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Mechanochemical Activation of Covalent Bonds in Polymers with Full and Repeatable Macroscopic Shape Recovery

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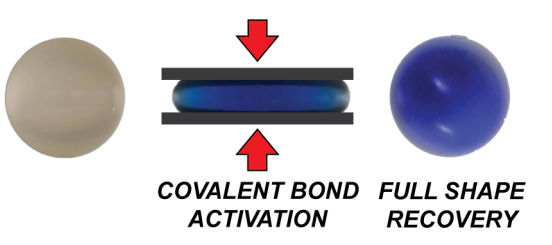
Supporting Information

ABSTRACT: Covalent mechanochemistry within bulk polymers typically occurs with irreversible deformation of the parent material. Here we show that embedding mechanophores into an elastomeric poly(dimethylsiloxane) (PDMS) network allows for covalent bond activation under macroscopically reversible deformations. Using the colorimetric mechanophore spiropyran, we show that bond activation can be repeated over multiple cycles of tensile elongation with full shape recovery. Further, localized compression can be used to pattern strain-induced chemistry. The platform enables the reversibility of a secondary strain-induced color change to be characterized. We also observe mechanical acceleration of a flex-activated retro-Diels–Alder reaction, allowing a chemical signal to be released in response to a fully reversible deformation.



The coupling of mechanical stresses in polymers to covalent chemistry (polymer mechanochemistry) has provided access to new chemical reactions,[1−7] mechanistic insights,[7−18] and polymer transformations.[1,19,20] In the bulk, chemomechanical activation has been used as the basis for new classes of responsive polymers that demonstrate stress/strain sensing,[15,16,21−25] molecular level remodeling and stress-strengthening,[26−32] and the release of small molecules that are potentially capable of triggering further chemical response.[33,34] These demonstrations have occurred in an increasing catalog of polymer morphologies spanning a range of mechanical properties. The potential utility of polymer mechanochemistry in functional materials is limited, however, by the fact that, to date, all reported covalent activation in the bulk occurs in concert with irreversible plastic yielding; the final form of the activated material is substantially different from its nascent form.[16,23,27,35−38] Mechanophores have been incorporated into and activated in elastomers,[16,37−42] but with the notable exception of the generation of mechanoradicals,[43] mechanochemically activated covalent chemistry at strains from which initial macroscopic shape can be fully recovered is largely unreported.

Shape recovery in concert with mechanophore activation would open the door for a variety of applications, including the ability to couple mechanochemical function into soft, active devices. Recently, Boydston et al. have demonstrated the release of small molecule agents over multiple compression cycles,[44] and here we report that a composite polydimethylsiloxane (PDMS) network provides a robust elastic substrate into which nonscissile mechanophores can be embedded and activated under strains from which the substrate regains its original shape. In the future, both the specific material and the general approach should be useful in enriching the responsive functionality of soft elastomeric materials and devices.

We chose filled PDMS as a platform because of its relatively high stretchability,[45] high mechanical strength,[46] optical transparency, and high functional group tolerance.[47] In addition, PDMS is a platform material for microfluidic[48−50] and electrolithographic devices,[51,52] pneumatically powered soft robotics,[53,54] and biomedical engineering applications,[55,56] and we speculated that, if shown to be accessible, covalent mechanochemical activation might provide a route to adding new responsive chemical functionality to an already highly functional material.

To test this idea, we initially turned to the colorimetric mechanophore spiropyran, developed previously by Davis et al.[23] Spiropyran reversibly opens in response to an appropriately coupled force, resulting in a colored merocyanine form (Figure 1B). Force-induced isomerization of the molecule allows for direct spatial and temporal visualization of stress accumulation in an otherwise insoluble network.

