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Mechanochemically Gated Photoswitching: Expanding the Scope of Polymer Mechanochromism
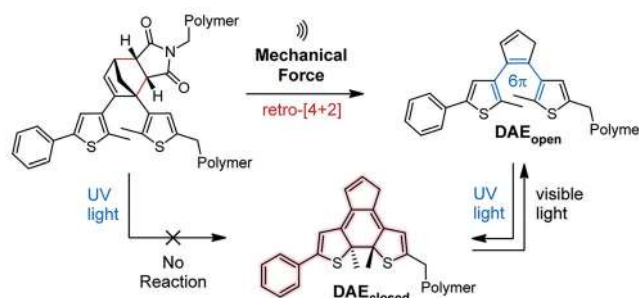
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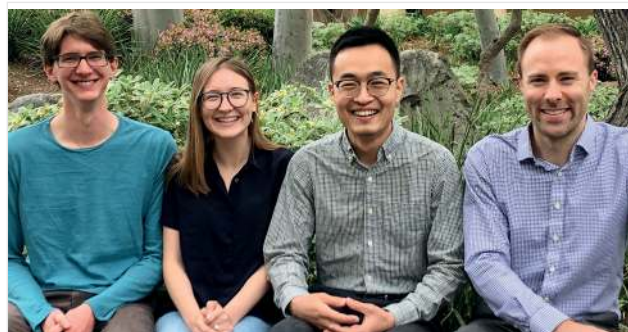mrobb@caltech.edu

Abstract Mechanophores are molecules that undergo productive, co-valent chemical transformations in response to mechanical force. Over the last decade, a variety of mechanochromic mechanophores have been developed that enable the direct visualization of stress in poly-mers and polymeric materials through changes in color and chemilumi-nescence. The recent introduction of mechanochemically gated photo-switching extends the repertoire of polymer mechanochromism by decoupling the mechanical activation from the visible response, en-abling the mechanical history of polymers to be recorded and read on-demand using light. Here, we discuss advances in mechanochromic mechanophores and present our design of a cyclopentadiene–maleim-ide Diels–Alder adduct that undergoes a force-induced retro-[4+2] cycloaddition reaction to reveal a latent diarylethene photoswitch. Fol-lowing mechanical activation, UV light converts the colorless diaryl-ethene molecule into the colored isomer via a 6π-electrocyclic ring-closing reaction. Mechanically gated photoswitching expands on the fruitful developments in mechanochromic polymers and provides a promising platform for further innovation in materials applications in-cluding stress sensing, patterning, and information storage.

Ross Barber (left) received his BA in Chemistry from Johns Hopkins University, where he performed research on fluorination methods un-der the guidance of Prof. Thomas Lectka. After graduating in 2015, he moved to Worcester, Massachusetts to join the team at Microbiotix, Inc., developing small-molecule antibiotics and antivirals. In 2017, he began his doctoral studies at Caltech, where he investigates polymer mechanochemistry under the guidance of Prof. Maxwell Robb.
Molly McFadden (second from the left) earned her BSc in biochemistry from Indiana University. There, she worked in the laboratories of Dr. Laura Brown and Prof. Kevin Brown on the synthesis of organic small molecules. After graduating in 2017, Molly began her graduate career at Caltech. Her PhD research in the Robb group focuses on the develop-ment of mechanochromic molecules.
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Maxwell Robb (right) was born and raised in Colorado. He obtained his BSc in chemistry in 2009 from the Colorado School of Mines under the mentorship of Prof. Daniel M. Knauss. Max carried out his PhD studies in the laboratories of Prof. Craig J. Hawker at the University of California, Santa Barbara, where his research focused broadly on the synthesis of functional organic materials. After graduating in 2014, he conducted postdoctoral research as a Beckman Institute Postdoctoral Fellow with Prof. Jeffrey S. Moore at the University of Illinois, Urbana-Champaign. Max joined the Division of Chemistry and Chemical Engineering at Caltech as an assistant professor of chemistry in September 2017.

