

# Shockwave Loading of Mechanochemically Active Polymer Coatings

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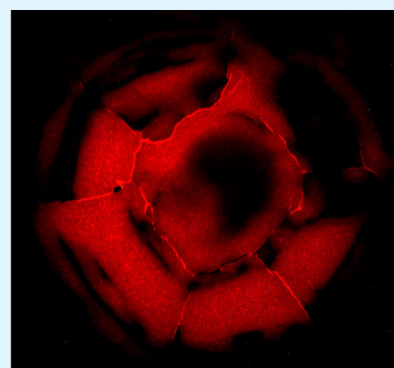
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## Supporting Information

**ABSTRACT:** Thin films of mechanochemically active polymer were subjected to laser-generated, high amplitude acoustic pulses. Stress wave propagation through the film produced large amplitude stresses ( $>100$  MPa) in short time frames (10–20 ns), leading to very high strain rates (ca.  $1 \times 10^7$  to  $1 \times 10^8$  s<sup>-1</sup>). The polymer system, spiropyran (SP)-linked polystyrene (PS), undergoes a force-induced chemical reaction causing fluorescence and color change. Activation of SP was evident via a fluorescence signal in thin films subject to high strain-rates. In contrast, quasi-static loading of bulk SP-linked PS samples failed to result in SP activation. Mechanoresponsive coatings have potential to indicate deformation under shockwave loading conditions.



**KEYWORDS:** mechanochemistry, spiropyran, thin films, laser spallation, polymers

## 1. INTRODUCTION

Mechanochemically active polymers elicit an advantageous chemical reaction in response to mechanical force.<sup>1,2</sup> A force-sensitive chemical unit (mechanophore) is linked into a polymer backbone and mechanical loading drives conversion of the mechanophore to a new chemical species.<sup>3–9</sup> Spiropyran (SP) is an effective mechanophore, undergoing a force-induced ring-opening reaction from SP to a merocyanine (MC) form under a variety of loading conditions in bulk polymers.<sup>10–13</sup> This conversion is accompanied by a color change and the emergence of a strong fluorescence signal in the visible range.<sup>12,13</sup> SP has previously been linked into both glassy and elastomeric polymer backbones. In elastomeric polymers, activation occurs at relatively high stretch ratios ( $\lambda > 3$ ) and exhibits high strain rate dependency.<sup>14</sup> Higher strain rates lead to activation at lower stretch ratios but require higher stress levels. In SP-linked glassy polymers, activation of mechanophores requires the onset of plastic deformation and also exhibits a strong strain rate dependence for activation.<sup>12,13</sup> For SP-cross-linked PMMA subject to torsion loading, activation stress increases with increasing shear rate.<sup>13</sup>

Motivated by the ability of thin films to deform plastically, as opposed to bulk polymers where brittle fracture can occur prior to the onset of plastic deformation,<sup>15</sup> we examine thin films of SP-linked polymer on a rigid substrate subject to high strain rate loading. Mechanochemically active polymer thin film

behavior was probed using a laser-induced stress wave technique first introduced by Stephens and Vossen,<sup>16</sup> and further developed by Gupta,<sup>17,18</sup> Wang,<sup>19</sup> and Grady.<sup>20</sup> In this method, a high energy laser pulse is incident on an absorbing surface, which converts laser energy into a high amplitude compressive stress pulse, and is ultimately transferred to a tensile stress pulse across the film (see Figure 1a). This test method was selected because the loading is highly repeatable and non-contact. Additionally, high strain rates are achieved in thin film specimens, and the method enables multiple tests without having to synthesize significant amounts of material. Strain rates achieved by this test method are typically on the order of  $1 \times 10^7$  to  $1 \times 10^8$  s<sup>-1</sup>, enabling characterization of mechanophore behavior under high strain rates and high stresses.<sup>16–23</sup>

