

Mechanical Adaptivity as a Process: Implications to New Materials and Material System Design

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AFRL Materials & Manufacturing Directorate



Report Documentation Page

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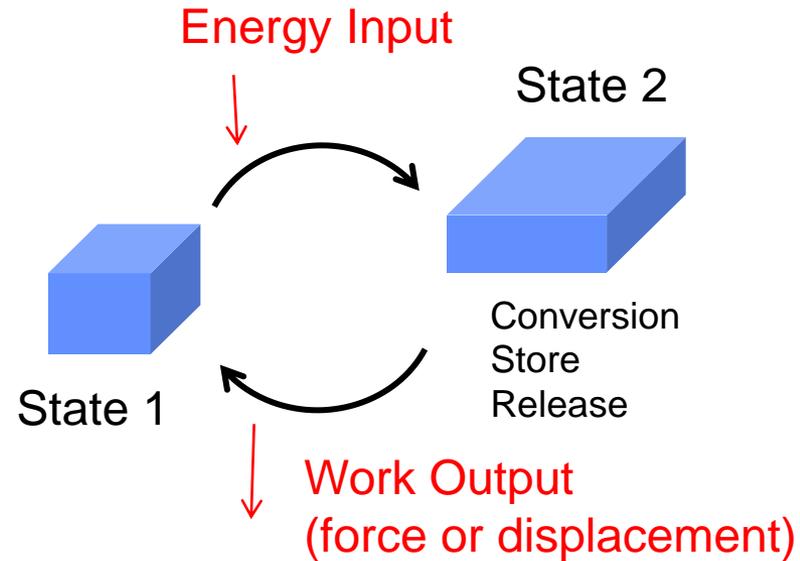
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What is Mechanical Adaptivity?

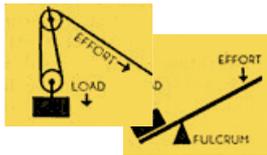


Energy Transduction Process Producing Force or Motion

- Conversion of Energy to Work
- Store Mechanical Energy and Release
- Combination



Mechanical Design Analogy:



Simple
Machines



Mechanical Design



Advanced
Functions



Building Blocks

Materials that display:

- 1) Autonomous behavior
- 2) Respond to multiple stimuli
- 3) 3D, rapid actuation

Knowledge & Predictive Models

Accurate math models
enable predictive design

Fabrication of Architecture: Greater than sum of the parts

Architecture design with responsive
materials leading to enhanced
functionality

Program Status



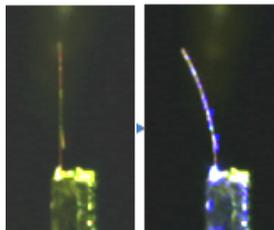
Building Blocks

HT Thermal Shape Memory



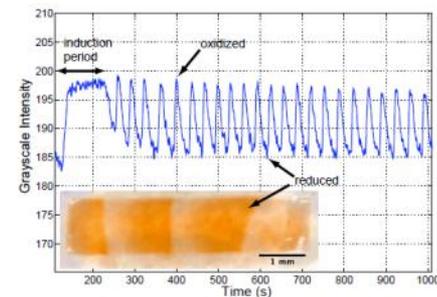
w/ L-S Tan, AFRL

PhotoChem-Mechanical

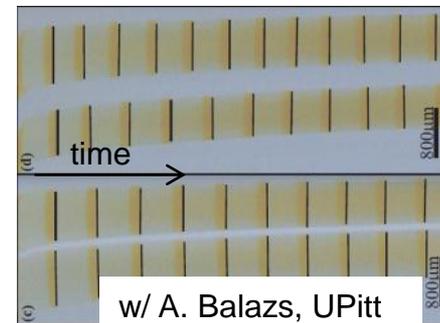
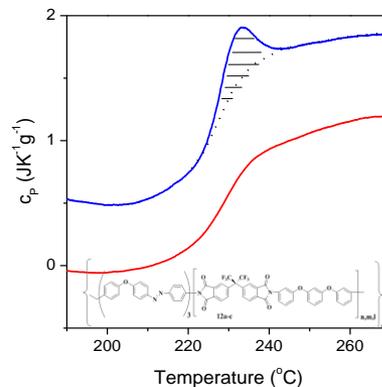
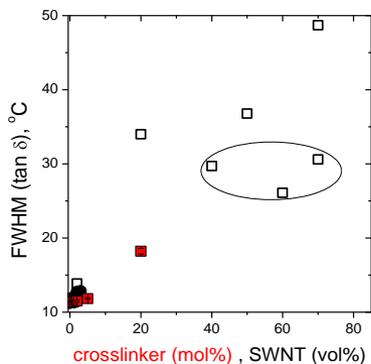


w/ T. White & L-S Tan, AFRL

Autonomic Chemo-Mechanical

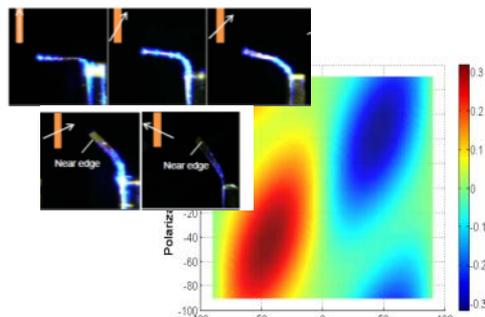
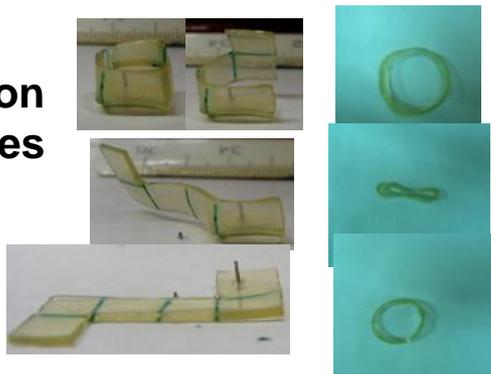


Predictive Models



w/ A. Balazs, UPitt
M. Smith, Hope C.

Fabrication of Devices



w/ T.White & M. Smith, Hope C.

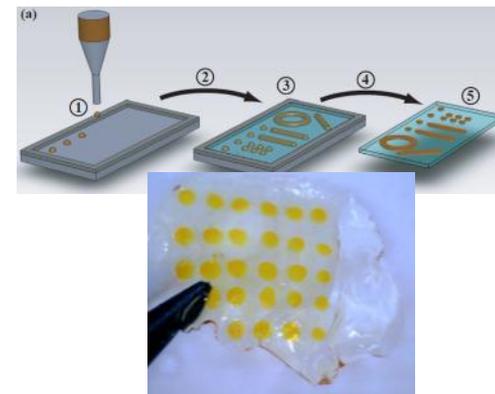
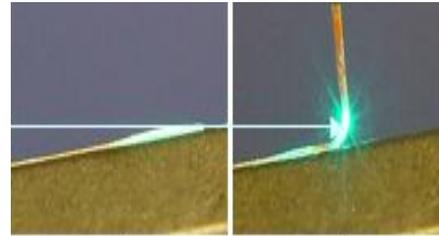
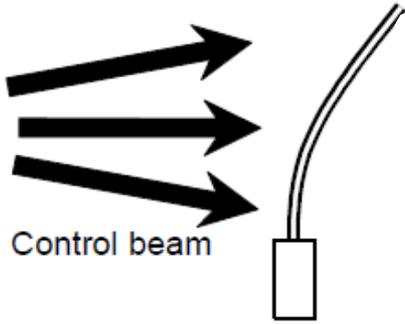




Photo Mechanical: Aerospace Applications



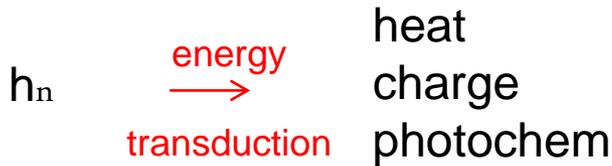
Beam Steering



Tabiryán et al BEAM
Unpublished. Bunning,
Optics Express, 2009.
Tabiryán & White
Optic Express 2010

Ar+ blocked

I = 4 mW/cm²



↓
amplification

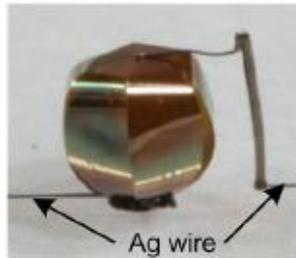
↓
phase change
concentration

↓
summation

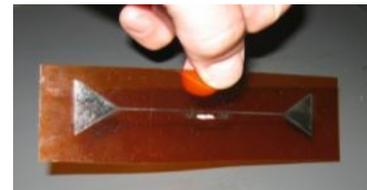
↓
gradient

Tuning Receivers and Packages

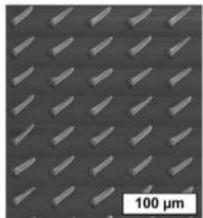
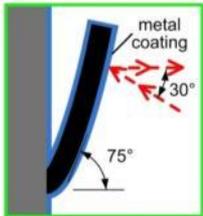
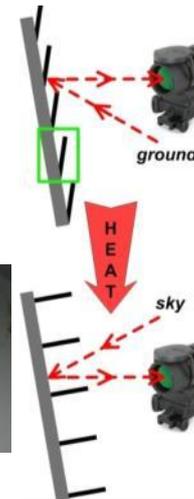
3D Photovoltaics



