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Twists and Turns in Glassy, Liquid Crystalline Polymer Networks

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Cite this: Macromolecules 2015, 48, 4, 1087–1092
Publication Date: January 30, 2015 ~
https://doi.org/10.1021/ma502563q
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Abstract



Three-dimensional shape control is an enabler of dexterous motion in nature. Herein, we report on the thermally initiated out-of-plane (torsional) responses observed in a series of glassy, liquid crystalline polymer networks prepared with a range of cross-link densities. The three-dimensional shape of these materials is strongly dictated by both cross-link density as well as the preparation conditions (polymerization temperature). All of the materials examined herein undergo torsional inversion of the handedness with increasing temperature. The temperature at which the material flattens (crossover between handedness inversion) can be positioned by the polymerization temperature. Monoliths prepared with either multimaterial composition or multidirector orientations are shown to exhibit spatial variation in shape adaptivity.

Introduction

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Plants and animals twist and turn (torsion) to facilitate mechanical integrity,(<u>1, 2)</u> energy storage,(<u>3)</u> or agility evident in the motion of insects,(<u>4-7</u>) birds,(<u>8</u>) or snakes.(<u>9</u>) The threedimensional shape control and actuation of biological systems often originate from anisotropic internal microstructures that can be emulated in synthetic materials. Macroscopic torsional deformation have been reported in various materials.(<u>10-22</u>) Recently, a number of contributions have elucidated the generation of anisotropic and three-dimensional shape change within liquid crystalline polymer networks (LCNs).(<u>14, 15, 18, 23-25</u>) These previous





dependence of the directionality of the thermal expansion coefficient. (26). In this study, liquid crystalline polymer networks are synthesized in twisted nematic (TN) geometry which exhibit a 90° twist of the director from top to bottom through the sample thickness. Liquid crystalline polymers are well-known to expand perpendicular to the director and contract parallel to the director upon heating. (26). This anisotropic dimensional change can be attributed to a reduction in the anisotropy of the conformation of the polymer chain. This conformational change arises from a reduction of order. The magnitude of this conformational change is a balance of the entropic penalty of the ordered system and constraint provided by cross-links within the polymer network. Hence, the thermal expansion of LCNs can be influenced by the cross-link density of the polymer network. It should be noted that moderately to highly cross-linked LCNs like the materials examined here do not undergo a nematic to isotropic phase transition, but instead exhibit a slight, broad reduction in order.

Previous examinations of liquid crystalline polymer networks have focused on the effect of temperature,(<u>14)</u> coefficient of thermal expansion,(<u>26)</u> liquid crystal alignment profile, (14, 15, 17) and film geometry (15, 17) on the mechanical response as well as temperature induced handedness inversion<u>(14)</u> and shape memory properties<u>(15, 18)</u> of torsional shapes. The goal of this work is to identify any association between the composition of the LCN material and the thermally induced torsional response and to demonstrate methodologies to introduce spatial variability in the shape adaptivity of monolithic specimens. Toward this end, the crosslink density of the materials examined here is varied through the copolymerization of diacrylate and monoacrylate liquid crystal monomers to form LCNs. The main-chain/side-chain orientation of the mesogens in the LCN materials is examined with wide-angle X-ray diffraction (WAXD) and Fourier transform infrared spectroscopy (FT-IR). In the materials examined here, a more than 7-fold decrease in cross-link density is achieved by the inclusion of as much as 40 wt % monoacrylate monomer. The thermomechanical deformation of the LCN materials traverses from coiled at room temperature through a flat state before inverting handedness. Hybridized shapes are demonstrated by employing surface alignment patterning and multimaterial compositions.