1   Introduction to Polymer Mechanochemistry

The burgeoning field of polymer mechanochemistry ex-plores the use of mechanical force to promote specific, and sometimes unusual, chemical reactions.[1,2] Polymer chains transduce external forces to particular covalent bonds in
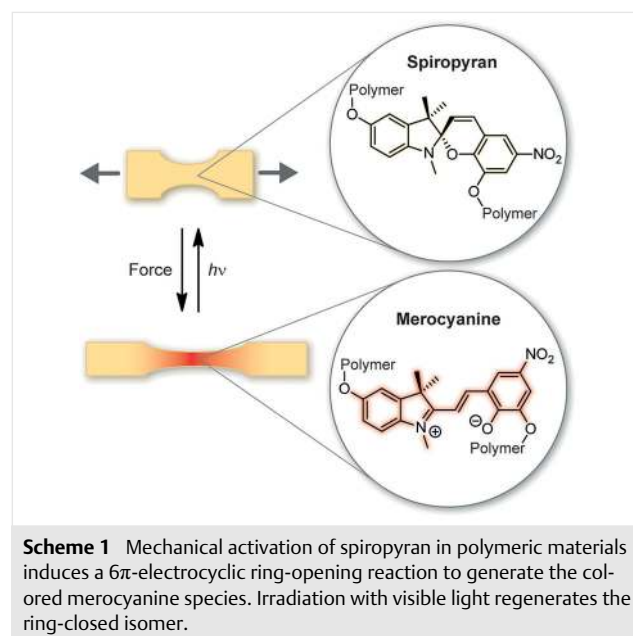
mechanically sensitive molecules known as mechanophores, resulting in productive chemical transformations.[3] Since the seminal report on site-specific activation of azo-linked polymers by Moore and coworkers in 2005,[4] the field has evolved to identify an exponentially growing number of mechanophores that display a wide variety of functionality. Force-driven reactivity includes activation of catalysts,[5] triggered depolymerization,[6] generation of reactive functional groups,[7–10] switching of electrical conductivity,[11] chemiluminescence,[12] and changes in color.[13–23] Mechanical force has also been shown to promote formally forbidden pericyclic reactions such as the disrotatory electrocyclic ring-opening reaction of *cis*-1,2-disubstituted benzocyclobutene[24,25] and the conrotatory ring-opening reactions of gem-dihalocyclopropanes.[26,27] Computational studies have established that the unique reactivity of mechanophores originates from a distortion of the potential energy surface under large forces, which fundamentally changes the reaction landscape and leads to different reaction pathways.[28–30]

2 Mechanochromic Reactions for Stress Sensing

Mechanophores that produce a visible change in color upon mechanical activation are particularly appealing targets for stress sensing. At the molecular scale, mechanical stress causes degradation typically characterized by homolytic bond scission along polymer backbones. As individual chains rupture, the mechanical integrity of a material diminishes and the likelihood of failure increases. Mechanochromic molecular force probes provide a convenient approach for visually detecting critical stress and/or strain in polymeric materials. Early reports of molecular strain sensors relied on changes in the fluorescent properties of dye aggregates in polymer blends;[31] however, the development of mechanophores has provided a platform for precisely tailoring the stress-responsive properties of materials within the framework of synthetic and physical organic chemistry.

The mechanically activated ring-opening reaction of spiropyran is one of the most ubiquitous transformations in the field of polymer mechanochemistry. Spiropyran is a well-known photochromic molecule that undergoes a 6π-electrocyclic ring-opening reaction upon irradiation with UV light to generate a highly colored merocyanine dye. In 2007, Moore and coworkers discovered that this same electrocyclic ring-opening reaction is promoted by mechanical force applied across the spiro C–O bond.[13] The mechanochromic transformation of spiropyran was originally demonstrated in solution by sonicating poly(methyl acrylate) (PMA) polymers containing a single spiropyran mechanophore located near the center of the chains, where sonication-induced elongational forces are maximized.[2] Later, in 2009, Sottos and coworkers demonstrated that the mechano-

chemical activation of spiropyran covalently incorporated into PMA and poly(methyl methacrylate) (PMMA) could be achieved in bulk polymeric materials (Scheme 1).[14] An intense color change corresponding to generation of the ring-opened merocyanine dye was observed in the materials under tensile loading, establishing a promising new strategy for stress sensing in polymers. Control experiments confirmed that the reactivity was mechanical in origin and the merocyanine dye was shown to convert back into the spiropyran form under visible light after stress relaxation.

Scheme 1 Mechanical activation of spiropyran in polymeric materials induces a 6π-electrocyclic ring-opening reaction to generate the colored merocyanine species. Irradiation with visible light regenerates the ring-closed isomer.

