Reaction with Mechanical Force

2014/1/27 Kiyoshi Aoki (B4)

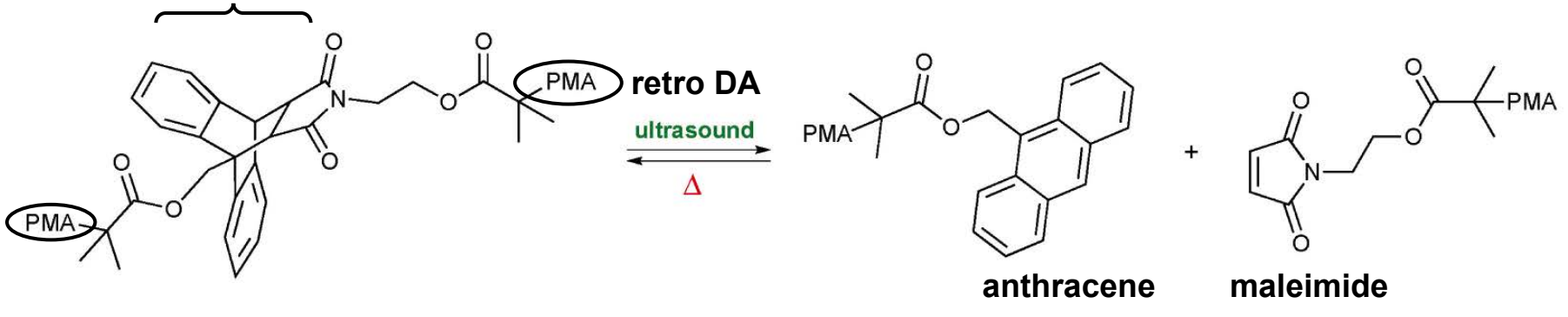
0. Introduction

what kind of mechanical force?

- compression
- cut
- extension
- ultrasound

one example (how to use ultrasound)

mechanophore (cf. p24)



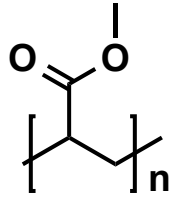
anthracene maleimide

C. W. Bielawski, *et al*. *J*. *Am*. *Chem*. *Soc*. **2011**, *133*, 7180.

ultrasound induced retro DA reation

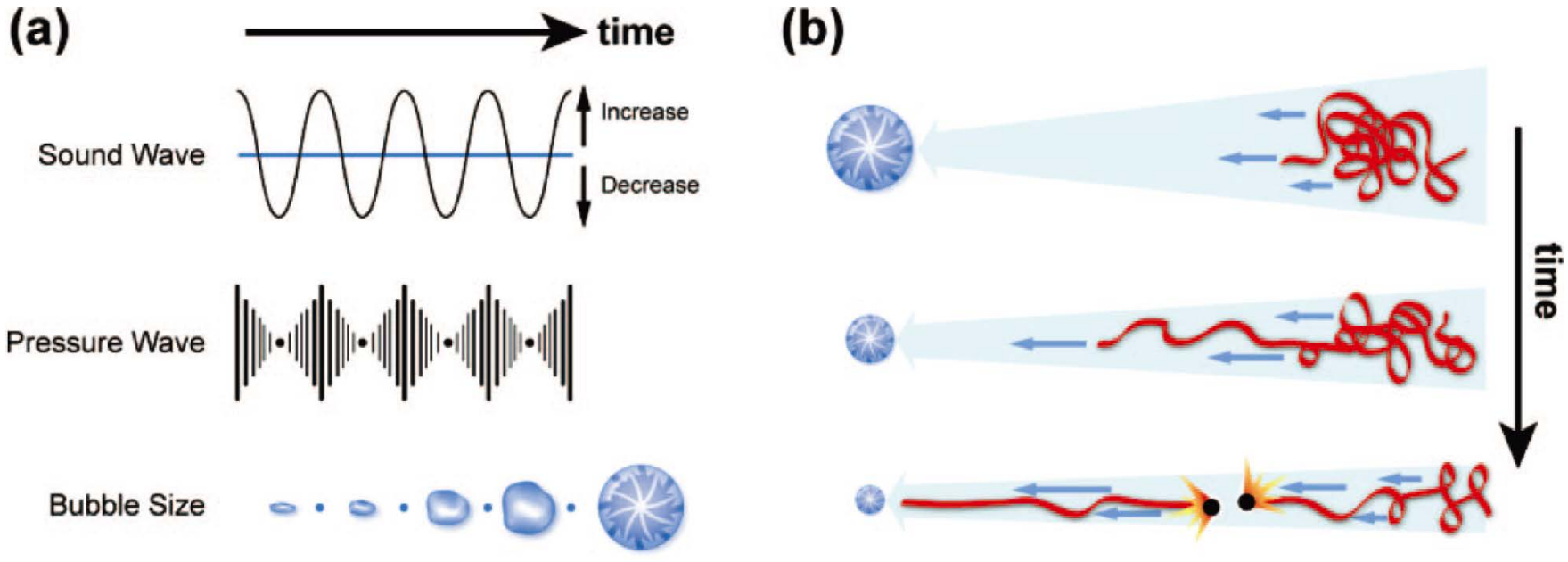
PMA backbone

ultrasound in CH_3CN, 9 ºC, 3 h



PMA

ultrasound (how to generate mechanical stress)

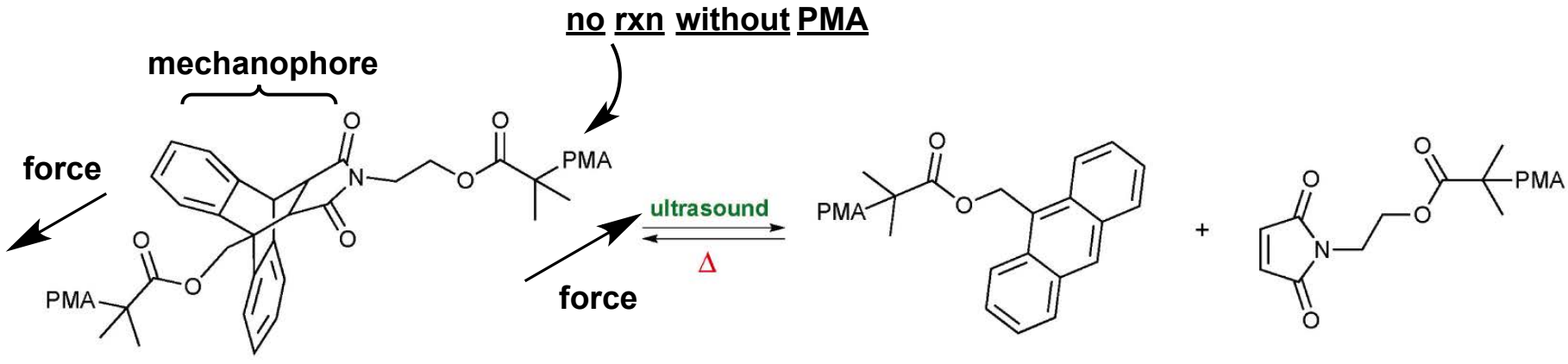


Chem. Rev. **2009**, *109*, 5755.

The mechanism of converting ultrasound waves to energy in the form of force on a polymer chain is through a process called cavitation.

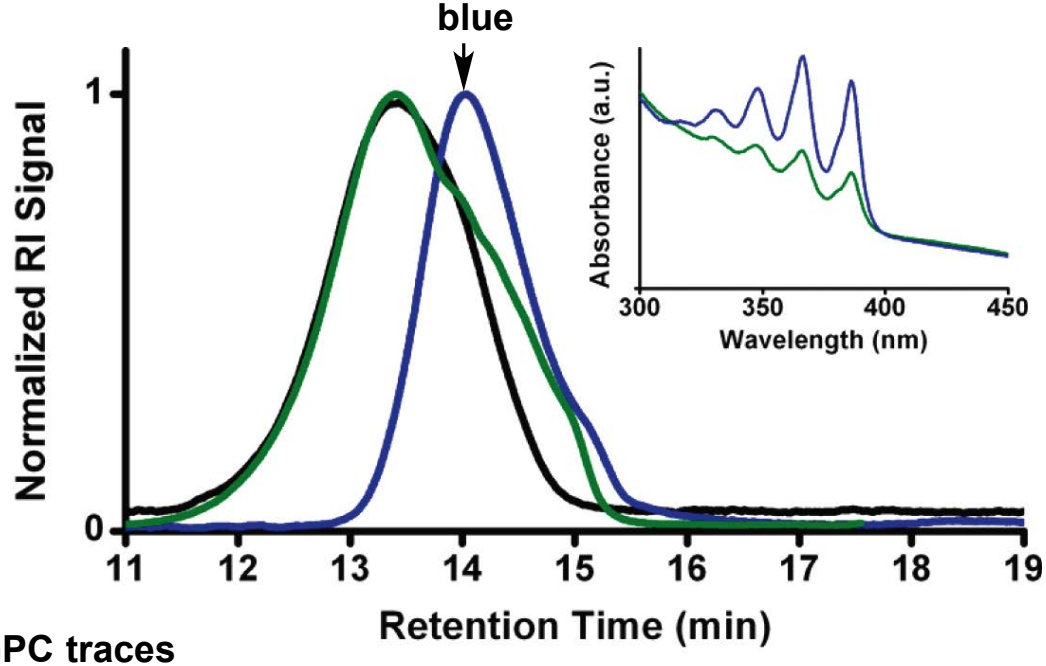
Cavitation is defined as the nucleation, growth, and collapse of bubbles in a liquid.

Polymer chains near a collapsing bubble experience solvodynamic forces as the proximal chain end is pulled toward the void creating by the imploding bubble.



C. W. Bielawski, *et al*. *J*. *Am*. *Chem*. *Soc*. **2011**, *133*, 7180.

Thermally prohibited retro Diels-Alder reaction was achieved. (cf. 110 ºC, 24 h)



GPC traces
black: before sonication
blue: after sonication
green: after heating

(When heating (60ºC, 48 h), recombination was observed.)

*Purpose of investigation
for reaction with mechanical force

There are two reaction types.

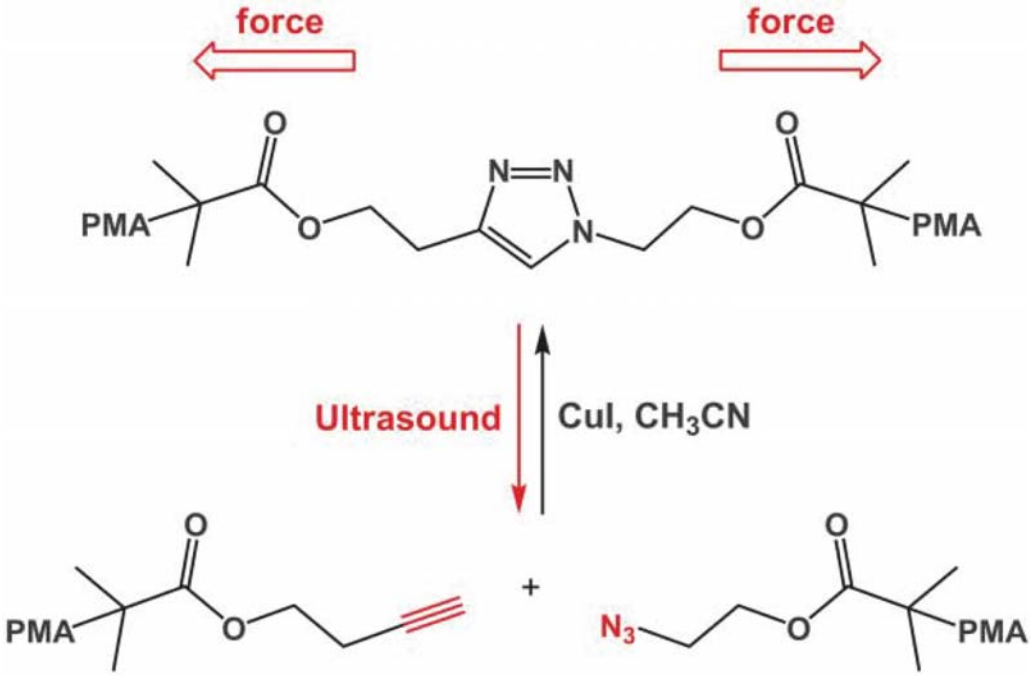
{ active use of mechanical force
to achieve otherwise impossible reaction

passive use of mechanical force
for material scientific application
(damage responsive polymer)

1. active use of mechanical force

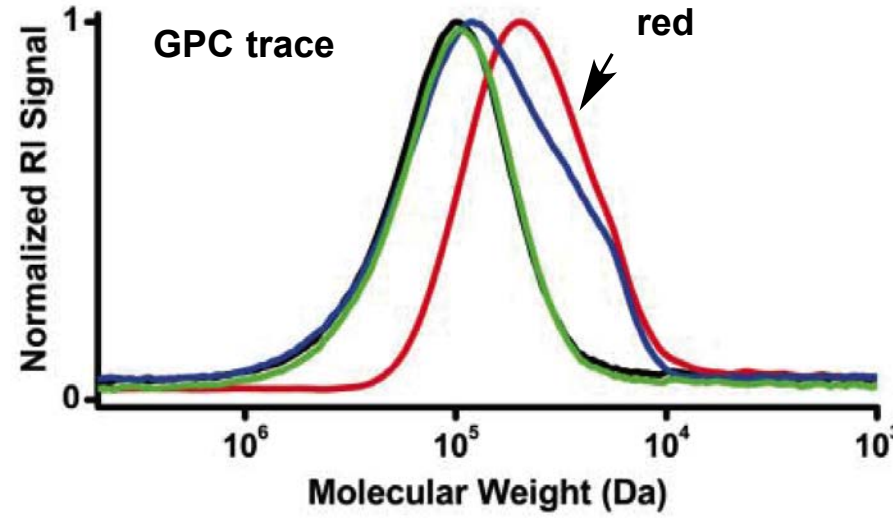
(1) triazole to azide and alkyne (unclicking)

C. W. Bielawski, *et al*. *Science* **2011**, *333*, 1606.



Ultrasound, CH_3CN, 0 ºC, 2 h, quant.

CuI, CH_3CN 80 ºC, 19 h ,86%



Triazole, although remarkably inert toward chemical and thermal perturbation, undergoes cycloreversion through the application of mechanical force.

function as mechanicall labile protecting group

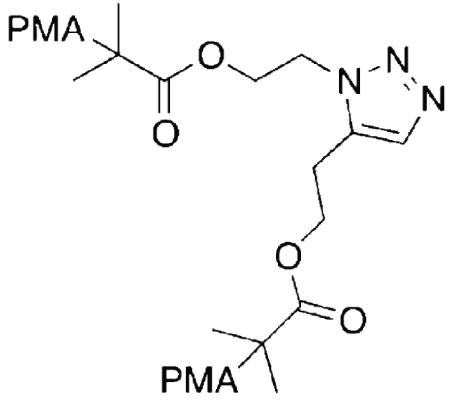
black: before sonication
red: after sonication
blue: after reclick
green: only heating
(258 ºC, 19 h)

cf. 力学的エネルギーで”逆”クリック!（chem-station)

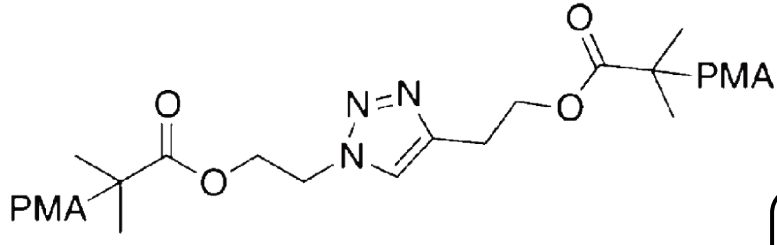
***Regiochemical Effects**

C. W. Bielawski, *et al*. *J*. *Am*. *Chem*. *Soc*. **2012**, *134*, 9882.

The rate of cycloreversion was found to be 20% greater for the 1,5-disubstituted regioisomer than for its 1,4-congener.



