Role of Mechanophore Orientation in Mechanochemical Reactions

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Ⓢ *Supporting Information*

ABSTRACT: The orientation of force-sensitive chemical species (mechanophores) in bulk polymers was measured via the anisotropy of fluorescence polarization. Orientation measurements were utilized to investigate the role of mechanophore alignment on mechanically driven chemical reactions. The mechanophore, spiropyran (SP), was covalently bonded into the backbone of poly(methyl acrylate) (PMA) and poly(methyl methacrylate) (PMMA) polymers. Under UV light or tensile force, SP reacts to a merocyanine (MC) form, which exhibits a strong fluorescence, polarized roughly across the long axis of the MC subspecies. An order parameter was calculated, based on the anisotropy of fluorescence polarization, to characterize the orientation of the MC subspecies relative to tensile force. For UV-activated SP-linked PMA samples, the order parameter increased with applied strain, up to an order parameter of approximately 0.5. Significantly higher order parameters were obtained for mechanically activated SP-linked PMA samples, indicating preferential mechanochemical activation of species oriented in the tensile direction. The anisotropy of fluorescence polarization in SP-linked PMMA also provided insight on polymer drawing and polymer relaxation at failure.
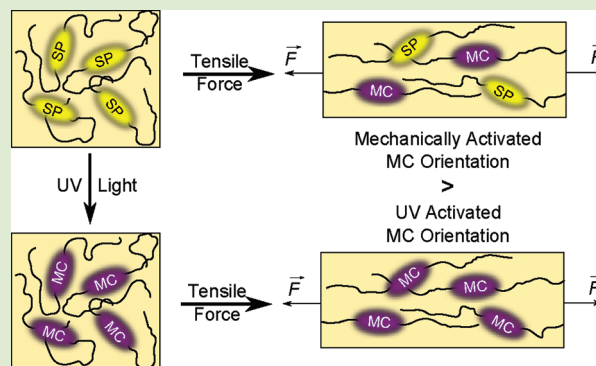
Mechanoresponsive polymeric materials elicit an advantageous response to mechanical force through a variety of transduction mechanisms.[1] Mechanical deformation has been used to change the ionic environment in polyelectrolyte films,[2] perturb ordering of agglomerates and crystalline regions,[3−5] and break covalent bonds at selective molecular sites.[6−13] In the latter case, force-induced chemical reactions are achieved in bulk polymers by incorporating force-sensitive molecules, that is, mechanophores, into the polymer backbone. These polymers have potential applications as damage sensing,[6,7,14−16] damage healing,[8,9] and catalyst-releasing[10−13] material systems. Recent work indicates that the alignment of polymer chains in the direction of stress is critical for effective force transfer across the mechanophore.[15−17] Here we show the correlation between the orientation of mechanophores in bulk polymers and their activation under uniaxial tensile deformation.

The mechanophore investigated was spiropyran (SP), which undergoes a reversible electrocyclic ring-opening reaction to a merocyanine (MC) form[18] (Scheme 1). The ring-closed SP form is colorless or yellow with virtually no fluorescence signal, while the ring-opened MC isomer is red or purple and strongly fluorescent (refer to Supporting Information (SI) for fluorescence spectra). The mechanophore can be driven to predominantly its closed SP form using visible light ($\lambda \approx 550$ nm). UV light ($\lambda = 385$ nm), elevated temperatures, and mechanical force drive SP toward its MC form.[6,7,14−16,18] In this study SP was linked into linear poly(methyl acrylate) (PMA) and poly(methyl methacrylate) (PMMA) backbones. Linear PMA is a thermoplastic elastomer ($T_g = 12$ °C), while PMMA is glassy ($T_g = 128$ °C). Properties for samples presented in this work are listed in Table 1. PMMA was either plasticized or tested at elevated temperatures to allow the drawing and mechanical activation of SP.[16] Details of synthesis for these polymers are provided in previous publications,[6,16] and optical images before and after testing can be found in the SI.

Fluorescent molecules (e.g., MC) emit photons with polarization in the direction of transition dipoles. Work by

Scheme 1. Ring-Opening of SP to MC, with the Approximate MC Transition Dipole, $\vec{r}$, Labeled

Non-Fluorescent SP   *Fluorescent MC*
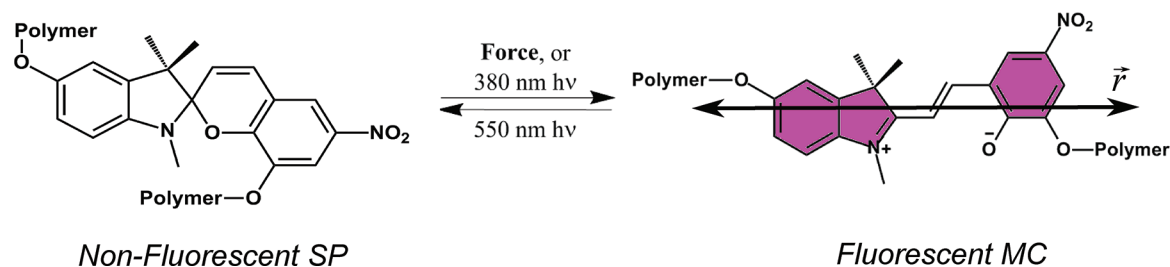
Table 1. Properties of SP-Linked Polymers

polymer	PMA	PMMA[a]	PMMA[b]
M_N (kDa)	230	180	180
PDI	1.1	1.8	1.8
T_g (°C)	12	128	
ε_{ult} (%)	~1500	35−70	65
σ_{ult}, Engr. (MPa)	4	20	15