We covalently incorporated a bis-alkene functionalized-spiropyran into PDMS (0.5−0.7 wt %) via platinum cure hydrosilylation, the same chemistry used to form the covalent network (Figure 1A). Further details of fabrication can be found in the Supporting Information. Solvent-cast films resemble the nascent PDMS material, but have pale yellow coloration from the embedded spiropyran. Stretching the films

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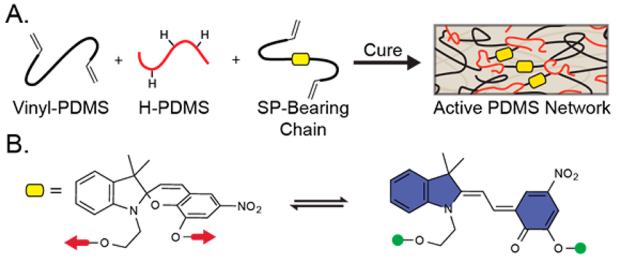

Figure 1. (A) Platinum-catalyzed hydrosilylation covalently incorporates a bis-alkene functionalized molecule among vinyl end-terminated PDMS and a hydrosilylated PDMS copolymer. (B) Ring-opening of spiropyran leads to the activated colored merocyanine compound.

by hand generates a vibrant color change (Figure 2) that persists once the film is relaxed (a tension-coupled secondary

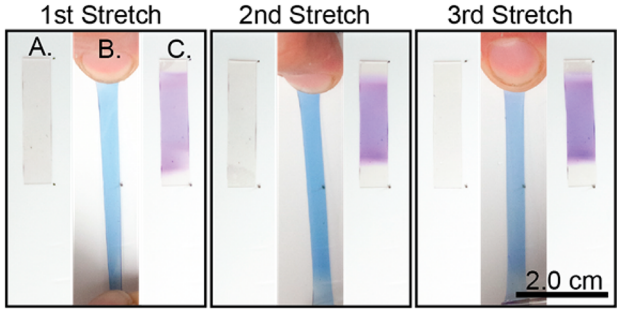

Figure 2. Covalent bond activation with full shape recovery. The original sample is clear and colorless under ambient conditions (A), but turns blue when stretched (B). When released, the material regains its initial shape (as indicated by the black reference spots), and the color switches to purple (C). Activation and shape recovery are repeatable over multiple cycles, as shown.

color change during relaxation is discussed below). Notably, the length of the relaxed film returns to that of the initial film, in marked contrast to prior reports of spiropyran activation in bulk materials. No activation was observed in control films containing a bis-functional, mechanically inactive control (see Supporting Information).

Activation is shown to be repeatable over multiple cycles. The film can be "reset" to the colorless form by illuminating the merocyanine with bright white light for about 10 s (or 1 h without light). The same stretch-induced color change, complete with shape recovery, can then be repeated over multiple cycles (Figure 2).

The stress–strain curves of a cyclic uniaxial extension to 175% strain shows hysteresis (Mullins effect)[57−60] typical of filled PDMS in the first stress/strain cycle (Figure 3A), but subsequent mechanophore activation (onset behavior described in Figure S3) occurs without further loss of mechanical properties. The subsequent 9 cycles are nearly identical in mechanical behavior, as shown by their overlapping curves (Figure 3C). After 10 cycles, the material was deformed to failure at about 200% strain (Figure 3C).

Localized compression can be used to pattern mechanophore activation within the films, by pressing or rolling patterned objects across the surface to generate lines, circles, or more complex patterns such as the cross-hatch grip of a flashlight (Figure 4). Large films cured onto a white surface can be used as a mechanochemical writing/drawing tablet that is activated

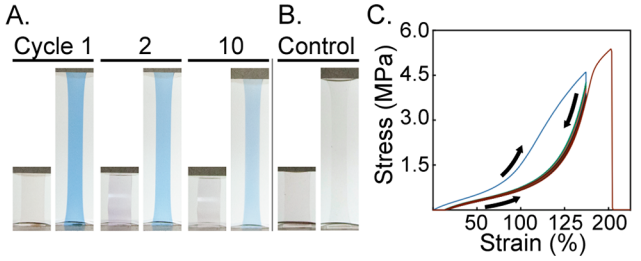

Figure 3. (A) Tensile elongation leads to covalent activation of spiropyran not observed in control films containing mechanically inactive spiropyran (B). Relaxing the sample to the initial position and illuminating with bright white light for 1 min returns the sample to its colorless state, and the activation is repeated over nine more cycles. (C) Stress–strain plot corresponding to (A), showing hysteresis in the first cycle, nine additional reversible cycles, and subsequent elongation to failure.