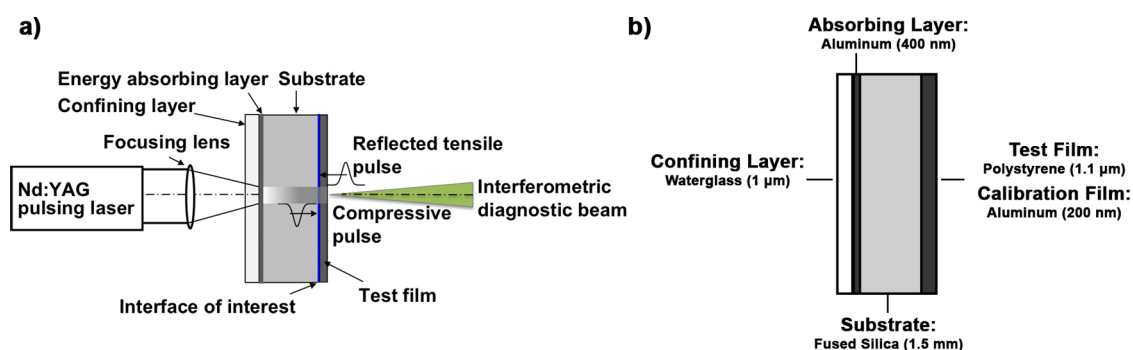
## 2. EXPERIMENTAL SECTION

SP-linked polystyrene (PS) was synthesized using an ATRP method, described by Matyjaszewski.<sup>24</sup> Following Davis et al.,<sup>10</sup> SP with  $\alpha$ -bromo ester functionality at two sites on the molecule acted as the living radical initiator for polymerization of styrene (Scheme 1, 1a). By this method a high molecular

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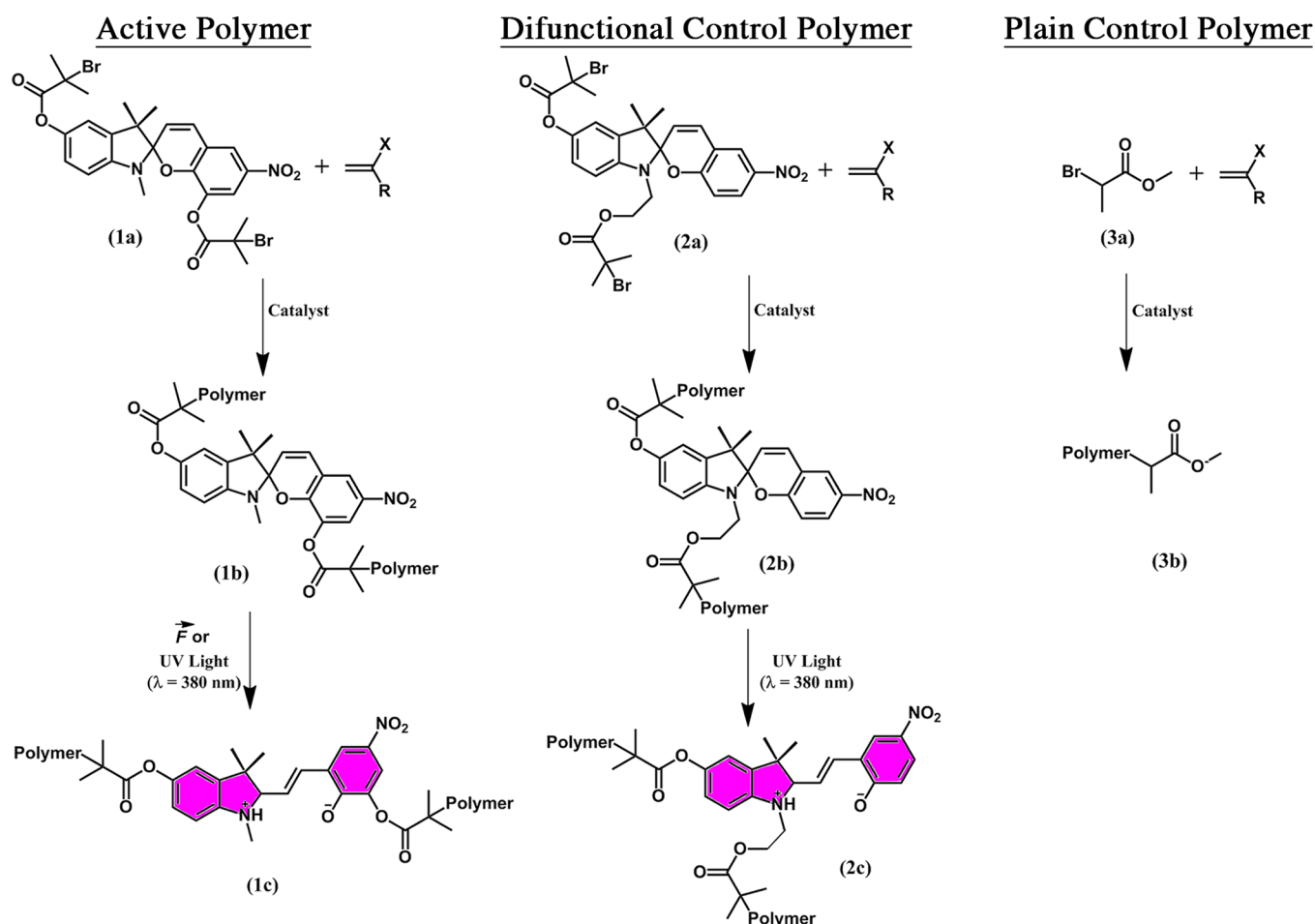
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**Figure 1.** High strain rate shockwave loading of mechanophore-linked polymer films. (a) Experimental setup for the laser-induced stress waves. (b) Schematic thin film/substrate specimens. Relevant layer thicknesses are included in parentheses.

