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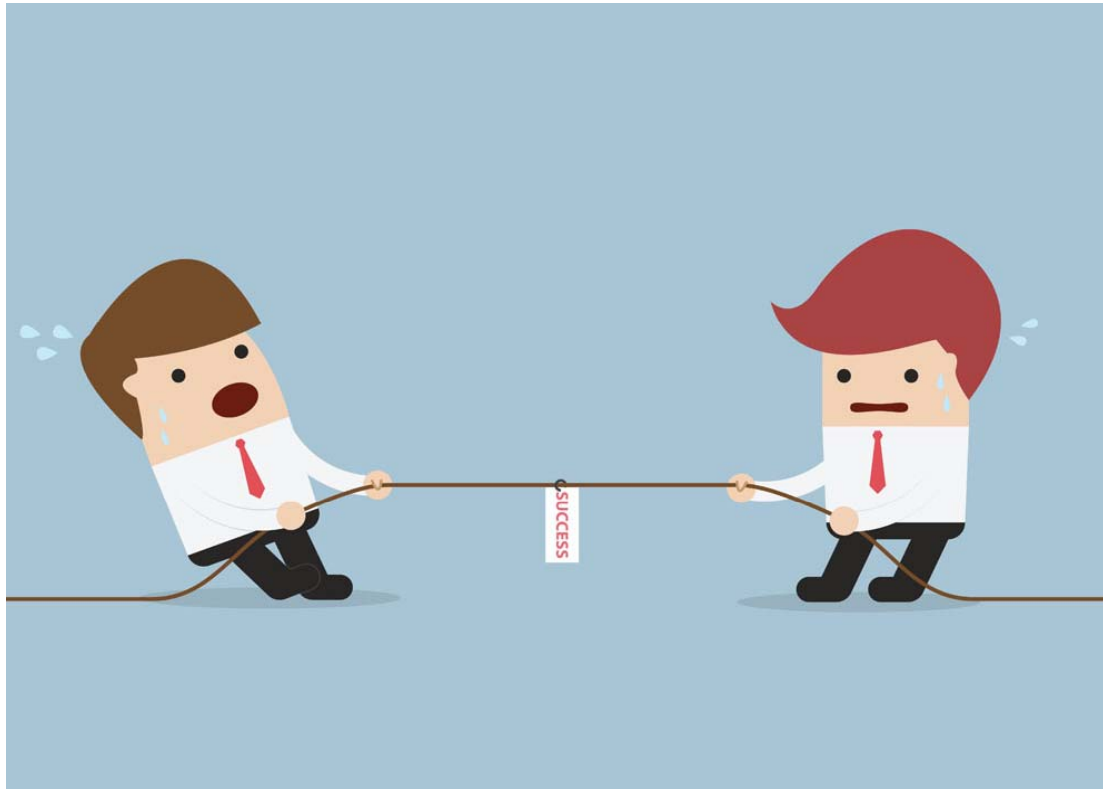
# Polymer Mechanochemistry

徐航勋

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<https://staff.ustc.edu.cn/~hxu>

中国科学技术大学高分子科学与工程系



# Chemical Reactions under Mechanical Force

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## Mechanochemistry

- ◆ 亚里士多德时期发现机械作用可以使物质发生变化并其有新物质生成
- ◆ 20世纪初，Ostwald 提出机械力化学概念

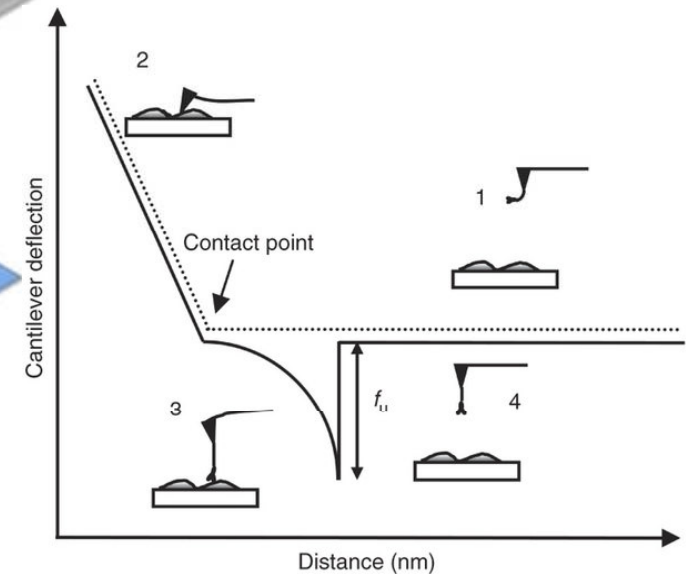
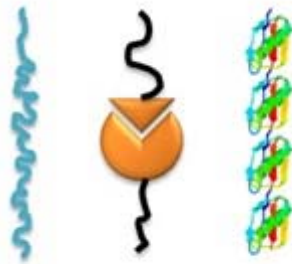
用于产生机械力化学研究的工具：

球磨、研磨、高速搅拌、原子力显微镜、流体力场和超声

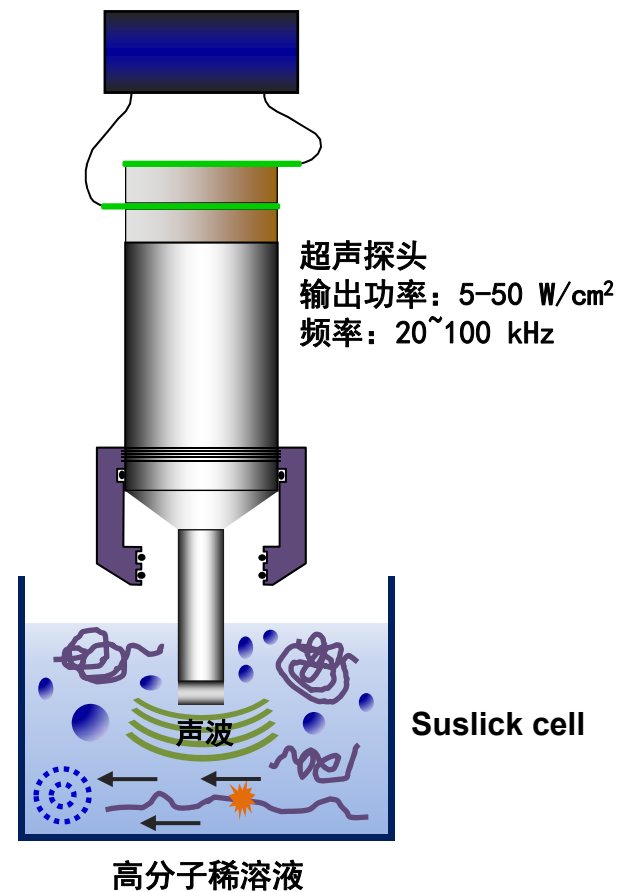
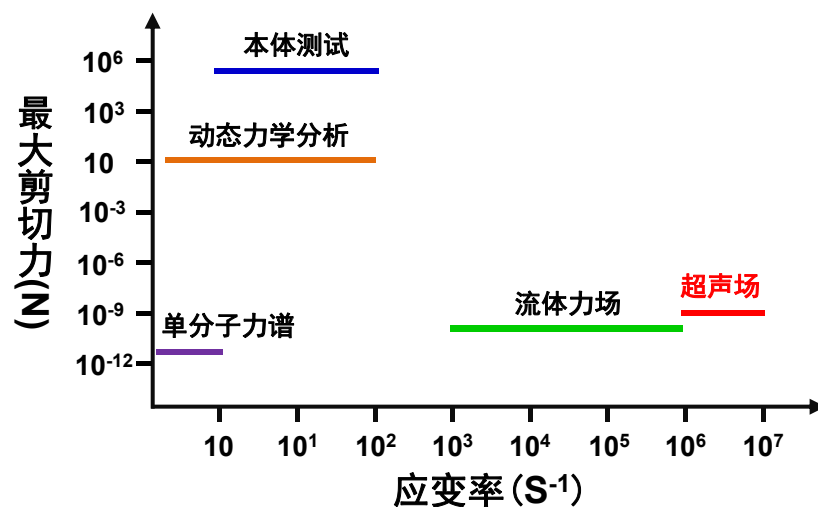
# Single-Molecule Force Spectroscopy