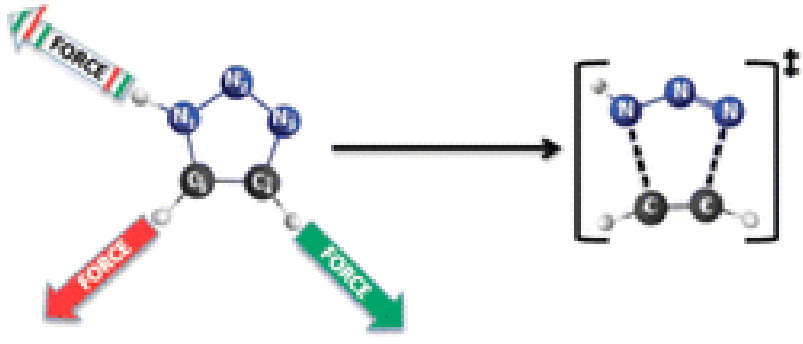
1,5-Disubstituted Triazole

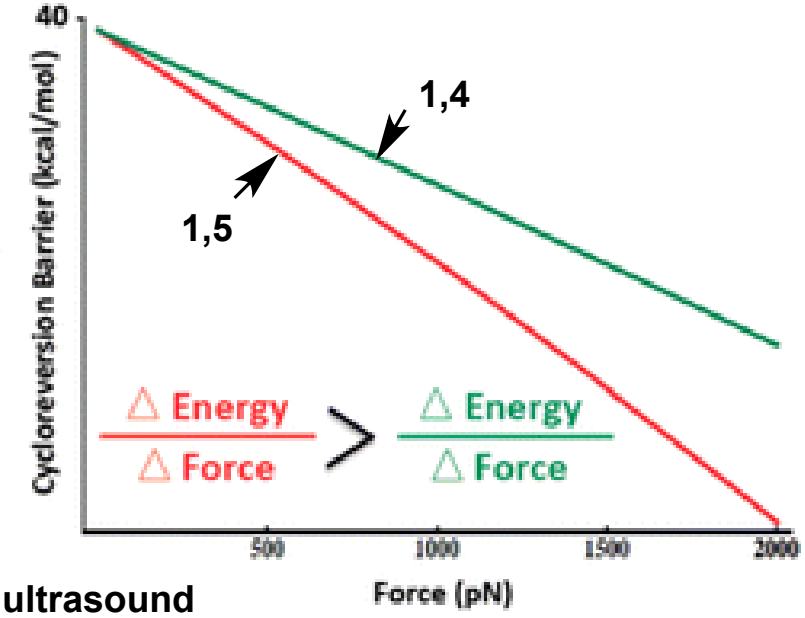


1,4-Disubstituted Triazole

This is explained by increased molecular compliance (steric interaction) for TS geometry and direct bond activation.

The relative regiochemistry of the polymer attachments on a mechanophore must be considered, when evaluating or designing mechanochemical systems.



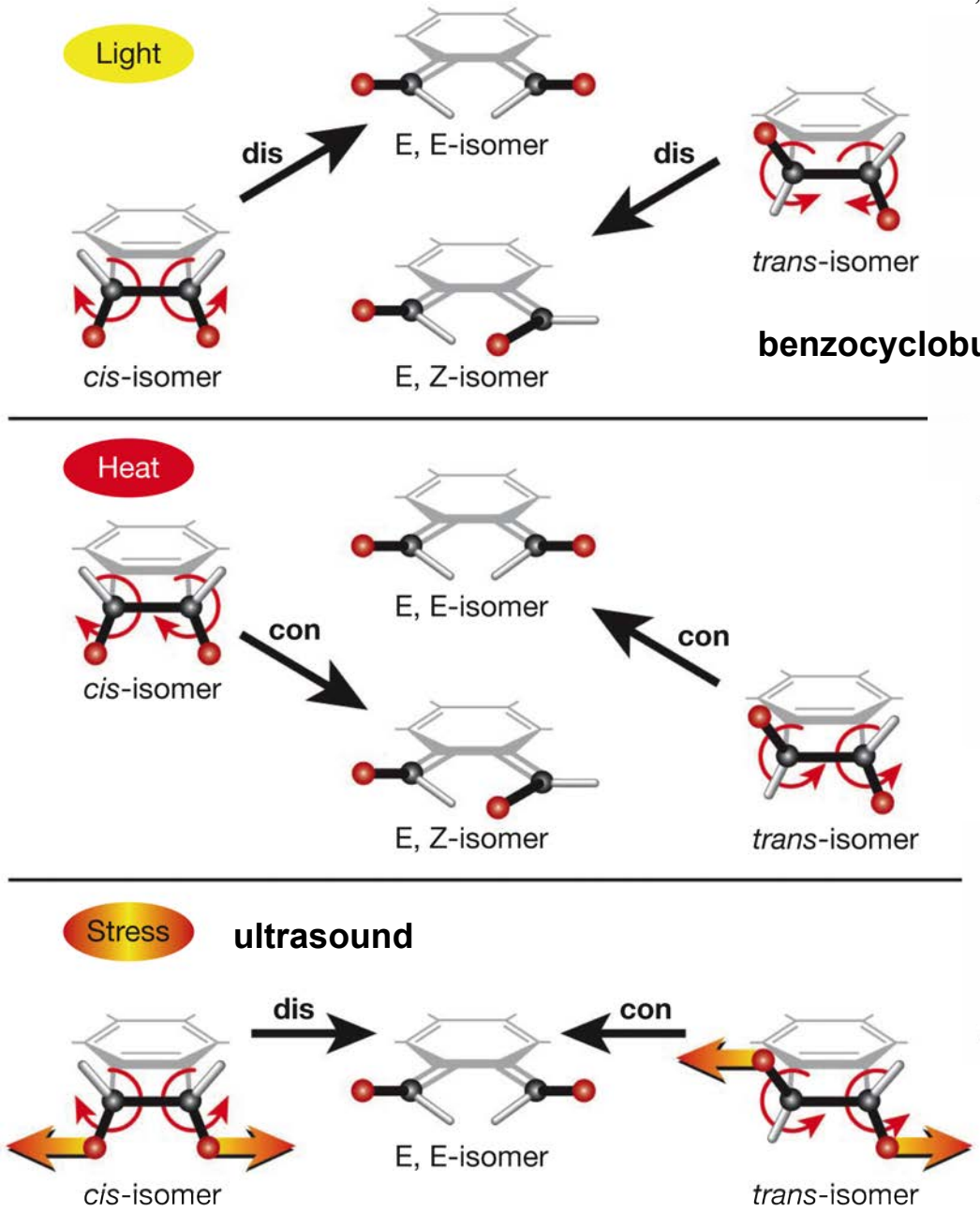


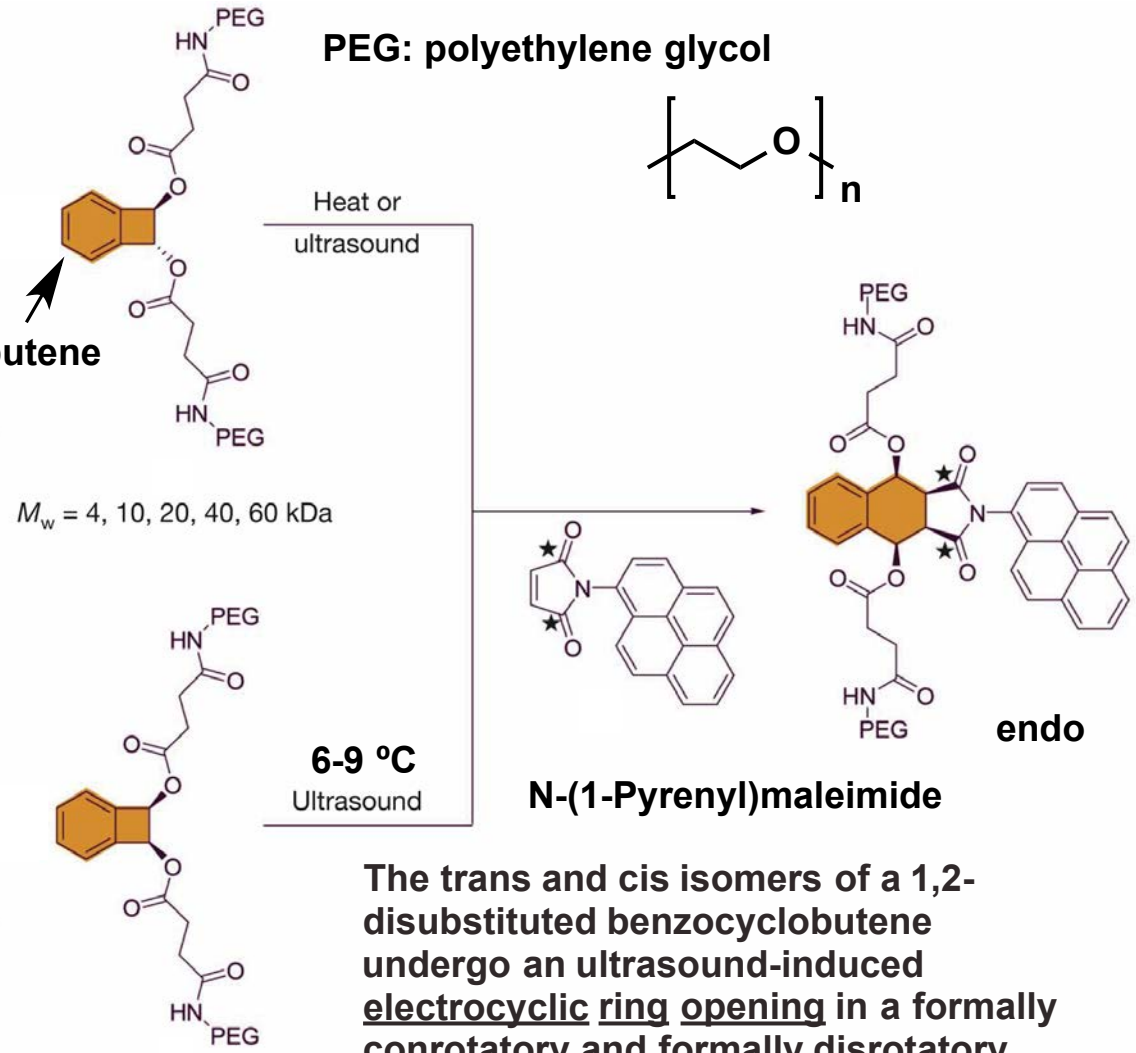
method: Irradiating acetonitrile solutions of these polymers with ultrasound

(2) violating Woodward-Hoffman rules

biasing reaction pathways with mechanical force

S. R. White, J. S. Moore, *et al*. *Nature* **2007**, *446*, 423.



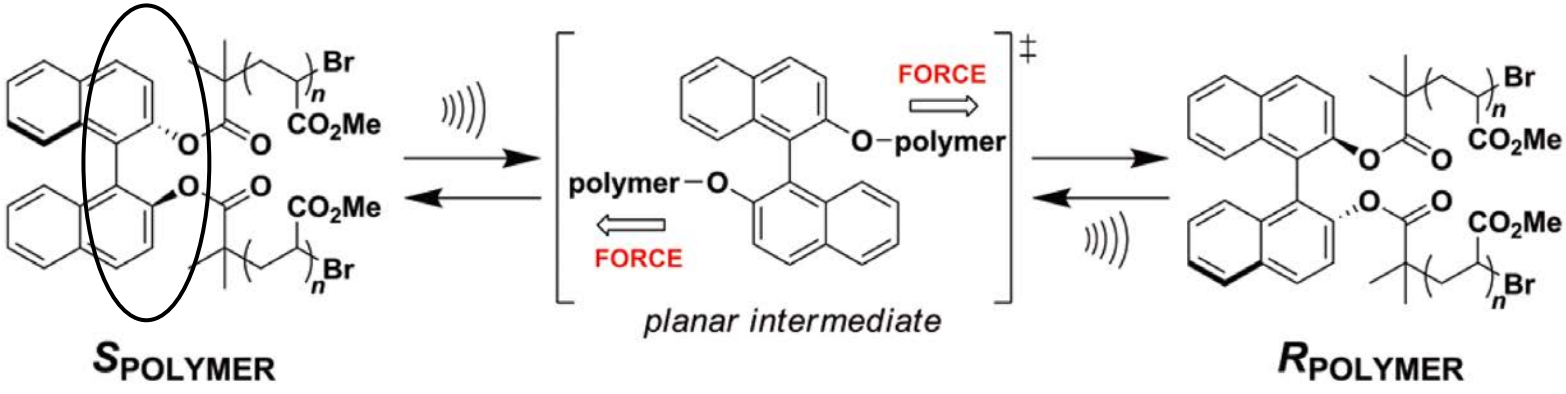


The trans and cis isomers of a 1,2-disubstituted benzocyclobutene undergo an ultrasound-induced electrocyclic ring opening in a formally conrotatory and formally disrotatory process, respectively, that yield identical products. (not following Woodward-Hoffman rules)

cf.ウッドワード・ホフマン則を打ち破る『力学的活性化』(**chem-station**)

(3)mechanical reconfiguration of stereoisomer (binol derivatives)

C. W. Bielawski, *et al*. *J*. *Am*. *Chem*. *Soc*. **2010**, *132*, 3256.



CH_3CN, 24 h

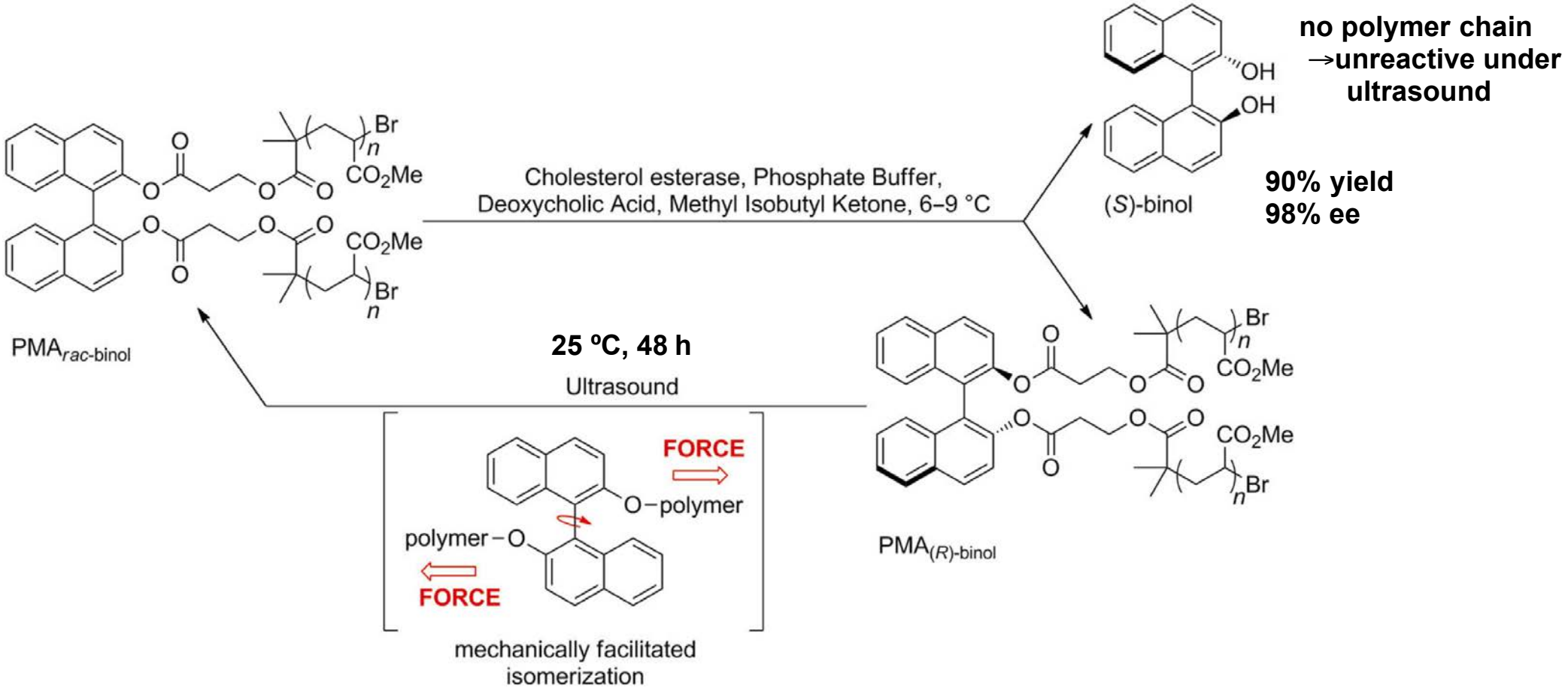
Thermally restricted isomerization barriers can be surmounted by force.

Upon heating these same materials to temperatures exceeding 250 ºC for longer than 72 h no isomerization was observed.