Nuzzo et al., *PNAS* 106
2009



Vaia et al 2012



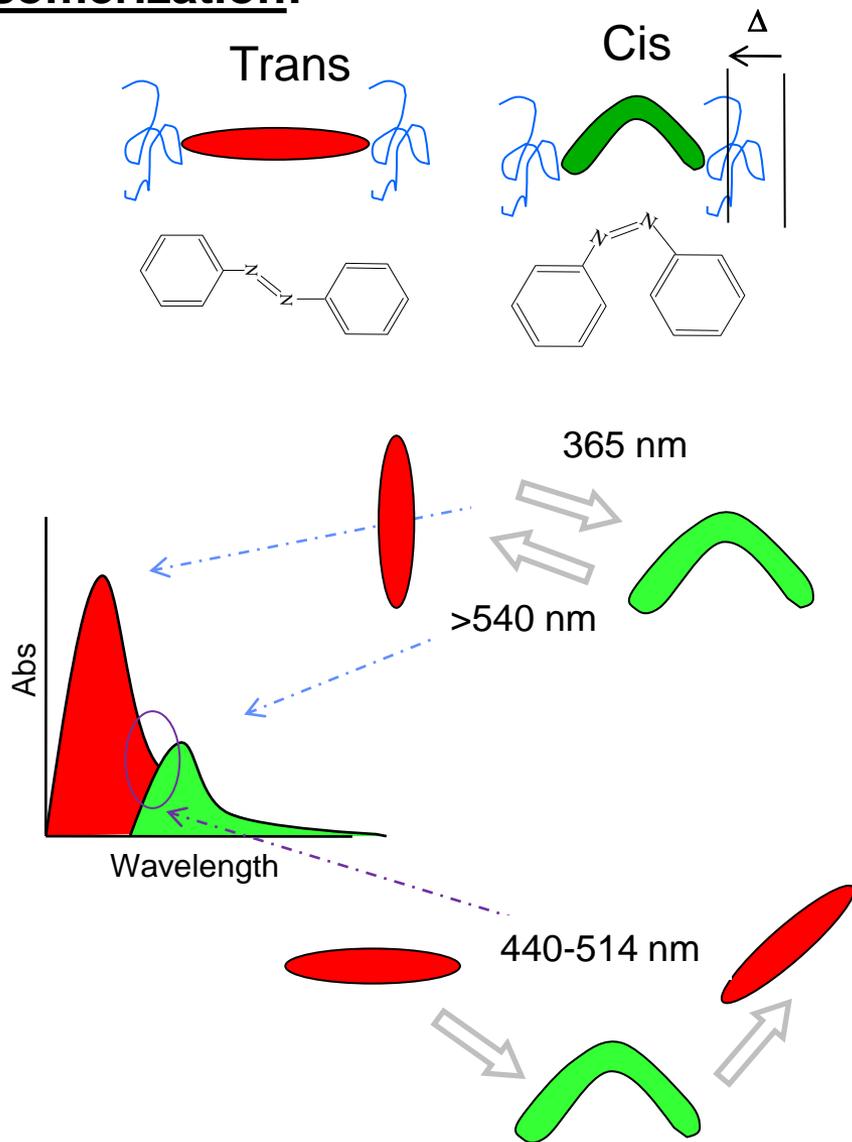
John Hart, Davor Copic,
University of Michigan

Remote & Focused Trigger

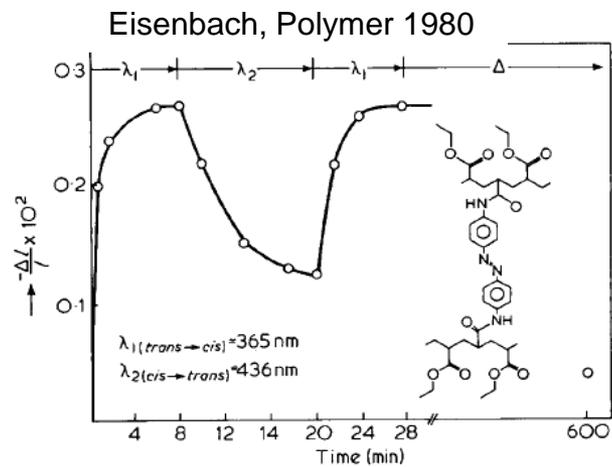
PhotoChem-Mechanical Response: Azo



Isomerization:

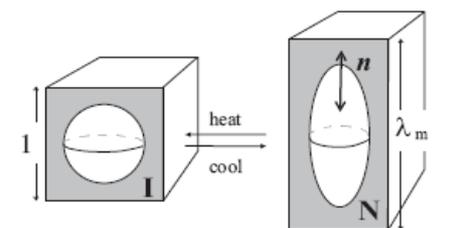
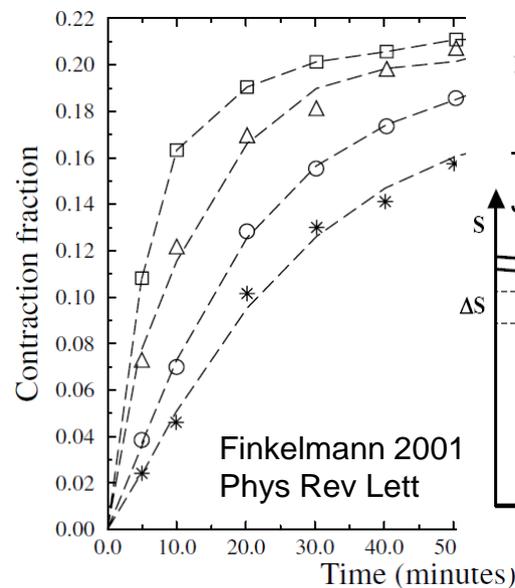


“Glassy” Networks: Azo & LC

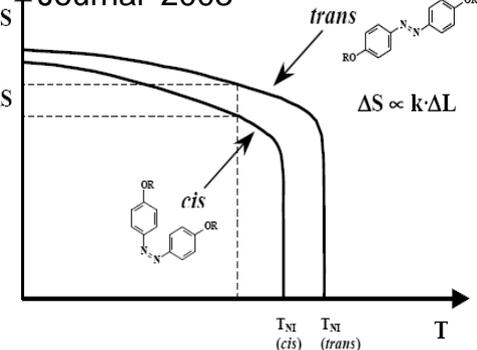


White, et al AFRL 2008

Elastomers: LC-Azo



Ternetjev EuroPhys
Journal 2003

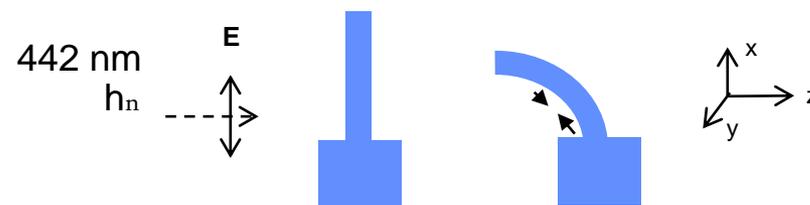
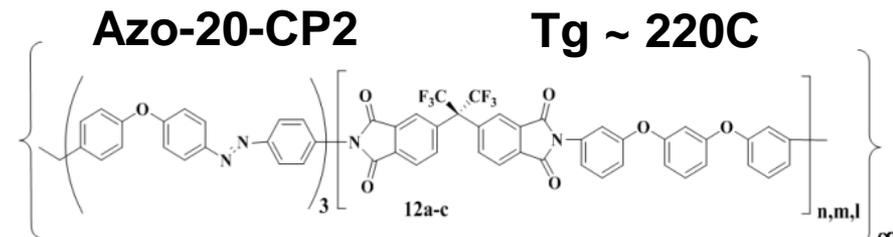


Tuning Photo-Mechanical Response with Process History

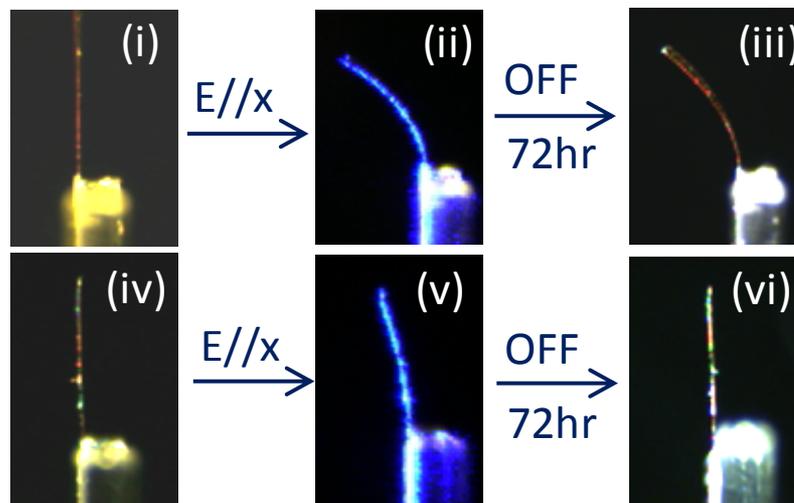


Photo-Plastic (Photo Set, Photo Hardening)
Remove light, retain shape

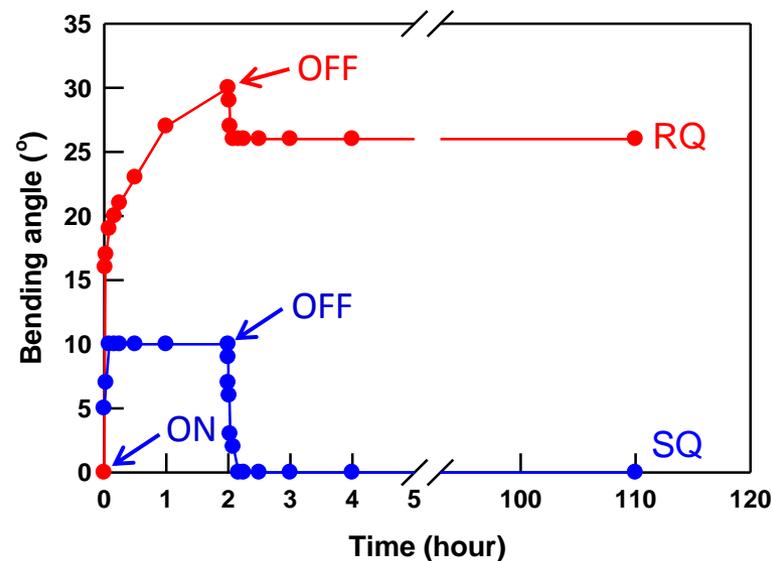
Photo-Elastic (Photo Recovery)
Remove light, recovery original shape