## Single-Molecule Force Spectroscopy (SMFS)

- Polymers
- Receptor-Ligand
- Proteins

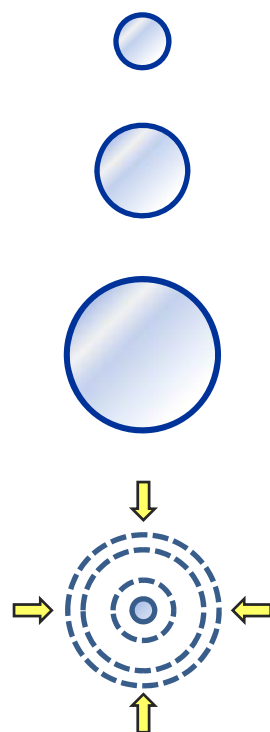


# Different Mechanical Tests

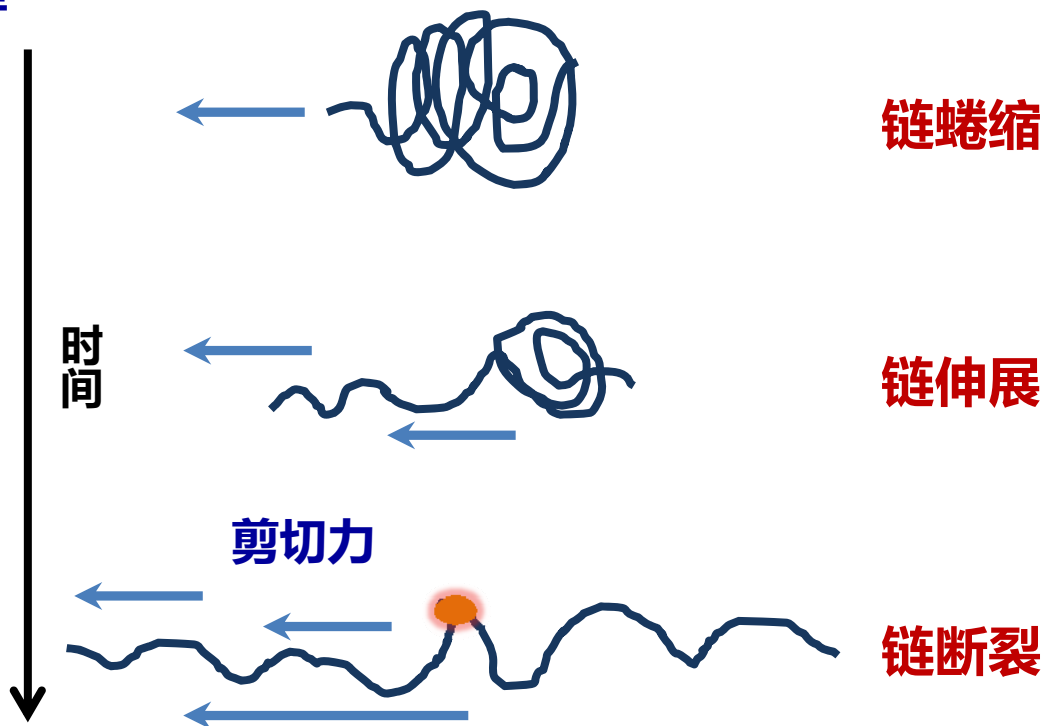


# Polymer Chains under Ultrasound

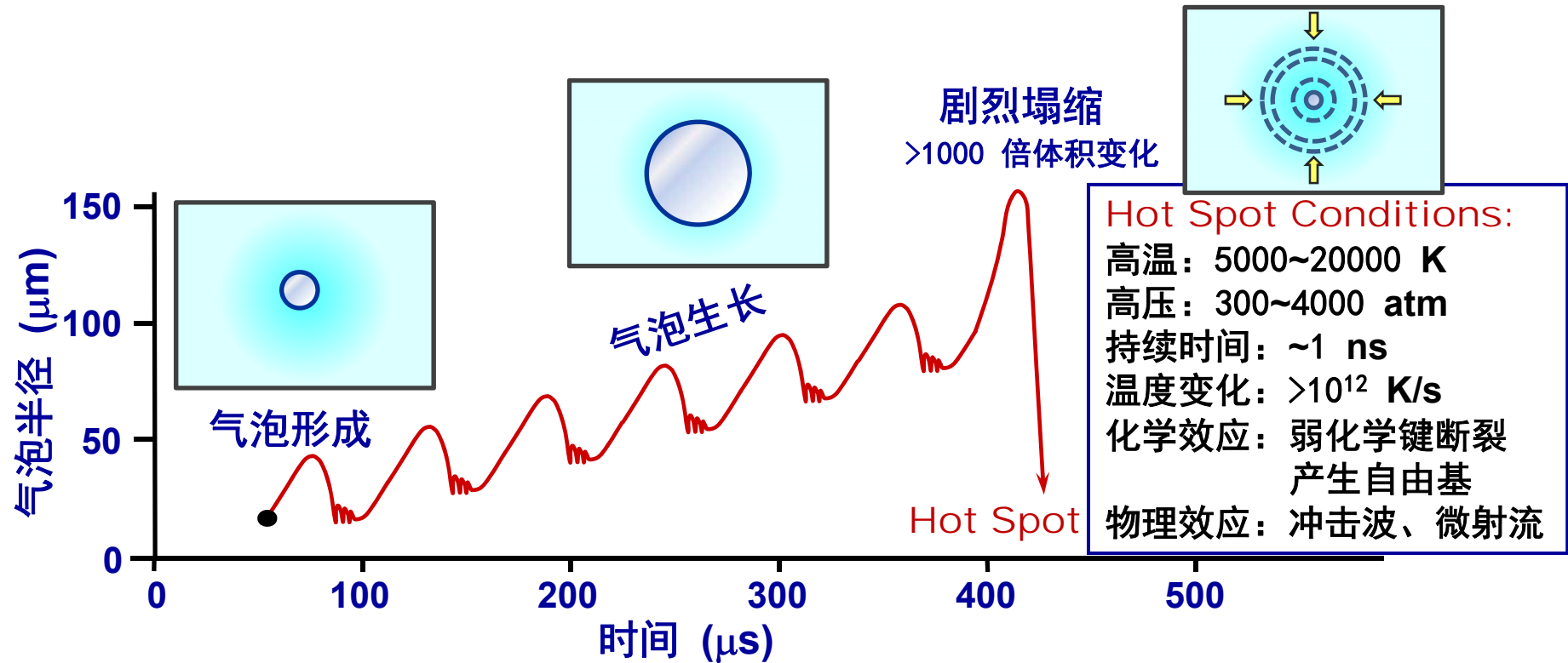
气泡塌缩过程



时间

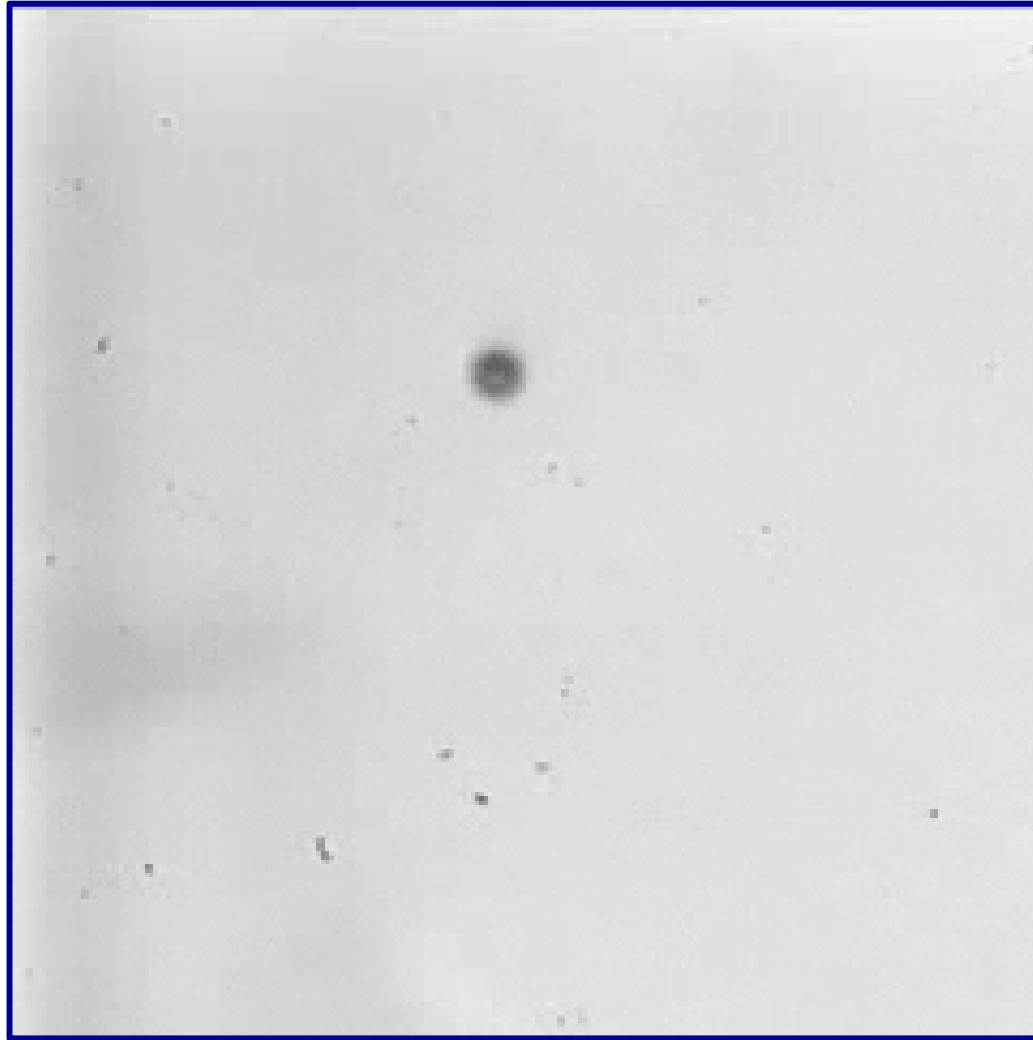


# Acoustic Cavitation



# An Acoustically Cavitating Bubble

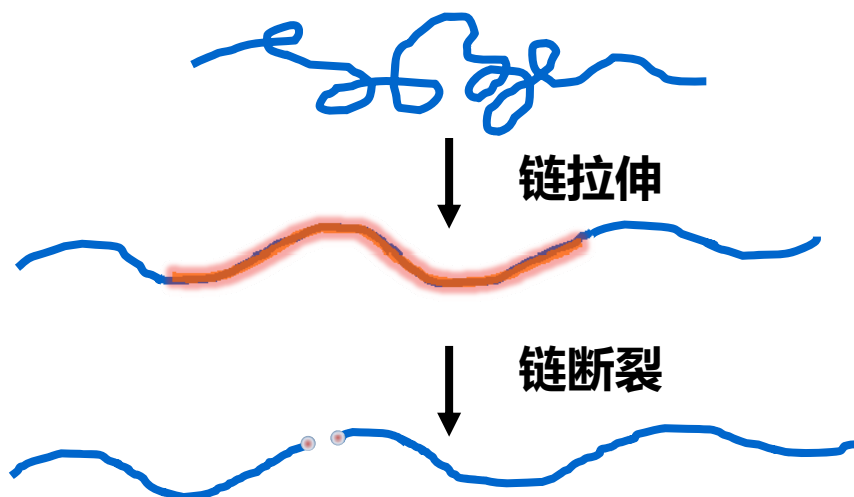
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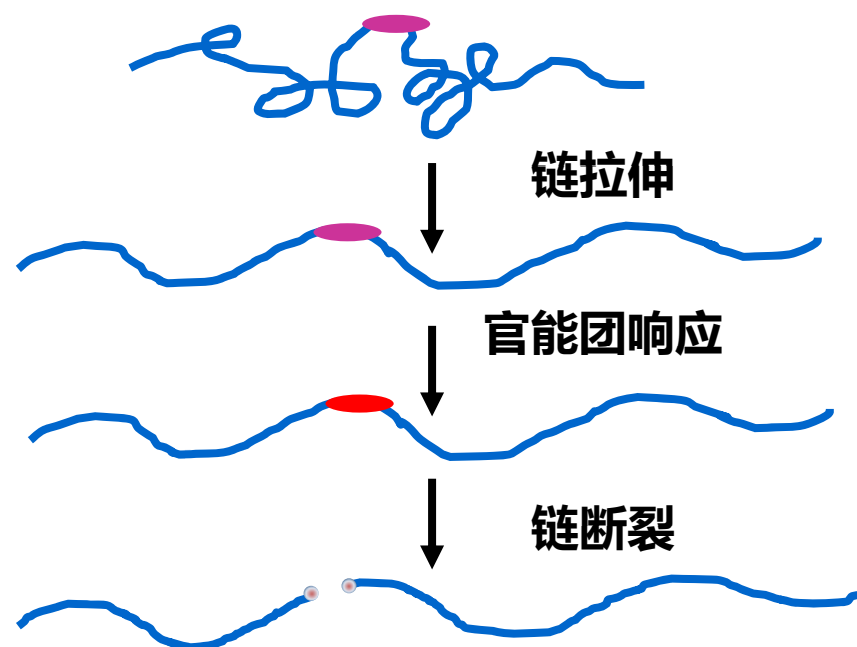
# Polymer Mechanochemistry

传统高分子链



链断裂基本发生在链中间，但具体位置不确定

含机械响应官能团高分子链



链断裂发生在官能团部位，位置确定

应用：改变化学反应进程、改变分子构型、催化

# Polymer Mechanochemistry



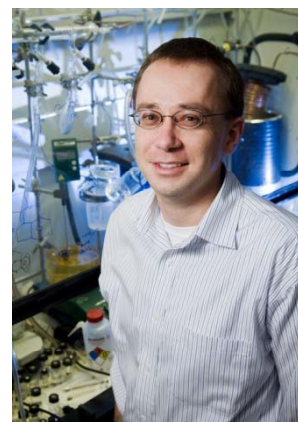
Jeff Moore



Stephen Craig



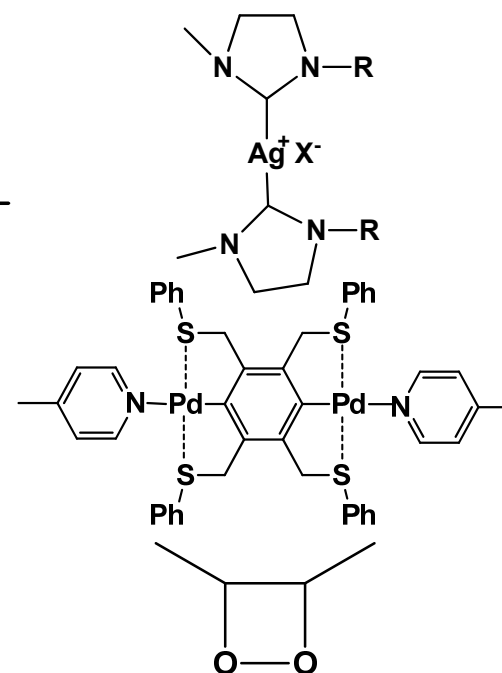
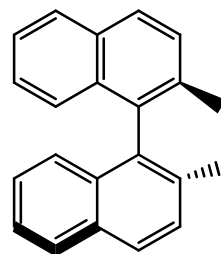
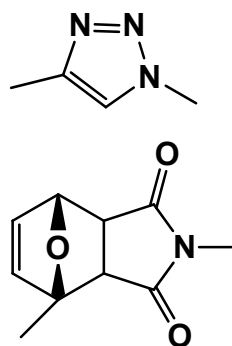
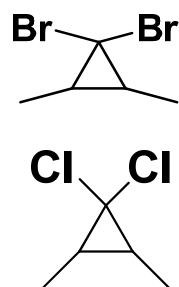
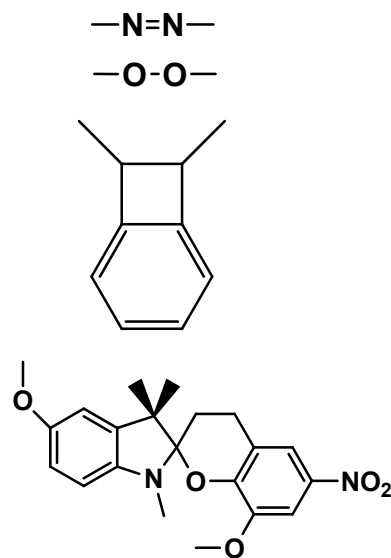
Chris Bielawski



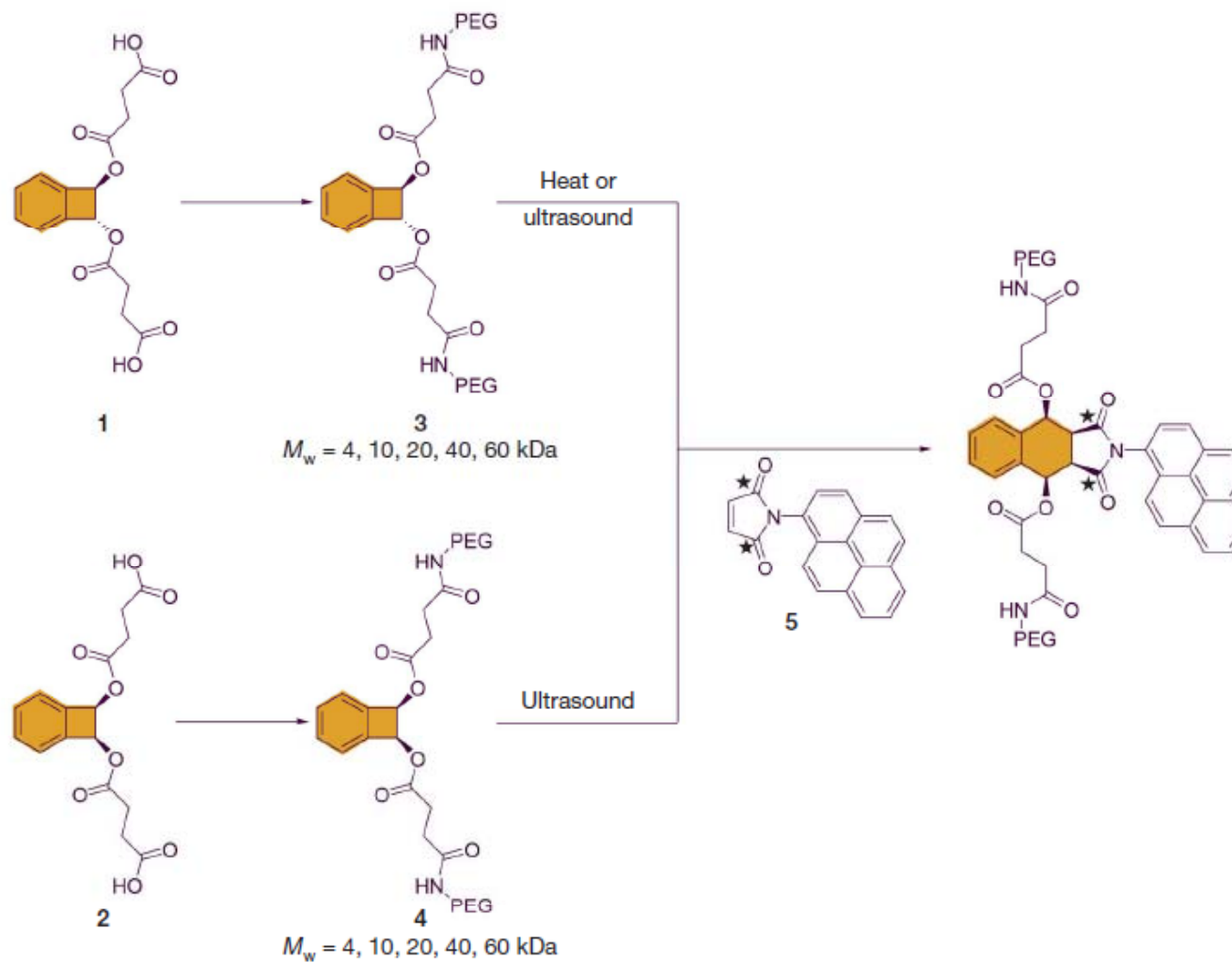
Roman Boulatov



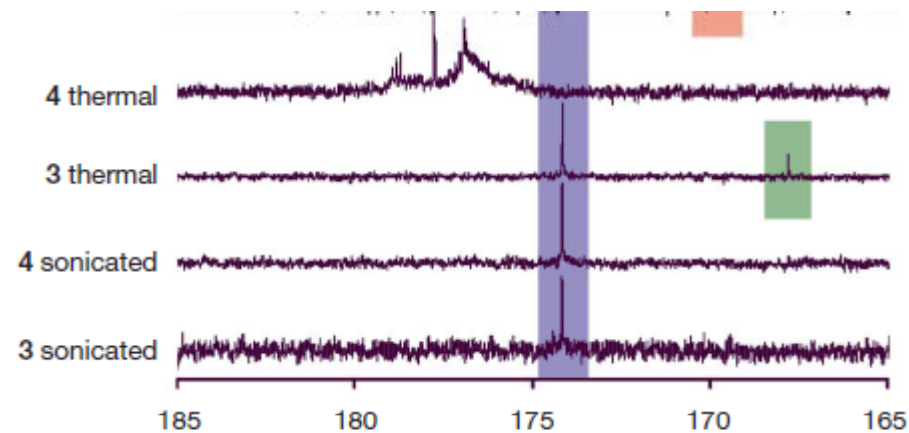
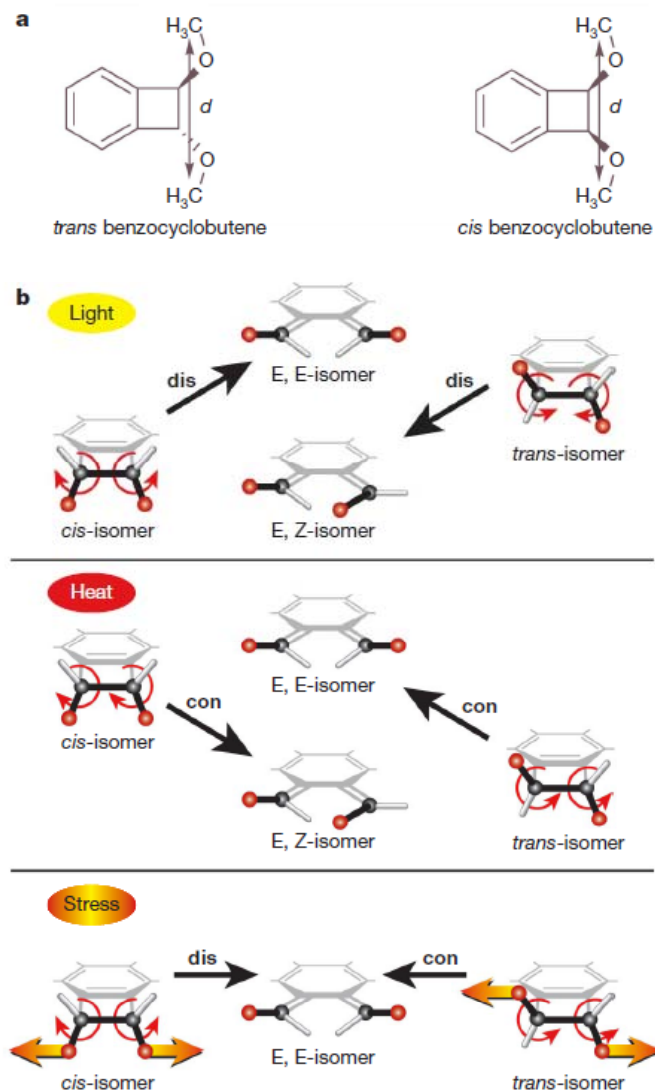
R. P. Sijbesma



