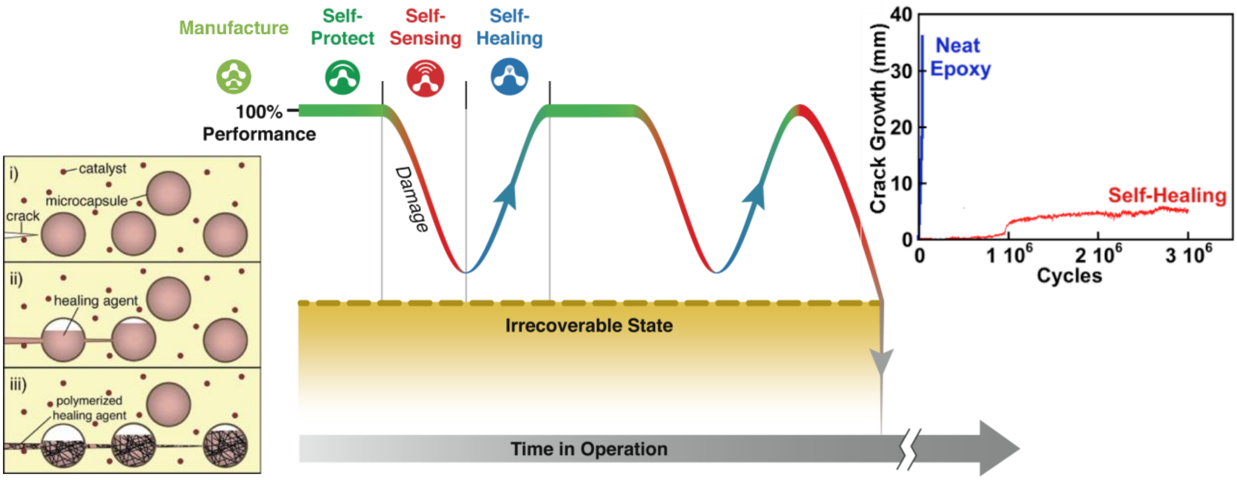
Mechanophore



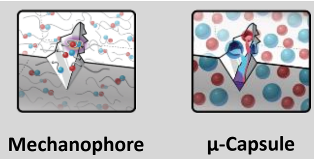
μ-Capsule

Patrick, Robb, Sottos, Moore, White, "Polymers with Autonomous Life-cycle Control", *Nature*, **2016**, *540*, 363-370.

32

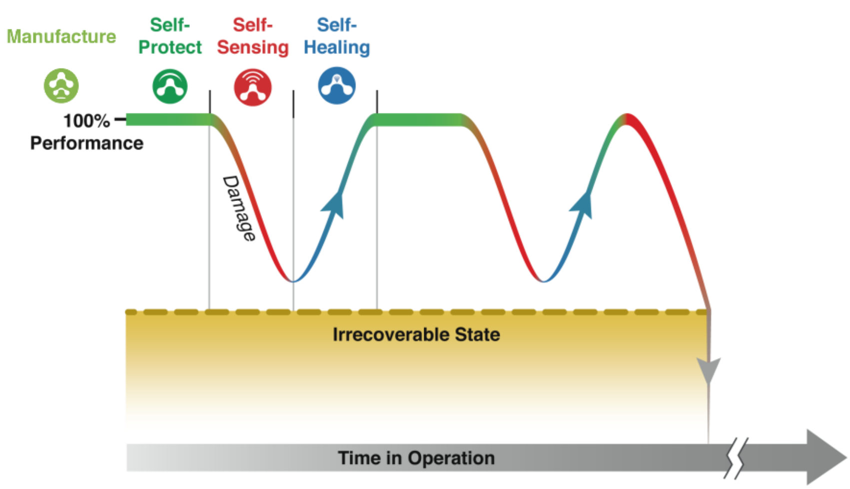


Toolbox of concepts

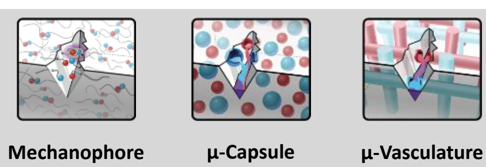


White, Sottos, Geubelle, Moore, Kessler, Sriram, Brown, Viswanathan, "Autonomic Healing of Polymer Composites," *Nature* **2001**, *409*, 794-797.

33



Toolbox of concepts



Patrick, Robb, Sottos, Moore, White, "Polymers with Autonomous Life-cycle Control", *Nature*, **2016**, *540*, 363-370.

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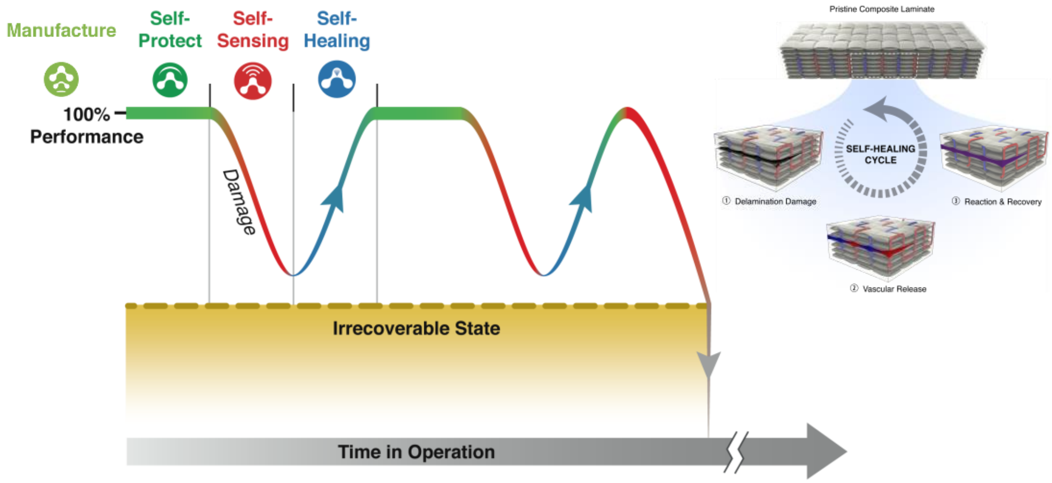

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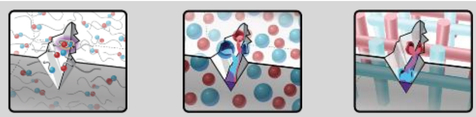

Mechanophore **μ-Capsule** **μ-Vasculature**

Patrick, Hart, Krull, Diesendruck, Moore, White, and Sottos, “Continuous Self-healing Life Cycle in Vascularized Structural Composites”, *Adv. Mater.*, **2014**, *26*, 4189-4396.

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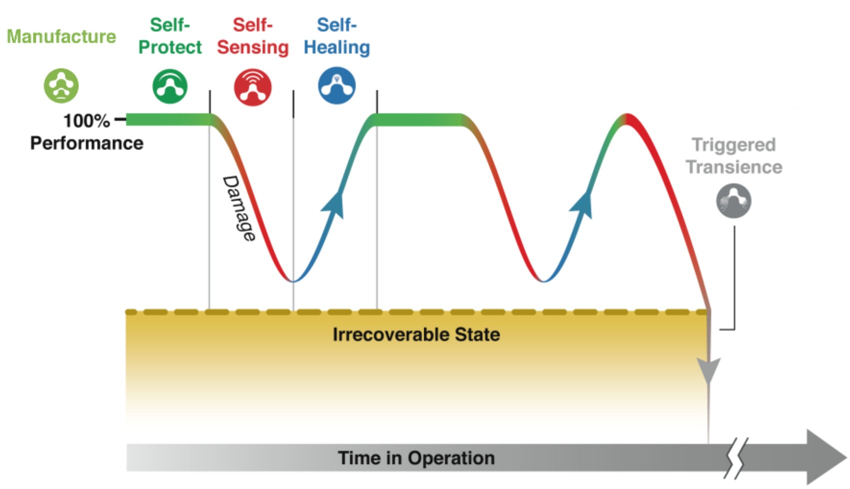
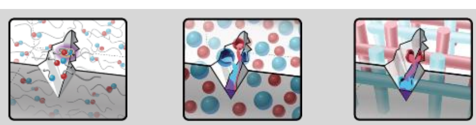


Toolbox of concepts



Mechanophore **μ-Capsule** **μ-Vasculature**

Patrick, Robb, Sottos, Moore, White, "Polymers with Autonomous Life-cycle Control", *Nature*, **2016**, *540*, 363-370.

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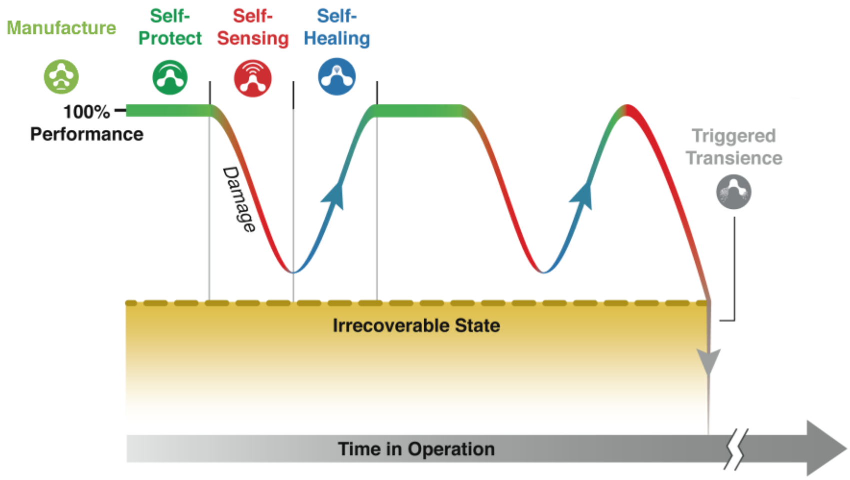
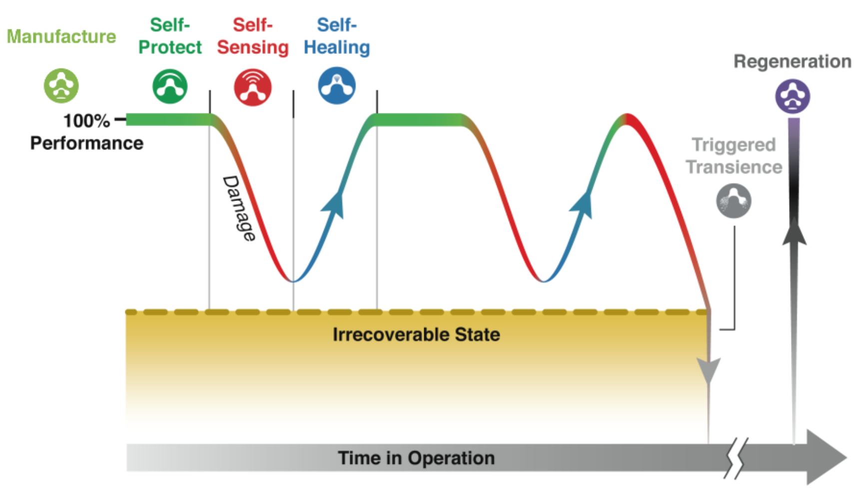


Toolbox of concepts

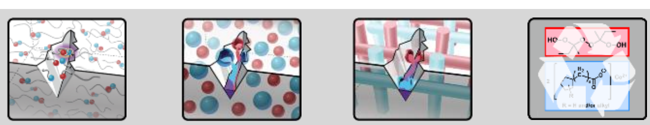
Mechanophore | μ-Capsule | μ-Vasculature | Multi-gen materials

Patrick, Robb, Sottos, Moore, White, "Polymers with Autonomous Life-cycle Control", *Nature*, **2016**, *540*, 363-370.