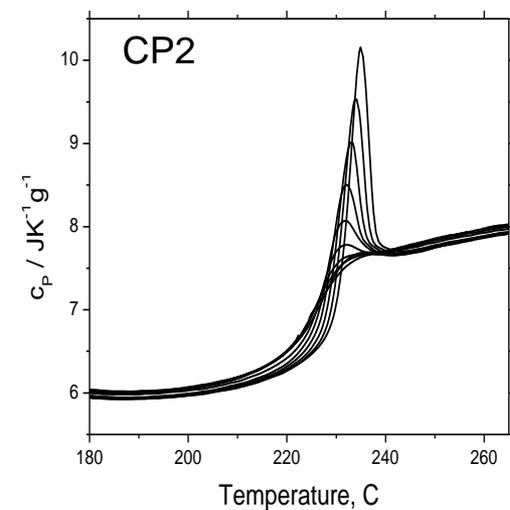
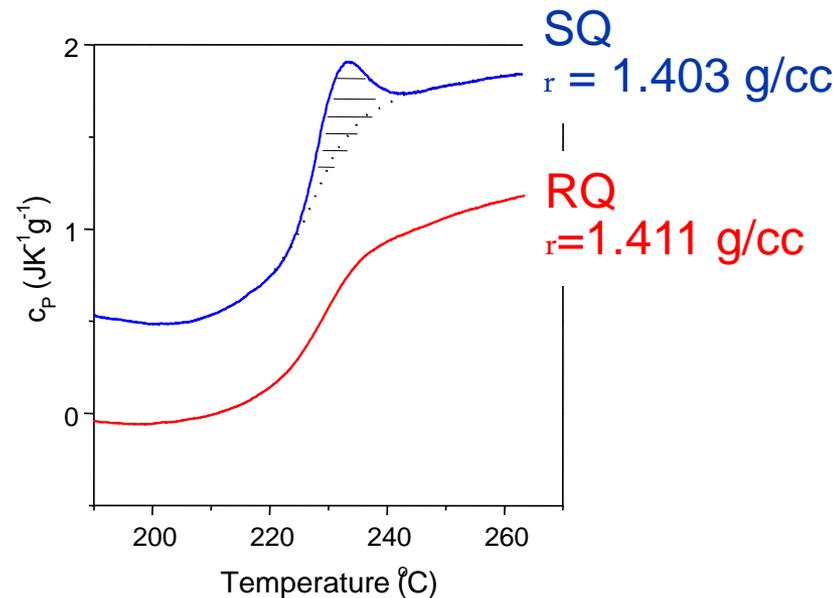
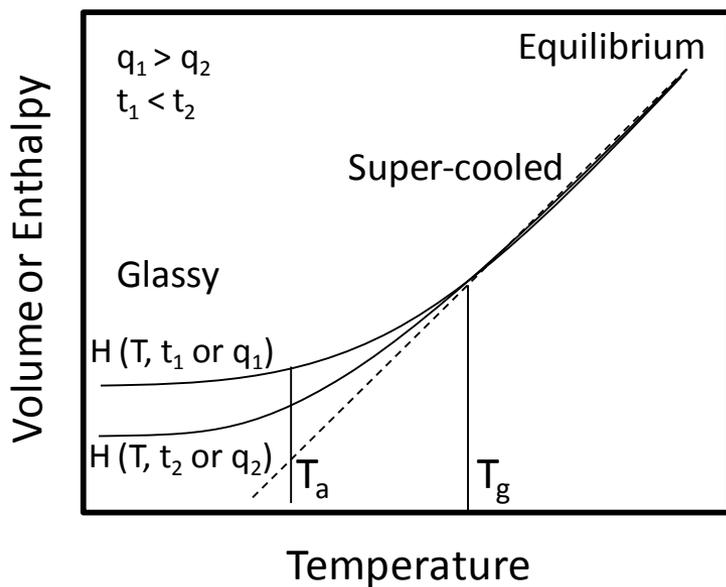
Rapid Quench



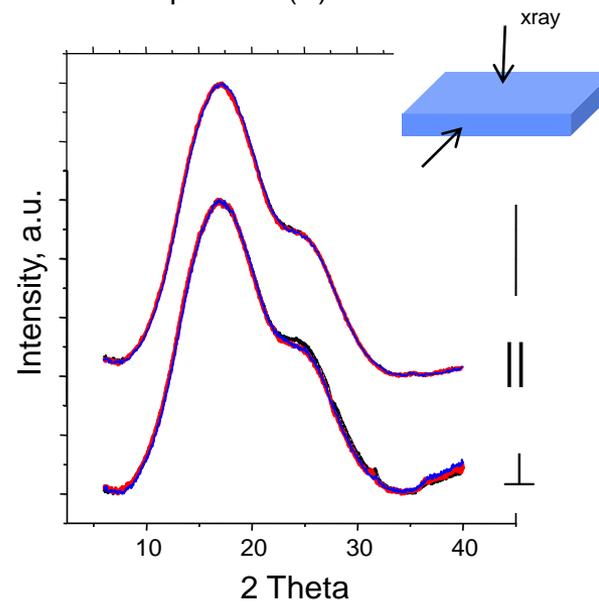
Slow Quench



Glass Structure

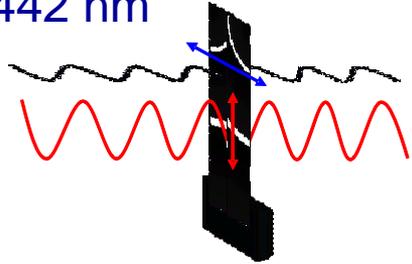


	T_g [K]	Δh [kJ/mol]	β	M
CP2	498	975	0.84	108
azo-5-CP2	500	980	0.71	110
azo-20-CP2	505	1500	0.46	150





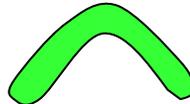
442 nm



Trans-
isomer

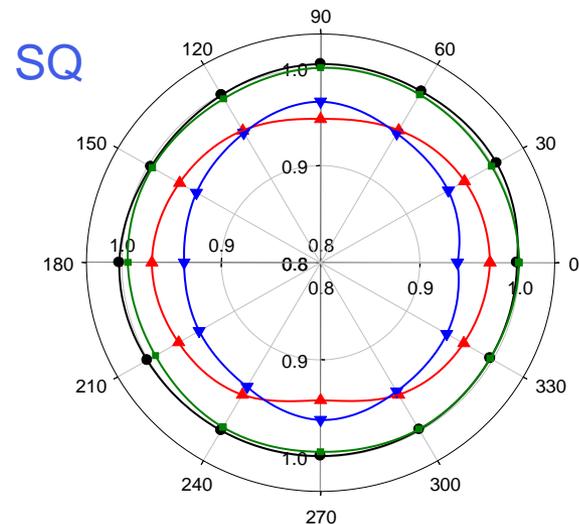
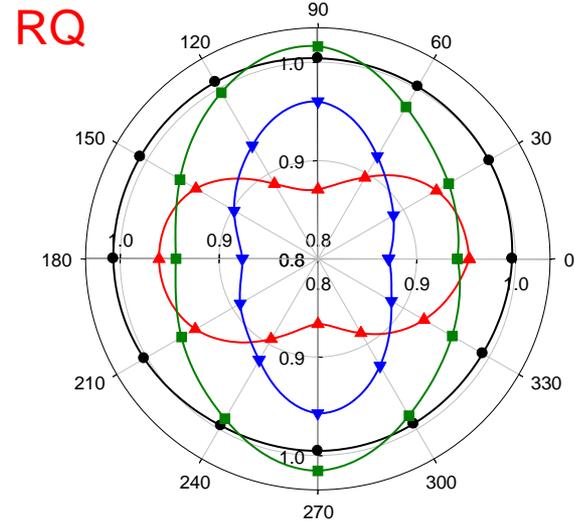


Cis-
isomer



- Isotropic trans distribution
- 442 illumination:
 - trans rotation + 3-5 % cis
 - RQ > SQ
 - Reversible & $\perp E$
- Dark state:
 - RQ partial recovery consistent with cis, trans enhancement
 - SQ initial state recovery

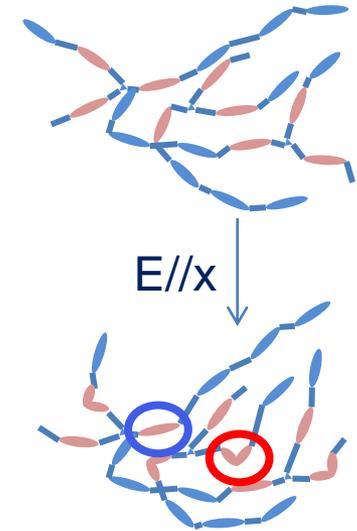
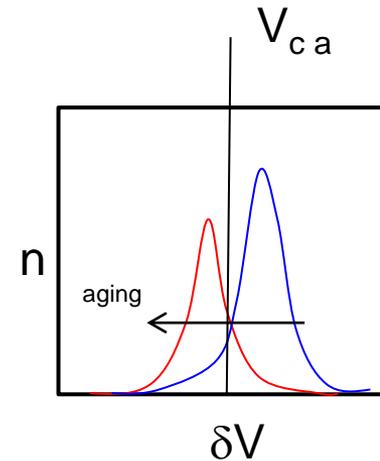
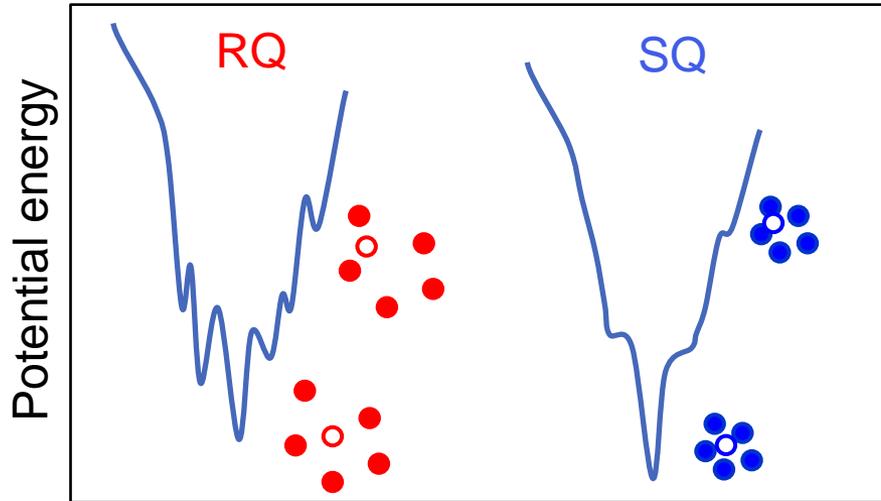
Relative Abs: Trans Isomer (355 nm)



Glass Energy Landscape for Photo Chemical to Mechanical Transduction

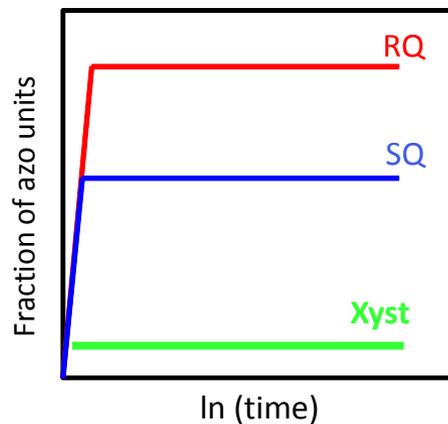


Configuration space

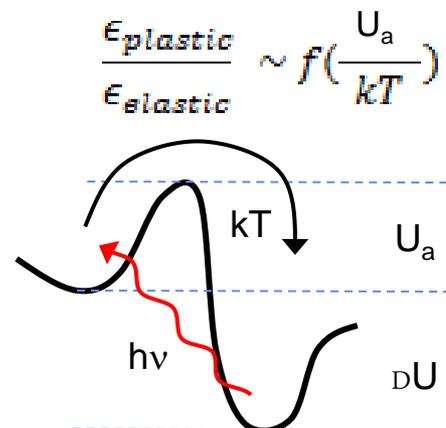


Photon to Isomerization

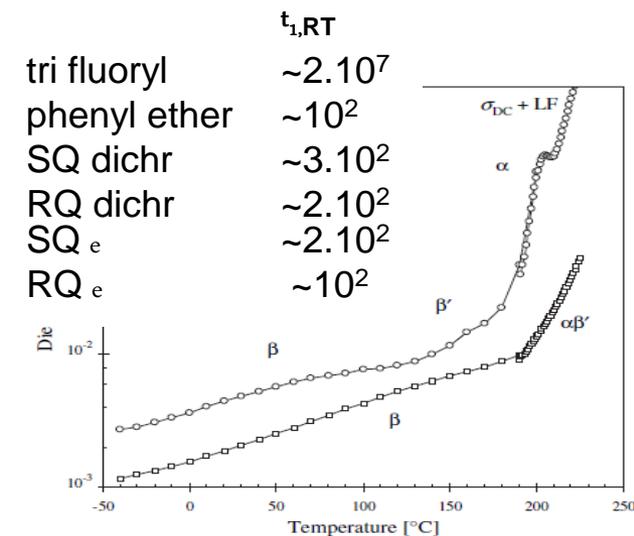
$$e \sim S f_{\text{isom}}$$



Internal Energy Storage & Recovery



Recovery Rates



Implications & Next Steps



Distribution of local “activation volume” controls first step for molecular to macroscopic transduction