# Biasing Reaction Pathways

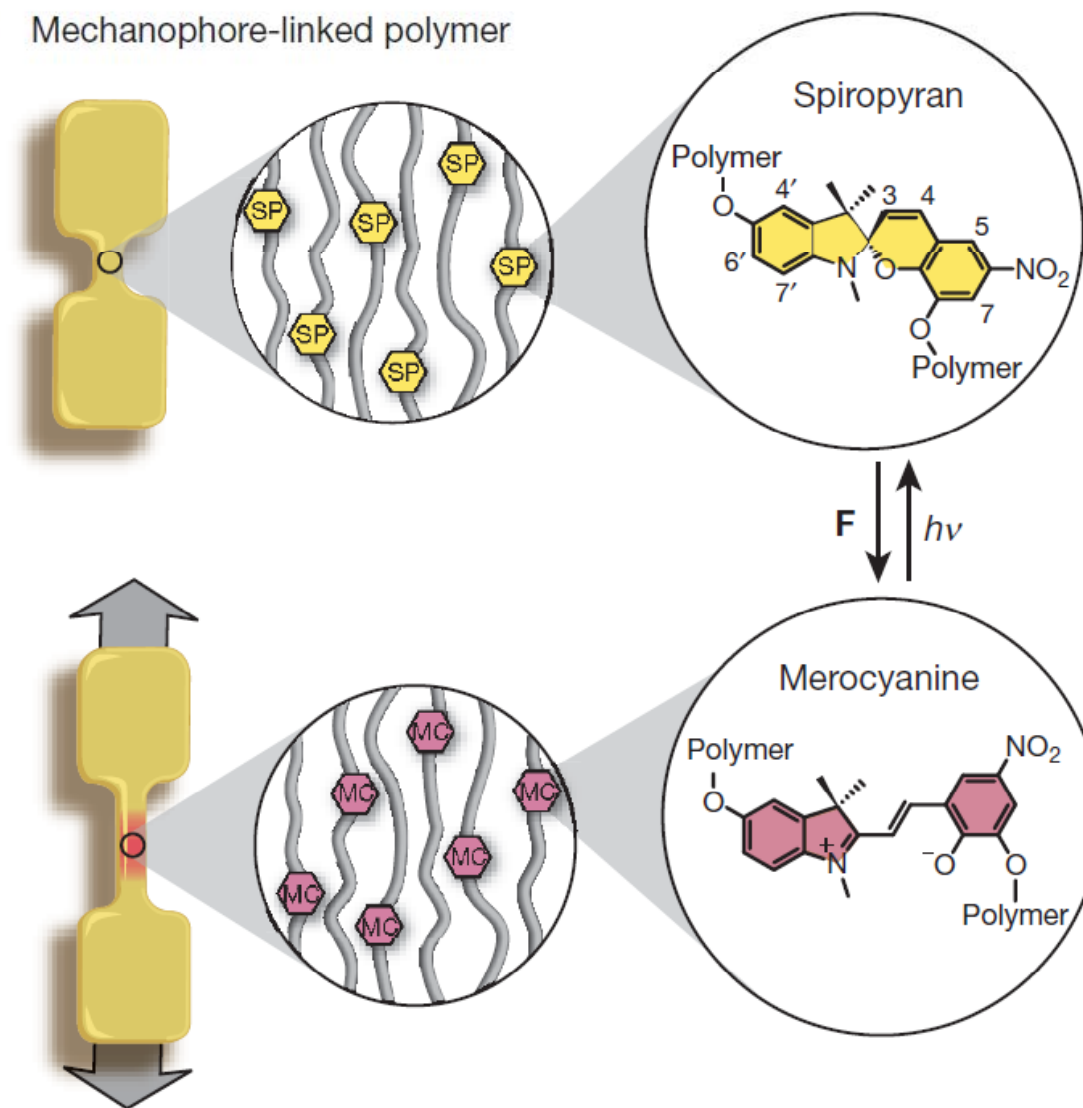


# Biasing Reaction Pathways

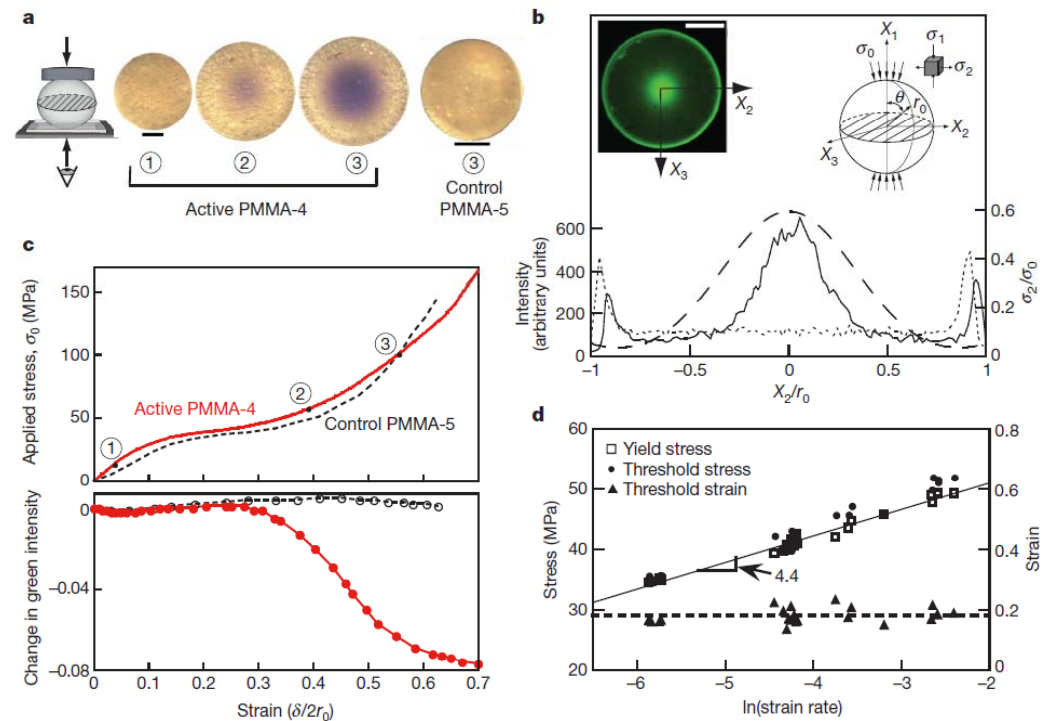
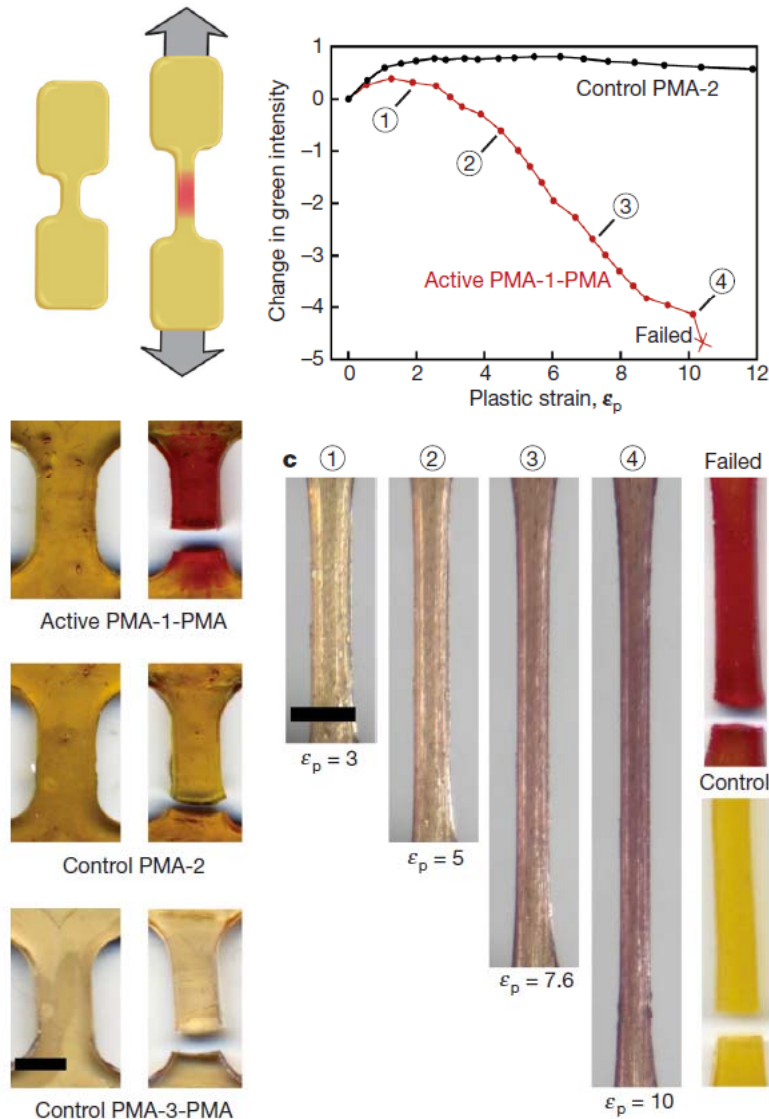


# Mechanical Reactions in Bulk Polymers

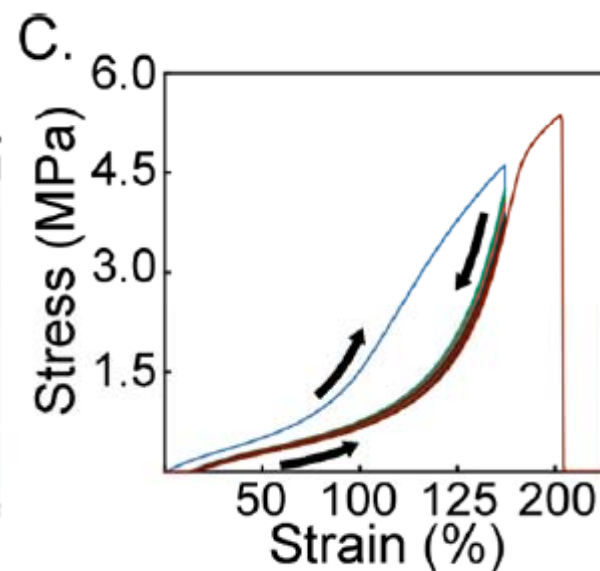
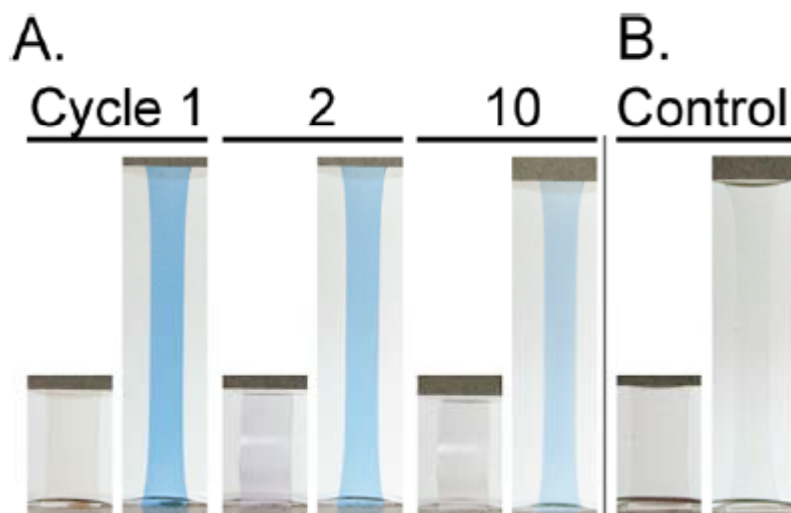
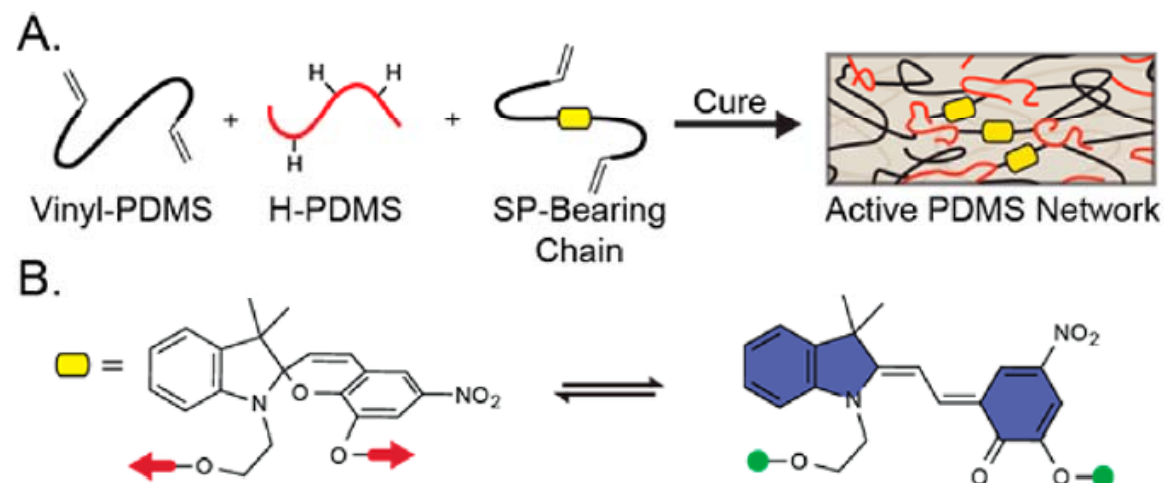
**a** Mechanophore-linked polymer



