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Communication **Description Description**

Autonomous, Hands-Free Shape Memory in Glassy, Liquid Crystalline Polymer Networks

Kyung Min Lee, Timothy J. Bunning, Timothy J. White 💌

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Abstract

Repeatedly forming temporary shapes can be a limitation to the employment of shape memory polymers. This work utilizes glassy, liquid crystal polymer networks to spontaneously form 3D shapes that are independent of a user. These shapes are autonomously fixed with rapid temperature cycling.



Dynamic control of shape has proven useful in applications ranging from heat shrinkable tubing to form fitting eyewear to the implantation of biomedical devices. <u>1</u> So-called shape memory materials–both alloys (SMAs) and polymers (SMPs)–are stimuli-responsive materials capable of energy transduction through shape change. SMAs are known for large force

generation coupled to limited displacement, while SMPs have proven capable of fixing large magnitude and complex shapes but exhibit comparably less force output.

This work focuses on SMPs, recently reviewed from a variety of perspectives.<u>1-7</u> Mather et al.<u>3</u> classify shape memory polymers into four material subclasses referred to as covalently crosslinked glassy thermoset networks (Class I), covalently crosslinked semi-crystalline networks (Class II), physically crosslinked glassy copolymers (Class III), and physically crosslinked semi-crystalline block copolymers (Class IV). In each of these classes, the polymeric material is heated through a transition temperature, subjected to a process composed of mechanical deformation (strain), thermal quenching under continuous mechanical deformation, and completed by release of the mechanical deformation. The subclasses of shape fixing are differentiated by the transition temperature while class II–IV materials utilize some combination of the glass transition temperature and crystalline melting temperatures. Through clever choice of materials and shape programming, it is possible to fix numerous temporary shapes.<u>8-13</u>

A number of recent papers have reported on shape memory in liquid crystalline polymer networks (LCNs)-as a means to fix multiple temporary shapes. 14-19 LCNs 20 are typically formed by photoinitiated polymerization of mesogenic monomers resulting in glassy polymeric films that exhibit moderate mechanical properties (storage moduli of as much as 2 GPa) and considerable mechanical adaptivity.21, 22 Importantly for the work presented here, the simplicity of the preparation of these materials by conventional liquid crystal alignment techniques readily yield monodomain and polydomain LCN materials aligned in planar, twisted nematic, homeotropic, and splay geometries. The domain orientation and geometry of LCN has repeatedly been exploited to dictate distinctive mechanical responses-triggered by both heat and light. Comparatively, photomechanical effects in azobenzene-based LCN materials have been more extensively examined–exhibiting planar23-28 and flexural-torsional29-31 responses that are elastic<u>26</u> or shape fixing.<u>28</u>, <u>32</u>, <u>33</u> Of particular relevance to the work here, heating glassy LCN films affects the order parameter of the material (reported previously as only a 5% reduction) which generates a contractile strain parallel to the nematic director.22 When the orientation of the nematic director varies through the thickness of a film, as in the twisted nematic or splay geometry, 22 the directionality of the thermally generated strain is nonuniform resulting in three-dimensional shapes.

All previous examinations of thermally-generated shape change in LCN materials immediately restore to the original shape upon removal of the stimulus. The goal of this work is to investigate thermally generated shape formation in a model LCN material system to repeatedly and reversibly generate three-dimensional shapes capable of fixing through the conventional and widely employed class I technique. Uniquely with respect to previous examinations of

shape memory polymers, this work generates shape without applied, external mechanical deformation. It is expected that the spontaneous formation of shape, dictated by the response of the LCN to heat, will significantly improve the ability to generate user-independent temporary shapes. The rich shape adaptivity<u>34</u> of twisted nematic (TN) LCN is employed here to generate wound, spiral ribbon, rippled, and other three-dimensional shapes.

The LCN material examined here was formed by photopolymerization of the commercially available liquid crystal monomer RM257 (**Figure 1**a). Upon heating, RM257 undergoes a $Cr \rightarrow N$ phase transition at 73 °C. To form twisted nematic LCNs, 25 a liquid crystal alignment cell was prepared in which the rubbing direction of the Elvamide alignment layers were orthogonal. This results in a 90° twist in the liquid crystalline director through the thickness of the material. Upon photopolymerization (initiated with 1 wt% Irgacure 784 and 532 nm irradiation), the TN orientation is retained. Samples were photopolymerized for one hour. The thickness of the LCN examined here was 15 µm. The thermomechanical properties of the LCN were measured by dynamic mechanical analysis (DMA) and plotted in Figure <u>1</u>a. As apparent in the plot of storage modulus (E') and tan δ as a function of temperature–the material is glassy at room temperature with a glass transition temperature (T_g) of 100 °C. Upon heating, the material undergoes considerable softening, as E' decreases from 1.3 GPa at 30 °C to 60 MPa at 160 °C.

