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Rapid viscoelastic switching of an ambient temperature range photo-responsive azobenzene side chain liquid crystal polymer

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ABSTRACT

We report the rheological properties of a new azobenzene side chain liquid crystal polymer (SCLCP) with photo-responsive behavior in the range of 0 °C to 50 °C as probed by small amplitude oscillatory shear (SAOS) rheometry with *in situ* UV irradiation. In the linear viscoelastic (LVE) strain regime, temperature sweeps measured G' and G'' from 80 °C to −5 °C and identified glass transition temperatures (T_g) at 2.2 °C and 0.3 °C for UV-off and UV-on, respectively. Also in the LVE strain regime, frequency sweeps identified G' and G'' cross-over frequencies at 5 °C and 0 °C. Most importantly, rapid shear modulus changes of between 7 and 35% were demonstrated at 50 °C, 25 °C, 5 °C, and 0 °C by successively turning the UV light on and off during time sweeps in the LVE strain regime. The elastic (G') and viscous (G'') shear moduli reversibly decreased by a maximum of 35% and 21%, respectively, with time constants (τ) from 6 s to 18 s as fit by a stretched exponential model. This significant, rapid, and reversible UV-triggered modulus switching at temperatures as low as 0 °C and up to 50 °C is noteworthy because it represents a bulk property change at temperatures that are in the ambient range for several geographic regions and has reasonable time constants across the range.

1. Introduction

Responsive Liquid Crystal Polymers (LCP) have gained interest for their ability to combine the functionality of liquid crystals with the elastomeric properties of polymers [1]. In particular, photo-responsive materials have gained interest for their ability to change properties by merely irradiating them with the correct wavelength of light in the appropriate temperature range. Of particular interest are photo-responsive azobenzene liquid crystal polymers (LCP), which are the most common of this class of materials [1,2]. The azobenzene moiety is a robust, reliable, and reversible chromophore that is well understood, and can be used as part of the LC moiety of an LCP. Liquid crystal polymers are useful because the photo-induced LC to isotropic phase transition provides the photo-response, and the polymer provides a permanent network structure and mechanical stability.

It is these properties that make azobenzene LCPs attractive as photo-responsive materials [1–3]. However, the quick, reversible, and large responses required for such applications have only been achieved at elevated temperatures or with relatively slow response times [4–6]. These responses are slow at room temperature because the glass transition temperature (T_g) of the polymer and/or the isotropization temperature (T_{iso}) of the LC are well above room temperature. There have been two approaches to circumvent this problem to obtain room temperature, rapid, and reversible photo-responses. The first is replacement of the azobenzene pendant group with a dissolved azobenzene chromophore. This technique has been used to prepare crosslinked nematic azobenzene polysiloxane thin films with response times ranging from milliseconds to seconds, depending on the irradiation intensity used [7,8]. A second approach involves complex alignment, mounting, and movement of the azobenzene LCP in conjunction with a high-powered polarized light source. Using this method, thin films and cantilevers of aligned crosslinked nematic azobenzene polyacrylates have shown very fast response rates, although they require relatively large light intensities [9,10]. However, these solutions are not practical under all circumstances. For example, in the first technique, the azobenzene moiety is no longer chemically linked and, therefore, requires specific processing strategies, and it cannot be used under conditions that interfere or change this processing. In the second technique, the glass transition temperature limitation was overcome by the use of a strong polarized laser and a complicated irradiation geometry and procedure.

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A more general solution to obtain a robust, rapid, and reversible photo-responsive material would be an azobenzene LCP with a low glass transition temperature and a low isotropization temperature [11]. Previously, we have synthesized a new azobenzene side-on side chain (SC) nematic LC polysiloxane that is such a material with a glass transition temperature of −7 °C and an isotropization temperature of 73 °C [12]. In the present work, we extend this previous study by performing rheological characterization of this material by small amplitude oscillatory shear (SAOS) rheometry with *in situ* UV irradiation. This provides complete characterization of the viscoelastic properties of the polymer, demonstrating that its photo-responsive behavior is, in fact, rapid, significant, and reversible over a substantial temperature range from well below room temperature to well above room temperature. This represents an improvement over current systems because it takes place in the bulk at ambient conditions and requires only a moderate intensity UV light source.

2. Experimental

2.1. Materials

The material used in the study was a photo-responsive nematic side chain liquid crystal polymer. Its synthesis was reported previously, and its chemical repeat structure is shown in Fig. 1 [12].

2.2. Instrumentation

Small Amplitude Oscillatory Shear (SAOS) [13] was performed on a Rheometrics ARES strain-controlled rheometer using a parallel plate geometry. The bottom plate was made of copper with a thin chromium-based coating by Micro-E, Electrolizing Inc., and its temperature was controlled by an ARES Peltier control system. The upper plate was an ARES UV Curing accessory, which consists of a 20 mm diameter transparent quartz plate. The plate is housed within a tube containing a 45° mirror onto which light is incident and transmitted to the sample. In situ UV irradiation was carried out with a Dymax Blue Wave 200 source with a Thorlabs, Inc. FGUV W53199 UV filter. Finally, UV light intensity was measured with a Dymax ACCU-CAL 50 radiometer.

