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Force-Induced Redistribution of a Chemical Equilibrium

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Abstract: Spiropyran (SP) mechanophores (mechanochemically reactive units) can impart the unique functionality of visual stress detection to polymers and have potential for use in smart materials with self-sensing capabilities. These color-generating mechanophores were incorporated into polyurethane via step growth polymerization. Polyurethane, which is inherently a versatile engineering polymer, possesses an optimized balance of mechanical toughness and elasticity to allow for investigation of the kinetics of the mechanochemical response of the SP mechanophore in the bulk polymer via fluorescence and absorbance measurements. The stress-induced 6-π electrocyclic ring-opening to the colored merocyanine (MC) form of the mechanophore was quantified by measuring the change in absorbance of the polymer, while it was held at constant strain. The closing kinetics of the mechanophore was also studied by fluorescence imaging. Finally, the effects of mechanical strain on the equilibrium between the SP and MC forms are reported and discussed.

Introduction

Mechanophores, molecules that respond in a productive fashion to mechanical stimuli, have the potential to dramatically increase the functionality of polymeric systems.[1] A major focus in this field is the discovery and development of mechanochromic mechanophores, that is, mechanophores that change color with the application of force. The ability of a material to autonomically react to changes in its environment lends itself to many potential applications in damage detection and catastrophic failure prevention. A variety of molecules with mechanochromic functionality have been investigated in literature. Mechanically induced changes in color and/or fluorescence have been due to the formation[2−5] or break up[2,6−13] of excimers, changes in conjugation,[14−21] or changes in charge state.[22] In these systems, the mechanically active species has generally been physically dispersed within a bulk polymer matrix.[6−13,23] Davis et al.[24] and more recently O'Bryan et al.[25] have reported on covalently linked spiropyrans (SP) as highly effective color-generating mechanophores that can provide visible detection and mapping of mechanical stresses through their mechanically induced transformation to the merocyanine (MC) conformation in glassy and elastomeric chain growth polymers. While the polymer systems explored by Davis et al.[24] were quite successful in demonstrating a mechanochemically induced visible color change, the physical properties of these polymers were not ideal for investigation of the kinetics or thermodynamics of the mechanically induced transformations of SP mechanophore in bulk polymers.