# Mechanical Reactions in Bulk Polymers

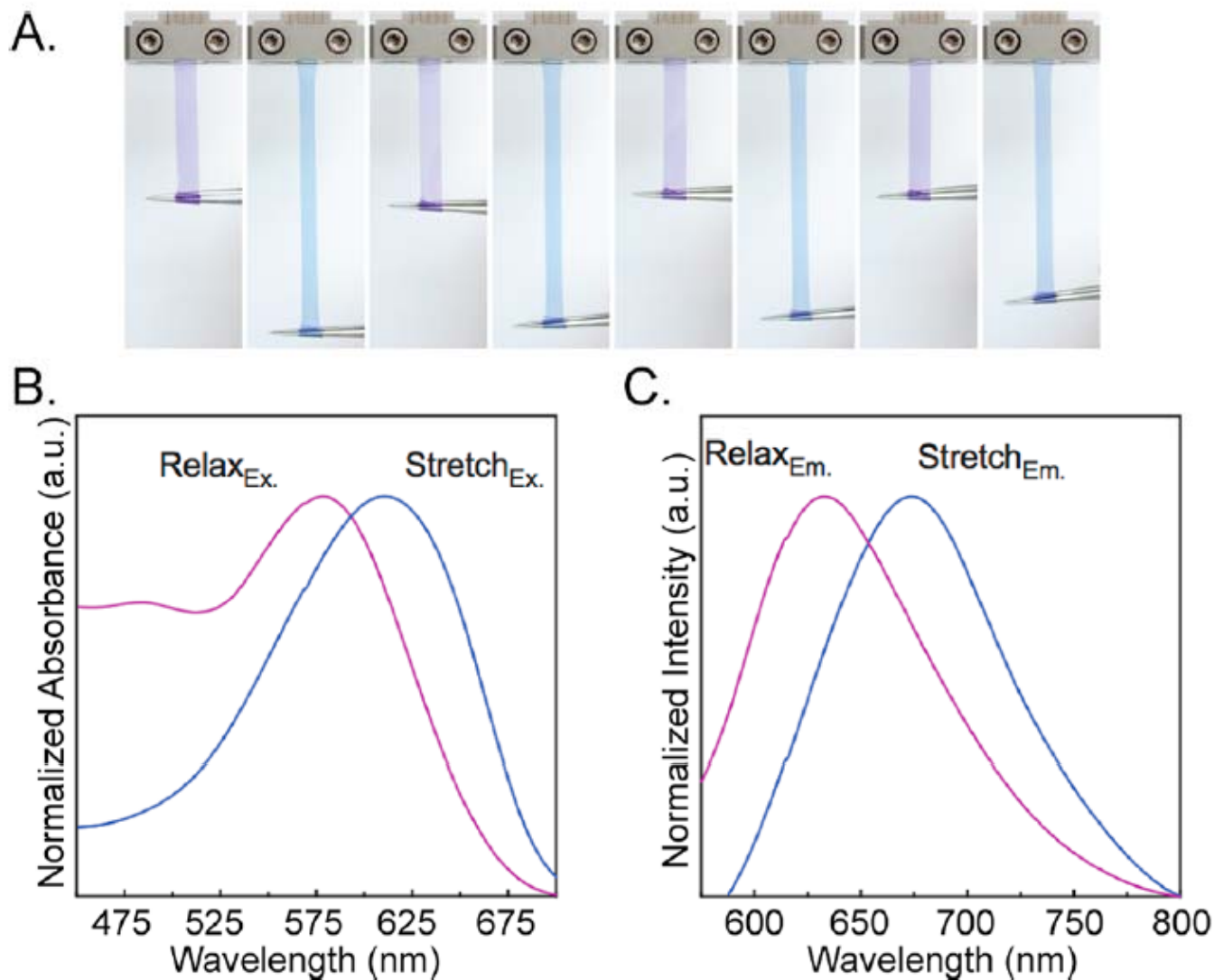


# Mechanical Reactions in Bulk Polymers



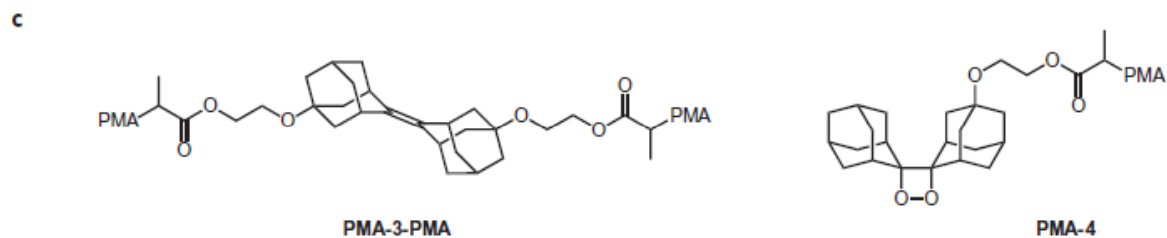
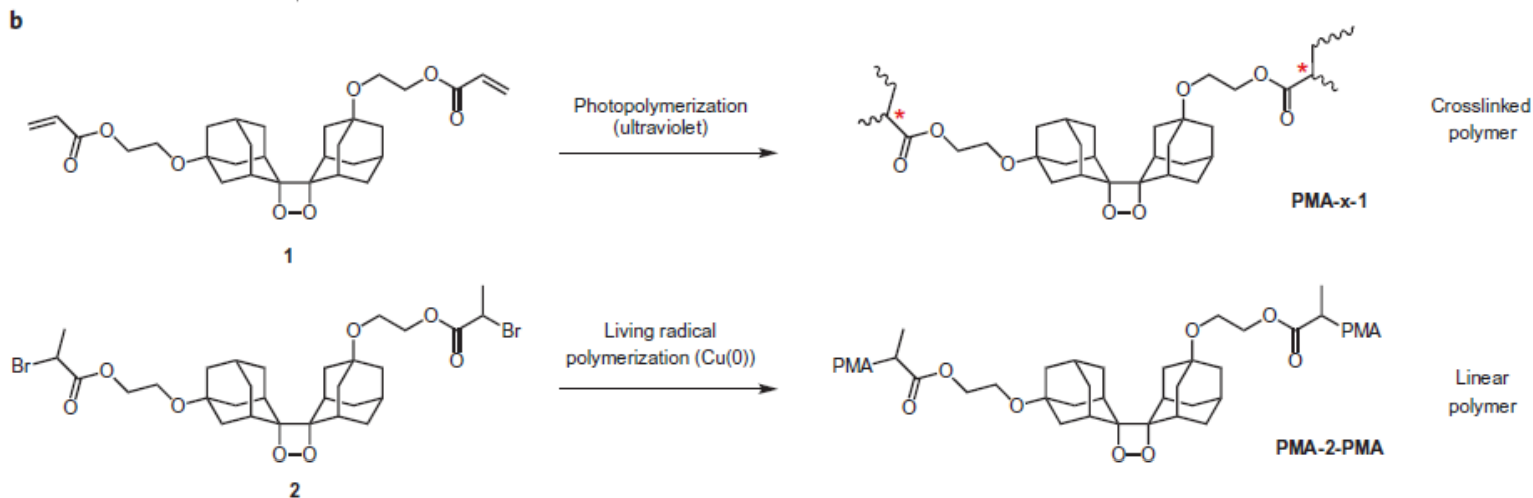
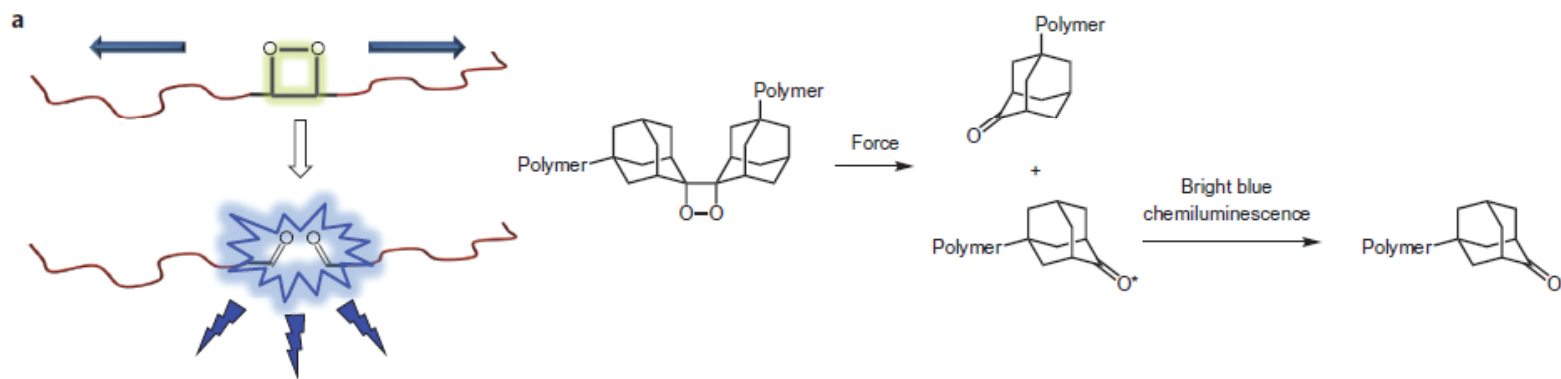