***the combination of ultrasound-induced isomerization and enzymatic resolution**

C. W. Bielawski, *et al*. *Angew. Chem., Int. Ed*. **2012**, *51*, 1640.

stereoselective enzymatic hydrolysis



no polymer chain
→unreactive under ultrasound

90% yield
98% ee

active use of mechanical force

- **developing field (few example)**
- **need polymer**

cf.「引っ張って光学分割」 (chem-station)

2. passive use of mechanical force

for material scientific application (damage responsive polymer)

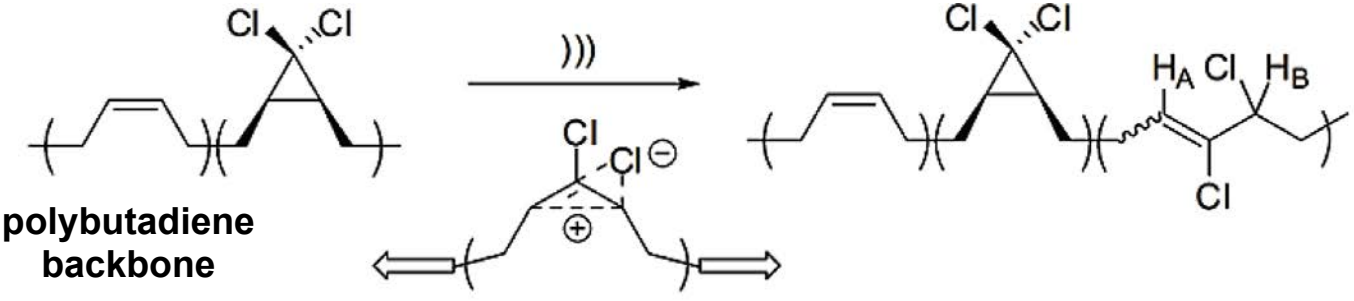
(1) Reaction with production of reactive species

(i) strengthening of a polymer

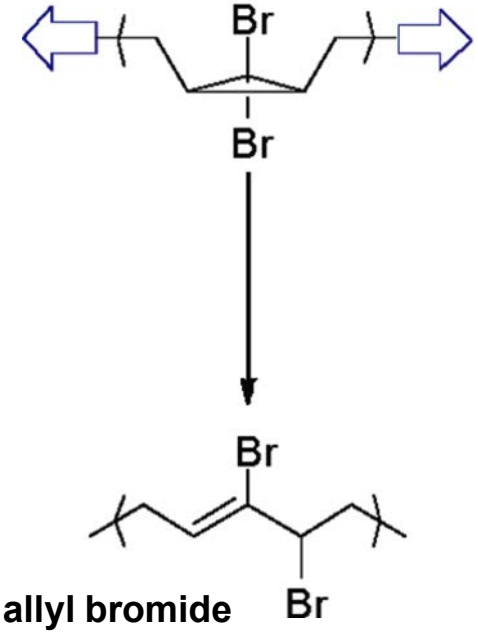
***gem - dichlorocyclopropane**

mechanically facilitated electrocyclic ring openings of *gem* - dichlorocyclopropanes

S.L. Craig, *et al*. *J*. *Am*. *Chem*. *Soc*. **2009**, *131*, 10818.



polybutadiene backbone



allyl bromide

polybutadiene backbone

Products were characterized by quantitative 1H NMR spectroscopy.

***gem*-dibromocyclopropane**

S.L. Craig, *et al*. *J*. *Am*. *Chem*. *Soc*. **2010**, *132*, 15936.

use Single-molecule force spectroscopy

***Mechanochemical strengthening of a synthetic polymer**

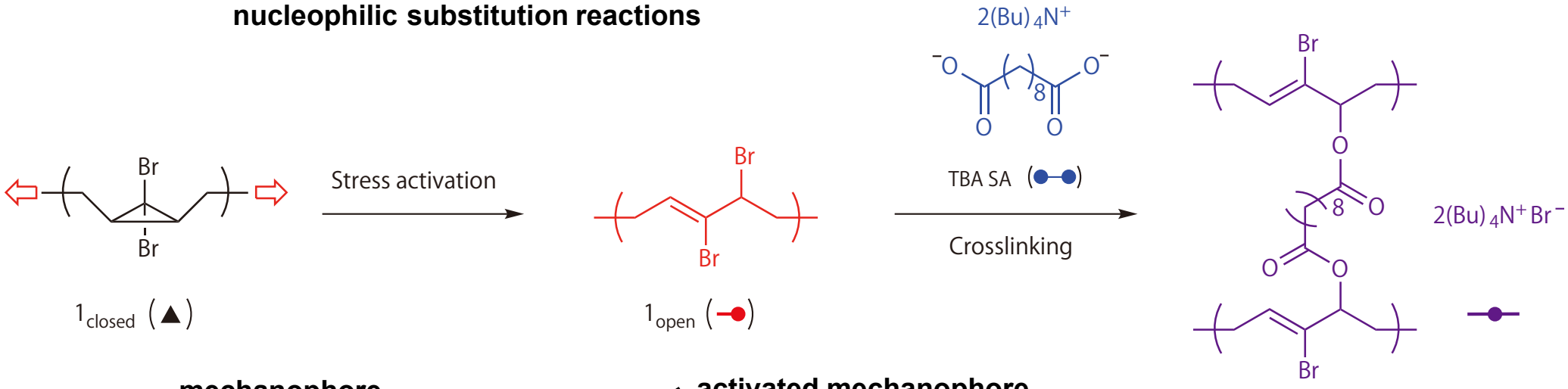
S. L. Craig, *et al*. *Nat*. *Chem*. **2013**, *5*, 757.

concept

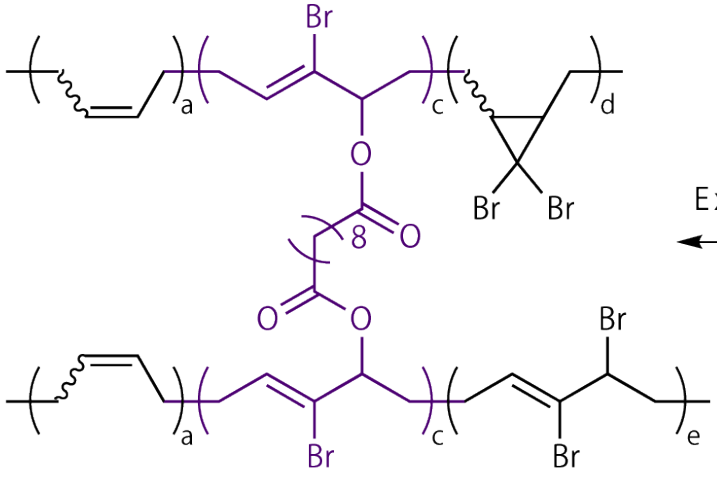
generation of allylic bromide

nucleophilic substitution reactions

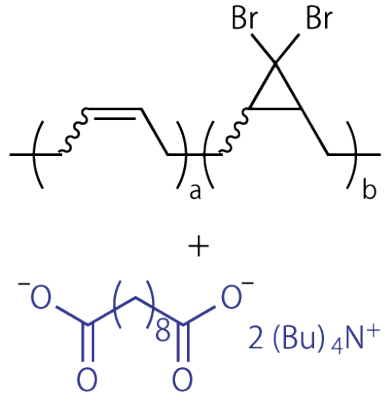
TBA SA: the di-tetrabutylammonium salt of sebacic acid



black: mechanophore red: activated mechanophore blue: crosslinker
backbone:polybutadiene

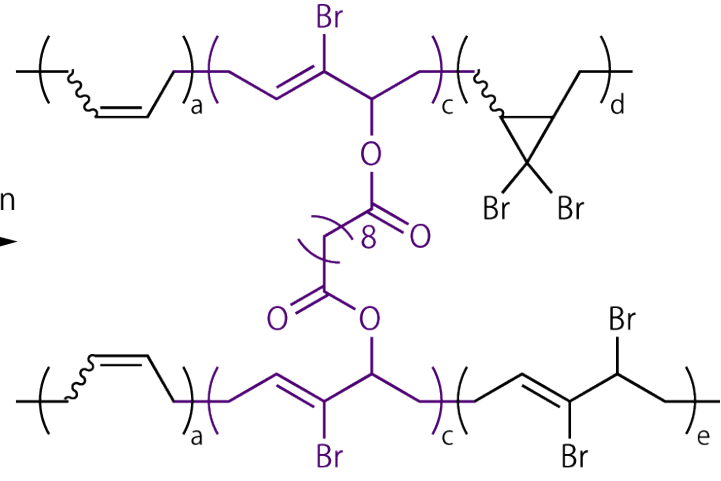


Extrusion

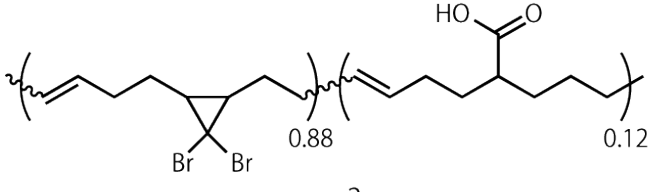


TBA SA

Sonication

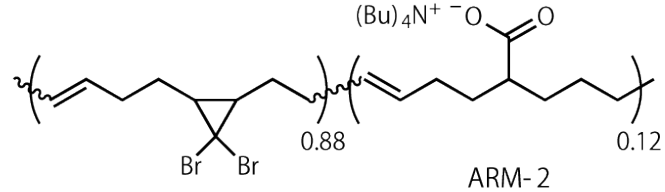


ultrasound in THF



2

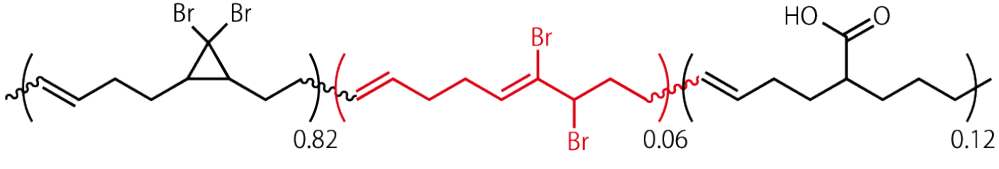
TBA $^{+}$OH $^{-}$

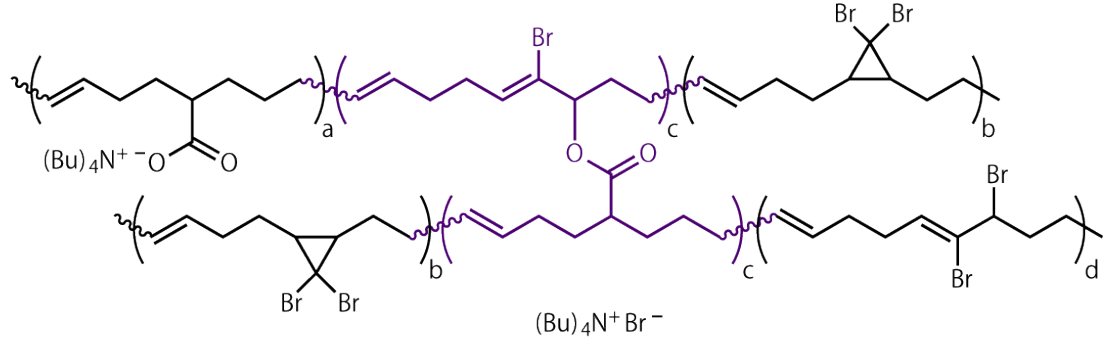


ARM-2

Sonication

Sonication





Support for this crosslinking was provided by infrared spectroscopy.

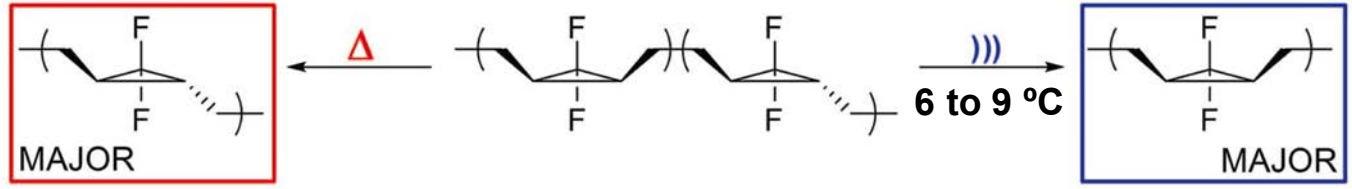
	Elastic Modulus(MPa)
polymer 1closed	7.6 ± 4.5
polymer 1open	7.8 ± 3.3
+TBA SA	1.7 ± 0.5
+TBA SA(extruded)	150 ± 85

achieved on demand strengthening

*gem-difluorocyclopropanes (gDFCs) ~different reactivity~

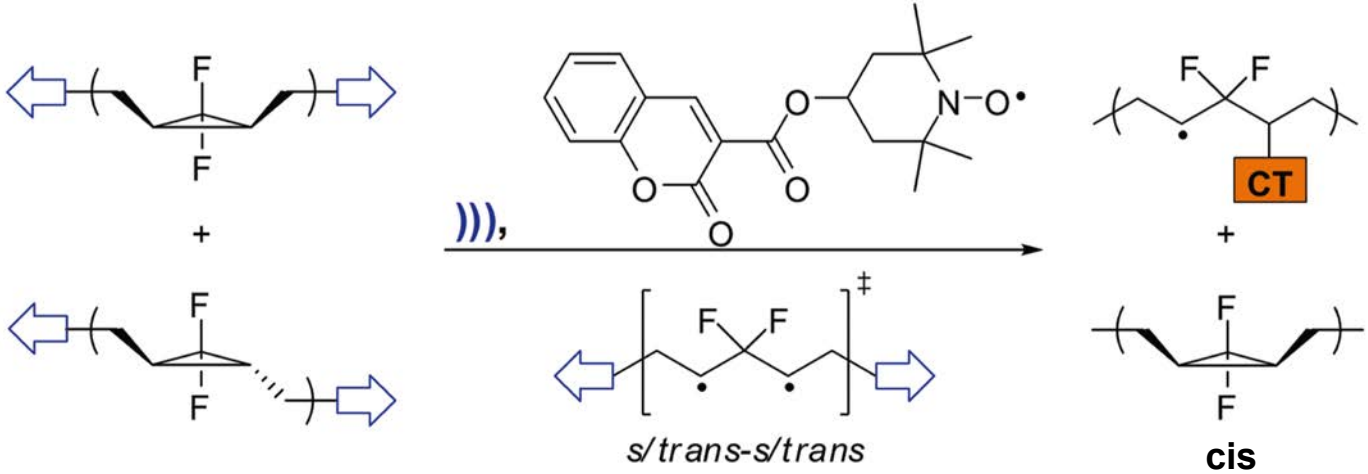
Trapping a Diradical Transition State
by Mechanochemical Polymer Extension

S. L. Craig, *et al*. *Science* **2010**, *329*, 1057.



backbone: polybutadiene

*Note that the trans isomers are more stable than the cis isomers.

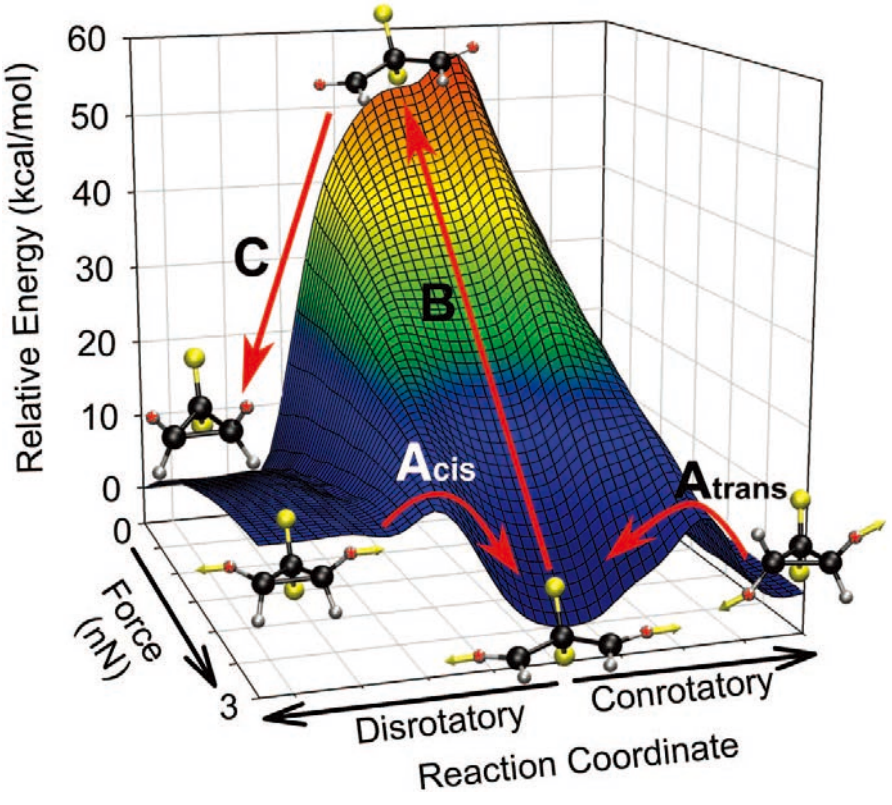


Radical trapping support diradical formation.

