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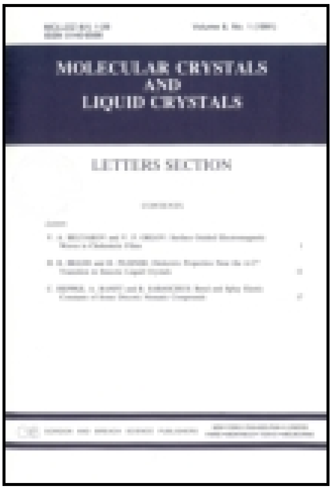

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Thermally and Optically Fixable Shape Memory in Azobenzene-Functionalized Glassy Liquid Crystalline Polymer Networks

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Thermally and Optically Fixable Shape Memory in Azobenzene-Functionalized Glassy Liquid Crystalline Polymer Networks

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Thermally and optically fixed shape memory is examined in glassy, azobenzene- functionalized liquid crystalline polymer networks (azo-LCN) in the twisted nematic (TN) geometry. The thermal and optical responses of two materials with a large difference in crosslink density are contrasted. The crosslink density was reduced through the inclusion of a monoacrylate liquid crystal monomer RM23. Reducing the crosslink density decreases the threshold temperature of the thermally-induced shape change and increases the magnitude of the deflection. Surprisingly, samples containing RM23 also allows for retention of a complex permanent shape, potentially due to differentiated thermal response of the pendant and main chain mesogenic units of the azo-LCN material.

Keywords Liquid crystal polymer; shape memory; azobenzene

1. Introduction

Stimuli-induced shape change in liquid crystalline polymer networks (LCNs) has been triggered by heat [1–5], pH [6–8], humidity [6, 9, 10], solvent [11], and light [12–17]. The mechanical adaptivity of LCNs has garnered considerable recent attention for potential relevance in microfluidics [18], optics [19, 20], structural mechanics [17, 21, 22], and medicine [23, 24]. One of the salient features of LCN materials versus other stimuli-responsive polymers [25–30] is the ability to easily control the local director [2, 31–34] or defect [35–39] pattern within the film. The ability to manipulate the local anisotropy has been recently shown to be a highly distinctive method to engineer the shape and topography of LCN materials.

Shape memory in polymeric materials is a process, not a property [40]. A number of approaches to the realization of shape memory in polymeric materials have been demonstrated and subject to recent reviews [41–43]. In nearly all cases to date, a polymeric material is subjected to heat and deformed into a temporary shape. Cooling the material through the transition temperature (while subjected to force maintaining the deformed shape) enables "memorization" of the deformed shape (referred to as the temporary shape). Heating the

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temporary shape of the material through the transition temperature restores the material to an equilibrium condition and reestablishes the permanent shape.

This work examines the thermal and optical response of azobenzene-functionalized LCN (azo-LCN). To date, the response of LCN materials to stimuli has primarily been elastic in nature (e.g., in the absence of the stimulus the material restores to the original shape). A few recent publications have examined shape memory in LCN materials [2, 44–47]. This work employs LCN materials in the twisted nematic orientation. The magnitude of the thermal and optical response of LCN has been shown to be considerably larger in this orientation when compared to polydomain or monodomain orientation [1, 2, 48–51]. As documented in recent reports, the shape of LCN in the twisted nematic orientation can generate planar and torsional deflections [2, 17, 50, 51]. The thermal and optical response of LCN in the twisted nematic orientation is attributable to a cooperative strain gradient in which the strain on one surface (contraction) is accentuated by the directionality of the strain on the opposite surface (expansion). In the case of thermal effects, the strain is attributable to the order-dependent "effective" coefficient of thermal expansion (CTE). For optical effects, the strain is caused by trans-cis or trans-cis-trans isomerization of azobenzene.

This work explores shape memory effects in two azo-LCN materials with a large difference in crosslink density. The reduction in crosslink density through the addition of a pendant (side-chain) monomer to the formulation is shown to reduce the glass transition temperature and modulus. Most notably, the reduction in crosslink density through the inclusion of pendant spacing groups is shown to distinguish the permanent shape of the materials. Shape change and shape memory processes induced via conductive heating (contact with body heat) and via a heat lamp are demonstrated. Due to the inclusion of the azobenzene chromophore, the ability to spatially manipulate the shape of the material is illustrated via a photothermal mechanism.

