The Effect of Polymer Chain Alignment and Relaxation on Force-Induced Chemical Reactions in an Elastomer

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Simultaneous measurements of mechanical response, optical birefringence, and fluorescence signal are acquired in situ during tensile testing of a mechanophore-linked elastomeric polymer. Mechanical stress, deformation, and polymer chain alignment are correlated with force-induced chemical reaction of the mechanophore. The mechanochemically responsive polymer under investigation is spiropyran-(SP)-linked poly(methyl acrylate) (PMA). Force-driven conversion (activation) of SP to its merocyanine (MC) form is indicated by the emergence of a fluorescence signal with 532 nm light incident on the sample. Increasing rate of tensile deformation leads to an increase in both stress and SP-to-MC conversion, indicating a positive correlation between macroscopic stress and activation. Simultaneously collected birefringence measurements reveal that rapid mechanophore activation occurs when maximum polymer chain alignment is reached. It is found that SP-to-MC conversion in PMA requires both a sufficient level of stress and adequate orientation of the polymer chains in the direction of applied force.

1. Introduction

Traditionally chemical reactions are driven by light, thermal, chemical, or electrical potential. Mechanically induced bond cleavage can also be achieved, but is typically non-selective and/or destructive.11 By synthesizing and linking force-sensitive molecules (mechanophores) into a polymer backbone, mechanical deformation can be used to drive site-specific in situ chemical reactions. A variety of mechanophore chemistries have been incorporated into polymer backbones, and numerous force-stimulated chemical reactions have been demonstrated using pulsed sonication in the solution state.12-13 Only a small number of mechanophores have shown activation in the solid state.11,13,14 Notably, Davis et al. achieved force-induced activation of spiropyran (SP), which undergoes a 6-π electro-cyclic ring-opening reaction under tensile deformation to a merocyanine (MC) form. The reaction of SP to MC is indicated by a strong color change, due to absorbance in the visible range, as well as the emergence of a fluorescence signal.13,15,16 This mechanically induced color change could serve as a sensor for mechanical deformation or stress in a polymer sample. Mechanochromic functionality has been demonstrated in previous polymer systems,17,18 but the mechanophore approach is unique in that covalent bonds are cleaved by force and chemical rearrangement of the mechanophore occurs.

Understanding the parameters influencing transfer of macroscopic stress in a bulk polymer to localized force on the mechanophore remains a topic of active research. The mechanophore, SP, has been incorporated into a variety of solid state polymers15,16,19,20 and the ease of monitoring the SP to MC conversion makes this system ideal for studying many of the key parameters affecting mechanophore activation in bulk polymers. However, the effects of applied stress, deformation and polymer chain orientation have not yet been fully explored. Previous publications have alluded to the importance of polymer orientation and alignment in the direction of applied force for achieving mechanochemical reactions.19,20 Recent work by Beiermann et al.21 examined the orientation of the mechanophore subunits within the polymer backbone using polarized fluorescence and found a preferential activation of mechanophores in the direction of macroscopic force. However, the orientation of polymer chains during loading and the influence of mechanophore activation have not yet been quantitatively correlated.

The proposed premise for mechanophore activation in bulk polymers is that linearly oriented polymer chains, aligned in the direction of macroscopic stress, transfer force to the mechanophore more efficiently than randomly oriented chains, which will first use the mechanical energy to align the chain in the direction of force. To investigate this hypothesis, we simultaneously measured stress, stretch ratio, mechanophore fluorescence, (a measure of SP activation to MC) and...
Glass transition temperatures ($T_g$) for active and control polymer were 12 °C and 13 °C, respectively, taken as the shoulder of differential scanning calorimetry curves. These values agreed closely with plain PMA (no SP). The effect of SP incorporation on polymer thermo-mechanical properties was considered negligible.