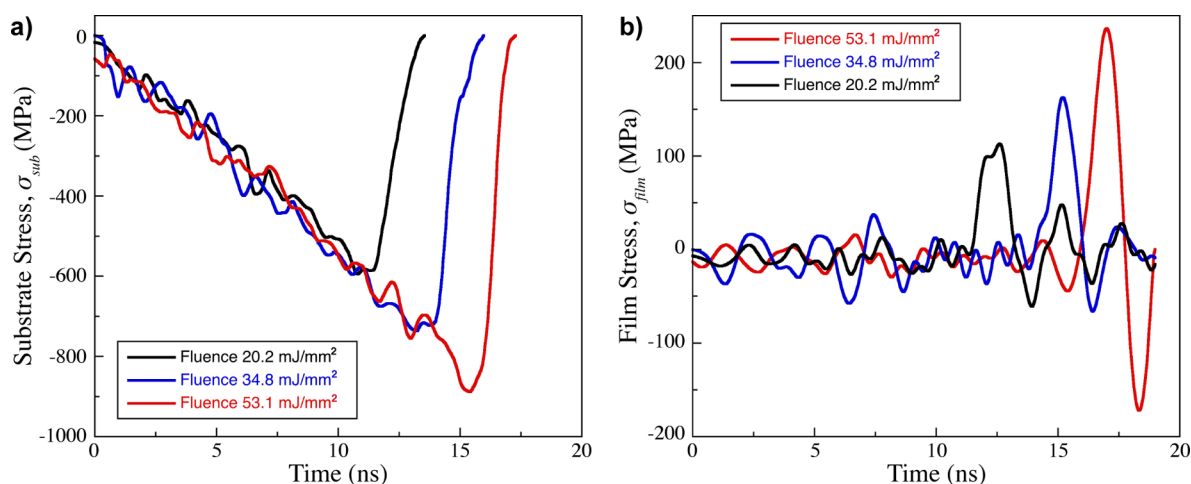
**Scheme 1.** Synthesis of Vinyl Polymers from  $\alpha$ -Bromo Ester Functionalized Initiators: (1a) Active SP, (1b) Active SP-Linked Polymer, and (1c) Ring-Opened MC-Linked Polymer; (2a) Difunctional Control SP, (2b) Difunctional Control SP-Linked Polymer, and (2c) Difunctional Control MC-Linked Polymer, Driven to This Form by UV Light; (3a) Methyl-2-bromopropionate and (3b) Plain Polymer Control