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(1) Caruso, M. M.; Davis, D. A.; Shen, Q.; Odom, S. A.; Sottos, N. R.; White, S. R.; Moore, J. S. *Chem. Rev.* **2009**, *109*, 5755–5798.
(2) Crenshaw, B. R.; Weder, C. *Macromolecules* **2006**, *39*, 9581–9589.
(3) Bruns, N.; Pustelny, K.; Bergeron, L.; Whitehead, T.; Clark, D. *Angew. Chem., Int. Ed.* **2009**, *48*, 5666–5669.
(4) Ikawa, T.; Shiga, T.; Okada, A. *J. Appl. Polym. Sci.* **1997**, *66*, 1569–1573.
(5) Yang, J.; Li, H.; Wang, G.; He, B. *J. Appl. Polym. Sci.* **2001**, *82*, 2347–2351.
(6) Löwe, C.; Weder, C. *Adv. Mater.* **2002**, *14*, 1625–1629.
(7) Crenshaw, B. R.; Weder, C. *Chem. Mater.* **2003**, *15*, 4717–4724.
(8) Kinami, M.; Crenshaw, B. R.; Weder, C. *Chem. Mater.* **2006**, *18*, 946–955.
(9) Kunzelman, J.; Crenshaw, B. R.; Kinami, M.; Weder, C. *Macromol. Rapid Commun.* **2006**, *27*, 1981–1987.
(10) Pucci, A.; Bertoldo, M.; Bronco, S. *Macromol. Rapid Commun.* **2005**, *26*, 1043–1048.
(11) Pucci, A.; Di Cuia, F.; Signori, F.; Ruggeri, G. *J. Mater. Chem.* **2007**, *17*, 783–790.
(12) Donati, F.; Pucci, A.; Cappelli, C.; Mennucci, B.; Ruggeri, G. *J. Phys. Chem. B* **2008**, *112*, 3668–3679.
(13) Crenshaw, B. R.; Burnworth, M.; Khariwala, D.; Hiltner, A.; Mather, P. T.; Simha, R.; Weder, C. *Macromolecules* **2007**, *40*, 2400–2408.
(14) Hammond, P.; Nallicheri, R.; Rubner, M. *Mater. Sci. Eng., A* **1990**, *126*, 281–287.
(15) Nallicheri, R. A.; Rubner, M. F. *Macromolecules* **1991**, *24*, 517–525.
(16) Rubner, M. F. *Macromolecules* **1986**, *19*, 2129–2138.
(17) Rubner, M. F. *Macromolecules* **1986**, *19*, 2114–2128.
(18) Lee, S. B.; Koepsel, R. R.; Russell, A. J. *Nano Lett.* **2005**, *5*, 2202–2206.
(19) Yoshino, K.; Nakao, K.; Onoda, M.; Sugimoto, R. *Solid State Commun.* **1988**, *68*, 513–516.
(20) Hess, B.; Kanner, G.; Vardeny, Z. *Phys. Rev. B* **1993**, *47*, 1407–1411.
(21) Iwasaki, K.; Fujimoto, H.; Matsuzaki, S. *Synth. Met.* **1994**, *63*, 101–108.
(22) Azzaroni, O.; Trappmann, B.; van Rijn, P.; Zhou, F.; Kong, B.; Huck, W. T. S. *Angew. Chem., Int. Ed.* **2006**, *45*, 7440–7443.
(23) Anuchai, K.; Weder, C.; Magaraphan, R. *Plast., Rubber. Compos.* **2008**, *37*, 281–287.
(24) Davis, D. A.; Hamilton, A.; Yang, J.; Cremar, L. D.; Van Gough, D.; Potisek, S. L.; Ong, M. T.; Braun, P. V.; Martinez, T. J.; White, S. R.; Moore, J. S.; Sottos, N. R. *Nature* **2009**, *459*, 68–72.
(25) O'Bryan, G.; Wong, B. M.; McElhanon, J. R. *ACS Appl. Mater. Interfaces* **2010**, *2*, 1594–1600.

10.1021/ja106332g

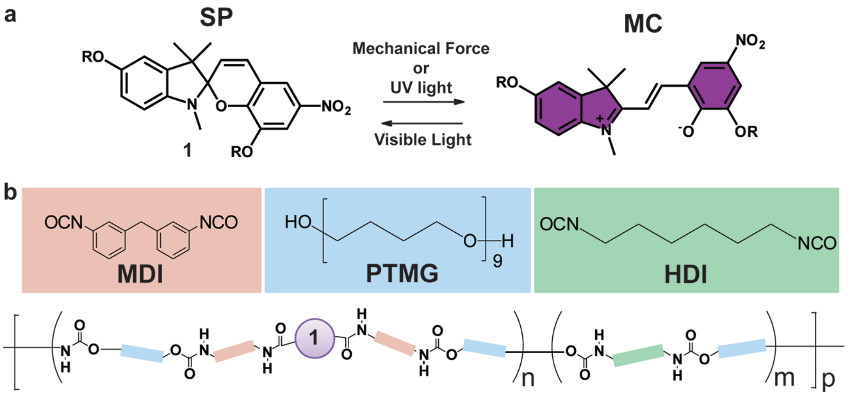

Figure 1. (a) Chemical structures of spiropyran (SP) and merocyanine (MC) and the mechanically or optically triggered conversion equilibrium between the colorless SP and colored MC forms. (b) Schematic of the incorporation of SP mechanophore **1** into PU via step growth polymerization where $m \gg n$.