In the decade following the discoveries of spiropyran mechanochromism in polymers, a number of other mechanophores that display mechanochromic properties have been developed. In addition to ring-opening and pericyclic reactions, Otsuka and coworkers have pioneered an alternative strategy to achieve mechanochromic materials that relies on homolytic dissociation of mechanophores into a pair of stable, colored free radicals under force. The mechanochromism of diarylbibenzofuranone (DABBF) was first demonstrated in polyurethane gels by freezing-induced mechanical activation (Scheme 2).[17] Formation of the blue-colored arylbenzofuranone radicals was confirmed using EPR spectroscopy. Low temperatures were required to suppress radical recombination. Subsequent research demonstrated that mechanochemical activation of DABBF could be achieved in elastomeric linear polyurethanes under uniaxial tension for colorimetric stress sensing.[32] The same group has also identified tetraarylsuccinonitrile (TASN)[33] and diarylbibenzothiophenone (DABBT)[34] as mechanophores capable of producing pink- and green-colored radical fragments, respectively. The intrinsic thermal instability of these radical-type dynamic covalent molecules, however, limits their
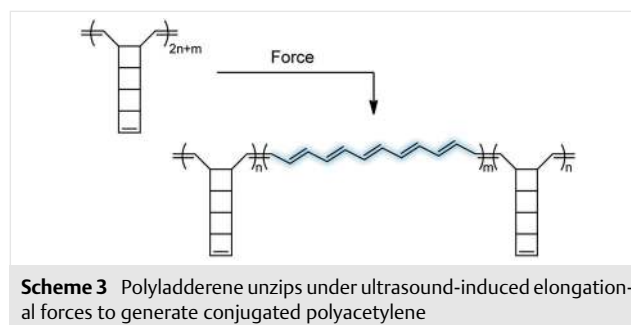
range of applications. To overcome this limitation, a thermally stable difluorenylsuccinonitrile (DFSN) mechanophore was recently introduced[35] that extends the utility of radical-type mechanochromic molecules and, importantly, enables their incorporation into well-defined materials prepared using controlled radical polymerization techniques.
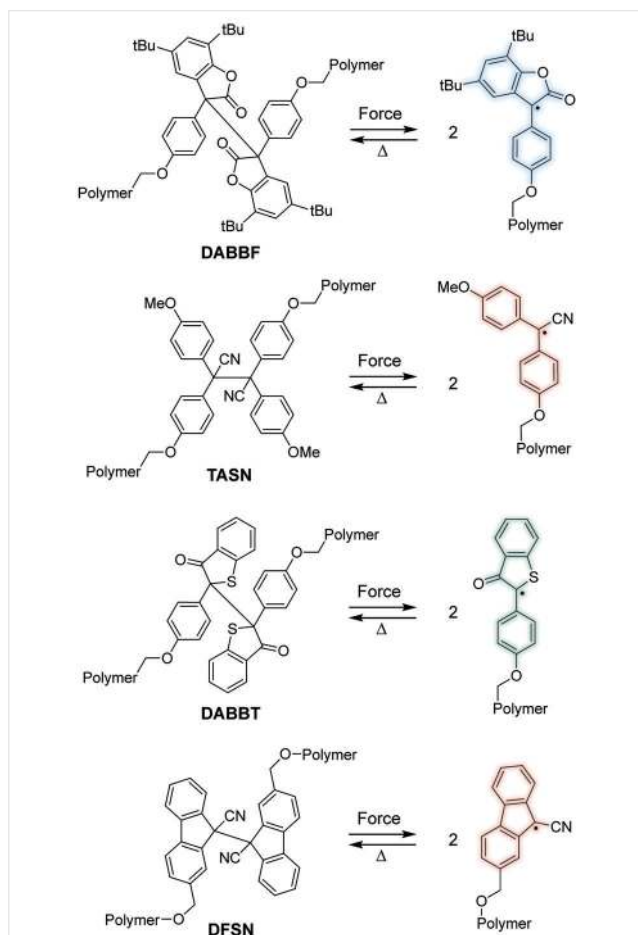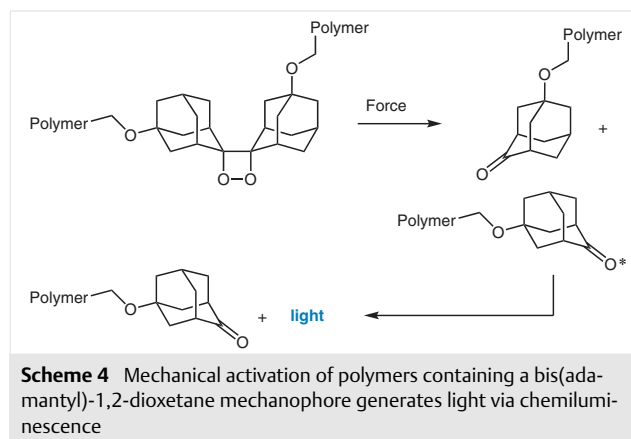

Scheme 2 Force-induced homolytic cleavage of dynamic-covalent mechanophores generates colored, stable radical fragments. The radical species thermally recombine to regenerate the mechanophores.