- Molecular structure *and* process history
- Fraction of successful photon-to-isomerization events
- Fraction of trapped events
- Rate of recovery of events

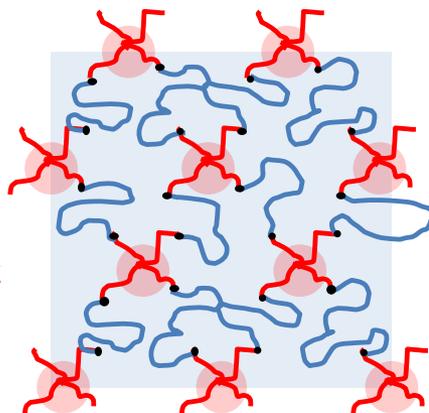
Material System Architecture to Optimize Speed and Efficiency

- $DU \sim r$ (isomerization) $I(x) E(x)$
- Local anisotropy – LCs v. semi-rigid v. flexible chains
- Network structure, secondary relaxations, local of “hinge”
- Photochemistry: rotation v. cis formation

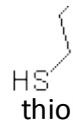
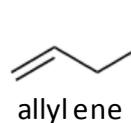
Telechelic Chain



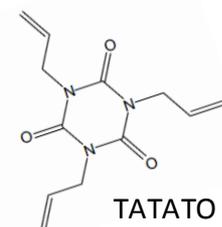
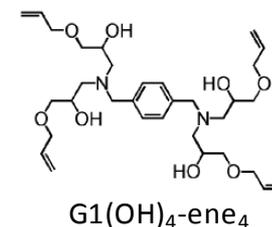
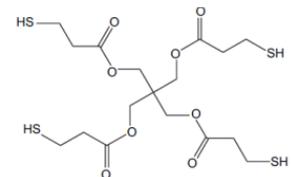
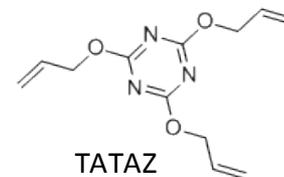
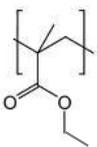
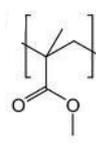
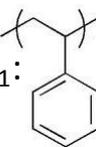
n-functional Crosslink



X:



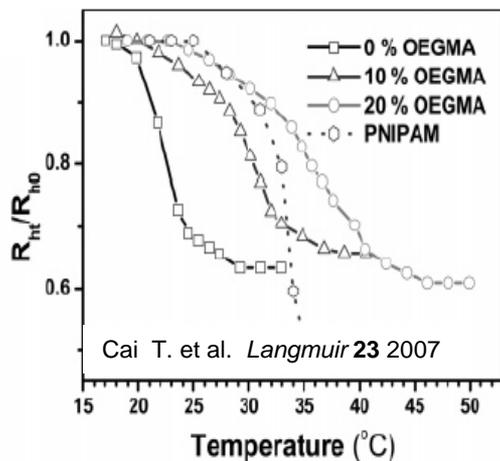
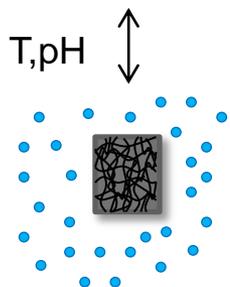
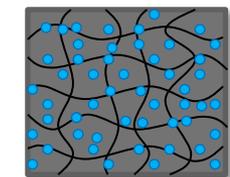
R₁:



Autonomic Chem-Mechanical Systems: Responsive Hydrogels & Chemical Oscillators

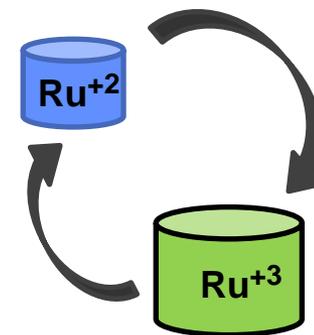
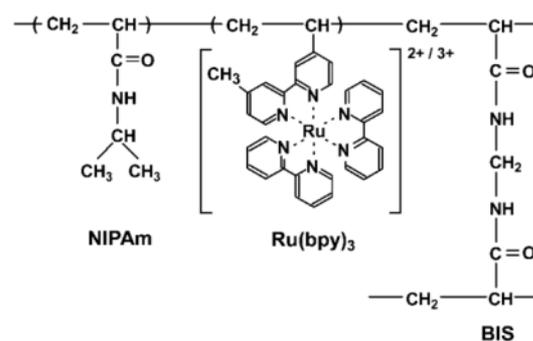


Responsive Hydro-gels



Autonomic Chem-Mechanical Systems

pNIPAAm-co-Ru(vbpy)



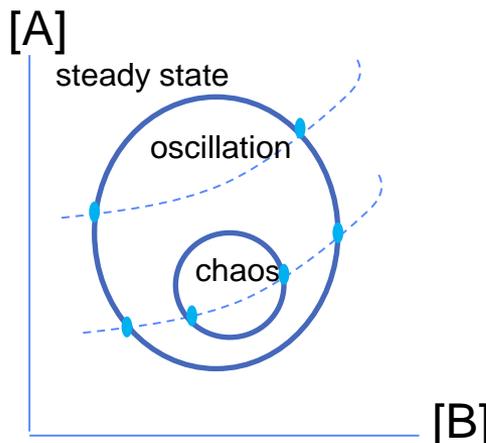
R. Yoshida

Chemical Oscillator

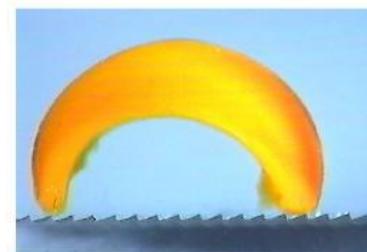
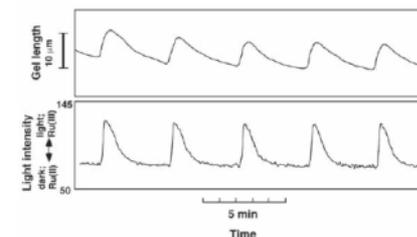
Stirred BZ reaction



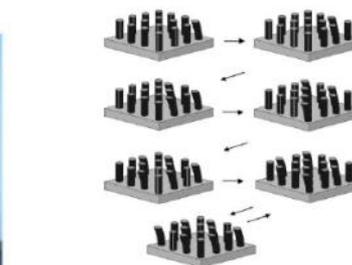
BZ Reaction



M. Smith



Maeda et al. *Int. J. Mol. Sci.* 2010



Tabata et al. *Sensor Actuat. A.* 2002

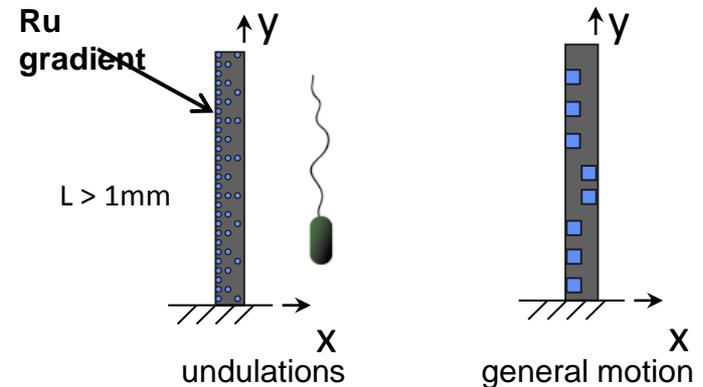
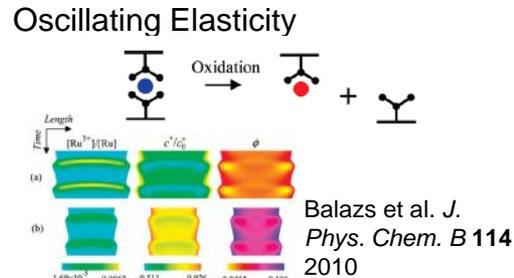
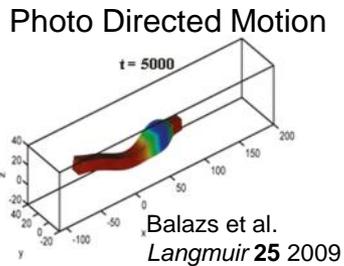
Heterogeneous Chem-Mechanical Design



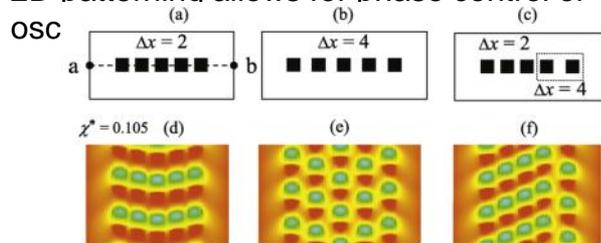
Heterogeneous Autonomic Systems = Composite w/ Active & Inactive Regions

- Homogenous Autonomic Gel = Strain Generator Unit
- Amplify Motion through mechanical architecture
- Coupled feedback through
 - Chemical Concentration gradients
 - Mechanical-Chem interactions

Potential routes for control



Coupled Oscillator patches:
2D patterning allows for phase control of OSC



Balazs et al. *Prog. Polym. Sci.* **35** 2010



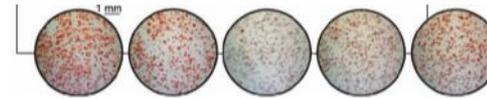
Westbrook and Qi. *J. Intell. Mater. Sys. Struct.* **19** 2008

Patterning Structure and Active Regions



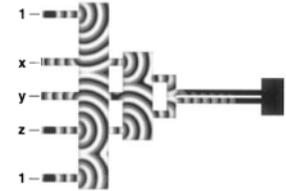
Assembly - arrange premade, discrete homogenous units

- Adv: Flexibility in design
- Dis: minimal mechanical coupling, weak structures, very slow, poor reproducibility



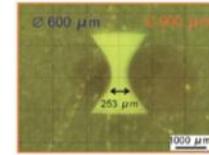
Showalter et al. *Science* **323** 2009
Steinbock et al. *Science*, **269** 1995

Steinbock et al. *J. Phys. Chem.* **100** 1996

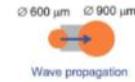


Photopolym - in plane patterning of monomer mixture

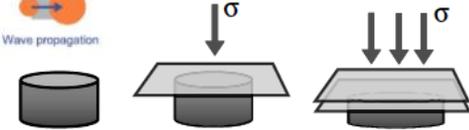
- Adv: Precision control to micron scale
- Dis: catalyst photo sensitive, limited flexibility (new form for new app)



Yashin, et al
J.Mater.Chem.,
2012

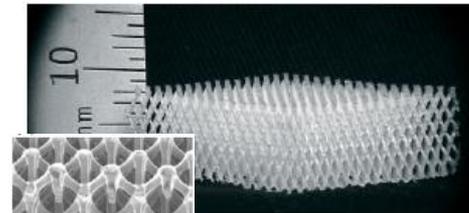


Van Vliet, *Adv. Func. Mater.*, 2012

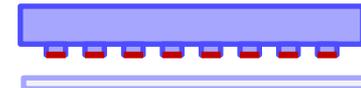
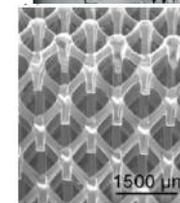


Postfunctionalization - separate form from pattern (add catalyst & x-linking later)

- Adv: Flexible for 2D (on-demand stamping), Pattern 3D structures
- Dis: Completeness of reaction, profiles dependent on diffusion



Jacobsen et al. *Adv. Mater.* **19** 2007



Vaia, Smith, *SPIE* 2012

Additive Manufacturing – printing 3D (involve postfunctionalization, thermo-gelling, etc..)