2.2. Simultaneous Measurement of Stress, Fluorescence, and Birefringence

Measurements for load, displacement, birefringence and fluorescence intensity were captured simultaneously during monotonic tensile testing using a novel optical and mechanical setup. A schematic and photo of the setup are shown in Figure 1a,b, respectively. A circularly polarized incident light source was incident on a polymer sample, which acted both as a monochromatic light source for photoelasticity (birefringence measurement) and an excitation source for fluorescence of the activated MC form (Species 1c in Scheme 1) of the mechanophore. The incident wavelength ($\lambda_{\text{light}} = 532 \text{ nm}$) was reflected off a dichroic beamsplitter at 45° incidence after passing through the sample for the photoelastic beam, while higher wavelengths ($\lambda_{\text{light}} > 580 \text{ nm}$) were transmitted through the dichroic beamsplitter for collection of the fluorescence signal. The photoelastic beam was then separated into four identical beams ($I_1 - I_4$, see Supporting Information for thorough description) using a two-dimensional diffraction grating, and the resulting images were passed through polarization optics such that the photoelastic state could be fully characterized. The birefringence signal was then calculated by a phase stepping procedure reported by Kramer et al. [23] By this method, full-field fluorescence and birefringence signals were simultaneously captured during tensile testing of dog-bone shaped specimens. Representative images for data collection are provided in Figure 2a–d, along with an optical image of a sample before and after tensile testing (Figure 2e). The experimental method is more thoroughly described in the Experimental Section.

Stretch ratio ($\lambda$, defined as instantaneous sample gauge length divided by the un-deformed gauge length) and true stress ($\sigma_{\text{true}}$, calculated based on optically measured sample width, and assuming the width and thickness stretch ratios were equivalent) were determined from the applied displacement and measured load. Representative data for a mecanochemically active sample tested at a stretch rate ($d\lambda/dt$) of 0.02 s$^{-1}$ are plotted in Figure 3. Stress increased consistently as a function of increasing stretch ratio until failure, which typically occurred at a stretch ratio between 10 and 12. An increase in slope of the stress versus stretch ratio plot ($d\sigma/d\lambda$), that is, hardening, occurred with increasing deformation. Birefringence ($\Delta n$) had
a negative value with respect to the tensile direction, agreeing with previously published data by Saiz et al.,[24] an effect likely due to bulky pendant methacrylate groups on the PMA backbone. In Figure 3 the birefringence value is plotted as the magnitude ($\Delta n$ multiplied by $-10^3$), which increased with increasing stretch ratio, indicating alignment of the polymer backbone in the direction of loading, and then leveled out as the polymer chains reached maximum alignment. The intensity of the measured fluorescence signal ($I_{fl,raw}$) was assumed proportional to the amount of reacted SP, that is, MC, in the beam path.[15] At room temperature (RT = 22 °C), a small equilibrium amount of MC was present in all specimens, which led to some fluorescence signal prior to stretching ($\lambda = 1$). During the initial loading, the fluorescence signal decreased due to sample thinning (i.e., a lower concentration of mechanophores in the fluorescence image field of view). With increasing stretch ratio, the fluorescence intensity began to increase, indicating mechanical activation of SP to the fluorescent MC form. The onset of detectable activation was defined where the increase in activation was significant enough to counteract the effect of thinning. Thus the activation stretch, $\lambda^*$, was identified as the lowest stretch ratio with a positive slope of raw fluorescence intensity, $I_{fl,raw}$ versus stretch ratio, $\lambda$, as indicated in Figure 3.

2.3. Effect of Stretch Rate

2.3.1. Stretch Rate Variation in Active SP-Linked PMA

Active PMA samples were tested at stretch rates of 0.004 s$^{-1}$, 0.02 s$^{-1}$, and 0.10 s$^{-1}$. The resulting polymer behavior (stress, birefringence, and fluorescence intensity) are plotted in Figure 4 for representative samples at each stretch rate. The stress (Figure 4a) in the polymer samples increased with increasing stretch rate as expected for an elastomeric material. In virtually all samples, hardening was observed with increasing stretch ratio. Birefringence (Figure 4b) also increased with increasing stretch rate. Birefringence values began to plateau for all stretch rates as the chains became maximally aligned in the direction of force. The fluorescence signal, $I_{fl,raw}$, was adjusted for the number of mechanophores in the field of view and normalized by the fluorescence intensity at ambient equilibrium ($\lambda = 1$) fluorescence intensity, as described in the Experimental Section.