We now demonstrate the incorporation of SP mechanophore into step-growth polyurethane (PU). The inherent mechanical toughness, elasticity, and low glass transition temperature ($T_g \approx -60$ °C) of PU enable the effects of mechanical force on the SP−MC equilibrium (Figure 1a) to be studied. The initial polymer systems studied were not amenable to kinetic analysis because they were either too soft [elastomeric poly(methyl acrylate)], resulting in mechanical activation only at high strains close to the strain of failure, or too glassy [poly(methyl methacrylate) (PMMA)], $T_g = 105$ °C. In PMMA, because of the high T_g, the rate of conversion from MC to SP form could not be investigated at room temperature.[24] We show that the SP mechanophore is mechanochromic in PU and that the equilibrium between the colored MC and colorless SP form can be directly controlled by mechanical strain. Because of the low T_g, equilibrium is reached in experimentally accessible times at room temperature. Here we report for the first time on the kinetics of the mechanically activated SP to MC conversion as well as the thermally activated conversion of MC to SP in a bulk polymer. PU is of specific interest not only because it is a ubiquitous engineering polymer but also because it is synthesized via step growth polymerization, so the mechanophore concentration can be modulated independently of molecular weight or cross-linking density. Finally, from a practical standpoint, the synthesis of the mechanochromic PU can be scaled to large volumes, simplifying mechanical testing studies.

Experimental and Methods

See also Supporting Information for details.

Polyurethane Synthesis. Dihydroxyspiropyran **1** (R = H) was first reacted with an excess of methylene diphenyldiisocyanate (MDI) in anhydrous tetrahydrofuran (THF), resulting in a diisocyanate-functionalized mechanophore. Still in solution, the functionalized spiropyran was then reacted with a hydroxyl-terminated poly(tetramethylene glycol) (PTMG, $M_n = 650$). The polymer was then put under vacuum at 70 °C to remove the solvent. Finally, hexamethylene diisocyanate (HDI) was added as a chain extender. Tensile specimens were prepared by pouring the polymer into Delrin "dog bone"-shaped molds and cured under a N_2 atmosphere at 60 °C for 2 days to yield the mechanophore-containing polymer (PU-**1**) with the general structure shown in Figure 1b. Different concentrations of **1** were incorporated (0.015−0.06 wt %). The resulting mechanochromic PUs all had similar molecular masses of 50−70 kDa and polydispersity indices of 3−6. For the following discussions, PU-**1** with an optimized concentration of 0.03 wt % **1** was used for fluorescence and absorbance experiments.

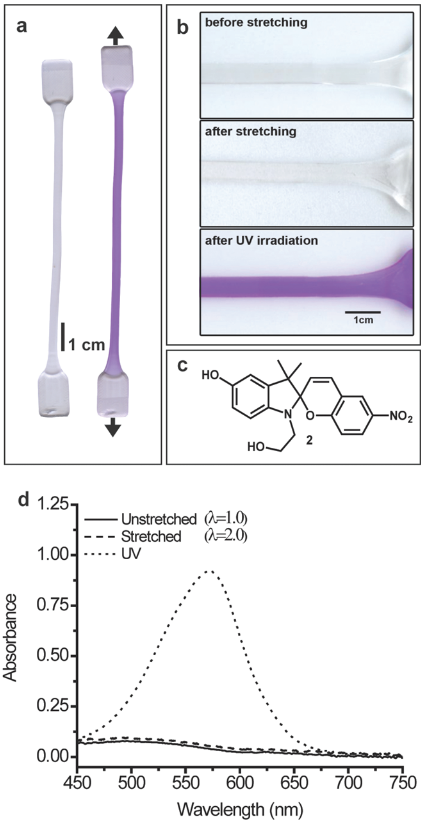

Figure 2. (a) Optical images of prestretched PU-**1** "dog bone" containing 0.03 wt % **1** before (left) and after (right) being stretched to a stretch ratio (final length/initial length) of 2.0 and released. (b) Optical images of PU-**2** before and after stretching compared to UV irradiation-induced conversion of the control SP mechanophore. (c) Difunctional control SP mechanophore. Polymer connectivity occurs at the hydroxyl functional groups and therefore does not bridge the spiro junction. (d) Absorbance spectra of PU-**2** showing no mechanical activation but a clear MC peak at about 580 nm after UV irradiation.