An unprecedented mechanochromic transformation was introduced in 2017 by Xia, Burns, Martinez, and coworkers with the demonstration of polyladderene mechanochemistry.[11] Mechanochemical unzipping of polyladderene in solution using ultrasound was revealed to generate semiconducting polyacetylene (Scheme 3). The initially colorless insulating polymer developed a deep purple color characteristic of polyacetylene with highly extended conjugation. Interestingly, resonance Raman and infrared spectroscopy suggested that mechanochemical activation of polyladderene forms exclusively *trans*-polyacetylene, requiring that a *cis*-to-*trans* isomerization of the terminal olefins also occurs simultaneously during chain extension. Calculations of the force-modified potential energy surface

suggested that the mechanochemical reaction occurs via a multistep mechanism involving two diradical transition-state structures that becomes barrierless above 3.0 nN of force.

Scheme 3 Polyladderene unzips under ultrasound-induced elongational forces to generate conjugated polyacetylene

A seminal report by Sijbesma and coworkers in 2012 described the mechanochemically induced chemiluminescent reaction of a 1,2-dioxetane mechanophore (Scheme 4).[12] Dioxetane and its derivatives are known to emit light in response to chemical or thermal stimuli by a reaction that generates a short-lived electronically excited ketone, which relaxes to the ground state through a radiative process. Mechanochemical activation of a bis(adamantyl)-1,2-dioxetane mechanophore covalently linked to PMA generated chemiluminescence upon ultrasonication. This effect was extended to the solid state by activating cross-linked PMA under tension, and the color of emission was tuned via energy transfer to different fluorescent dye molecules incorporated into the polymeric material. While not technically a mechanochromic transformation, chemiluminescence provides an advantage in stress-sensing applications due to the absence of background signal, enabling highly sensitive detection of polymer-chain-scission events with excellent temporal and spatial resolution.[36–38] Nevertheless, the transience of chemiluminescence emission precludes any record of the stress history of materials. It is interesting to note that bis(adamantyl)-1,2-dioxetane remains the only reported chemiluminescent mechanophore.

Scheme 4 Mechanical activation of polymers containing a bis(adamantyl)-1,2-dioxetane mechanophore generates light via chemiluminescence

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3 Regiochemical Effects on Mechanophore Activation

Regiochemistry has been implicated as a critical structural parameter that influences mechanochemical reactivity. In 2016, Moore and coworkers demonstrated the regioisomer-specific mechanochromism of naphthopyran, which undergoes a 6π-electrocyclic ring-opening reaction under force to generate a yellow merocyanine dye (Scheme 5, a).[19] Three naphthopyran regioisomers were prepared, each having a different polymer attachment point on the naphthalene ring. Remarkably, only the naphthopyran molecule substituted at the 5-position exhibited mechanochromic behavior in cross-linked polydimethylsiloxane (PDMS) elastomers under tension. This trend was also supported by density functional theory (DFT) calculations. The mechanochemical reactivity of naphthopyran substituted at the 5-position was attributed to more efficient chemomechanical coupling due to better alignment of the C–O pyran bond with the direction of external force applied along the reaction coordinate. The angle between the C–O pyran bond and the external force vector at maximum extension was calculated to be a relatively narrow 31°, while the angle was significantly wider for the other two unreactive naphthopyran regioisomers (Scheme 5, b). It was proposed that mechanical activation of a specific covalent bond is achieved only when it is sufficiently aligned with the force vector, introducing a useful conceptual framework for the design of new mechanophores.

