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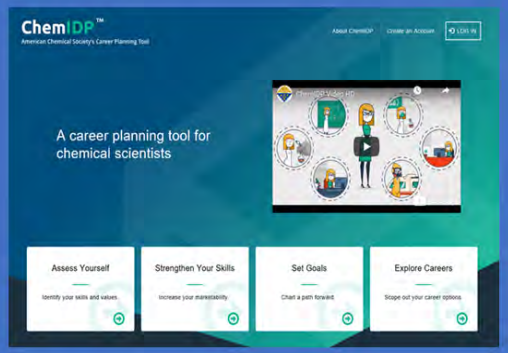

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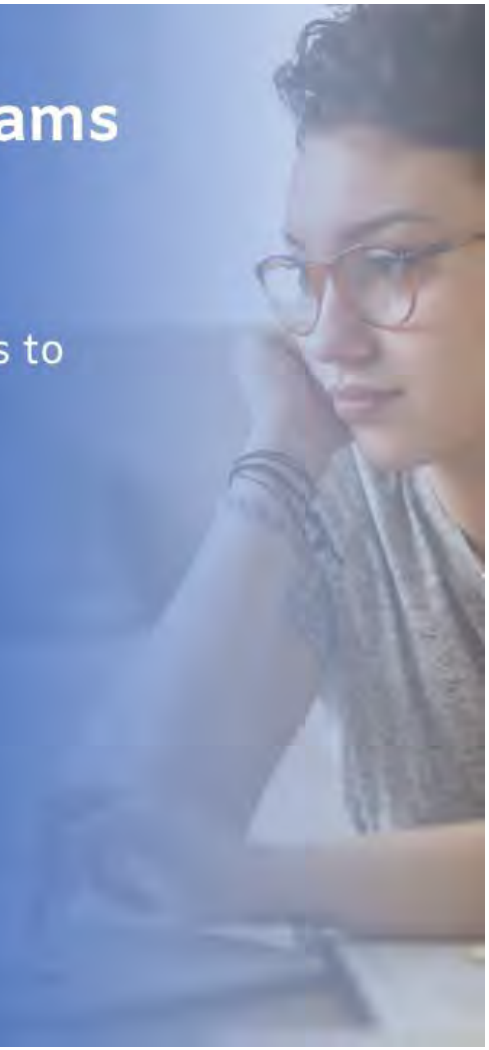

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What You Will Learn

- What types of fabrics and household cloth are effective in particle filtration and why
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- How to disinfect N95 masks and how many times you can do it without reducing filtration efficiency

Co-produced with: ACS External Affairs & Communications and ACS Publications

Monday, June 22, 2020 at 2-3pm ET
Speakers: Bob Corlett and Aileen Hedden of Staffing Advisors
Moderator: Brooke Lockhart, Staffing Advisors

Register for Free!

What You Will Learn

- How virtual interviewing differs from in-person interviewing and how you can use the format to your advantage
- How to make an effective case for yourself (without bragging)
- How to apply timeless principles that are successful in any interview setting and at every career level

Co-produced with: ACS Industry Member Programs

Tuesday, June 23, 2020 at 2-3pm ET
Speakers: Mark Jones, Dow Chemical
Moderator: Bryan Tweedy, American Chemical Society

Register for Free!

What You Will Learn

- Accessible communication does not mean simplistic communication
- Brevity is both appreciated and improves clarity
- Self-editing is the surest way to improve clarity and attain brevity

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ACS Division of Polymer Chemistry, Inc.

2019 POLY Chair
Sarah Morgan





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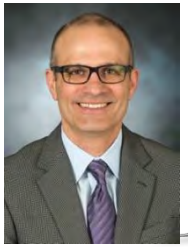

"….the next generation of polymer scientists is where we put a lot of our focus and we've really established a tremendous network of scientists at all points in their career. …our more seasoned members are active in helping support and foster the growth of the next generation through mentoring and a very active awards program."

Marc Hillmyer, 2017 POLY Chair
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Self Healing Polymers and Vitrimers

Brent Sumerlin
George B. Butler Professor, Department of Chemistry, University of Florida

Marek Urban
J.E. Sirrine Foundation Endowed Chair and Professor, Department of Materials Science and Engineering, Clemson University

Christopher Bowman
Distinguished Professor, Clinical Professor of Restorative Dentistry, Co-Director of the NSF I/UCRC for Fundamentals and Applications and Photopolymerizations, University of Colorado, Boulder

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SELF-HEALING POLYMERS

Marek W. Urban

Department of Materials Science and Engineering

Center for Optical Materials Science and Engineering (COMSET)

Clemson University, USA

URBAN RESEARCH GROUP

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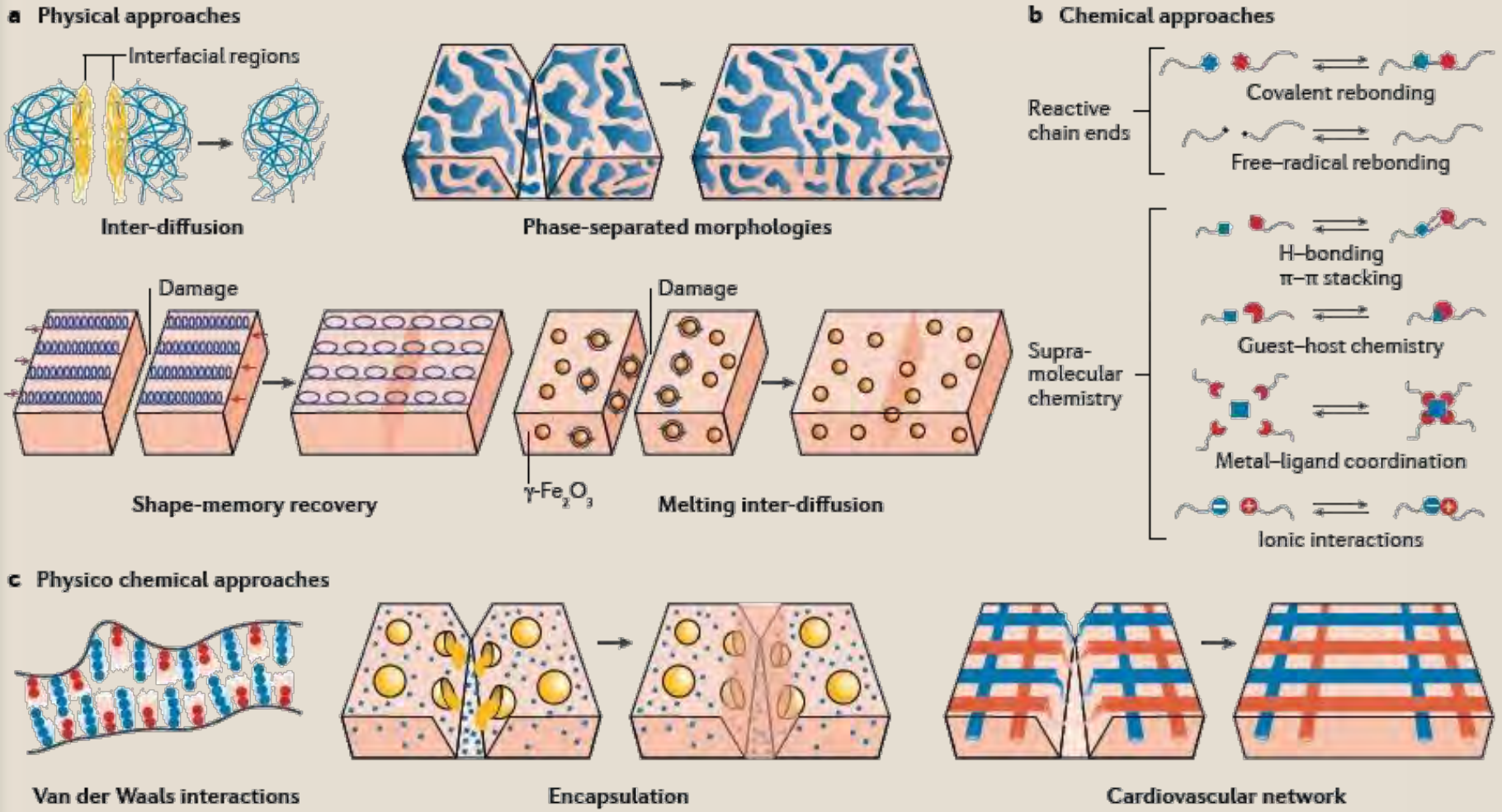
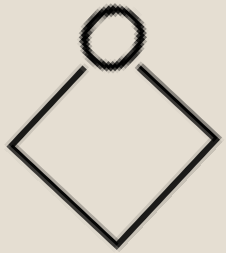
SELF-HEALING APPROCHES IN POLYMERS



Nature Reviews Mat., 2020.
www.nature.com/articles/s41578-020-0202-4

WHAT IS AN ESTIMATED LIFE-TIME OF 4- or 5-MEMBER HETEROCYCLIC RADICALS?

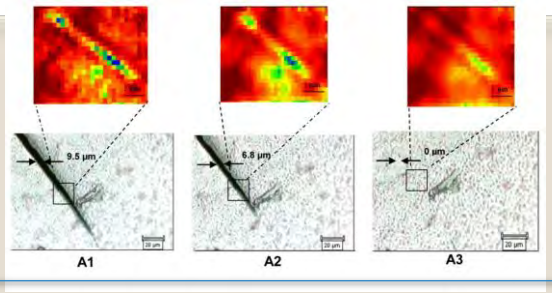
- 10 msec
- 25 sec
- 2 days
- ~1 month
- 10 psec



Prog. Polym. Sci., 2020, 102, 101208

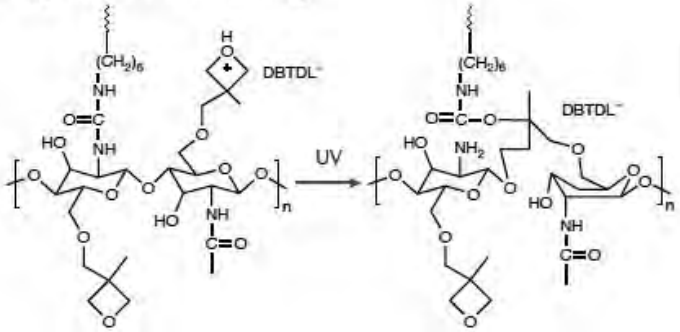
REFORMATION OF COVALENT BONDS

Urban Research Group

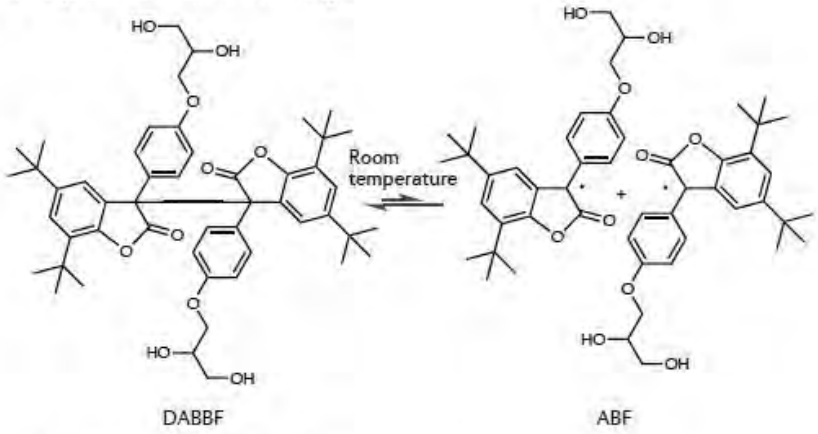


Exposure to UV Light	0	15	30 MIN

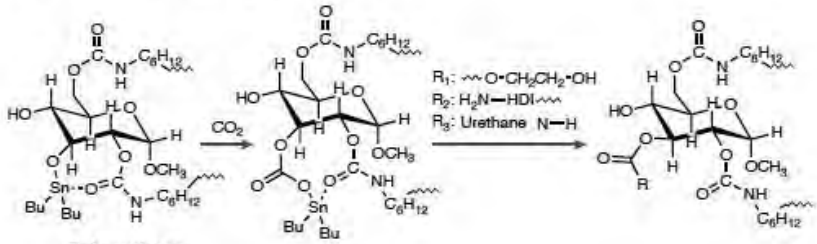
a Polyurethane-radical rebonding



b Polycarbonate-radical rebonding

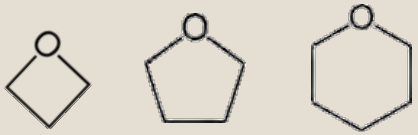


c Generation of reactive groups

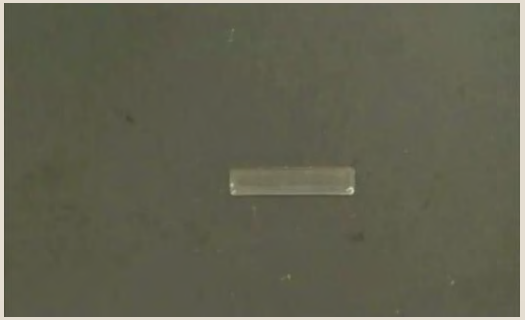


Science, 2009, **323**, 1458.
J. Mater. Chem., 2011, **21**, 14473

Heterocyclic Compounds



Angew. Chem. Int. Ed. 51, 1138–1142 (2012).

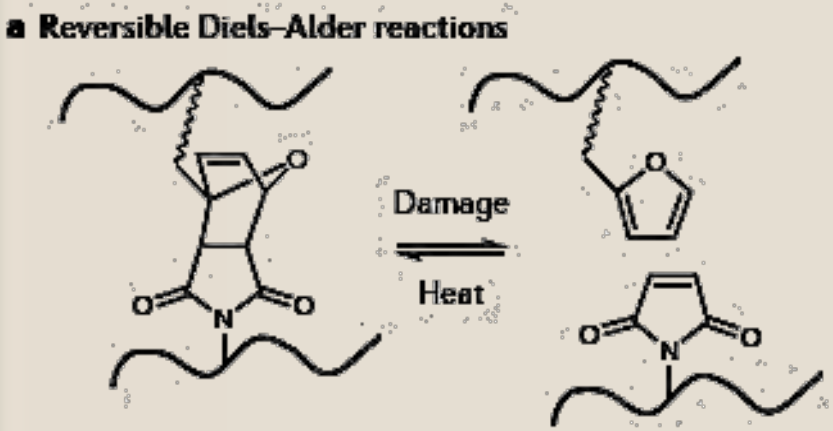


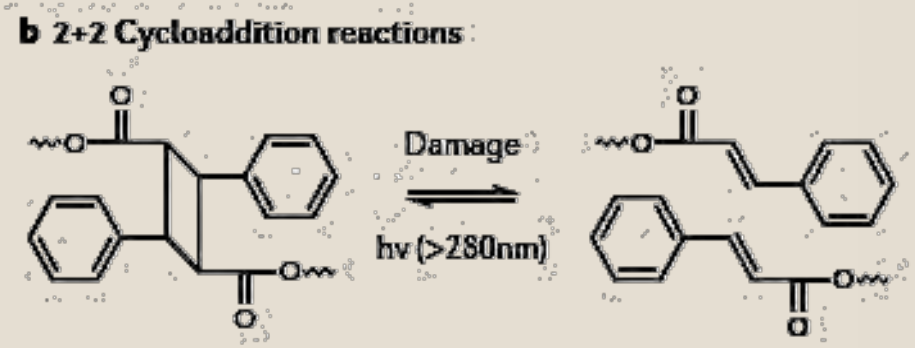
Angew. Chemie, 2014, **53**, 12142 –12147

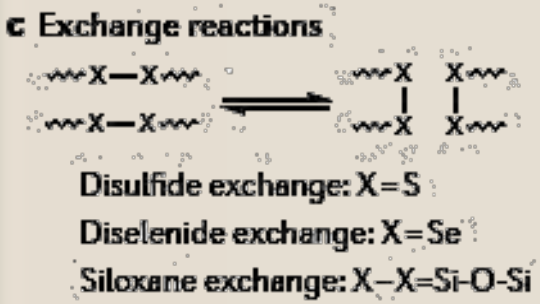
REVERSIBLE REACTIONS ENABLING REFORMATION OF COVALENT BONDS

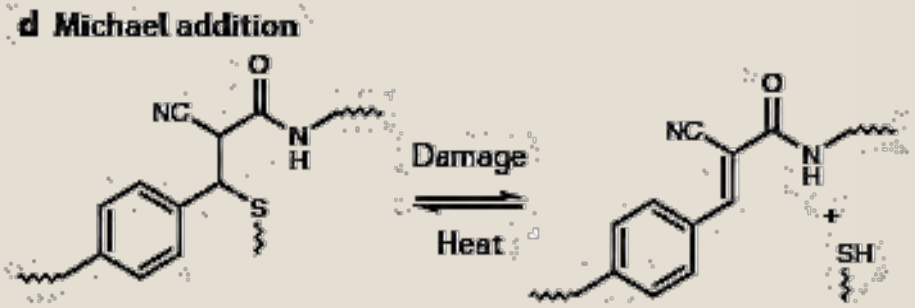
Science 295, 1698–1702 (2002).

Chem. Mater. 16, 3982–3984 (2004).









Macromolecules 43, 4133–4139 (2010).

Macromol. Chem. Phys. 217, 2541–2550 (2016).

DYNAMIC REFORMATION OF COVALENT BONDS

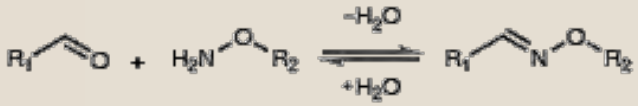
a Schiffs base bond regeneration

Adv. Mater. 27, 3518–3524 (2015).

b Acylhydrazone rebonding

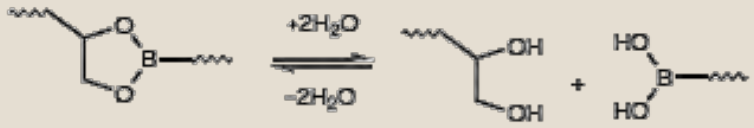
Adv. Funct. Mater. 25, 3295–3301 (2015).

c Oxime rebonding



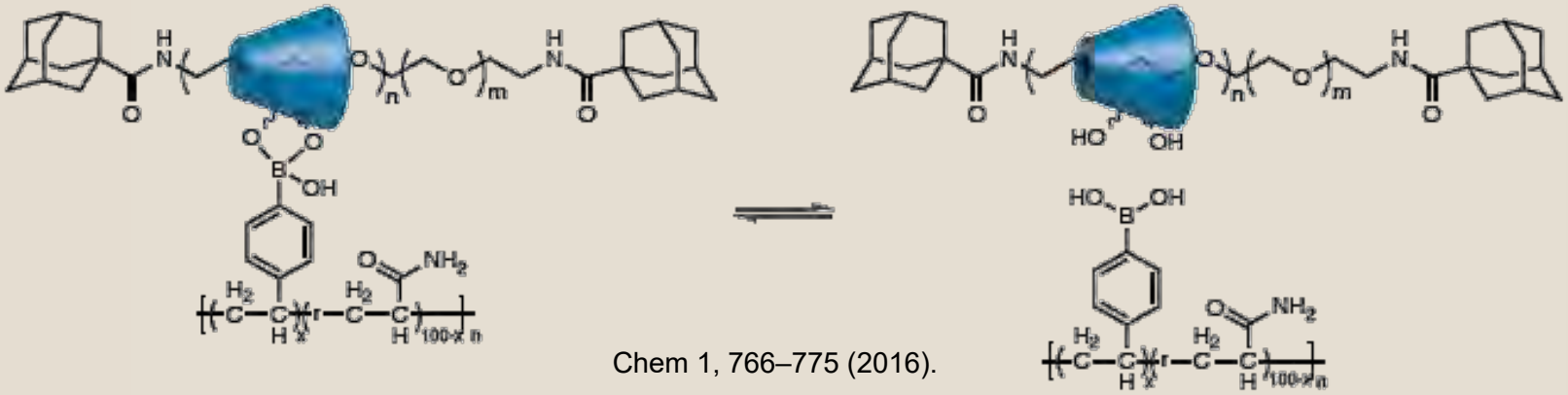
Soft Matter 11, 6152–6161 (2015).

d Boronic ester reformation



Macromolecules 48, 2098–2106 (2015).

e Boronic ester reformation in rotaxane-based polymers

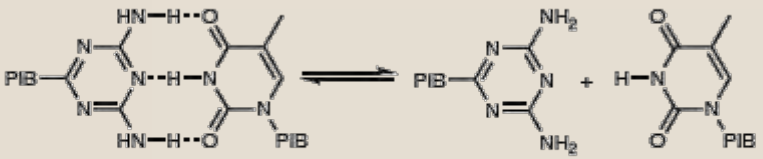


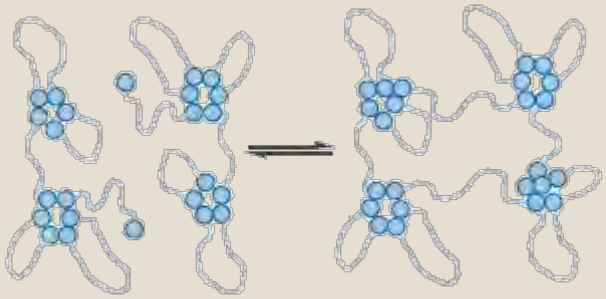
Chem 1, 766–775 (2016).