[a]Tested at 90 °C, unplasticized. [b]Plasticized with 17 wt % methanol (MeOH), tested at room temperature.

Bletz et al.[19] revealed that the predominant emission dipole moment ($\vec{r}$) for the MC species is coincident with the long axis of the molecule (Scheme 1). We analyzed polarized fluorescence emission to determine the average orientation of mechanophores using the experimental setup diagrammed in Figure 1a.
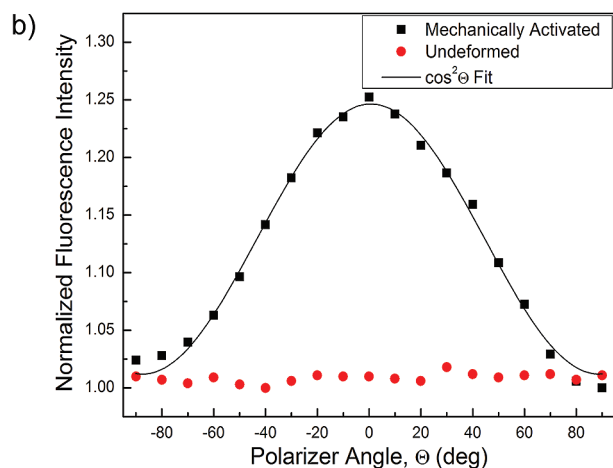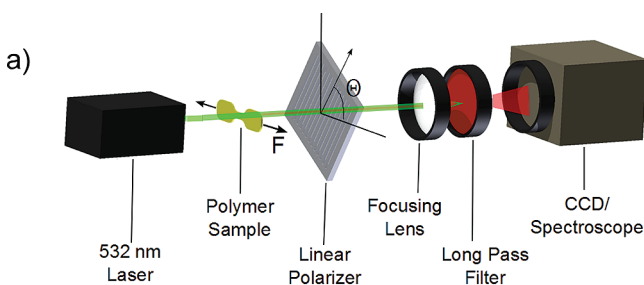

a)

532 nm Laser   **Polymer Sample**   **Linear Polarizer**   **Focusing Lens**   **Long Pass Filter**   **CCD/ Spectroscope**

b)

Figure 1. Analysis of mechanophore orientation. (a) Experimental setup for analysis of polarized emission. (b) Fluorescence intensity vs polarizer orientation for mechanically activated (ε = 35%) and undeformed thermally activated SP-linked PMMA.

We first investigated the effect of varying polarizer angle, Θ, with respect to the uniaxial tensile direction, on the fluorescence signal of SP-linked PMMA samples. Relative fluorescence intensity is plotted as a function of polarizer orientation in Figure 1b for two samples: mechanically activated and thermally activated SP-linked PMMA. The mechanically activated sample was drawn to ε = 35% at 90 °C, resulting in a strong purple color in the gauge section. The fluorescence signal was anisotropic with a maximum intensity when the polarizer was oriented parallel to the tensile direction, indicating that the transition dipole of MC was oriented predominately in the direction of applied force. The data closely fit the expected $\cos^2 \Theta$ relationship for a preferred orientation of the fluorescent molecule. In contrast, un-deformed SP-linked PMMA, thermally activated at 170 °C during molding, shows no preferential orientation.

The degree of orientation is evaluated by an order parameter, S, based on the second-order Legendre polynomial, P_2:[20]

$$\langle P_2 \rangle = \frac{\langle 3 \cos^2(\beta) - 1 \rangle}{2} \equiv S \qquad (1)$$

where β is the angle between a laboratory frame (i.e., the tensile direction) and a component director (i.e., the dominant MC transition dipole). Order parameter values vary between 0 (random distribution) and 1 (perfectly aligned) in this study. An order parameter can be derived from eq 1 based on the measured fluorescence intensities with the analyzing polarizer oriented parallel and perpendicular to the tensile direction:[21−23]

$$S = \frac{(I_{\parallel} - I_{\perp})}{(I_{\parallel} + 2I_{\perp})} \qquad (2)$$

where $I_{\parallel}$ and $I_{\perp}$ denote the total fluorescence intensity with the polarizer parallel and perpendicular to the tensile direction, respectively. Eq 2 assumes that the mechanophore is rotationally fixed during measurement.