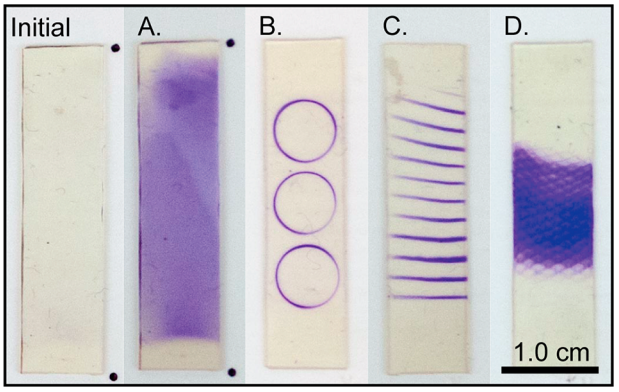

Figure 4. Spatial localization of probe activation by localized compression on film surfaces. A film can be activated by tension (A) or by rolling a patterned object across the surface to generate circles (B), lines (C), or a cross-hatch pattern (D). The same sample was used for all images.

by nondestructively dragging a stylus across the surface (see movie in Supporting Information).

The reversibility of the substrate enabled the reversibility of a second force-coupled colorimetric response in spiropyran to be characterized. When activated under tension, the PDMS-spiropyran films are a deep blue color, but when that same film relaxes, the color turns purple. The activated film reversibly changes color between blue and purple with subsequent change in stress/strain state (Figure 5A). This change is instantaneous, can be switched back and forth hundreds of times and can be quantified spectroscopically. Both the absorption (Figure 5B) and fluorescence emission (Figure 5C) spectra are red-shifted with increasing strain, by approximately 25 and 50 nm at strains of 25 and 125%, respectively. Notably, the emission spectrum of the photochemically activated merocyanine resembles the purple form (see Supporting Information). This secondary color transition has been noted previously,[40,41] and can also be can retrospectively be identified as a transient state in some previous reports.[23,36,37] It is unambiguous here largely because of the ability to reversibly and repeatedly deform the PDMS substrate. We hypothesize that the secondary color transition is the result of an isomerization about the methine bridge of the activated merocyanine (see Supporting Information).

Having demonstrated elastic shape recovery in the PDMS platform, we wondered if we could incorporate other stress responsive functionality and achieve the release of a small

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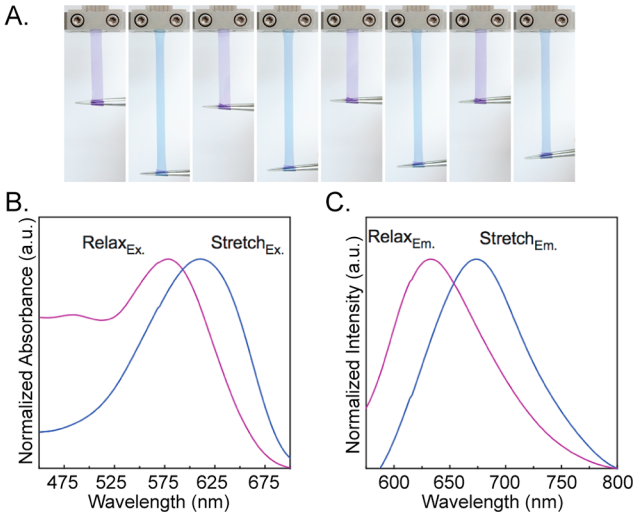

Figure 5. Mechanically activated film is blue under strain but purple when relaxed, and the transition between colors is instantaneous and repeatable over multiple cycles (A). The purple and blue states show different characteristics in both their absorption (B) and emission (C) spectra.

molecule. Noting the potential of flex activation for this purpose,[34] we chose a phenyltriazolinedione-anthracene adduct that we speculated could be triggered to release a small molecule through the force-induced planarization of the anthracene component (Figure 6A). This putative mechanophore had the added benefit that its activation would unveil a fluorescent anthracene product that would facilitate detection.