SUPRAMOLECULAR DYNAMIC CHEMISTRY

Urban Research Group

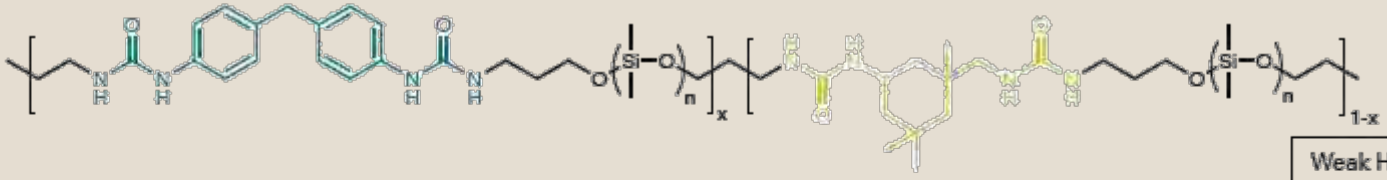
a Triple H-bonding





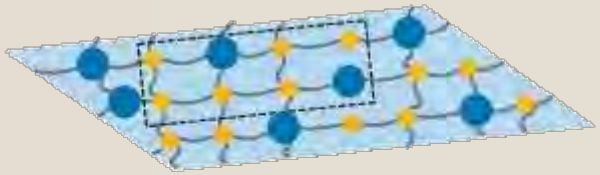
Polym. Chem. 3, 3084–3092 (2012).

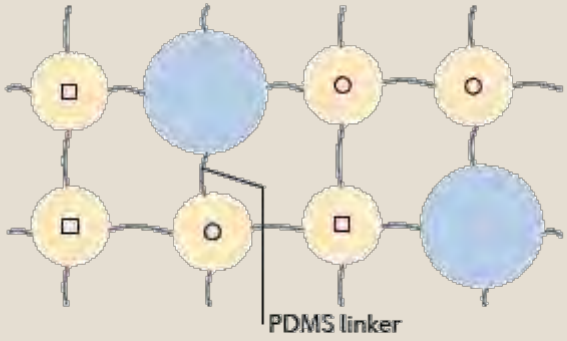
b Combining strong and weak H-bonds

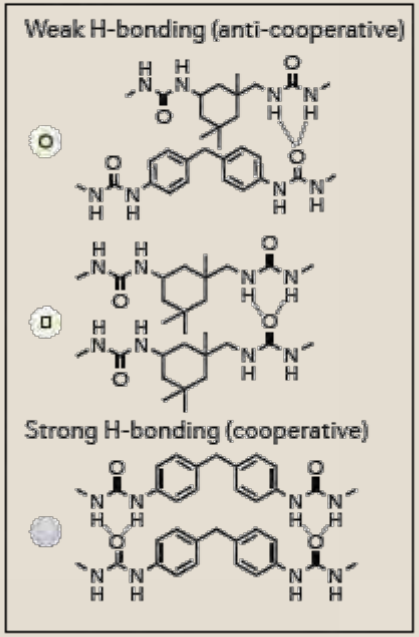


Strong H-bonding

Weak H-bonding







Adv. Mater. 30, 1706846 (2018).

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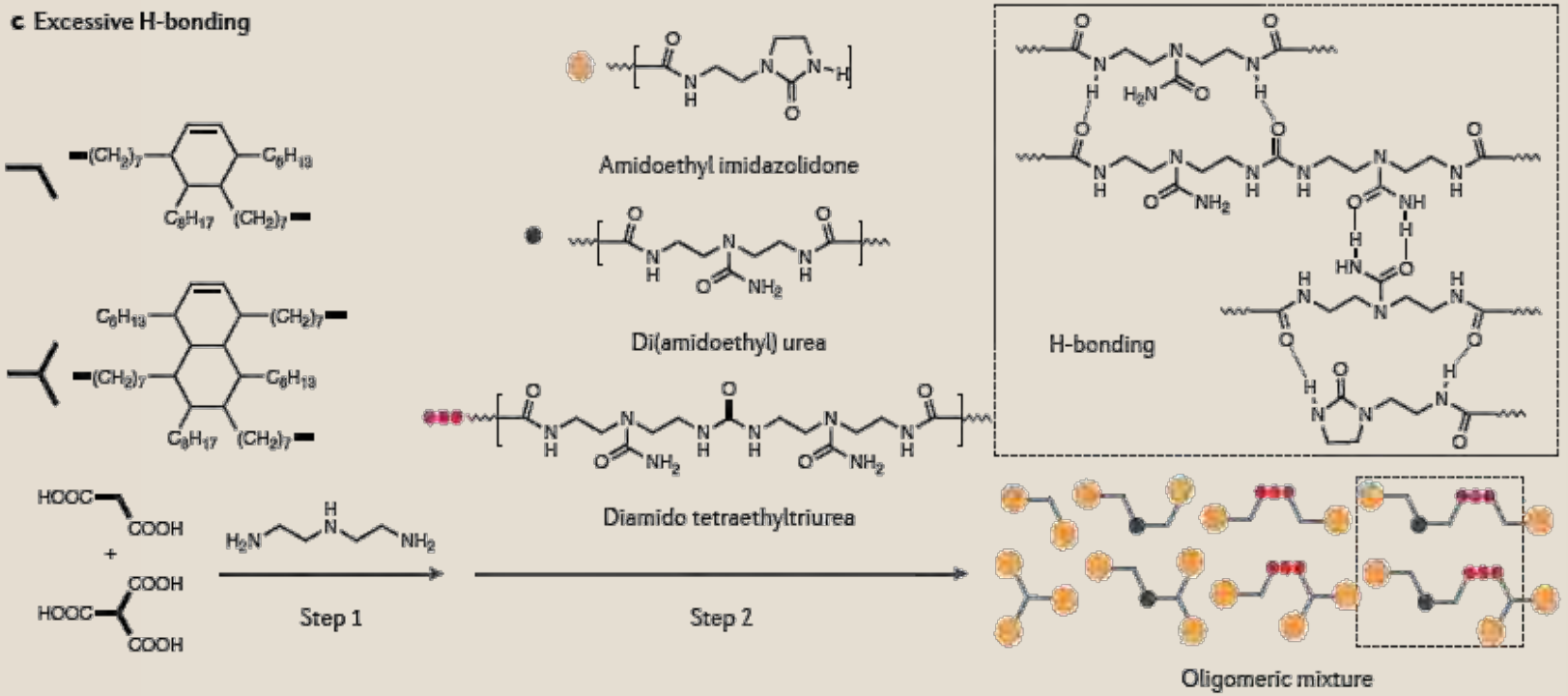
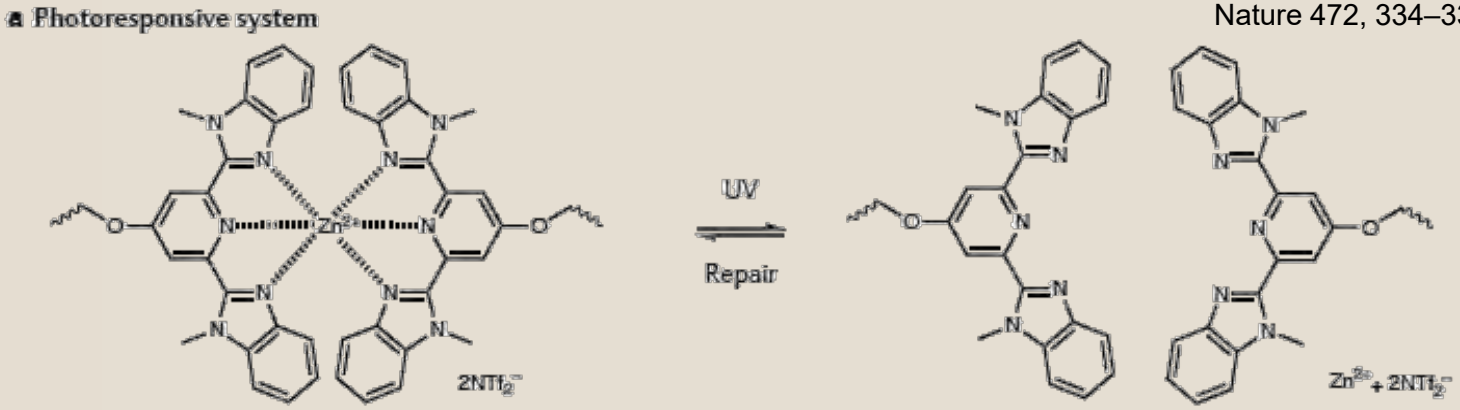


Nature 451, 977–980 (2008)

SELF-HEALING USING METAL–LIGAND COORDINATION CHEMISTRY

Nature 472, 334–337 (2011).



J. Am. Chem. Soc. 138, 6020–6027 (2016).

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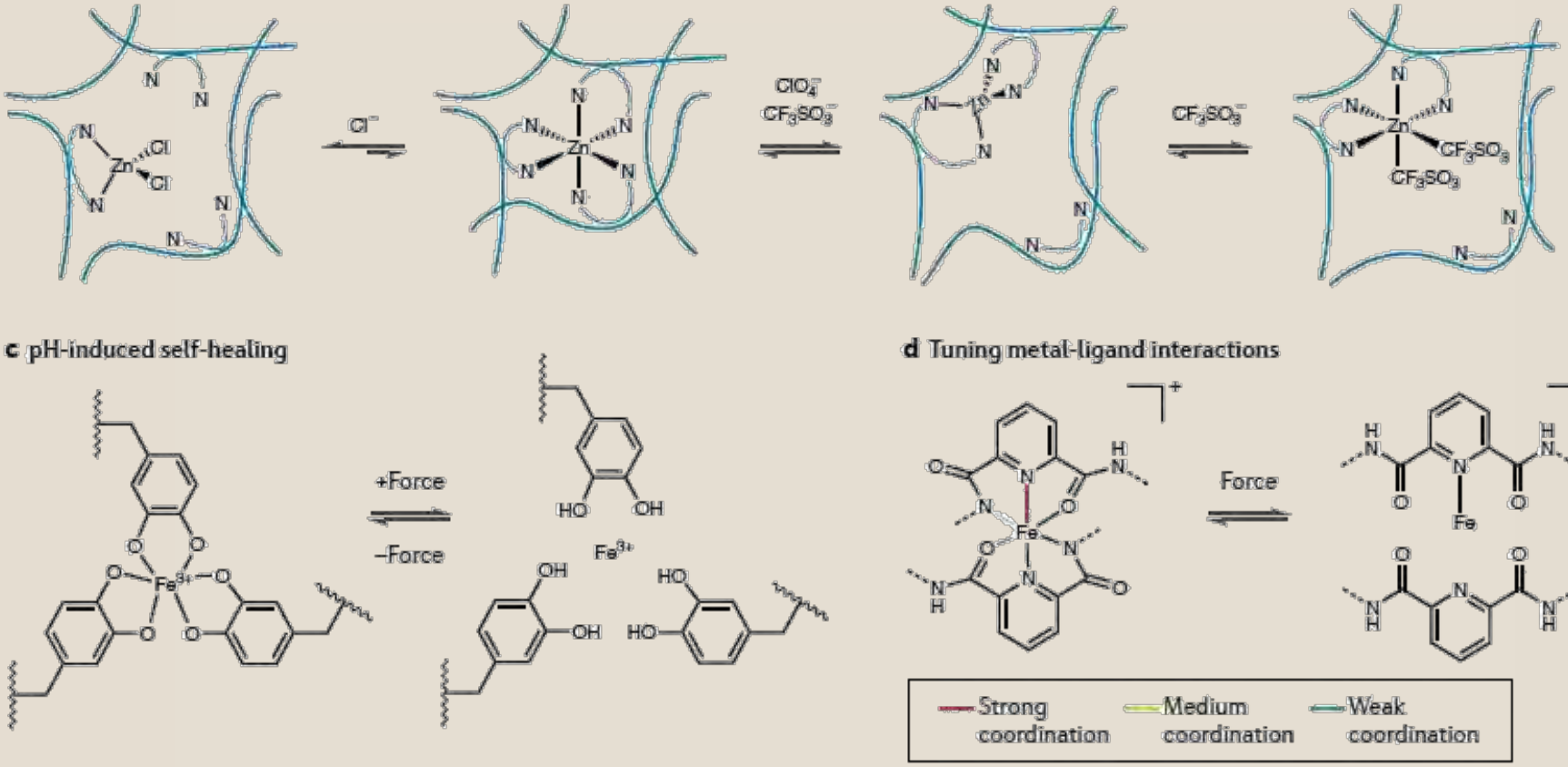
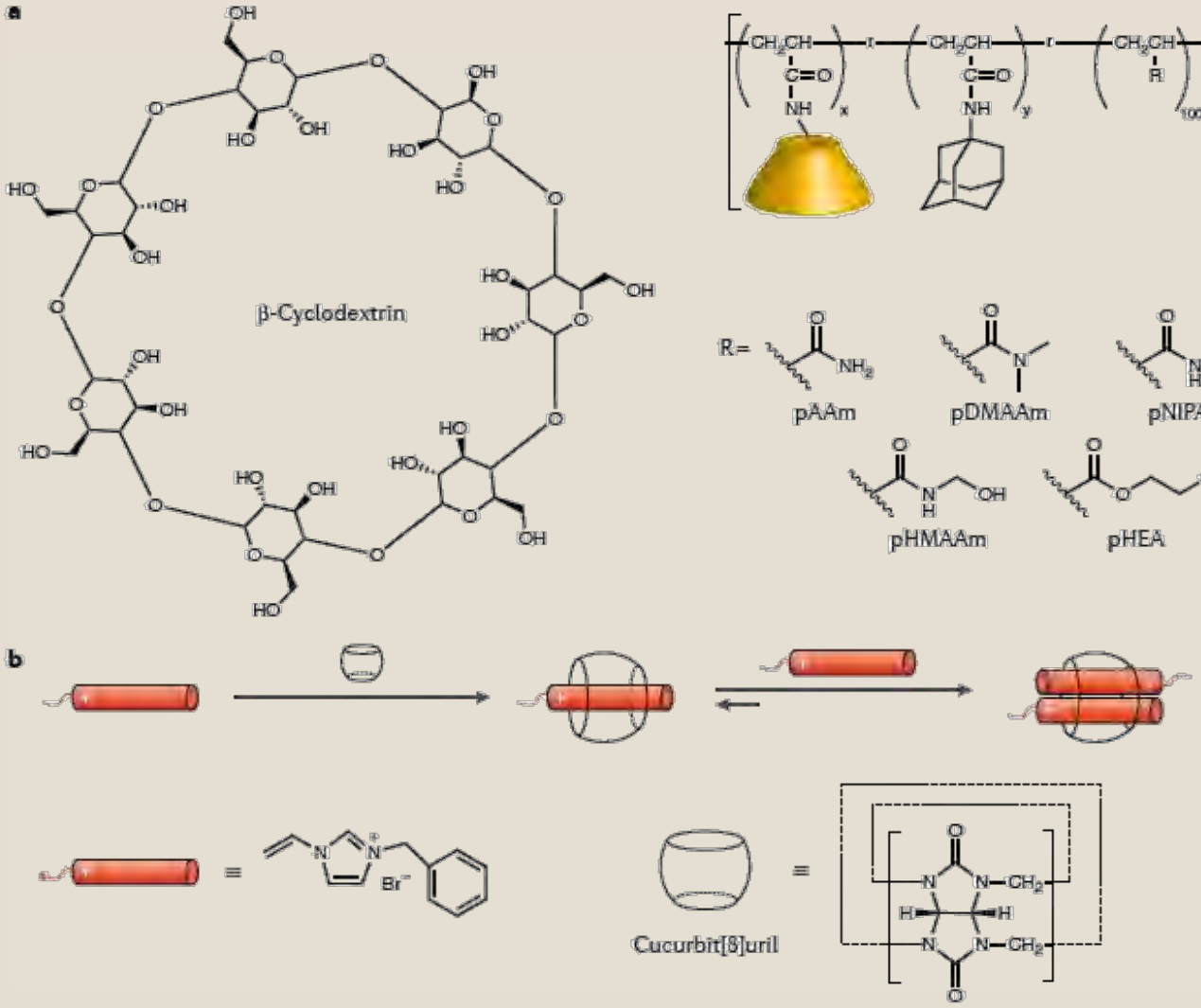


Adv. Funct. Mater. 23, 2081–2090 (2013).

Nat. Chem. 8, 618–624 (2016).

