Photoresponsive Polymers

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Reversible Switching of the Shear Modulus of Photoresponsive Liquid-Crystalline Polymers[**]

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Liquid-crystalline polymers (LCPs) are of interest because of their ability to combine the properties of small-molecule liquid crystals with those of polymers.[1] LC moieties can be designed to exhibit a conformational change on the molecular level in response to thermal,[2,3] pH,[3] electrical,[4] or optical[5,6] stimulation. LC polymeric materials benefit from the rheological integrity that the polymer component provides to the system. Siloxane-based LCPs present specific advantages associated with the very low glass transition temperature (T_g) of the siloxane backbone,[7,8] which allows the materials to retain their properties over a wide temperature range, particularly at room temperature.

The photoisomerization of LC moieties to produce actuator materials was first proposed by de Gennes.[5] This class of materials can be stimulated by exposure to particular wavelengths of electromagnetic radiation (e.g., visible light), which results in the desired confirmational changes that can lead to changes in the rheological or dimensional properties of the materials to give photoresponsive shape-memory polymers[9] or films that exhibit a bending actuation when one surface is exposed to light.[8,10] Several molecules have generated great interest because of their abilities to photoisomerize and thus generate useful properties in polymers.[11,12] One such class of molecules is azobenzene-containing moieties, which undergo a *trans* to *cis* photoisomerization upon exposure to UV (366 nm) light. The moiety relaxes to the equilibrium *trans* conformation when the UV irradiation is removed; the relaxation can also be accelerated with heat or exposure to longer wavelength light (> 540 nm). The photoisomerization of azo moieties incorporated into a polymer matrix has been shown to disrupt the stability of nematic[13] and smectic[14] LC mesophases. Thus, a reversible and isothermal smectic to isotropic transition can be achieved through the disruption of the smectic LC mesophase by isomerization of the azo moieties.[11,15]

Herein, we report the effects of UV stimulation on the morphology and rheological properties of azo-containing siloxane-based LCPs. To date, a very limited number of studies have addressed the light-tunable rheological properties of photoresponsive polymeric systems. Among these, the recent work by Ketner et al.[16] revealed the remarkable potential of aqueous micellar solutions, the viscosity of which can be reduced by more than four orders of magnitude upon UV exposure. The limiting factor in the study of such systems is the irreversible character of the transformation; however, in the present study, we have demonstrated reversible rheological property changes. Such properties are of particular interest for light-activated damping mechanisms, actuable armor, and related applications in fields such as robotics and sensors. We have investigated azo-containing moieties attached to a siloxane polymer backbone that can undergo a reversible conformational change upon exposure to UV light. This molecular rearrangement disrupts the LC phase, which affects the global conformation of the chain, thus allowing dynamic switching of the rheological properties of the system.

The polymer backbone used in this study is a poly(vinylmethylsiloxane) (PVMS) with a number average molecular weight (M_n) of 14800 g mol^{-1} and a polydispersity index (PDI) of 1.23.[17] The homopolymer can be modified with a broad range of attachment percentages by using previously reported approaches that rely on platinum-catalyzed hydrosilyation. Azo-containing LC moieties were attached to the polymer backbone with an attachment percent of 67% to yield a functionalized siloxane polymer (LCP$_{azo}$81, Figure 1 a) with a total molecular weight of 80700 g mol^{-1}. The smectic to isotropic transition temperature (T_{iso}) of LCP$_{azo}$81 was measured to be $T_{iso} = 124$ °C by using differential scanning calorimetry (DSC).

Small-angle X-ray scattering (SAXS) was used to characterize the morphological response of the liquid-crystalline polymers to UV exposure. To achieve sufficient LC response over reasonable timeframes, the LCP film was first heated to 100 °C (which is close to the clearing point temperature) in the