The tension-induced stabilization of the 1,3-diradical in the polymer affords the opportunity to reactively probe this trapped transition state structure.

→provides a tool for the study of reactive intermediates

(another example of active use of mechanical force)



The s-trans/ s-trans diradical is formed regardless of the cis or trans arrangement.

When coupled to the applied force, the ring- opened diradical is lower in energy than the ring- closed cyclopropanes.

*epoxides

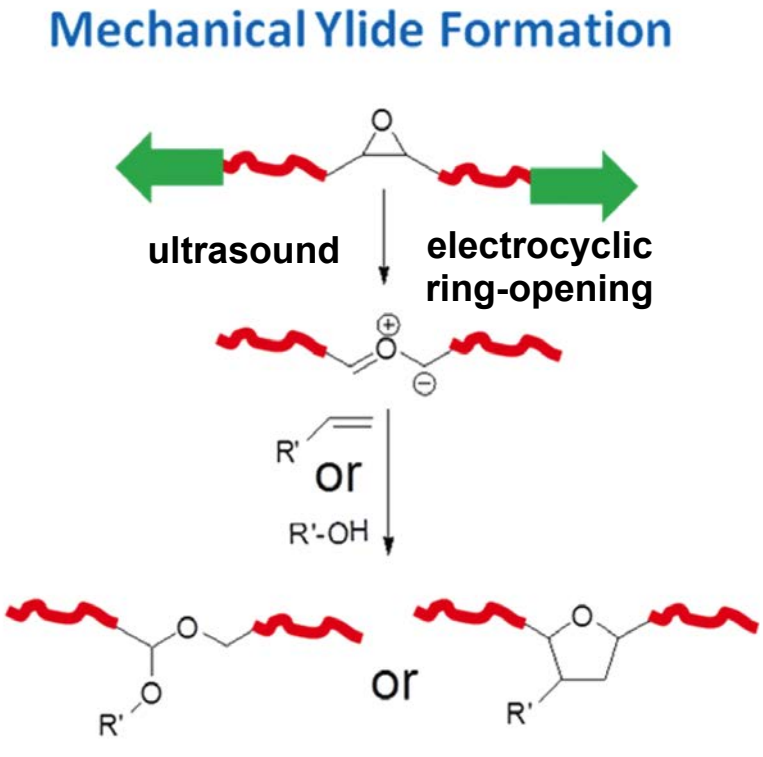
hypothesis

Epoxides also undergo mechanically triggered ring-opening to carbonyl ylides?

electrocyclic ring openings of epoxides and the influence of polymer backbone

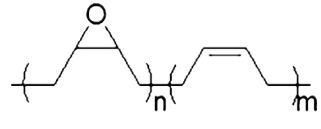
S.L. Craig, *et al*. *J*. *Am*. *Chem*. *Soc*. **2012**, *134*, 9577.

cf. regiochemical effect (p5)

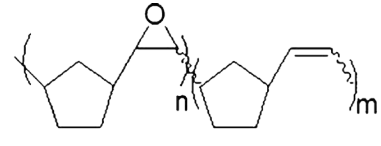


When epoxidized polybutadiene was sonicated, there was no observable small molecule addition to the polymer.

In contrast, when epoxidized polynorbornene was subjected to the same conditions, addition of ylide trapping reagents was observed.



polybutadiene



polynorbornene

The cyclopentyl groups increase the efficiency of force transduction? (not steric effect)

cf. The critical force for reaction of gem-dihalocyclopropane (gDHC) (cf.p9) drops by about one-third in the polynorbornene scaffold relative to polybutadiene.

S. L. Craig, *et al*. *Nat*. *Chem*. **2013**, *5*, 110.

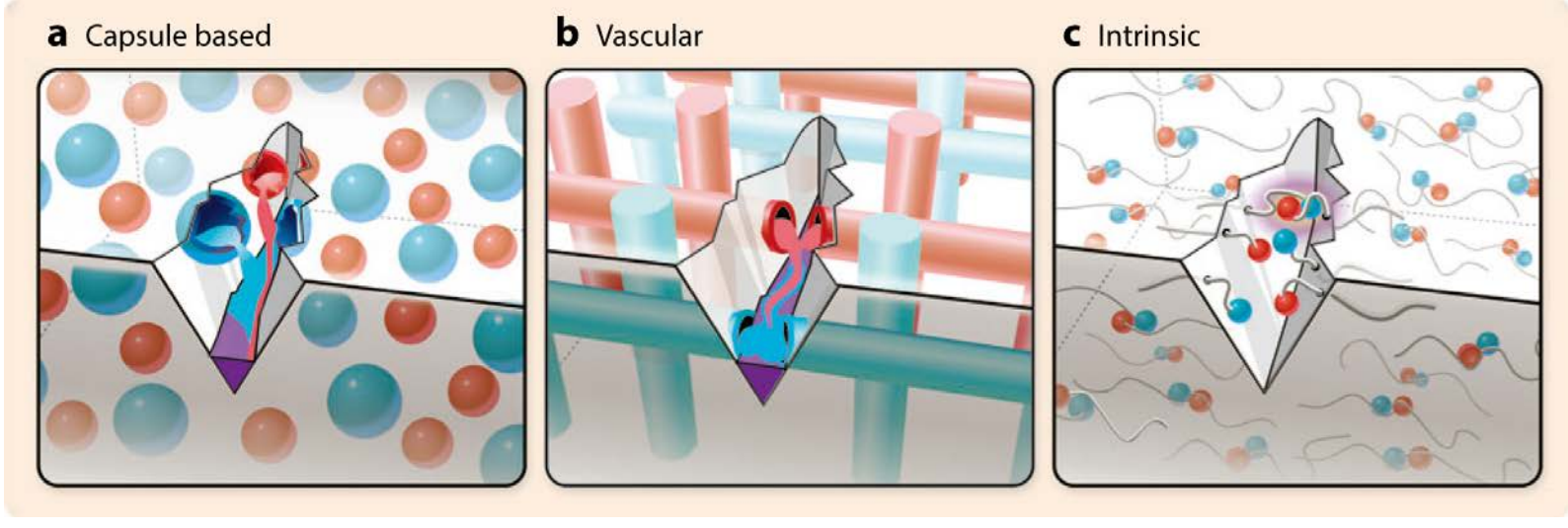
PMA is often used because it is robust.

~ self healing ~

cf. Y. Wang, *Self-healing polymers and composites* (Lit. Seminar)

repairing crack or failure

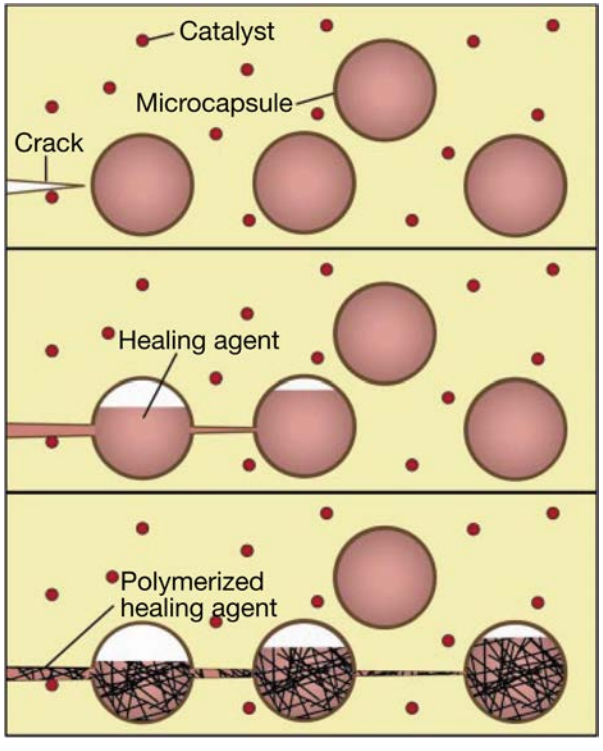
Three primary conceptual approaches to self healing



Annu. Rev. Mater. Res. **2010**, *40*, 179.

a. Capsule - Based Healing System

S. R. White, J. S. Moore, *et al*. *Nature* **2001**, *409*, 794



use of Grubbs catalyst in an epoxy matrix

2.5% (by weight) Grubbs' catalyst and 10% (by weight) microcapsules

microcapsules consists of Urea Formaldehyde Resin

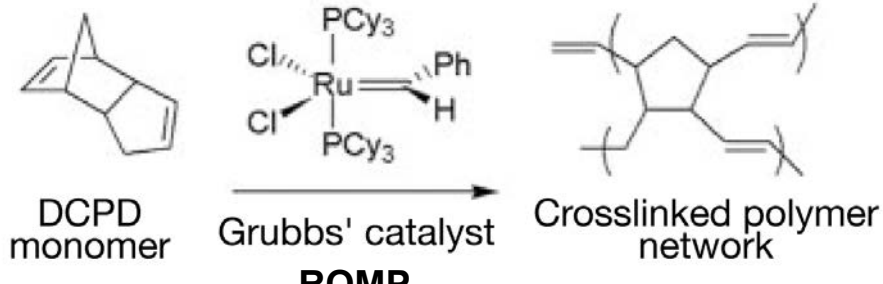
The material incorporates a microencapsulated healing agent that is released upon crack intrusion.

Polymerization of the healing agent is then triggered by contact with an embedded catalyst, bonding the crack faces.

After failure, the crack allowed to heat at rt with no manual intervention (48 h).

75% recovery in toughness

high cost of Grubbs catalyst

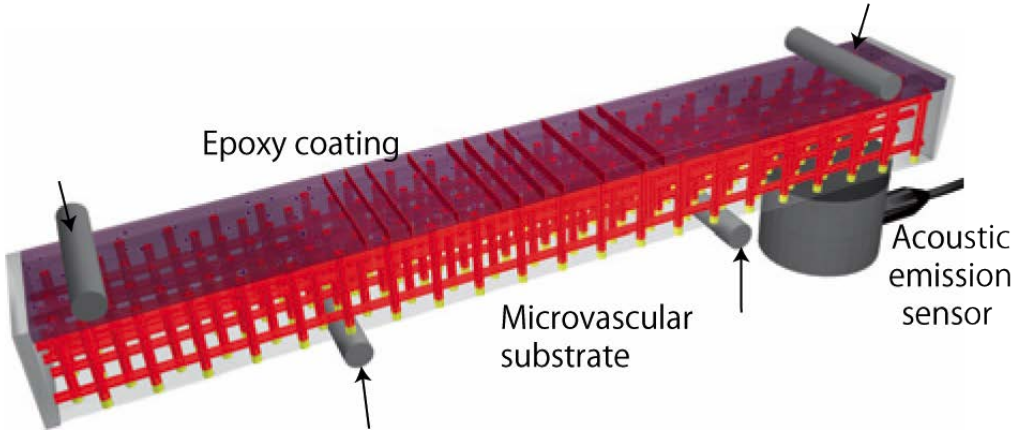


ROMP

DCPD: dicyclopentadiene

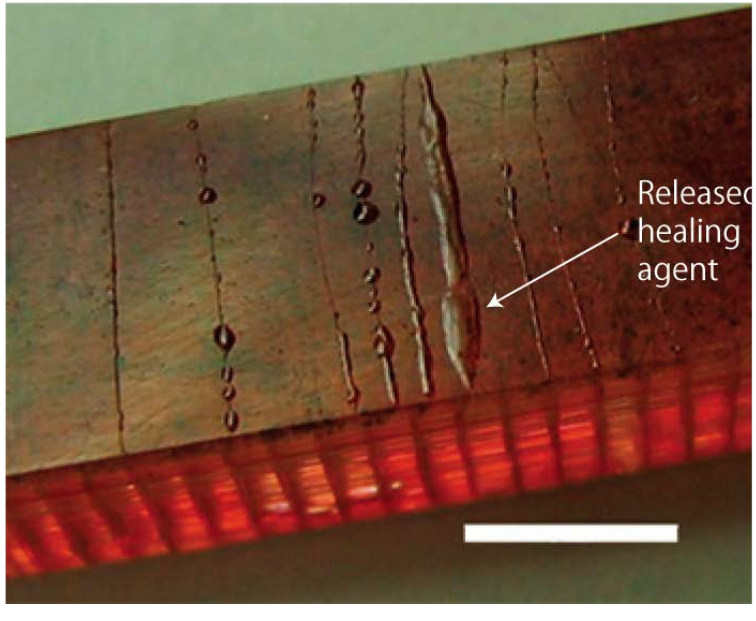
b. Vascular-Based Healing System

S.R. White, J. S. Moore, *et al*. *Nat*. *Mater*. **2007**, *6*, 581.



three-dimensional microvascular network

***There is no mechanophore applied in two strategies to date.**



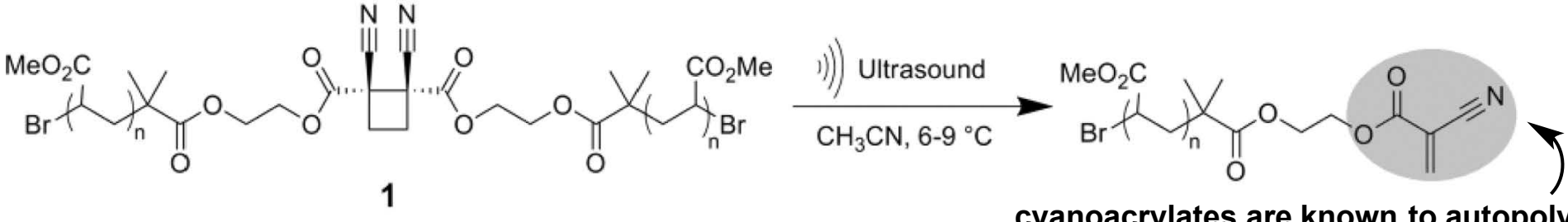
c. Intrinsic Healing Systems

cf. Y. Wang, *Self-healing polymers and composites* (Lit. Seminar)

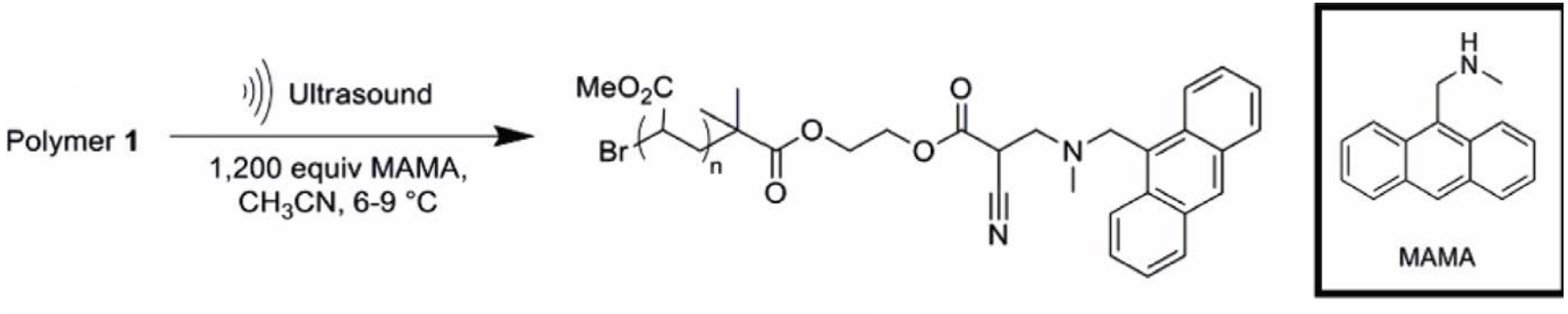
(ii) dicyano-substituted cyclobutane (self healing approach)