37



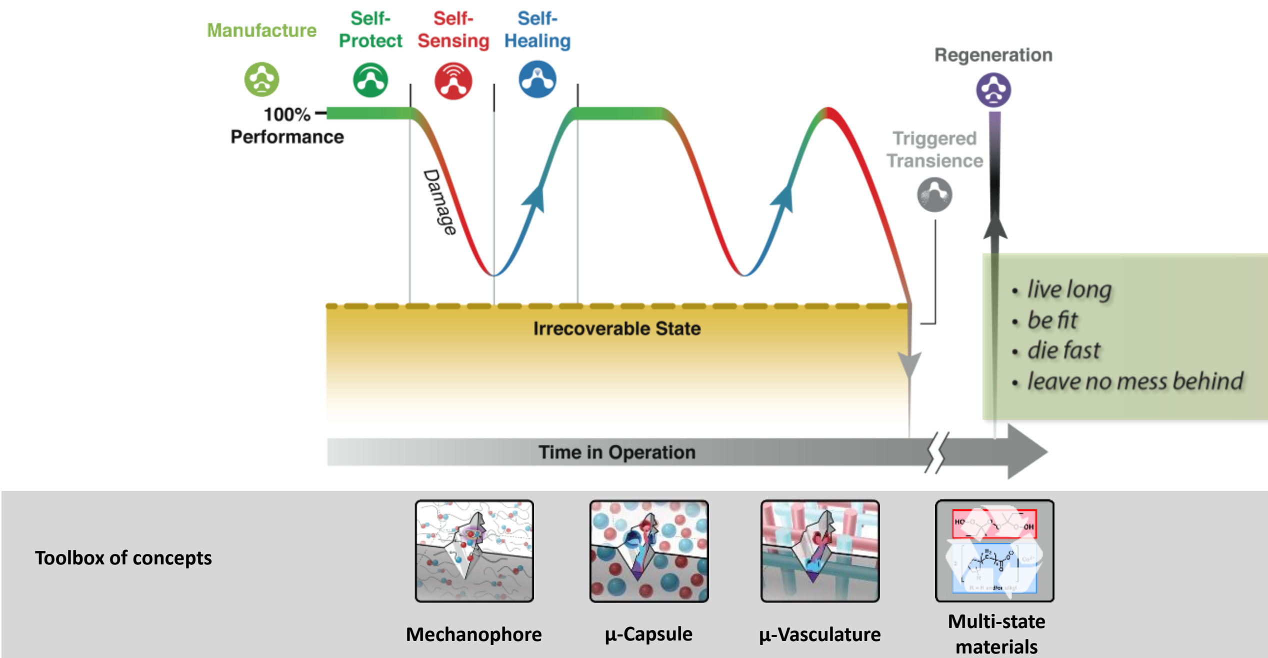
Toolbox of concepts



Mechanophore | μ-Capsule | μ-Vasculature | Multi-gen materials

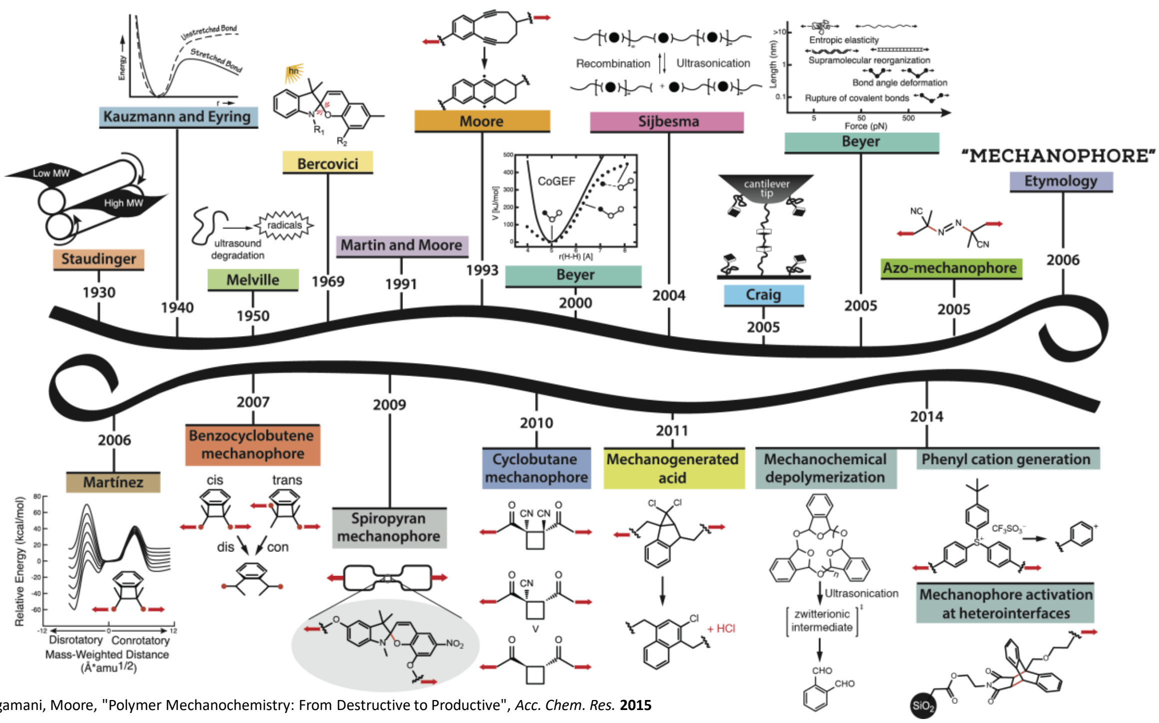
Patrick, Robb, Sottos, Moore, White, "Polymers with Autonomous Life-cycle Control", *Nature*, **2016**, *540*, 363-370.

38



Patrick, Robb, Sottos, Moore, White, "Polymers with Autonomous Life-cycle Control", *Nature*, **2016**, *540*, 363-370.

39



Li, Nagamani, Moore, "Polymer Mechanochemistry: From Destructive to Productive", *Acc. Chem. Res.* **2015**

40

Mechanochemistry’s Historical Roots in Polymer Science

My first introduction to mechanochemistry came from the annual UIUC – Northwestern Polymer Science Symposia

Polymer Fracture—A Simple Model for Chain Scission

B. CRIST, JR., *Department of Materials Science and Engineering and Materials Research Center, Northwestern University, Evanston, Illinois 60201*, JENS ODDERSHEDE* and J. R. SABIN, *Departments of Physics and Chemistry and Quantum Theory Project, University of Florida, Gainesville, Florida 32611*, J. W. PERRAM, *Department of Mathematics, Odense University, DK 5230 Odense, Denmark*, and MARK A. RATNER, *Department of Chemistry and Materials Research Center, Northwestern University, Evanston, Illinois 60201*

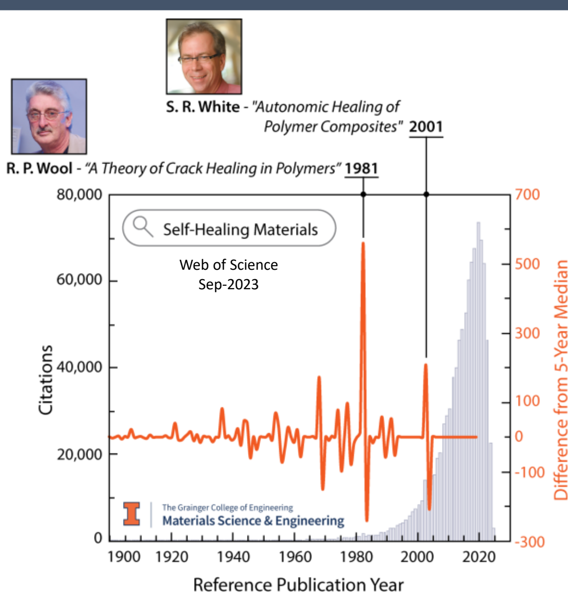
Synopsis

A simple model for calculating the fracture process for a single extended-chain molecule such as polyethylene is considered. The model consists of a chain of N coupled Morse oscillators. There exists a critical overall extension ΔL_c below which the fracture is energetically unfavorable but above which fracture is favored both energetically and kinetically. This elongation ΔL_c scales as $N^{1/2}$. For the critically stretched chain, the activation energy for rupture increases with N. Long chains must be stretched beyond this critical value to fail within experimentally meaningful times. Chains of all lengths subjected to the same force will fail with the same activation energy, provided this force is large enough to stretch each chain to $\Delta L > \Delta L_c$. Observed activation energies are less than $\frac{1}{3}D_e$, where D_e is the bond energy.

Journal of Polymer Science: Polymer Physics Edition, Vol. 22, 881–897 (1984)
 CCC 0098-1273/84/050881-17$04.00

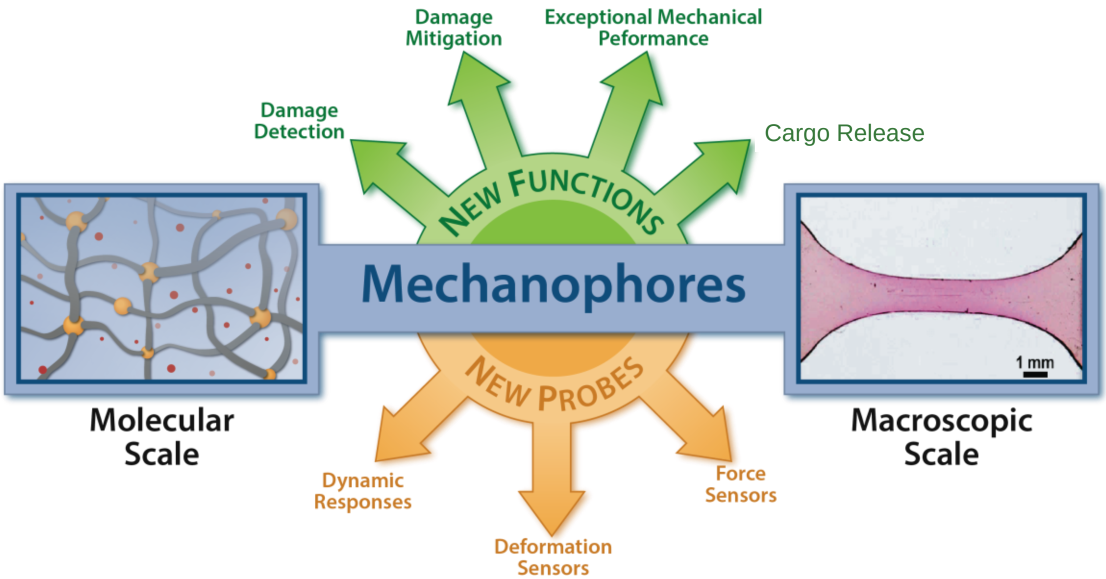
41

Mechanochemistry for Mechanoresponsive Materials

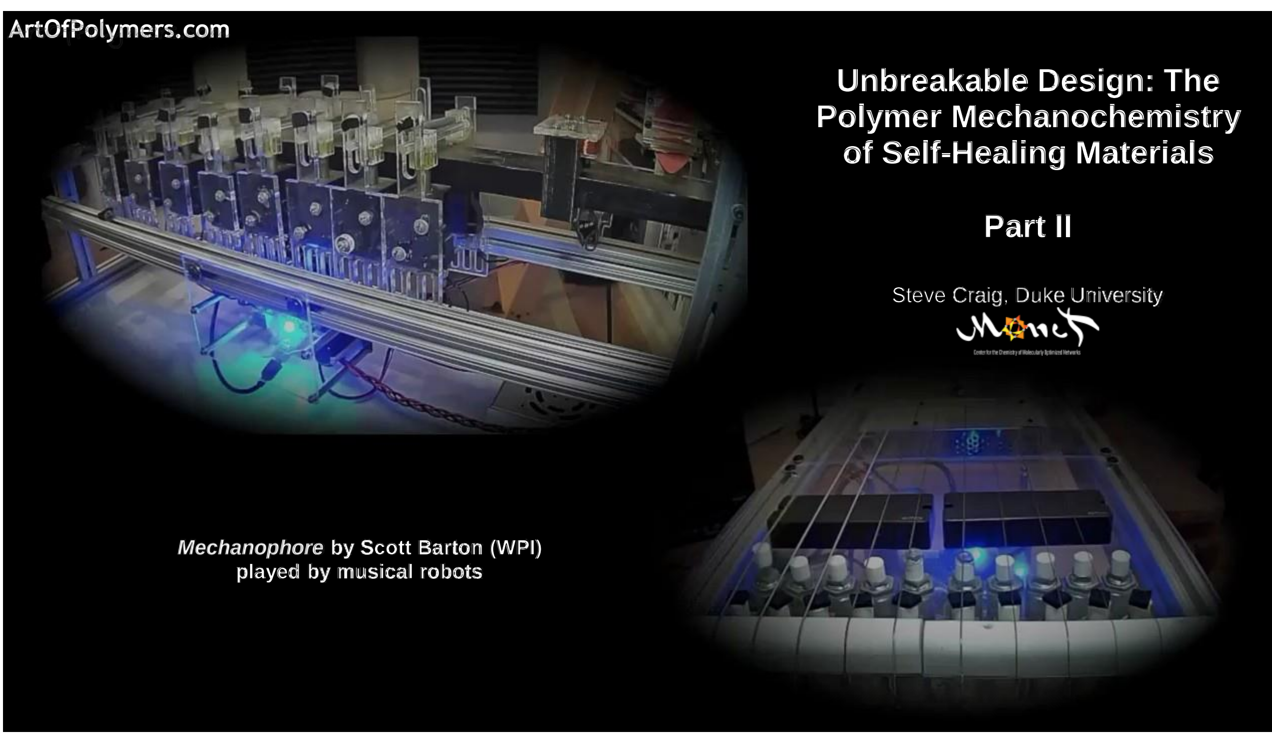


42

Mechanophores: from Concepts to Mechanoresponsive Materials

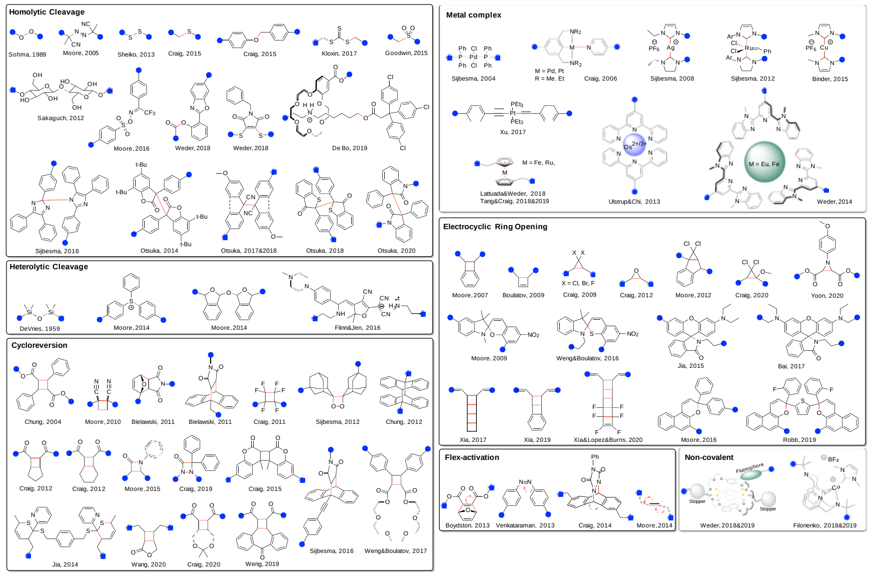


43



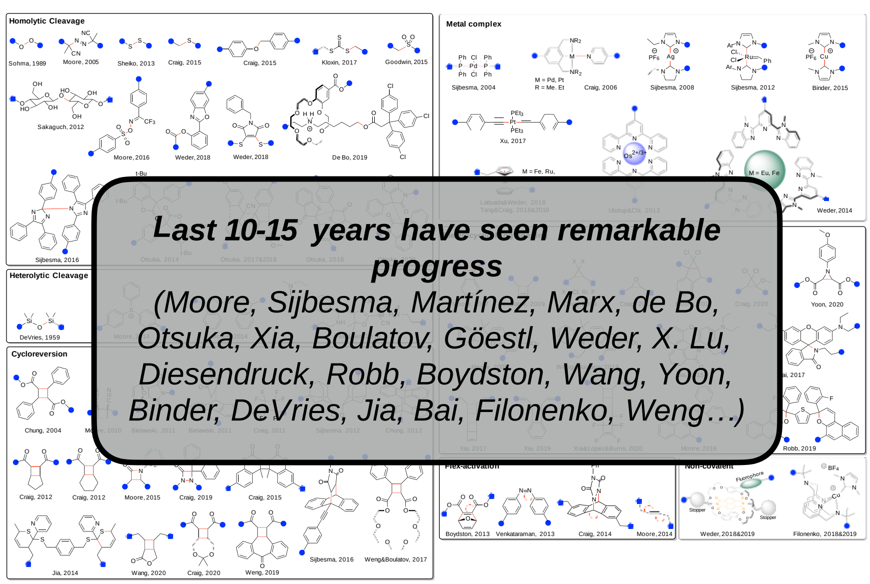
44

Mechanophore Toolbox (*c.* 2019)