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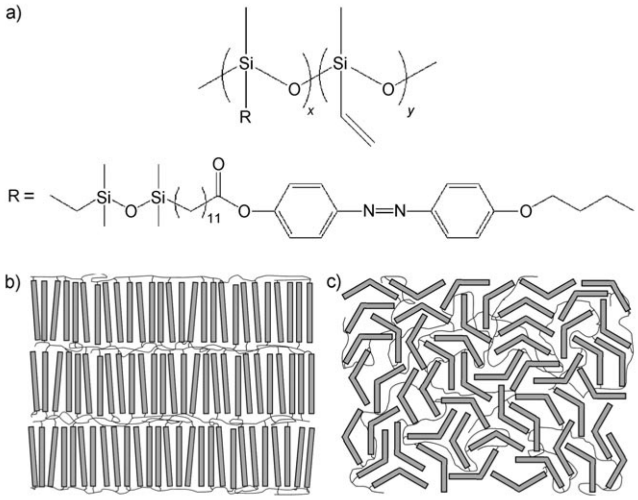

Figure 1. a) Chemical structure of the side-chain liquid-crystalline polymer, where *x* and *y* are random and R is the azobenzene-containing moiety. Schematic of LCP in b) the *trans* conformation and c) the *cis* conformation, which result in the smectic and isotropic LC mesophases, respectively.

absence of UV light using a commercially available SabreTube furnace,[18] which was custom-mounted for in situ X-ray experiments. A *trans* to *cis* conformational change was induced by exposing the LCP film to UV light at constant temperature, which resulted in a disruption of the smectic LC mesophase and a corresponding decrease in the scattering intensity. Figure 1 b shows a schematic diagram of the LCP in the *trans* conformation, which results in a smectic LC mesophase; Figure 1 c shows a schematic diagram of the LCP in the *cis* conformation, which results in an isotropic LC mesophase.

As the UV exposure time increased, a decrease in the scattering intensity from the smectic layers is observed; one-dimensional scattering profiles as a function of UV exposure time are shown in Figure 2. The low q scattering arises from the larger smectic layers, which are more readily disrupted, thus leading to a shift in the peak upon continued exposure; the larger smectic layers are less tightly packed and thus the photoisomerization has a lower enthalpic barrier that must be overcome. A similar phenomenon was previously observed in related systems, in which larger smectic layers had a lower smectic-to-isotopic transition temperature.[17]

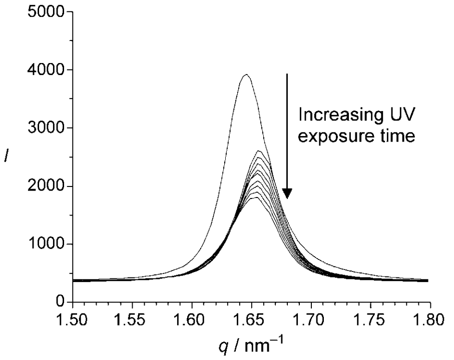

Figure 2. Morphological response to UV light measured by using small-angle X-ray scattering (SAXS). One-dimensional scattering curves as a function of exposure to UV light are shown, the scattering intensity decreases with increasing exposure time.

Small- and large-amplitude oscillatory shear tests (SAOS and LOAS, respectively) were performed at 100 °C ($T < T_{iso}$) in order to characterize the rheological properties of the liquid-crystalline polymer in response to UV light. Exposure of the LCP to UV light during oscillatory shear experiments significantly affects the viscoelastic behavior of the system. Strain amplitude sweep tests, with amplitudes ranging from $1\% \leq \gamma_o \leq 1000\%$, were performed at a frequency of $\omega = 1\ \mathrm{rad\,s^{-1}}$ on the LCP without and with exposure to UV light (Figure 3). In the case of exposure to UV light (represented by the open symbols), the signals obtained for strain amplitudes less than 5 % are close to resolution of the force rebalanced transducer on the rheometer. The unexposed material (UV light switched off, and shielded from ambient light) shows a linear viscoelastic response for strain amplitudes up to about 4 %, above which the dynamic moduli begin to decrease slowly with increasing strain amplitude. Figure 3 shows how exposure to UV light reduces the modulus by close to an order of magnitude and extends the linear viscoelastic regime of the LC melt to a strain amplitude of about 20 %. Both the storage (G') and loss (G'') moduli are reduced upon exposure to UV light; however, the extent of this reduction depends on the imposed strain amplitude. Within the linear viscoelastic regime, the relative decrease in the storage modulus $(G'_{off})/(G'_{on})$ and loss modulus $(G''_{off})/(G''_{on})$ is comparable. For strain amplitudes $1\% \leq \gamma_o \leq 4\%$: $(G'_{off})/(G'_{on}) = 8.4 \pm 0.9$, and $(G''_{off})/(G'_{on}) = 7.0 \pm 1.1$. As the strain amplitude is increased into the nonlinear viscoelastic regime, the elastic modulus of the LCP network begins to decrease dramatically and is more than an order of magnitude lower than the elastic modulus without exposure to UV light at strain amplitudes greater than 100 % and $(G'_{off})/(G'_{on}) \gg (G''_{off})/G''_{on})$. Frequency sweep experiments were performed with a strain amplitude of 2 % at 100 °C with and without