Figure 1

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(a) Chemical structure of the liquid crystalline diacrylate monomer RM257 and thermomechanical properties of resulting liquid crystal polymer network (LCN) homopolymer (E' (•), tan δ (\bullet)). (b) Spontaneous shape change (flat to coiled) in twisted nematic (TN) LCN aligned in the "X" geometry (45° to -45°) as a function of aspect ratio upon heating through the Tg of the material (130 °C). (c) Resulting thermal response of the L and S geometry TN LCN films upon heating through the Tg of the material (130 °C). The orientation of the nematic director through the film thickness is depicted graphically. The thickness of the LCN films was 15 µm.

Figure <u>1</u>b illustrates the response of a TN LCN cut in the so-called "X" geometry,<u>34</u> in which the nematic director is oriented ±45° to the long axis of the film. To ascertain the contribution of aspect ratio, the 15 mm long films were cut with 1.2, 0.8, and 0.3 mm widths. The originally flat films (Figure <u>1</u>b-i) spontaneously coil upon heating to 130 °C, above the T_g of the LCN. The film remains liquid crystalline at this elevated temperature. 20 The shape of the films is strongly influenced by the aspect ratio, with the low aspect ratio film forming a spiral ribbon-like shape, while the larger aspect ratio film exhibits a helicoidal-like shape.<u>34</u> Urayama and coworkers

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have recently reported on the dependence of coiled shapes on aspect ratio realized in swollen twisted nematic elastomers, drawing parallels to biological systems.<u>34</u> Due to the broad T_g of the material, the tightness of the coiling can be readily controlled with temperature (Supporting Information, Figure S1). The shape and handedness of the thermal response can also be controlled by varying the orientation of the nematic director to the principal axes of these high aspect ratio films. The variation of the nematic director through the thickness is plotted in Figure <u>1</u>c for the geometries examined here. When the nematic director rotates from a negative angle to a positive angle through the film thickness (S geometry), the originally flat materials spontaneously form a left handed coil upon heating. Comparatively, when the nematic director rotates from a positive angle to a negative angle through the film thickness (L geometry), the originally flat films spontaneously form a right handed coil upon heating. As highlighted in Figure 1c, the orientation of the nematic director at the midplane (positive or negative) of the sample thickness (7.5 µm) is an indicator of the resulting handedness of the response. The thermal response of the TN LCN materials is illustrated in the images in Figure 1c. Evident in Figure <u>1</u>c-i, heating a TN LCN with conventional alignment above the T_g (130 °C) causes the film to spontaneously wind itself into a wheel-like shape, as reported previously.22 When the film is cut such that the nematic director is offset between -15 to -45° to the long axis of the film-large differences in the nature of the thermally induced coils are observable as demonstrated for the S geometry in Figure 1c ii-iv. As the alignment of the nematic director to the surface of the films shifts from -15° to -30° to -45°, the film shifts from a tightly wound coil to an elongated spiral ribbon. Reversing the rotation of the director through the film thickness (L geometry), represented here as 15 to 45°, reverses the handedness of the coiling (Figure 1 c v-vii).

To assess the performance of the material system as a shape memory polymer, we subjected the TN LCN to a typical shape memory cycle in a DMA. It should be noted that the geometry of the TN LCN in the gauge during DMA testing was aligned in the conventional geometry, evident in Figure <u>1</u>c-i. As plotted in **Figure 2**a, the TN LCN was initially heated to 150 °C (through the T_g of the material). At this elevated temperature, the sample was subjected to a stress of 4 MPa, straining the material approximately 9.6% (step i). To thermally fix this strain, the material was cooled to 0 °C under constant stress (step ii). At 0 °C the stress was released (step iii) and the material retained a considerable portion of the strain, evident in a fixity of 96%. Upon heating to 160 °C, the material releases the fixed strain and recovers to the original shape, exhibiting a degree of recovery of 92%. This cycle was repeated three times (fixity and recovery ratios reported in Supporting Information, Figure S2). The limited strain in this model TN LCN material is not surprising due to the substantial crosslink density of the film (e.g., low molecular weight between crosslinks).