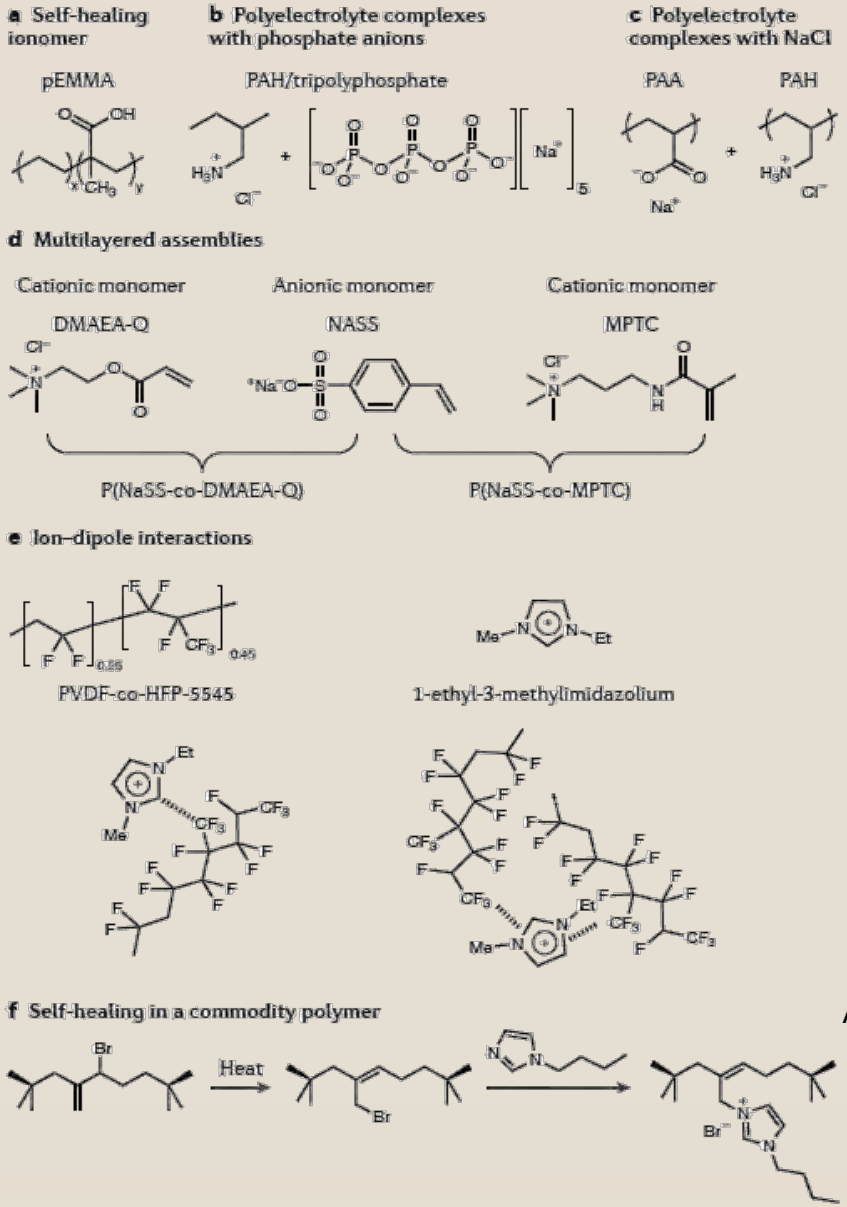
HOST–GUEST CHEMISTRY

Macromol. Rapid Comm. 37, 86–92 (2016).



Adv. Mater. 29, 1605325 (2017).

IONIC INTERACTIONS APPLIED IN SELF-HEALING



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SELF-**HEALING "Key-and-Lock" ACRYLIC COPOLYMERS**

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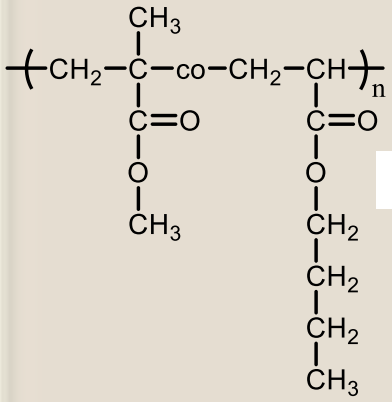
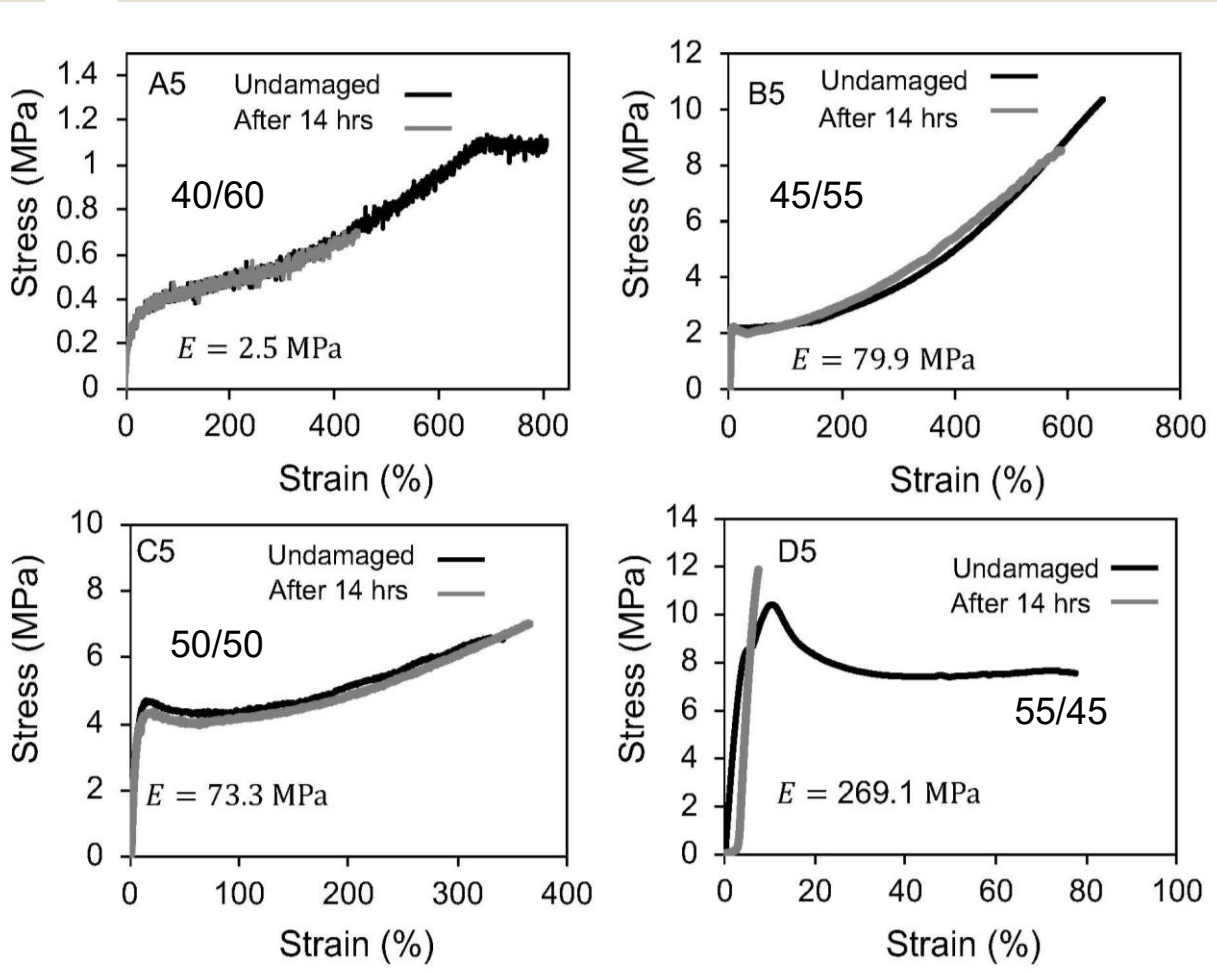
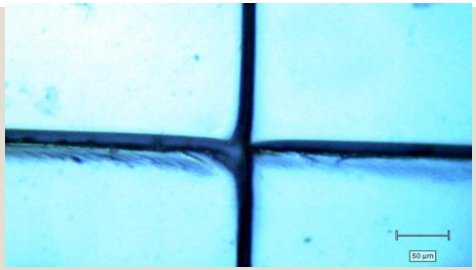
Poly(methyl methacrylate/n-butyl acrylate) (pMMA/nBA)

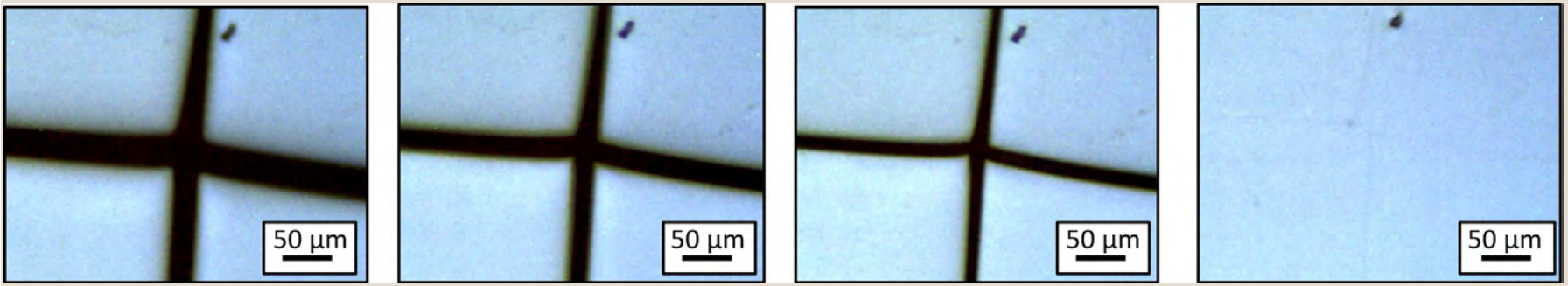


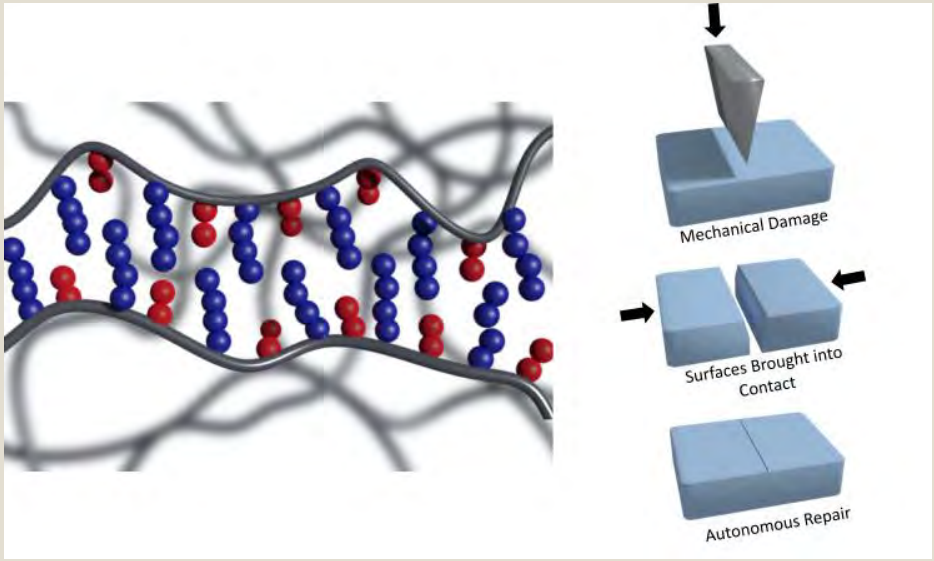
Self-healing occurs within a narrow compositional range

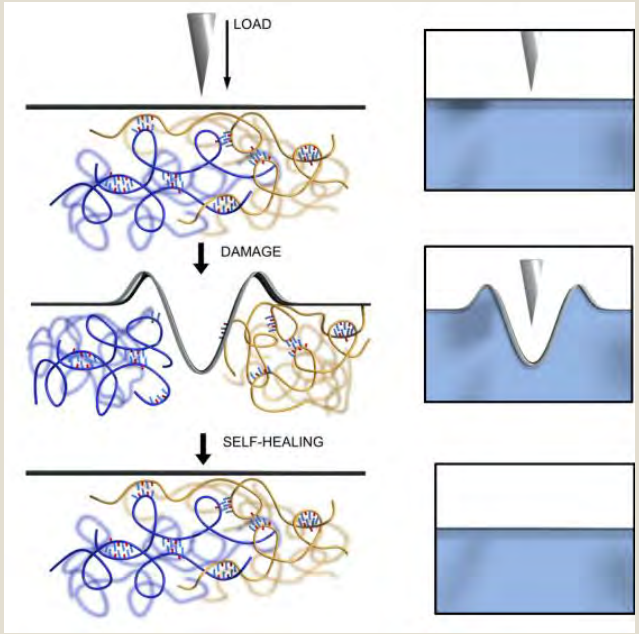


Science, 2018, 362, 220.

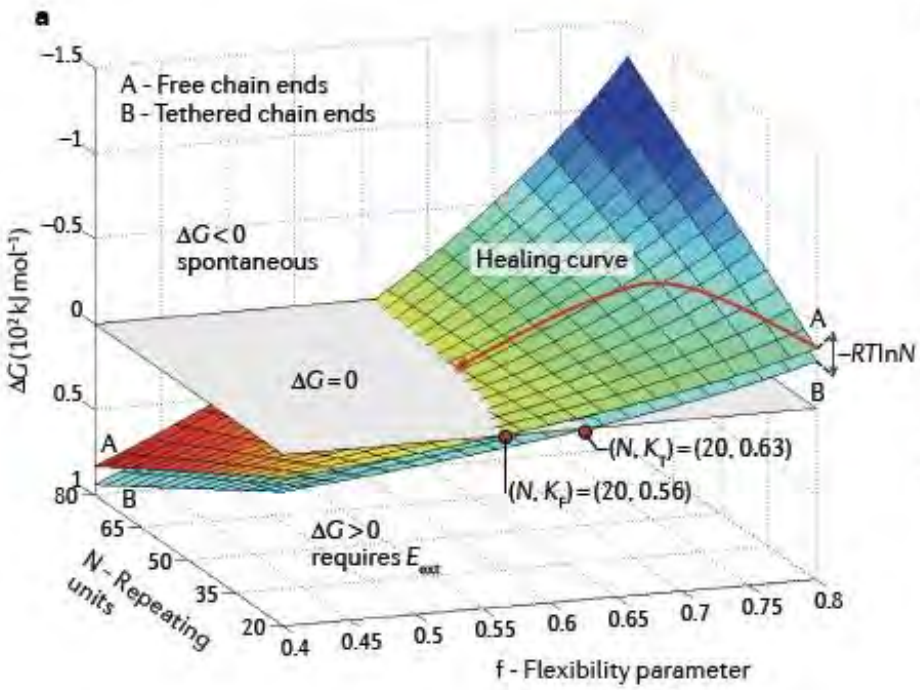


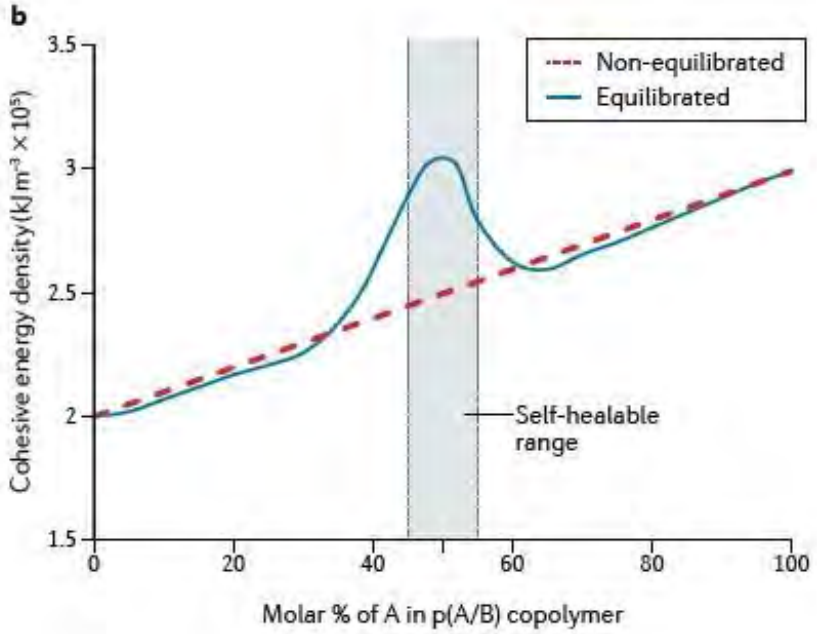






Science, 2018, 362 (6411), 220-225.





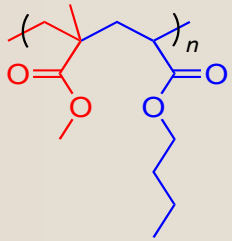
"Self-Healing Polymers; Thermodynamics and Chemistry," in Healable Polymer Systems, RSC Polymer Chemistry Series, 2013.

Science, 2018, 362 (6411), 220-225.

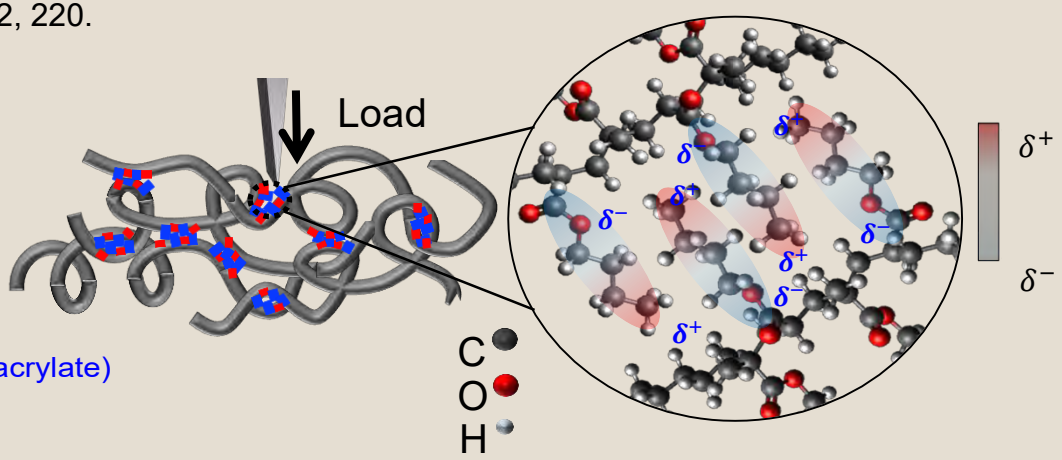
van der Waals (vdW) INTERACATIONS IN SELF-HEALING

Science, 2018, 362, 220.

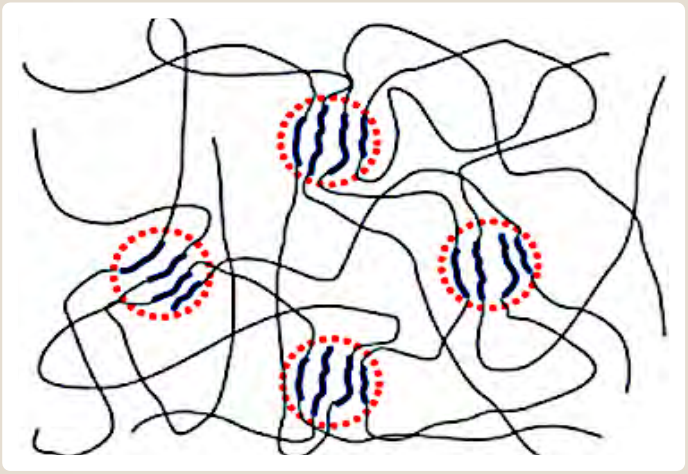
a



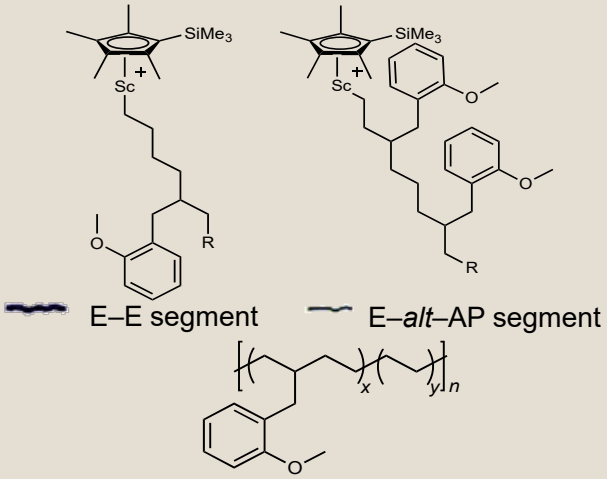
Poly(methyl methacrylate/*n*-butyl acrylate)



b



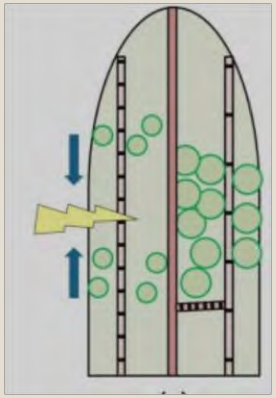
Crystalline nanodomain of E–E segments



Multi-block copolymer with relatively long E–*alt*–AP segment and short E–E segment

J. Am. Chem. Soc. 141, 3249–3257 (2019).

Self-Healing of Plants – Delosperma Cooperi



Delosperma cooperi plants (Pink Carpet or Iceplant) in the Freiburg Botanical Garden.