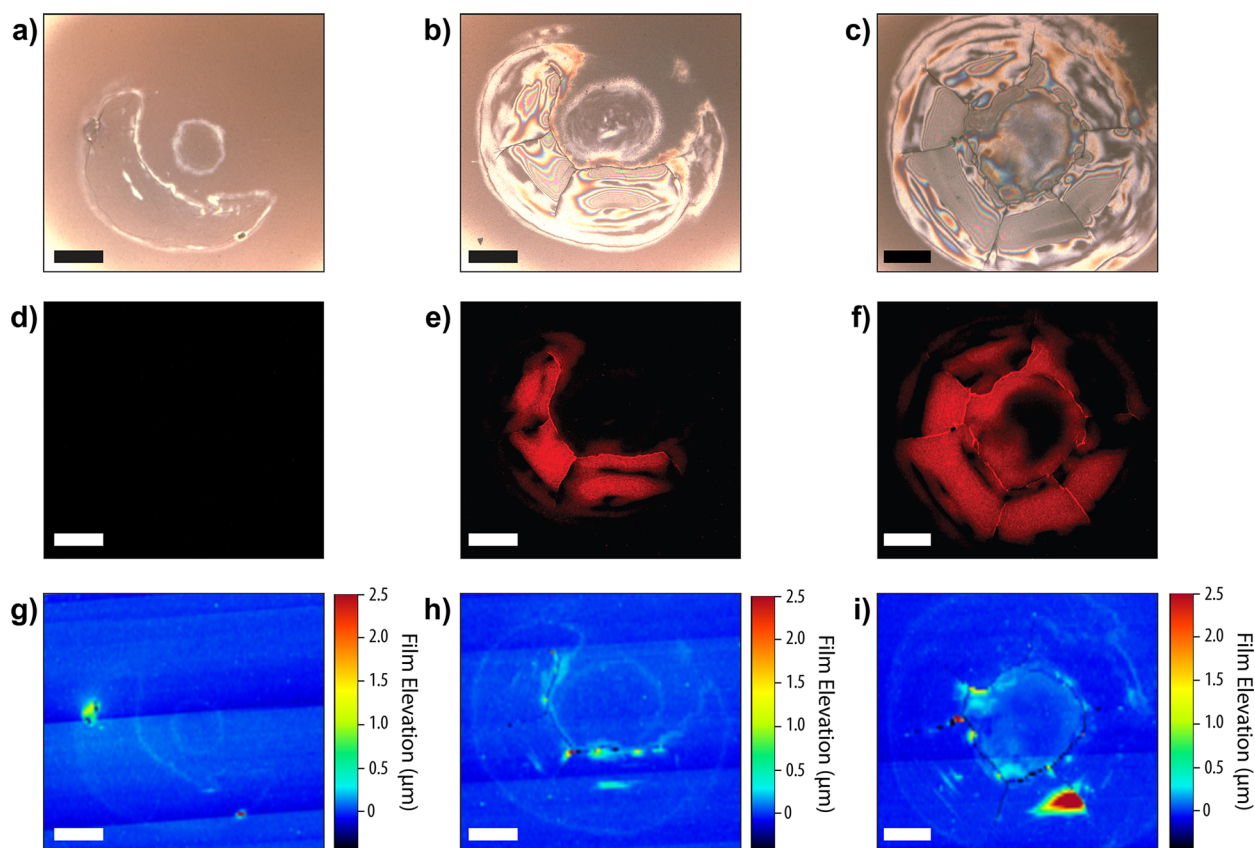
weight (160 kDa) polymer with a  $T_g$  of 105 °C and PDI of 2.0 was synthesized with SP covalently bonded roughly into the center of the polymer backbone. Active SP-linked PS was structured such that the polymer chain transmitted force across the force-sensitive spiro bond of the mechanophore. A difunctional control SP-linked PS polymer was synthesized with the SP in the center of the chain (similar to the active mechanophore) but with the polymer chains only linked to one side of the spiro-junction (Scheme 1, **2b**). This placement allowed the transfer of force to the SP but not the spiro-fused