Another important class of mechanochemical transformations are retro-[4+2] cycloaddition reactions, which have been demonstrated for anthracene–maleimide,[39–41] anthracene–triazolinedione,[15] furan–acetylene,[42] and furan–maleimide[43–46] Diels–Alder adducts. The geometrical analysis used for naphthopyran was extended to furan–maleimide adducts in a key paper by Stevenson and De Bo in 2017, which further elucidated the effects of regiochemistry and stereochemistry on mechanochemical reactivity (Figure 1).[46] Four different isomers, constructed with an *endo* or *exo* configuration and *proximal* or *distal* pulling geometry, were incorporated into PMA polymer chains, and their mechanochemical activity was investigated in solution using ultrasonication. In contrast to thermal activation in which *endo* and *exo* stereochemistry primarily dictates the relative reactivity, the regiochemistry of polymer attachment to the furan–maleimide adducts was determined to be crucial to the mechanochemical activity. Adducts with *endo* and *exo* stereochemistry bearing a pulling position α (*proximal*) to the diene/maleimide junction reacted faster than the *distal-endo* adduct with one of the polymer chains attached at the β position. Interestingly, the *distal-exo* adduct was mechanochemically unreactive due to weak che-
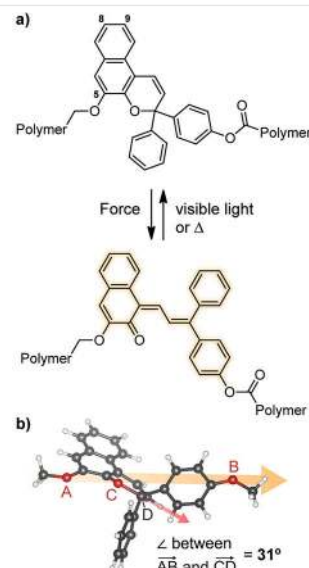
Scheme 5 a) The naphthopyran regioisomer substituted at the 5-position undergoes a mechanically facilitated 6π-electrocyclic ring-opening reaction in polymeric materials to produce a colored merocyanine dye, while regioisomers with polymers attached at the 8- and 9-position are mechanochemically inert. b) Regioisomer-specific mechanochromism is attributed to better alignment of the force vector with the C–O pyran bond along the reaction coordinate. Adapted with permission.[19] Copyright 2016, American Chemical Society.
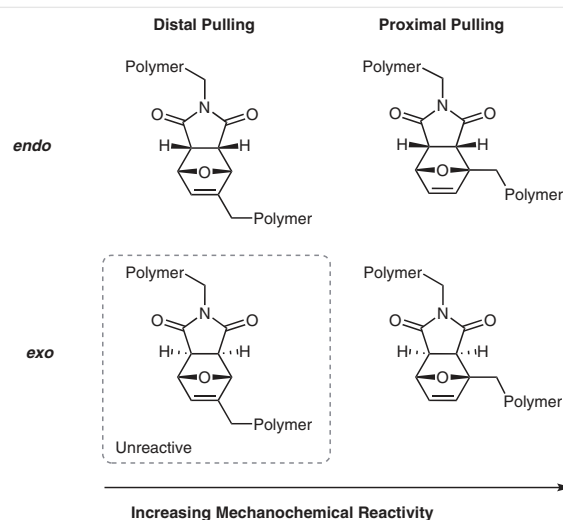
Figure 1 Furan–maleimide adducts with an *endo* or *exo* configuration and *distal* or *proximal* polymer attachment geometry display different rates of mechanochemical activation using ultrasound. In contrast to the thermal reactivity, the regiochemistry of polymer attachment critically influences mechanochemical activity. The *distal-exo* adduct is mechanochemically inert due to poor alignment of the scissile bonds with the direction of applied force.

momechanical coupling, which arises from poor geometrical alignment between the scissile bonds and the external force vector.

4 Mechanochemically Gated Photoswitching

The mechanochromic mechanophores presented previously undergo force-induced covalent-bond transformations that lead directly to a visible color change or chemiluminescence, which reports on critical stress and/or strain in materials and signals potential damage caused by polymer-chain scission. Despite their utility, mechanochromic transformations are often transient, which limits some applications. For example, the ring-opening reactions of spiropyran and naphthopyran are reversible under visible light; radical-type mechanophores undergo radical recombination; and the oxidative instability of polyacetylene leads to degradation. The development of alternative strategies for visible stress sensing in which mechanical activation is decoupled from the visible response would allow the mechanical history of a material to be more permanently preserved for future detection.