How does the elastic component contribute to damage closure of polymer?

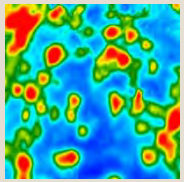
Speck, Olga et al. “Humidity-Dependent Wound Sealing in Succulent Leaves of *Delosperma Cooperi* – An Adaptation to Seasonal Drought Stress.” Ed. Stanislav N Gorb. *Beilstein Journal of Nanotechnology* 9 (2018): 175–186. *PMC*. Web. 8 Oct. 2018.

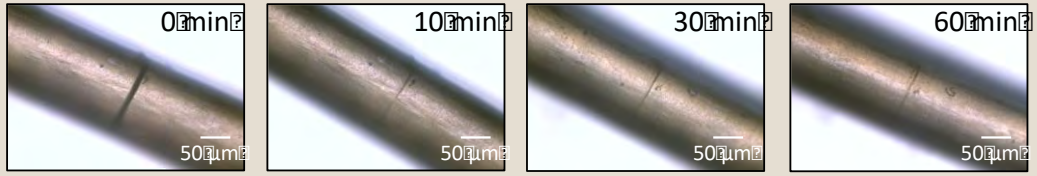
SELF-HEALING vs. PHASE MORPHOLOGY

IR IMAGES

OPTICAL IMAGES

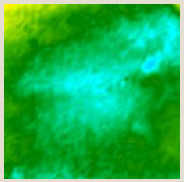
PCL-PUR (P)
Polymerization induced phase separation

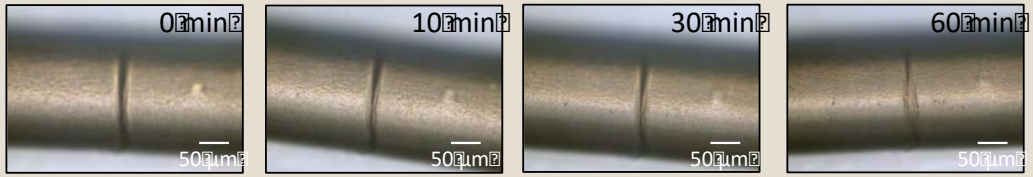




T_m = 51 and 168°C (DSC)

PCL-PUR (M)
Thermally induced phase separation

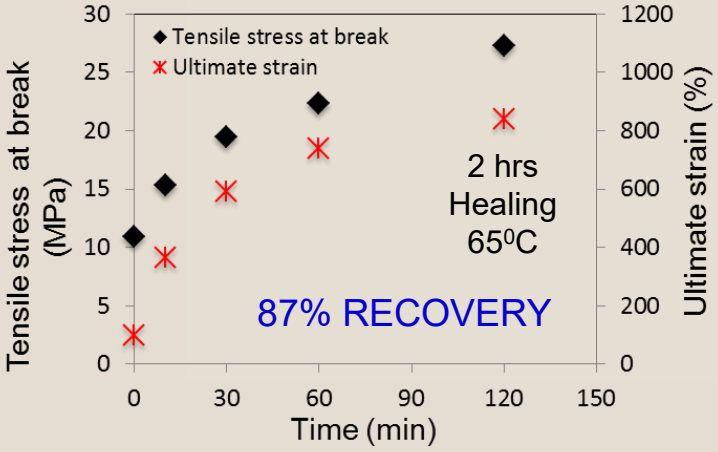




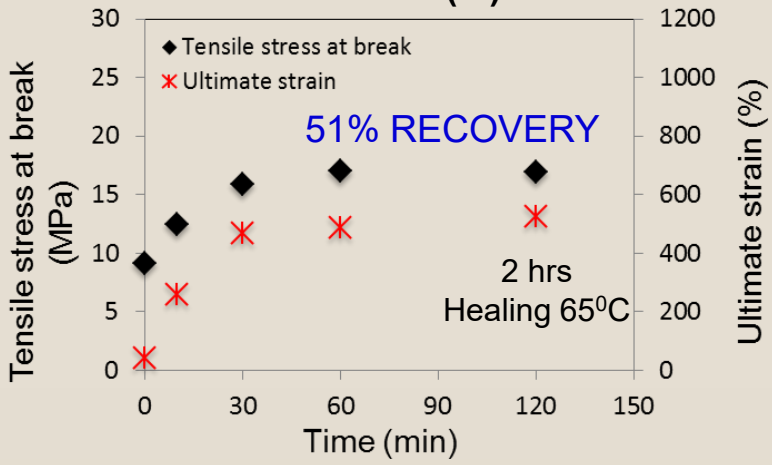
T_m = 51 and 162°C (DSC)

TENSILE PROPERTIES

Micro-phases separated PCL-PUR (P)



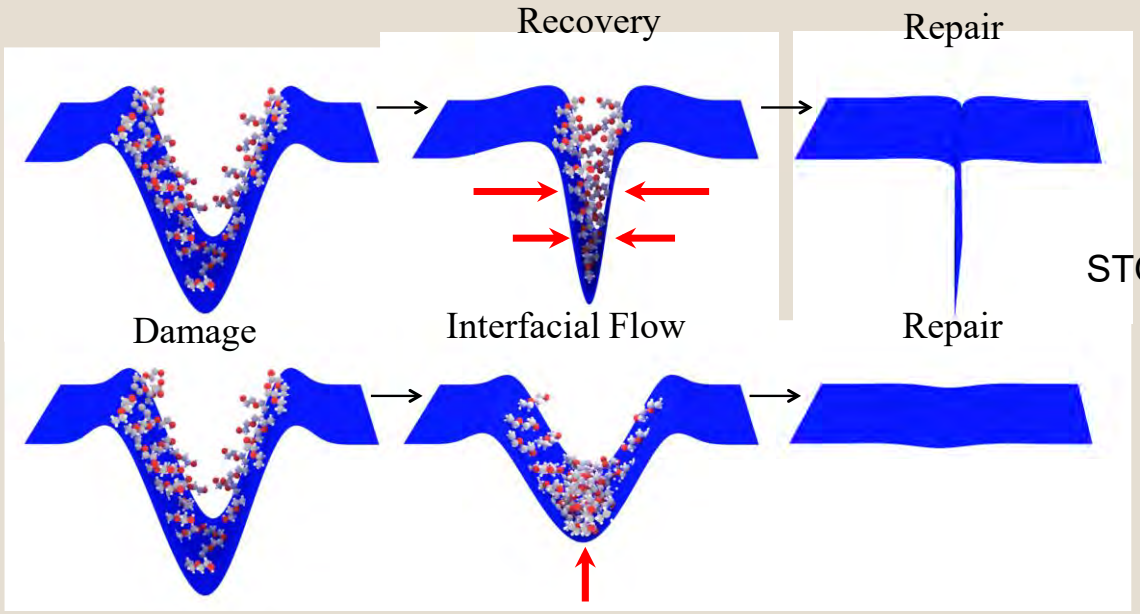
Nano-phase separated PCL-PUR (M)



Chem, 2018, 4, 1928.

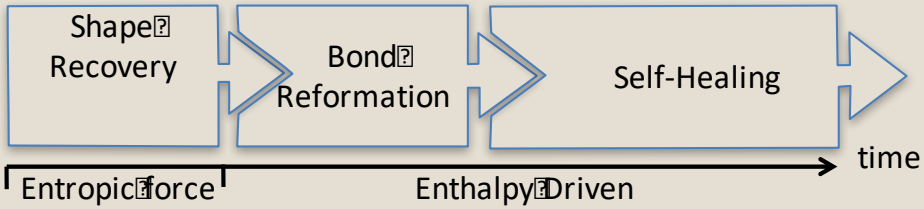
Self-Healing Polymers Inspired by Leaves

CHEM, 2018, 4, 1928



ENTROPIC ENERGY STORED DURING DAMAGE

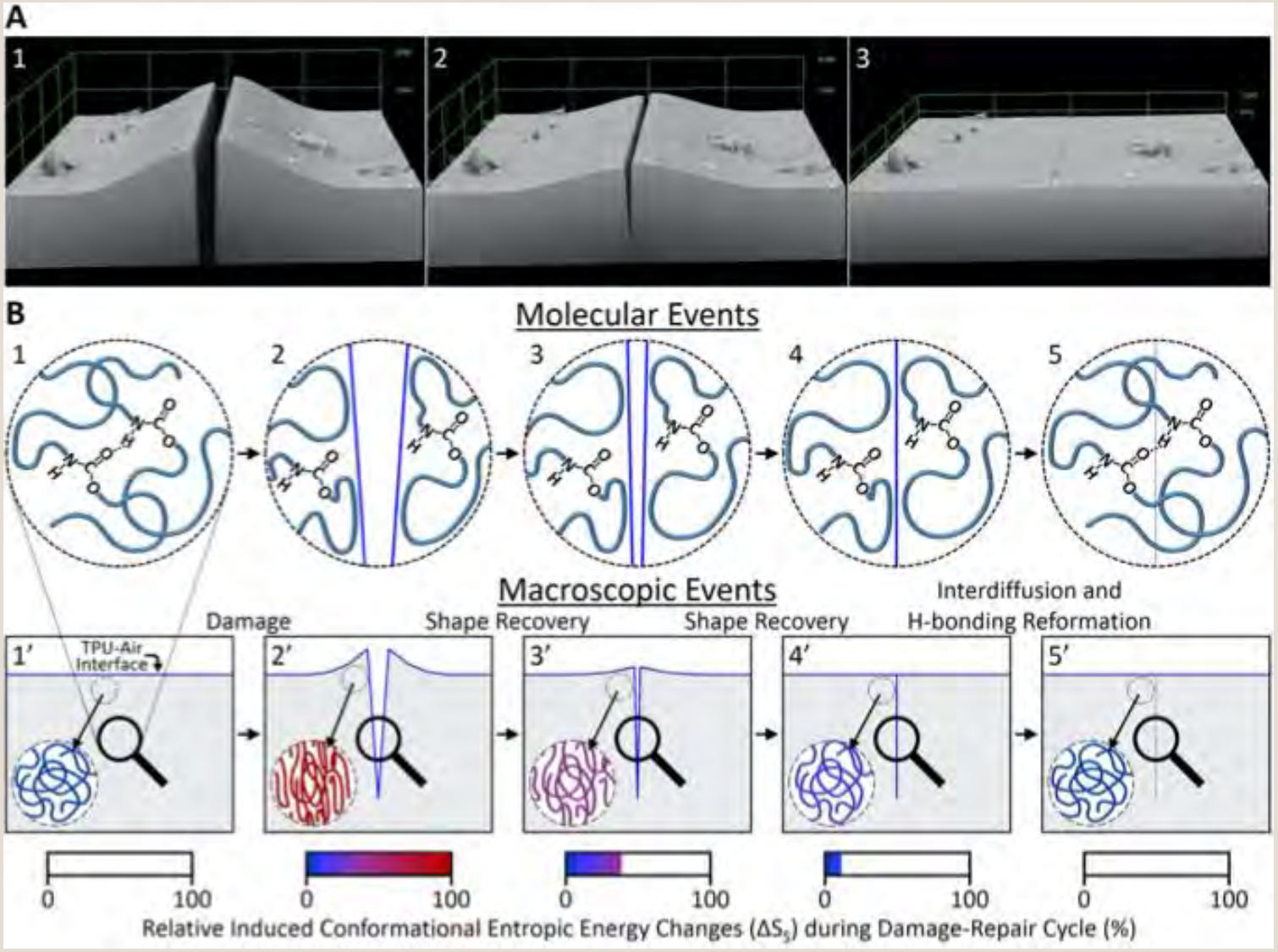
INTERFACIAL DIFFUSION



Nano- to Macro-Scale Self-Healing

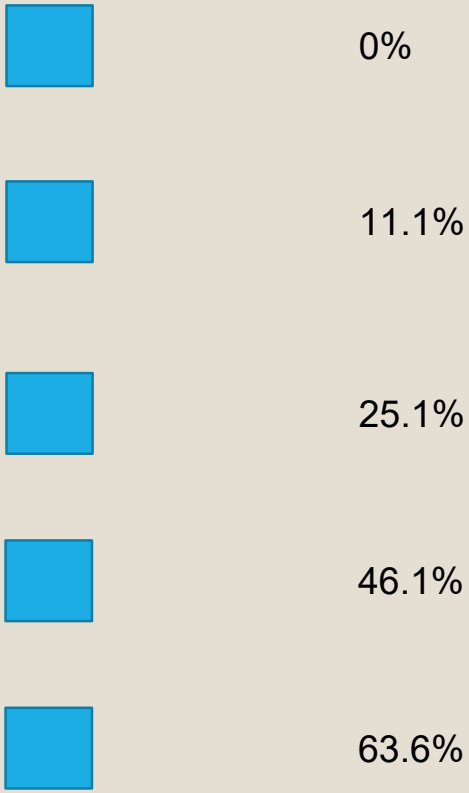
Shape Memory Effect vs Rebonding

Adv. Mat., 2017, 29, 1603334.



Nature Comm. 2020, 11:1028.

WHAT IS ANTICIPATED GROWTH OF SELF-HEALING POLYMER TECHNOLOGIES IN USA BY 2025?



0%

11.1%

25.1%

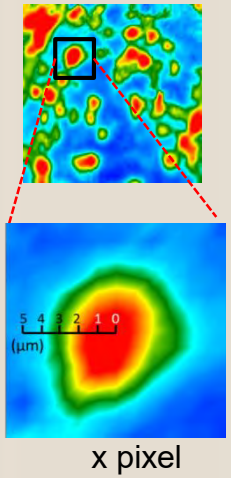
46.1%

63.6%

SUMMARY

Urban Research Group

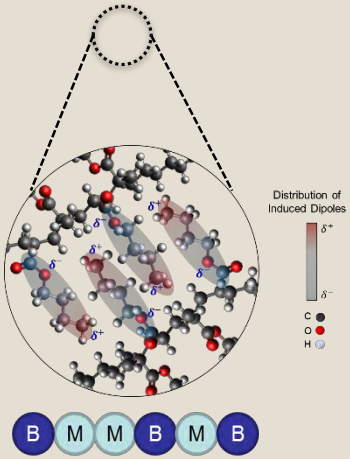
Phase Separation & Interphase



Molecular chemical events are responsible for macroscopic responses without intervention

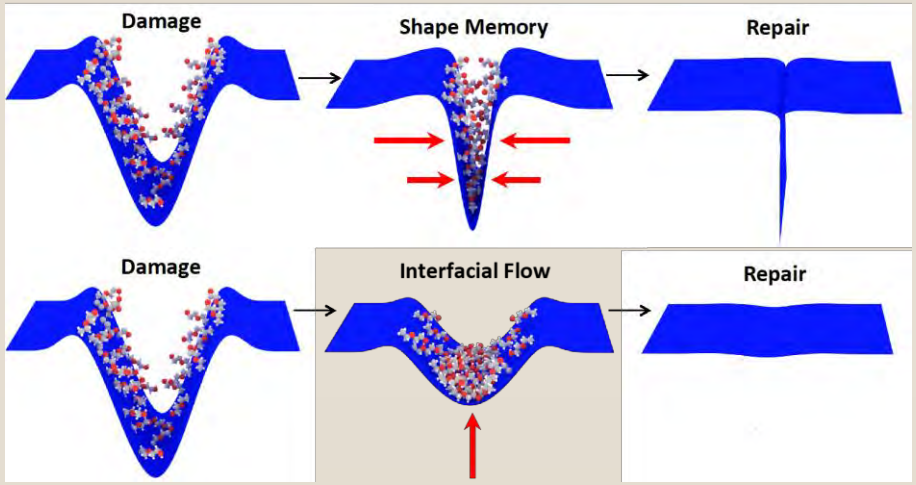
Morphology control may facilitate energy storage and recovery during damage-repair cycles.

Chain Topology & Key-and-Lock vdW Interactions



Narrow monomer molar ratios in simple alternating/random copolymers offers repeatable self-healing properties of thermoplastic polymers

A key characteristic feature are enhanced van der Waals (vdW) interactions rather than the reformation of hydrogen or covalent bonds.



Self-healing driven by entropic energy recovery stored during damage

Self-healing driven by interfacial flow and diffusion

Nature Reviews Mat., www.nature.com/articles/s41578-020-0202-4

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www.clemson.edu/cecas/urbanresearch

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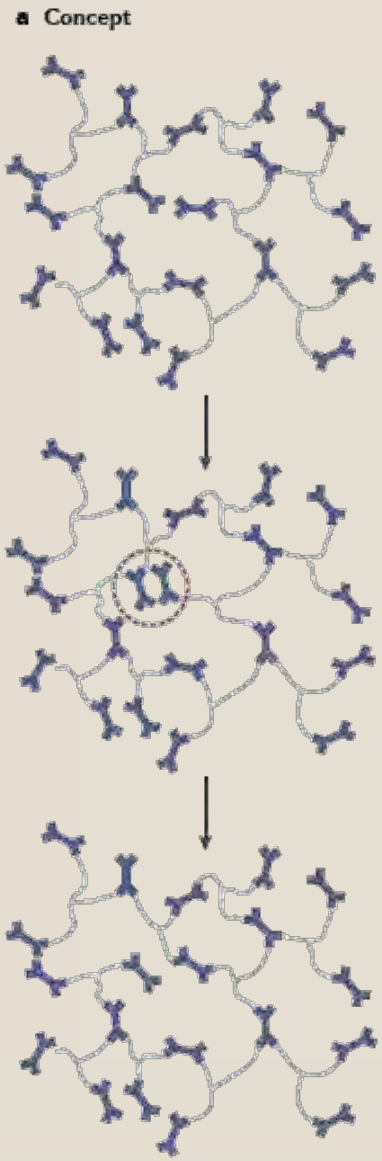
  OIA-1655740
- Department of Energy: DE-EE0008827
- US Army Research Center
- J.E. Sirrine Foundation Endowment at Clemson University
- Industrial Sponsors

Vitrimers



b Transesterification exchange reactions

Science 334, 965–968 (2011).

c Transamidation exchange reactions

Funct. Mater. 25, 2451–2457 (2015).

d Transcarbamoylation exchange reactions

J. Am. Chem. Soc. 137, 14019–14022 (2015).

e Transamination of vinylgous amides or urethanes

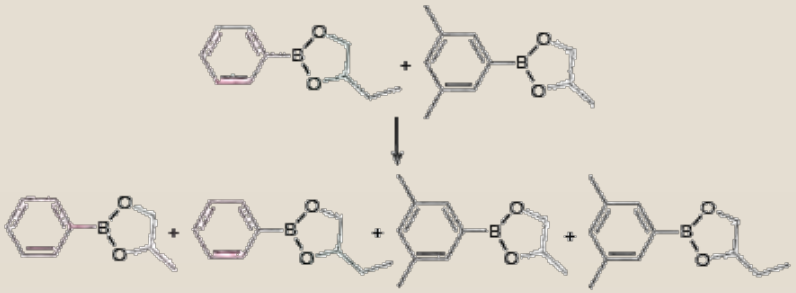
X=CH_2: Vinylogous amide
X=O: Vinylogous urethane

Adv. Funct. Mater. 25, 2451–2457 (2015).

f Transcarbonation exchange reactions

Macromolecules 51, 389–397 (2018).

g Dioxaborolanes metathesis



Science 356, 62–65 (2017).