Masked Cyanoacrylates Unveiled by Mechanical Force

J. S. Moore, *et al*. *J*. *Am*. *Chem*. *Soc*. **2010**, *132*, 4558.



cyanoacrylates are known to autopolymerize
→ self healing application



trapping experiments

(2)Reaction with Activation of Catalytic Speices

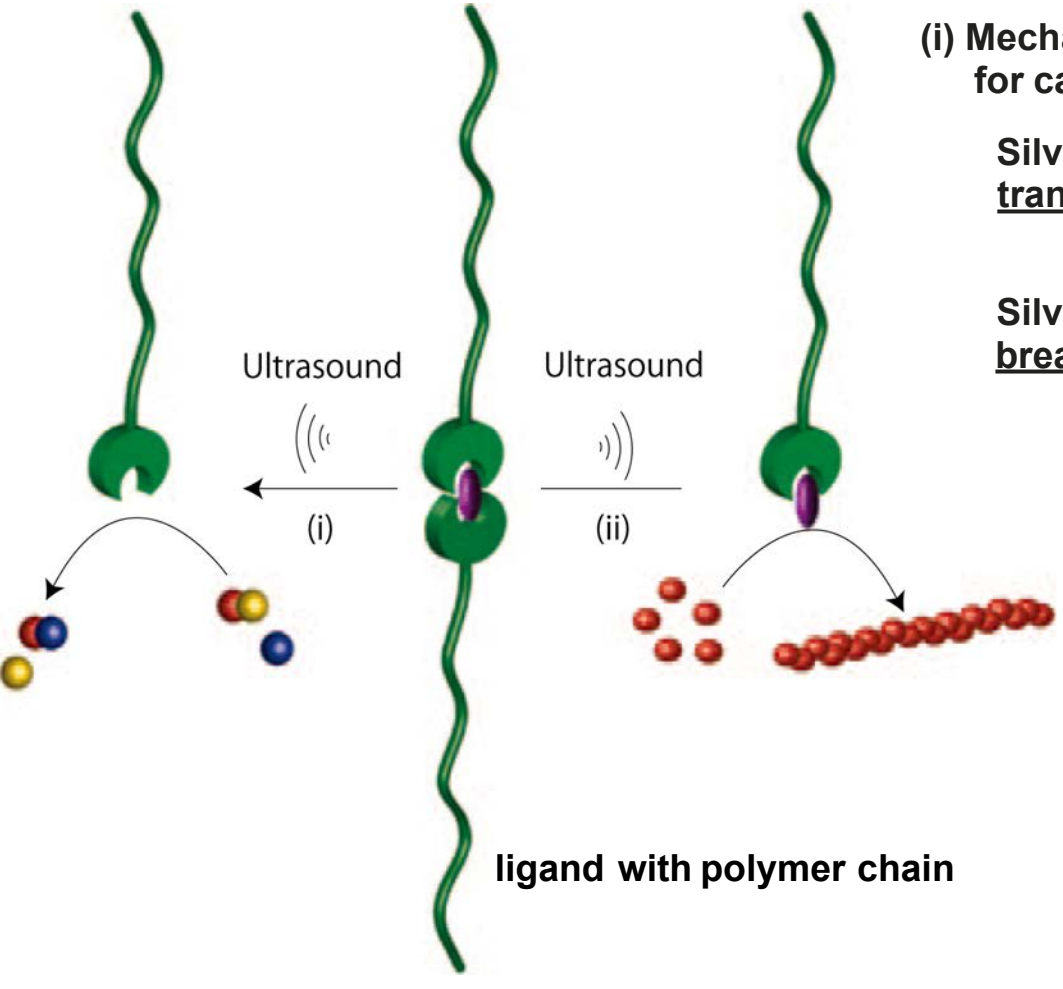
mechanocatalyst

(a) NHC and Grubbs catalyst

Activating catalysts with mechanical force

R. P. Sijbesma, *et al*. *Nat*. *Chem*. **2009**, *1*, 133.

Strategy



ligand with polymer chain

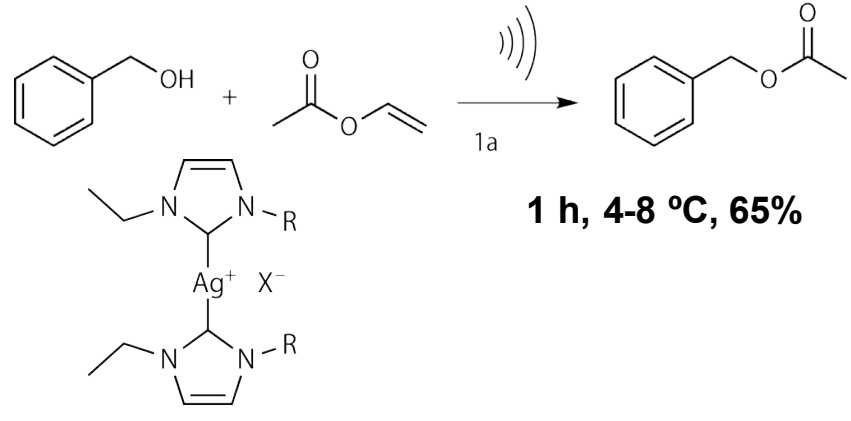
(i) Mechanochemical activation of silver–NHC complexes for catalysis of transesterification (proof of concept)

Silver(I) complexes of NHCs have been used as transesterification catalysts that can be activated thermally.

R. M. Waymouth, J. L. Hedrick, *et al*. *J*. *Org*. *Chem*. **2005**, *70*, 2391.

Silver(I) complexes with polymer-functionalized NHC ligands break when exposed to ultrasound.

R. P. Sijbesma, *et al*. *J*. *Am*. *Chem*. *Soc*. **2008**, *130*, 14968.

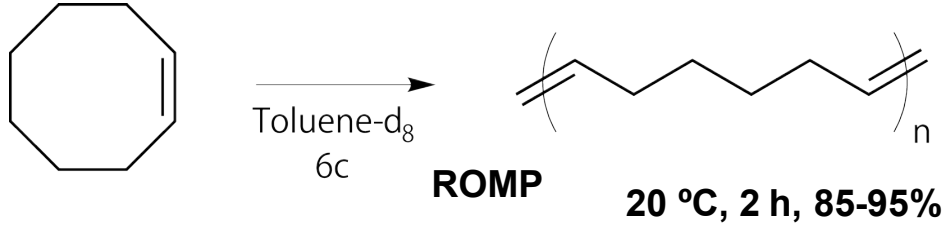


1 h, 4-8 ºC, 65%

X = PF_6 ; R = pTHF-OCH_3

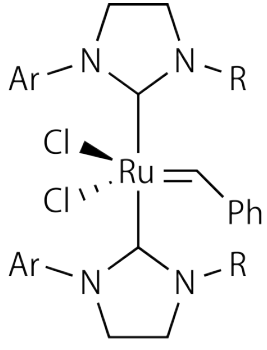
1a: M_n(pTHF) = 5 kDa

(ii) Mechanochemical activation of a catalytic ring-opening metathesis polymerization (ROMP)



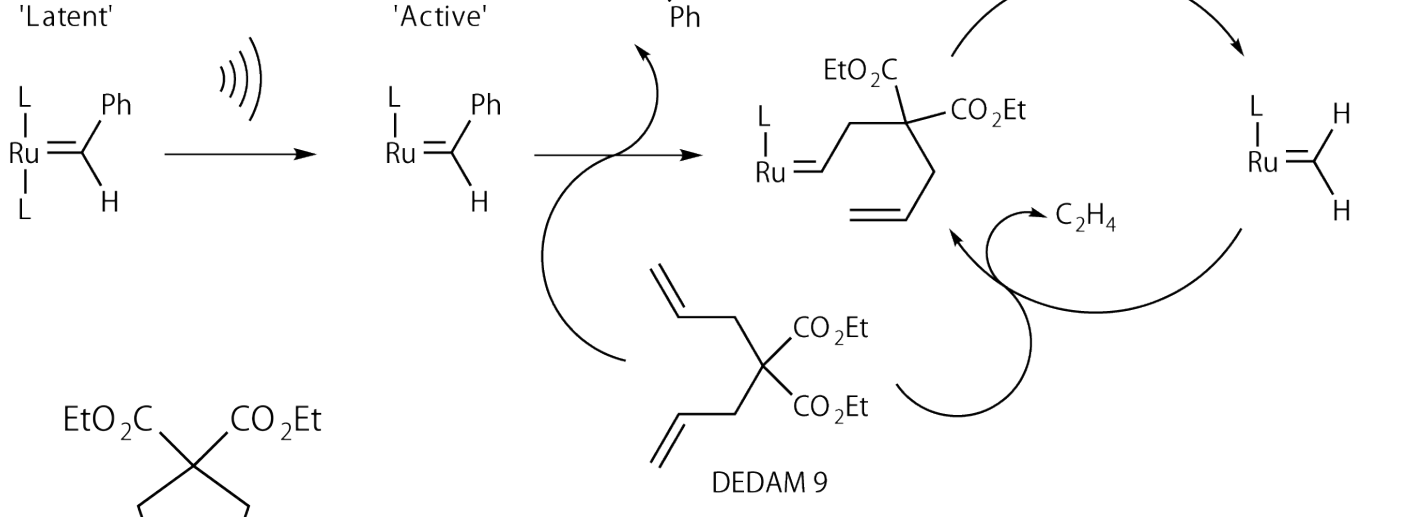
ROMP

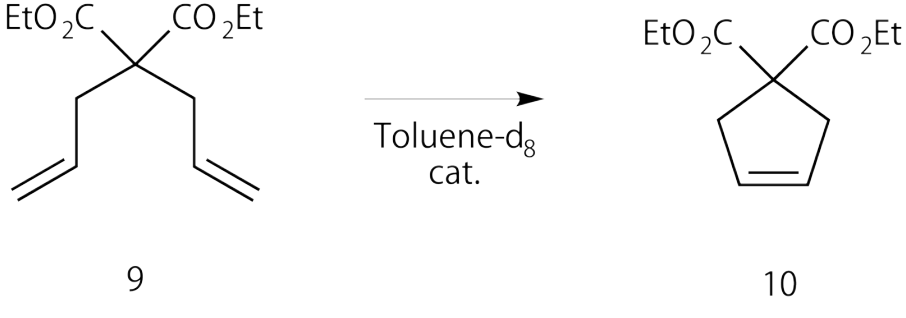
20 ºC, 2 h, 85-95%



R = pTHF-OCH 3

6c: M_n(pTHF) = 21 kDa





9 10

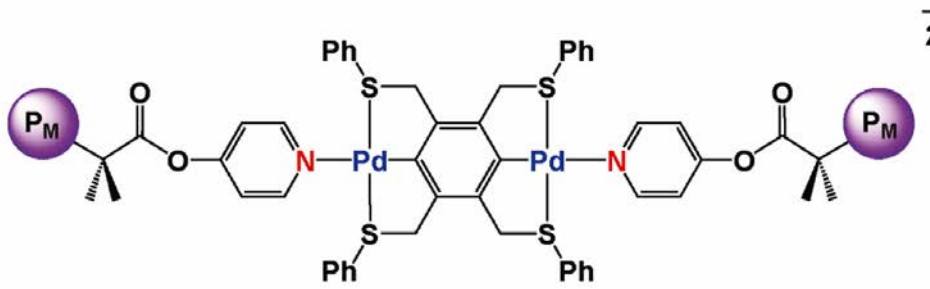
(Cl ligands have been omitted for clarity.)

***for self healing application**
(cf. strategy a (p16) <u>without</u> <u>capsule</u>)

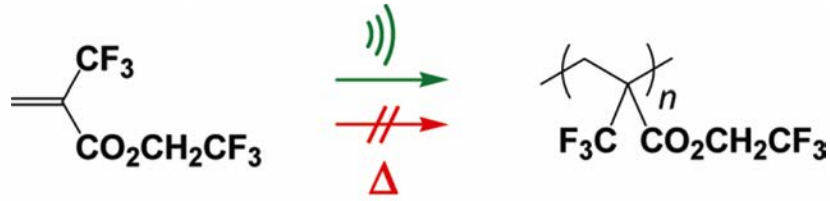
(b) Mechanical Activation of Catalysts for Anionic Polymerization Reactions

C. W. Bielawski, *et al*. *J*. *Am*. *Chem*. *Soc*. **2010**, *132*, 16631.

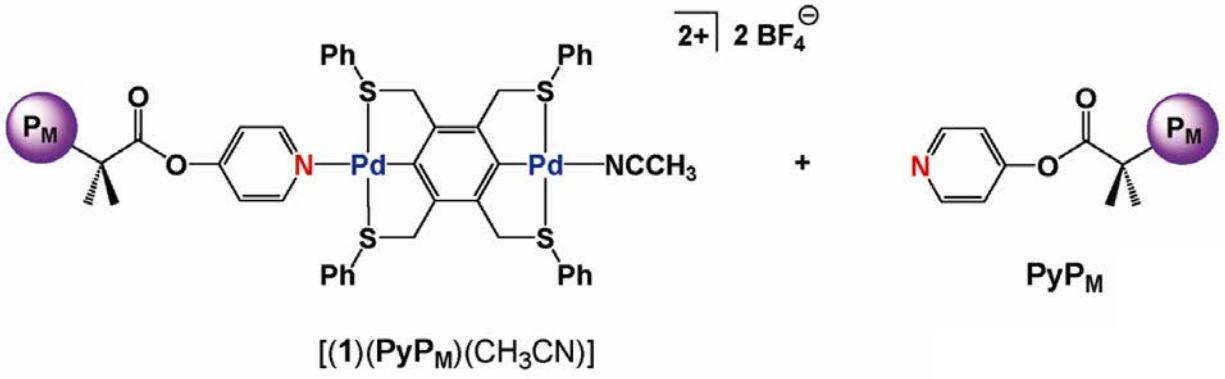
type(i) (p23)

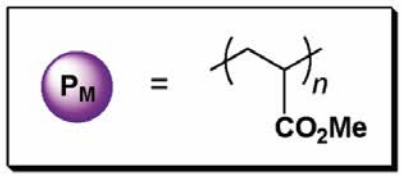


Pyridine-Catalyzed Anionic Polymerization



[(1)(PyP$_{66}$)$_2$] 0.025mol%
CH$_3$CN, 4 ºC, 22 h, 42%



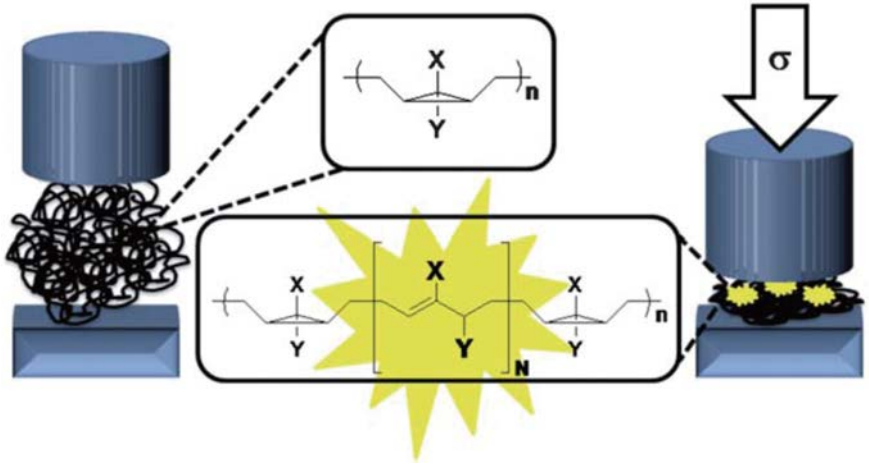


P$_M$:PMA (MkDa)

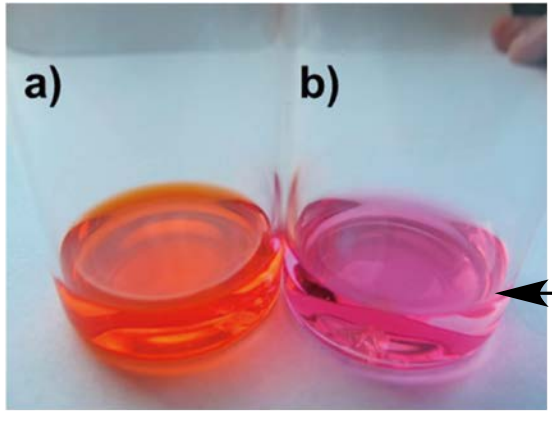
(c) mechanophore with acid-releasing capability

S. R. White, J. S. Moore, *et al*. *J*. *Am*. *Chem*. *Soc*. **2012**, *134*, 12446.

Previous Results



J. S. Moore, S. L. Craig *et al*. *J*. *Mater*. *Chem*. **2011**, *21*, 8454.

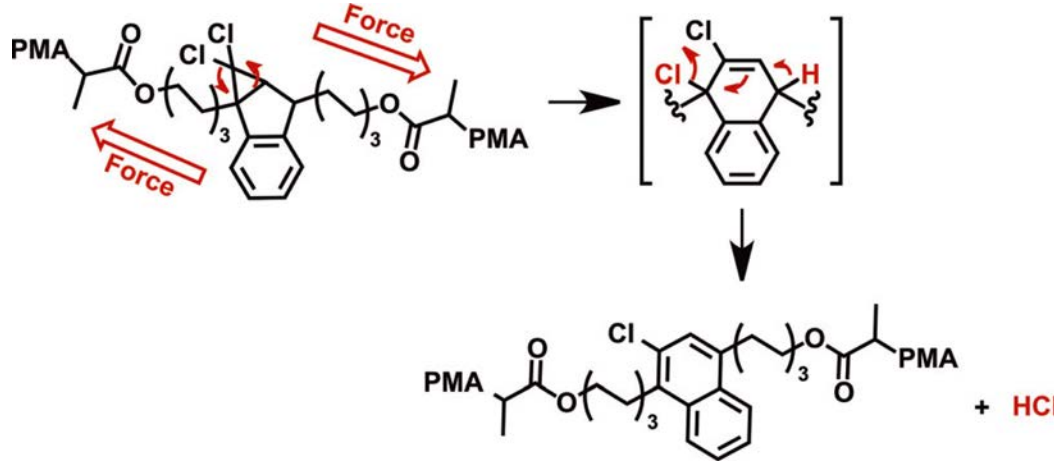


pink

Methyl red in acetonitrile added to compressed polymers containing (a) unbound and (b) covalently bound

The color becomes pink when acid is present.