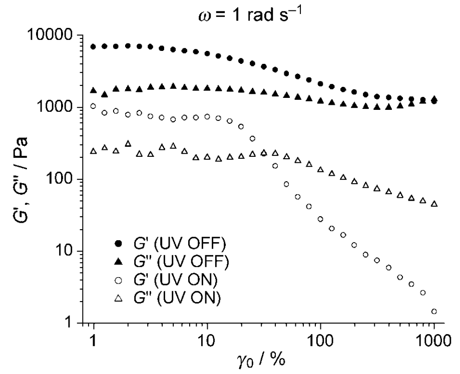

Figure 3. Strain amplitude sweep without (solid symbols) and with (open symbols) exposure to UV light. The storage modulus (G') is represented by the circles and the loss modulus (G'') is represented by the triangles. The data were obtained at 100 °C at an angular frequency of $\omega = 1\ \mathrm{rad\,s^{-1}}$.

exposure to UV light (Figure S4 in the Supporting Information).

The transient response of this photorheological polymer melt to UV irradiation was investigated with in situ UV dynamic oscillatory shear experiments. The effects of repeated exposure to UV irradiation on the storage and loss moduli at 100 °C are shown for both small ($\gamma_0 = 2\,\%$) and large ($\gamma_0 = 100\,\%$) strain amplitudes in Figures 4 a and b, respectively. The experiment began without UV exposure, and, once the steady state was reached, the LCP was exposed to UV light, which resulted in a decrease in the G' and G'' values. Once a new steady state was established (after a period of approximately 500 s), the UV light was turned off so that the system could relax to its initial state. The decay in both the integrated scattering intensity and the storage modulus (G') can be described by an exponential as a first-order approximation (see the Supporting Information for details).

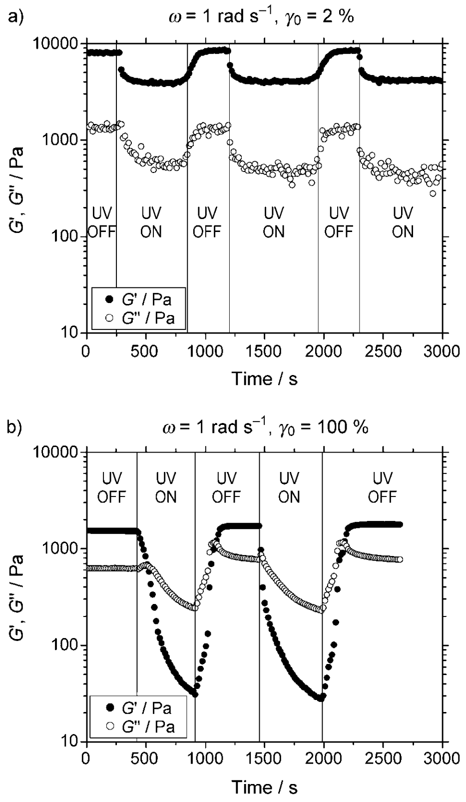

Figure 4. a) Rheological dynamic properties measured over several exposure cycles at a strain amplitude of 2%; b) rheological dynamic properties measured over an exposure cycle at a strain amplitude of 100%. The storage modulus (G') is represented by the solid circles and the loss modulus (G'') is represented by the open circles. The data were obtained at 100 °C at an angular frequency of $\omega = 1$ rad s^{-1}.