Covalent Adaptable Networks as Stimuli Responsive Materials

Or...

How Can We Make a Square Peg Fit Into a Round Hole?

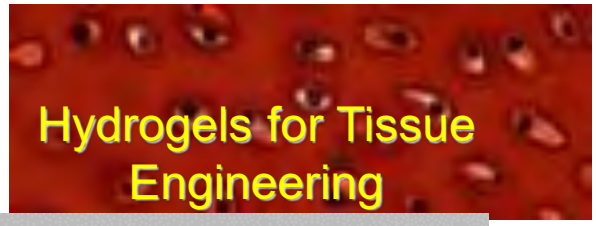
Christopher N. Bowman
Department of Chemical and Biological Engineering
Materials Science and Engineering
Department of Restorative Dentistry
University of Colorado

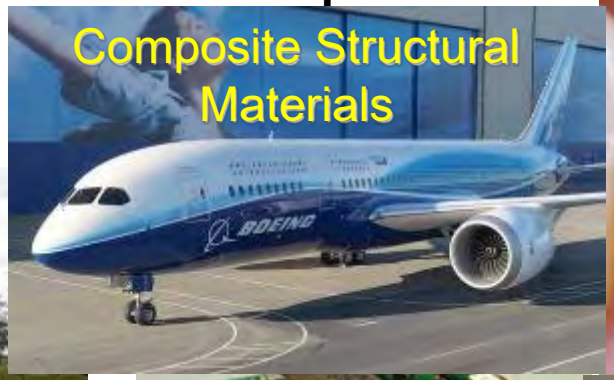
Conflict of Interest Disclosure

CNB has a financial interest in patents and royalties from those patents that have been licensed related to addition fragmentation in dental and other materials

Covalently Crosslinked Networks (i.e., Thermosets)

Covalently crosslinked polymeric materials are ubiquitous but suffer from significant shortcomings





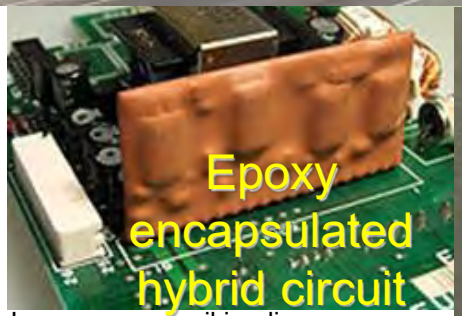


Image source: wikipedia

Cell Phone and Other Optics

Question…

What opportunities and alterations in material properties would be possible if the bond structure wasn't "permanent"?

Question…

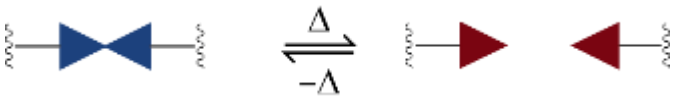
What opportunities and alterations in material properties would be possible if the bond structure wasn't "permanent"?

- ***Recycling and reprocessing***
- ***Stress relaxation***
- ***Actuation***
- ***Adhesion***
- ***Self-healing***
- ***Etc.***

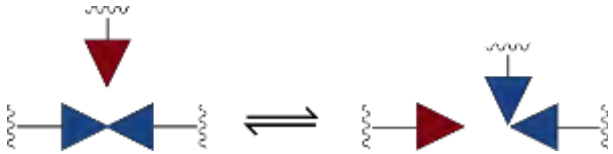
Dynamic Covalent Chemistry

Broadly there are two categories of reversible reactions that we can consider:

Reversible Addition Reactions



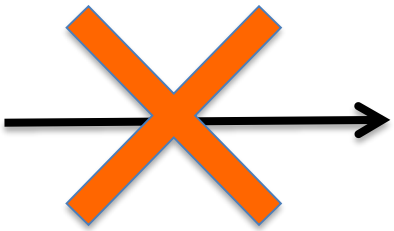
Reversible Exchange Reactions



So, why would we care about these reactions and what would they enable in crosslinked networks?

Covalent *Adaptable* Network Paradigm

Non-Equilibrium State

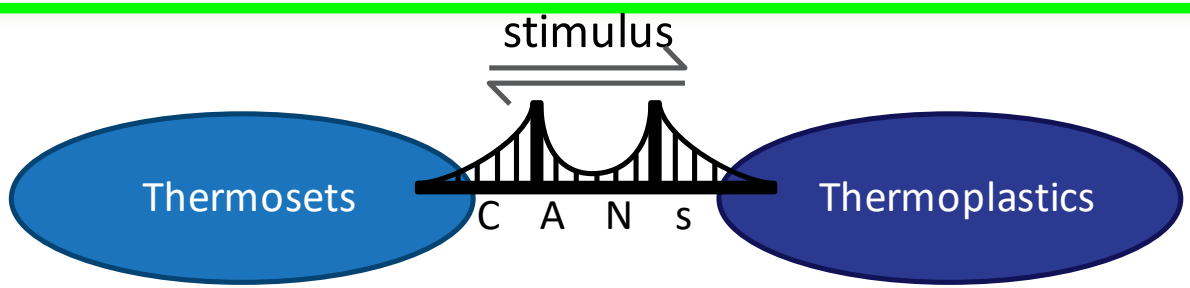


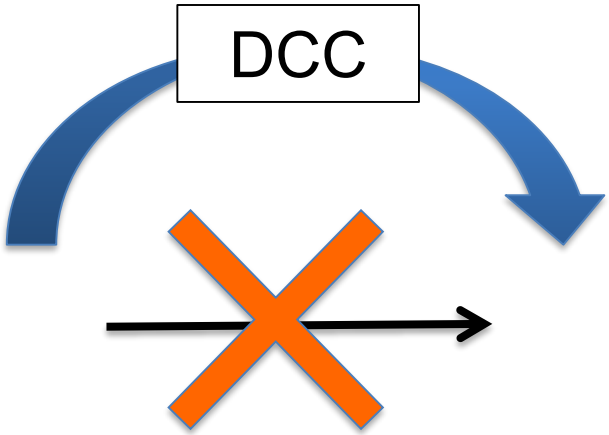
Relaxed State

Stress, Molecular Alignment, Birefringence, Interfaces, Phase Separation, Healing, Shape, Etc.

Macromolecules, 43, 2643 (2010), *Angewandte Chemie, 51* ,4272 (2012), *Chemical Society Reviews*, *41,* 7161 (2013)

Covalent *Adaptable* Network Paradigm





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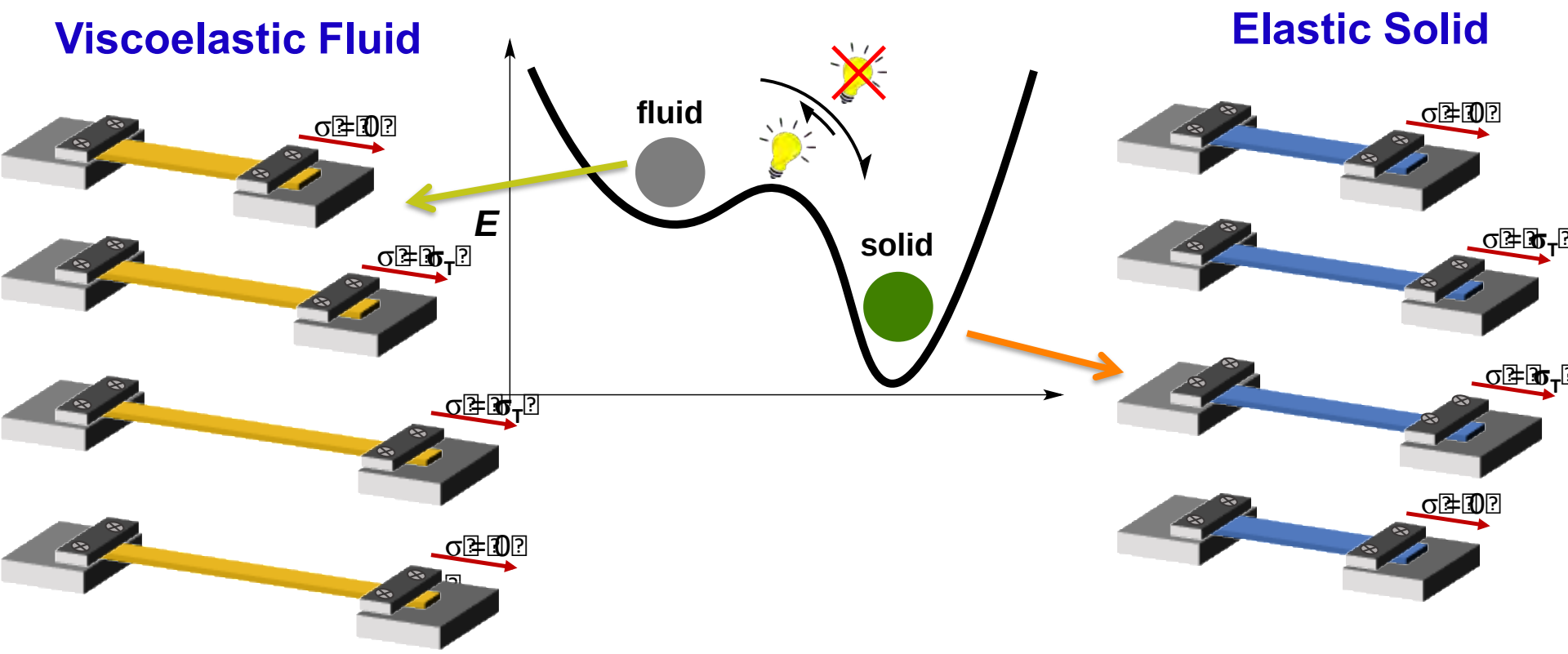
Macromolecules, 43, 2643 (2010), *Angewandte Chemie, 51* ,4272 (2012), *Chemical Society Reviews*, *41,* 7161 (2013)

Covalent Adaptable Network Paradigm: Inducing a Solid-to-Fluid Transition

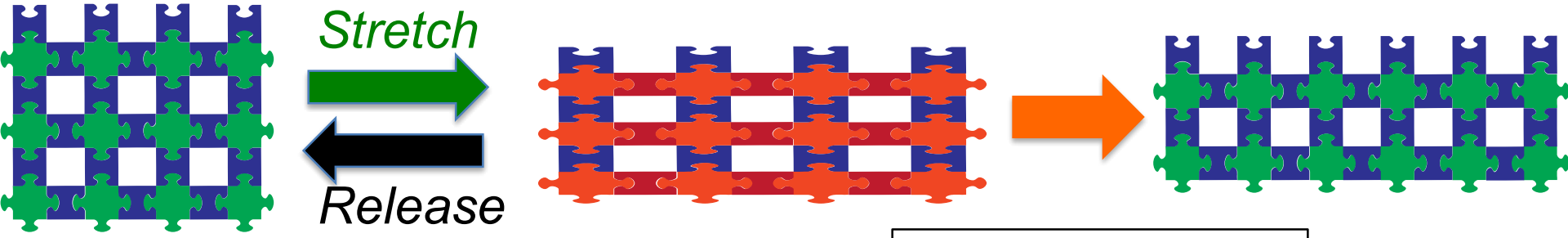


During Light Exposure the Dynamic Covalent Chemistry is Activated, Leading to the Formation of a Fluidic Material

Once the Light is Extinguished, the Material Returns to its Solid State

Covalent Adaptable Networks: Permanent Network Rearrangement

Permanent Shape Change Achieved When Bond Exchange Is Activated During Strain

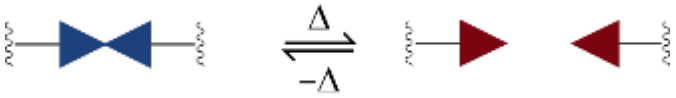


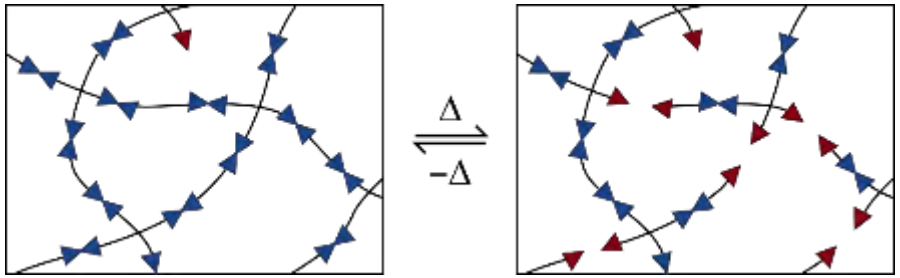
Bond Exchange Stress Relaxation

Altering Shape: The Most Important Property

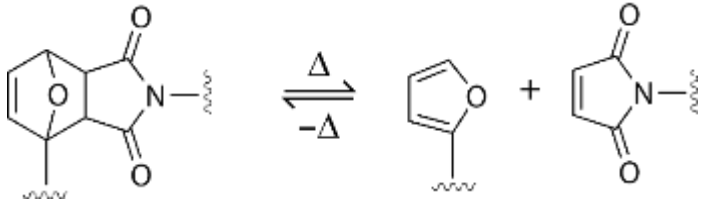
Nature of the Dynamic Covalent Crosslinks Constitutes the Type of Covalent Adaptable Network

Reversible Addition Reactions



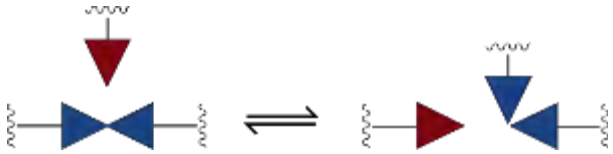


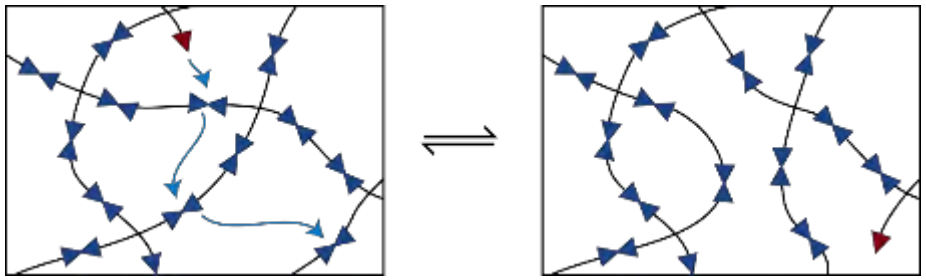
Diels-Alder Reactions



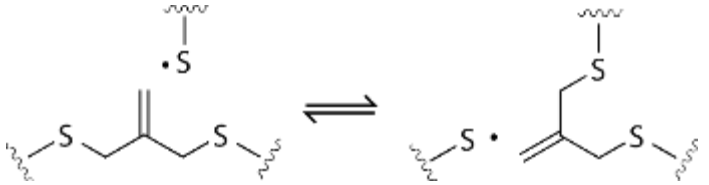
X. X. Chen, M. A. Dam, K. Ono, A. Mal, H. B. Shen, S. R. Nutt, K. Sheran, F. Wudl, *Science* **2002**, 295, 1698 – 1702.

Reversible Exchange Reactions



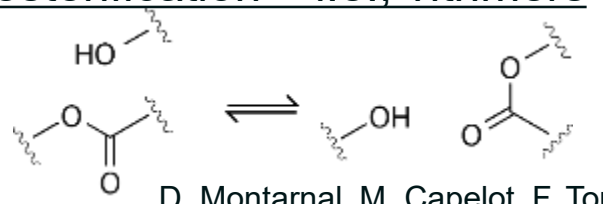


Addition—Fragmentation Chain Transfer



T. F. Scott, A. D. Schneider, W. D. Cook, C. N. Bowman, *Science* **2005**, 308, 1615 – 1617

Transesterification – i.e., vitrimers



D. Montarnal, M. Capelot, F. Tournilhac, L. Leibler, *Science* **2011**, 334, 965 – 968

C.J. Kloxin and C.N. Bowman *Chem. Soc. Rev.,* 2013, **42**, 7161--7173

C.N. Bowman and C.J. Kloxin *Angew. Chem. Int. Ed.* **2012**, 51, 4272 – 4274

Covalent Adaptable Networks:
An old concept with new applications

Tobolsky 1956: "**In actual fact**, we discovered that **all rubbers show $E_r(t)$ curves that decay to zero stress** at sufficiently high temperatures, and we **attributed this stress decay to chemical reactions** such as chain scission by oxidative cleavage or reorganization of the network structure by ionic interchanges" – This includes *polyesters, polyurethanes, vulcanized rubbers*

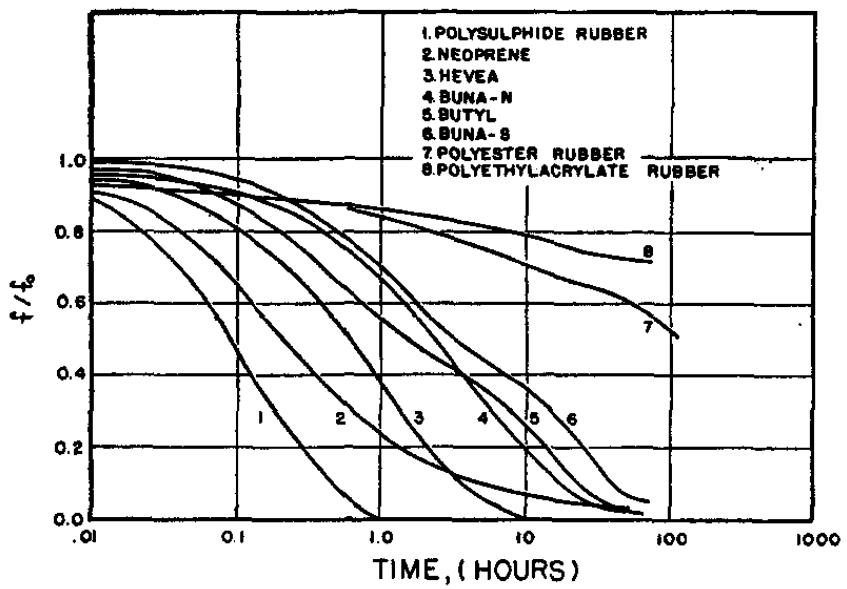
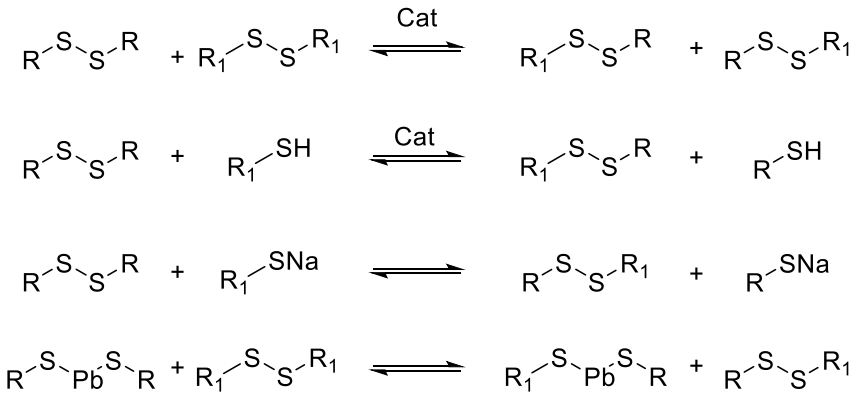


FIG. 1. Chemical stress relaxation for various vulcanized rubbers at 130° (reference 25).