Figure 1. Design of optical setup. a) Over-head view schematic showing two of the four photoelastic (PE) beams ($I_1$ and $I_2$). $I_3$ and $I_4$ are mirrored across the x-z plane. Optical elements are indicated by P – linear polarizer, Q – quarter wave plate, and f – focusing lens. b) Photo with incident (green) and fluorescent light (red) illustrated. A monochromatic laser was used for both photoelasticity measurements and excitation of fluorescence. The photoelastic and fluorescence signals were separated with a dichroic beam splitter. The fluorescence light was imaged using a color camera. The photoelastic light was split using 2D diffraction, and the $a_1$ and $a_2$ beams, shown as the four green first-order diffraction spots in the inset in (a), were passed through appropriate polarization optics for $I_1$–$I_4$ and redirected to a single camera.
and activation were considerably more apparent in the fastest testing rate (0.10 s\(^{-1}\)) when compared with middle and slowest stretch rates (0.004 s\(^{-1}\) and 0.02 s\(^{-1}\)). This finding implies that larger macroscopic stress at higher stretch rate leads to greater chain alignment and force across the mechanophore, causing more extensive activation of SP.

Figures 5a–c reveal the trend in stretch ratio, stress, and birefringence, at the activation point, as defined in Section 2.2, averaged over three samples at each stretch rate. The stretch value at activation, \(\lambda^*\), shows a marked decrease at the fastest stretch rate. The true stress at the activation point, \(\sigma^*\), shows an increasing trend, indicating that although macroscopic stress is positively correlated to SP activation, the same macroscopic stress does not necessarily translate to the same force and activation of SP at the molecular scale. This effect is attributed to rate dependent hardening of the bulk polymer (Figure 4a), which leads to viscoelastic redistribution of intermolecular forces, i.e., chain slip and relaxation. Activation birefringence, \(\Delta n^*\), values were similar between stretch rates, indicating that a similar degree of chain alignment was present at the onset of SP activation, regardless of the stretch rate. Finally, the rate of change of fluorescence intensity with respect to stretch ratio \((dI_{fl,norm}/d\lambda)\) was averaged between stretch ratios of 8 and 9, where all samples showed an increasing fluorescence signal, but none had failed. The results plotted in Figure 5d show a clear trend of higher rate of fluorescence change (i.e., SP activation) with increasing stretch rates.

### 2.3.2. Stretch Rate Variation in Difunctional Control SP-Linked PMA

Difunctional control SP-linked PMA was tested in tension at the same stretch rates as mechanochemically active polymer. Stress, birefringence and normalized fluorescence data are shown in Figure 6. The mechanical and birefringence behavior were similar to the mechanochemically active case. Despite being linked in a manner that should not transmit force from the covalently bonded polymer chains across the mechanophore, an increase in fluorescence signal (activation) was seen with increasing stretch ratio. The extent of fluorescence increase was lower than the active case, but still showed stretch rate dependence (higher stretch rate led to greater activation). In contrast to active specimens, color change was not visually detectable in the gauge section of difunctional control SP-linked samples after tensile testing (see Figure S2 in the Supporting Information).

The fluorescence increase in difunctional control PMA had a virtually identical spectroscopic fluorescence peak as the active sample (refer to Figure S1 in the Supporting Information),
and no fluorescence signal was present in polymer without SP incorporated, providing evidence that fluorescence increase in the difunctional control was due to SP ring opening. Fluorescence increase in the difunctional control SP-linked PMA may be due to a frictional force on the pendant group containing the force sensitive C–O spiro bond (Scheme 1, Species 2). This effect is discussed in more detail in Section 2.4.2.

2.4. Stress Relaxation Behavior of SP-Linked PMA

2.4.1. Active SP-linked PMA

Active SP-linked PMA samples were drawn at a stretch rate of 0.10 s⁻¹ to a stretch ratio of 9 and held at constant deformation. The relaxation response of stress, birefringence and activation were measured as a function of time and are shown in Figure 7. The stress and birefringence during the stress relaxation stage were fit to exponential decay curves with effective time constants (τeff) of 54 s and 83 s, respectively (Figure S3 in Supporting Information).