Mechanical Testing. Tensile testing was done at room temperature on a rail frame with loads data determined by use of a 50 lb capacity Futek LSB300 load cell via a panel meter (Omega Engineering Inc., DP25B-S-A), DAQ card (National Instruments), and Labview software from National Instruments. Before absorbance and fluorescence testing, the tensile specimens were prestrained to a length 5 times the initial gauge section, which caused the samples to neck and cold draw (Figure 2a, left). The prestrained specimens were then reloaded to increasing levels of stretch, where stretch is defined as the final length over the initial length (after prestraining). Typical load−stretch plots (see Supporting Information) of PU-**1** and plain PU were very similar, suggesting that the

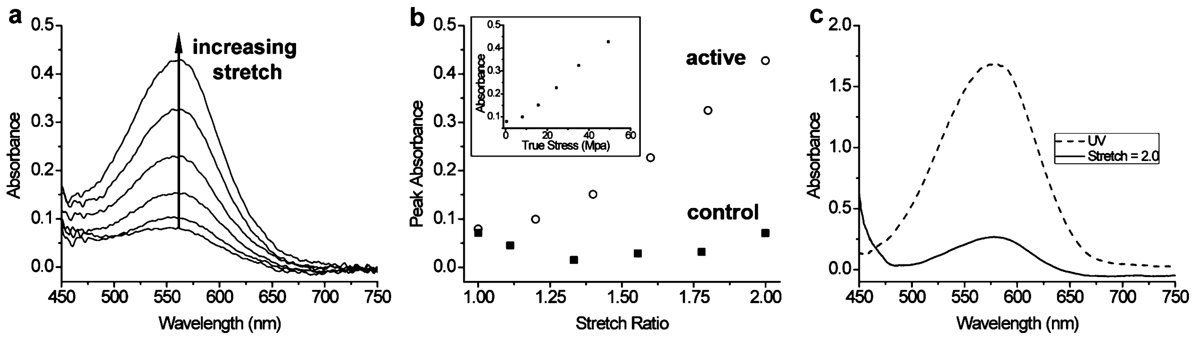

Figure 3. (a) Absorbance spectra of PU-**1** as a function of increasing stretch ratio (1.0, 1.2, 1.4, 1.6, 1.8, and 2.0). (b) Peak absorbance (average of absorbance between 570 and 580 nm) of PU-**1** and difunctional control mechanophore (PU-**2**) as a function of stretch ratio. (Inset) Peak absorbance as a function of true stress. Sufficient time was allowed between stretch steps for the mechanically induced SP to MC conversion to reach equilibrium. (c) Absorbance spectra of a mechanically activated PU-**1** stretched and held at a constant stretch of 2.0 compared to the same PU-**1** sample irradiated with UV (365 nm) for 5−10 min. The peak absorbance (570−580 nm) of the mechanically activated sample is, on average, ≈20−30% of the UV-activated peak absorbance.

low concentration of SP had negligible effects on the tensile properties of the polymer.

Absorbance and Fluorescence Measurements. After prestraining of the tensile specimen, absorbance data were collected by use of an Ocean Optics HL-2000 tungsten halogen light source and Ocean Optics HR2000+ spectrometer. For collection of absorbance data, the samples were mechanically tested on a custom-built rail frame. Displacement control was established through a bidirectional screw-driven Lintech rail table. A fluorescence light microscope (Zeiss Axiovert 200M) was used to capture fluorescence images, and ImageJ was used for image analysis.

Results and Discussion

Mechanical Activation and Controls. When the polymer was uniaxially stretched, a deep purple coloration appeared along the entire gauge section of the PU-**1** sample (Figure 2a), demonstrating the stress-induced formation of the open, MC form of the mechanophore (Figure 1a). To confirm that activation of the SP mechanophore was indeed mechanical and not due to thermal or photo means of activation, a difunctional control SP molecule **2** (Figure 2c) was synthesized and incorporated into PU (PU-**2**) by the same synthetic procedure as PU-**1**. The control SP was a hydroxyl-functionalized version of the difunctional control used by Davis et al.,[24] where the SP is coupled into the polymer backbone in such a fashion such that force is not transferred to the spiro C−O bond, and thus conversion from the SP to MC form is not mechanically triggered. Upon uniaxial stretching, no color change was observed for plain PU (containing no mechanophore) or PU containing the difunctional control SP (PU-**2**) (Figure 2b). Absorbance measurements confirmed the lack of mechanical activation displaying no MC peak for both unstretched and stretched spectra (Figure 2d). In the control system, the difunctional control samples could be activated with ultraviolet (UV) light, thus confirming the presence and photochemical activity of the spiropyran (Figure 2b,d).