Chemorheology:
Stress relaxation due to chemical reactions

Proposed DCC in vulcanized rubbers



Tobolsky. Journal of Applied Physics **27**, 673 (1956)

Question…

What stimuli would be desirable to use as activators for turning the dynamic covalent chemistry on/off?

(a) Temperature Change

(b) Irradiation

(c) Molecular Detection

(d) Solvent Condition Change

(e) None of the above

Question…

What stimuli would be desirable to use as activators for turning the dynamic covalent chemistry on/off?

(a) Temperature Change – easily activated and controlled

(b) Irradiation – spatiotemporal control

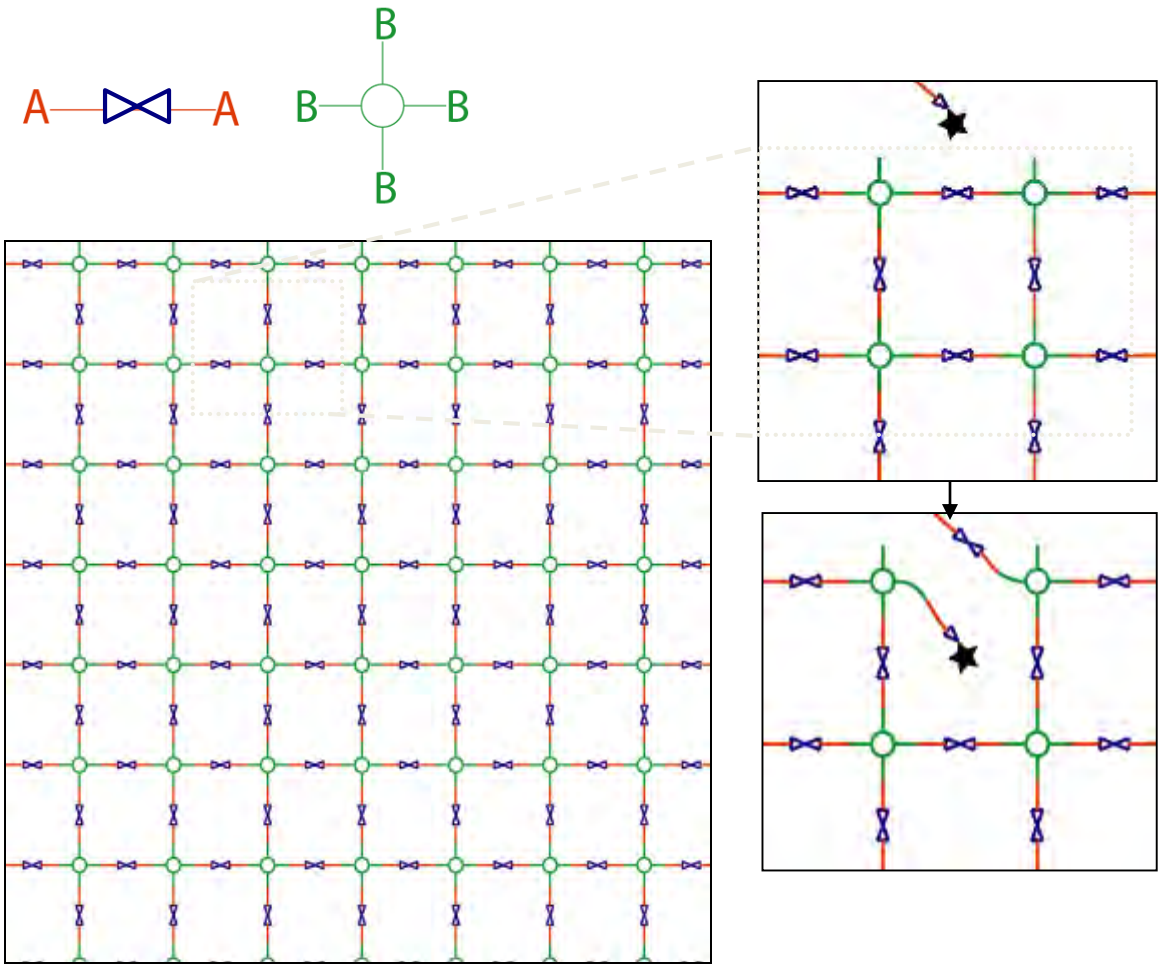
(c) Molecular Detection – useful as a sensor

(d) Solvent Condition Change – biological applications

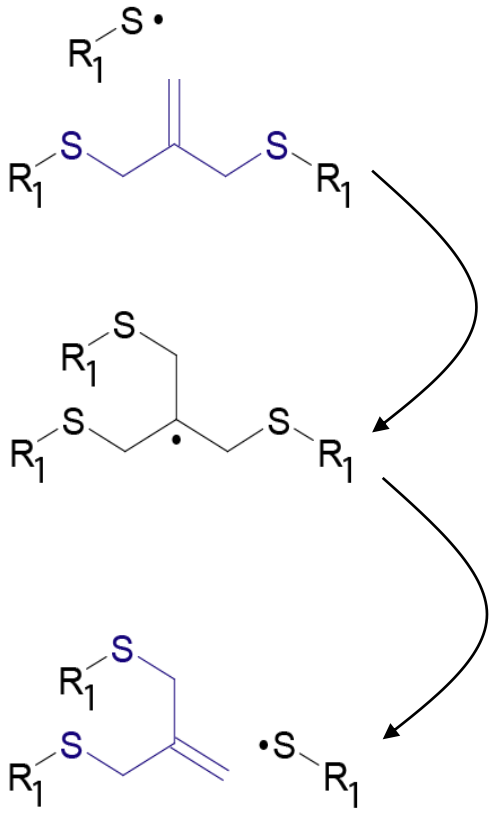
(e) None of the above

Photoplasticity: Covalent Adaptable Networks (CANs)

Addition-fragmentation in the network alleviates stress as bonds are broken and reformed

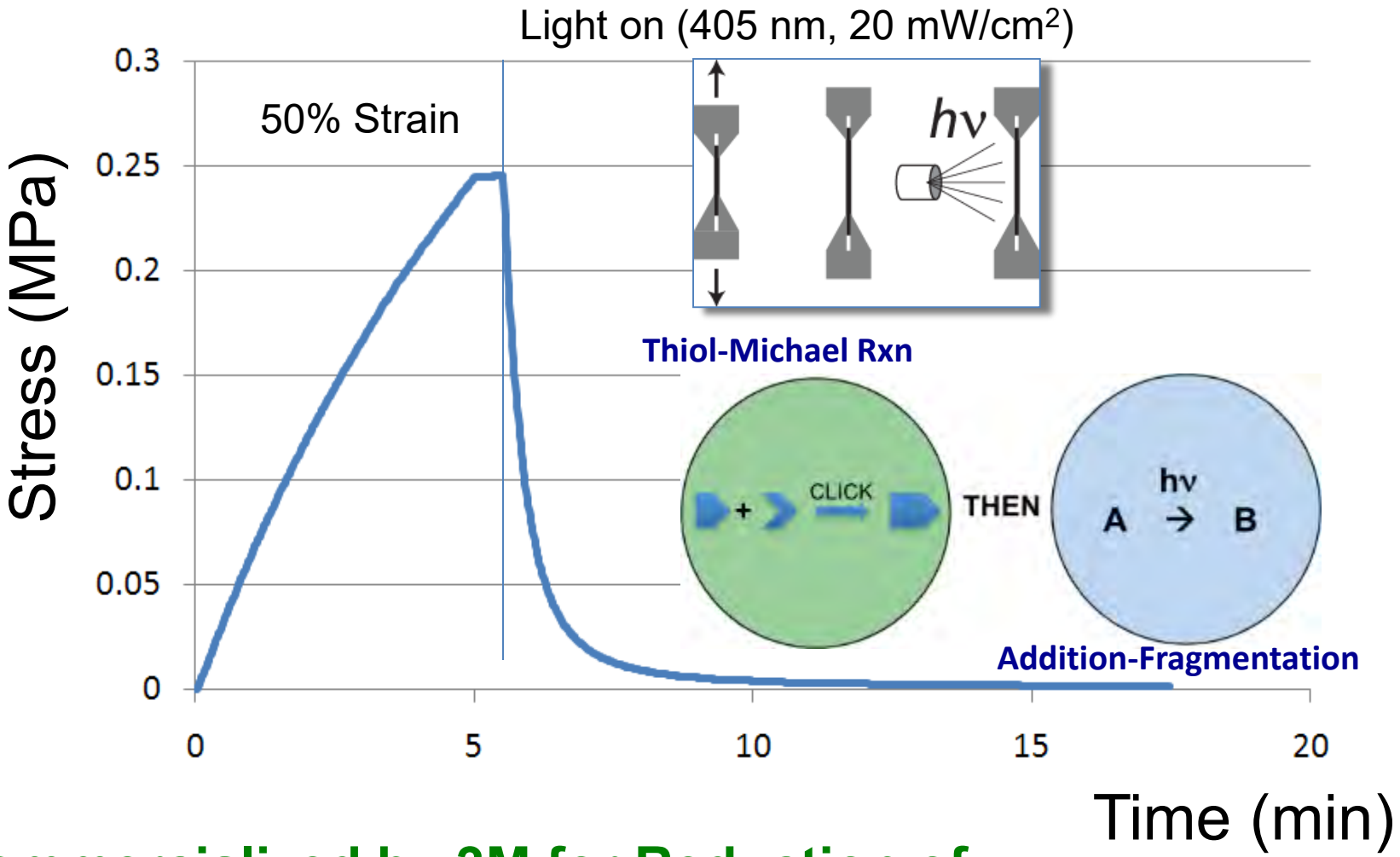


Addition-Fragmentation of Allyl Sulfides



Science, 308, 1615 (2005); *Advanced Materials, 18,* 2128 (2006)

Stress Relaxation via Photoinduced Plasticity

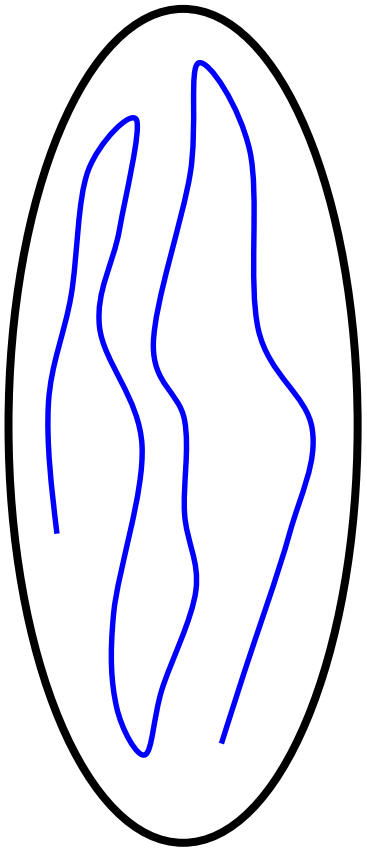


Commercialized by 3M for Reduction of Polymerization Stress

Networks formed by Thiol Click Michael Addition are Capable of Complete Relaxation of Stress

C.J. Kloxin *et al., Advanced Materials*, 2011

Phase Transitions in LCNs: Reversible Phase and Shape Changes

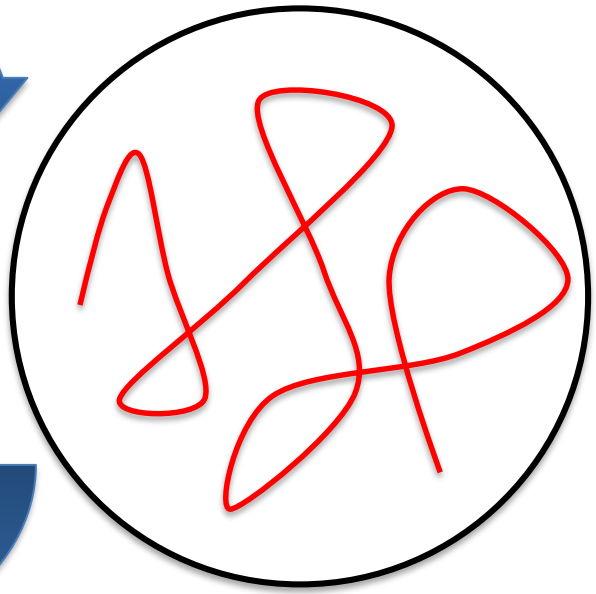


RAFT

Thermal Cycle

Crosslinking

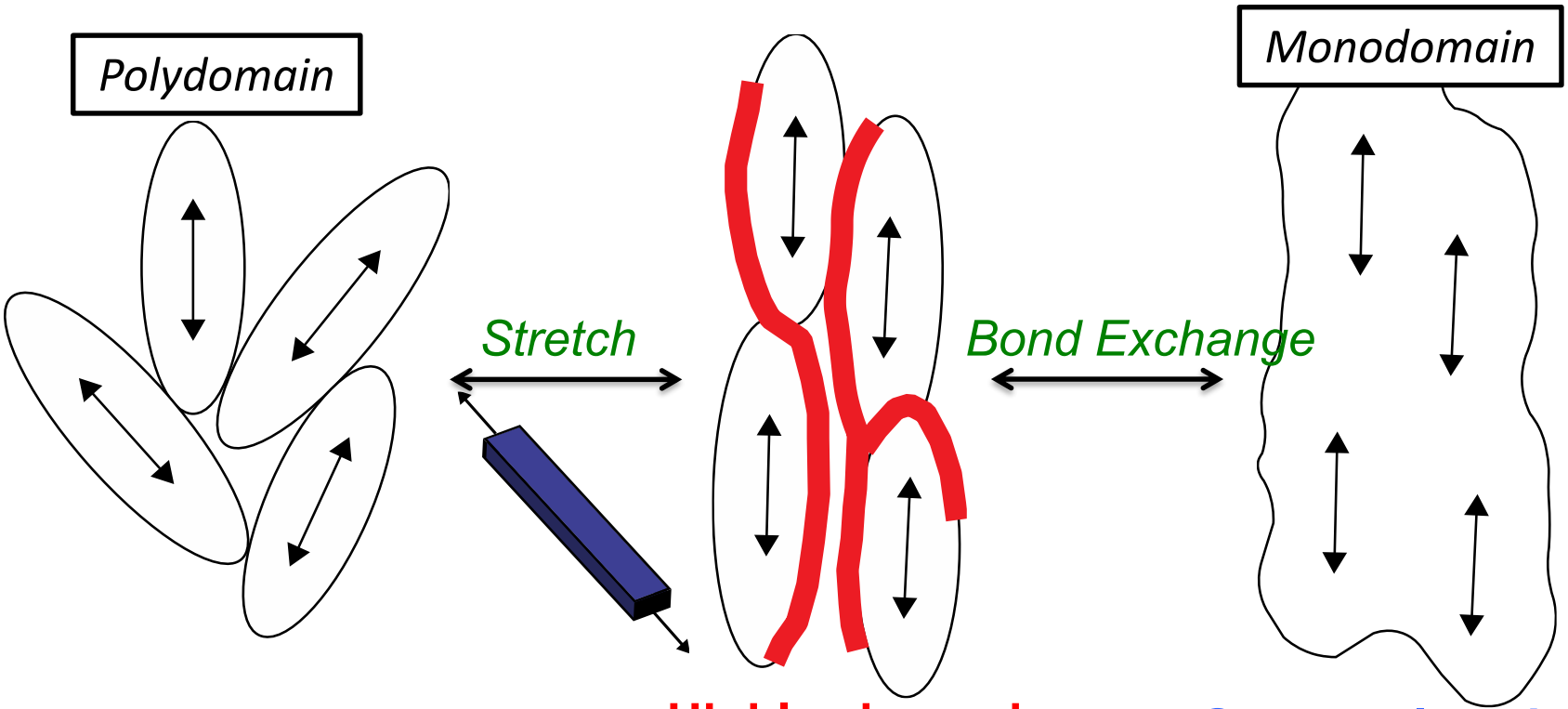
RAFT



Liquid Crystal Phase "Order"

Isotropic "Disorder"

Programming Monodomain to and from Polydomain



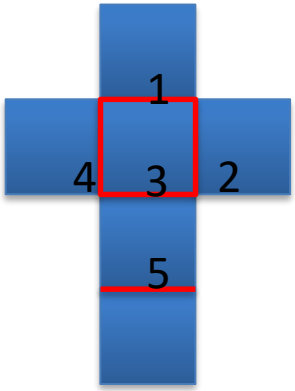
Stress relaxation occurs through allyl sulfide exchange in the polymer and stress-rich regions at the wall

Fully Reversible Surface and Bulk Shape Control

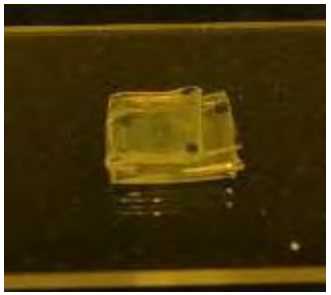
Cube

Strained area

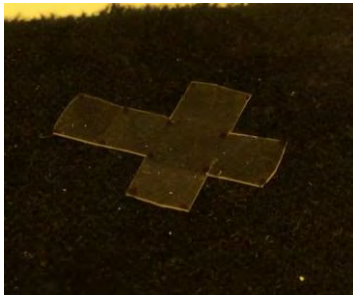
Note: Only strained regions will program



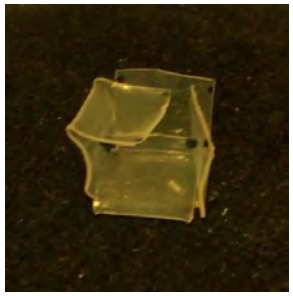
Strain sample by folding
Irradiate with light