45

Mechanophore Toolbox (*c.* 2019)



Last 10-15 years have seen remarkable progress

(Moore, Sijbesma, Martínez, Marx, de Bo, Otsuka, Xia, Boulatov, Göestl, Weder, X. Lu, Diesendruck, Robb, Boydston, Wang, Yoon, Binder, DeVries, Jia, Bai, Filonenko, Weng…)

46

Questions for today

1. How do I think about kinetics and reactivity in polymer mechanochemistry?

2. Can embedded mechanochemistry redefine polymer material performance limits?

3. Can I use polymer materials for the top-down manipulation of reaction pathways?

big picture; happy to address details in Q&A

47

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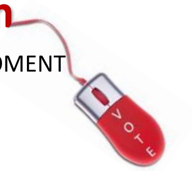
big picture; happy to address details in Q&A

48

Audience Survey Question

ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT

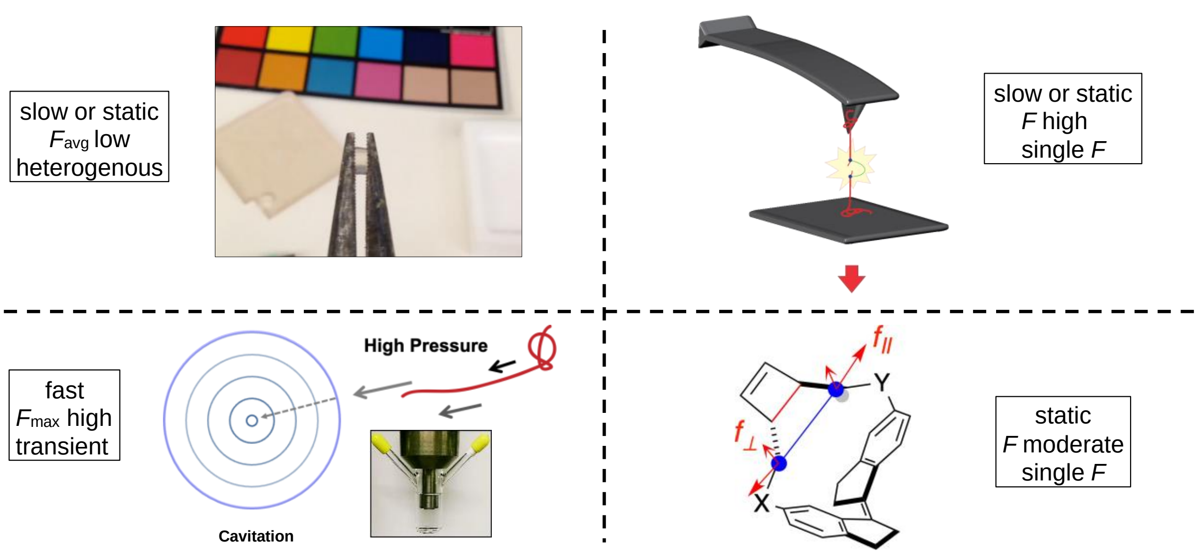


In polymer mechanochemistry:

- **A.** All of the energy needed for a reaction to occur is provided by an external force, without any energy input from heat or light.
- **B.** Traditional chemical intuition is no longer useful, because force-free potential energy surfaces are not related to force-coupled potential energy surfaces.
- **C.** The range of system sizes and timescales associated with mechanochemistry means that connections between different experiments are almost impossible.
- **D.** All of the above are false.
- **E.** All of the above are true.

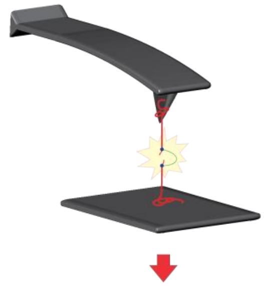
49

Observed in many different contexts



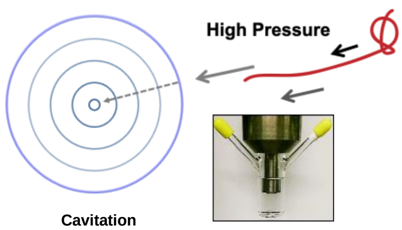
Observed in many different contexts

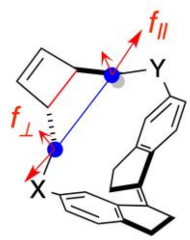
slow or static
F_{avg} low
heterogenous



slow or static
F high
single F

fast
F_{max} high
transient



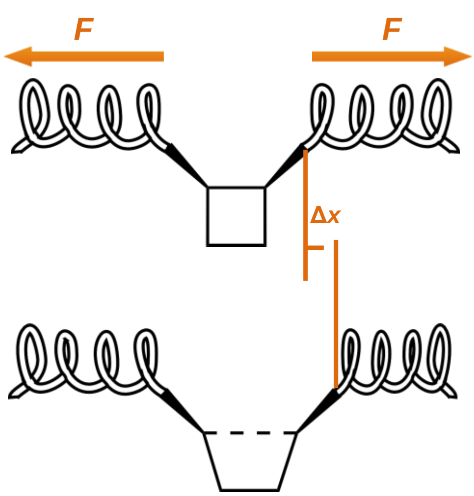


static
F moderate
single F

very different environments, but principles the same

51

Force-coupled reactivity



1. Distortion of the reactant, TS (minor)

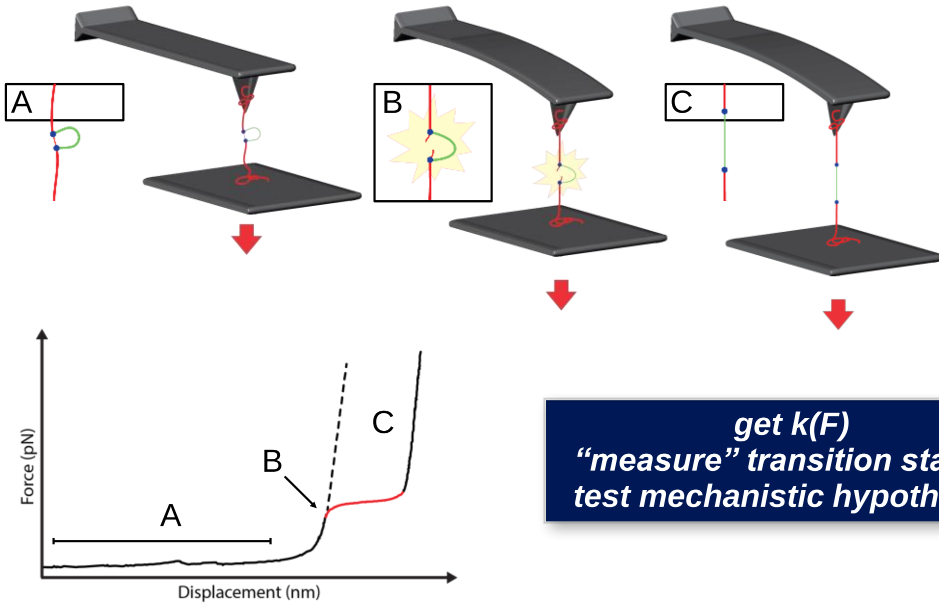
2. Work coupled to reaction path (major)

$$\ln(k_{rel}) = \Delta\Delta G^{\ddagger} = F\Delta x$$

- ***still a thermal barrier; rxn accelerated by force***
- ***same reactivity concepts remain relevant (but mechanism & TS position can change)***
- ***k vs. F is opportunity to "measure" position of TS***

52

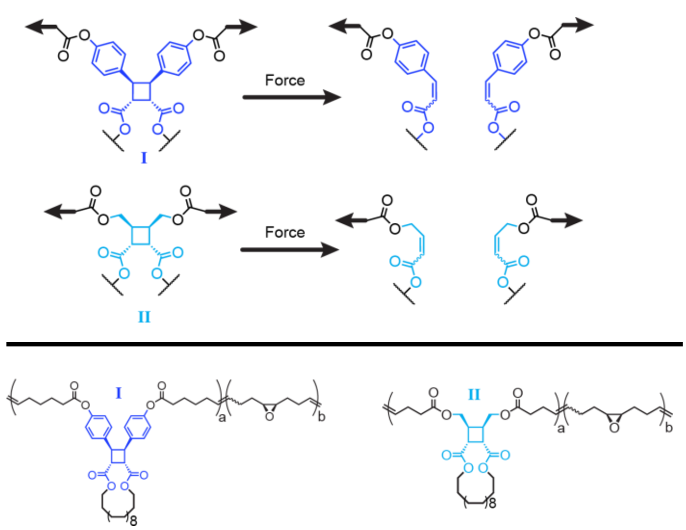
Quantifying molecular response

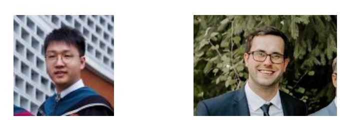


get k(F)
"measure" transition states
test mechanistic hypotheses

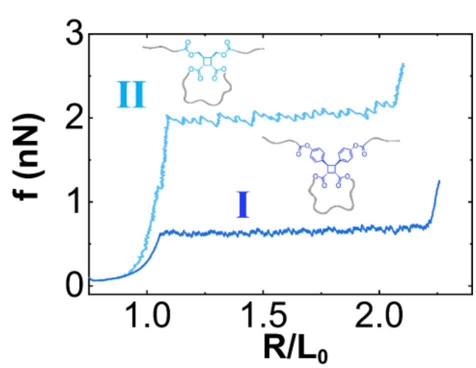
53

Mechanophore design





Shu Wang **Brandon Bowser**

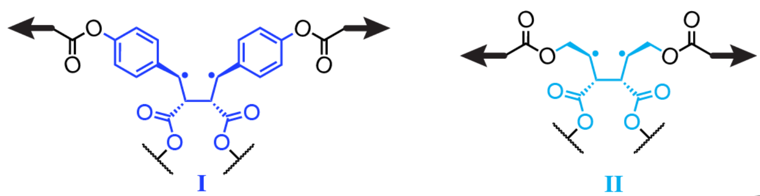


J. Am. Chem. Soc. **2021**, *143*, 5269–5276

54

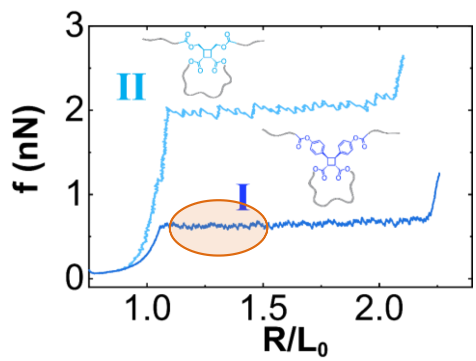
Mechanophore design

diradical character in rate-determining step



Shu Wang

Brandon Bowser



- Resonance stabilization of the diradical character in transition state

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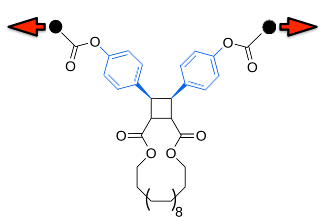
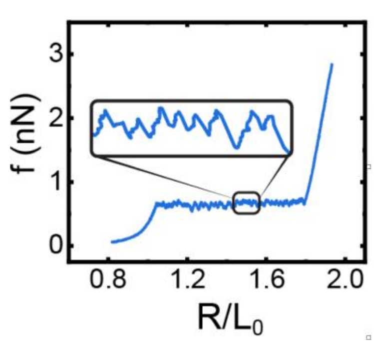
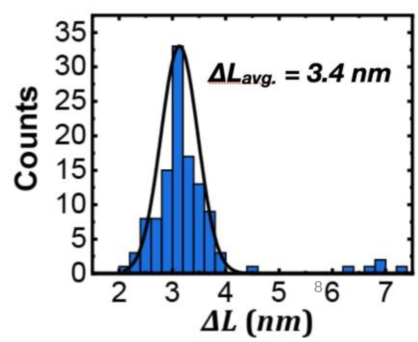
7