The viscoelastic properties of the LCP melt are dependent upon the morphology of the system; when the azo moieties are in their equilibrium *trans* conformation, the smectic LC mesophase provides interchain interactions that reinforce the LCP, thus leading to higher values of the storage and loss moduli. In general, it is known that smectic LC phases have a high viscosity; the closely packed and ordered smectic layers present additional resistance to deformation that is manifested as a higher shear modulus. Upon exposure to UV irradiation, a local *trans* to *cis* isomerization is induced, thus resulting in a disruption of the smectic LC mesophase and a subsequent decrease in the storage and loss moduli. This effect is most prominent at larger strain amplitudes; the large imposed deformation helps to disrupt the long-range order of the mesogens. The reversibility of the system is demonstrated by the rapid relaxation of the rheological properties upon removal of the UV light. Multiple cycles of this switching response can be achieved at strain amplitudes of 2 % or 100 %.

Close examination of Figure 4 a,b shows that the photorheological evolution in the properties of the LCP melt is more complex than a simple exponential decay in the nonlinear viscoelastic regime.[19] Upon UV irradiation, and after short time periods, the elastic modulus G' decreases approximately linearly with time and the loss modulus G'' initially increases. As the UV irradiation continues, the order of the LC mesophase is increasingly disrupted by the shearing and both the loss and storage modulus decrease dramatically. The nonlinear nature of the viscoelastic response at large strains can be more clearly demonstrated by Lissajous plots of the stress $\sigma(t)$ and strain $\gamma(t)$ at a given frequency ω.[20] When represented in this form, a perfectly elastic material response would appear as a straight line with a slope equal to the elastic modulus. For strain amplitudes of 2 %, the response is clearly linearly viscoelastic, both with and without UV exposure, as shown by the elliptical trajectories in Figure 5 a. Exposure to UV light leads to a decrease in the slope of the curves which indicates an elastic softening because of the disruption of the LC smectic mesophase. This is in agreement with the results shown in Figure 3 and 4 and the relative decrease in the storage modulus is $(G'_{\mathrm{off}})/(G'_{\mathrm{on}}) \approx 9.4$. In the linear viscoelastic regime, both the viscous and elastic contributions to the complex modulus $G^*(\omega)$ are affected to equal extents following exposure to UV light. The decrease in the linear viscoelastic moduli over a range of frequencies can be described by a single vertical shift factor that depends on the intensity and duration of the UV irradiation (see Figure S4 in the Supporting Information for an example of this shift).

For the larger strain amplitudes of 100 %, we observe pronounced distortions from ellipticity in the shape of the Lissajous curves in Figure 5 b (both with and without UV exposure), which indicates nonlinear behavior. The large-amplitude deformations induce a macroscopic orientation of the LC smectic mesophase that lead to the nonlinear viscoelastic behavior. This more complex material response can be described in multiple ways; for example, in terms of higher order Fourier coefficients[21] or using the Chebyshev representation introduced by Ewoldt et al.[20] to describe nonlinear elastic and viscous responses. By using the latter approach, we can quantify both the first-order changes in the modulus of the material and the evolution in the nonlinear strain-stiffening response using a series of elastic material coefficients $e_1, e_3, \dots$ The ratio of the third-order to first-order elastic Chebyshev coefficient increases with UV exposure: from $(e_3^{\mathrm{off}}/e_1^{\mathrm{off}}) = 5.5 \times 10^{-2}$ to $(e_3^{\mathrm{on}}/e_1^{\mathrm{on}}) = 8.9 \times 10^{-2}$, which indi-

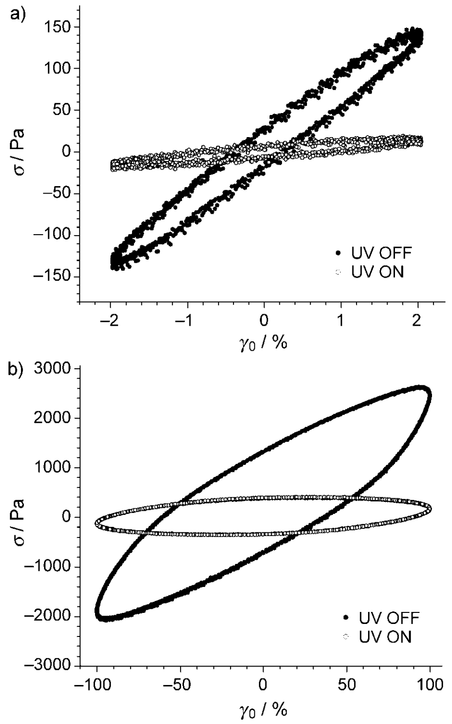

Figure 5. Lissajous figure of the shear stress σ as a function of the oscillatory strain for a maximum strain amplitude of a) 2% and b) 100%. The steady state data were obtained at 100°C with (open symbols) and without (solid symbols) exposure to UV light at an angular frequency of $\omega = 1\ \mathrm{rad\,s^{-1}}$ and after a UV exposure time of 750 s corresponding to a) 33τ and b) 8τ, where τ is determined according to Equation (2) in the Supporting Information.

