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Photoinduced Topographical Feature Development in Blueprinted Azobenzene-Functionalized Liquid Crystalline Elastomers

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Abstract

All-optical deformation and recovery of complex topographical features is demonstrated within elastic sheets composed of main-chain type azobenzene-functionalized liquid crystalline elastomers (azo-LCEs). The azo-LCEs are synthesized via an orthogonal, two-step reaction between commercially available LC monomers and *n*-butylamine. By employing surface alignment, the local orientation of the nematic director is spatially complex ("blueprinted"). Exposing the blueprinted LCE films to light as an actinic stimulus generates a photomechanical response which yields reversible shape changes between 2D and 3D shapes. The deformation of azo-LCEs strongly depends on the azobenzene concentration as well as the network structure (i.e., crosslink density). Blueprinting complex director profiles within azo-LCEs yield reconfigurable elastic sheets that can be addressed both remotely and selectively which may have benefit in a variety of applications in aerospace, medicine, and optics.

1 Introduction

The conversion of light energy into mechanical work in polymeric materials has been a subject of intense research in recent years and dates back to the pioneering work of Lovrien. <u>1</u> A variety of materials have been prepared and examined—ranging from rubbery elastomers<u>2-6</u> to high-performance polyimides.<u>7-11</u> Key to the realization of practical utility of photomechanical effects is the efficient generation of mechanical force or shape (topography). Light is potentially

a "smart" stimulus that can uniquely allow for wireless (remote) spatio-temporal control of the force or shape change.

A considerable volume of recent research has focused on photomechanical effects in azobenzene-functionalized liquid crystalline polymer networks (azo-LCNs) and elastomers (azo-LCEs) both experimetnally and theoretically.<u>12-27</u> In these numerous efforts, azobenzene has been used as a molecular switch to convert input light energy into conformational change which subsequently generates strain in the polymeric materials. Two related but distinguished photochemical processes have been employed including (i) *trans-cis* photoisomerization of azobenzene typically initiated with UV irradiation 28 and (ii) trans-cis-trans reorientation of azobenzene initiated with blue-green irradiation. 12, 14, 29, 30 These photoinduced conformational changes convert input photonic energy into a mechanical output by distorting the local polymer network. *Trans-cis-trans* reorientation has recently been subject to intense fundamental studies focused on the athermal softening of the material at the molecular and macromolecular level. 30, 31 The photogenerated strain has correspondingly been demonstrated to induce motion including bending, oscillation, and torsion. 19, 32, 33 For aligned azo-LCNs and azo-LCEs, the strain is anisotropic and oriented parallel to the nematic director. For example, the photogenerated strain in a monodomain (nematic) LCN results in inplane deformation 29, 34 while offsetting the orientation of the director profile to the sample geometry results in out-of-plane deformation yielding twisting. 15, 16, 32, 35, 36

Spatial variation in the orientation (programming) of liquid crystalline monomers using surface alignment techniques such as photoalignment has many potential benefits. 32, 37, 38 In the work presented here, we employ a commercial photoalignment material also based on azobenzene. This material is formulated in solution and applied to glass substrates by spin coating, subsequently evaporating solvent, and then subjecting the surface layer to patterned linearly polarized light. The azobenzene molecules on the surface layer orient orthogonal to the electric field vector of the incident linearly polarized light. Upon filling the cell after photoalignment, the LC monomer orients to the local surface and retains this alignment during polymerization. When exposed to external stimuli, the resulting LCNs or LCEs display complex topographical changes dictated by spatial variation of the nematic director within the materials.38-40 Recently, main-chain LCEs amenable to photoalignment have been prepared, allowing for arbitrary spatial alignment of the nematic director over area as small as 0.01 mm².<u>41</u>, <u>42</u> These materials were prepared by a two-step synthesis in which oligomers were formed by Michael addition of a nematic diacrylate to a primary amine followed by free-radical photopolymerization of the acrylate end-capped oligomers. This reaction proceeds in one pot (in this case an alignment cell) and the resulting LCEs exhibit complex topographical changes with strain up to 55%. Comparatively, LCNs prepared by radical photopolymerization of diacrylates exhibit strains <5%. Other materials prepared from thiol-ene/acrylate formulations

have also been reported that are conducive to photoalignment and exhibit strain of as much as 150%. <u>43</u> Unfortunately, these LCEs can require heating to as much as 175 °C to generate such large strain that is undesirable for many applications. Prior examinations of main-chain LCEs prepared by hydrosilylation of vinyloxy-terminated mesogens with a flexible crosslinker produce materials with a considerably lower nematic-isotropic temperature (T_{ni} below 50 °C), but the use of solvent during the reaction prevents the use of surface alignment. <u>44</u>