Activation versus Stretch. The mechanical activation of PU-**1** as a function of stretch was studied. It was observed that the MC absorbance peak centered on 580 nm grew as a function of strain (Figure 3a,b), supporting the hypothesis that mechanical forces are directly responsible for converting the mechanophore from SP to MC form. Increasing levels of strain correlate to larger amounts of mechanical force on the mechanophore, which in turn opens an increasing percentage of the mechanophores from SP to MC, resulting in the growing MC peak centered at about 580 nm. PU-**2** was also tested with varying strain levels and resulted as expected with no change in absorbance (Figure 3b).

The increase of absorbance with strain as well as with stress for PU-**1** appears linear, at least up to a stretch of 2.0 (Figure 3b). Higher stretch values of about 2.3 were tested and resulted in continued increases in absorbance (see Supporting Information); however, higher stretch ratios led to slippage of the polymer samples in the testing grips. The linear increase of absorbance with strain leads us to believe we are far from activating all the mechanophore incorporated into the PU, since the absorbance must asymptotically reach some value. When the already mechanically activated PU-**1** was held at a stretch of 2.0 and then irradiated with UV light for 5−10 min, the polymer became noticeably darker purple and the MC absorbance peak increased (Figure 3c). Analysis of these results indicates that the mechanical activation of PU-**1** activates ca. 20−30% of the SP relative to the amount activated by UV irradiation.

Nearly complete mechanophore activation must simply require levels of mechanical force on the mechanophore not attainable with the current experimental system. In part, this is an experimental problem in that the sample slips out of the grips at high strain, but also, on the molecular level, this partial activation could reflect on the force distribution on individual mechanophores due to both the finite chain lengths in the sample and the distribution in mechanophore alignment in the sample. Significant color change was generally observed only after the necking event (Video S1 in Supporting Information) during the prestrain step. Even though substantial plastic deformation and thus chain alignment takes place upon prestraining, some fraction of mechanophores are likely to be oriented in such a direction that they do not activate under uniaxial tension. Overall this lends evidence to the hypothesis that chain alignment may play a key role in activation of the SP mechanophore as postulated by O'Bryan et al.[25] It is also quite likely that the stress required for nearly complete activation would result in fracture of the polymer dog bone.

Kinetics Studies. In PU-**1**, which has a $T_g \approx -60$ °C (see Supporting Information), the mechanically induced 6-π electrocyclic ring-opening conversion from SP to MC fully reverts to the SP form after about 1 h of exposure to fluorescent room light; this behavior can be repeated multiple times with the same sample. We previously reported that the MC to SP reversion in elastomeric poly(methyl acrylate) ($T_g \approx 10$ °C) occurred after

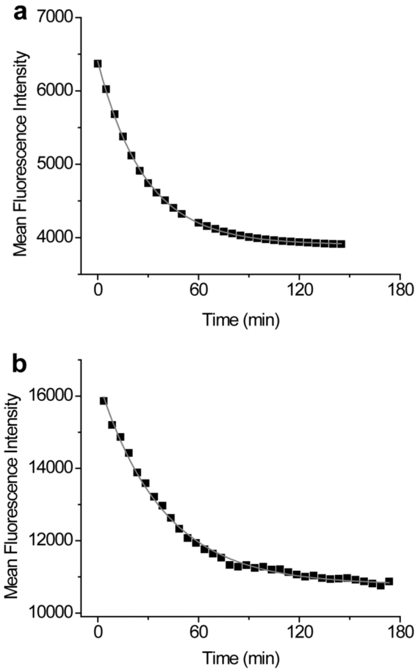

Figure 4. (a) Mean fluorescence intensity decay of UV-activated PU-**1** plotted against time and fitted to a single-exponential decay function with $\tau \approx 30$ min. (b) Mean fluorescence intensity decay of mechanically activated PU-**1** fitted to a single exponential with $\tau \approx 38$ min.