# Mechanical Reactions in Bulk Polymers

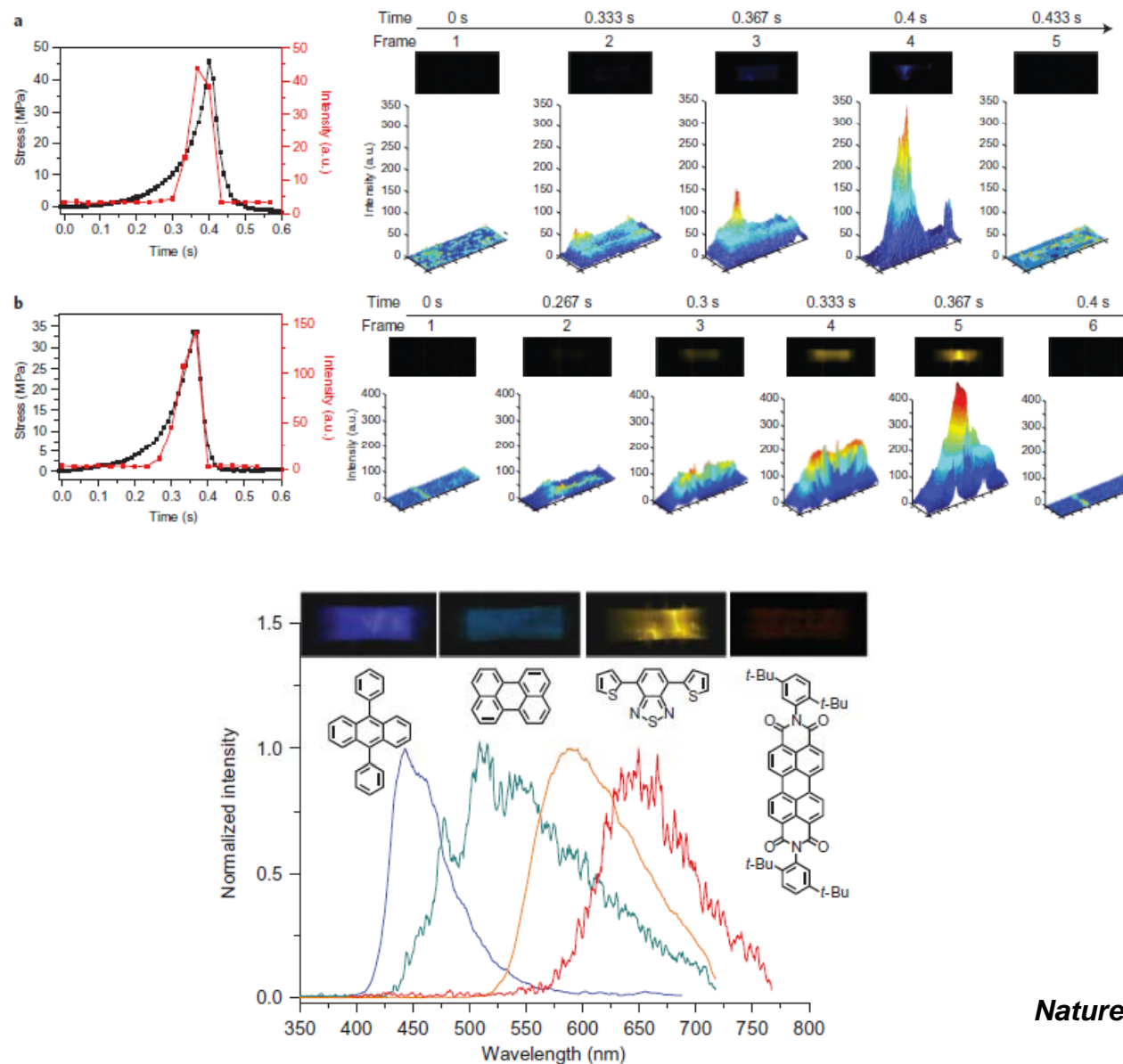




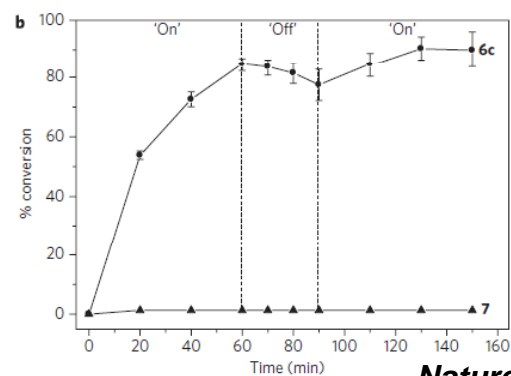
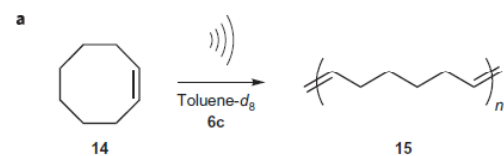
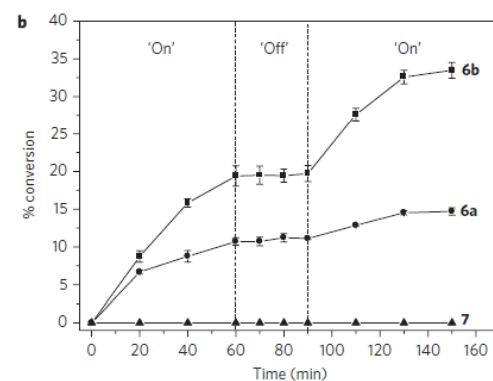
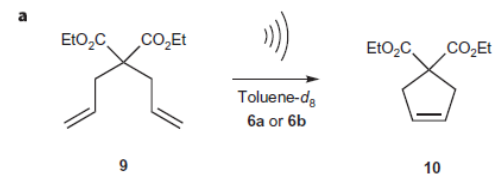
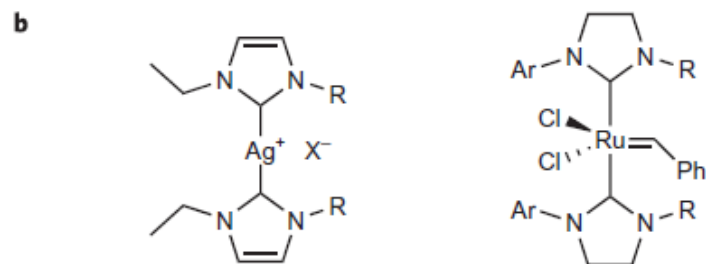
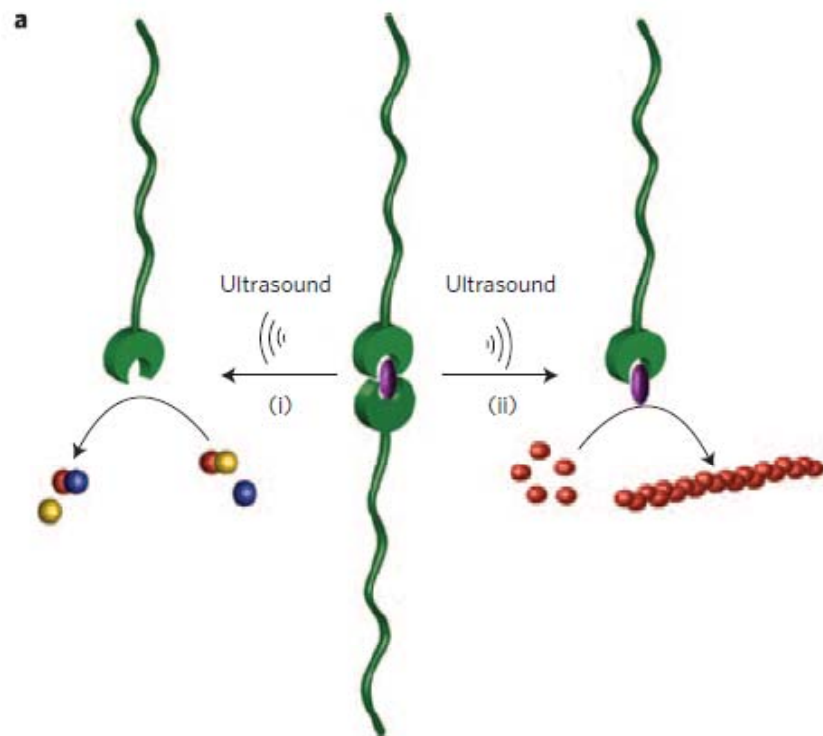
# Mechanically Induced Chemiluminescence



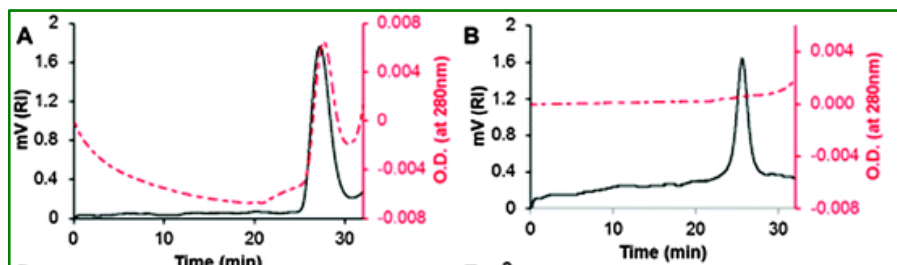
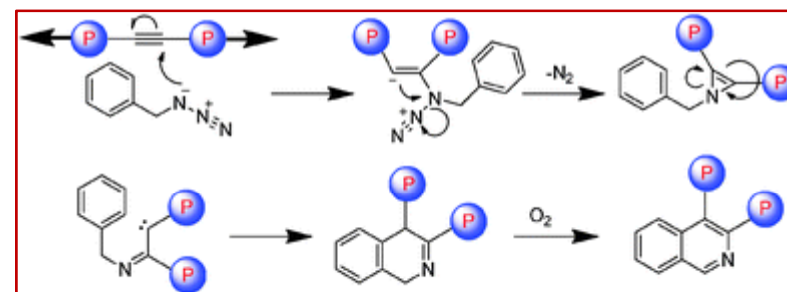
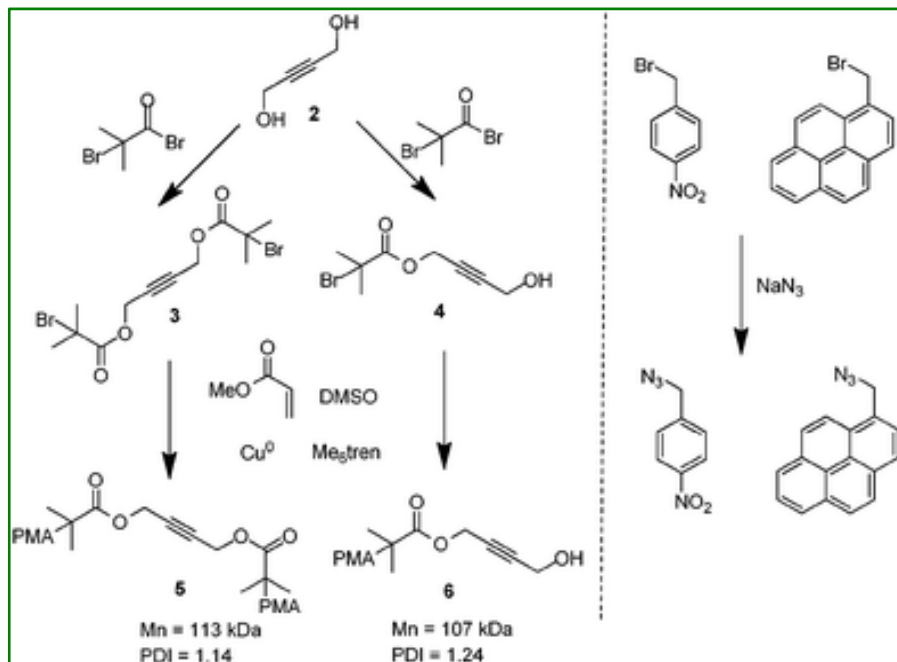
# Mechanically Induced Chemiluminescence



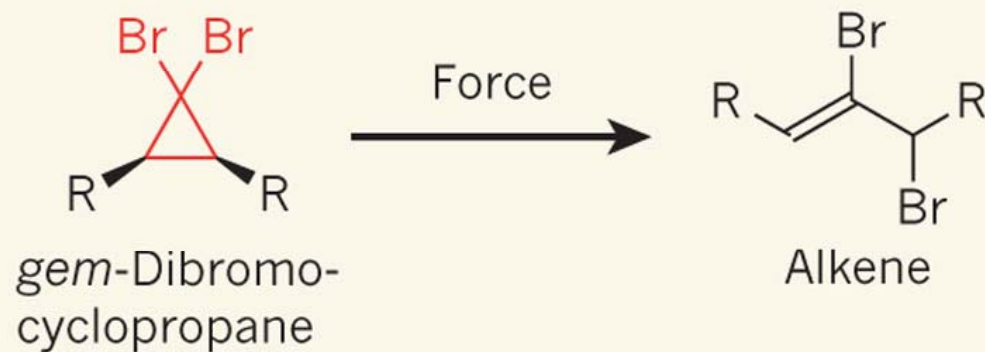
# Polymer Mechanochemistry for Catalysis



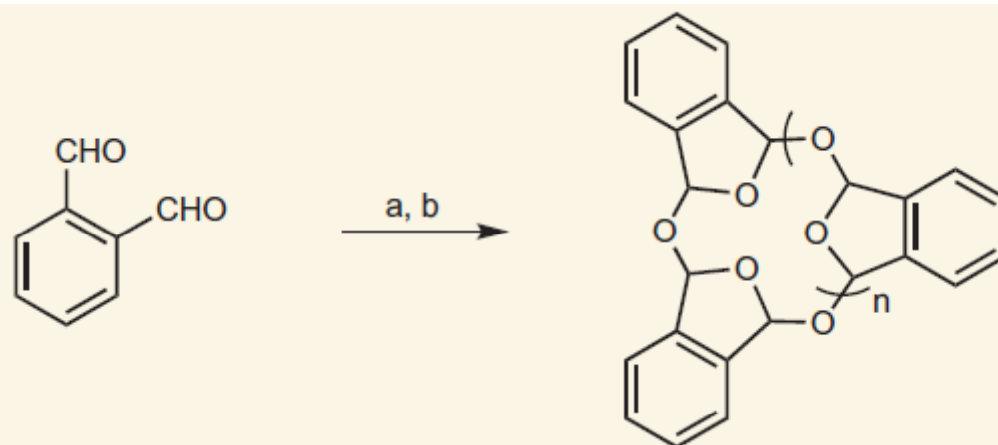
# Polymer Mechanochemistry for Catalysis