In this work, we employ light as a contactless stimulus to realize all optical deformation and recovery of complex topographical features generated within sheets composed of azo-LCEs at room temperature. The photosensitivity of the materials is enabled by the inclusion of a diacrylate azobenzene monomer that is copolymerized with a nematic diacrylate monomer during aza-Michael addition with an amine. The chemistry is conducive to surface alignment by photoalignment layers, allowing for spatial programming ("blueprinting") of the local director orientation of azo-LCEs. Through variation of crosslink density and azobenzene concentration, the optical deformation as well as mechanical relaxation of both azo-LCEs is demonstrated.

2 Results and Discussion

2.1 Preparation of Spatially Programmed Azobenzene-Functionalized Liquid Crystalline Elastomers

The photoresponsive elastic sheets examined here are composed of azo-LCEs synthesized by the copolymerization of 1,4-bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]-2-methylbenzene (RM82), 4,4'-bis[6-(acryloyloxy)hexyloxy]azobenzene (2Azo), and *n*-butylamine (*n*-BA) with crosslinking initiated by Irgacure 784 (I-784) prepared using methods similar to a recent report.<u>41</u> The polymerization proceeds in two stages, but "one pot" including (1) a slow aza-Michael addition between the diacrylates and primary amine resulting in chain-extended diacrylate end-capped LC oligomers and (2) photopolymerization of resulting LC oligomers. Importantly, this chemistry is amenable to surface alignment. The overall reaction scheme, the fabrication process, and the preparation of patterned alignment cells (via photoalignment) are illustrated in **Figure 1**. The crosslink density (molecular weight between crosslinks) is easily tuned by adjusting the ratio of acrylate to amine functional groups where larger concentrations of *n*-BA lead to an increase in the chain extension of RM82<u>42</u> to increase the molecular weight between crosslinks within the materials.

Figure 1

a) Chemical structures and reaction scheme for the preparation of the azobenzene-functionalized liquid crystalline elastomers (azo-LCE) examined here. The polymerization proceeds in two steps: (i) aza-Michael addition reaction and (ii) photopolymerization of the end-capped diacrylate oligomers. b) The formulations are amenable to surface alignment. Complex director profiles were blueprinted into the azo-LCE materials by preparing surface alignment cells with light (photoalignment). The process for preparing the azo-LCE in alignment cells is illustrated for the example of a 3 × 3 array of +1 topological defects.

We contrast the photomechanical response of five samples spanning the azo-LCE to azo-LCN continuum to explore the relationship between azobenzene concentration as well as crosslink density on the resulting shape change. The formulations are detailed in **Table 1**. Nematic phases are observed for all mixtures and oligomers (Figure S1, Supporting Information). Compositions 1–3 are prepared with similar crosslink densities but with increasing azobenzene concentration. Phase transition temperatures of the mixtures and oligomers of compositions 1–3 determined by polarized optical microscope (POM) under temperature control show a decrease in T_{ni} with increasing 2Azo concentration. The T_{ni} of the oligomers are a few degrees higher than the *T*_{ni} of the LC mixtures due to the increase in molecular weight. The gel fractions of the materials examined here decrease as the 2Azo concentration is increased, which indicates that the photopolymerization is impeded by the absorbance of the incident wavelength (532 nm) by the 2Azo monomer or inhibited by uncharacterized side reactions. Samples prepared from compositions 1–3 are elastomers (azo-LCE) with glass transition temperatures (T_g) ranging from -3 to 7 °C. Comparatively, samples prepared from compositions 3–5 maintain the identical azobenzene concentration but the ratio of amine:acrylate is decreased to increase the crosslink density. The T_{ni} for both the LC mixtures and LC oligomers increase considerably with decreasing concentration of *n*-BA. The gel fraction of the azo-LCEs also increases with decreasing *n*-BA concentration (increasing crosslink density) at nearly constant 2Azo concentration which is expected from prior examinations of acrylate photopolymerization.45 The increase in crosslink density results in an increase in T_g from -3 to 26 °C as shown in Table 1 and Figure S2.