2. Experimental Section

Thermally and optically triggered shape memory was examined in two compositions prepared from the liquid crystalline monomers RM257, RM23, and 2-azo (chemical structures given in Fig. 1a). The azobenzene-functionalized liquid crystalline polymer networks (azo-LCN) were synthesized by photopolymerization of mixture of LC monomers in 8 μm (unless thickness otherwise specified) thick self-prepared alignment cells. The alignment cells were prepared from two glass substrates coated with Elvamide (Du Pont) that were directionally rubbed. To generate the twisted nematic (TN) orientation, the glass substrates were aligned such that the rubbing direction of the layers were aligned 90° to one another. The cell was filled by capillary filling of the molten liquid crystal mixtures at 120 °C. After filling, the cells were cooled to 75 °C into the nematic phase. Photopolymerization was initiated with 60 mW/cm^2 of 532 nm light (Nd:YAG laser) for 1 h. Both formulations included 1 wt% of the photoinitiator Irgacure 784 (I-784, Ciba), 0.1 wt% of chiral dopant R1011 (Merck), and 20 wt% of 4-4′-bis[6-(acryoloxy)hexyloxy]-azobenzene (2-azo, BEAM Co.). The sample referred to as "TN-0" was prepared from the copolymerization of RM257 (78.9 wt%, Merck) and 2-azo. The sample referred to as "TN-15" was prepared by diluting the concentration of RM257 (63.9 wt%) by adding 15 wt% of RM23 (Merck).

The thermomechanical properties (storage modulus – E', loss tangent – tan δ) of the materials were measured by a TA Instruments dynamic mechanical analyzer (DMA, RSA III)