cates an increase in the relative degree of elastic nonlinearity of the material upon UV irradiation. However, the absolute strength of the elastic network of the material is decreased because of the disruption of the smectic mesophase. Quantitative analysis of the Lissajous curves shows that both the linear and nonlinear coefficient decrease after exposure to UV light with $(G'_{\mathrm{off}})/(G'_{\mathrm{on}}) = (e_1^{\mathrm{off}}/e_1^{\mathrm{on}}) = 14.9$ and $(e_3^{\mathrm{off}}/e_3^{\mathrm{on}}) = 9.2$. Similar analysis of the viscous contributions to the oscillating stress in Figure 5 b show an increase in the relative degree of viscous nonlinearity upon UV irradiation. Under the combination of UV light and large strain, the material is thus broken down from a predominately elastic LC material with a high modulus to a weakly nonlinear viscoelastic gel-like response.

This study has demonstrated how the the morphology of side-chain liquid-crystalline polymers, which contain azo moieties, can be reversibly altered. The changes are induced upon exposure to UV light, which induces a *trans* to *cis* isomerization that disrupts the smectic LC mesophase, as shown by in situ SAXS experiments. This morphological rearrangement can be used to manipulate the rheological properties of the material over several orders of magnitude. In both the linear viscoelastic regime (strain amplitude of $\gamma_0 \leq 4\%$) and in the nonlinear viscoelastic regime (strain amplitude of 100%), we have shown that UV irradiation can be used to reversibly modify and control the storage (G') and loss (G'') moduli of the material. Future work includes investigating the effects of LC architecture and attachment percentage upon the responsive properties of this class of materials as well as the temperature dependence of the photorheological response.

Experimental Section

The synthesis of the poly(vinylmethylsiloxane) homopolymer has been previously reported.[17,22] A detailed description of the synthesis of the LC moieties is provided in the Supporting Information. Solvent-cast films were prepared from a 2 wt% solution of LCP in toluene, which resulted in films approximately 100 μm thick. A Dymax Blue Wave 200 light source with a Thorlabs, Inc. FGUV W53199 ultraviolet (UV) filter, with peak at transmission at 360 nm, was used for UV exposure experiments. Information regarding the transmission spectrum of the FGUV filter is provided in the Supporting Information. The power output measured at the point where the sample is mounted for the UV rheometry experiments was $10\ \mathrm{mW\,cm^{-2}}$. A TA Instruments Q1000 was used for differential scanning calorimetry (DSC), the heating and cooling rate was $10\ {}^{\circ}\mathrm{C\,min^{-1}}$ in all cases. SAXS experiments were performed at the G1 beamline at the Cornell High Energy Synchrotron Source (CHESS). The wavelength of the X-rays was 1.239 Å, and silver behenate was used to calibrate the sample to detector distance with a first order scattering vector of q of 1.076 nm-1 (with $q = 4\pi\ \sin\theta/\lambda$ where 2θ is the scattering angle and λ is the wavelength). A slow-scan CCD-based X-ray detector, home built by Drs. M. W. Tate and S. M. Gruner of the Cornell University Physics Department, was used for data collection. All scattering data were processed and analyzed using Polar software (Stonybrook Technology and Applied Research Inc., NY, USA). The SAOS and LAOS measurements were performed at the Hatsopoulos Microfluids Laboratory in the Massachusetts Institute for Technology (MIT). We used a parallel plate photocuring accessory mounted on an Advanced Rheometric Expansion System (ARES) strain-controlled rheometer (TA Instruments, New Castle DE, USA). The photocuring accessory consists of an upper tool with a reflecting mirror directing the UV source towards the quartz lower plate (20 mm diameter), which is in contact with the sample. The lower plate is made of copper with a thin coating (6.35 μm) of a chromium-based material (Micro-E, Electrolizing Inc.) and was used with the ARES Peltier control system.

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