- Adv: 3D structures (additive manufacturing)
- Dis: Resolution limits, processing variables



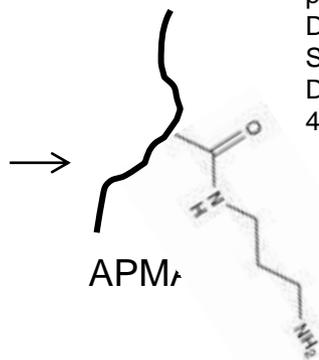
Vaia, et al 2012

Postfunctionalization: Polyacrylamide



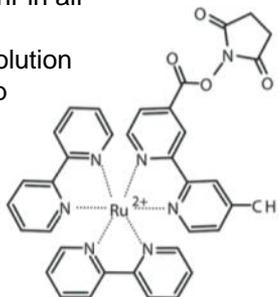
95.5% AAm
2.5% APMA
2% MBA

Initiate:
APS, TEMED
Cast in mold



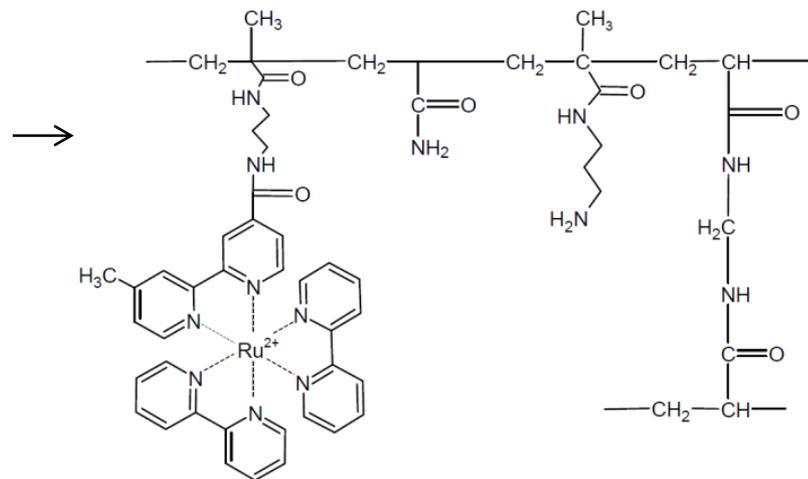
pH 7.2 buffer
Dehydrate for 1hr in air
Soak gel in Ru,
DMSO, water solution
4hrs, room temp

+



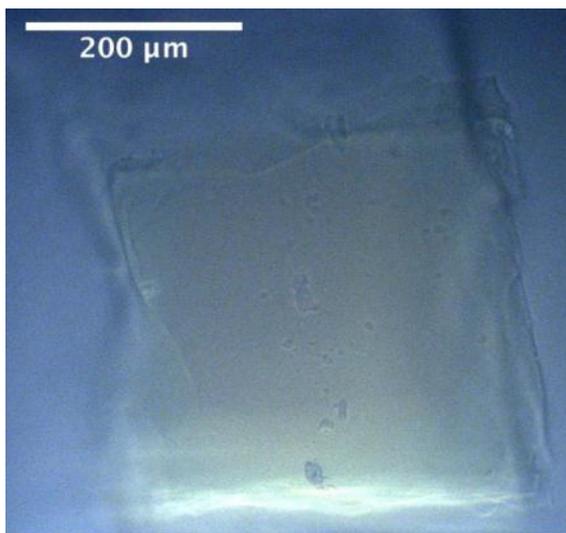
Polymer *or*
Swollen Network

poly(AAm-co-AMPA-co-Ru)

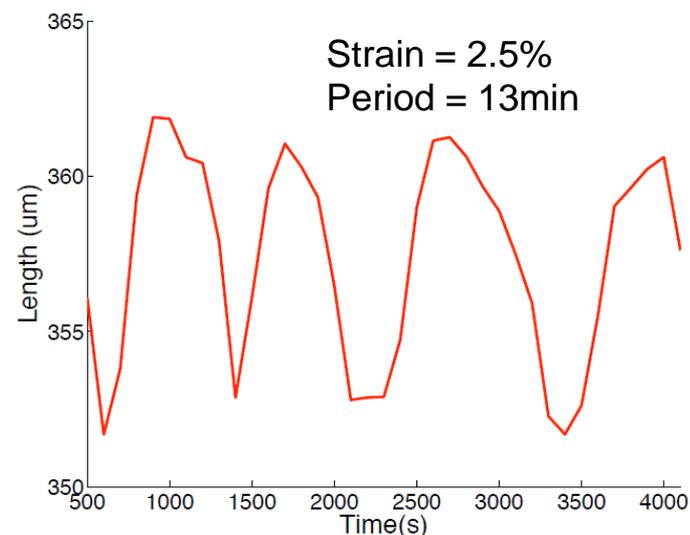


Immerse in
BZ Soln

0.08M Sodium
Bromate
0.04M Malonic Acid
0.7M Nitric Acid

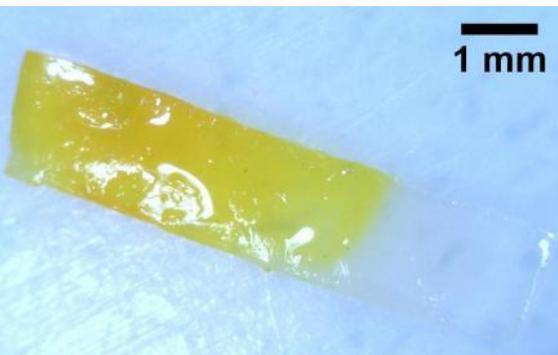
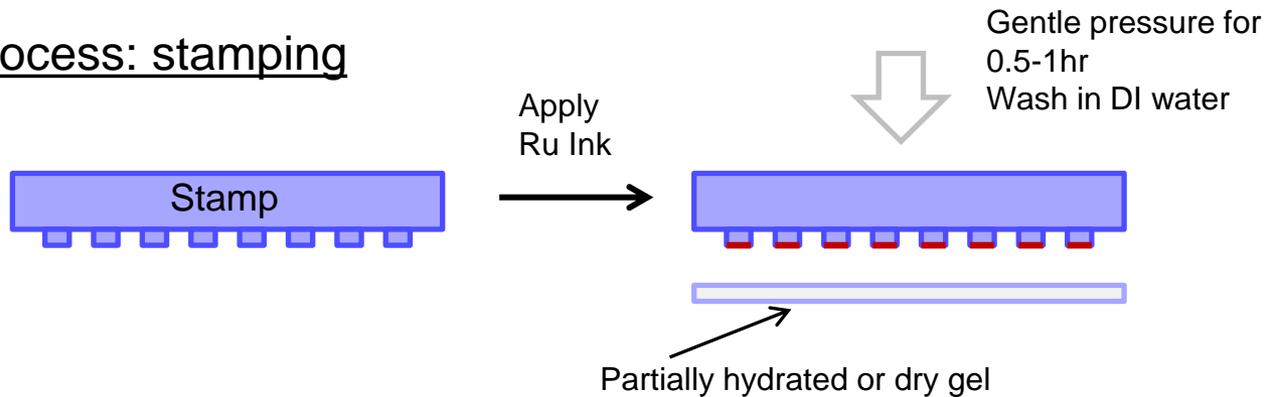


Literature: Typical strains = 2-20%

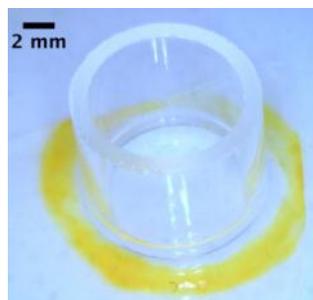
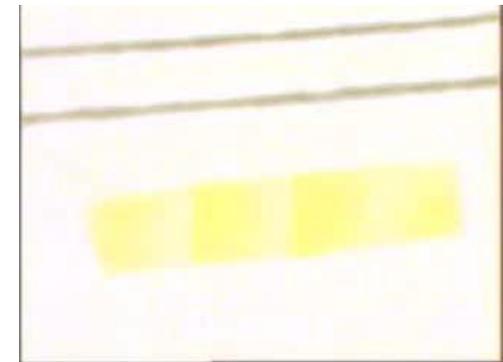
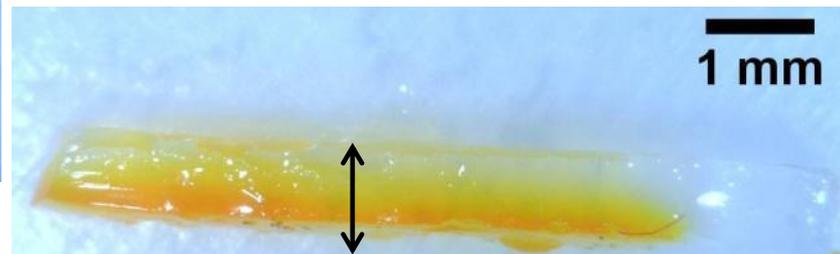


Patterning poly(AAm-co-APMA)