Experimental Section

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Synthesis of Liquid Crystalline Polymer Networks

Liquid crystal polymer networks (LCNs) were synthesized by copolymerizing the diacrylate liquid crystal monomer RM82, 1,4-bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]-2-methylbenzene (Merck), and the monoacrylate liquid crystal monomer RM23 (Merck), 6-(4-cyano-biphenyl-4'-





Elvamide-coated rubbed glass cells in the planar or TN geometry. The LCNs were polymerized in the nematic state with 60 mW/cm² of 532 nm laser light for 60 min. The phase diagram and photopolymerization temperatures of these mixtures are summarized in Figure 1b. The synthesized LCNs were harvested from the alignment cells after polymerization.

Figure 1



Figure 1. (a) Chemical structures of the liquid crystal monomers RM82 and RM23. (b) Phase diagram of the liquid crystal monomer mixtures determined by DSC and POM, plotting the melting temperature (T_m , \Box) and the nematic to isotropic transition temperature (T_{NI} , \circ). The ratio of the polymerization temperature (T_p) to T_{NI} (T_p/T_{NI} , Δ) is plotted on the right axis.

Characterization Methods

The melting (T_m) and nematic-to-isotropic transition (T_{NI}) temperatures of the monomer mixtures were determined by differential scanning calorimetry (DSC, Netzsch differential scanning calorimeter) and polarized optical microscopy (POM, Nikon) (<u>Supporting Information</u> Figures S1 and S2). The orientation and alignment of the patterned LCN samples were also confirmed by POM.

The thermomechanical properties of twisted nematic LCN samples of dimension 6 mm (l) × 3 mm (w) × 8 µm (t) were determined by dynamic mechanical analysis (DMA) (RSA III, TA Instruments) at frequency of 1 Hz with a heating rate of 2.5 °C/min in a nitrogen atmosphere. The glass transition temperatures (T_g) are taken from the maximum of the tan δ curve. Cross-link density was determined from the thermomechanical data using Flory's rubber elasticity theory.(27).

The order and orientation of the LCNs was examined with transmission wide-angle X-ray diffraction (WAXD) and FT-IR. WAXD experiments were carried out by using a Rigaku Ultrax18 using Cu Kα radiation on a Statton box camera. The sample was positioned 53 mm from the





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The LCN films were cut such that the nematic director was 30° (top) and −60° (reverse) offset from the primary film axis. The LCN films were immersed in a silicon oil bath that was gently stirred to ensure uniform heating. Thermally induced mechanical deformation was monitored between 30 and 150 °C. Images were collected after 10 min of temperature equilibration.

Results and Discussion

This investigation examines LCN materials prepared from the diacrylate liquid crystalline monomer (LCM) RM82 (Figure 1a) which was copolymerized with up to 40 wt % of the monoacrylate LCM RM23 (Figure 1a). The chemical compositions of the five samples examined here are summarized in Table 1. The concentrations of the photoinitiator (Irgacure 784, I-784) and the chiral additive (R1011) were held constant for all compositions. Increasing the concentration of RM23 in the prepolymer mixtures impacts the phase behavior by reducing the temperature of both the crystalline to nematic (T_m) and nematic to isotropic (T_{NI}) transitions (Figure 1b). The $T_{\rm m}$ and $T_{\rm NI}$ were determined by DSC and POM, respectively. It should be noted that significant undercooling of these mixtures broadens the nematic phase regime on cooling. This enables polymerization below the equilibrium $T_{\rm m}$. As discussed in detail in the Experimental Section, the mixtures of the LCMs were photopolymerized in the nematic state within alignment cells in the planar or TN geometry at the polymerization temperature (T_p). The ratio between T_p and T_{NI} has been previously shown to strongly affect the coefficient of thermal expansion (CTE) of LCN materials. (26) Accordingly, to facilitate comparison of the thermomechanical response of the materials, T_p was varied to maintain a T_p/T_{NI} of approximately 0.93 (Figure 1b) unless otherwise noted.

| sample | RM23 (wt %) | RM82 (wt %) | I-784 (wt %) | R1011 (wt %) |
|----------|-------------|-------------|--------------|--------------|
| LCN-16.6 | 0 | 98.4 | 1.5 | 0.1 |
| LCN-11.5 | 10 | 88.4 | 1.5 | 0.1 |
| LCN-8.9 | 20 | 78.4 | 1.5 | 0.1 |