approximately 6 h of exposure to fluorescent room light, whereas reversion in glassy poly(methyl methacrylate) ($T_g \approx 105$ °C) required several weeks.[24] The MC to SP ring closing kinetics appears to vary greatly with the local environment, with T_g being a major determinant.

Fluorescence imaging was used to quantify the time required for MC to revert to SP under no load within PU. We took advantage of the photochromic properties of SP.[26] UV light was used to activate a solution-cast film of PU-**1**, converting the SP mechanophore to the colored/fluorescent MC conformation. A thick film was used to eliminate any signal variation from the slightly different thicknesses of the "dog bone" sample as well as scratches and defects on the surface, which could lead to scattering. Over several hours, fluorescence images of the activated region were captured by brief exposures in the dark. The mean fluorescence intensity of the activated region was plotted versus time and fitted to a single-exponential decay with a time constant of $\tau \approx 30$ min (Figure 4a). This shows that in just over an hour, kT at room temperature is sufficient to allow the MC form to revert back to the SP form favored at equilibrium.

Fluorescence-based characterization was also performed on a mechanically activated PU-**1** "dog bone"-shaped sample. The sample was stretched to a stretch ratio of 2.0 and then unloaded, placed in a dark container, and taken to the fluorescence microscope. The time at which the sample was unloaded and removed from the rail frame was defined as time zero. Results for the mechanically activated PU-**1** sample were similar except for a slightly longer time constant, $\tau \approx 38$ min (Figure 4b), when fitted to a single-exponential decay function and slightly noisier due to thickness and imperfect surface of the "dog bone" shape. We suspect that the slight increase in time constant τ could be a result of slowly relaxing residual strain in the polymer preventing the mechanophore from closing as quickly.

Mechanically Biased Equilibrium. The relatively rapid interconversion between SP and MC forms, coupled with the robust mechanical properties of PU-**1**, enable a quantitative analysis of the effects of strain on the equilibrium between the SP and MC forms. Visible color change of PU-**1** occurs immediately after mechanical activation, but the full color change is not instantaneous. When the sample is held at constant strain, over time it becomes increasingly purple and the MC peak (570−580 nm) increases (Figure 5a). The peak absorbance versus time of the PU-**1** sample held in the dark at a stretch of 2.0 shows the absorbance approaches a steady-state value after 1−2 h. In contrast to the mechanically activated PU-**1** sample used for the fluorescence decay measurements (Figure 4b), which demonstrates the reversion of stress-induced MC form back to the more thermally stable SP form; the mechanically activated MC in the PU-**1** sample held under constant load does not revert. The plateau in absorbance seen in Figure 5a and the lack of MC to SP reversion suggest that the mechanophore has reached a new mechanically biased equilibrium in the strained state.

After PU-**1** is allowed to come to equilibrium, no change is expected to occur without changes to the ambient conditions, such as light exposure and temperature. For instance, irradiation with visible light should drive the equilibrium toward the closed SP form, even if the strain in the sample is held constant. If indeed the equilibrium ratio of MC to SP in the absence of light is determined by the force on the sample, upon removal of the visible light source, the amount of MC present should return to the no-light levels. A PU-**1** sample was mechanically activated in the dark at a stretch of 2.0 and allowed to equilibrate in the