# Polymer Mechanochemistry for Catalysis

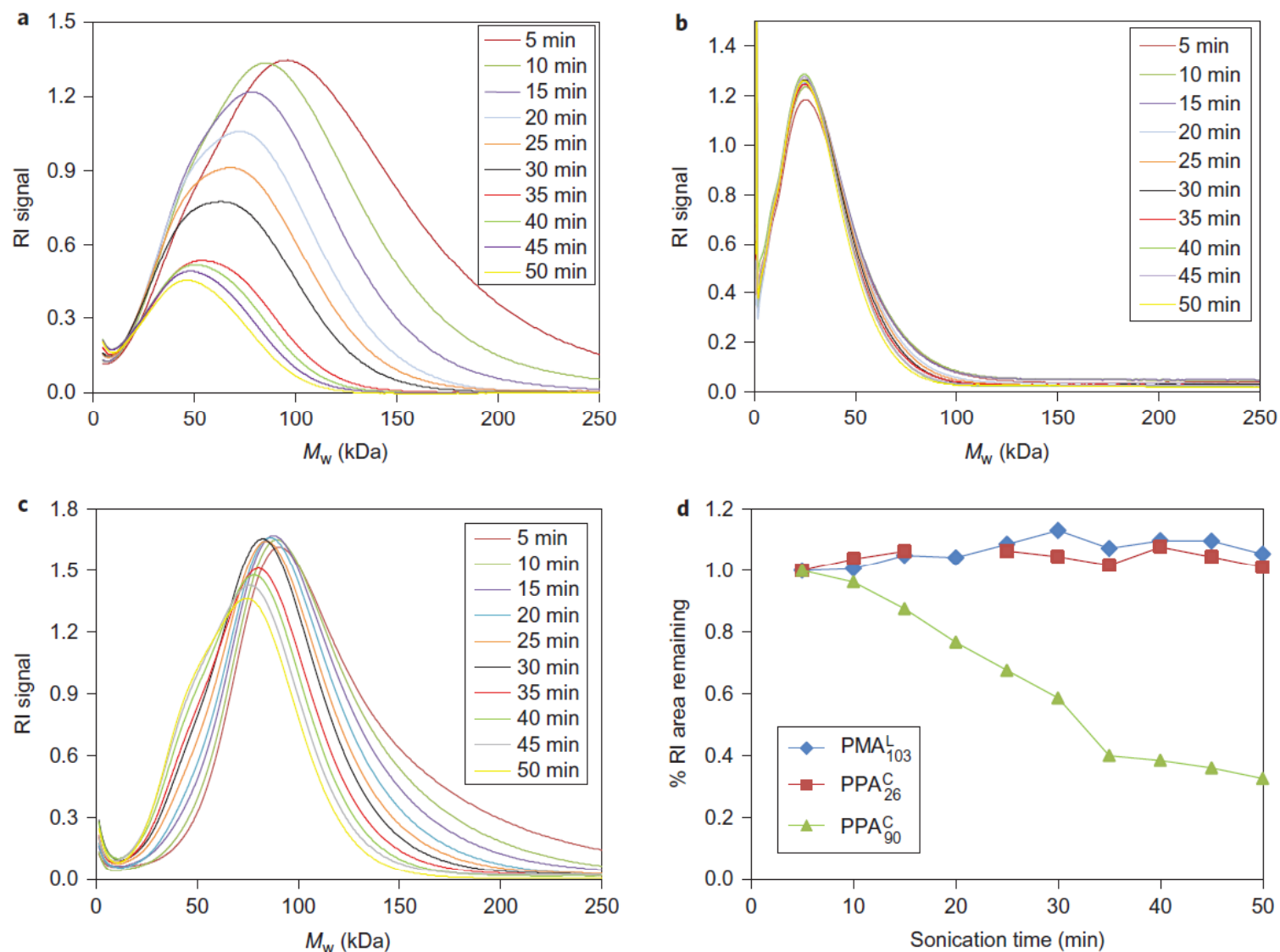


# Mechanically Induced Depolymerization

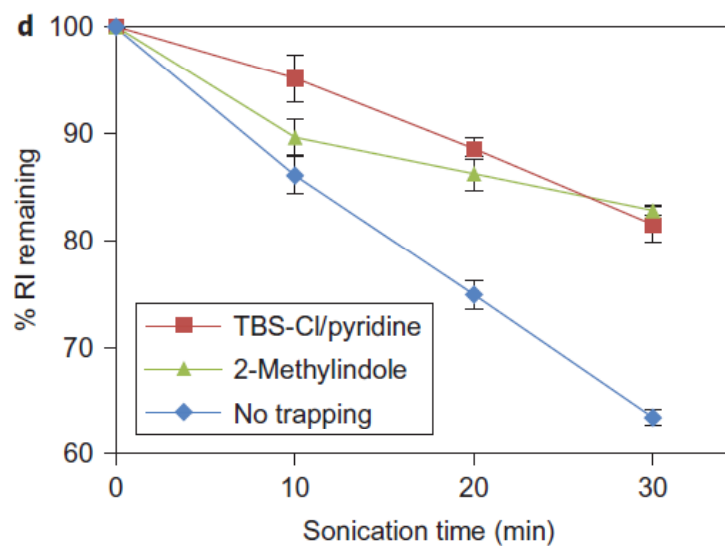
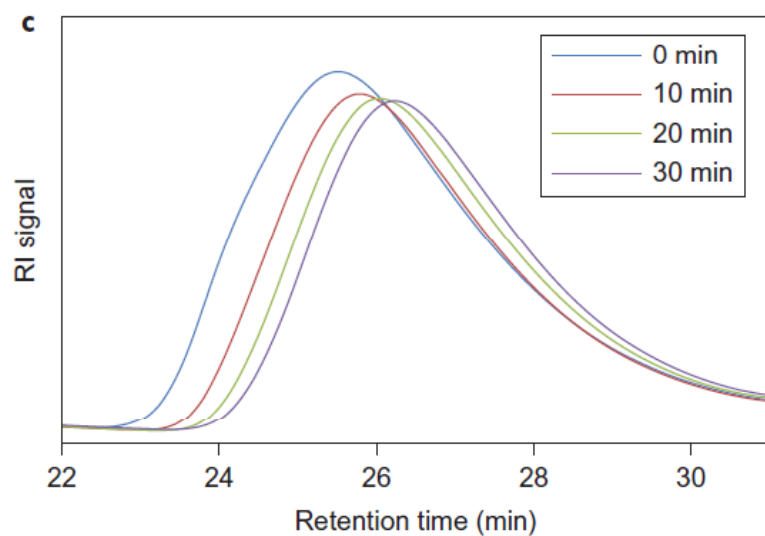
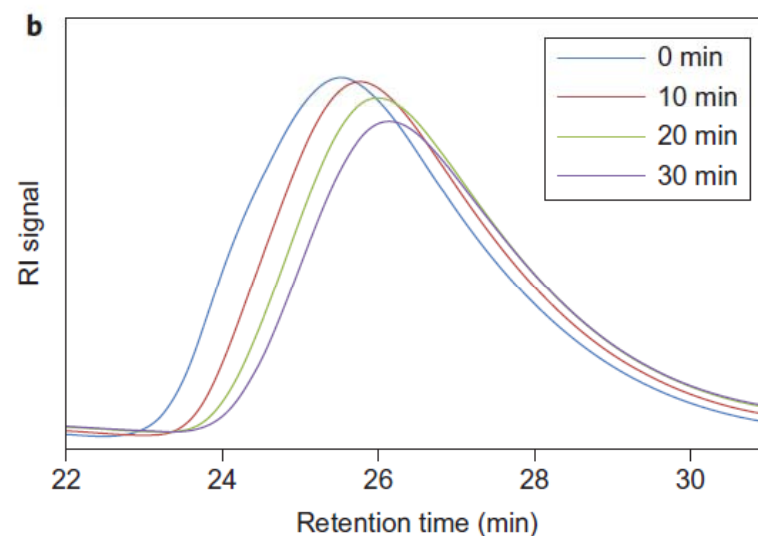
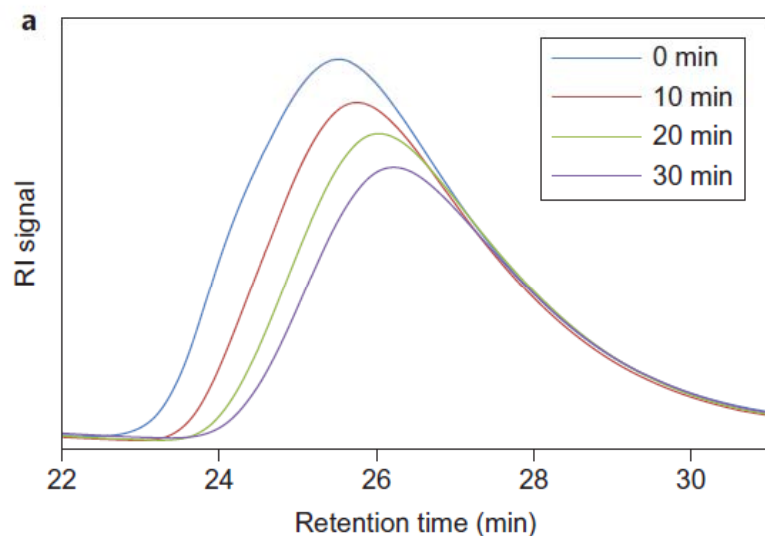


Polymer	$M_n$ (kDa)	$M_w$ (kDa)	PDI
PPA <sub>26</sub> <sup>C</sup>	16.5	25.6	1.6
PPA <sub>90</sub> <sup>C</sup>	58.2	89.6	1.5
PPA <sub>458</sub> <sup>C</sup>	254	458	1.8
PMA <sub>103</sub> <sup>L</sup>	86.4	103	1.2

# Mechanically Induced Depolymerization



# Mechanically Induced Depolymerization

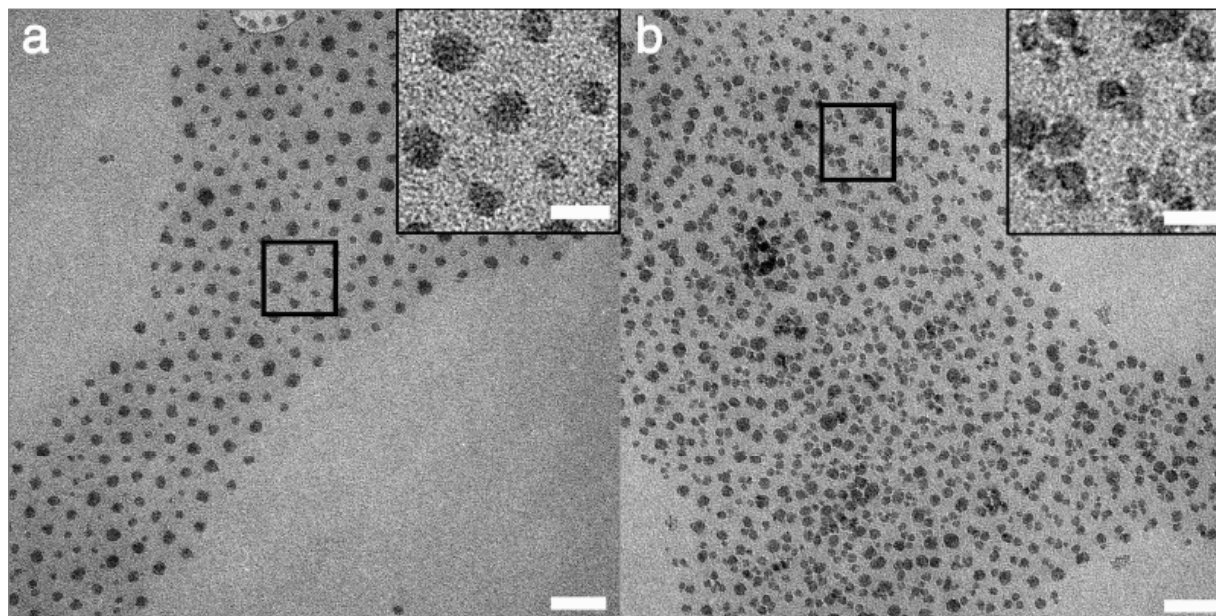
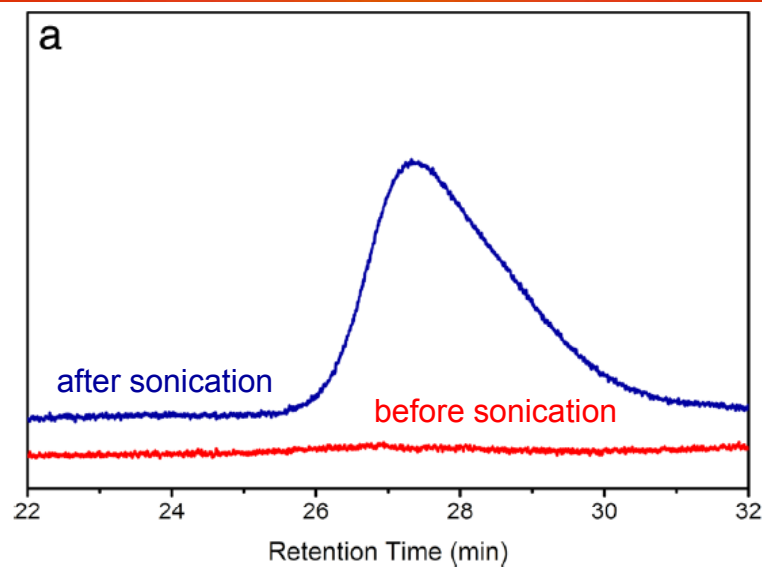




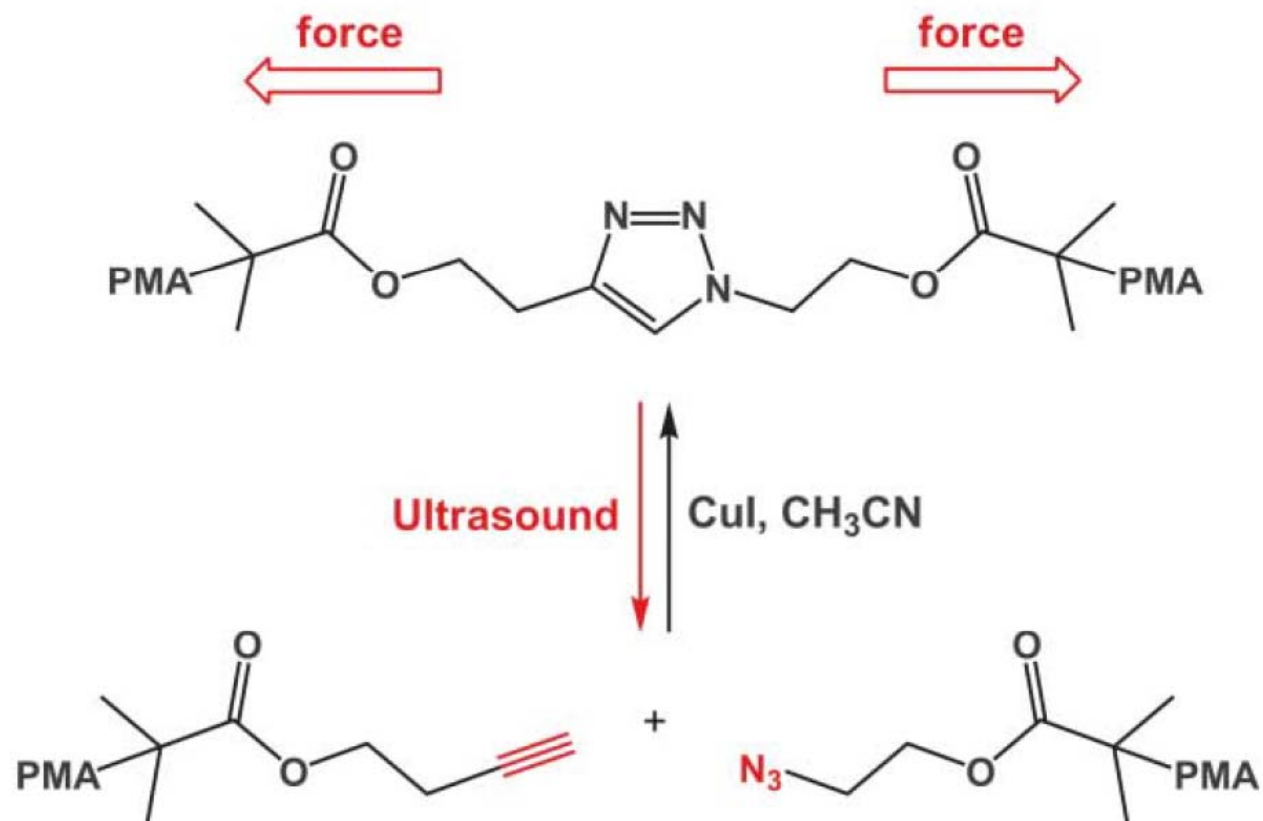
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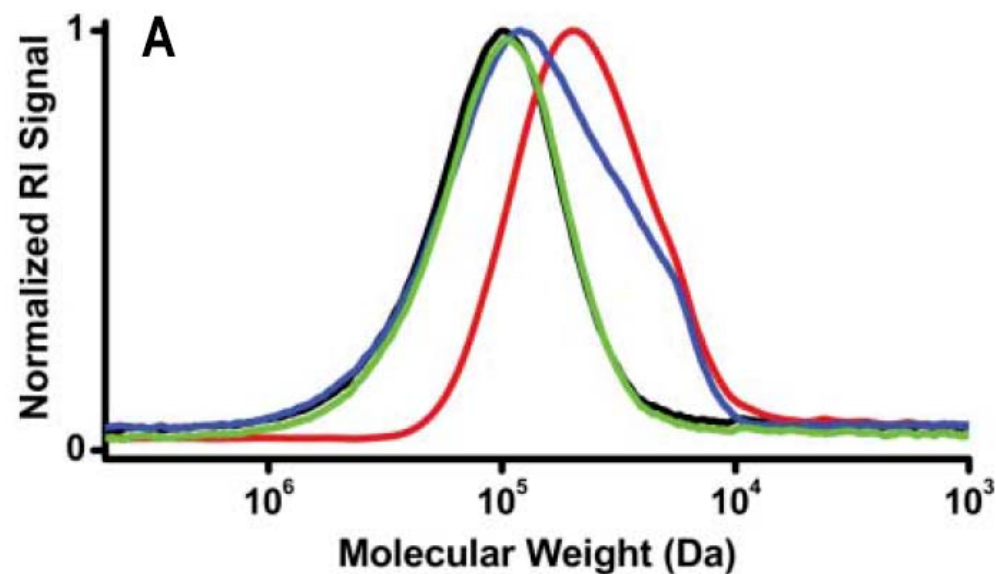
# Polymer Mechanochemistry at Solid Interface



# Polymer Mechanochemistry



# Polymer Mechanochemistry

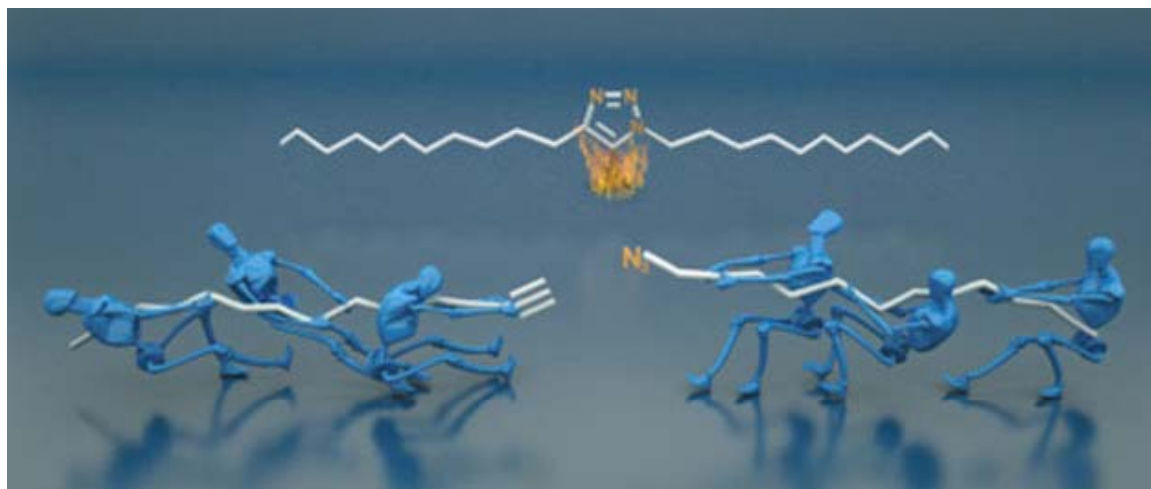


	Presonication		Postsonication		Sonication time
Name	$M_n$ (kD)	PDI	$M_n$ (kD)	PDI	(hours)
TriP <sub>160</sub>	160	1.2	84	1.3	2
TriP <sub>96</sub>	96	1.3	48	1.4	2
TriP <sub>63</sub>	63	1.3	32	1.4	5
TriP <sub>36</sub>	36	1.3	33	1.3	7
TriP <sub>16</sub>	16	1.4	16	1.4	7

# Polymer Mechanochemistry

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## Mechanically Throwing a Reaction into Reverse



# Polymer Mechanochemistry

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**This article has been retracted**  
**An Expression of Concern has been published for this article**  
*Science* 16 September 2011:  
Vol. 333 no. 6049 pp. 1606-1609  
DOI: 10.1126/science.1207934

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**Unclicking the Click: Mechanically Facilitated 1,3-Dipolar Cycloreversions**  
Johnathan N. Brantley, Kelly M. Wiggins, Christopher W. Bielawski<sup>\*</sup>  
 Author Affiliations  
 <sup>\*</sup>To whom correspondence should be addressed. E-mail: [bielawski@cm.utexas.edu](mailto:bielawski@cm.utexas.edu)

ABSTRACT

The specific targeting of covalent bonds in a local, anisotropic fashion using mechanical methods offers useful opportunities to direct chemical reactivity down otherwise prohibitive pathways. Here, we report that embedding the highly inert 1,2,3-triazole moiety (which is often prepared using the canonical "click" coupling of azides and alkynes) within a poly(methyl acrylate) chain renders it susceptible to ultrasound-induced cycloreversion, as confirmed by comprehensive spectroscopic and chemical analyses. Such reactivity offers the opportunity to develop triazoles as mechanically labile protecting groups or for use in readily accessible materials that respond to mechanical force.