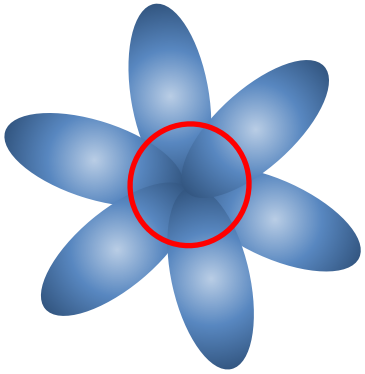
Heat to 120°C

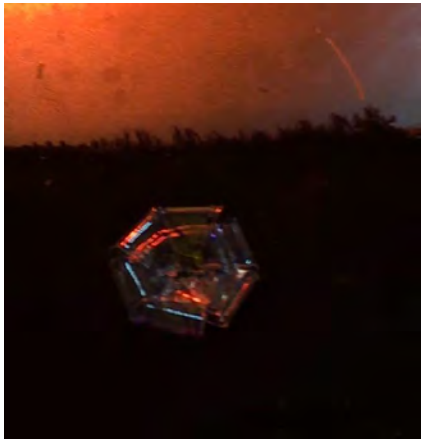


Allow to cool to 25°C



Flower

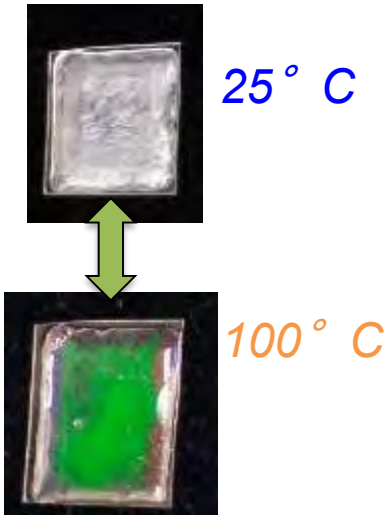




Miura Ori

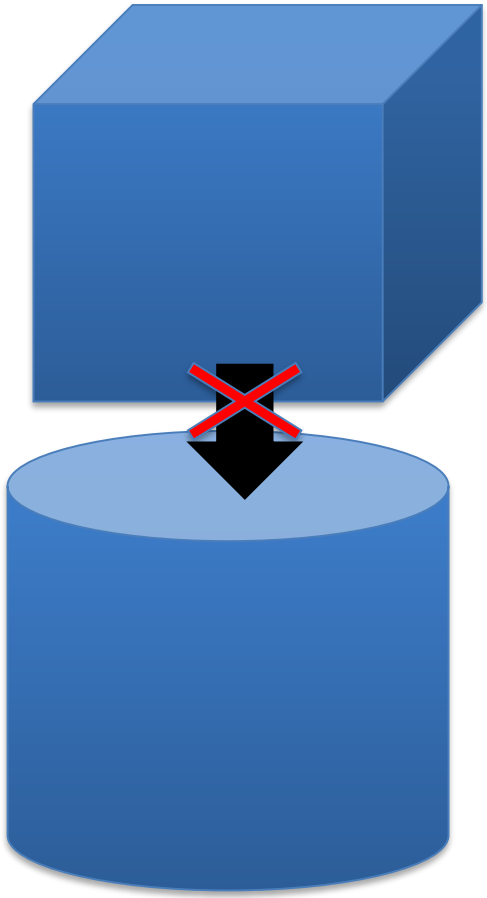
Actual time

Nanoimprint

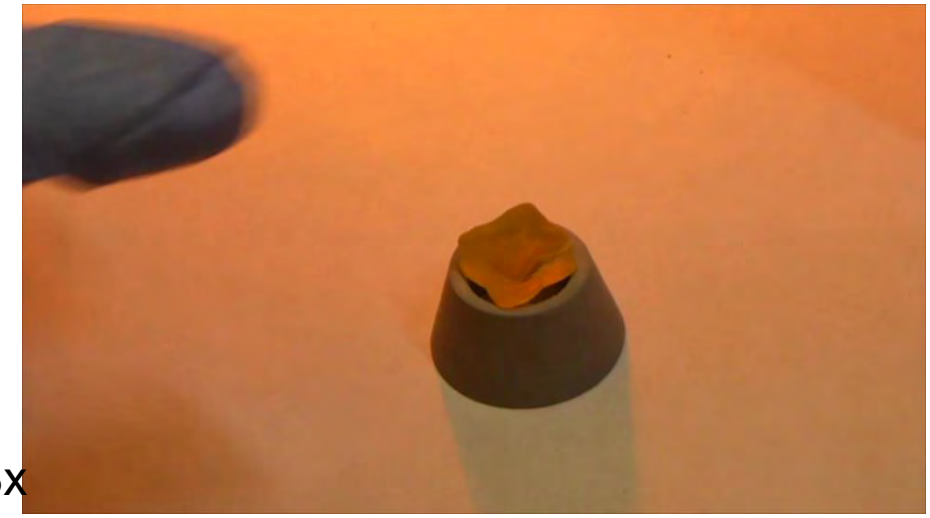


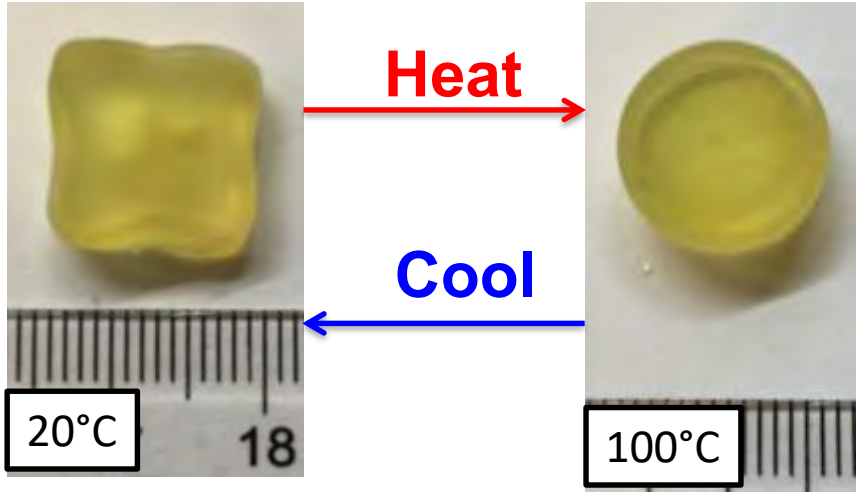
McBride et al., *Science Advances,* 2018

Does a Square Peg Fit into A Round Hole?



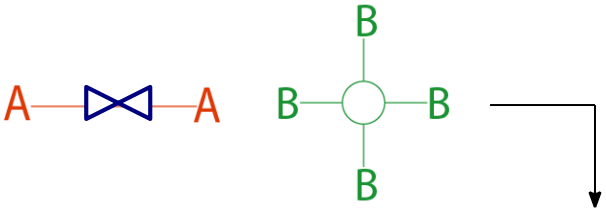
Speed 8x

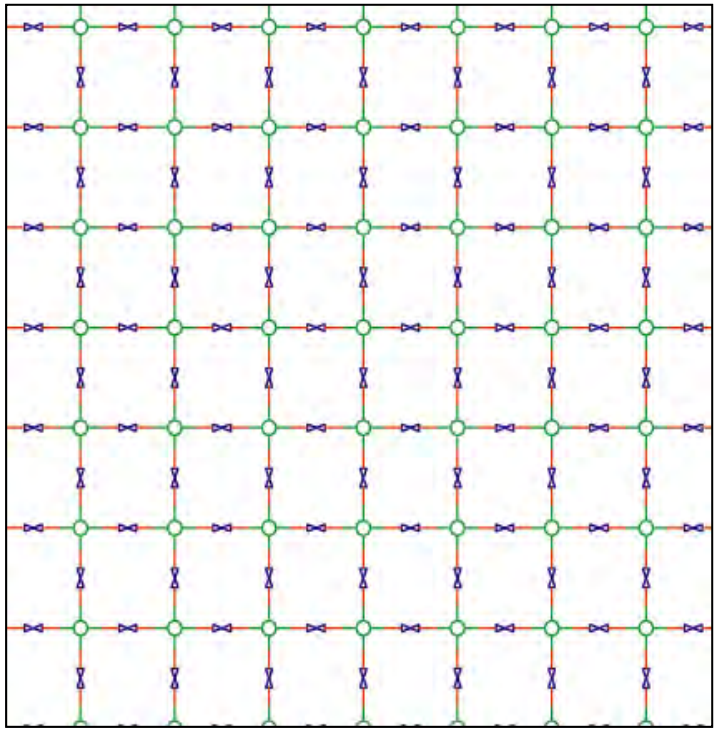




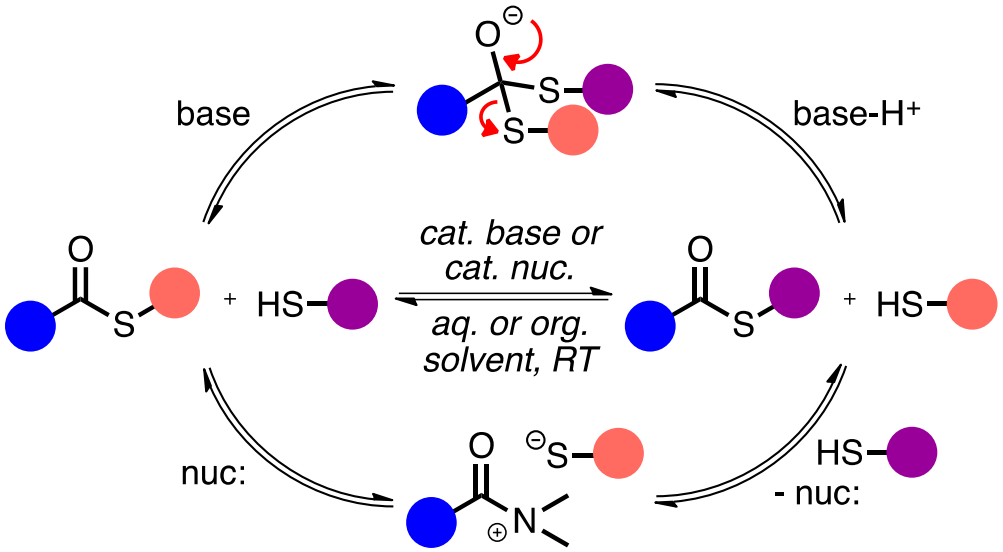
McBride et al., *Science Advances,* 2018

Covalent Adaptable Networks (CANs): Dynamic Thiol-Thioester Exchange

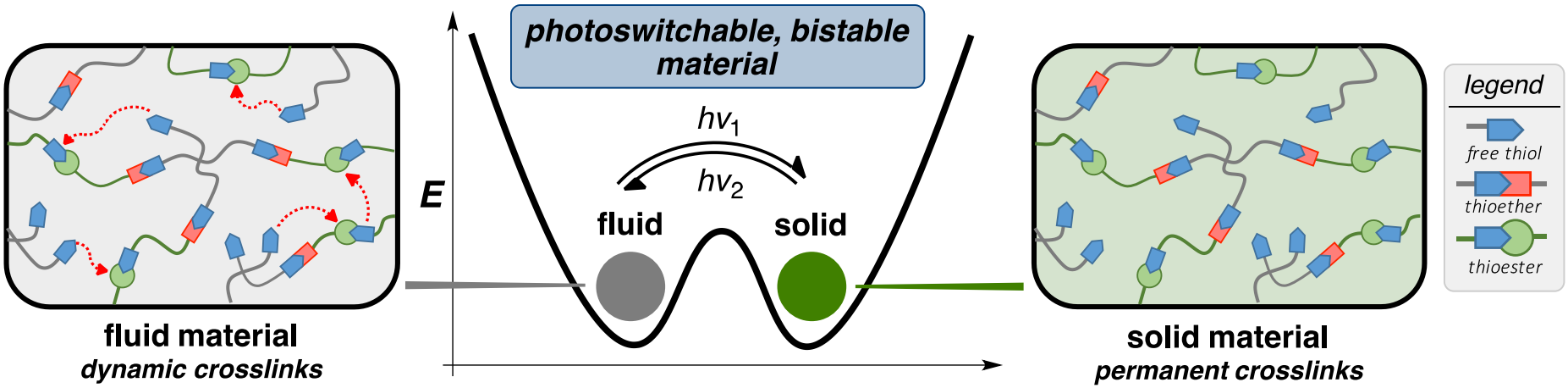




Thiol-Thioester Exchange



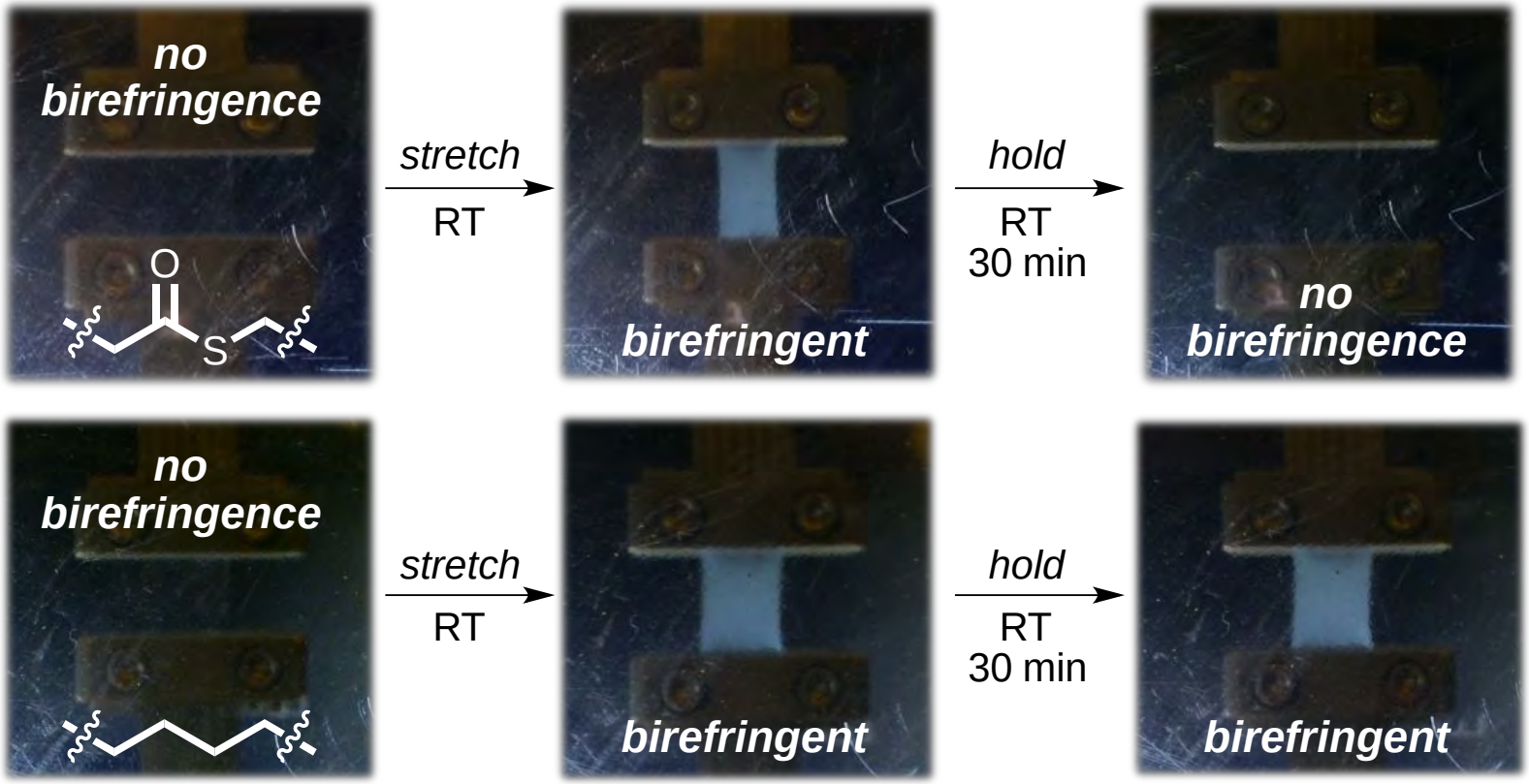
Inducing a Solid-to-Fluid Transition: Switching from One State to Another



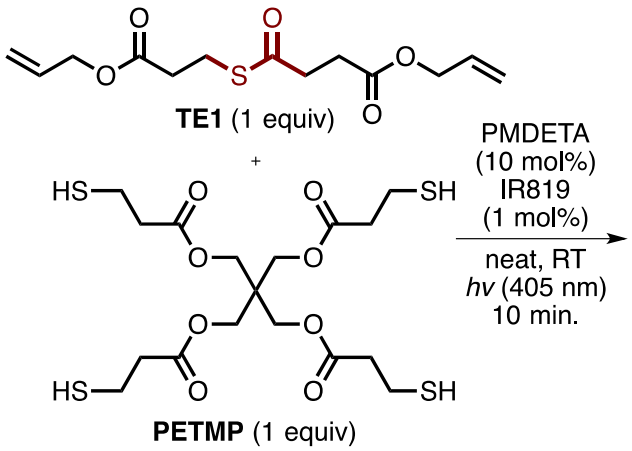
During Light Exposure the Dynamic Covalent Chemistry is Either Activated or Deactivated By Generating or Eliminating a Catalyst

Once the Light is Extinguished, the Material *Remains* in its New State – It is Thus Bistable

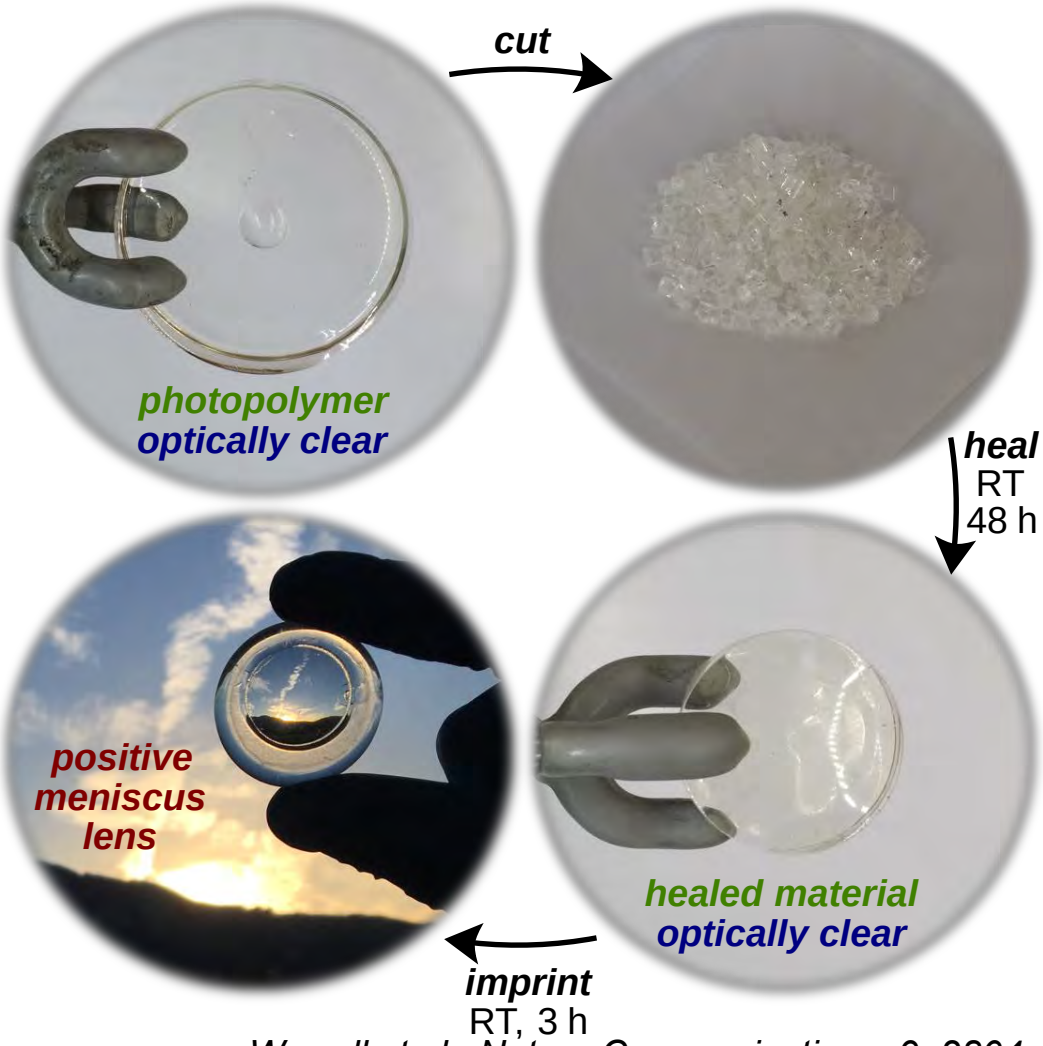
Thioester Based Networks are Reconfigurable Under Ambient Conditions