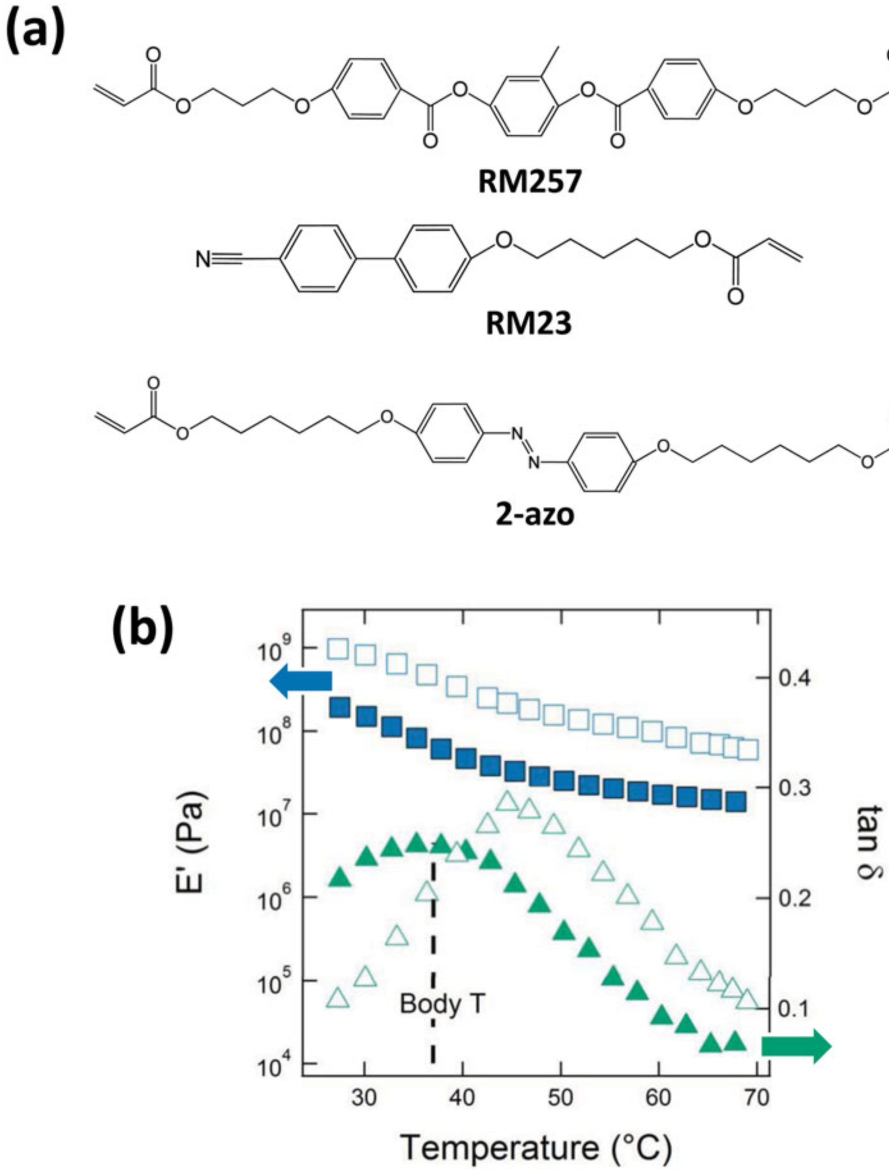

Figure 1. (a) Chemical structure of liquid crystal monomers used in this study. (b) Thermomechanical properties of the azo-LCN materials "TN-0" (open symbols) and "TN-15" (solid symbols). Storage modulus (rectangles) and tan delta (triangles) were measured as a function of temperature.

at 1 rad/s of frequency with a 3 °C/min temperature ramp rate for sample measuring 3 mm × 8 mm × 30 μm (width, length, and thickness, respectively). Polarized optical microscopy (POM, Nikon) was utilized to characterize the phase behavior of the liquid crystal mixtures and azo-LCN materials after polymerization.

3. Results and Discussion

We previously reported on thermally and optically fixable shape memory in an azo-LCN prepared in the polydomain orientation (of the identical composition of the sample referred to as "TN-0") [2] This work is distinguished from the prior work in that it examines shape memory in azo-LCN materials in the TN geometry (which is accompanied by a considerable increase in magnitude of photogenerated work and deflection). The thermal and optical response of two materials are contrasted throughout the work ("TN-0" and "TN-15") to elucidate the role of materials composition and crosslink density on shape memory. The storage modulus (E') and loss tangent (tan δ) of TN-0 and TN-15 were determined with DMA as a function of temperature (Fig. 1b). As apparent from Figure 1b, the addition of RM23 reduces the storage modulus throughout the temperature cycle. Not surprisingly, the addition of RM23 also reduces the T_g (reported here from the maxima in tan δ) by approximately 9 °C to a value slightly below the human body temperature (as denoted by the line in Fig. 1b). The crosslink density of TN-0 and TN-15 was calculated using the equation 1 [52]:

$$v_e = E'_{high}/3RT_{high} \tag{1}$$

where υ_e is the cross-link density, E'high is the storage modulus in rubbery plateau regime, R is the ideal gas constant, and T_{high} is the temperature at plateau modulus (summarized in Table 1). The substitution of 15 wt% monoacrylate causes a four-fold decrease in crosslink density from 6.2 mol/dm^3 (TN-0) to 1.15 mol/dm^3 (TN-15). The inclusion of pendant LC groups in TN-15 also broadens the loss tangent curve as a function of temperature, due to larger heterogeneity in polymer segmental motions. Notably, the modulus, T_g, and crosslink density of TN-0 are considerably different than previous examinations of polydomain [53, 54] and monodomain [55, 56] azo-LCN materials prepared under identical compositions and polymerization conditions.