Chemical reactivity can be gated in certain systems, wherein desired chemical changes occur only after specific regulating events. In 2016, Craig and Boulatov reported the mechanically gated reaction of a molecule containing two distinct mechanochemically active groups that underwent sequential activation in response to mechanical force.[47] In this example, activation of the second mechanophore unit was gated by the first. The gating concept is conventionally applied to photoswitching reactions, where light either triggers a chemical change to reveal a new structure with unique reactivity, or a chemical reaction generates a photochemically active motif. Otsuka and coworkers have elegantly expanded the former concept by establishing the photochemical modulation of thermally[48] and mechanochemically induced polymer-chain scission.[49]

A notable early example of photogated reactivity was reported by Branda and coworkers in which the photoactivation of a diarylethene (DAE) molecular switch regulated a retro-Diels–Alder reaction for light-triggered small-molecule release.[50] DAE photoswitches undergo 6π-electrocyclic ring-closing reactions under UV irradiation to generate intensely colored conjugated species, while the colorless ring-opened form is regenerated using visible light. The authors leveraged the reorganization of π bonds that accompanies the electrocyclic ring-closing reaction of DAEs to photochemically lock a reversible dithienylfulvene–dicyanofumarate Diels–Alder adduct in a thermally stable state (Scheme 6). Upon irradiation of the ring-closed DAE photoswitch with visible light, the two exocyclic double bonds isomerized to regenerate the dithienylethene architecture, facilitating the retro-Diels–Alder reaction that proceeded at room temperature to release the dienophile.
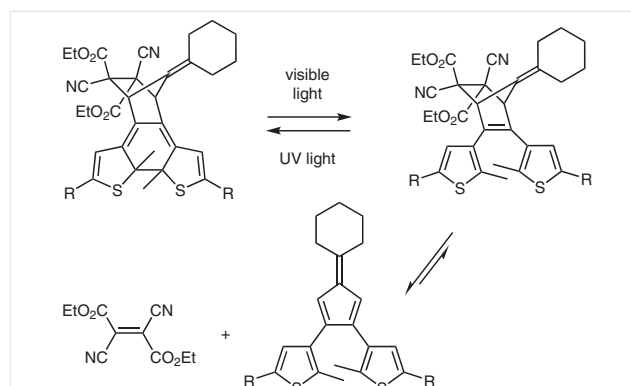

Scheme 6 Isomerization of π bonds upon photoirradiation of a thermally locked, ring-closed DAE photoswitch with visible light enables a retro-[4+2] cycloaddition reaction to release the dicyanofumarate dienophile.

Inspired by Branda's work, we recently set out to design a system using the gating concept to mechanically regulate the formation of a photochromic switch in polymers.[51] Materials with mechanochemically gated photoswitching capabilities are promising for applications in stress sensing, enabling the mechanical history of a material to be recorded and then read on-demand using light. In addition to stress sensing, we envisioned that the spatial control provided by mechanochemical activation would make this concept useful for lithographic and information storage applications, where patterns written by mechanical force could be visualized under UV light and subsequently erased with visible light.

Our strategy for achieving mechanochemically gated photoswitching is illustrated in Scheme 7. We designed a cyclopentadiene–maleimide Diels–Alder adduct (**1**) that was anticipated to generate the dithienylethene photoswitch **DAE**$_{open}$ via a mechanochemical retro-[4+2] cycloaddition reaction. Following mechanical activation of **1**, **DAE**$_{open}$ would reversibly photoisomerize between the colorless ring-opened and colored ring-closed states upon irradiation with UV and visible light. Importantly, the Diels–Alder adduct is photochemically inert because it does not possess the 6π-electronic framework necessary for electrocyclization, so no photoswitching reaction should occur in the absence of mechanical force. Moreover, cyclopentadiene–maleimide adducts are known to possess high thermal stability,[52] suggesting that the transformation would be selective toward mechanical activation.

To initially test our hypothesis, we performed DFT calculations using the constrained geometries simulate external force (CoGEF) method,[53,54] which qualitatively predicted the desired retro-[4+2] cycloaddition reaction upon molecular elongation. Encouraged by this result, we set out to synthesize a polymer containing the cyclopentadiene–maleimide Diels–Alder adduct in order to investigate its mechanochemical behavior experimentally (Scheme 8). Dithienylethene **2** was prepared via an acylation reaction