55

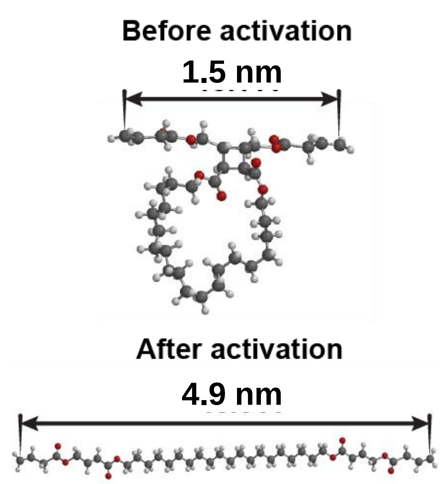
Mechanophore design





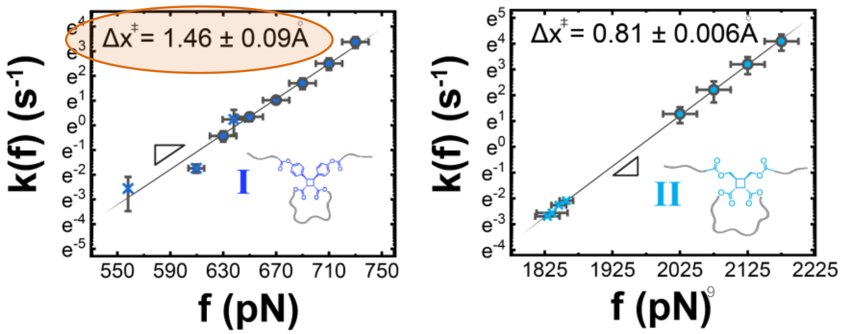


experiment matches modeling



56

Rate-force dependence



$\ln(k_{rel}) = -\Delta\Delta G^{\ddagger} = F\Delta x$

larger Δx indicates better coupling

these two mechanophores with characterized reactivities are used in the next story

J. Am. Chem. Soc. **2021**, *143*, 5269–5276

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same kinetic and mechanistic principles — coupled to force

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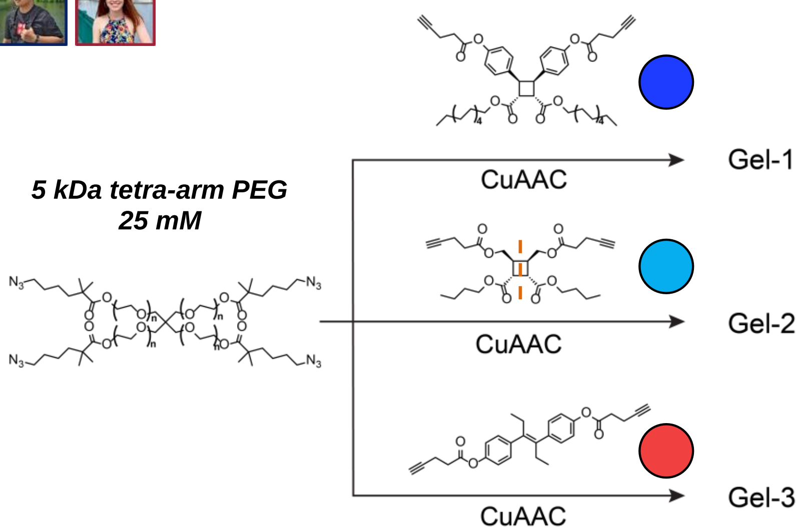
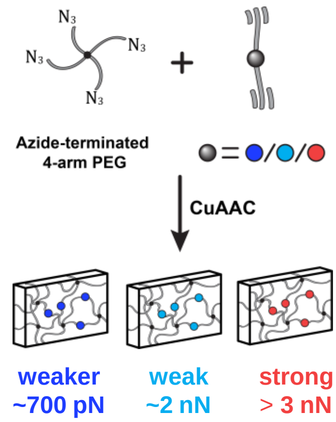
59

60

Networks held together by mechanophores





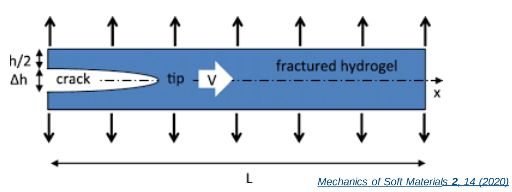
force depends on timescale
focus here on <u>relative</u> behavior

JACS, **2021**, *143*, 3714–3718.

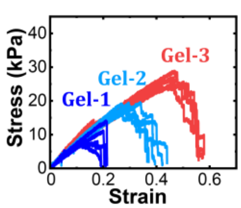
61

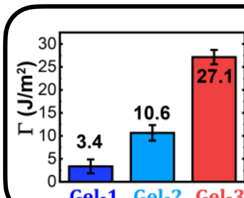
Networks held together by mechanophores

make films, stretch until they tear

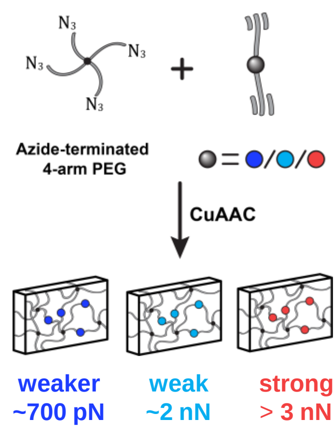


notched films





tear resistance



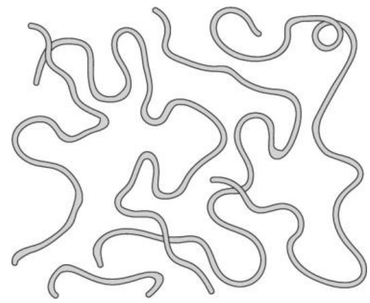
single unit per chain, huge effect!

JACS, **2021**, *143*, 3714–3718.

62

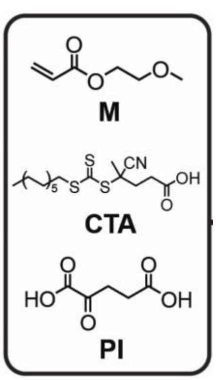
From end-linking to cross-linking

17

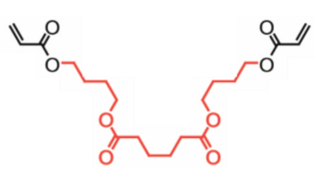


melt of linear chains
poor mechanical properties

From end-linking to cross-linking



Control strand length (gray)
within and across networks



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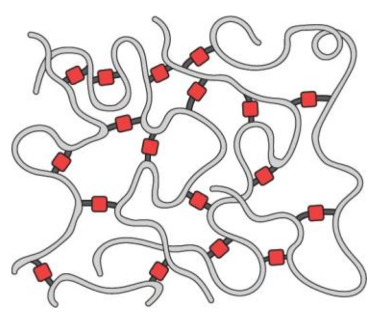
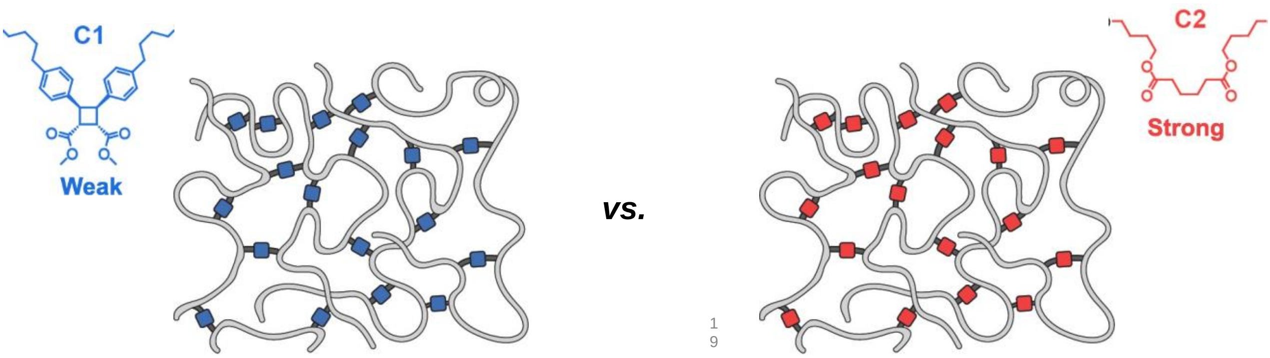


cross-linked chains
good mechanical properties

From end-linking to cross-linking

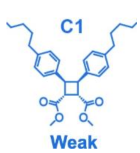


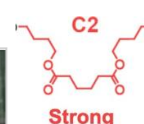
effect of easily broken cross-linkers?

cross-linked chains
good mechanical properties

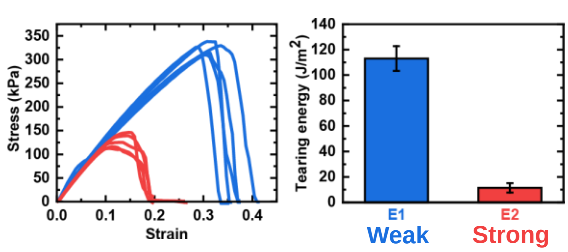
65

Tearing comparison





otherwise identical



still a large effect,
but opposite direction!

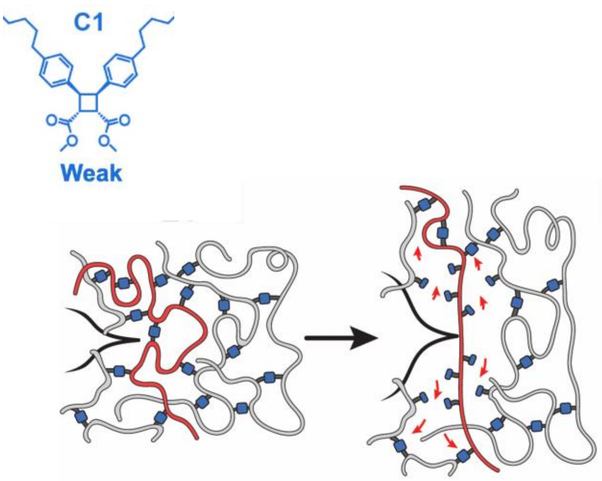
same behavior in gels, different monomers, fatigue…
but magnitude very much depends on network

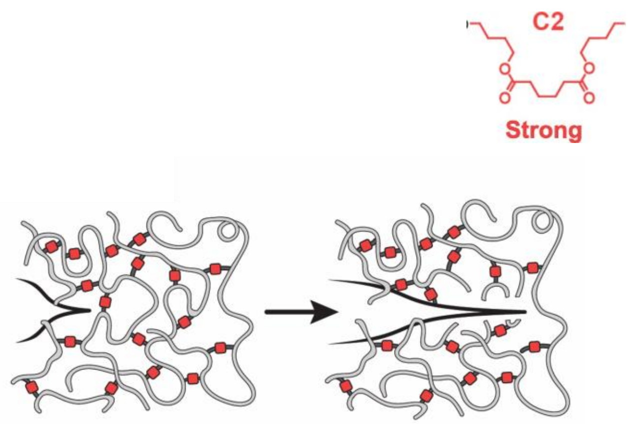
See also: Otsuka, *Macromolecules*, **2022**, *55*, 5795-5802.

20

66

Mechanistic hypothesis

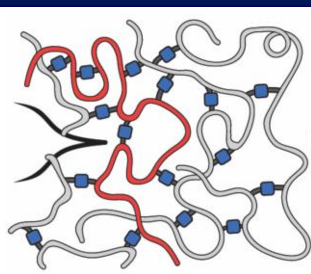




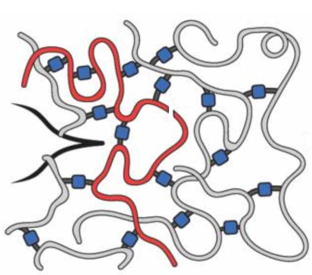
Simulations by Sapir & Rubinstein support this picture

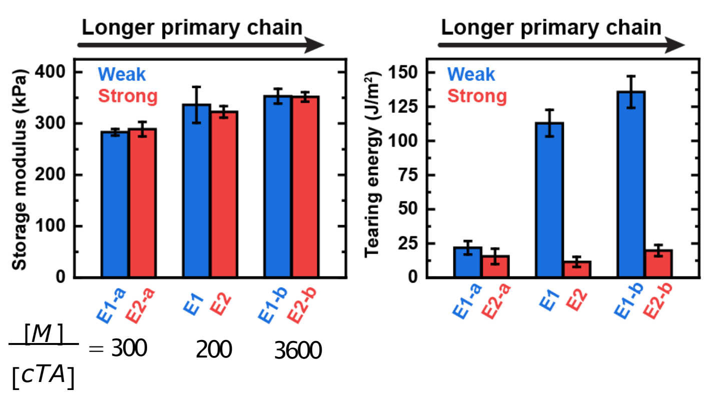
67

Vary primary chain length



vs.