Table 1. Chemical Compositions for LCNs

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The thermomechanical properties of the LCN were characterized with a strain-controlled dynamic mechanical analyzer (DMA, RSA3). Figure 2a plots the storage modulus (*E*) as a function of temperature. All five materials exhibit classical and expected behavior for cross-linked polyacrylates typified by a broad transition between the glassy and rubbery plateau regions. The RM82 homopolymer yielded the highest storage modulus. The introduction of RM23 results in a monotonic decrease in storage modulus. The cross-link density (v_e) of the LCN materials was calculated from Flory's rubber elasticity theory:(27).

$$v_{\rm e} = E_{\rm high}^{\prime}/3RT_{\rm high}(1)$$

where E_{high} is the storage modulus in rubbery plateau regime, *R* is the ideal gas constant, and T_{high} is the temperature within the rubbery plateau region (T_g + 50 °C). As expected, the crosslink density of polymer networks decreased with increased RM23 concentrations. Accordingly, this series of polymers is referred to as LCN-*xx.x*, where *xx.x* refers to the measured cross-link density value of the sample. Notably, adding 40 wt % RM23 reduces the cross-link density of the RM82 (LCN-16.6) homopolymer by nearly a factor of 8. The influence of cross-link density is also observed in the glass transition (T_g) temperatures of the materials, taken from the maxima of tan δ data reported in Figure 2b. The thermomechanical properties and calculated cross-link densities of the LCN-*xx.x* materials are summarized in Table <u>2</u>.

Figure 2



Figure 2. Thermomechanical properties of the liquid crystalline polymer networks examined here. (a) Storage modulus (*E*) plotted against temperature for LCN-16.6 (open circle), LCN-11.5 (open square), LCN-8.9 (open up triangle), LCN-6.9 (open down triangle), and LCN-2.2 (open tilted square). (b) Loss tangent (tan δ) plotted against temperature for LCN-16.6 (open circle),



| sample | <i>T</i> g (°C) | T _{high} (K) | <i>E</i> _{high} ' (MPa) | υ _e (mol/dm³) |
|----------|-----------------|-----------------------|----------------------------------|--------------------------|
| LCN-16.6 | 84.2 | 407.4 | 168.8 | 16.61 |
| LCN-11.5 | 73.9 | 397.1 | 114.1 | 11.52 |
| LCN-8.9 | 69.5 | 392.7 | 86.7 | 8.85 |
| LCN-6.9 | 55.0 | 378.2 | 64.7 | 6.86 |
| LCN-2.2 | 51.4 | 374.6 | 20.7 | 2.22 |

The sample preparation, harvesting, and characterization of the LCN-*xx.x* materials are illustrated in Scheme <u>1</u>. The LCN-*xx.x* films were prepared in liquid crystal alignment cells in which the alignment direction of the two glass plates was offset by 90°. The inclusion of a small amount of chiral additive (R1011) biases the handedness of the resulting TN orientation to ensure uniformity in the twist direction. As described in prior reports,(<u>14, 15, 17</u>) torsional responses are observed in LCN materials when the director profile is offset to the principal axes of the specimen. LCN materials in the TN orientation exhibit considerably larger torsional deflections compared to planarly oriented LCNs owing to dependence of the coefficient of thermal expansion on the nematic director rotates from 30° to -60° through thickness direction. The torsional response of the LCN-xx.x films was measured as a function of temperature in an oil bath.