LCN materials in the TN or hybrid orientation generate large deflections when subjected to an optical or thermal stimulus. The deflections are caused by a gradient in the directionality of the "effective" coefficient of thermal expansion (CTE) across the sample thicknesses. When the nematic director of the surfaces of an LCN in the TN orientation are aligned parallel and perpendicular to the principal axes of a film – a planar deformation is observed (bending). When the nematic director of the surfaces of an LCN in the TN orientation are offset to the principal axes of a film – flexural-torsional deformation is observed (coiling, twisting). The onset and magnitude of the thermally-triggered deflections of the azo-LCN films for TN-0 and TN-15 are compared in Figure 2 when actuated with a heat lamp. The temperature was measured by a non-contact IR temperature sensor (Omega). In both cases, the nematic director of the surfaces of the azo-LCN materials was aligned parallel and perpendicular to the principle axes of the cantilever strip. Upon heating, both films exhibit a planar deflection (images inset into Fig. 2). Notably, the onset of deflection begins to occur at lower temperature for TN-15. The first measureable deflection is observed for TN-0 at 40 °C. It is clear from Figure 2 that the reduction in crosslink density in TN-15 allows for a considerable increase in the deflection at a given temperature.

One of the salient features of LCNs as shape memory polymers is the ability to autonomously generate shape that are ultimately dictated by the local anisotropy of the liquid crystalline alignment. In a previous examination, we reported on the ability to accomplish "hands-free" shape memory [2]. Due to the T_g of the material employed in our previous examination, the samples were heated above 100 °C and did not show shape

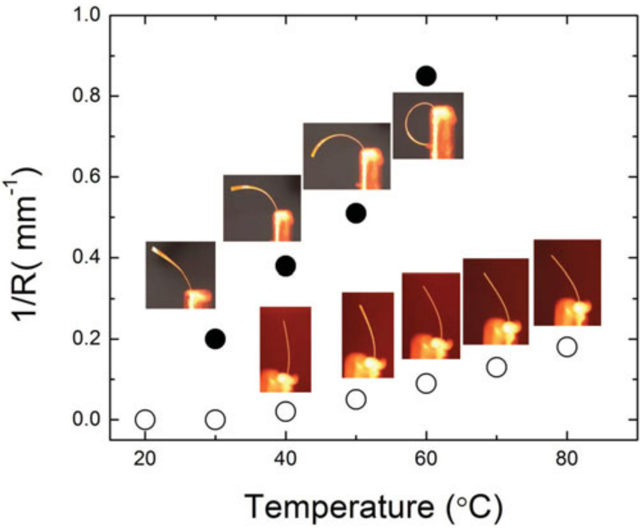

Figure 2. Radius of curvature of TN-0 (unfilled circle) and TN-15 (filled circle) in a cantilever geometry (6 mm (L) × 0.5 mm (W) × 8 μm (T)) upon illumination (heating) by an infrared lamp. The nematic director of the TN samples were aligned such that director was parallel to the long axis of the cantilever on the front surface. The data and images depicted were collected after 15 min of equilibration at each temperature.

fixing unless subjected to force (adhesive or mechanical) or subject to rapid temperature cycling. The "shape restoring" nature of the previously examined material (a homopolymer of RM257) was identical to that observed in TN-0 (Fig. 3a). As evident in Fig. 3a, upon heating the material through the T_g, a coiled shape is formed. However, on cooling – the sample restores to the original flat shape. The response of TN-15 is distinguished. In images labeled Figures 3b-i and 3c-i, the films are flat after removal from the alignment cells. The material was heated by conduction by simply placing the flat sheet onto a hand to warm the TN-15 films to 37 °C. Identical results were observed with more conventional heating methods. As evident in Figures 3b-ii and 3c-ii, heating the TN-15 to this temperature causes the films to change shapes (in Fig. 3a-ii – planar rolling; in Fig. 3b-ii – flexural-torsional coiling). After removing the films from the heat source (hand), the samples retain their deformed shape (Figs. 3b-iii and 3c-iii). The shapes observed in Figs. 3b-iii and 3c-iii are in fact the permanent shape of these samples. Subsequently heating the materials above the T_g does not restore the original flat shape of the materials. Only by heating to more than 50 °C above the T_g is the flat shape restored explicitly by thermal means. As shown in Figures 3b-iv and 3c-iv the coiled shape can be flattened by force. Heating the material in these conditions can be used to fix the films into a temporary shape that is flat.