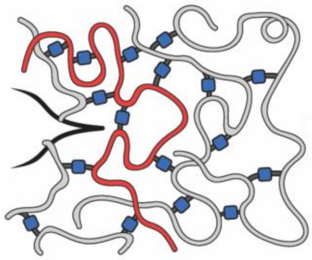




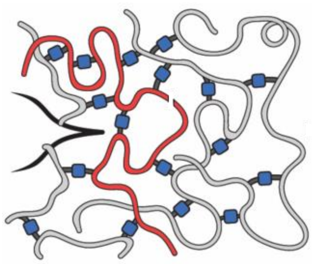
***Strong** xlinks have almost no dependence on N*
***Weak** xlinks have strong dependence on N*

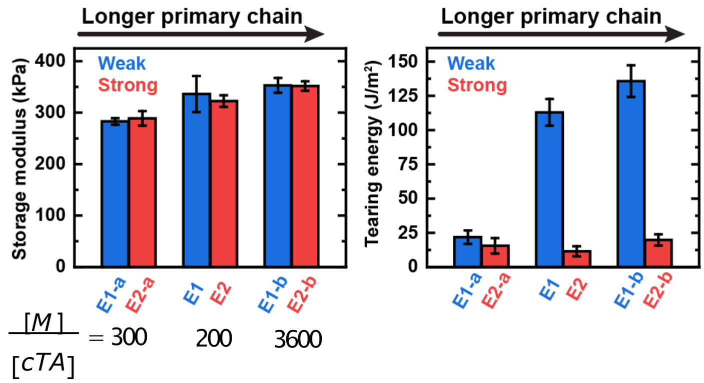
68

Vary primary chain length



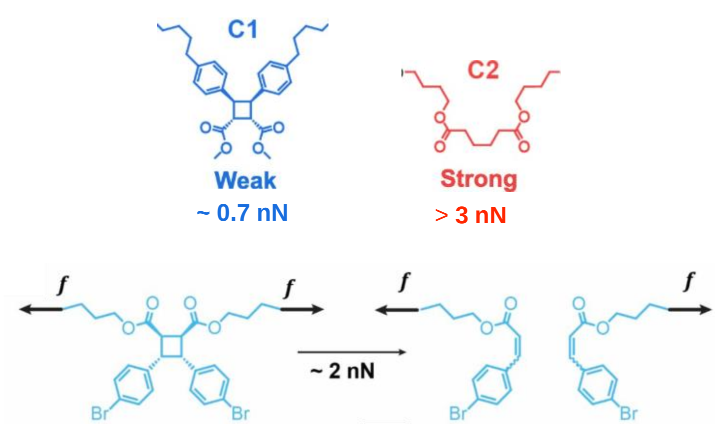
vs.

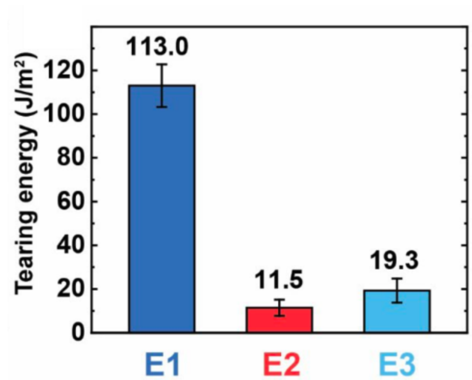




Strong xlinks have almost no dependence on N
Weak xlinks have strong dependence on N
What about mechanophore reactivity?

Effect of mechanophore reactivity

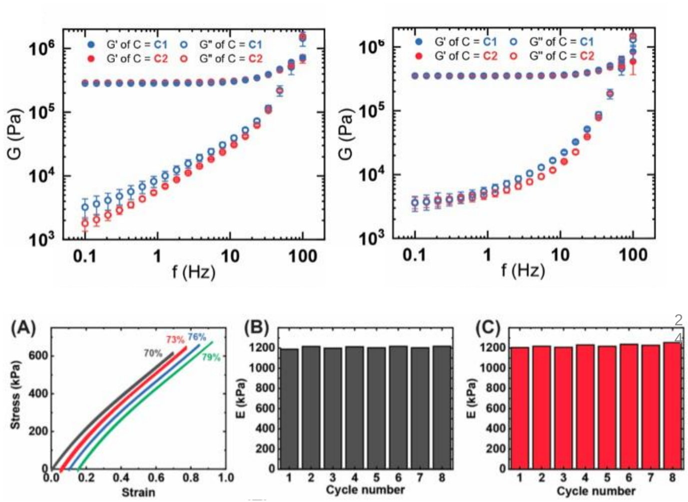




Is it enough to just be more reactive than the primary chain?

***No.* Mechanochemical reactivity matters**
Ongoing: "optimal" mechanophore?

Other attributes are indistinguishable



mechanophore

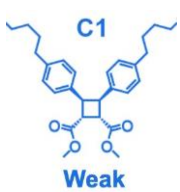
conventional xlink

indistinguishable network properties

no hysteresis in cyclic loading

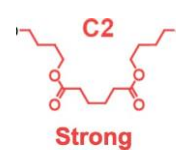
71

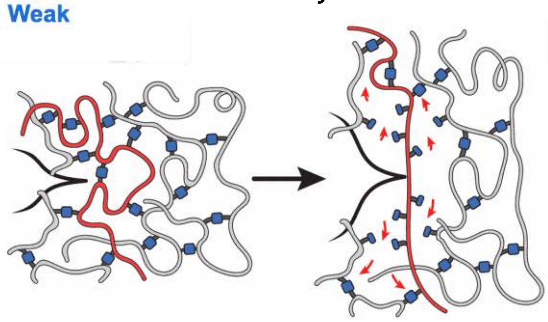
Consequences

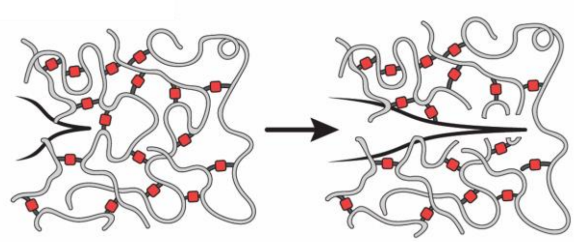


Need enough mechanochemical lability to redirect molecular fracture

Need enough thermal stability to otherwise stay intact & function







path forward is molecular! reactivity, network topology

25

72

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same kinetic and mechanistic principles — coupled to force

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yes! consequences depend on network & mechanophore

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73

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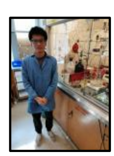
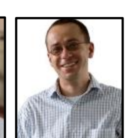
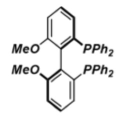
3. Can I use polymer materials for the top-down manipulation of reaction pathways?





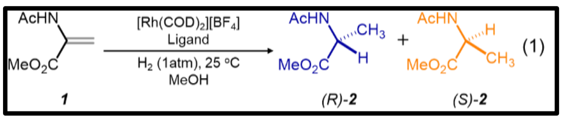
74

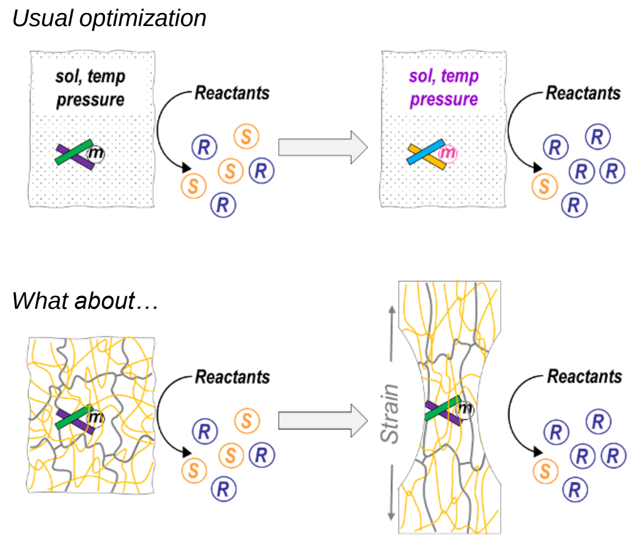
Catalysis



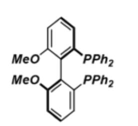
(R)-MeOBiphep

Ligand



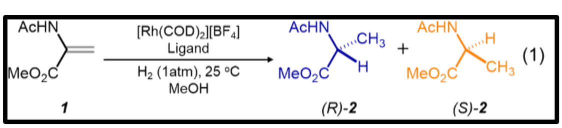


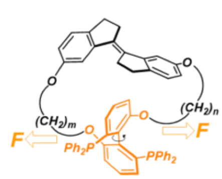
Catalysis



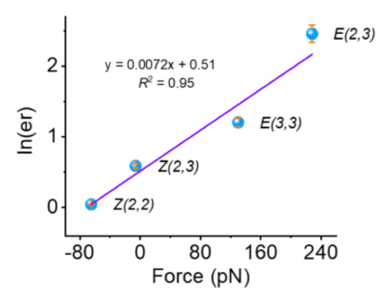
(R)-MeOBiphep

Ligand





Tension
E(m,n)

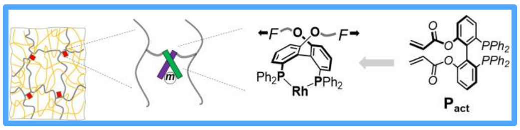


reaction with ligand = MeOBiphep improves selectivity with tension in small molecule force probe systems.

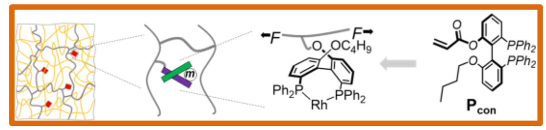
translate to bulk?

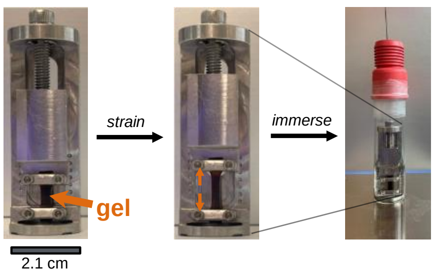
DOI: 10.26434/chemrxiv-2023-vt45d

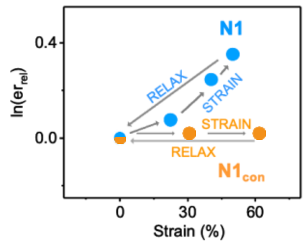
Catalysis

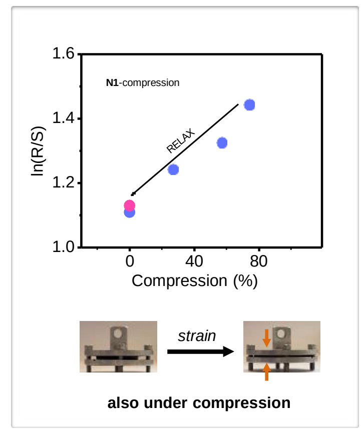


mechanically decoupled control









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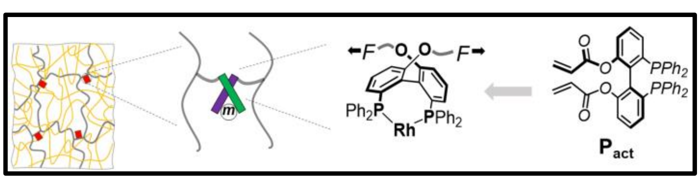
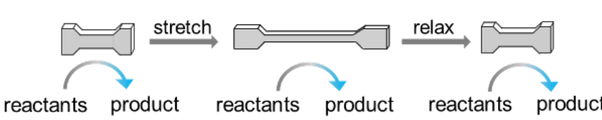
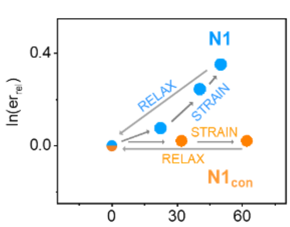
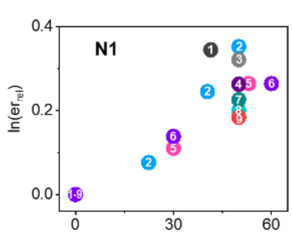
77

Catalysis









Key points

- Effect is reproducible, but small (from 50% ee to 60% ee)
- Very heterogenous — some catalysts unaffected. But…
- Small molecule probes and computations suggest some sites might undergo up to 300-fold improvement (e.g., racemic to 99.7% ee)

Top-down manipulation of catalytic reaction pathways is possible

DOI: 10.26434/chemrxiv-2023-vt45d

78

Questions for today

1. How do I think about kinetics and reactivity in polymer mechanochemistry?

2. Can embedded mechanochemistry redefine polymer material performance limits?

yes! consequences depend on network & mechanophore

3. Can I use polymer materials for the top-down manipulation of reaction pathways?

yes! opportunities for reaction and material/device design

79

Questions for today

1. How do I think about kinetics and reactivity in polymer mechanochemistry?

same kinetic and mechanistic principles — coupled to force

2. Can embedded mechanochemistry redefine polymer material performance limits?

yes! consequences depend on network & mechanophore

3. Can I use polymer materials for the top-down manipulation of reaction pathways?

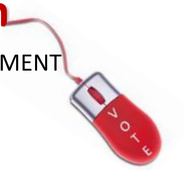
yes! opportunities for reaction and material/device design

Thank you (and back to Jeff)!

80

Audience Survey Question

ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT



How did the understanding of polymer mechanochemistry change about 20 years ago, shifting from a focus on destruction and limits of polymer strength?