Scheme 1



Scheme 1. Illustration Depicting the Preparation Procedure of 30 to −60° Twisted Nematic (TN) LCN Film and the Test Method for Its Thermomechanical Deformation

The torsional deflections of the LCN-*xx.x* materials oriented from 30° to -60° are shown in Figure 3 as a function of cross-link density. The initial shape of the LCN-*xx.x* films was flat (not shown) upon harvesting. After initial heating through the T_g of the given LCN-*xx.x* material, the shape of the materials at room temperature is nonflat, as in prior reports.(<u>14, 18)</u> The presence of twisted (nonflat) shapes at room temperature indicates that the materials maintain a residual stress. One potential source of residual stress is shrinkage from the polymerization. However, as in this report, polymerization shrinkage stress in LCN materials is anisotropic, primarily occurring along the director axis in most cases.(<u>28</u>) Accordingly, this would cause a stress gradient that would result in the same handedness as the variation in CTE.

Figure 3

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Figure 3. Thermally induced shape of the LCN-*xx.x* materials. At a given temperature, the shape was allowed to equilibrate for 10 min. All samples were of dimension 10 mm (l) × 1 mm (w) × 8 μ m (t).

To further explore this dependence, the LCN-xx.x composition was prepared over a range of $T_{\rm p}$'s to isolate the contribution of preparation conditions to T_{flat} . As evident in Figure 4a, T_p and T_{flat} exhibit a seemingly linear relationship. As the material is cross-linked in a flat state at T_{p} , there is a minimum in the thermal stresses near this temperature. On cooling, a net expansion along the director and contraction perpendicular to the director generates a stress gradient in the film that is opposite in sign to the gradient observed on heating. This leads to the handedness inversion below $T_{\rm p}$. As evident in the images in Figure 3, reducing the cross-link density of the LCN-xx.x samples increased the magnitude of the torsional responses as a function of temperature. A similar sensitivity to cross-link density has been reported recently in shape memory polymers. (29) The thermomechanical response of the LCN-xx.x materials is similar in that the samples flatten at an intermediate temperature before inverting handedness. The magnitude of the thermomechanical responses observed in Figure 3 are affected by the geometrical stiffness (in this case largely influenced by the modulus, Table 2) and by the inherent thermal responsivity of the material. The material response is most adequately described by an "effective" coefficient of thermal expansion (CTE). The word "effective" is used to gualify the CTE measurements reported here, as this measurement is affected by conventional factors known to influence CTE as well as by slight change in order parameter. To prove and quantify this hypothesis, the CTE values for these compositions were measured in planarly aligned samples, both parallel and perpendicular axes to the nematic director. As shown in Figure 4b and c, the CTE has a negative sign (contraction) along the nematic director and positive sign (expansion) for perpendicular to the nematic director as in prior reports. (28, 30) Above the $T_{\rm q}$, the slope of the CTE variation





difference (Δ | α |) for LCN-16.6 at 150 °C was only 316 ppm °C⁻¹, while the CTE difference (Δ | α |) for LCN-2.2 at 90 °C (T_{flat}) is 416 ppm °C⁻¹. The Δ | α | at 150 °C is plotted against the calculated cross-link density values for the five samples (see Figure 4d) to illustrate the relationship of these values.

Figure 4



Figure 4. (a) Flattening temperature of LCN-2.2 polymerized at different temperatures (T_p). The y = x trend line is drawn to guide the eye. (b) Coefficient of thermal expansion (CTE, α) for LCN-16.6 as a function of temperature. (c) Coefficient of thermal expansion for LCN-2.2 as a function of temperature. For (b) and (c), the CTE is measured for parallel (blue solid circle) and perpendicular (red solid circle) directions, and the difference between these two is reported as $\Delta |\alpha|$. (d) $\Delta |\alpha|$ values at 150 °C is plotted against cross-link density. All CTE measurements employed film dimension of 6 mm (l) × 3 mm (w) × 8 µm (t).