Process: stamping



Gel Cross Section - Ru Gradient



Large Circular Pattern

Chemical wave periods: 4-10min

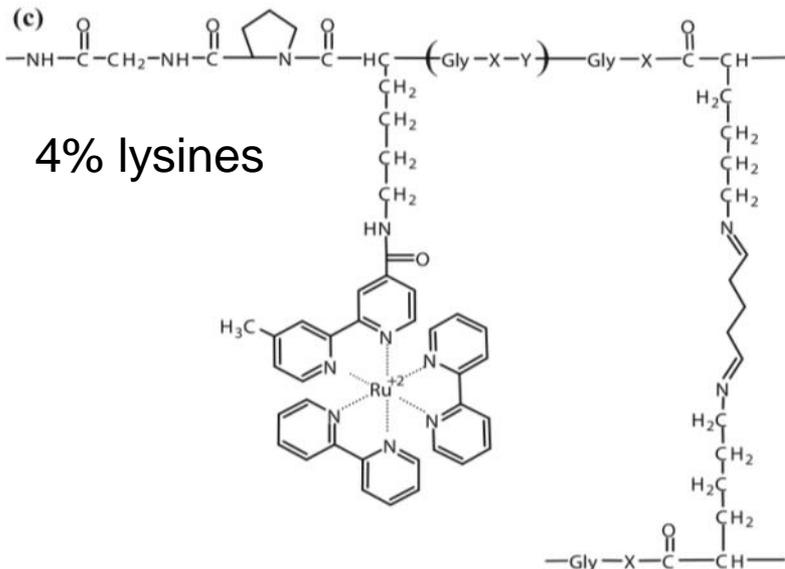
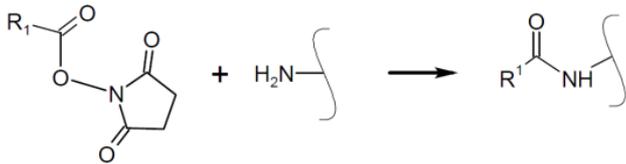
Current Challenge: Improve control over diffusion and pattern size

BZ-Gelatin for Thermogelling

Thermogel

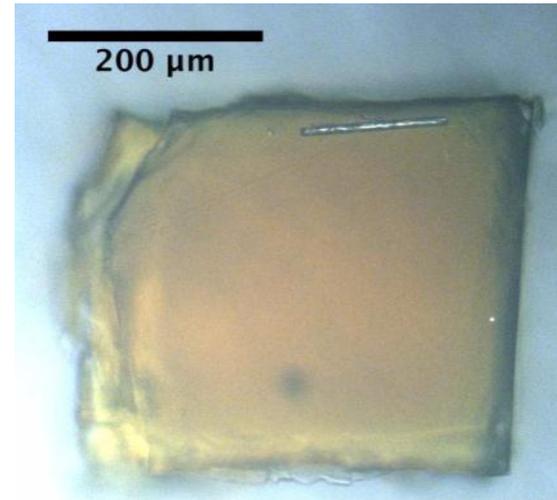
- physically crosslinked (H-bonds, xystals)
- melts above a critical temperature

Type A BZ Gelatin

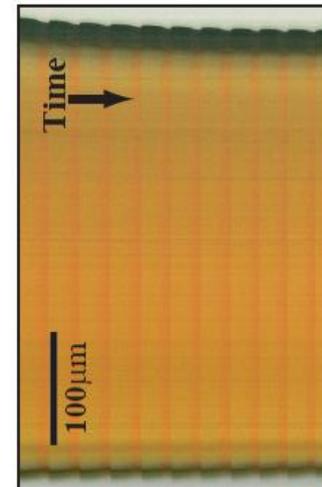
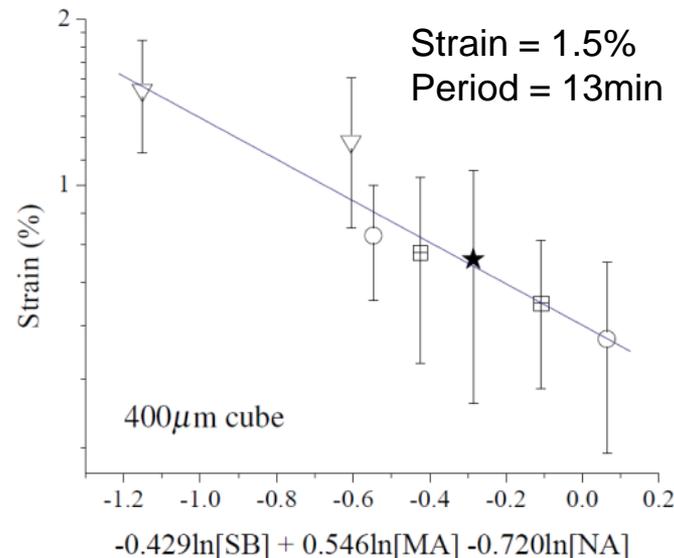


Ru conc:
0.04-0.05%

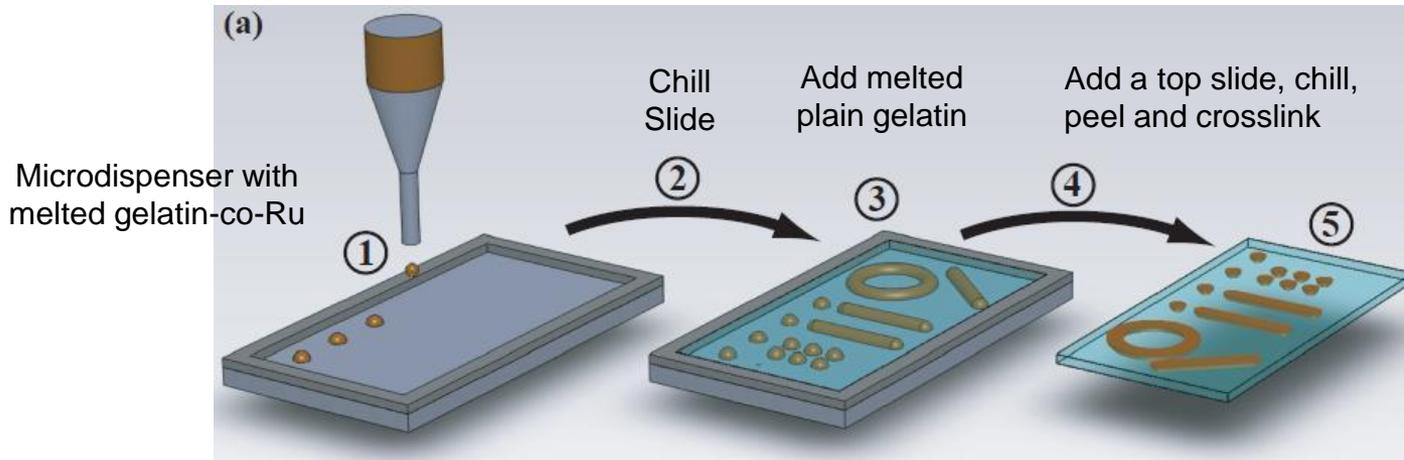
Chemical
wave periods
(>1mm):
2-6min



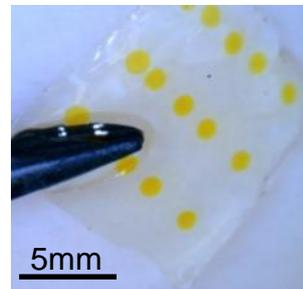
0.08M Na Bromate
0.04M Malonic Acid
0.7M Nitric Acid



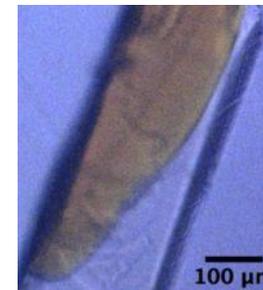
Additive Mfg: Patterned Gelatin



Heterogeneous Gel



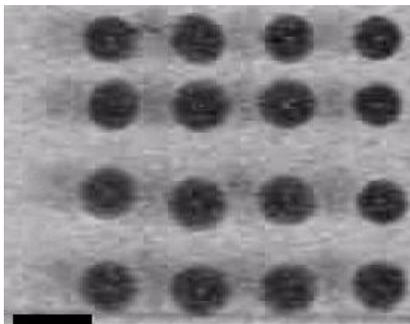
Cross Section



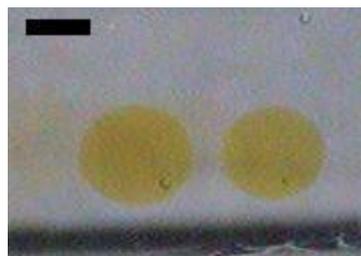
3D Pattern



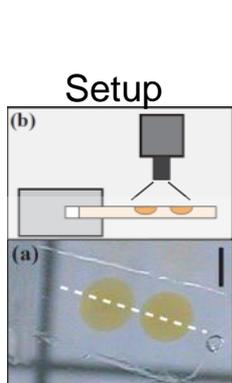
Array of Freestanding Dots in BZ Solution



0.08M Sodium Bromate
0.06M Malonic Acid
0.7M Nitric Acid



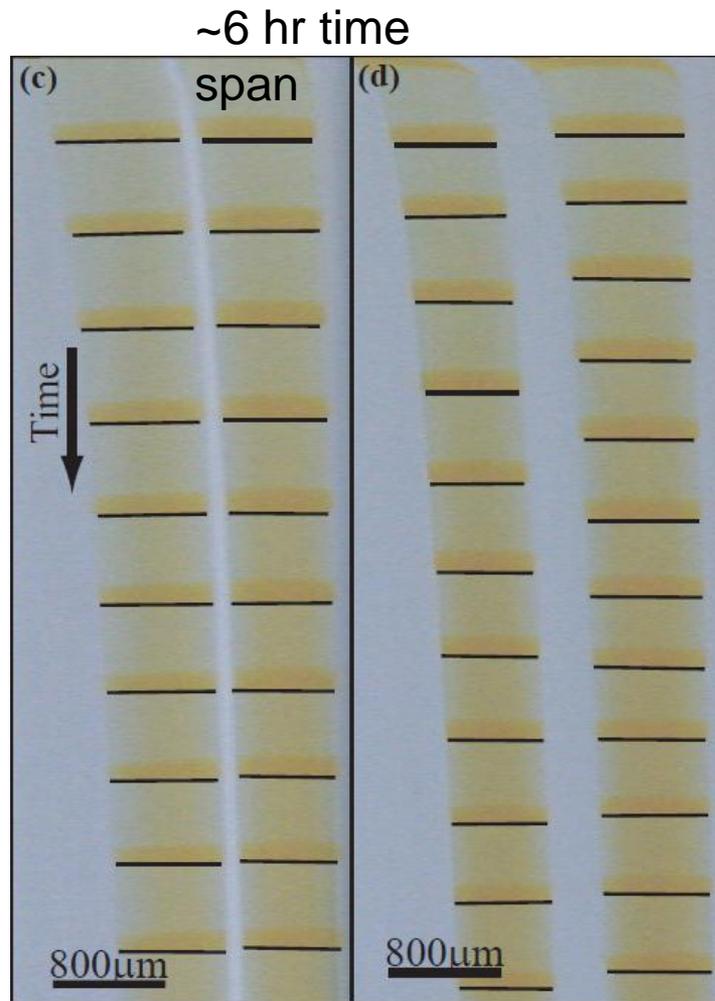
Adjacent Patches: Effects of Spacing



Coupled
Osc.