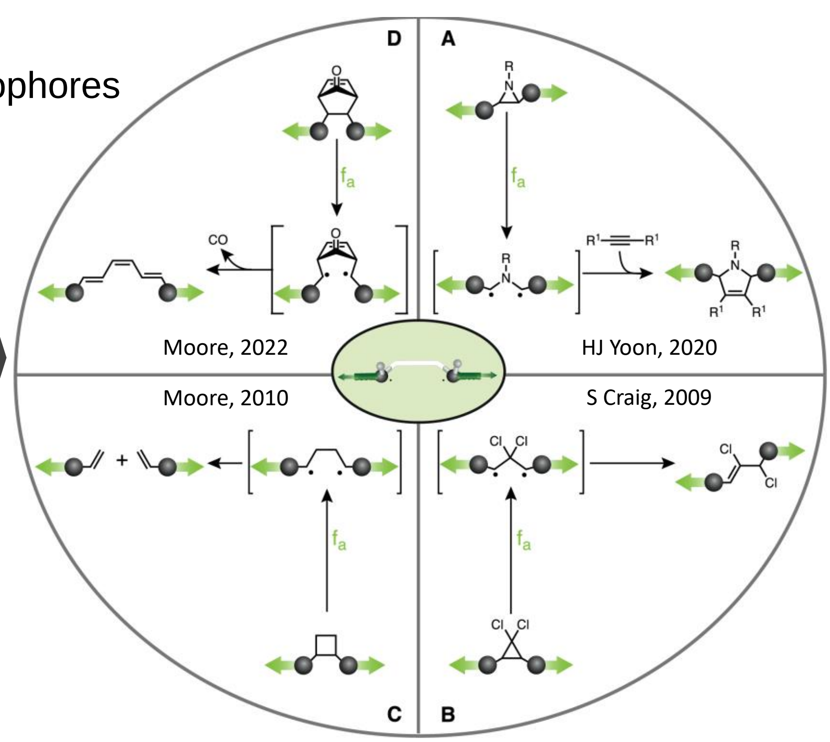
- **A.** Mechanical forces were found to uniformly degrade polymers, regardless of their structure.
- **B.** Mechanical forces were realized to selectively trigger chemical changes in certain polymers, leading to mechanoresponsive materials.
- **C.** It was determined that all polymers exhibit similar strengths and weaknesses under mechanical stress.
- **D.** Mechanical stress was deemed irrelevant in altering polymer properties at the molecular level.

81

81

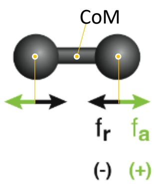
Representative Mechanophores

Many mechanophores are based on selective C-C bond scission

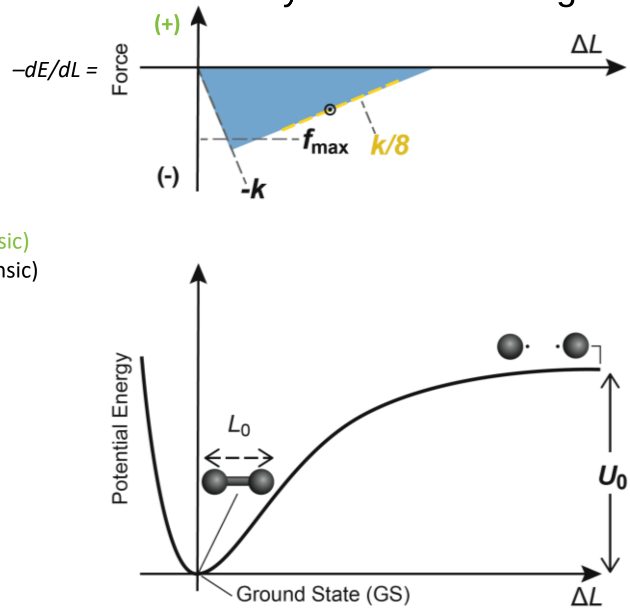


82

Making Sense of Mechanochemistry – The Restoring Force Triangle



f_a = applied force (extrinsic)
f_r = restoring force (intrinsic)

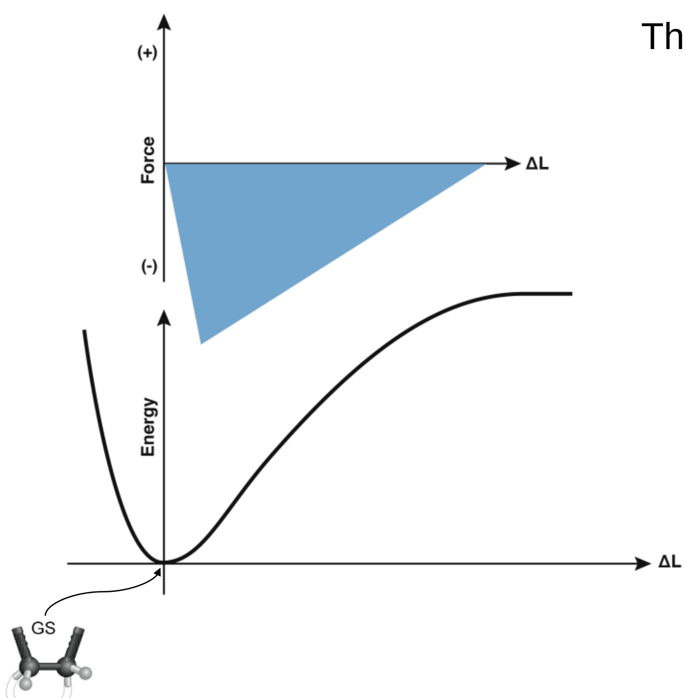


https://chemrxiv.org/engage/chemrxiv/article-details/64c326d1ce23211b20accfc5 [chemrxiv.org]

Morse, P. M. (1929). "Diatomic molecules according to the wave mechanics. II. Vibrational levels". *Phys. Rev.* 34 (1): 57–64

83

The Tension Activated Bond



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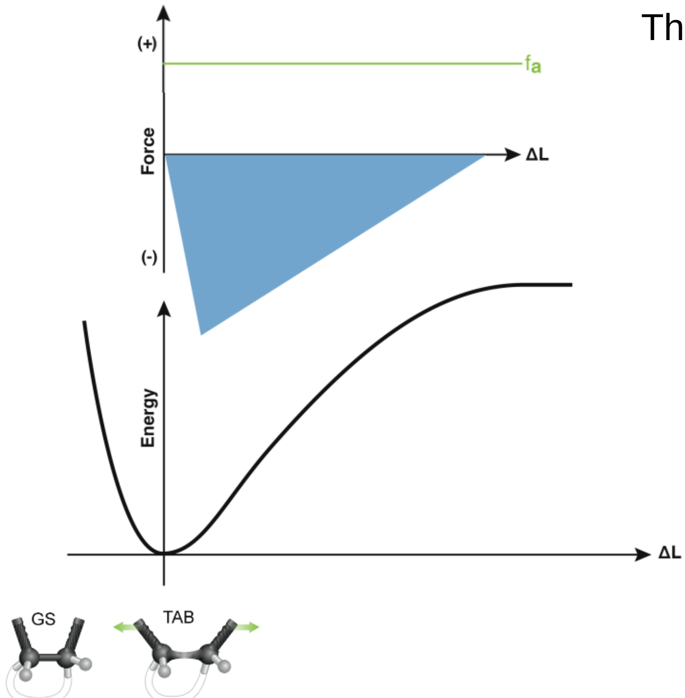
The Tension Activated Bond



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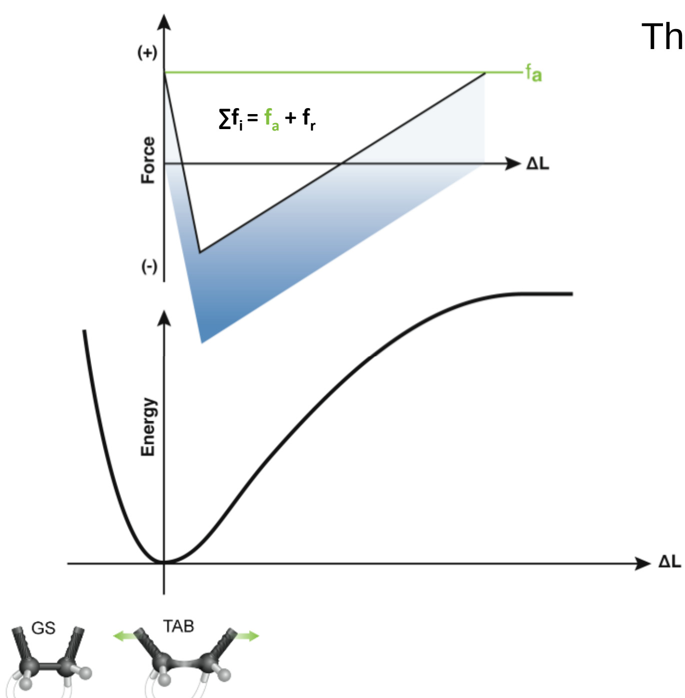
The Tension Activated Bond



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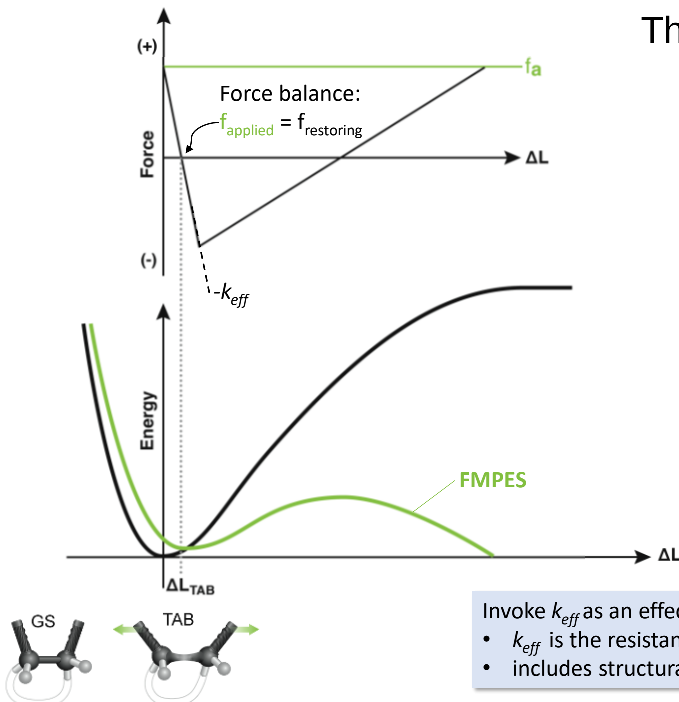
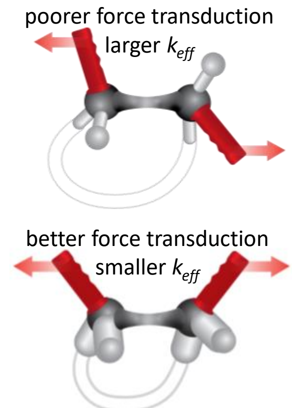
The Tension Activated Bond

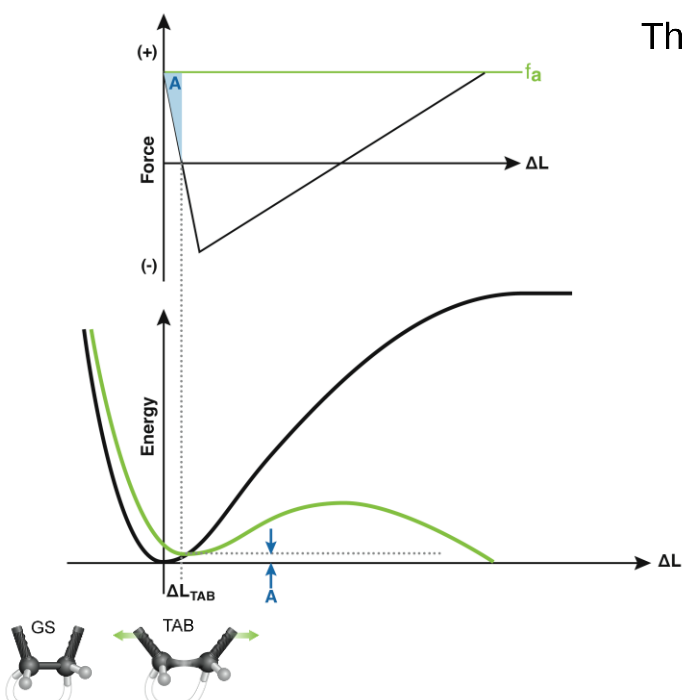




Invoke k_{eff} as an effective bond force constant
- k_{eff} is the resistance to deformation under applied force
- includes structural features that transduce force to bond