Our choice of dieneophile was motivated by Lehn's earlier report that these Diels–Alder adducts are reversible at or near room temperature.[61] In our hands, these adducts are much less reactive than reported previously and require elevated temperatures. We evaluated the effect of tension by comparing reactivity as a function of temperature in films held under 175% strain to that in unstrained films. The strained films exhibit both a lower critical temperature for measurable activation and greater activation at elevated temperatures, as compared to the control films (Figure 6). The differential fluorescence in the films under tension suggest that mechanical activation is on the order of ∼1% at 125 °C and several percent at higher temperatures (see Supporting Information). Importantly, as with spiropyran activation, this activation occurred with full shape recovery.

Noncovalent mechanically triggered responses with shape recovery have been reported previously,[29] but the expansion to covalent activation in concert with macroscopic reversibility has many potential consequences. First, the ability to trigger stress-adaptive mechanical responses such as self-strengthening, demonstrated previously under irreversible shear deformation,[28] might now be brought to materials that retain their structure and, therefore, intended function. Second, the reversibility of the secondary color transition offers an opportunity for new, high-resolution spectroscopic probes of equilibrium stress state in PDMS. Third, the bulk shape recovery provides for the first time a platform for mechanochemical devices and soft, active materials, in which reactivity can be turned on and off with spatiotemporal resolution within an intact device. Small molecule release is demonstrated here at elevated temperatures, and subsequent generations of mechanophores should bring the response to

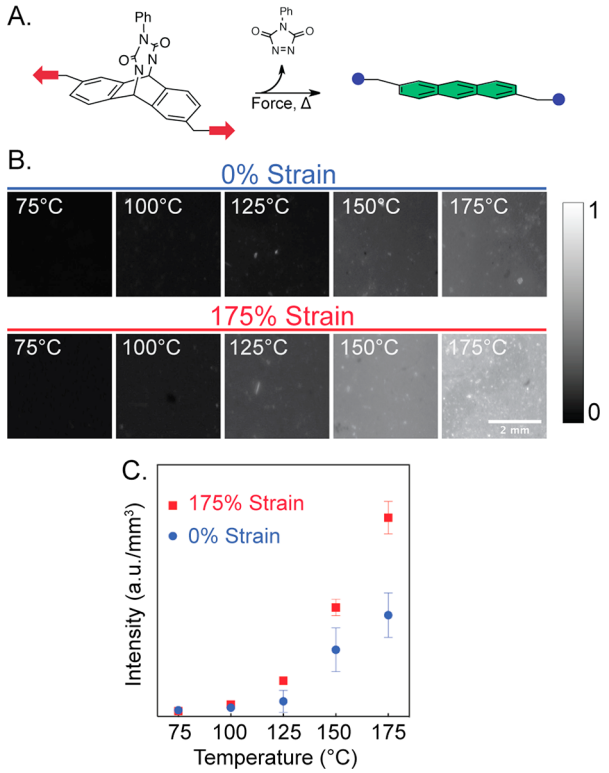

Figure 6. Functional Diels–Alder adduct of anthracene and phenyltriazolinedione (A) is incorporated as a cross-linker in PDMS. Tension accelerates the flex-activated retro-Diels–Alder reaction, leading to dienophile release and unveiled fluorescence of anthracene. The reaction is accelerated in films under 175% strain relative to the corresponding strain-free control films, as seen in the images (B) and integrated fluorescence intensities (C). Error bars represent standard deviations of measurements on multiple images within a given film.

room temperature. More generally, the majority of mechanophores reported to date are, like the materials in which they are embedded,[39] irreversibly activated by force. Macroscopically reversible activation therefore motivates the future pursuit of reversible molecular responses and function beyond the color change provided by spiropyran.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic procedures, digital image processing, control experiments, and additional details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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