Figure 2

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(a) Three shape memory cycles of the TN LCN in a conventional alignment to the gauge (as in Figure <u>1</u>c-i). After heating the material to 150 °C the sample was subjected to a 4 MPa stress, straining the material to 9.6% (step i). Under constant stress (4 MPa), the sample was cooled to 0 °C (step ii) at which the stress was released (step iii). Upon heating through the glass transition temperature of the material the temporary state is restored to the permanent state (step iv). (b) Demonstration of spontaneous shape formation and fixing of a TN LCN film in the "X" geometry. (i) Permanent shape (flat), (ii) spiral ribbon formed upon heating to 130 °C, (iii-iv) shape fixing by applied mechanical force (human) and room temperature cooling, (v-vi) shape fixing by applied mechanical force (adhesion), and (vii-viii) autonomous shape fixing by rapid temperature cycling. If slowly cooled without mechanical constraint, the sample returns to the permanent shape (ix). (c) Shape fixing of a TN LCN in conventional alignment. Upon heating the permanent shape (i) forms the temporary shape (ii and iv). If the system is subjected to mechanical force (ii) or rapid temperature cycling the wheel-like shape is retained (iii). However, in the absence of mechanical force or rapid temperature change the sample restores to the original permanent shape (v). The thickness of the LCN films was 15 µm.

The ability to autonomously generate and subsequently fix three-dimensional shapes, such as those demonstrated in Figure 1, is shown in Figure 2b. A TN LCN material (Figure 2b-i) in the "X" geometry (\pm 45°) was heated through the T_g (Figure 2b-ii). If the material is removed from the heat source, the film unwinds as it cools and restores to the original flat form (Figure 2b-ix). However, if the material is removed and allowed to cool to room temperature while both ends are held by tweezers (Figure 2b iii-iv) or by adhesion (Figure 2b v-vi)–the film retains its three-dimensional shape. Additionally, if the film is rapidly quenched from the hot state by immediate exposure to a cold state (transition into liquid nitrogen, Figure 2b vi-viii) the film also retains the complex shape realizing an autonomous, hands-free shape memory cycle. As apparent in this Figure, due to the association of shape and temperature (Figure S1)–when the sample is unconstrained (free-standing as in Figure 2b vii-viii) near-instantaneous temperature cycling is required. However, in constrained systems (tweezers and adhesion in Figure 2b iii-iv and 2bv-vi) the cooling rate can be slow–analogous to previous reports of shape memory in polymeric materials.

One unique opportunity afforded to liquid crystalline systems is the ease in which domain orientation can be spatially controlled to yield a single monolithic film engineered to yield a desired response. Most commonly, spatial variation of the domain orientation of liquid crystal devices is enabled by the utilization of so-called command surfaces and photopatterning (holographic and masking).<u>35</u> To prepare LCN with spatial variation of the domain orientation an azobenzene material (procured from BEAM Engineering for Advanced Measurements) was

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spin cast onto a glass substrate as a command surface. This substrate was then paired with a rubbed, polyimide coated piece of glass to form a liquid crystal alignment cell. The cell was subjected to patterned linearly polarized 442 nm light (photomask) to align the azobenzene chromophores to yield a cell which periodically varies from TN to planar alignment (confirmed with polarized optical microscopy). In **Figure 3** a, the periodicity of the alternating TN and monodomain regions was 2 mm. The photoaligned cells were then filled with the LC monomer and photopolymerized with 532 nm irradiation (to avoid disruption of the photoalignment pattern). The LCN retained the patterned alignment upon removal from the substrates as well as after temperature cycling. The thermal response of the TN-MD monolith with 2 mm periodicity is shown in Figure <u>3</u>a. Upon heating, the MD portion of the film undergoes uniaxial contraction while as in Figure 1c-i, the TN portions expand-resulting in the formation of a periodic ripple. This shape is fixed by subjecting to immediate immersion in a cold environment (liquid nitrogen). Other combinatorial shapes can be generated as well (Figure <u>3</u>b)–for example when the periodicity of the TN and MD is expanded to 8 mm the sample remains flat in the middle (MD portion) while the TN regions roll into wheel-like shapes (as in Figure 1c). Once again, without externally applied force or rapid temperature change-this shape immediately restores back to the original flat shape. However, immersion in liquid nitrogen allows this shape to be fixed. Finally, the ability to fix samples that twist (shear) is demonstrated in Figure 3c, in which the alignment of the TN and MD are offset to the principal axis of the film geometry. Accordingly, shear strain (as in Figure <u>1</u>c) is generated upon heating which results in the film forming a three-dimensional "S" like shape. This shape is once again fixed by rapid cooling.