0.08M Sodium Bromate
0.02M Malonic Acid
0.7M Nitric Acid



Summary

1 patch

- Period = 2039 +/- 251

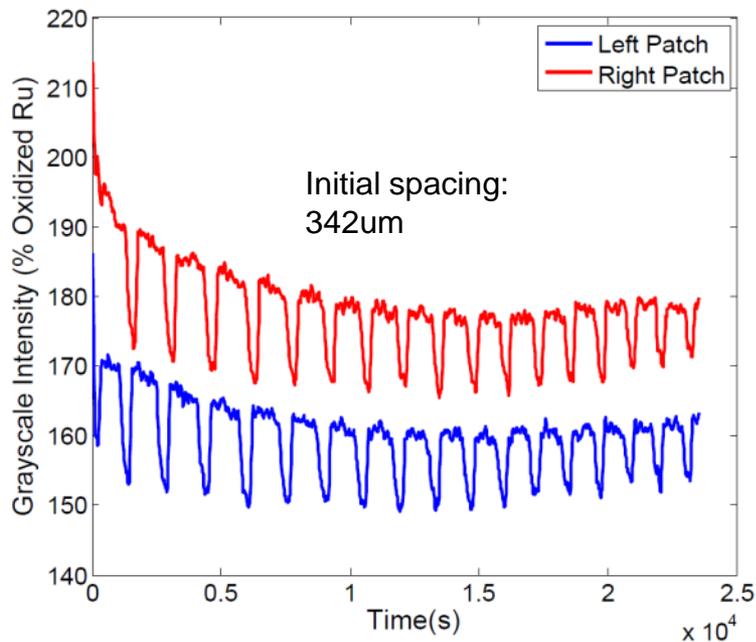
2 close patches

- Inner spacing = 117 +/- 13um
- Period = 1613 +/- 244
- Ave diff in period: 0-34s

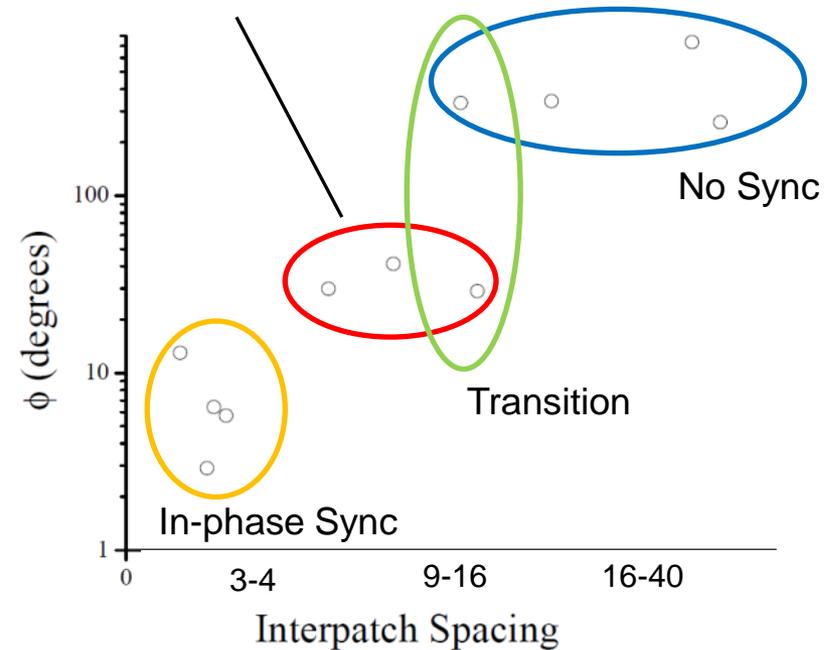
2 far patches

- Inner spacing = 628 +/- 160um
- Short (clamp) = 1547 +/- 332
- Long (free end) = 1962 +/- 429
- Ave diff in period: 120-751s

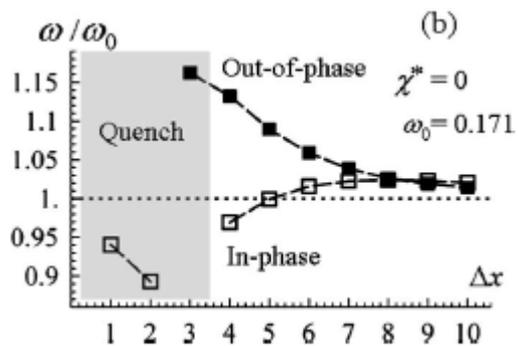
Synchrony Comparison to Simulation



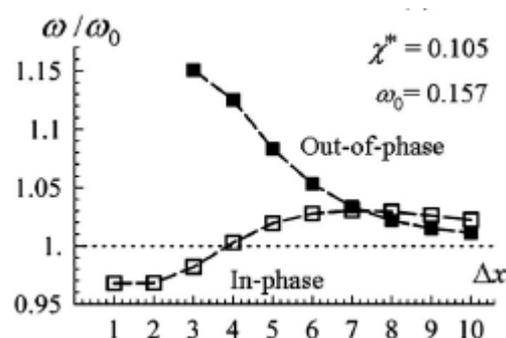
Out-of-phase Sync



No Mechanical Coupling



With Mechanical Coupling

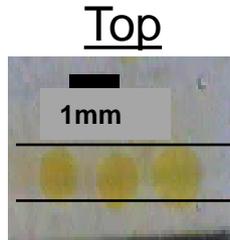


Balazs Group Simulation

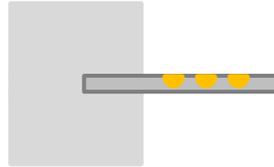
Putting Blocks Together: Three Patch Actuator



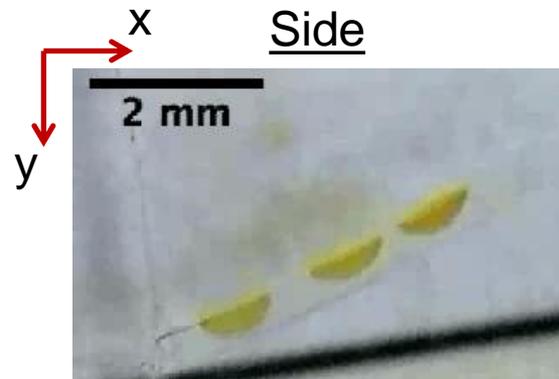
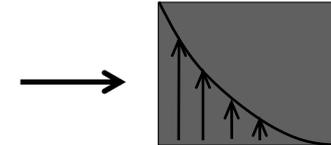
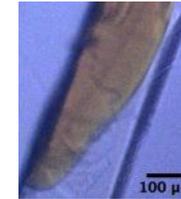
Cut actuator from
patterned sheet



Clamp in PDMS

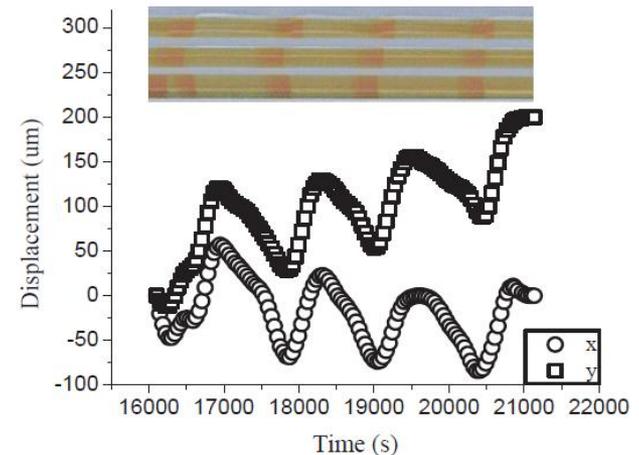
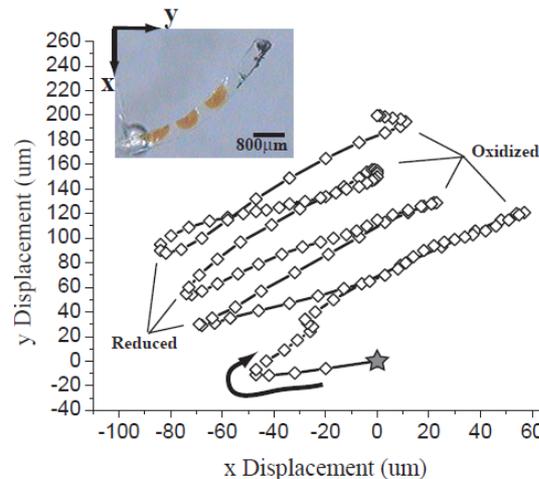


Gradient in Ru leads to gradient in
strain upon swell-deswell



5x1x0.4mm
cantilever
Period: 30 min.

0.08M Sodium Bromate
0.02M Malonic Acid
0.7M Nitric Acid



1 patch cantilever

- Amp 38.6 +/- 7.4 um
- Period = 1369 +/- 107um

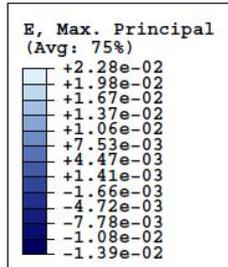
3 patch cantilever

- Amp 162 +/- 36 um
- Period = 1587 +/- 410um

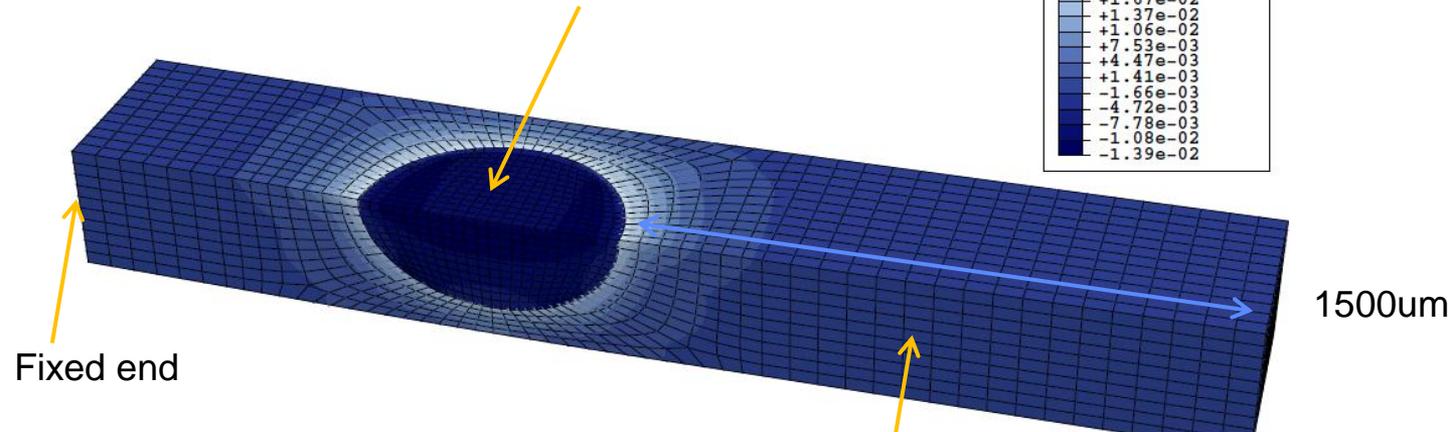
Pattern design and mechanics leads to cooperative swell-deswell with motion amplification of 15x over cube