The two materials examined here are distinguished in the shape that is retained after first heating. In the terminology of shape memory, these are referred to as permanent shapes. As evident in Figure 3a, it is clear that upon heating TN-0 through the T_g the material coils (due to the strain mismatch across the sample thickness). Upon cooling, the strain is lost and the sample restores to the flat shape. Evident in Figures 3b and 3c, upon first heating the TN-15 materials deform into the expected shapes. However, on cooling, the material retains these complex shapes. Heating the material to a large temperature (T_g+50 °C) is actually shown to flatten the shape, in a similar fashion to recent reports [2, 51]. However,

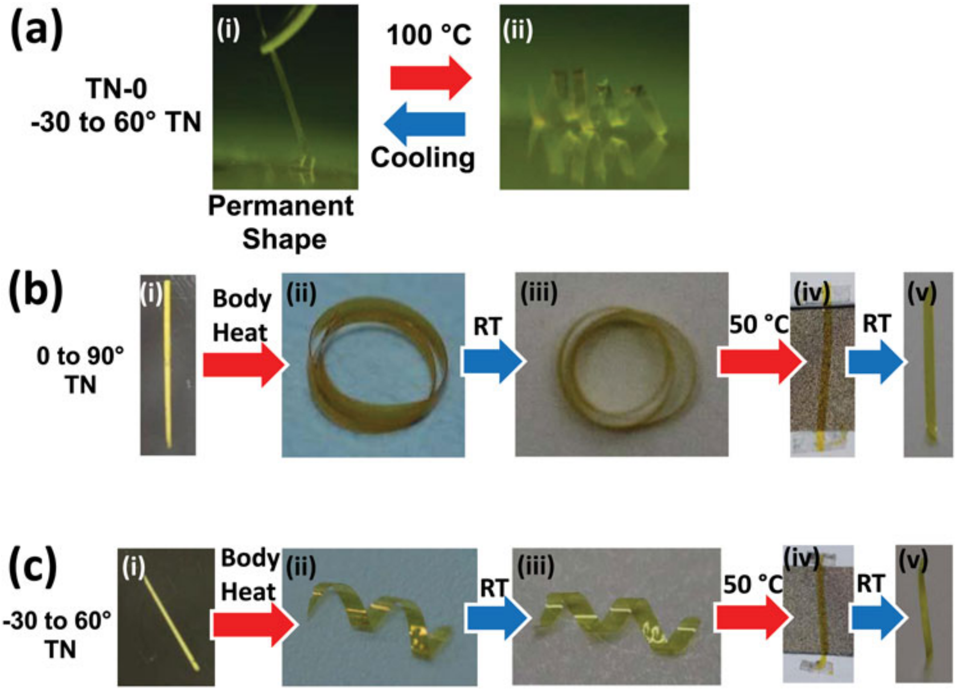

Figure 3. Thermally fixable shape memory in azo-LCN. (a) Thermally induced and reversible out-of-plane deformation (ii) was demonstrated when initially flat (i) TN-0 (−30 to 60° TN) films were heated to 100 °C. Upon cooling, the sample restored to the original flat shape (i). (b) An initially flat TN-15 sample (i) was heated with by contact heating with the body for 10 min to generate in-plane deformation (ii). Upon removal, the sample retained the coiled shape (iii). Heating the material above 50 °C under load (iv) allows fixation of a temporary flat shape (v). (c) An initially flat TN-15 sample (i) aligned with the nematic director oriented −30° to the long axis of the film was heated by contact heating with the human body for 10 min to generate out-of-plane deformation (ii). Upon removal, the sample retained the torsional shape (iii). Heating the material above 50 °C under load (iv) allows fixation of a temporary flat shape (v).

on cooling, the material restores the complex shape once again. From the thermomechanical characterization presented in Figure 1b, TN-0 and TN-15 have a large difference in crosslink density that is rooted in a difference in network morphology. The inclusion of RM23 in the formulation decreases the crosslink density by interspersing amongst the RM257 and 2-azo main chain units. While morphology characterization is ongoing, it is expected that the RM23 units are pendant to the primary direction of the main chain LCN. Thus, one explanation of the difference in permanent shapes for the two materials examined here may be attributable to the inclusion of the pendant mesogenic spacing units.