2.3. Procedure

After set-up of the equipment, the UV light was aligned with the mirror on the upper rheometer plate at a gap large enough for the radiometer head to fit (∼4 mm), and the intensity of the UV light transmitted through the quartz plate was measured at 125 mW/cm^2. The gap was then set to around 0.2 mm, and the UV light was re-aligned. Next, approximately 80 mg of crystalline LCP was placed on the bottom plate at room temperature. The plate was then heated to 80 °C for several minutes and sheared to completely melt the crystalline phase and produce an aligned monodomain of the LCP. Subsequently, the gap was set to 0.28 mm in order to completely fill the parallel plate geometry with the nematic phase, which is less dense than the crystal phase. Prior to measurement, auto-tension as well as manual gap adjustment were used to minimize tension or compression on the sample. Finally, a series of temperature sweeps, time sweeps, amplitude sweeps, frequency sweeps, and SAOS experiments, all with UV-off and with UV-on, were performed.

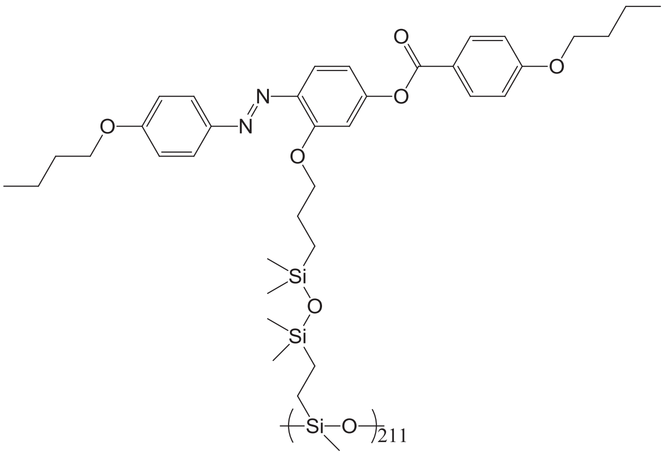

Fig. 1. Structure of the photo-responsive nematic SCLCP in the SAOS experiments.

3. Results and discussion

3.1. Thermal and temporal effects

With the LVE strain regime established (see Appendix A, Supplementary material for details) within the functional temperature range of the material, the structure of which is in Fig. 1, thermal and temporal characterization was performed with temperature and frequency sweeps, respectively. In Fig. 2, temperature sweep data is reported with the UV source both off and on from −5 °C to 80 °C at 5 °C/min at an applied frequency and strain amplitude of 10 rad/s and 1%, respectively. Even though 1% strain was commanded, the actual strain attained at the lowest temperatures was reduced because of instrument compliance. The data in Fig. 2a exhibits shear storage (G') and loss (G'') moduli which vary by six orders of magnitude over temperatures ranging from the glass transition temperature to the isotropization temperature due to the concomitant increase in free volume of the LCP. At temperatures above 55 °C, the material exhibits soft viscoelastic solid-like behavior with constant values for G' and G'' and with $G' < G''$ [14]. In this regime, the difference in G'' between UV-off and UV-on is quite small, due to the decreased order in the nematic phase near the isotropization temperature [15]. Between 55 °C and around 2 °C, the polymer is a viscoelastic fluid, but as the temperature approaches the glass transition, the material becomes gel-like as it begins to form "preglassy elastic clusters," [14] and ultimately the moduli increase by 4 orders of magnitude (Fig. 2a), much as described for other LC elastomers. This behavior coincides with the glass transition observed for the polymer in our previous work [12] and is consistent with previously reported data on siloxane based LC homopolymers [15–17]. At room temperature and below, a significant difference in moduli between UV-off and UV-on develops (Fig. 2b). These differences in G' and G'' achieve maximal values of 44% and 23% at 4.7 °C and 5.6 °C, respectively. In this temperature range, a crossover with $G' > G''$ is observed with decreasing temperature as the material transitions to a glassy response. Defining the glass transition as the crossover in G' and G'', the values for the glass transition temperature are 2.2 °C and 0.3 °C for UV-off and UV-on, respectively. At even lower temperatures G'' goes through a maximum at 0.6 °C and −1.6 °C for UV-off and UV-on, respectively, and decreases as the material is cooled further. These results show that UV light significantly decreases the isotropization temperature of the LCP so that, under ambient temperature conditions, the application of UV light destroys the nematic phase and decreases the rigidity of the LCP. [12]. Finally, below −2.5 °C, the difference between G' for UV-off and UV-on again vanishes, demonstrating that, below the glass transition temperature, the polymer chains are insufficiently mobile to rearrange upon UV irradiation.

The results of the temporal characterization are consistent with that of the thermal characterization and the principle of time–