We used the order parameter calculated from eq 2 to determine the average orientation of the MC form within SP-linked PMA. Fluorescence images or spectra were taken at increments of odd integer values for the stretch ratio, λ, defined as the instantaneous sample gauge length divided by the initial length. The order parameter was averaged over the gauge section for a number of samples. Sample details, testing procedures, and analyses are more thoroughly described in the SI. A plot of order parameter as a function of stretch ratio is shown in Figure 2 for UV-activated and mechanically activated SP-linked PMA.

Activation by UV light drove virtually all SP subspecies to the fluorescent MC form. The order parameter for unstrained material was nearly 0, indicating a randomly oriented sample.
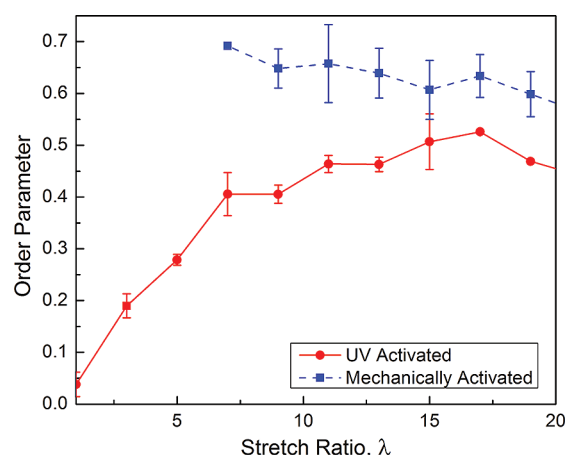
Figure 2. Average MC order parameter as a function of the stretch ratio, λ, for UV activated and mechanically activated SP-linked PMA. Error bars represent the standard deviation between three samples for each sample type.

The small degree of orientation present was due to a prestress on the sample before testing. With an increasing stretch ratio, the UV-activated MC subspecies became increasingly oriented in the tensile direction, reaching a maximum order parameter of ca. 0.5.

Prior to testing, mechanically activated samples were irradiated with visible light to drive any MC form to the closed SP form. Because the SP form has virtually no fluorescence signal, the order parameter remained undefined until the samples began to exhibit a detectable fluorescence (i.e., activation). The onset of mechanical activation occurred at $\lambda_{onset} \approx 6$, well before polymer failure. The order parameter for mechanically activated samples was significantly higher than in the UV-activated case, indicating that SP subspecies which were more aligned with the tensile force activated preferentially.

While SP-linked PMA exhibited a relatively consistent degree of fluorescence anisotropy throughout the gauge section (Table SI in the Supporting Information), activation and degree of orientation were highly localized in SP-linked PMMA. SP-linked PMMA was plasticized with MeOH (17 wt % uptake). A region of interest (ROI) (refer to the SI, Figure S8a) was monitored for MeOH-plasticized SP-linked PMMA, which was driven to the SP form using visible light prior to testing. The sample was tested in tension with increments of 5% strain between fluorescence measurements (Table 2). After the polymer yielded and began to draw, the fluorescence increased with increasing strain. When the fluorescence signal was sufficient to define an order parameter, the order parameter initially demonstrated relatively high values (0.4−0.5), again indicating that the mechanophores oriented in the direction of force are preferentially reacting. Both fluorescence and order parameter were spatially heterogeneous and localized across the ROI. After failure, the order parameter dropped to levels below 0.1 near the failure surface. The same trend was evident in unplasticized SP-linked PMMA samples tested at elevated temperature (90 °C) and examined ex situ (see Figure S8 in the SI). The authors hypothesize that this decrease in order parameter at failure, particularly near the failure surface, indicates significant polymer recoil and relaxation.

Fluorescence anisotropy of MC enabled the measurement of the orientation of subspecies covalently bonded into bulk polymers under a tensile load. In situ testing of mechanophore-

Table 2. Fluorescence Images and Calculated Order Parameter in the Gauge Section of SP-Linked PMMA under Tensile Deformation[a]

[a]Tensile force applied in the horizontal direction. Fluorescence images shown were taken with a polarizer oriented parallel to tensile force. Approximate sample edges have been outlined in white.

linked PMA revealed increasing overall mechanophore orientation with increasing strain. Mechanophores aligned along the tensile direction were shown to be preferentially activated by force. These measurements provide the first quantitative evidence that mechanophore orientation in the direction of force promotes activation. These findings apply not only to the SP/MC mechanophore investigated here, but to any mechanophore-linked polymer, and provide insight for design and testing of new, more efficient mechanophores. We provide evidence suggesting substantial relaxation of polymer chains at failure in SP-linked PMMA. Results indicate that MC fluorescence polarization may provide an effective molecular probe to study the full-field orientation of polymer chains during deformation and failure.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed description of mechanical/optical testing and analysis of SP-linked polymers. 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.

■ ACKNOWLEDGMENTS

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