We conclude this examination by demonstrating the ability to assimilate multiple responses into a single monolithic element. In the first case, a film is prepared wherein half of the sample is composed of LCN-2.2 and the other half of the sample is composed of LCN-16.6. This sample was prepared in a conventional twisted nematic cell (as described hereto). The cell was then filled with the molten isotropic LCN-2.2 and LCN-16.6 mixtures from opposite ends which fill the cell by capillary action (as illustrated in Figure 5a). We expect that the two formulations mix in





sample is flat in the LCN-16.6 region and coiled in the LCN-2.2 region. When the sample was cooled to 90 °C, the LCN-2.2 region is now flat (as in Figure 3 at this temperature) while the LCN-16.6 region exhibits some curvature. Upon cooling to 30 °C, LCN-2.2 now coils in the opposite handedness and the LCN-16.6 region is slightly bent.

Figure 5



Figure 5. (a) Procedure to prepare a monolithic film containing LCN-2.2 and LCN-16.6. (b) Thermally induced coiling of a monolith film prepared with LCN-2.2 and LCN-16.6 at 30, 90, and 150 °C. Film dimension is 10 mm (l) × 1 mm (w) × 8 µm (t).

A second example of assimilating multiple shapes into a monolithic film is demonstrated in Figure 6. Here, a TN cell was prepared in which half of the cell was rubbed such that the LCN-2.2 film would form a right-hand twist and the other half of the cell was rubbed such that the LCN-2.2 film would form a left-hand twist. An interfacial, planarly aligned region was inserted in between the two oppositely handed twisted nematic areas to allow the handedness inversion to





Figure 6



Figure 6. (a) Alignment of LCN-16.6 material having two different handedness. (b) POM images showing sharp and clear transition between the 30° to -60° TN (LH) and planar region. Scale bar is 500 µm. (c) Thermally induced coiling of a monolith film having both right and left handedness at 30, 90, and 150 °C. Film dimension is 25 mm (*I*) × 1 mm (*w*) × 8 µm (*t*).

Conclusions

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In this study, glassy liquid crystal polymer networks (LCNs) were synthesized by copolymerizing a diacrylate liquid crystalline monomer with a monoacrylate liquid crystalline monomer (0–40 wt %) to vary cross-link density and affect the thermomechanical response. Thermomechanical effects in these materials were examined in the twisted nematic geometry with the director profile of the LCN-*xx.x* samples offset at 30° and –60° to the long axis of the films. Accordingly, upon heating, the films undergo out-of-plane deformation (torsion). The magnitude of the

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The temperature dependence of the mechanical response of the films was also elucidated. After first heating through the glass transition temperatures, all five materials exhibited nonflat shapes at room temperature. The temperature at which the films flatten upon heating (T_{flat}) exhibits a seemingly linear relationship with the polymerization temperature, indicating that the residual stresses may be attributed to deviation of the LCN materials from their equilibrium chain configurations. Upon heating through T_{flat} , the materials invert handedness. Upon cooling, the films unwind, once again flatten at an intermediate temperature, and invert handedness. Notably, the variation in temperature sensitivity of the materials is used to prepare a monolithic sample that is a hybrid of high and low cross-linking densities in which torsion is selectively observed in the films. Similarly, samples were prepared with rubbing conditions to generate TN films in which half the sample exhibited a left handed deflection and half the sample exhibited a right handed deflection. Upon heating, the film flattens and both sides of the sample invert handedness.

Supporting Information

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DSC measurements to determine melting temperature of liquid crystal monomer mixtures; POM measurements to determine nematic to isotropic transition temperature (T_{NI}) of liquid crystal monomer mixtures; 2D-WAXD patterns and scattering intensity profiles; polarized FTIR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

J.J.W., K.M.L., and T.H.W.: Also with Azimuth Inc. The authors declare no competing financial interest.

Acknowledgment

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This work was completed at Air Force Research Laboratory (AFRL) at the Wright-Patterson Air Force Base with funding from Materials and Manufacturing Directorate as well as Air Force Office of Scientific Research. We are grateful for discussions with Michael McConney, M. Ravi Shankar, and Matthew L. Smith. We thank Hilmar Koerner (WAXD), Carl Liebig (DSC), Marlene Houtz (DMA), and Andrew Harbach for experimental assistance.

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