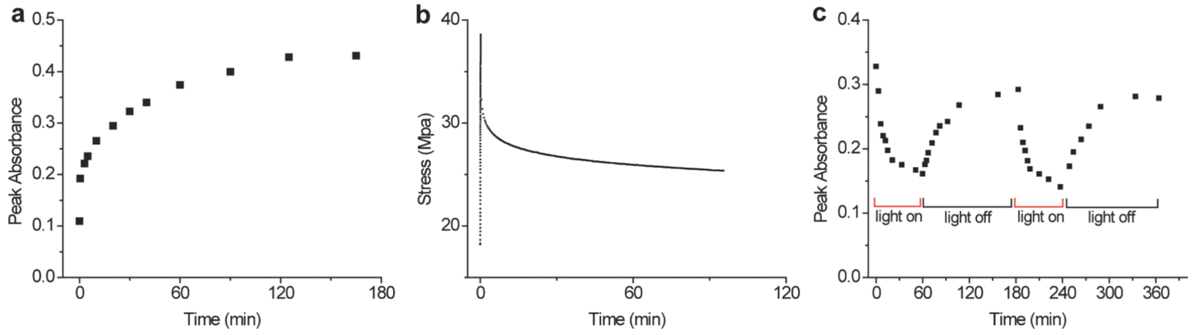

Figure 5. (a) Peak normalized absorbance at 580 nm of mechanically activated PU-**1** held at a constant stretch ratio of 2.0 vs time. (b) Typical stress relaxation of PU-**1** held under constant strain. Plot represents "dog bone"-shaped PU-**1** with initial gauge length of 10.2 cm stretched at 1 mm/s to a displacement of 6 cm, and then held for over 90 min. (c) Peak absorbance (570−580 nm) plotted versus time. The PU-**1** sample had been held at constant stretch of 2.0 for 2 h, and at time = 0 min a bright halogen light source is continuously irradiated onto the PU-**1** sample for 1 h and then removed for 2 h; this is repeated, demonstrating the altering of the equilibrium between SP and MC by strain.

strained state (approximately 1−2 h). Then, while still strained, the equilibrated sample was exposed to a bright visible light driving the sample toward the SP form. This could be observed as the color rapidly faded (≈30 min). Upon removal of the light, the color returned in 1−2 h (the strain on the sample was constant over these experiments). This could be repeated multiple times, for as long as the sample stays in the strained state (Figure 5c). This not only provides further indication that the SP to MC conversion is induced by force and not some other effect (such as some effect during the initial mechanical deformation) but also shows that mechanical force is altering the potential energy surface such that the MC form becomes more favored under strain compared to the no-strain situation.

Stress relaxation of the PU-**1** tensile specimen was also monitored at different levels of strain (Figure 5b). PU-**1** was stretched at a strain rate of 1 mm/s to different levels of displacement. Between each increasing step of displacement, sufficient time was allowed to ensure that the sample had relaxed and that the absorbance measurements were indeed taken at the new equilibrium. After 90 min in constant strain, the stress values indeed were close to a steady-state value of stress relaxation, establishing that the dynamical values of stress in the tensile specimen had also equilibrated.

The thickness, cross-sectional area, and overall volume were monitored throughout the mechanical testing to ensure that measured physical dimensions of the sample over time remained constant. Thickness and cross-sectional area decreases correlated consistently with increases in gauge length of the tensile specimen, and the sample volume change remained fairly constant with only a slight increase in volume with stretch ratio (see Supporting Information). The minimal volume change indicates that although the sample is held under strain for long periods of time, there is minimal grip slippage and also further supports that the measured equilibrium values are valid.

In conclusion, we have developed a new method of incorporating mechanophore into step-growth polymers, specifically PU, and have demonstrated bulk mechanical activation of the SP mechanophore in this system. By use of visible spectroscopy, the absorbance was shown to increase linearly with strain, and when held at constant strain, the MC form did not revert back to the thermodynamically preferred (under no load) SP form, indicating a strain-induced change in the energy landscape of the SP mechanophore system. We envision that the transfer of this mechanophore incorporation method to other step growth polymers is possible, leading to the possibility of developing a variety of different engineering polymers with local stress-sensing capabilities.

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Supporting Information Available: Text, two schemes, six figures, and two videos describing experimental details, synthetic procedures, mechanical testing procedures, and absorbance and fluorescence procedures and spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) Minkin, V. I. *Chem. Rev.* **2004**, *104*, 2751–2776.