C–O bond specifically. After synthesis, the polymer was dried under vacuum.

Bulk polymer specimens were prepared by compression molding polymer powder into dog-bone specimens (ca. 0.6 mm thick) using a closed mold. A pressure of 200 psi was applied to the mold at a temperature of 130 °C for 10 min. The mold was then quenched in water. Before testing, all specimens were polished and SP-linked polymers were held at 80 °C and were irradiated with a 530 nm diode lamp for 24 h to drive the active species toward the ring-closed SP form (Scheme 1, **1a**).



**Figure 2.** Experimental data for calibration samples tested at laser fluences of 20.2, 34.8, and 53.1 mJ/mm<sup>2</sup>. (a) Substrate stress pulse profiles and (b) corresponding film stress calculated by finite element analysis for polystyrene films.



**Figure 3.** Images of active SP-linked PS films after Nd:YAG-induced shockwave loading at interfacial tensile stress levels of 166 MPa, 186 MPa, and 216 MPa, from left to right. (a–c) Optical images of polymer films. (d–f) Optical fluorescence images, indicating SP activation. (g–i) Corresponding contour plots of surface elevation measured by profilometry. Scale bars in each image are 150  $\mu\text{m}$ .

Thin film specimens were prepared by spin coating a 50 mg/mL solution of polymer/THF on to substrates with a 5 s ramp to 1500 rpm for 60 s. After film deposition the sample was held under vacuum for 30 min to remove residual solvent and minimize any plasticization of the polymer. Three sample types of polymer films were investigated: plain polystyrene without SP linked into the backbone, difunctional SP-linked control PS, and mechanochemically active SP-linked PS. All sample films were spun cast under the same conditions. Polymer film thickness was on average 1.1  $\mu\text{m}$  as determined by stylus

profilometry. Substrates for Nd:YAG laser-induced shockwave loading (Figure 1b) consisted of a fused silica wafer (1.25" diameter, 1.5 mm thick) with an aluminum layer (400 nm thick) deposited on one side via electron beam deposition, and a 1  $\mu\text{m}$  sodium silicate (waterglass, spin-coated at 3000 rpm) layer deposited from solution on top of the aluminum. Polymer films for testing were spun cast on the opposite side of the substrate. Additional calibration samples were produced with aluminum (200 nm thick) as the test film.

A rapid, high-amplitude acoustic wave was initiated by the impingement of an Nd:YAG pulsed laser (New Wave Tempest) on the aluminum energy absorbing layer on the back surface of the substrate (Figure 1a). Because of the confinement of a sodium silicate (waterglass) layer, rapid expansion of Al generated an acoustic wave that propagated through the substrate in compression. After reflection at the thin film free surface, the wave loaded the thin film–substrate interface in tension. The relatively thick fused silica substrate (1.5 mm) sufficiently isolated the test film from thermal effects of the laser impact.<sup>17</sup>

In prior work, thin film stress amplitudes were inferred from interferometric measurements.<sup>16–23</sup> The thin film polymer specimens in this work are not specular, precluding in situ interferometric data collection. To determine the substrate and interface stresses for a given laser fluence (energy per area), we carried out a set of interferometric measurements on calibration specimens with highly reflective thin Al films (200 nm) on the top surface of identical substrates to the polymer thin film test specimens. The displacement of the free surface and corresponding substrate stress was recorded as described previously by Wang et al.<sup>19</sup> Using the measured stress pulses as input for a 1D finite element model, the interface stress and resulting strain was calculated over a range of fluences for polystyrene films on fused silica substrates. The difference in thickness and stiffness between the aluminum calibration films and the polystyrene films was accounted for in the stress calculations. Details of the stress analysis are described by Grady et al.<sup>20</sup> and also provided in the Supporting Information.