The 1,3-dipolar cycloaddition of azide and alkyne moieties (1, 2), which allows access to a variety of substituted triazoles, is included under the umbrella of "click" chemistry. This reaction has found broad applicability over the past decade because it exhibits rapid kinetics under mild conditions, high functional group and solvent tolerance, and good atom economy, and it has a propensity to generate relatively chemically inert and thermally stable products. In addition to finding compelling use in molecular and polymer functionalizations, this coupling motif has been applied to robust, chemically orthogonal ligations for the study of biological systems (3–11). However, a consequence of the high kinetic stability of these triazole products is that simple chemical or thermal treatments capable of cleanly reverting the coupling reactions into their

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**Mechanically Throwing a Reaction into Reverse**  
Frank A. Leibfarth, Craig J. Hawker  
*Science* 16 September 2011: 1582-1583.

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# Polymer Mechanochemistry

The screenshot shows the C&EN (Chemical & Engineering News) website. The main article is titled "Doubts About Unclick Reaction" by Bethany Halford. The article discusses a 2011 paper in *Science* by Christopher W. Bielawski, Johnathan N. Brantley, and Kelly M. Wiggins, which reported on a mechanically facilitated 1,3-dipolar cycloversion. The article mentions that the authors of the *Science* paper were questioned about the reliability of their data, and that a correction was submitted. The article also includes a quote from the *Science* editor-in-chief, Marcia McNutt, and a quote from Bielawski. The article is categorized under "Mechanochemistry" and "Unclick Chemistry".

## Retraction Watch

Tracking retractions as a wind

### Chemistry paper in *Science* earns expression of concern for unreliable data

with 15 comments

A 2011 paper in *Science* has been subjected to an expression of concern and has led to an investigation by the Texas university where the work was done.

Here's the [expression of concern](#), signed by *Science* editor in chief Marcia McNutt (and paywalled):

“In the 16 September 2011 issue, *Science* published the Report “Unclicking the click: Mechanically facilitated 1,3-dipolar cycloversions” by J. N. Brantley *et al.* ([1](#)).

After concerns were raised in an e-mail to the editors from a reader, the corresponding author supervised a comprehensive evaluation of all data presented in the original manuscript by tracing all figures back to their raw data files. In over 50% of the figure parts, the authors deemed the data unreliable due to uncertainty regarding the origin of data or the manner in which the data were processed. A confidential investigation that is relevant to these concerns is currently being conducted by the University of Texas at Austin.

Pending the conclusion of the investigation, *Science* is publishing this Editorial Expression of Concern to alert our readers to the fact that serious questions have been raised about the validity of findings in the Brantley *et al.* paper.

*Chemical & Engineering News* [has some details](#) after talking to corresponding author [Christopher W. Bielawski](#):

“Bielawski tells C&EN that a former group member, whom he declined to identify, came forward and admitted to manipulating data in the *Science* paper. Bielawski says that his lab “successfully repeated the experiments in question and found that the conclusions of the report were unchanged.” He has submitted a correction to *Science* to address the concerns. Neither Brantley nor Wiggins could be reached for comment.

The paper has been cited 75 times, according to Thomson Scientific's Web of Knowledge.

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Written by Ivan Oransky  
June 27th, 2014 at 8:30 am

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« Republished Seralini GMO-rat study was not peer-reviewed, says editor  
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# Polymer Mechanochemistry

## Retraction Watch

Tracking retractions as a window into the scientific process

### Archive for the 'christopher bielawski' Category

#### Bielawski and Wiggins retraction count grows to six

with 3 comments

A group of chemists whose work was investigated by the University of Texas–Austin has had another paper retracted, this one of a *Chemical Science* study [previously subjected to an Expression of Concern](#).

That makes six retractions for [Christopher Bielawski and Kelly Wiggins](#).

Here's the [notice](#) for "Homonuclear bond activation using a stable N,N'-diamidocarbene", signed by all three authors of the paper: [Read the rest of this entry](#) »



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Written by Ivan Oransky  
April 22nd, 2015 at 9:30 am

Posted in [chemical science](#), [chemistry retractions](#), [christopher bielawski](#), [faked data](#), [freely available](#), [misconduct investigations](#), [rsc publishing](#), [united states](#)

#### Bielawski and Wiggins up retraction count to five with three in JACS

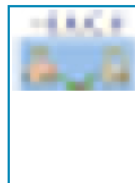
with 6 comments

The *Journal of the American Chemical Society* (JACS) has retracted three articles that had [earned expressions of concern](#) by chemistry researchers who were under investigation at the University of Texas, Austin.

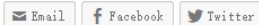
[Kelly Wiggins](#) and [Christopher Bielawski](#) have already received two other retractions and several EoCs.

The newly retracted articles have each been cited more than 50 times, according to Thomson Scientific's Web of Knowledge.

The three papers are: [Read the rest of this entry](#) »



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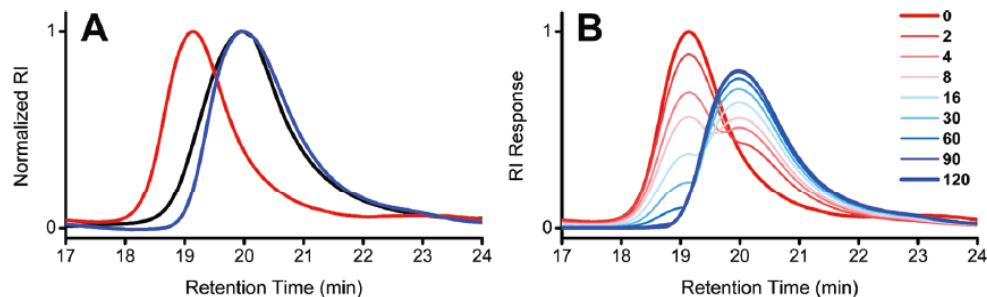
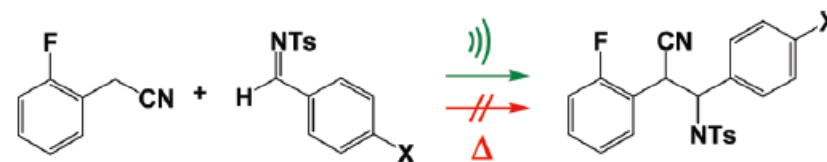
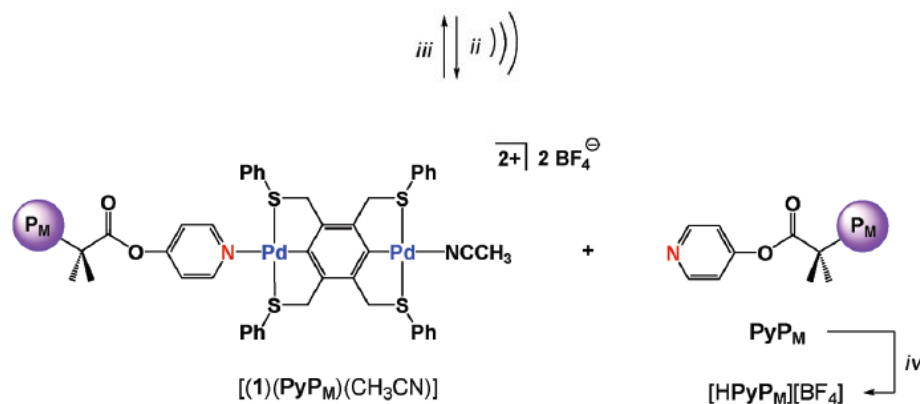
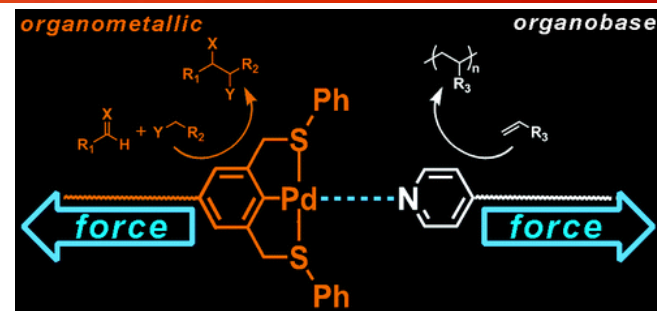
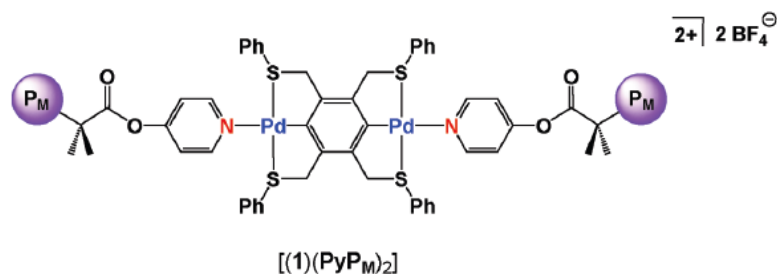
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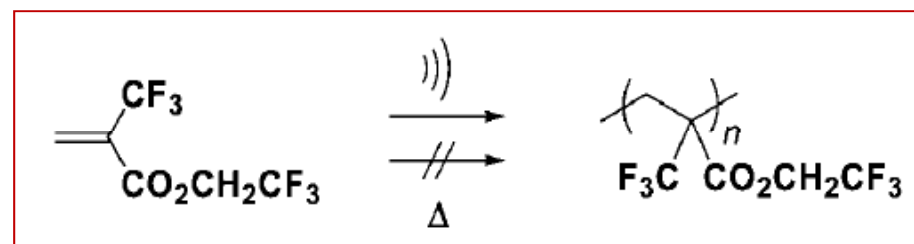
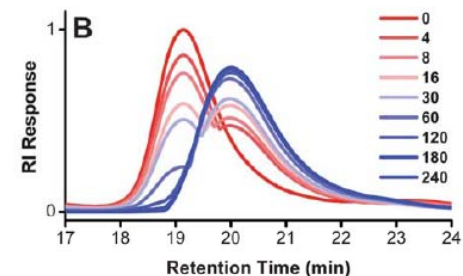
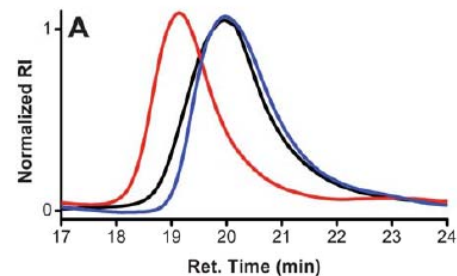
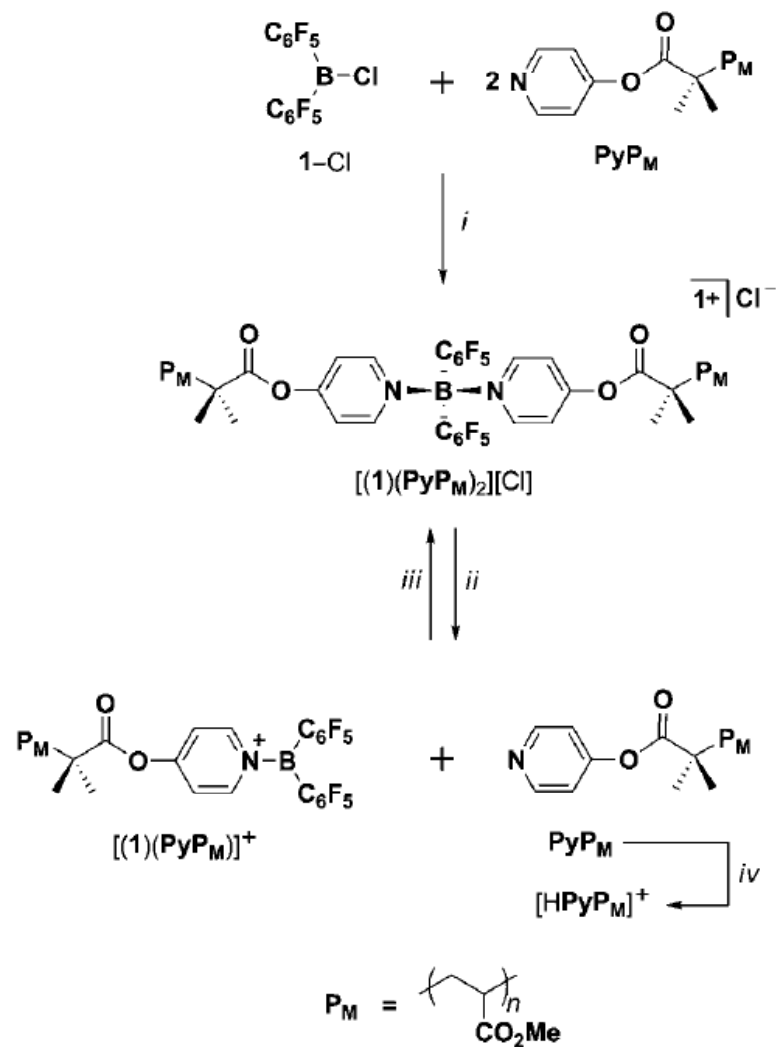
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# Polymer Mechanochemistry



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This paper was retracted on March 11, 2015 (*J. Am. Chem. Soc.* 2015, 137, DOI: 10.1021/jacs.5b01990).