This time results



(cited by *Angew*. *Chem*., *Int*. *Ed*. **2013**, *52*, 3806.)

cf. p9

Aromatization provides the driving force to elimination.

compress at 88-352 MPa using KBr pellet press (high pressures are required)

monotonic rise in activation against applied pressure

exposing a piece of insoluble compressed polymer to a pH indicator solution

(3) rearrangement

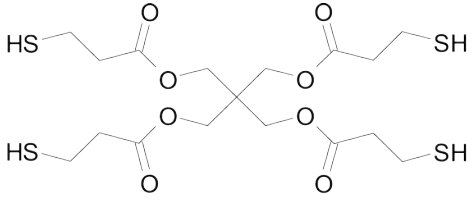
***stress relaxation**

<u>expanding</u> <u>the</u> <u>concept</u> <u>of</u> <u>mechanophore</u>

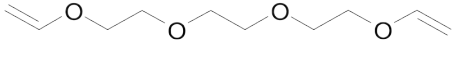
(i) allyl sulfide groups in Cross-Linked Polymers

C. N. Bowman, *et al*. *Science* **2005**, *308*, 1615.

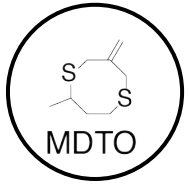
use light to produce radicals



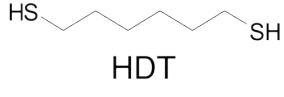
PETMP



TEGDVE

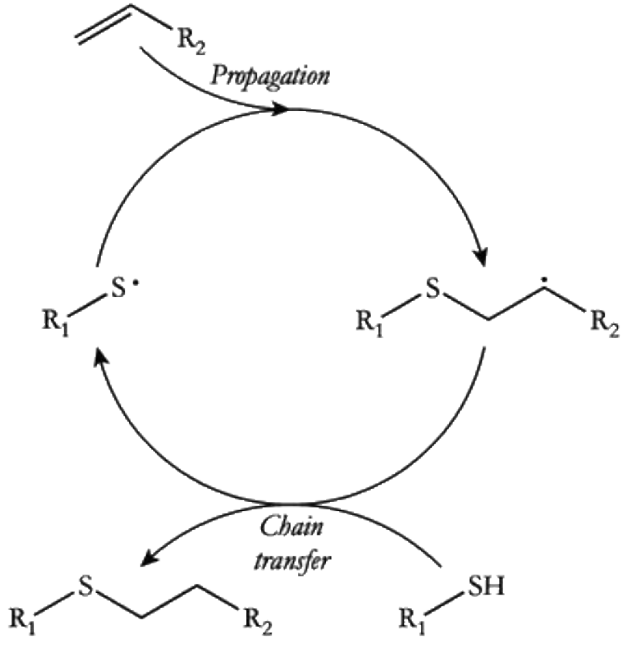


MDTO



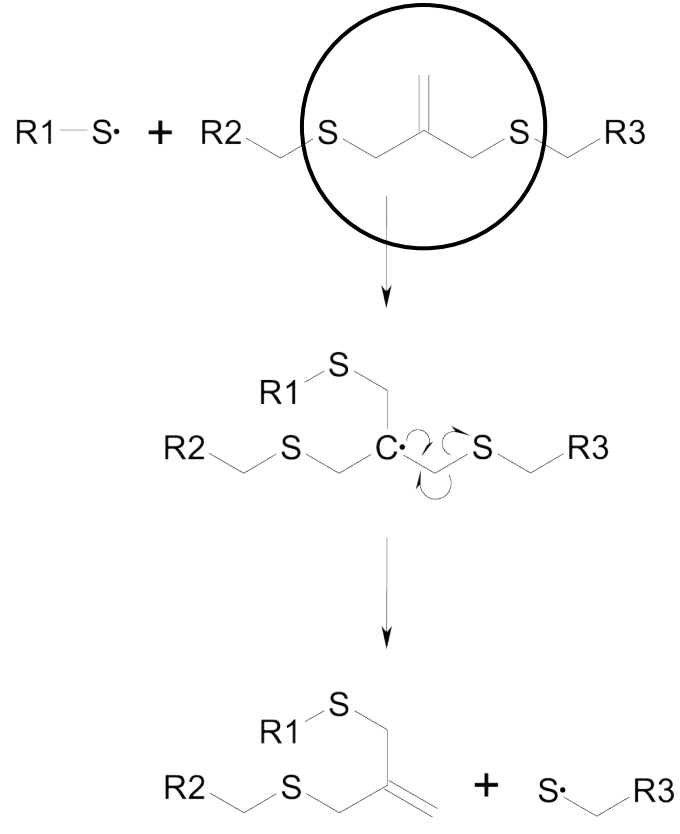
HDT

Monomers used to produce the networks.

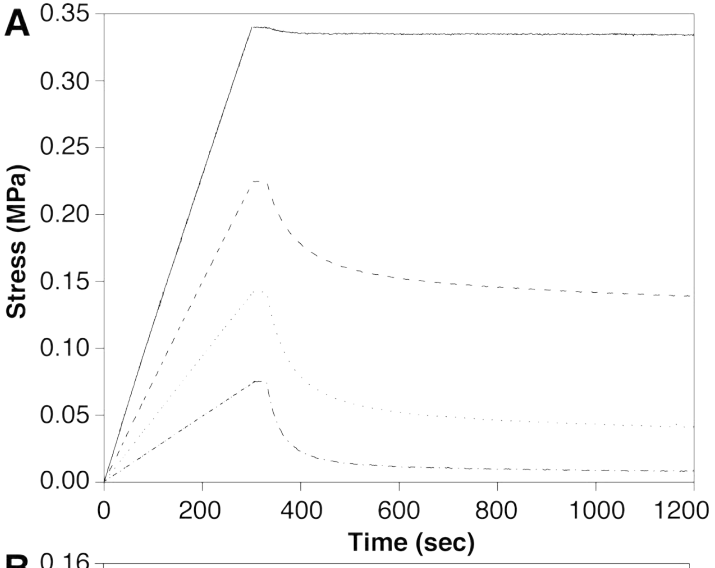


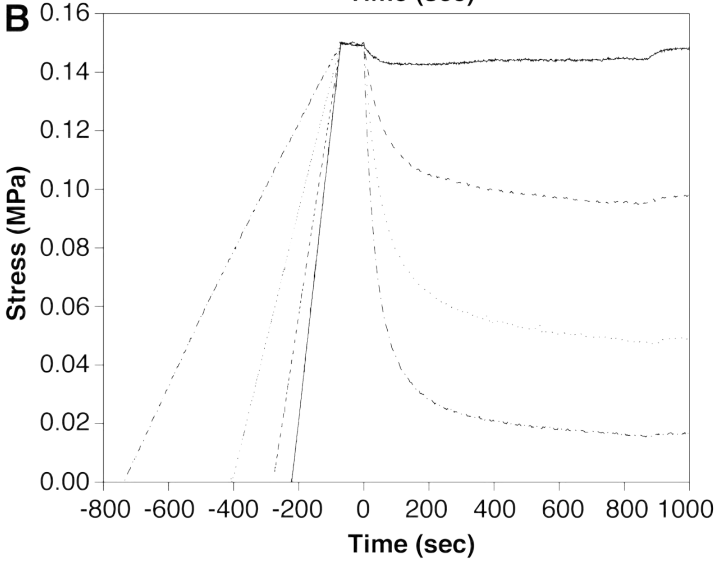
thiol-ene polymerization (radical mechanism)

mechanophore



Reaction mechanism for chain transfer within the polymer backbone.





Stress versus time for four MDTO concentrations (solid line, 0 wt %; dashed line, 25 wt %; dotted line, 50 wt %; dashed-dotted line, 75 wt %). (A) Constant strain (irradiation started at t 0 330 s). (B) Constant initial stress (offset to align the start ofirradiation at 0 0, irradiation stopped at 900 s). The specimens were irradiated at 320 to 500 nm, 20 mW cm^{-2}.

***Allyl sulfide groups in the network are essential to stress/strain relaxation.**

radicals via photocleavage of residual photoinitiator in the polymer matrix

***termination reaction**

mechanophore ~definition~

bonds or chemical functionalities that are especially susceptible to undergoing a chemical change caused by mechanical stress

J. S. Moore, *et al*. (2013). *Self-healing polymers*. Wiley

functional groups that respond to mechanical perturbation in a controlled manner

C. W. Bielawski, *et al*. *Polym. Int.* 2013, 62, 2.

Tensile moduli of specimens before and after experiments performed in A.

MDTO (wt%)	Ratio of cross-links to allyl sulfide groups	Modulus before extension and irradiation (MPa)	Modulus after extension and irradiation (MPa)
0	1: 0	11.5	11.8
25	1.17: 1	7.33	7.72
50	0.390: 1	4.58	5.17
75	0.130: 1	2.38	2.92

(ii) Siloxane ~ mechanophore or not? ~

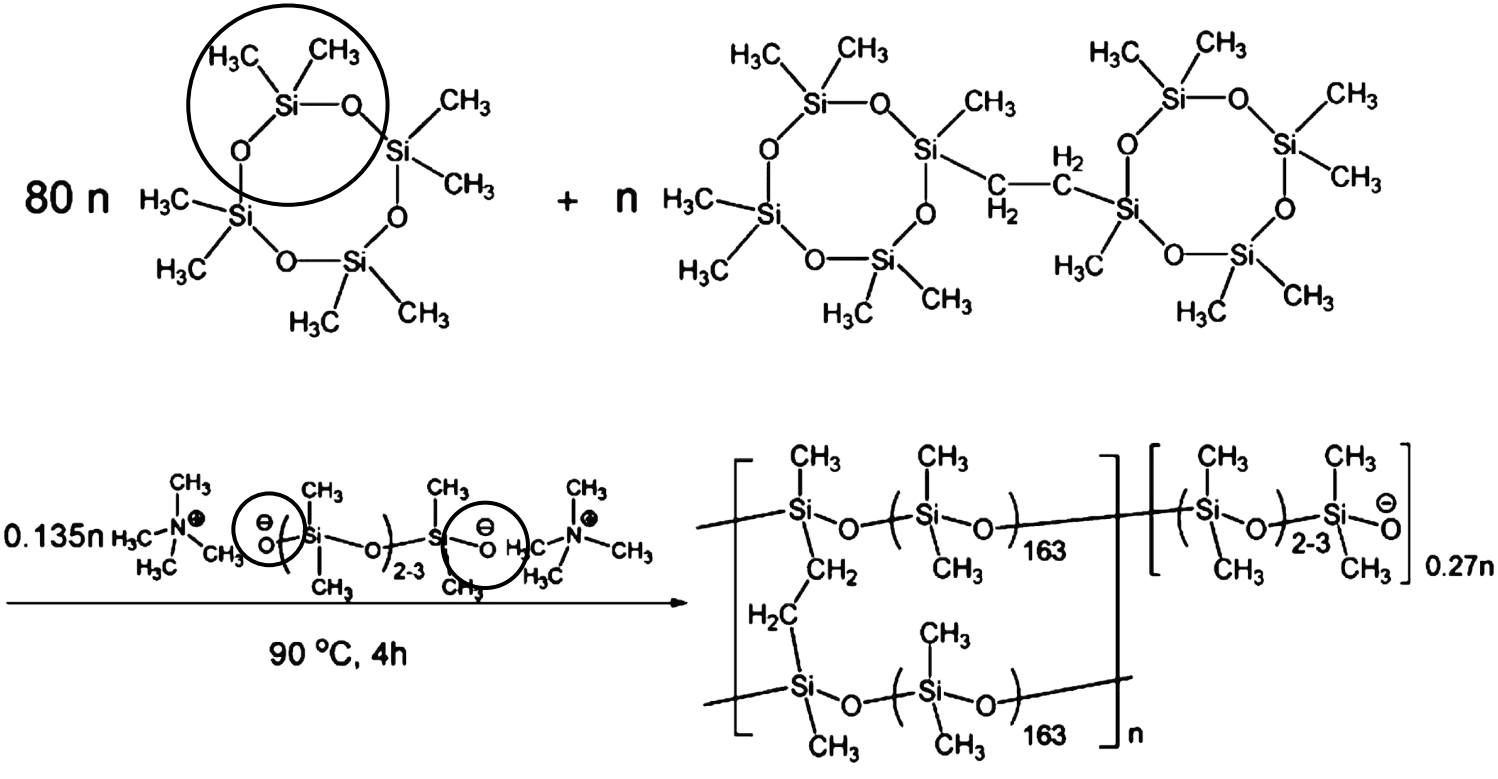
T. J. McCarthy, *et al*. *J*. *Am*. *Chem*. *Soc*. **2012**, *134*, 2024.

***Use Siloxane Equilibration**

E ≒ 0.4MPa

achieve self healing

introduced as mechanophore in Moore's review J. S. Moore, *et al*. (2013). *Self-healing polymers*. Wiley



Mini Summary

~ passive use of mechanical force ~

- **production of reactive species (strengthening, self healing)**
- **production of catalytic species (mechanocatalyst, polymerization to self healing)**
- **rearrangement (damage relaxation)**

(4) breaking hydrogen bond (and supramolecular network) (cf. mechanocatalyst)

cf. Y. Wang, *Self-healing polymers and composites* (Lit. Seminar)

UPy motif

Titin ~ Biomimetic approach ~

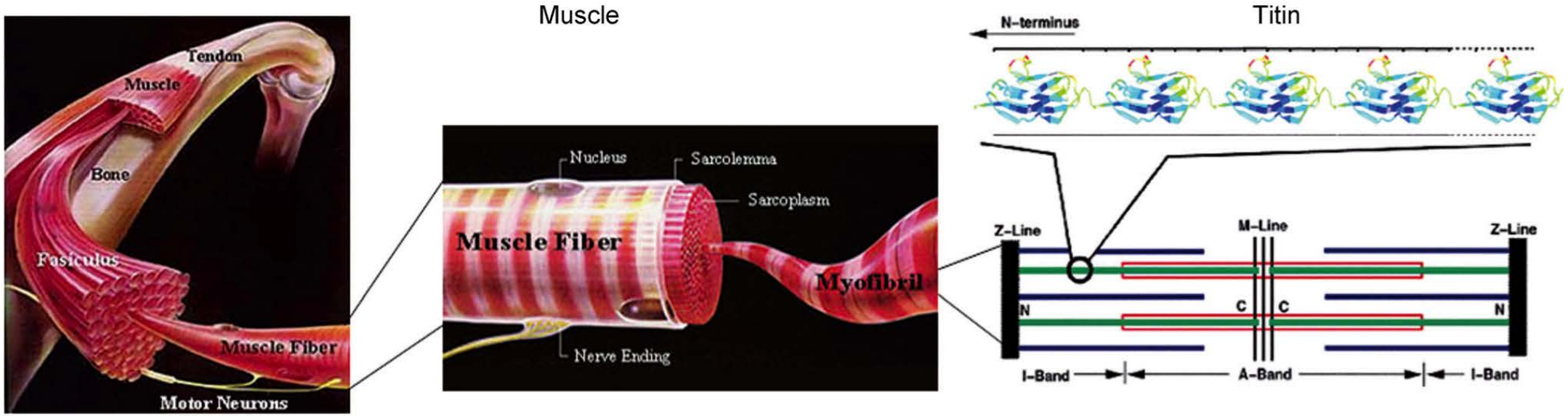
Z. Guan, *et al*. *J*. *Am*. *Chem*. *Soc*. **2009**, *131*, 8766.