Laser fluence was varied by incrementally adjusting the energy of the Nd:YAG laser while keeping the beam diameter constant at 1.9 mm. Aluminum calibration films and polymer films were tested over the same range of laser fluences at a number of sites on the same film. Separation between impact sites along the sample was greater than 3x the radius of the laser beam. Representative substrate stress profiles from the calibration and the corresponding interface stress from finite element analysis are shown in Figure 2 for a 1.1  $\mu\text{m}$  polystyrene film tested at laser fluences of 20.2, 34.8, and 53.1  $\text{mJ}/\text{mm}^2$ .

Polymer films were imaged after testing at each stress level and analyzed ex situ optically and under fluorescence microscopy with 532 nm excitation light and collection at  $\lambda > 575$  nm. The field of view, incident light intensity, and fluorescence exposure were held constant for all imaging. Fluorescence intensity due to SP activation was quantified by averaging the red pixel intensity over the entire image field of view.

### 3. RESULTS AND DISCUSSION

Active and control polymer thin films were tested at various fluences using laser-induced stress waves. The intensity of the laser pulse increased with increasing input laser energy. For the highest laser fluence (53.1  $\text{mJ}/\text{mm}^2$ ) substrate stress amplitudes reached values of nearly 1 GPa. The corresponding stress wave in the film (Figure 2b) was calculated from the substrate stress (Figure 2a) and material properties as described in the Supporting Information. Film stresses greater than 200 MPa were achieved at strain rates on the order of  $1 \times 10^8 \text{ s}^{-1}$ . The mechanical responses of plain PS control, difunctional control SP-linked PS, and active SP-linked PS, were qualitatively similar, whereas optical responses varied significantly.

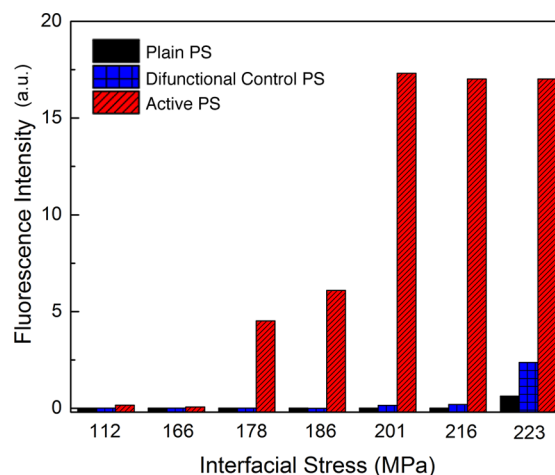
Representative optical, fluorescence and profilometry images for mechanochemically active SP-linked PS films loaded at a

range of film stresses from 166 to 216 MPa are shown in Figure 3. In the optical images, the dark coloring of the background occurred where the laser was incident on the back surface. Light areas and coloration indicated polymer film delamination from the surface and deformation out of the plane of the image. At a peak film stress of 160 MPa, the polymer film began to delaminate from the silica substrate (Figure 3a). Images b and c in Figure 3 show the increasing delamination zone with increasing peak film stress (186 and 216 MPa, respectively), which is roughly circular, in accordance with the incident laser beam.

Activation of SP was indicated by fluorescence signal from the MC form. Fluorescence signal was not detectable in the polymer films prior to testing, implying that the mechanophore was predominantly in the SP form. SP activation occurred at peak film stress levels greater than 180 MPa (Figure 3e, f). Although delamination initiated at lower stresses ( $\sigma_f \approx 160$ –175 MPa), SP activation was not detectable at these values.