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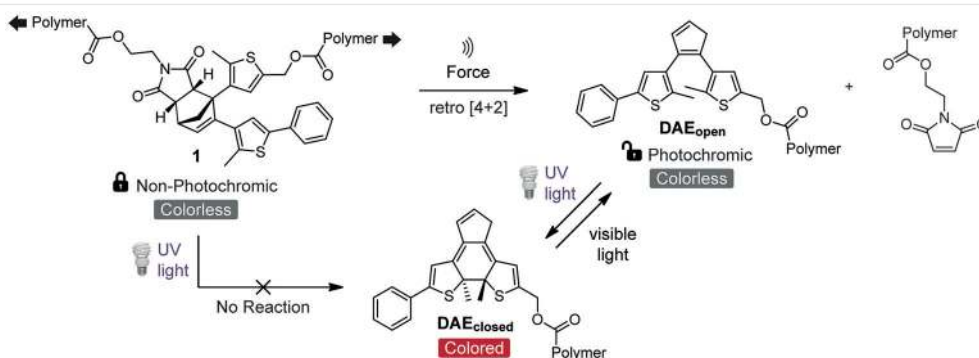
Scheme 7 Mechanochemically gated photoswitching. Mechanical activation of a polymer-chain-centered cyclopentadiene–maleimide mechanophore (**1**) generates a diarylethene photoswitch (**DAE**$_{open}$), which is converted into the colored ring-closed isomer (**DAE**$_{closed}$) under UV light. No photochromic transformation occurs in the absence of mechanical force. Adapted with permission.[51] Copyright 2018, American Chemical Society.

between 2-chloro-5-methylthiophene and glutaryl dichloride, followed by a McMurry reaction to form the annulated product, and finally Suzuki–Miyaura coupling to install a single phenyl substituent.[55,56] The phenyl substituent was included to extend the conjugation and shift the absorption of the ring-closed DAE compound to longer visible wavelengths. Formylation of the chloro-substituted DAE afforded aldehyde **3**, which was reduced to the alcohol and protected to generate **4**. Oxidation of the cyclopentene to a cyclopentadiene was facilitated by bromine, resulting in a mixture of three different cyclopentadiene tautomers. Reacting this mixture with N-(2-hydroxyethyl)maleimide afforded a mixture of Diels–Alder adducts which were separated chromatographically. Based on the analysis by De Bo on the regio- and stereochemical effects on the mechanochemical activity of furan–maleimide adducts,[46] we focused our in-

vestigation on the *endo* cyclopentadiene–maleimide adduct with a *proximal* pulling geometry. Removal of the TIPS protecting group with TBAF afforded dihydroxy compound **7**, which was unambiguously characterized by single-crystal X-ray diffraction. Finally, installation of α-bromoisobutryl esters provided **8**, which was used as a difunctional initiator for the controlled radical polymerization of methyl acrylate using the Cu/Me$_6$TREN catalyst system in DMSO to afford chain-centered PMA polymer **1** with a number average molecular weight of 90 kg/mol and a dispersity of 1.09.

Pulsed ultrasonication was used to evaluate the mechanochemical activity of polymer **1** incorporating the chain-centered cyclopentadiene–maleimide adduct. The molecular weight of the polymer steadily decreased with increasing sonication time, as characterized by gel permeation chromatography (GPC) with refractive index and multian-
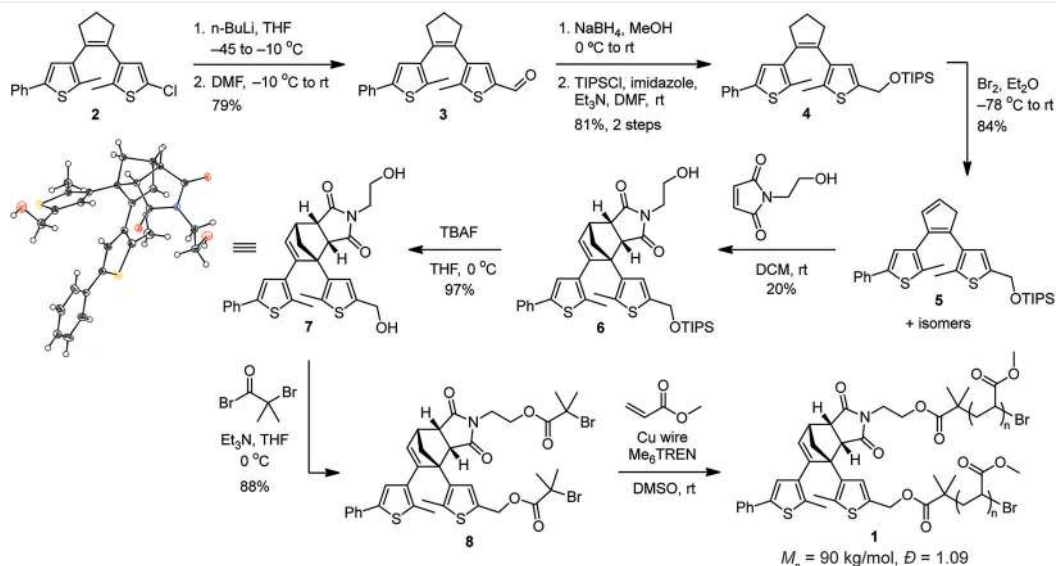
Scheme 8 Synthesis of poly(methyl acrylate) polymer **1** incorporating a chain-centered cyclopentadiene–maleimide mechanophore for mechanochemically gated photoswitching. Adapted with permission.[51] Copyright 2018, American Chemical Society.