Figure 3

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Spontaneous shape formation and fixing of combinatorial shapes formed in liquid crystal alignment cells with photopatterned alignment. (a) A monolithic LCN film is formed with alternating regions of TN and monodomain (MD) regions with periodicity of approximately 2 mm. Upon heating the initially flat film (i), the film spontaneously ripples (ii). The rippled film restores to the permanent shape (i) with slow cooling and can be fixed with rapid cooling (iii). (b) A monolithic LCN film composed of a 6 mm TN region, a 6 mm MD region, and a 6 mm TN region (permanent shape illustrated in (iv) is heated to form a combinatorial shape of a flat region with two wheel-like ends (v). With slow cooling, the film restores to (iv) while with rapid cooling the shape is partially fixed (vi). (c) A monolithic LCN film composed of from a 6 mm offset-TN (15 to -85°) region, a 6 mm offset-MD region, and a 6 mm offset-TN region (15 to -85°) (vii) is heated to form a combinatorial shape of a flat region with two coiling ends

(viii). With slow cooling, the film restores to (vii) while with rapid cooling the shape is fixed (ix). The thickness of the LCN films was 15 μm.

In summary, glassy liquid crystalline polymer network (LCN) materials in the twisted nematic (TN) geometry are shown to spontaneously form a variety of three-dimensional shapes upon heating that can be autonomously fixed via rapid temperature cycling. The resulting shape of large aspect ratio LCN films can be readily controlled with temperature or adjusting the orientation of the alignment of the TN to the sample geometry. Furthermore, the distinctive responses of the TN geometries examined here are assimilated into a single monolith by employing photoalignment techniques. Combinatorial effects such as those demonstrated here will be an important tool in the hands of an integrator seeking highly engineered and tailorable shape memory. Shapes have been observed to be stable over the course of many months. It is expected that the spontaneous formation and fixing of shape, dictated by the response of the LCN to heat, will significantly improve the ability to generate user-independent temporary shapes–a limitation to the employment of shape memory polymers in applications in aerospace and medicine.

Experimental Section

Synthesis of Twisted Nematic Liquid Crystalline Network: Twisted nematic iquid crystal polymer networks (TN LCN) were synthesized by polymerizing RM257 (Merck) with 1 wt% of the inorganic photoinitiator Irgacure 784 (I-784) (Ciba). The chemical structure of RM257 is shown in Figure <u>1</u>a. To prepare TN LCNs, a liquid crystal alignment cell was prepared in which the Elvamide rubbing materials were rubbed orthogonally. A mixture of RM257 and I-784 was melted and mixed at 100 °C and drawn by capillary action into 15 µm thick Elvamide-coated orthogonally rubbed glass cells. For photocuring, the sample was cooled to 75 °C and subjected to 60 mW/cm² of 532 nm laser light for 1 hour. After photocuring, the film was removed from the glass substrates and washed in methanol to remove residual Elvamide alignment material. The spatially patterned LCN was prepared by using an azobenzene command surface (BEAM Co.) which was spin cast onto glass. The command surface substrate was then paired with a rubbed, polyimide coated substrate to form a liquid crystal alignment cell. The cell was patterned with linearly polarized 442 nm light through photomasks to align the azobenzene chromophores in desired periodic patterns to yield a cell which periodically varies from TN to planar alignment. Alignment was confirmed with polarized optical microscopy both before and after polymerization, as well as after temperature cycling.

Characterization Methods: The TN structure was confirmed by polarized optical microscopy (POM, Nikon). Thermomechanical properties of the TN LCN films were examined in cantilevers of 6 mm × 1 mm × 15 μ m (width, length, and thickness, respectively). Storage modulus (E'), loss modulus (E''), and loss tangent (tan δ were determined by dynamic mechanical analysis (DMA)

(RSA III, TA Instruments) operating at a strain of 0.5% and frequency of 1 Hz with a heating rate of 2.5 °C/min over the temperature range of 20 to 200 °C. Glass transition temperatures (T_g) are reported from the peak value of the tan δ curve.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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