During stress relaxation, the fluorescence intensity in the polymer continued to increase, indicating a time dependence of force-induced chemical reactions. Although macroscopic deformation had stopped, stress in the system was sufficient to drive the reaction forward without further deformation. The fluorescence reached a maximum as the stress decayed and eventually decreased slightly over time due to the incident light source (λ = 532 nm) driving MC to SP. SP to MC activation continued to proceed forward until the stress in the sample was below ≈10 MPa. This relaxation behavior was repeatable over multiple samples. The stress relaxation region of Figure 7 in which normalized fluorescence intensity increased was fit to an exponential curve. The effective time constant of the fluorescence increase was 53 s, virtually the same as the stress relaxation time constant. After returning to zero load, some fluorescence increase remained in the sample.

Effective time constants measured from stress and birefringence relaxation conditions (fitted to exponential decay for 400 s after the onset of relaxation) were between 50–100 s at all loading rates. These relaxation time scales were similar to the test times for the fastest stretch rate (dλ/dt = 0.10 s⁻¹). Slower stretch rates (dλ/dt = 0.004 s⁻¹ and dλ/dt = 0.02 s⁻¹) corresponded to test times substantially longer than the relaxation times (ttest ≈ 5–25 τeff), giving more time for polymer relaxation. The pronounced increase in stress, birefringence, and activation at the highest stretch rate of 0.10 s⁻¹ (refer to Figure 4) is attributed to a less prominent relaxation effect over short test durations.

2.4.2. Difunctional Control SP-linked PMA

Difunctional control SP-linked PMA specimens were subjected to stress relaxation testing similar to the active case. The response of the difunctional control polymer over time is included in Figure 8. The fluorescence signal increased during deformation, implying activation of SP to MC. In contrast to the active samples, the fluorescence signal did not continue to increase in the stress relaxation stage. Instead the fluorescence
A novel experimental set-up was designed to simultaneously apply a mechanical load to polymer samples and collect in situ optical measurements of fluorescence and polymer chain alignment. The SP-to-MC conversion was monitored via the fluorescence signal of the MC form, excited by a 532 nm laser and collected at $\lambda > 580$ nm. Birefringence provided a relative measure of the polymer chain alignment, which was correlated to the mechanophore activation. The findings indicate that rapid activation of SP occurred when birefringence began to plateau and reach a maximum, thus when polymer chains were most aligned in the direction of macroscopic force.

The effect of tensile stretch rate was studied and showed that for increasing stretch rate, the macroscopic stress in the polymer increased and a corresponding increase in the rate and degree of activation ensued. Stress relaxation behavior of SP-linked PMA indicated that SP activation is a time dependent process, and mechanochemical conversion will continue at a constant deformation, provided that the stress remains sufficiently high (above ~10 MPa).

An SP-linked control was incorporated into the PMA backbone such that force was not transferred across the sensitive C–O spiro bond of the mechanophore. In this configuration, some amount of fluorescence increase, that is, SP activation, was detected in the control under tension. The fluorescence increase was of smaller magnitude and did not continue under stress relaxation conditions, indicating a different mechanism for activation in the control case.

4. Experimental Section

Sample Preparation: Active and difunctional control SP-linked PMA were synthesized via single electron transfer living radical polymerization reactions with SP serving as the initiator as described by Davis et al. \cite{13} Polymer was dissolved into THF, filtered through fumed silica and dried under vacuum at 50 °C for 24 h. This step was critical to removing all solvents involved in synthesis and attaining maximum polymer stiffness. PMA was then molded at a pressure of 200 psi at 150 °F (66 °C) for 10 min in a closed mold.