gle laser light-scattering detectors. Attenuation of the original polymer peak and formation of a new peak at approximately one-half the original molecular weight was observed, which is characteristic of a process involving midchain scission. Remarkably, photoirradiation of the sonicated samples with UV light immediately prior to analysis by GPC revealed a new elution peak measured using a UV-vis absorption detector monitoring at 460–550 nm. The retention time of this new peak matched the low molecular weight fragment peak in the refractive index traces, indicating that a photochromic moiety covalently bound to the polymer was generated during ultrasonication.

UV-vis absorption spectroscopy was performed to further probe the photochemical changes that accompanied ultrasound-induced mechanical activation of polymer **1** (Figure 2). Over the course of 90 minutes of sonication, the solution remained colorless and displayed changes in absorption only at wavelengths below approximately 350 nm. Irradiation of the sonicated polymer solution with UV light (λ = 311 nm), however, revealed a new absorption peak centered at 505 nm that increased in optical density with longer ultrasonication times. These spectroscopic changes associated with mechanical activation of **1** were reflected in the color of the polymer solution, which changed from colorless to red upon UV irradiation. Importantly, no color change was observed under UV light without prior mechanical activation, and the absorption spectra obtained after sonication and subsequent UV irradiation matched that of the isolated ring-closed DAE small molecule. In addition, the photoswitching behavior of polymer **1** after mechanical activation was reversible over several cycles of alternating UV and visible-light irradiation. Control experiments performed on a polymer containing the cyclopentadiene–maleimide adduct at the chain end, which is not subjected to mechanical force during ultrasonication, did not result in the generation of a photochromic product, indicating that the reactivity observed for **1** was mechanochemical in nature.

5 Conclusions

Mechanochromic reactions are an important class of mechanochemical transformations that enable the direct visualization of stress in polymers. We recently introduced the concept of mechanochemically gated photoswitching, which expands the scope of mechanochromic reactions by decoupling the mechanical activation of a mechanophore from the visible response. We designed a cyclopentadiene–maleimide Diels–Alder adduct that produces a diarylethene (DAE) photoswitch via a retro-[4+2] cycloaddition reaction. Once generated mechanochemically, the photoswitch isomerizes under UV light to form an intensely colored species via a 6π-electrocyclic ring-closing reaction that is reversible using visible light. Conceptually, this strategy pro-

vides a promising platform for recording the mechanical history of materials, which can be revealed on-demand using light. Ongoing research is exploring new chemistries and the translation of mechanically gated photoswitching from solution to solid state polymeric materials for a range of applications including patterning, information storage, and stress sensing.

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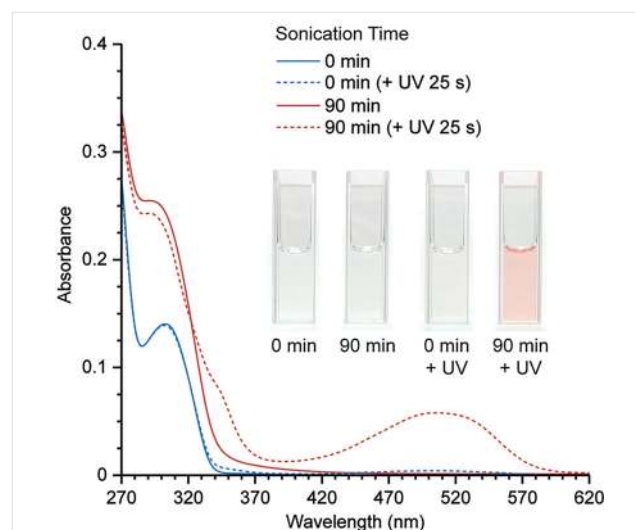
Figure 2 UV-vis absorption spectra of **1** before and after ultrasonication for 90 min and subsequent UV irradiation. Ultrasound-induced mechanical activation generates a diarylethene (DAE) photoswitch that photoisomerizes under UV light to form the colored ring-closed species. Both mechanical force and UV light are required to cause the color change. Reproduced with permission.[51] Copyright 2018, American Chemical Society.

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