Titin: skeletal muscle protein in Myofibril

It functions as a molecular spring which is responsible for the passive elasticity of muscle.

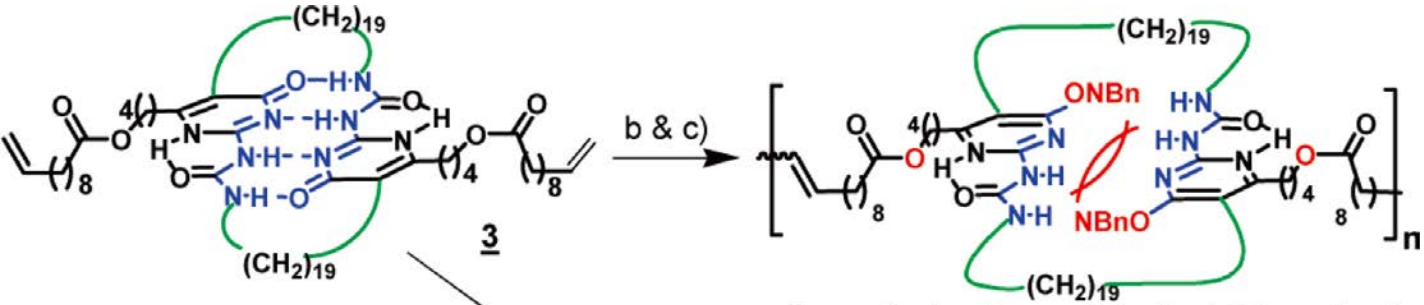
the ability to absorb energy by the reversible rupture of intramolecular secondary interactions, followed by refolding induced recovery

The load-bearing region has six hydrogen bonds between β strands.



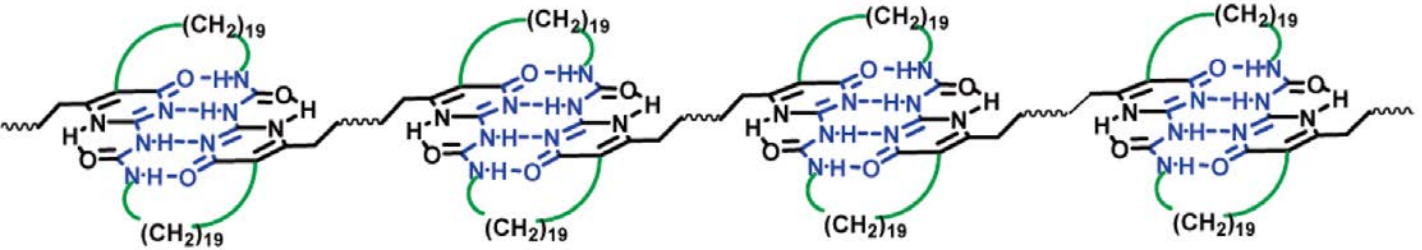
cited from *Angew*. *Chem*., *Int*. *Ed*. **2011**, *50*, 9026.

the quadruple hydrogen bonding 2-ureido-4[1*H*]-pyrimidone (UPy) motif as the modular domain- forming mimic



2, control polymer (blocked H-bonding)

a)

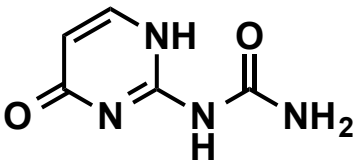


1, *titin*-mimicking modular polymer

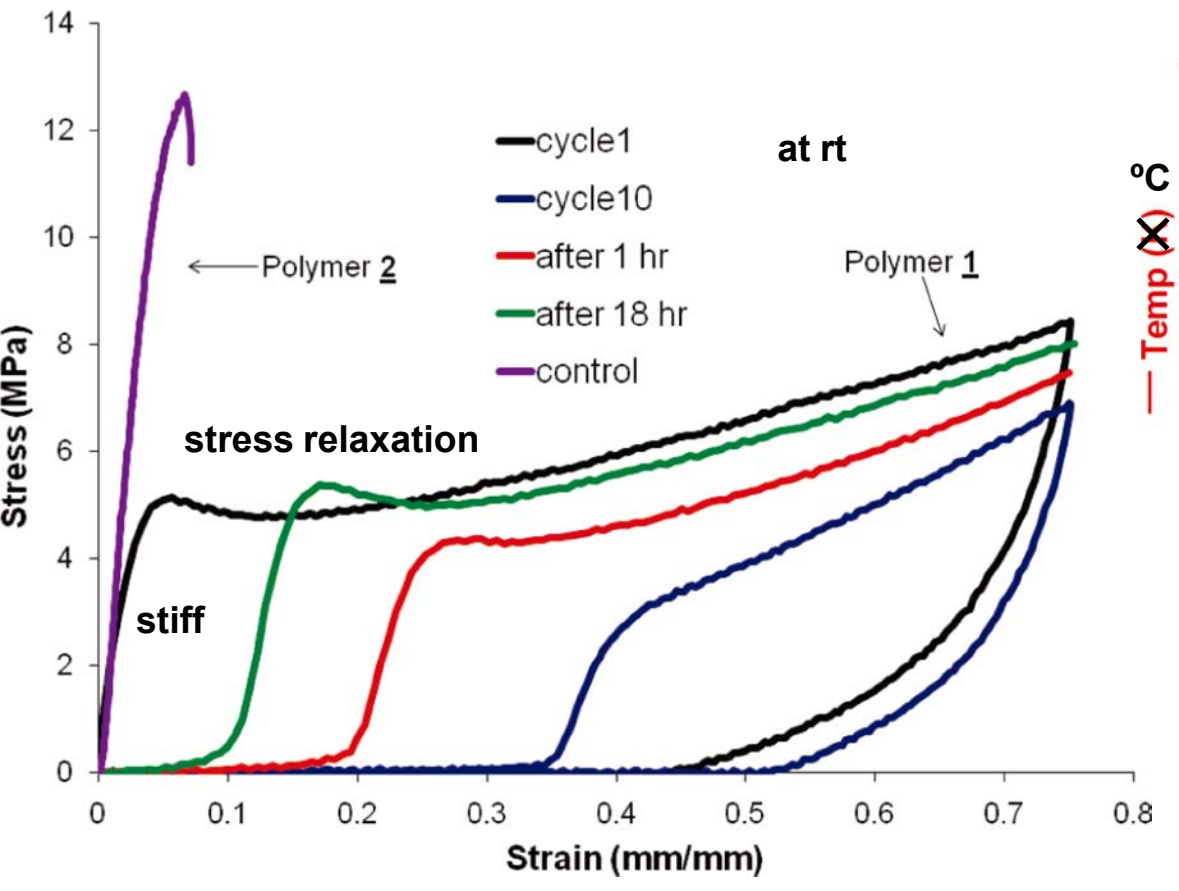
modular structure of *titin* protein

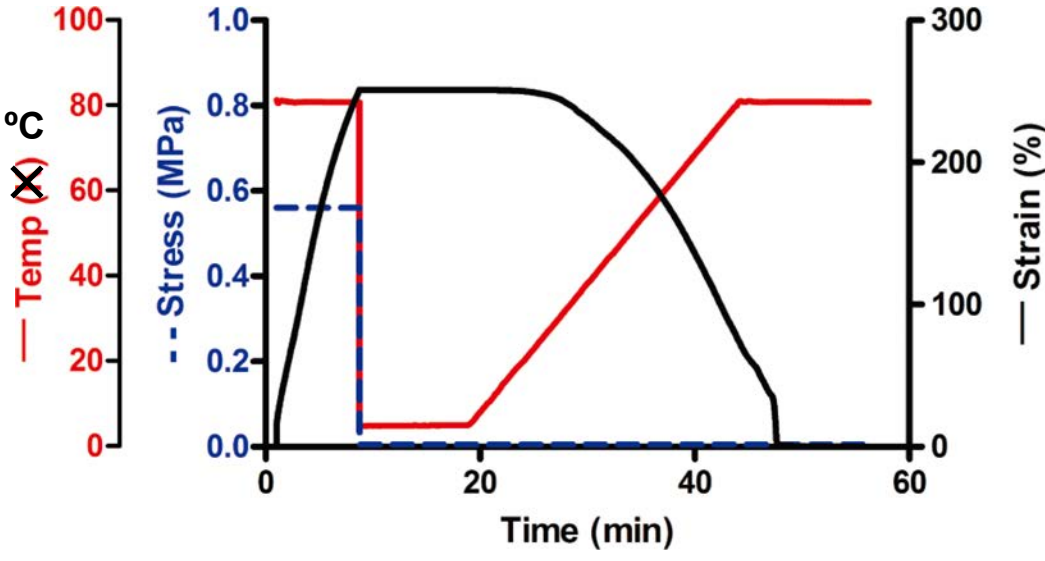
a) Grubbs Gen-2 cat, 1,2,4-TCB, 70 ºC, 84%. b) o-NBnBr, K_2CO_3, DMF, 70 ºC, 52%
c) Grubbs Gen-2 cat, $CHCl_3$, reflux, 75%.

the polymer combines high toughness and self-healing like properties in one material.



2-ureido-4[1H]-pyrimidone
UPy

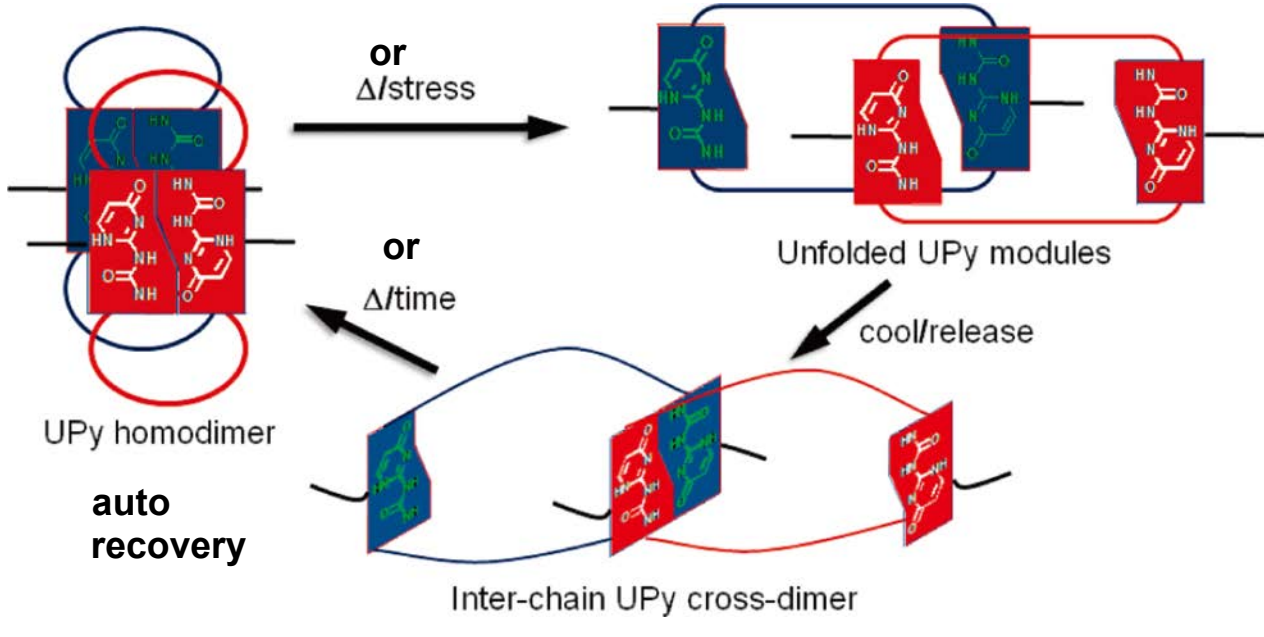




Young's modulus ~200MPa

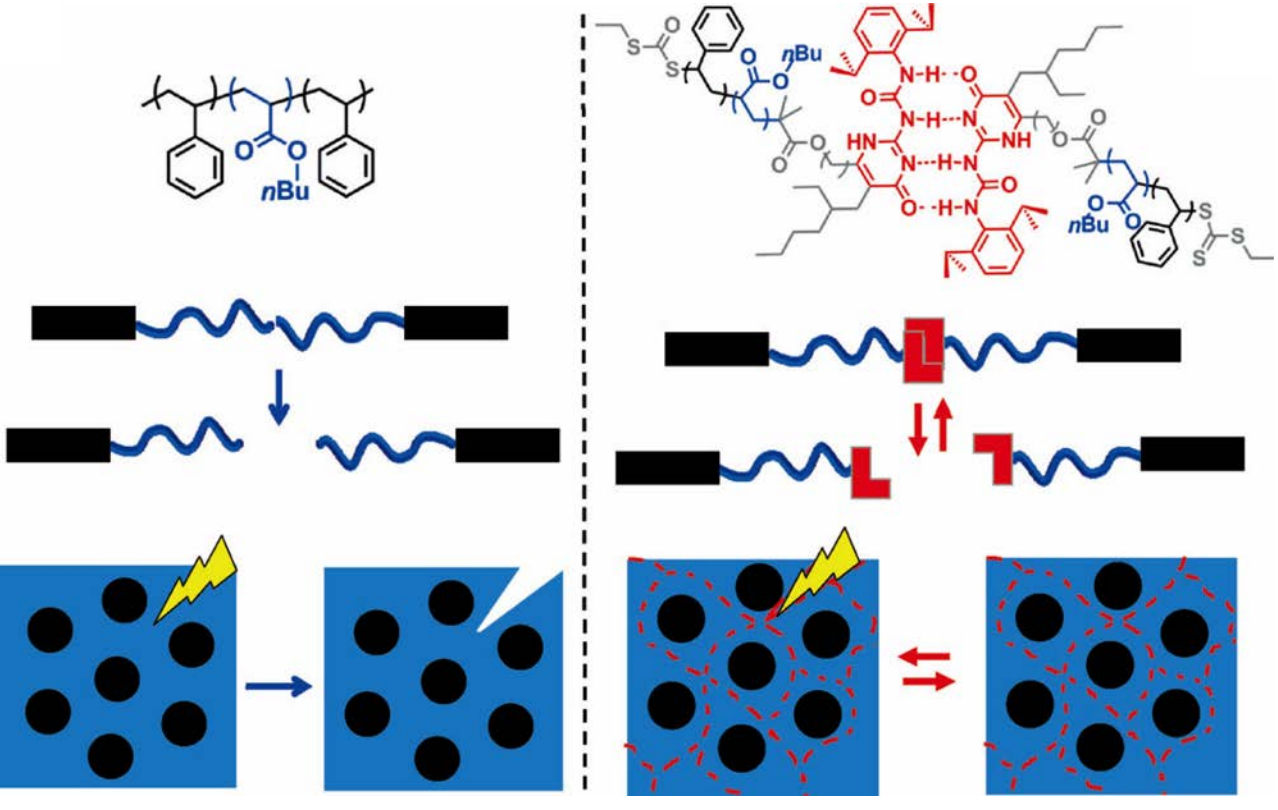
Deformation could gradually recover with time (at rt) or upon heat treatment. (80 °C, 30s)

proposed mechanism



***use UPy to develop self healing supramolecular block copolymer**

Z. Guan, *et al*. *Angew. Chem., Int. Ed.* **2012**, *51*, 10561.



use poly(n-butyl acrylate) (PBA) as the soft block and polystyrene (PS) as the hard block

The supramolecular healing motifs located within the soft phase remain dynamic and reversible, providing self- healing capability.

utilizing a 2,6-diisopropyl- phenyl group to disrupt π –π stacking between UPy dimers

samples show the characteristic stress-strain behavior of thermoplastic elastomers

E 21.1MPa

after cutting, gently pressed together for 1min and left for 18 h at 45 ºC

recovery of tensile strength (> 90 %) and strain at break (ca. 75 %)

Summary

theme: Reaction with Mechanical Force

- active use of mechanical force
- passive use of mechanical force

key characters of Reaction with Mechanical Force

- mechanophore
- polymer backbone
- regiochemical effect

(1) active use of mechanical force

- deprotection (unclicking) cf. retro DA
- vias reaction pathway (violating WH rules)
- reconfiguration of stereoisomer (atropisomer)
- stabilize intermediate (radical trapping)

(2) passive use of mechanical force

- production of reactive species (strengthening, self healing)
- production of catalytic species (mechanocatalyst, polymerization to self healing)
- rearrangement (damage relaxation)
- breaking hydrogen bond (damage relaxation, self healing)