87

The Tension Activated Bond



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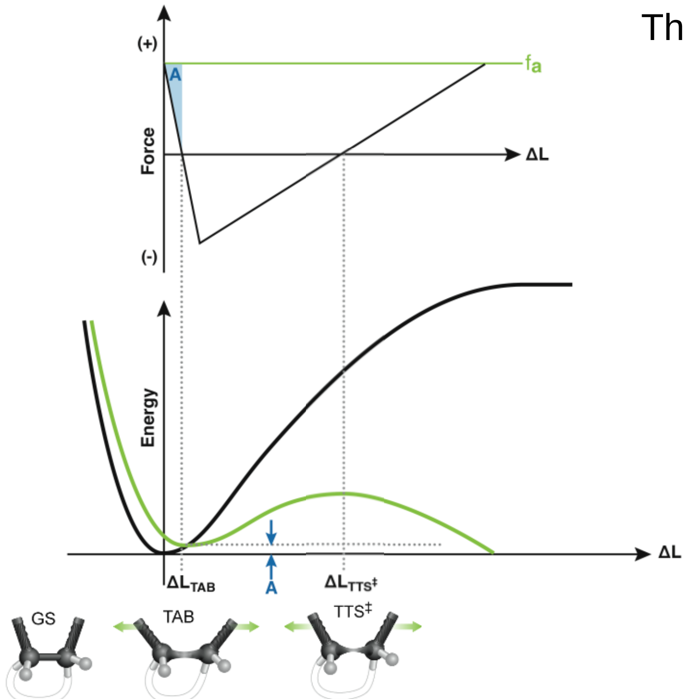
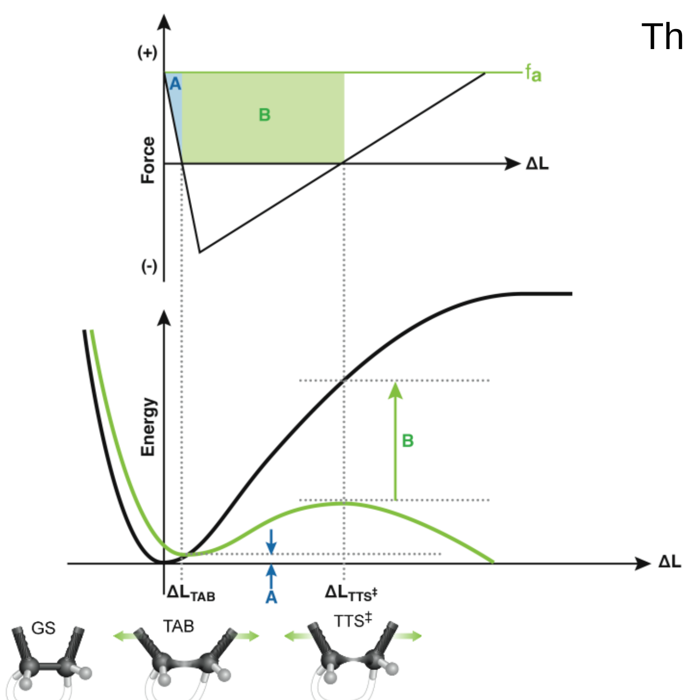


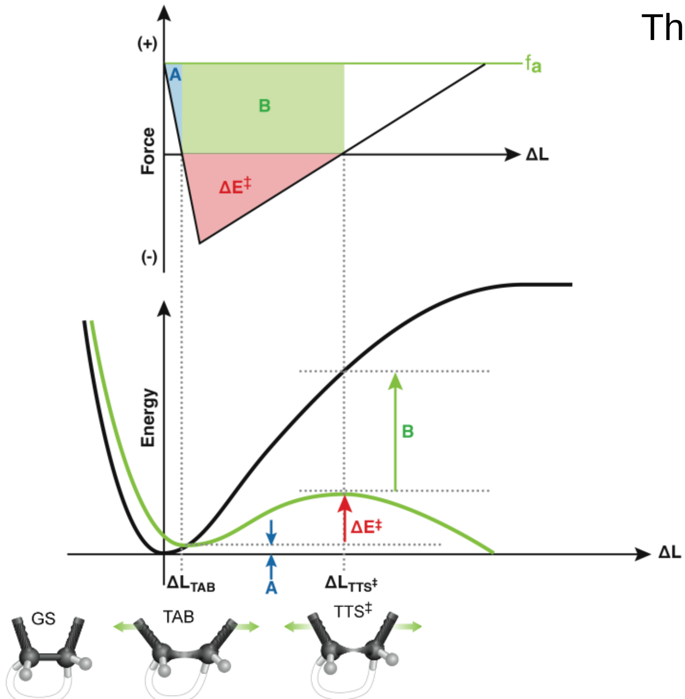
The Tension Activated Bond

89



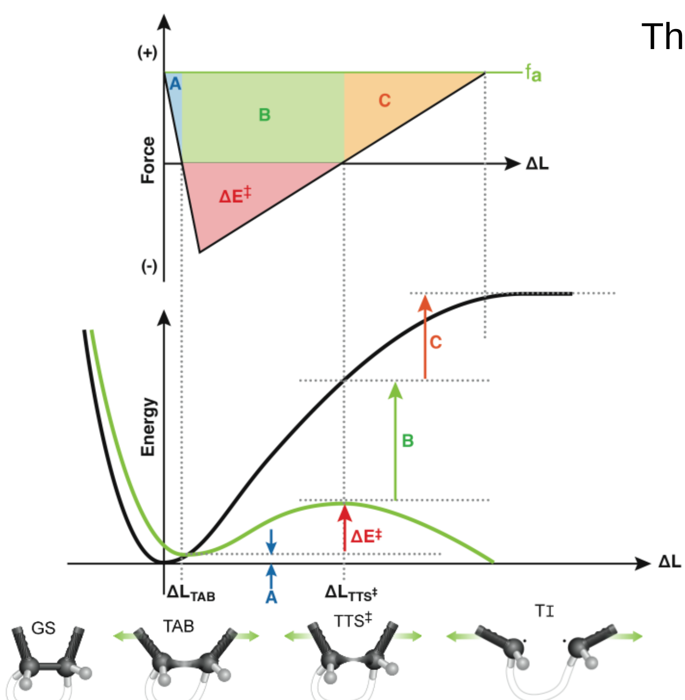
The Tension Activated Bond

90



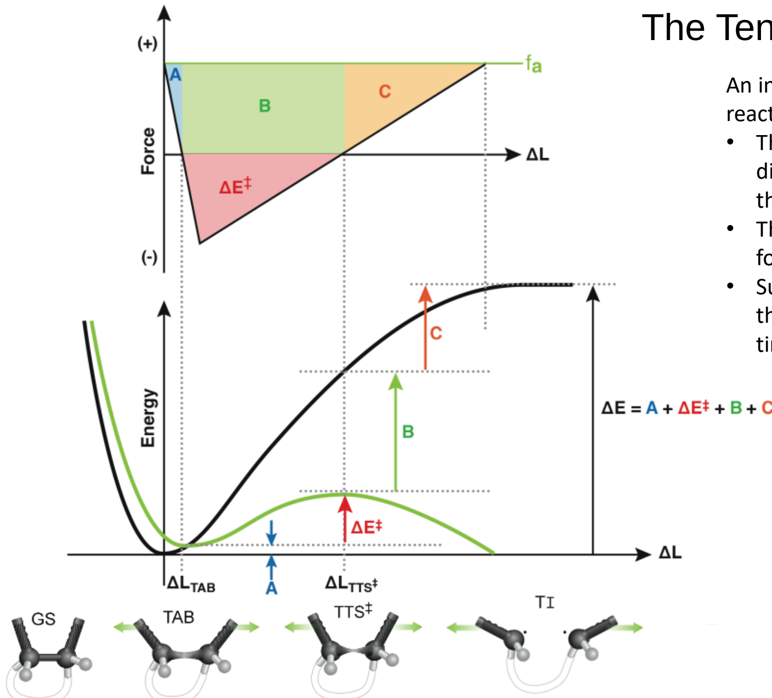
The Tension Activated Bond

91



The Tension Activated Bond

92



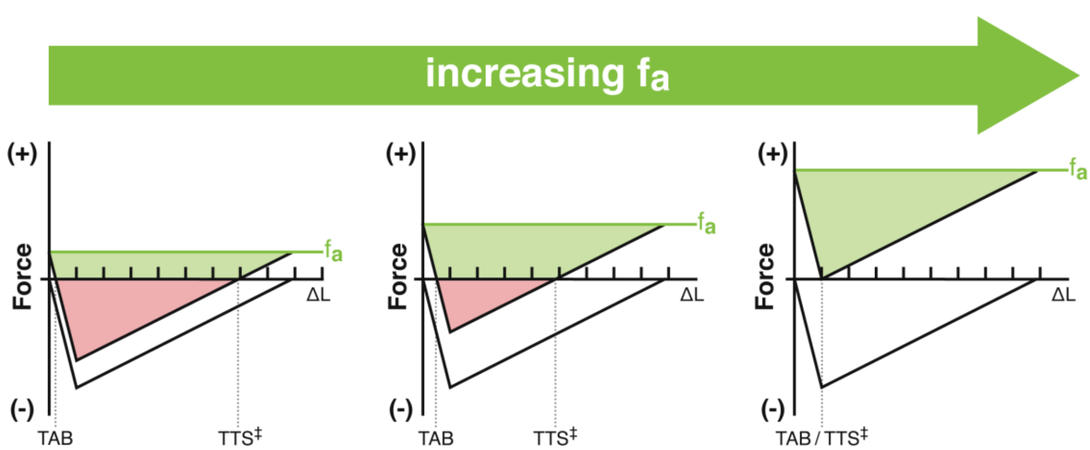
The Tension Activated Bond

An intuitive, easy-to-compute reactivity model for the TAB

- The larger the △E (force-free dissociation energy) the larger the force to activate
- The larger k_{eff}, the larger the force to activate
- Surmounting △E‡ depends on the reaction conditions and timescale of the experiment

93

Dependence of TAB, ΔE‡, and TTS‡ on Applied Force



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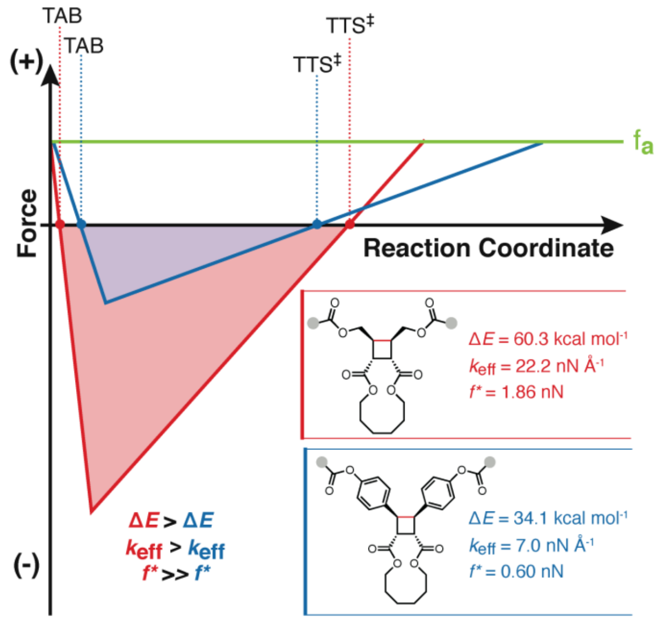
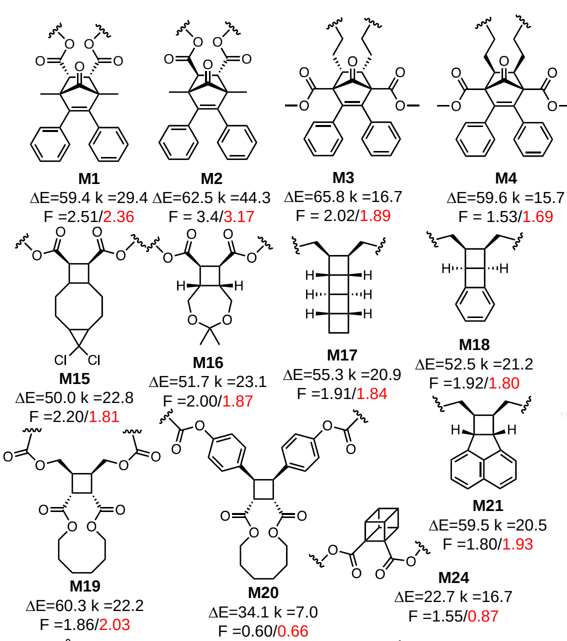
Application of the Restoring Force Triangle

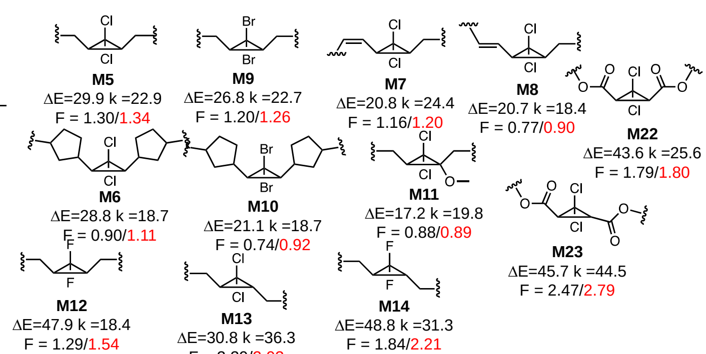


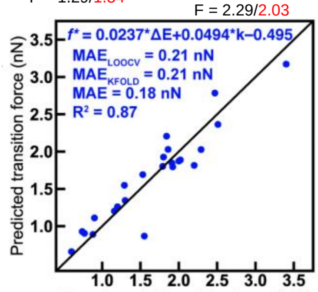
95

Predictions from the Tension Activated Bond Model

With H Kulik (MIT) and S Craig (Duke)







- Cubane is the outliner
- Easy computational workflow compared to CoGEF (1-2 days for >20 mechanophores)

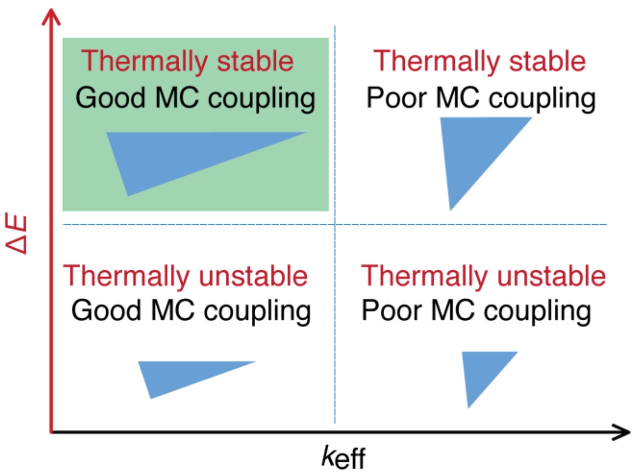
k: nN/ Å ; ΔE (diradical intermediate) : kcal mol-1