## Mechanically Facilitated Retro [4 + 2] Cycloadditions

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Supporting Information

**ABSTRACT:** Poly(methyl acrylate)s (PMAs) of varying molecular weights were grown from a [4 + 2] cycloaddition adduct of maleimide with furan containing two polymerization initiators. Subjecting the corresponding PMA (>30 kDa) chains to ultrasound at 0 °C resulted in a retro [4 + 2] cycloaddition reaction, as observed by gel permeation chromatography (GPC) and UV–vis spectroscopy, as well as labeling of the liberated maleimide and furan moieties with appropriate chromophores featuring complementary functional groups. Similar results were obtained by sonicating analogous polymers that were grown from a thermally robust [4 + 2] cycloaddition adduct of maleimide with anthracene. The generation of anthracenyl species from these latter adducts allowed for the rate of the corresponding mechanically activated retro [4 + 2] cycloaddition reaction to be measured. No reduction in the number average molecular weight ( $M_n$ ) or liberation of the maleimide, furan, or anthracene moieties was observed (i) for polymers containing the cycloaddition adducts with  $M_n < 20$  kDa, (ii) for high molecular weight PMAs ( $M_n > 60$  kDa) featuring terminal cycloaddition adducts, or (iii) when the cycloaddition adducts were not covalently linked to a high molecular weight PMA. Collectively, these results support the notion that the aforementioned retro [4 + 2] cycloaddition processes were derived from a vectorially opposed mechanical force applied to adducts embedded within the polymer chains.

## INTRODUCTION

Ultrasound has recently been demonstrated as a powerful technique for directing bond dissociation<sup>1</sup> and isomerization<sup>2</sup> reactions through high energy pathways. For example, Moore has shown that sonicating solutions of benzocyclobutenes appropriately outfitted with polymer chains facilitates thermally and photochemically disallowed electrocyclic ring-opening reactions.<sup>2a</sup> In these enabling processes, the ultrasound induces the formation and growth of microbubbles, which later collapse. The dissolved polymer segments closest to these collapsing bubbles move at higher velocities than those that are more distant, causing the polymer chain to elongate.<sup>3</sup> For polymers of sufficiently high molecular weight, the tension formed can selectively activate certain chemical processes, often at centrally located sites where the force is maximized. Ultimately, this process translates mechanical force into unique chemical reactivity.<sup>1,2,4</sup> Despite the extreme temperatures and pressures that may form in solutions under sonication, extensive control experiments have supported the notion that the aforementioned activation processes are derived from mechanical force.<sup>5</sup>

Although ultrasound has been used to facilitate other periodic rearrangements, including spirocyclic-to-merocyanine isomerizations<sup>6</sup> and dihydrocyclopropane ring-openings,<sup>2,22</sup> we report herein the first use of mechanical force to facilitate retro [4 + 2] reactions.<sup>6</sup> Beyond establishing new tools for controlling molecular processes with high activation barriers and fundamentally new reactivities, mechanical methods for forming reactive cycloaddition adducts are expected to find applications in self-healing materials that use the physical processes associated with the formation of damage to initiate essential repair processes.<sup>7</sup>

Diels and Alder disclosed the first cycloaddition reaction in 1928,<sup>8</sup> modifications of which have subsequently found extraordinary utility in synthetic organic chemistry for the formation of carbo- and heterocycles.<sup>9</sup> Many cycloaddition reactions are reversible when heated, a feature that has been used to generate reactive species *in situ*.<sup>10</sup> However, such retro cycloadditions, especially those which involve carbocycles, typically require elevated temperatures. While the applied heat often results in undesired side reactions, frequently to the detriment of the desired reactivity,<sup>11</sup> Barney Kowalik has elegantly demonstrated<sup>12</sup> that the activation temperature may be finely tuned through structural modifications. We envisioned overcoming prohibitively high thermal barriers associated with retro cycloadditions using mechanical force. Our hypothesis was that the application of ultrasound-induced tensile stress to polymer chains properly attached to a cycloaddition adduct should destabilize the ground state of the system or lower the activation barrier, facilitating the entropy-driven cycloreversion process at relatively low temperatures. To test our hypothesis, a variety of retro [4 + 2] cycloaddition reactions involving derivatives of two dienes (furan and anthracene) and a common dienophile (maleimide) were investigated.

## RESULTS AND DISCUSSION

Initial efforts were directed toward polymerizing methyl acrylate (MA) from the known<sup>13</sup> oxanorbornene-based, difunctional initiator DAI<sup>14</sup> using Cu-mediated single-electron-transfer living

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## Mechanical Reconfiguration of Stereoisomers

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Atropisomers are chiral molecules whose asymmetric structures are derived from hindered rotations about sterically congested bonds.<sup>1</sup> They have found utility in a broad range of applications, including asymmetric synthesis and catalysis, supramolecular and polymer chemistry, and chemical sensors.<sup>2</sup> Certain atropisomers, such as 1,1'-bi-2-naphthol (binol),<sup>3,4</sup> 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (binap),<sup>5,6</sup> and their derivatives, have isomerization barriers that typically exceed 30 kcal mol<sup>-1</sup> and therefore do not readily undergo thermal equilibration.<sup>1–3</sup> Although these high energy barriers facilitate chiral resolution, stereoselective syntheses are currently required to access enantiopure forms of these molecules in the most efficient manner.<sup>7</sup> In view of the recent advances in mechanochemistry,<sup>8</sup> in which known or conceived reaction pathways may be activated or even biased to proceed in atypical directions,<sup>9</sup> we demonstrate here that thermally restricted isomerization barriers can be surmounted by force, thus establishing a new method for reconfiguring stereoisomers.

As shown in Scheme 1, we reasoned that planar intermediates should be accessible by applying a tensile force to binol derivatives outfitted with polymer chains of sufficient molecular weight, ultimately converting one enantiomer to the other. To test this hypothesis, poly(methyl acrylate) (PMA) was grown from the bifunctional initiator (S)-1,1'-binaphthyl-2,2'-bis(2-bromoisobutyrate) (S)<sub>2</sub> using Cu-mediated single-electron-transfer living radical polymerization (SET LRP).<sup>10</sup> (Methyl acrylate)/[S]<sub>2</sub> = 1:160 in dimethyl sulfoxide (DMSO) followed by precipitation from CH<sub>2</sub>OH.

The resulting polymer (S)<sub>2</sub> exhibited a number-average molecular weight ( $M_n$ ) of 98.7 kDa and a polydispersity index (PDI) of 1.03, as determined by gel-permeation chromatography (GPC).<sup>10</sup> After the optical profile of this material was measured using circular dichroism (CD) and UV–vis spectroscopy, (S)<sub>2</sub> was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (0.75 mg/mL) and subjected to sonication<sup>11</sup> in a Suisick cell<sup>12</sup> placed in an ice bath.<sup>13</sup> As shown in Figure 1, CD analysis of aliquots<sup>14</sup> removed periodically from this solution revealed a smooth decrease in signal intensity over time. Comparison of the intensity of the signal measured at 230 nm after 24 h of sonication with that of the pre-sonicated (S)<sub>2</sub> revealed that >95% of the material had undergone racemization.<sup>15</sup> Although the polydispersity of the post-sonicated material was slightly higher (PDI = 1.13) than that of the pre-sonicated (S)<sub>2</sub> (97.2 kDa) was comparable. Likewise, the UV–vis and <sup>1</sup>H NMR spectra of the pre- and post-sonicated materials revealed no significant differences (see Figures S1 and S2 in the Supporting Information). Similar results were obtained when the aforementioned experiments were performed with (R)<sub>2</sub>, a polymer prepared from methyl acrylate and (R)-1,1'-binaphthyl-2,2'-bis(2-bromoisobutyrate) (R)<sub>2</sub> (see Figure 1 and Table 1).

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Scheme 1. Mechanically Facilitated Reconfiguration of Stereoisomers

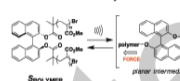


Table 1. Selected Molecular Weight and PDI Data

	pre-sonication	
polymer <sup>a</sup>	$M_n$ (10 <sup>3</sup> Da)	PDI <sup>b</sup>
(S) <sub>2</sub>	98.7	1.03
(R) <sub>2</sub>	98.4	1.07
(S) <sub>2</sub>	48.9	1.16
(R) <sub>2</sub>	26.5	1.09
(S) <sub>2</sub>	9.66	1.03

<sup>a</sup> All of the materials were dissolved in CH<sub>2</sub>Cl<sub>2</sub> and subjected to sonication for 24 h. <sup>b</sup> The 88–99% isolated yield from methyl acrylate. <sup>c</sup> Nonracemic: the letter indicates the o-embedded in the polymer chain and the s-polymer's approximate molecular weight number-average molecular weight of the initiator (PDI) was calculated using the eq  $M_w$  is the weight-average molecular weight determined using GPC.<sup>10</sup> The standard measurements were calculated to be < 0.05.

To support the observation of a racemization, a series of control experiments were performed. A solution of (S)<sub>2</sub> in Ph<sub>2</sub>O (bp = 25 °C for 72 h) showed no decrease in its CD signal. This result is consistent with the

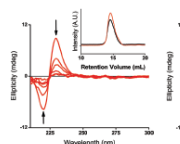


Figure 1. CD spectra of CH<sub>2</sub>Cl<sub>2</sub> solution (0.1 mg/mL) as functions of time under the influence of sonication. The x-axis is Wavelength (nm) and the y-axis is Ellipticity (mdeg). The arrows indicate the direction of change over time. The chromatograms of (S)<sub>2</sub> and (R)<sub>2</sub> before (black) and after sonication (red).

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## Mechanical Activation of Catalysts for C–C Bond Forming and Anionic Polymerization Reactions from a Single Macromolecular Reagent

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Coupling of pyridine-capped poly(methyl acrylate)s, **PyPMA** (where M corresponds to the number-average molecular weight in kDa), to the SCS-cyclometallated palladium complex [(1)(CH<sub>3</sub>CN)<sub>2</sub>] afforded **PyPMA** polymers [(1)(PyPMA)] with a concomitant doubling in molecular weight. Ultrasonication of staining [(1)(PyPMA)] effected the mechanical scission of a palladium–pyridine bond, where **PyPMA** was trapped with excess HBF<sub>4</sub> as the corresponding pyridinium salt, harnessed to effect reductive deprotonation of a colorimetric indicator, or used to catalyze the anionic polymerization methyl-2,2,2-trifluoroethyl acrylate. The mechanically induced chain scission also unmasked active palladium species which was used to facilitate carbon–carbon bond formation between de- and *tert*-butoxy imines. Spectroscopic and macromolecular analyses as well as a series of experiments demonstrated that the aforementioned structural changes were derived from mechanical forces originating from ultrasound-induced dissociation of the polymer chains connected to the active Pd complexes.

Recently received significant attention for chemical structures, properties, and materials via mechanical force, a process referred to as mechanochemistry.<sup>1–5</sup> During the application of tension to polymers, bubbles are created which induces velocity gradients and elicits polymer chains.<sup>6</sup> For macromolecular length, this mechanical force may ultimately enable access to otherwise inaccessible sites.<sup>7</sup> There has been substantial interest in activated catalysts. For example,

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recent efforts by Sijbesma have highlighted the promise for using sonomechanically induced changes in polymer structure to drive catalytic olefin metathesis and transesterification reactions.<sup>6</sup> More broadly, mechanochemical catalysts<sup>4b</sup> are anticipated to uncover fundamentally new chemistries, enable transformations not currently feasible,<sup>7</sup> and endow stimulus-responsive materials with novel functions and applications.<sup>8</sup> Achieving many of these goals, however, hinges on using mechanical force to access new reaction pathways, particularly those that are thermally inaccessible or prohibited.

To guide the design of such mechanically activated catalysts, we first considered the components necessary for a mechanochemical catalyst: (i) a mechanochemical catalyst, which undergoes an electronic or structural change in response to mechanical force and (ii) an actuator, which translates exogenously supplied energy into useful mechanical force at the mechanochemical site.<sup>9</sup> Polymers have been extensively employed as actuators, given that they respond to mechanical stress at both the macro- and microscopic level and can be covalently linked to small

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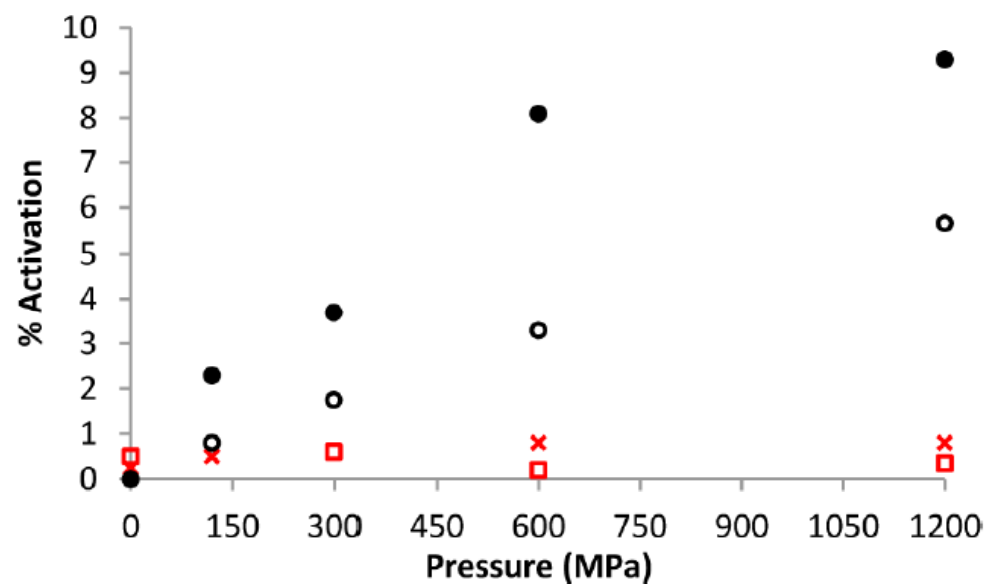
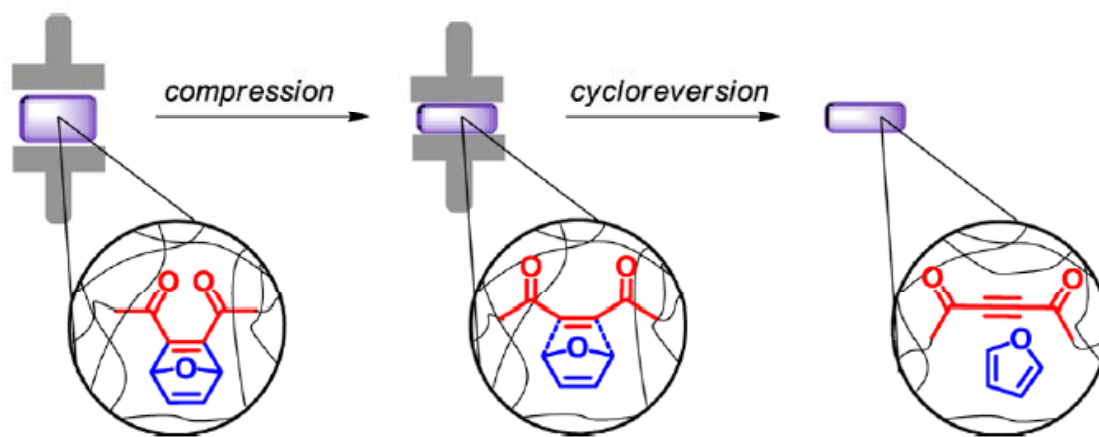
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# Flex Induced Polymer Mechanochemistry



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