Apply temp locally to impart
1.5% strain in patch



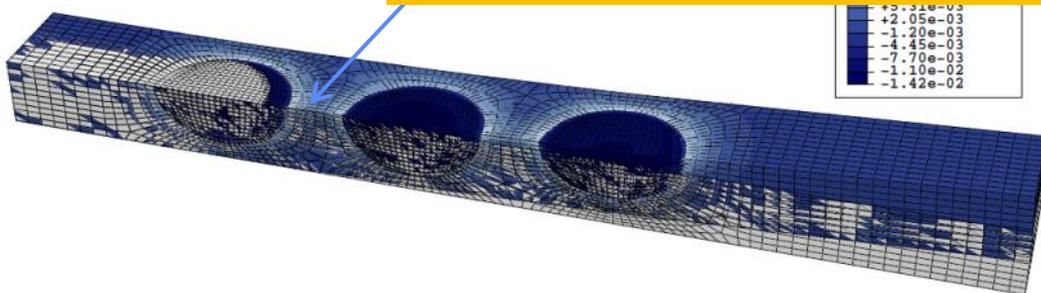
Half of the
cantilever is
modeled



- Max principal strain outside patch: 2.3%
- Max principal strain drops to zero beyond ~300um, <0.5% after 200um
 - Within these distances we expect mechanical effects on coupling

- 1 patch tip displacement = 42um
- 3 patch tip displacement = 191um

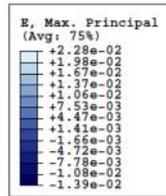
Experimental = 38.6um
Experimental = 162um



FEA: Optimal Stain Generator Profile

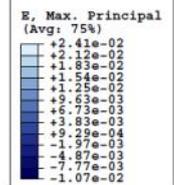


- Apply 1.5% strain
- Tip displacement = 42.3um



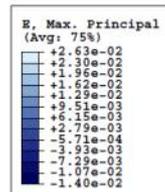
270um

Tip displacement = 28.7um

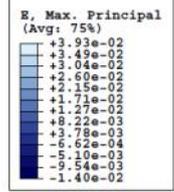


100um

Tip displacement = 44.1um



Tip displacement = 30.4um

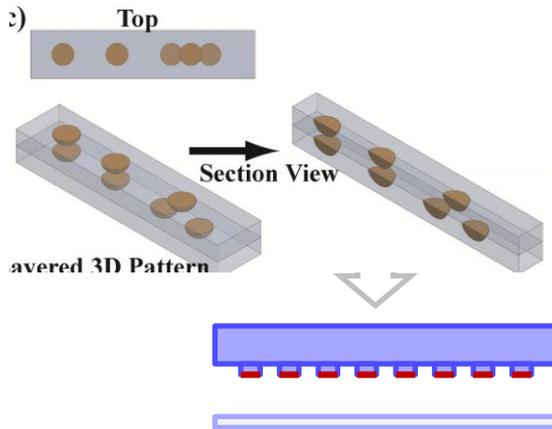


- Which shapes give greatest degree deflections?
 Which shapes lead to greatest coupling through strain?
 How do varying material properties affect behavior?

Next Step: Heterogeneous Autonomic Gels

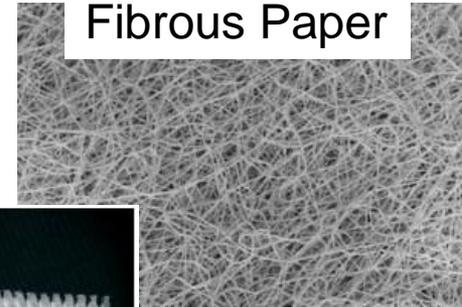


Patterning: Additive Mfg, 2D Stamping, 3D microtrusses, 3D BZ colloid mixtures

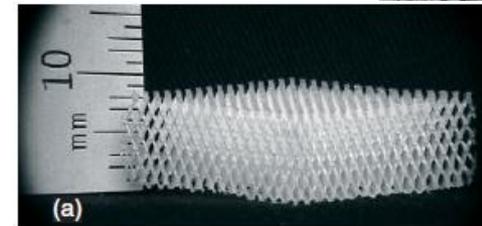


Puopolo, Vaidyanathan OSU

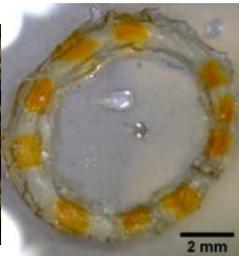
Fibrous Paper



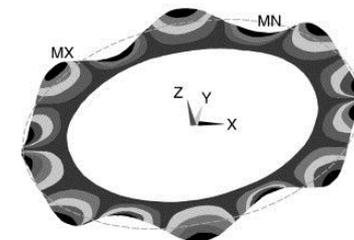
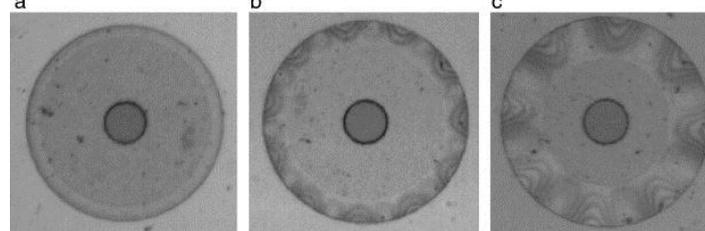
Jacobsen et al. *Adv. Mater.* **19** 2007



Mechanical Design: Bi- / meta- stability for speed; wave interference



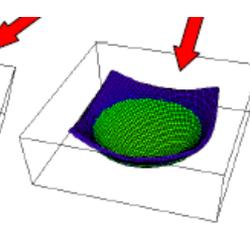
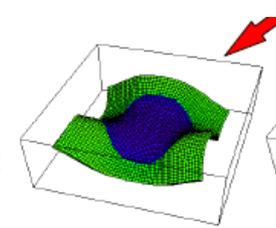
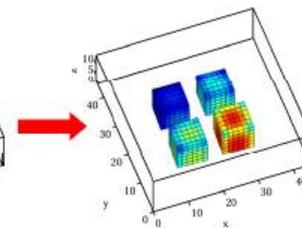
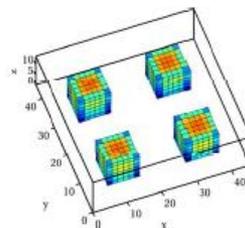
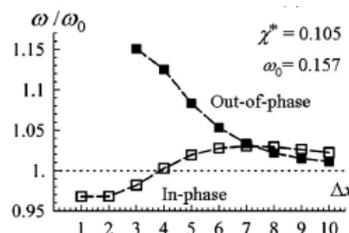
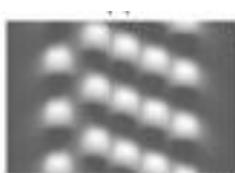
Philip Buckohl



Thin Film Solids, 516, 2008, 4070

Model Validation: crosslink network, transduction, material properties

Balazs et al.





Program Status



HT Thermal Shape Memory

PhotoChem-Mechanical

Autonomic Chemo-Mechanical

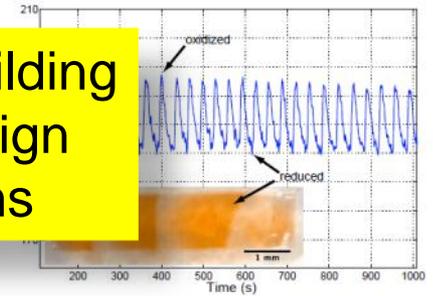
Building Blocks



w/ LPS tan, ATR

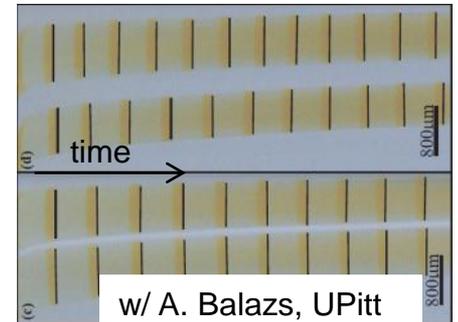
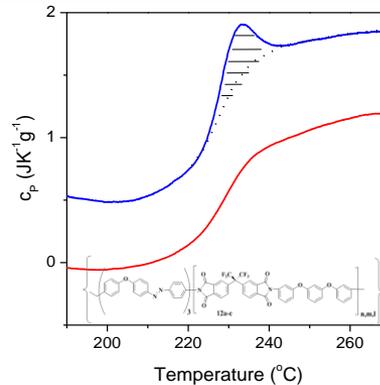
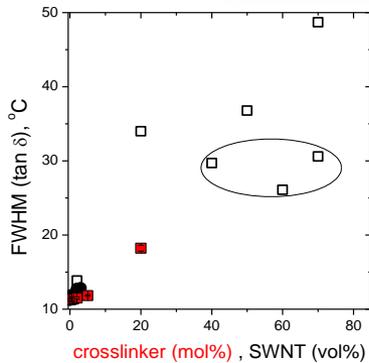


w/ T. White & LPS tan, ATR



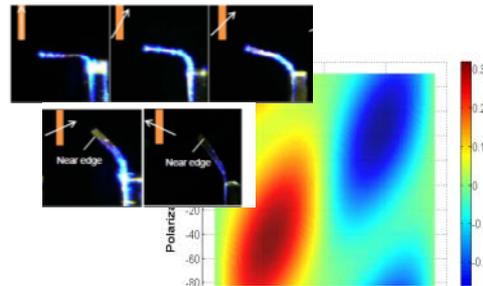
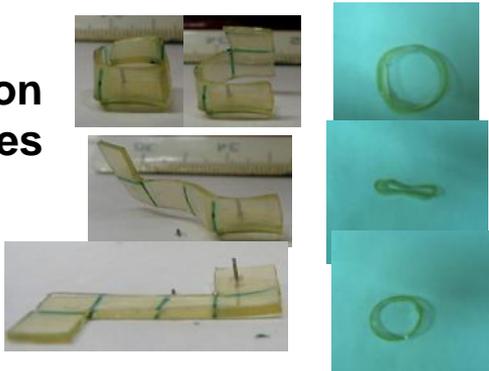
Goal: Develop responsive material building blocks & fabrication to establish design tools for functional material systems

Predictive Models



w/ A. Balazs, UPitt
M. Smith, Hope C.

Fabrication of Devices



w/T. White & M. Smith, Hope C.