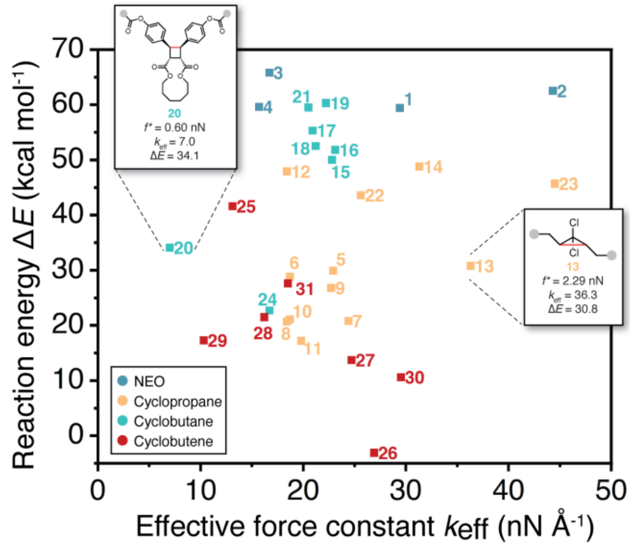
experimental/predicted force

96

96

Thermally Stable, Mechanically Active





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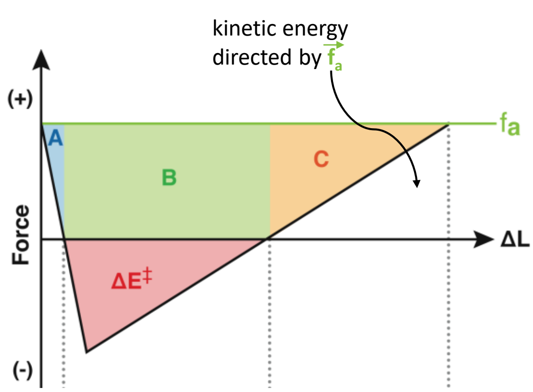
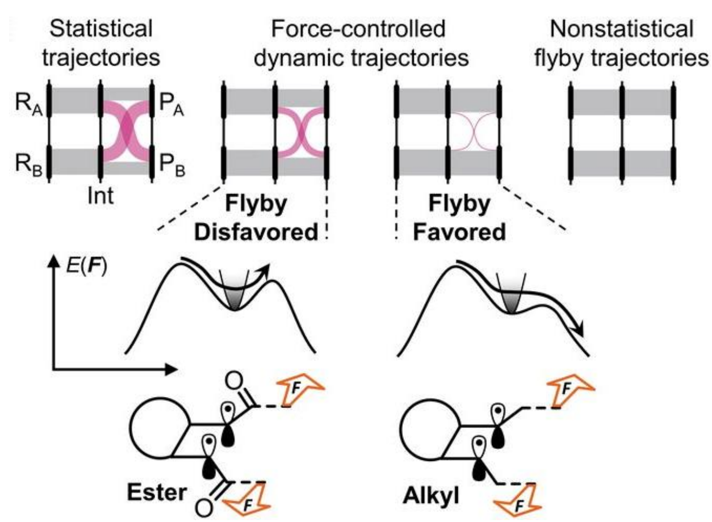
Excess Force Leads to Flyby Trajectories



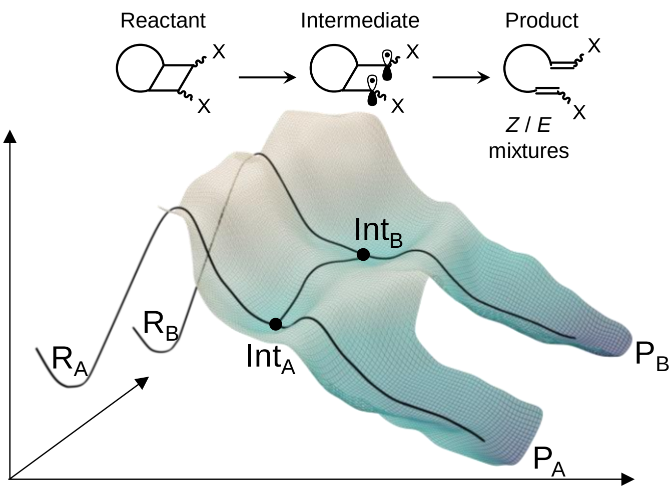


Liu et al. *Science* 2021, 373, 208-212 “Flyby Reaction Trajectories”

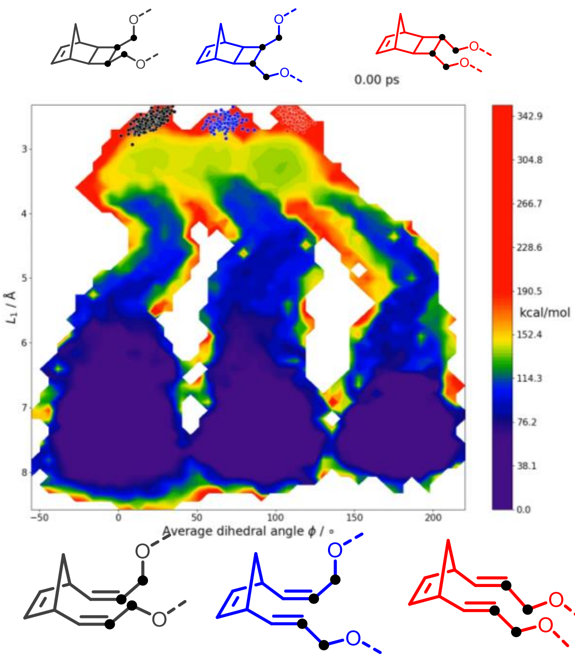
98

Force-Driven Dynamic Trajectories

With T Martinez (Stanford)

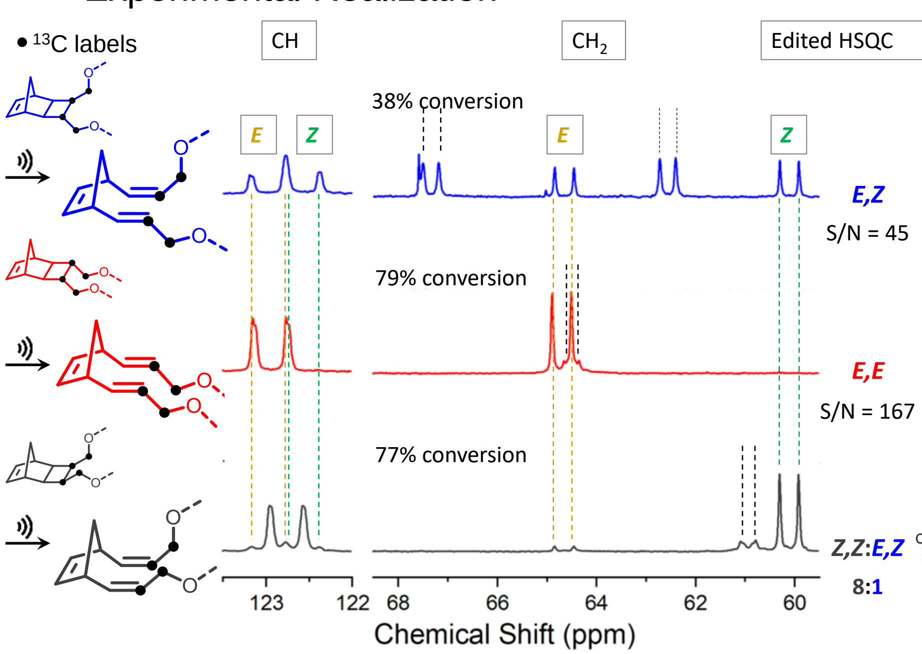


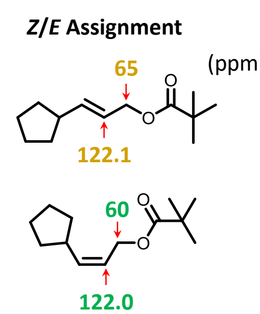
Liu et al. *Science* 2021, 373, 208-212 “Flyby Reaction Trajectories”

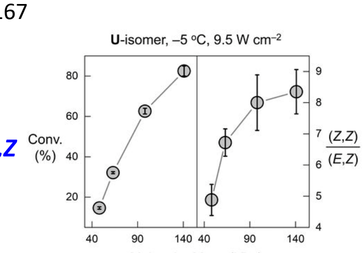


99

Experimental Realization







Ultrasound: 8 h on time, 8.9 W cm^{-2}, 1 s on, 2 s off; –10 °C bath, THF, Ar, ~100 kDa, 1.5 mg mL^{-1}

100

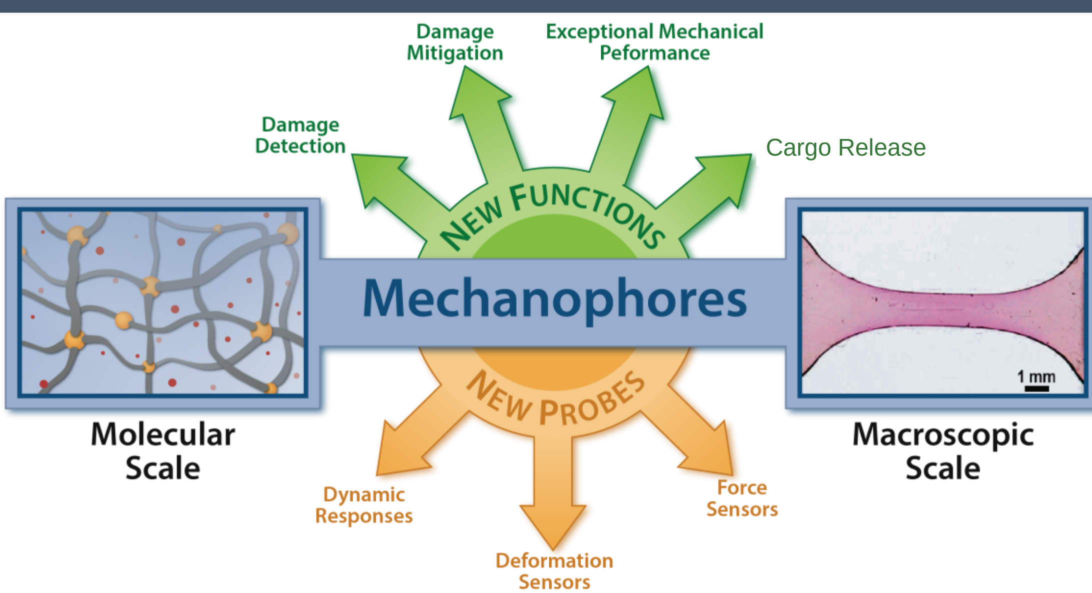
Linking the Molecular and Macroscopic Scales

Force | Work done to activate | Stress | Toughness

Molecular deformation | Molecular deformation rate | Strain | Strain rate

101

Mechanophores: from Concepts to Mechanoresponsive Materials



102

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Dr. Yun Liu
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Dr. Lingyang Zhu

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Tatiana Kouznetsova

Simulation:
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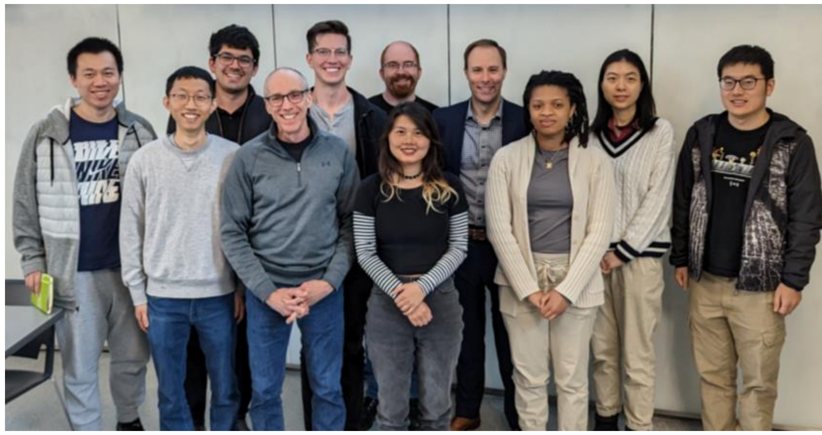
Prof. Heather Kulik
Dr. Ilia Kevlishvili
Dr. Soren Holm
Dr. Jan Meisner



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103

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104

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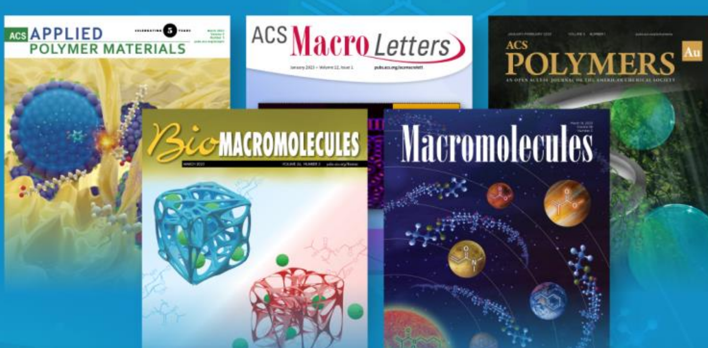

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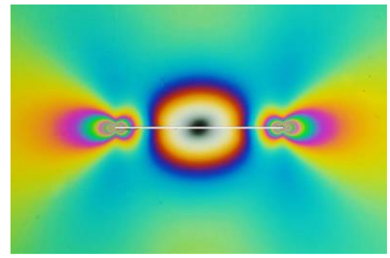

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109