Tensile Testing Protocol: For monotonic tensile testing, displacement control was used at stretch rate was 0.1 s$^{-1}$, 0.02 s$^{-1}$, and 0.004 s$^{-1}$. Images were acquired at periods of 1 s, 5s, and 25 s for the three testing rates, respectively. For the stress relaxation testing, samples were stretched to approximately $\lambda = 9$, held at constant displacement. The image acquisition rates were the same as the monotonic tests. True stress was calculated during testing based on the load, $F$, in the sample and the optically measured sample width, $w$, based on photoelastic image. The thickness ($T$) stretch ratio, $\lambda^T = T/T_0$, was assumed equal to the optically measured width stretch ratio, $\lambda^w = w/w_0$, therefore true stress was defined as

$$\sigma_{true} = \frac{F}{w_0 T_0 (\lambda^w)^2}.$$ (1)
Combined Mechanical and Optical Experimental Setup: The experimental setup, shown in Figure 1, incorporated a uniaxial load frame with a hybrid optical measurement technique combining fluorescence imaging and photoelasticity. This setup allowed for simultaneous measurement of load-displacement data, fluorescence detection (indicating SP activation to MC), and optical birefringence (a relative measure of polymer chain orientation) using a photoelastic polariscope. A custom uniaxial load frame from IMAC Motion Control Corporation utilized two opposing actuators so that the center of a tensile sample remained in the field of view. A 5-lb (22 N) capacity Honeywell Sensotec Load Cell (Model 31) was attached to one of the actuators to monitor load. Displacement of the actuators was controlled through NI LabVIEW. The load frame was oriented horizontally on an optical table to allow for the hybrid optical techniques.

A 532-nm laser diode was the source for both photoelasticity and fluorescence imaging excitation. The laser beam was expanded to a 12-mm diameter collimated beam, passing through polarization optics to control the light intensity and to create a circularly polarized beam for the first portion of the photoelastic polariscope. After the light was transmitted through the sample, a dichroic beamsplitter from Chroma Technologies reflected the incident light wavelength ($\lambda = 532$) for photoelastic imaging and transmitted emitted fluorescence from the MC form, which has a broad emission peak centered at 600–650 nm when excited with 532 nm light (see Supporting Information for spectra). To determine the optical birefringence from the photoelastic signal, we utilized phase-stepped photoelasticity requiring four different images obtained from four different combinations of analyzing polarization optics after the sample, typically obtained by rotating these optics for sequential image capture. Since PMA is a time-dependent

Figure 6. Behavior of difunctional control SP-linked PMA loaded in tension at three stretch rates. a) Stress vs stretch ratio, and b) birefringence vs stretch ratio, and c) thickness-corrected, normalized fluorescence intensity vs stretch ratio.

Figure 7. Stress relaxation testing of active SP-linked PMA loaded at a stretch rate of 0.10 s$^{-1}$ including stretch history, stress relaxation, birefringence relaxation, and normalized fluorescence intensity as a function of time.
viscoelastic material, it did not allow sequential phase-stepping photoelastic images. Therefore diffraction gratings were used to split the photoelastic signal into four beams that were captured by the same camera (AVT Stingray F145b), allowing for four simultaneous phase-stepped images. A mathematical description of the birefringence calculation is included in the Supporting Information. The optical birefringence of the polymer was determined from the four phase-stepped photoelastic images, as described in detail in the Supporting Information. In summary, the intensities of the four interference patterns were averaged over the same central area of interest in the gauge section of the sample, and then used to calculate the isochromatic phase, $\delta$, which is a measure of the relative retardation of the polarized light through the sample. The isochromatic phase is directly related to the optical birefringence, $\Delta n$, by

$$\delta = \Delta n \frac{2\pi T}{\lambda}$$

where $T$ is the current thickness (as determined from the width stretch ratio) and $\lambda$ is the wavelength of the incident light.

Supporting Information

Supporting Information is available from Wiley Online Library or from the author.

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Figure 8. Stress relaxation and activation in difunctional control SP-linked PMA loaded at a stretch rate of 0.10 s$^{-1}$. The normalized intensity of the color image, averaged over pixels in the gauge section of the field of view. The equation relating the normalized fluorescence to the raw fluorescence, measured length stretch ratio, $\lambda$, and width stretch ratio, $\lambda_w$ is

$$I_{\text{fl,norm}} = I_{\text{fl,raw}} \lambda^{\frac{\lambda_w}{\lambda}}$$

This calculation is derived in the Supporting Information.