Surface topology of the failed films was characterized by stylus profilometry (P6 KLA Tencor) for each fluence (Figure 3g–i). Slight elevation changes in the film (10s of nm) were measured for film stresses above approximately 160 MPa, indicating partial delamination of the film off of the substrate. Below this stress level (<160 MPa), the film surface was uniform. At higher stresses, foldlike features with elevation on the order of micrometers were present, as well as film cracking.

Mechanochemically induced fluorescence was compared for identical loading conditions in active, difunctional control, and plain polystyrene, plotted in Figure 4. For active SP-linked PS,



**Figure 4.** Fluorescence intensity (average red pixel intensity), indicating SP activation in active, difunctional control, and plain control (no SP) PS films at varying stress amplitude. One measurement was taken at each interfacial stress.

the relative amount of fluorescence increased with increasing applied load. At film stresses greater than 200 MPa, fluorescence intensity plateaued, reaching a level of saturation. Plain PS, without SP incorporated into the polymer backbone, emitted no detectable fluorescence. The fluorescence signal detected for difunctional control was negligible compared with active SP-linked PS. This difference in signal provided evidence that the fluorescence increase in the active polymer was due to force transfer across the molecule (Scheme 1).

For comparison, bulk tensile specimens of PS were tested under quasi-static conditions. Optical images of specimens and



a representative stress–strain curve are included in the Supporting Information. Bulk polymer samples deformed elastically at room temperature and experienced brittle failure at stresses of ca. 60 MPa. In contrast to thin film specimens, this mode of deformation and failure did not lead to detectable activation of SP in bulk specimens as evaluated by fluorescence microscopy. In previous studies, successful activation of mechanochemical species in glassy polymers was only achieved after plasticizing the polymer or elevating the test temperature to promote plastic deformation.<sup>12</sup> This study utilized thin films of mechanochemically active polymer (as opposed to bulk material) and a shockwave loading method as a means for activating SP in a glassy polymer system. Although the SP-linked PS films are a model system, the ability to activate colorimetric mechanophores under high strain rate conditions may lead to future applications as visual indicators of dynamic loading.

#### 4. CONCLUSION

Mechanochemically induced fluorescence was observed in glassy SP-linked polystyrene thin films under high strain rate conditions. Activation of SP via fluorescence microscopy occurred after a stress threshold of approximately 180 MPa, corresponding to a strain of 7%. Increased stress levels led to higher intensity of fluorescence until reaching saturation. Interestingly, bulk specimens tested at slow strain rates showed no evidence of activation via fluorescence microscopy, even at failure strains of approximately 8%. Under these loading conditions, thin films deposited on a substrate were able to accommodate plastic strains prior to failure and result in more efficient conversion of SP to MC. Through the testing of thin films, we were able to demonstrate that mechanochemical reactions in polymer films can occur on very short time scales, approaching that observed in sonication-induced activation of mechanophore-linked polymer solutions.<sup>4</sup> Moreover, mechanophores designed specifically for activation under high energy, high strain rate shock loading could lead to useful functional responses under extreme conditions.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

Chemical structures, details of shockwave loading calculations, and bulk spiropyran-linked polystyrene tensile testing. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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##### Author Contributions

The manuscript was written through equal contributions of all authors. All authors have given approval to the final version of the manuscript.

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##### Notes

The authors declare no competing financial interest.

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#### ■ ABBREVIATIONS

SP, spiropyran  
PS, polystyrene  
PDI, polydispersity index  
 $M_w$ , molecular weight  
Nd:YAG, neodymium-doped yttrium aluminum garnet  
MPa, megapascals  
 $\epsilon$ , strain  
 $\sigma_{\text{film}}$ , film stress  
 $\sigma_{\text{sub}}$ , substrate stress

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