Healing/Imprinting Conditions Retain Optical Clarity

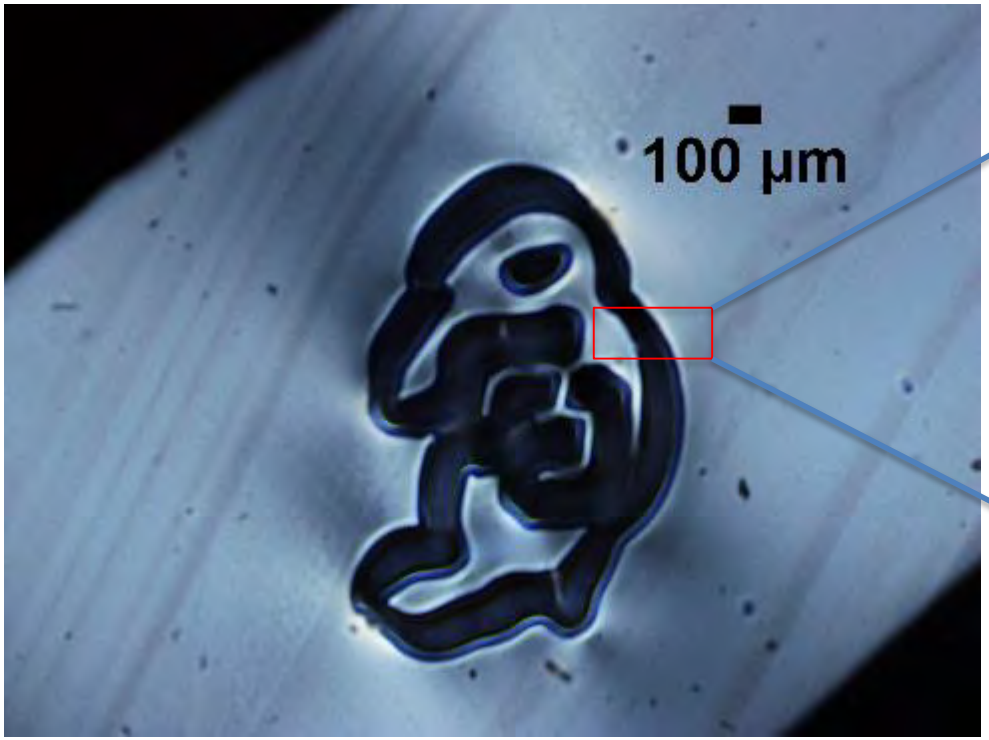


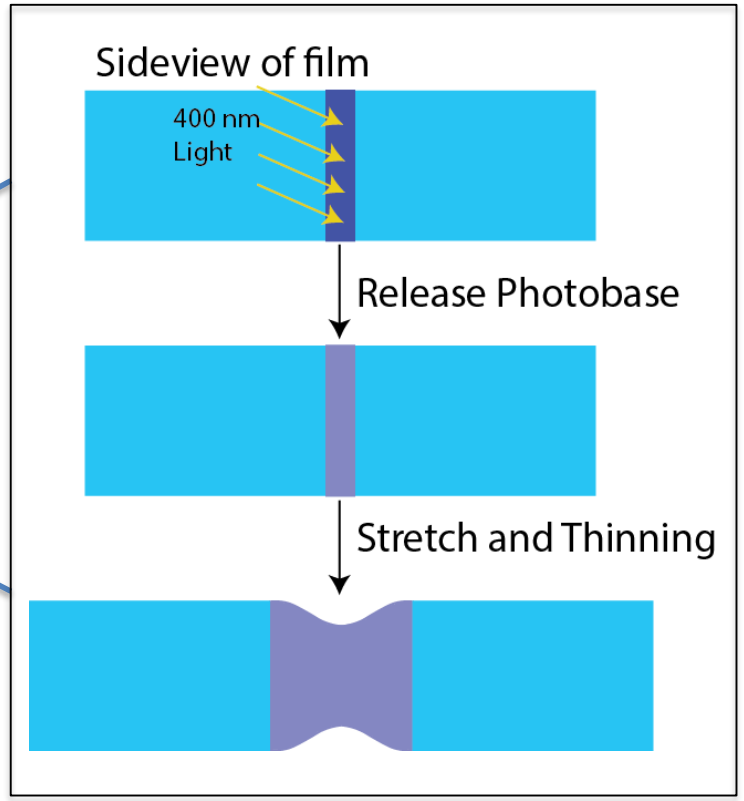
Polymerizing ~10 grams of material into an optically clear puck, it was cut, healed at room temperature by loading into a syringe and applying mild pressure.

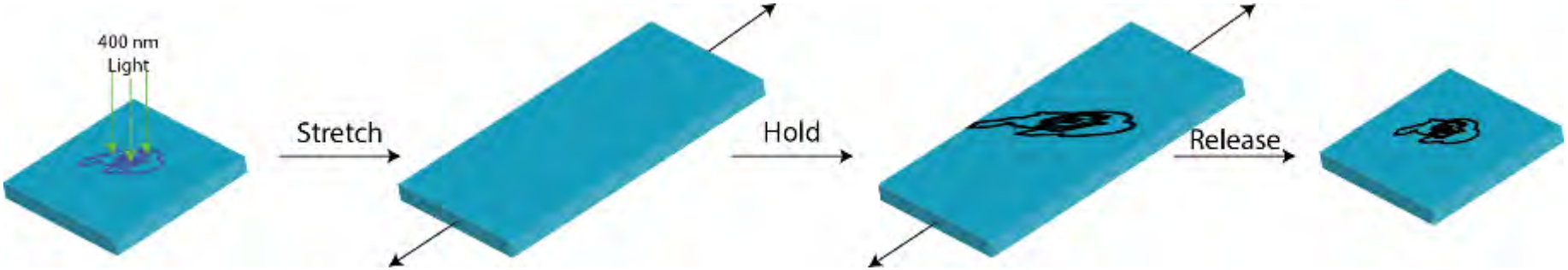


Worrell et al., Nature Communications, 9, 2804 (2018)

The "ON" Switch: Demonstration of Spatial Control via Photobase Generation







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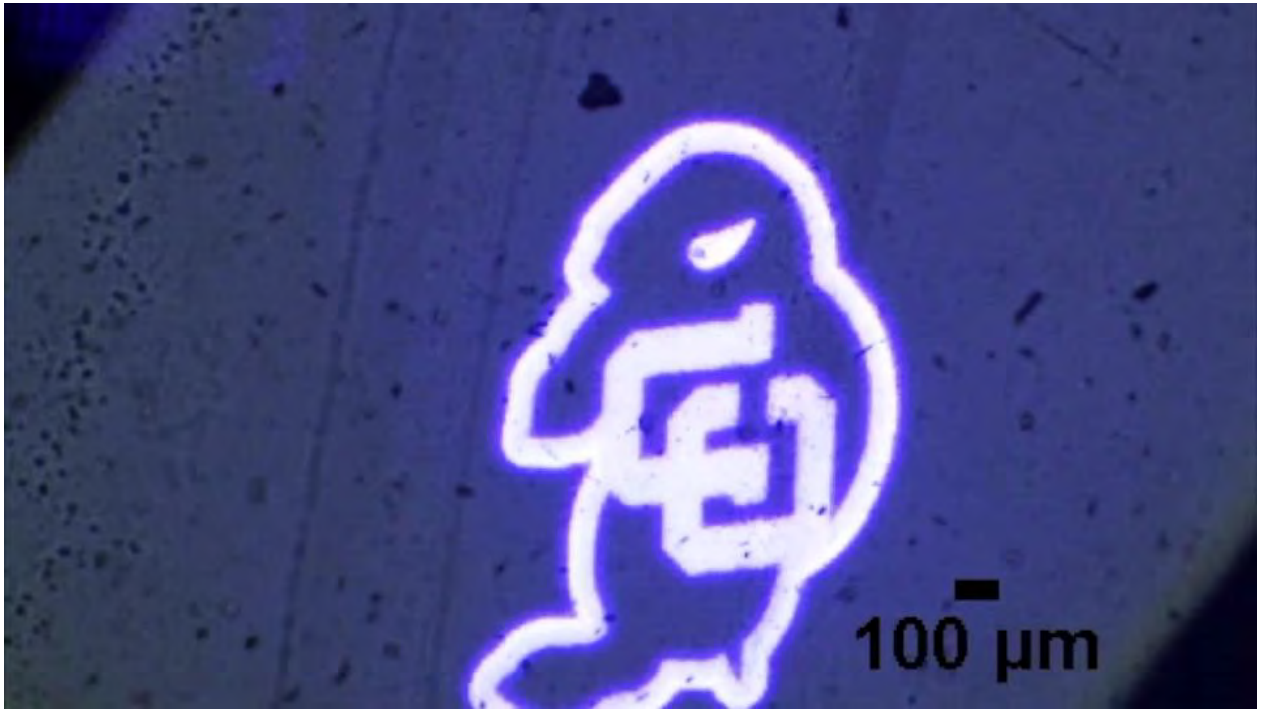

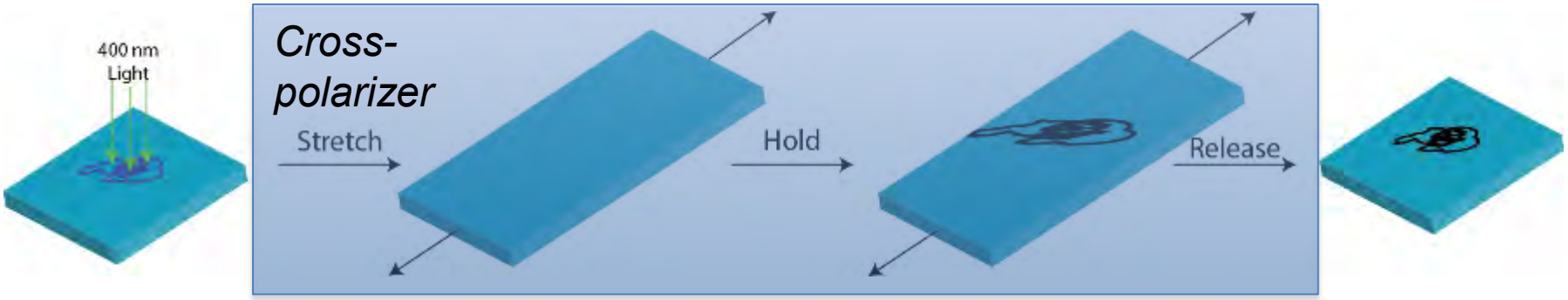

Question:

In Conventional Composite Systems Where the Filler Is Much Higher Modulus, Where Do the Stresses Generally Concentrate?

a) The resin phase

b) The filler phase

c) The interface between the filler and the composite

d) All of the above

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While all regions in a composite bear stresses, the *interface* between the filler and the polymeric matrix is often a region of concentrated stresses that have a significant influence on the mechanical performance and lifetime of composite materials

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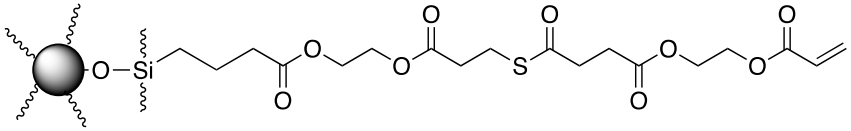
While all regions in a composite bear stresses, the *interface* between the filler and the polymeric matrix is often a region of concentrated stresses that have a significant influence on the mechanical performance and lifetime of composite materials

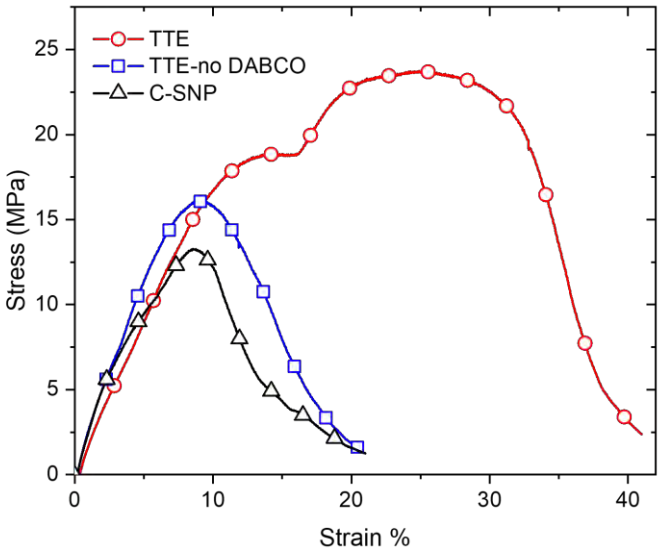
Hypothesis: ***Triggered DCC activated in the resin during formation combined with perpetual DCC at the interface is optimal.***

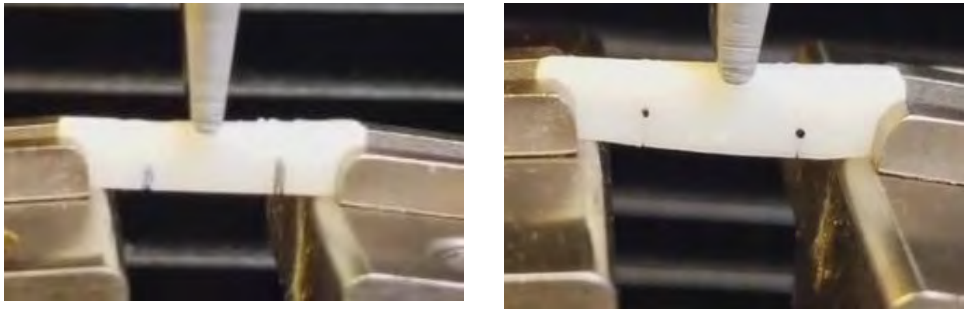
Implementation of TTE at the Resin-Filler Interface

Activated TTE Interface composite failure

Thioester filler with DABCO catalyst







TTE sample fails at the small notch, requiring more than twice the total energy to fail the material– unlike any other conventional material.

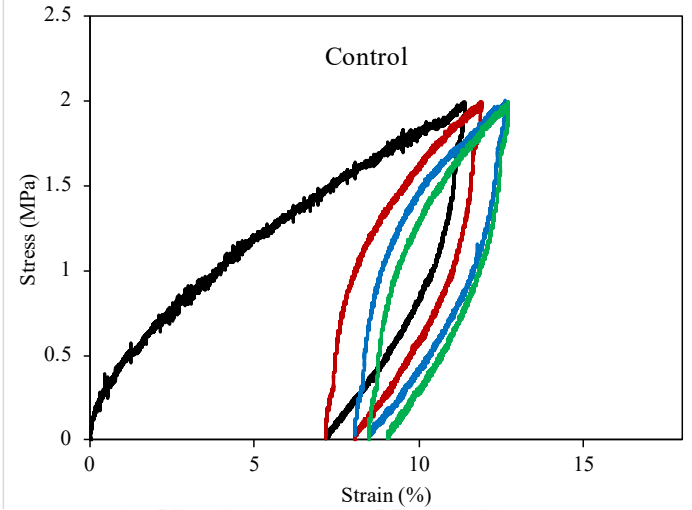
(1.1:1) Thiol:ene, 10 wt% SNPs, 6 mol% DABCO, 1 wt% I 819. Crosshead speed = 1 mm/min

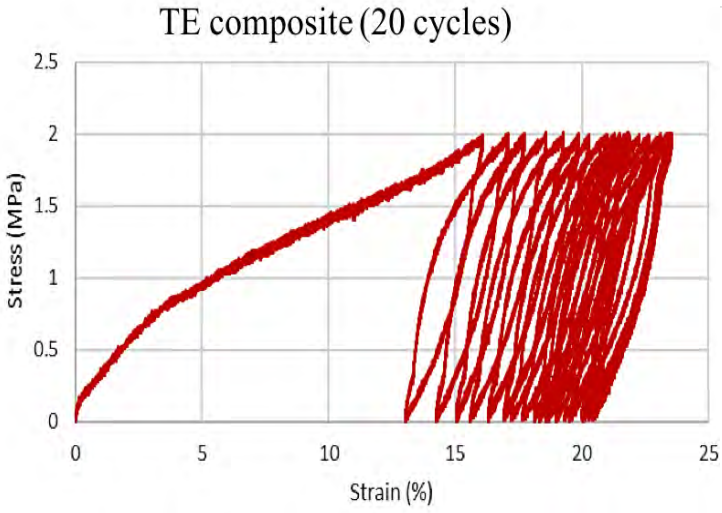
Sowan, Polymer Chemistry, In Press

Implementation of TTE at the Resin-Filler Interface: Cyclic Loading and Fatigue

Dynamic composites and improvement in cyclic behavior

	Control	TTE
Stress (MPa)	12 ± 3	28 ± 6
Strain (%)	20 ± 8	30 ± 10
Toughness (MJ/m³)	1.9 ± 0.5	6.1 ± 0.9





The **thioester-modified composite** was found to survive more than **20 cycles** while the **control** composites were only able to survive **3-4 such cycles**.

(1.1:1) Thiol:ene, 10 wt% SNPs, 1 wt% DABCO, 1 wt% I 819. Curing conditions: (400-500) nm, with 50 mW/cm^2 intensity.

Sowan, Polymer Chemistry, In Press

Summary

- **Implementation of Dynamic Covalent Chemistry in Crosslinked Networks Represents a Powerful Approach to Identify and Control Polymer Properties**

- **Breadth of Chemistries and Triggers Possible**

- **Control is possible of**
  - **Type of reaction**
  - **On/Off trigger**
  - **Timescale of reaction**
  - **Implementation relative to the lifecycle of the material**

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Brady Worrell
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Sudhi Mavilla
Lewis Cox
Maciek Podgórski

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Charles Musgrave, Jeffrey Stansbury

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NSF MRSEC Program
NIH

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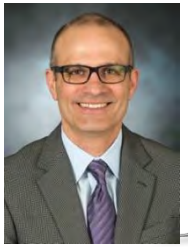
Diana Gerbi, 2018 POLY Chair
3M(retired)



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Marc Hillmyer, 2017 POLY Chair
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Moderator: Laura Cassiday, American Chemical Society

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- What types of fabrics and household cloth are effective in particle filtration and why
- The basics of particle filtration and data on filtration efficiencies as a function of size for common fabrics that are used in cloth masks
- How to disinfect N95 masks and how many times you can do it without reducing filtration efficiency

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- Brevity is both appreciated and improves clarity
- Self-editing is the surest way to improve clarity and attain brevity

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- Brevity is both appreciated and improves clarity
- Self-editing is the surest way to improve clarity and attain brevity

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