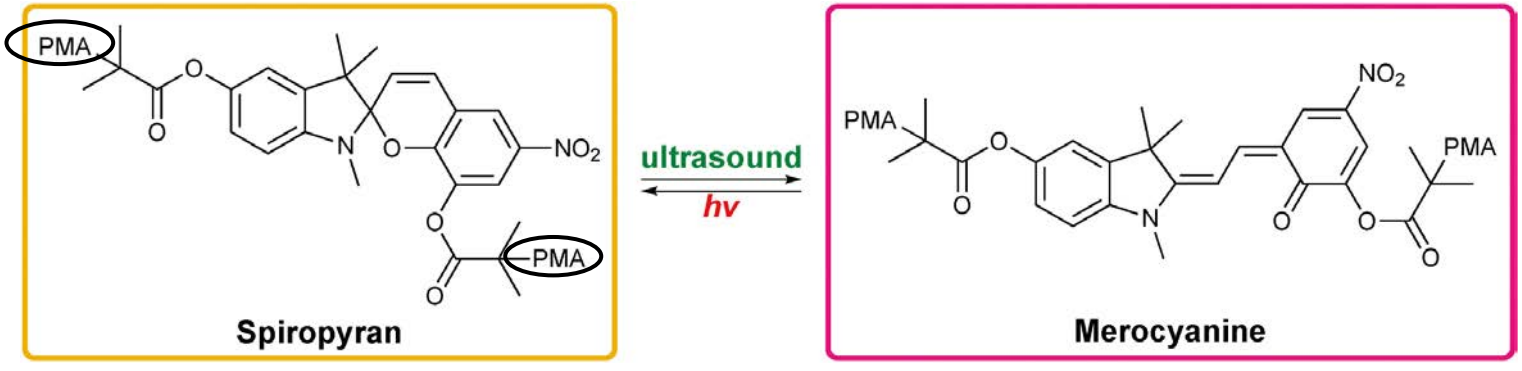
(other application: damage sensing)

Appendix: selected other reactions

*damage sensing

(i)Spiropyran

S. R. White, J. S. Moore, *et al*. *J*. *Am*. *Chem*. *Soc*. **2007**, *129*, 13808.



cited from *Chem*. *Soc*. *Rev*. **2013**, *42*, 7130.

condition: US, CH_3CN, 6-9 ºC

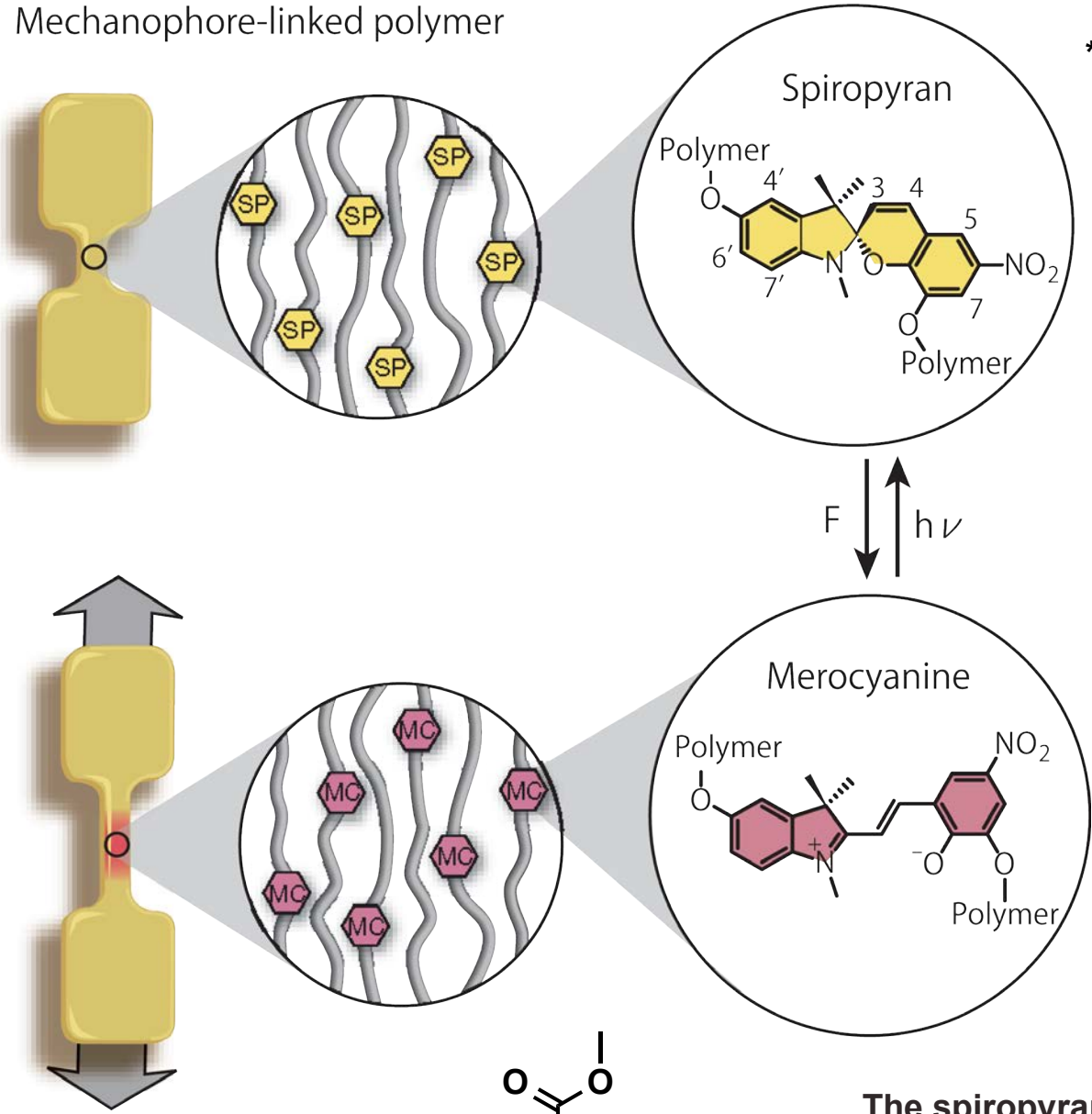
Spiropyran mechanophore undergoes 6π–electron electrocyclic ring opening.

The colorless polymer solution turned pink.

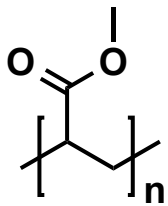
Exposure to ambient light for 40 min at room temperature caused the color to disappear.

Application in damage sensing

Mechanophore-linked polymer



Polymer:PMA



PMA

***application in solid state**

S. R. White, J. S. Moore, *et al*. *Nature* **2009**, *459*, 68.

find mechanophore in solution by using US

↓

application in solid state

reversible ring-opening reaction under tensile stress

Colour change could be reversed after 6 h of exposure to fluorescent room light.

If it fails, it can not be repaired.

The spiropyran mechanophore can function as a molecular force sensor, providing visible detection and mapping of mechanical stresses within bulk polymeric materials.

cf.力を加えると変色するプラスチック（chem-station)

(ii)1,2-dioxetane

response to strain by emitting light

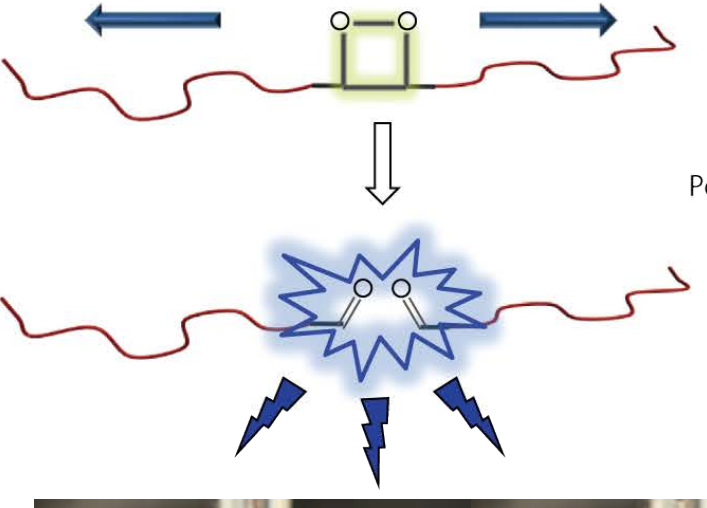
R. P. Sijbesma, *et al*. *Nat*. *Chem*. **2012**, *4*, 559.

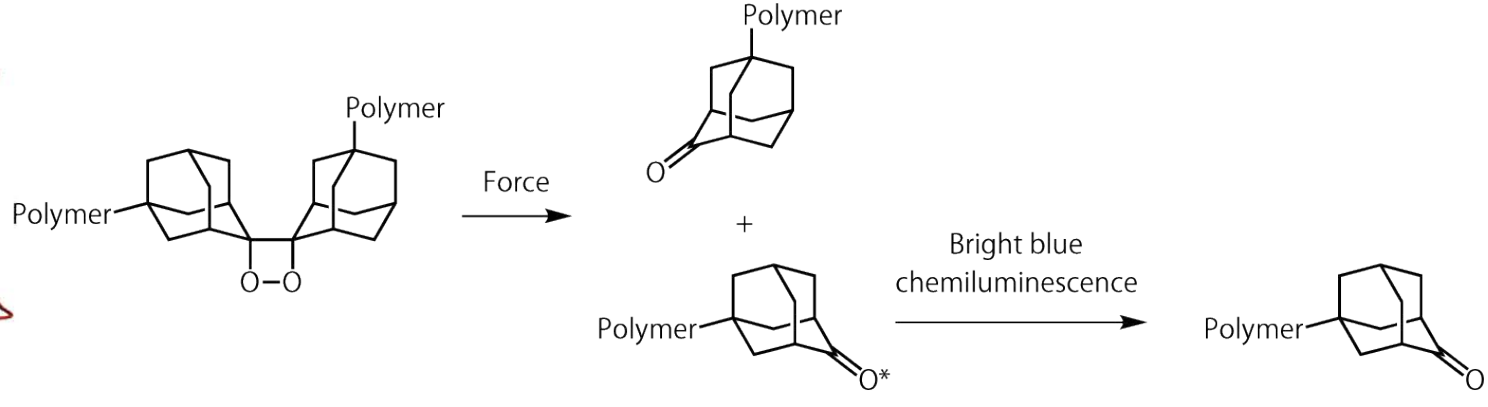
cycloreversion process that generated electronically excited ketone intermediates

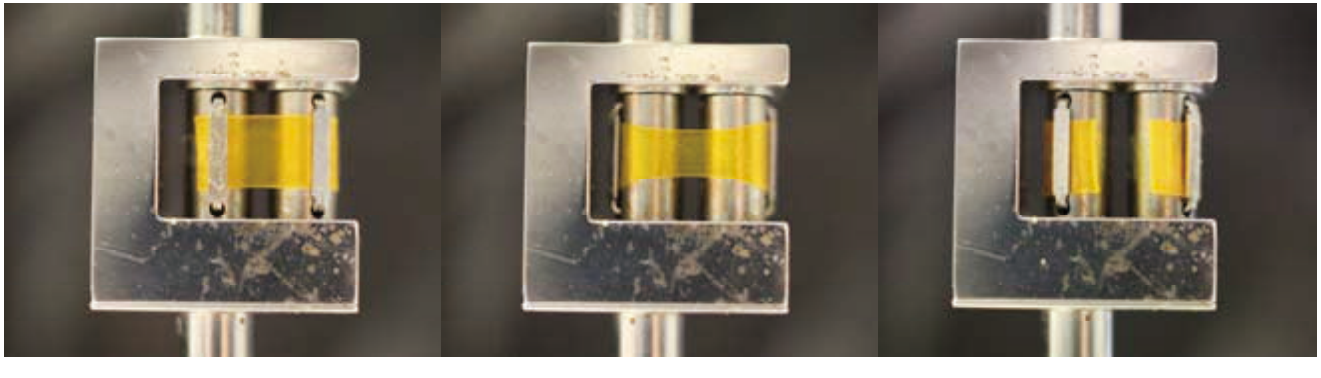
The 1,2-dioxetane unit is well known as an efficient source of electronically excited products when it is activated thermally.

Acc. Chem. Res. **1974**, *7*, 97.

On relaxation, blue light (at 420 nm) is emitted.





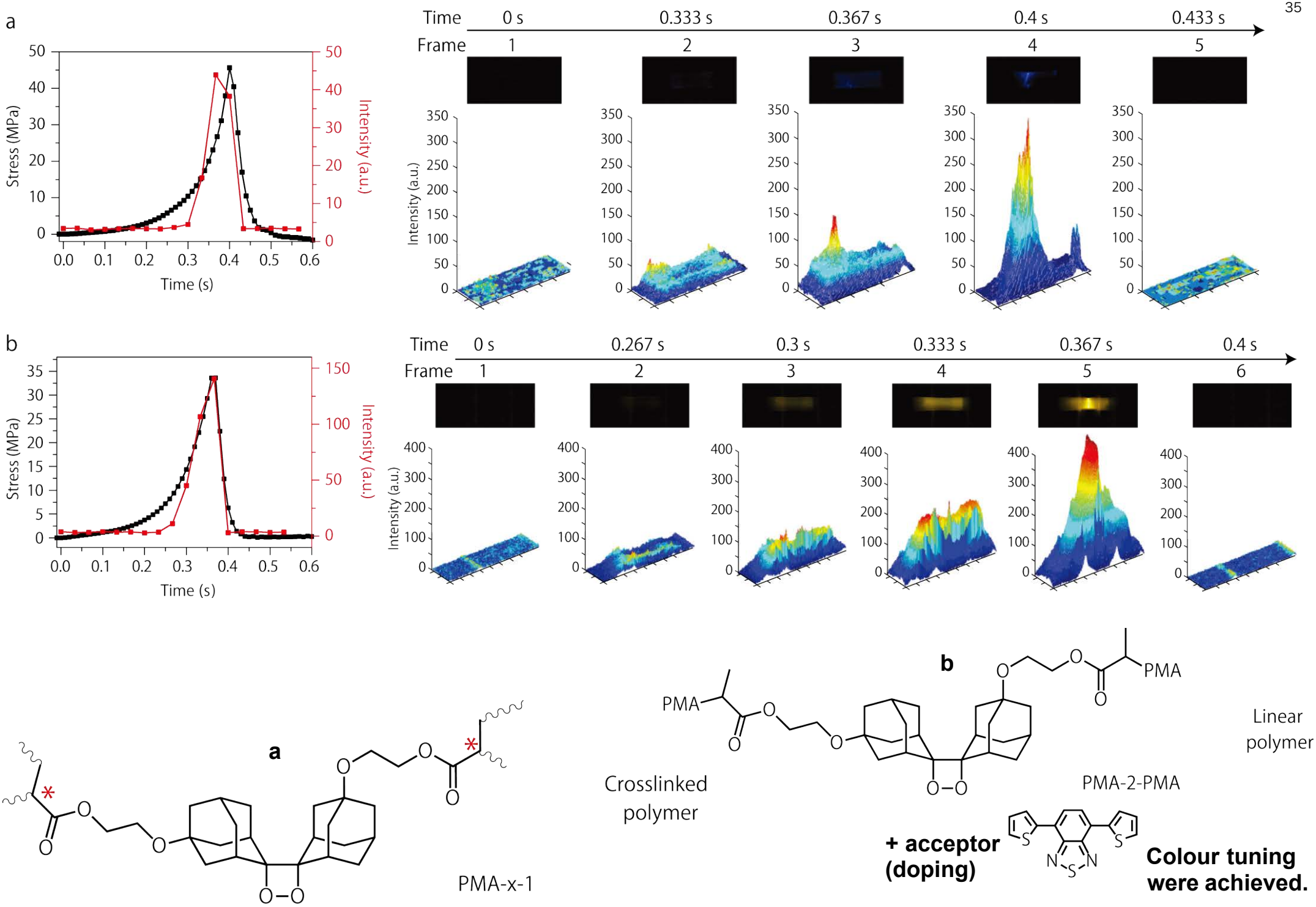


Application

crosslinking (by ketone formation)

damage sensing

use film


a
Stress (MPa)
Intensity (a.u.)
Time (s)
Time
0 s
0.333 s
0.367 s
0.4 s
0.433 s
Frame
1
2
3
4
5
Intensity (a.u.)
b
Stress (MPa)
Intensity (a.u.)
Time (s)
Time
0 s
0.267 s
0.3 s
0.333 s
0.367 s
0.4 s
Frame
1
2
3
4
5
6
Intensity (a.u.)
a
PMA-x-1
Crosslinked polymer
b
PMA
PMA-2-PMA
Linear polymer
+ acceptor (doping)
Colour tuning were achieved.