Photothermal effects in elastomeric and glassy LCN materials have recently been reported, primarily facilitated through the inclusion of carbon nanomaterial [4, 57, 58] or a heat transfer dye [32, 34]. Here we leverage the large absorption coefficient of azobenzene to generate photothermal effects at large light intensities. As previously reported in azo-LCN materials with similar absorption coefficients, exposure to 445 nm light exceeding 120 mW/cm^2 induces nonnegligible macroscopic heating [56]. As presented in Figure 4, light can be used to adjust and fix a temporary shape. The permanent shape of TN-15

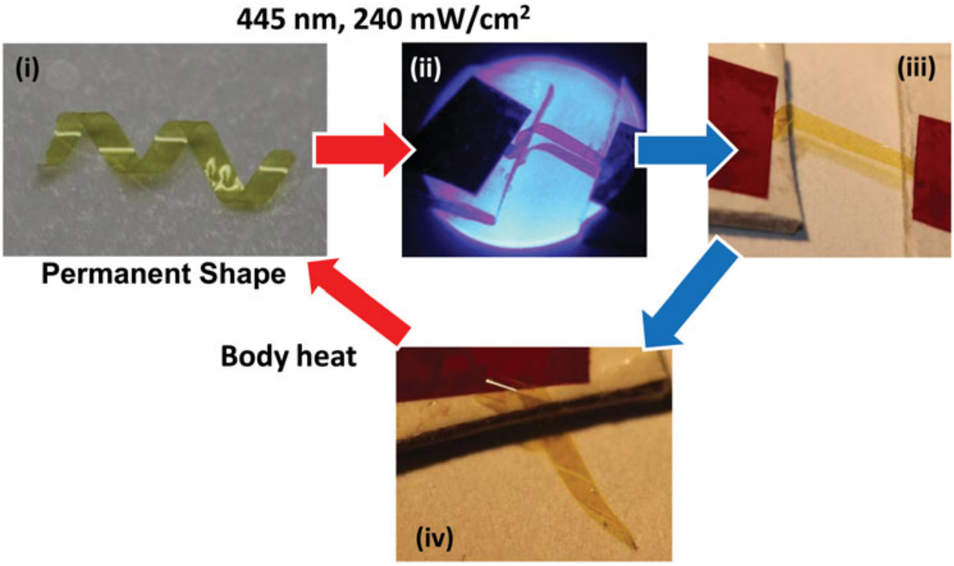

Figure 4. Photothermal shape change and shape memory in the TN-15 sample. The permanent shape of TN-15 (i) was partially untwisted under force (adhesion) (ii). The sample was irradiated with 445 nm light at 240 mW/cm^2 for 30 min. After removal of the light (iii) the load mechanical deformation was removed and the sample is shown to exhibit a new, phothermally fixed temporary shape (iv).

aligned +30° to −60° to the principle axes of the strip is shown in Figure 4i. The coiled permanent shape was unwound one time (leaving a single twist) and irradiated with 240 mW/cm^2 445 nm laser light at room temperature. A laser was employed to enable selective unlocking and adjustment of the azo-LCN material. Due to the photothermal heating, the shape is undone and due to boundary conditions of the film (e.g. locked in place with adhesion to a substrate), as the film cools through the T_g the shape is retained (Figs. 4iii and 4iv).

4. Conclusions

Thermally and optically fixable shape memory is examined in glassy azo-LCN materials in the twisted nematic orientation. Adding 15 wt% of the liquid crystal monomer RM23 reduces the crosslink density by a factor of four and the glass transition temperature by more than 9 °C. The reduction in T_g and its close proximity to the temperature of the human body allows for simple and facile shape control. Due to the inclusion of azobenzene, the employment of high intensity light to induce photothermal effects is shown to tune the shape of an azo-LCN in the TN orientation. The control and retention of shape in soft polymeric materials has wide ranging potential utility in optics and photonics, aerospace, and medicine.

Conflicts of Interest

The authors declare no conflict of interest.

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