Table 1. Formulation and materials characterization

Sample	Molar composition ^{a)} (LC mixture)			Molar composition ^{b)} (LC oligomer)		Nematic- isotropic temperature ^{C)}		Gel fraction (LCE)	Glass transition (LCE)	
	Acryl/amine	RM82	2Azo	<i>п</i> - ВА	RM82	2Azo	7 _{ni} [°C] ^{d)}	T _{ni} [°C] ^{e)}	G [%] ^{f)}	7 _g [°C <mark>≸⁾</mark>
1	1.26	1.17	0.09	1	93	7	88	94	86	7

Sample	Molar composition ^{a)} (LC mixture)				Molar composition ^{b)} (LC oligomer)		Nematic- isotropic temperature ^{C)}		Gel fraction (LCE)	Glass transition (LCE)
	Acryl/amine	RM82	2Azo	<i>п</i> - ВА	RM82	2Azo	7 _{ni} [°C] ^{d)}	7 _{ni} [°C] ^{₽)}	G [%] ^{f)}	<i>Т</i> _g [°С <mark>^{g)}</mark>
2	1.24	1.04	0.20	1	86	14	85	91	73	-1
3	1.25	1.00	0.25	1	81	19	81	85	71	-3
4	2.10	1.68	0.42	1	81	19	84	88	90	15
5	3.17	2.57	0.6	1	82	18	93	95	99	26

^{a)}LC mixture in the feed;

^{b)}Determined by ¹H NMR in CDCl₃;

^{c)}Determined by polarized optical microscope while cooling from isotropic state;

^{d)}*T*_{ni} for LC mixture;

 $^{e)}\textit{T}_{ni}$ of LC oligomers after aza-Michael addition reaction;

^{f)}Determined by comparing ratio of mass before and after extraction in CHCl₃;

^{g)}Determined by second heating cycle of DSC.

2.2 All Optical Control of Topographical Features

Using the materials and patterning methodology described in Figure <u>1</u>, the five compositions detailed in Table <u>1</u> were prepared with a +1 azimuthal defect subsumed in the center of a 5 × 5 mm² film. The director profile of +1 azimuthal defect and a representative photograph of azo-LCE film taken between cross polarizers are shown in Figure <u>2</u>a,b, respectively. All five samples were \approx 50 µm thick. Evident in Figure <u>2</u>c, upon irradiation with 365 nm at 100 mW cm⁻² for 15 min the azo-LCE materials form the expected conical deformation, which is a comparable shape observed upon thermal activation.<u>41</u> The photomechanical response is attributable primarily to the decrease in nematic order within the materials resulting from UV induced *trans* to *cis* isomerization of azobenzene. Notably, these irradiation conditions are also accompanied by absorptive heating of \approx 20–30 °C at these concentrations. As evident in the photographs, the magnitude of the deflection depends on both azobenzene concentration (compositions 1–3) and crosslink density (compositions 3–5). It should be noted that the deflection of the films illustrated here and throughout this work were taken at the photostationary state (PSS). The transient process within which the material forms these shapes is complex and subject to

ongoing examination. From Figure 2d,e, which were taken ≈ 5 s and 2 min after removal of the UV light (sufficient time for the samples to cool to room temperature), the samples nearly completely retain the deformed state. Based on these results, the deflections evident in Figure 2c are nearly completely attributable to a photochemical mechanism rather than a photothermal mechanism. The deformed shapes evident in Figure 2b-e are not permanent and slowly return to the initial shape as metastable *cis* isomers relax back to *trans* isomers by thermal relaxation.22, 23 Evident in Figure 2f, irradiation with 532 nm (50 mW cm⁻² for 10 min) light can rapidly drive *cis*-to-*trans* isomerization within the materials which also reduces the photogenerated strain within the films to approximately zero. It should be noted that the films do not restore to a completely flat shape but rather retain some deformation. The non-flat shape seems to take on the form of a so-called anti-cone (especially for compositions 1, 4 and 5).46 Predictions from Warner and Modes indicate that the anti-cone is expected to occur upon cooling from the flat shape whereas a cone is expected to appear on heating (or light irradiation).46 The flat shape can be restored by increasing the temperature to the photopolymerization temperature (75 °C).

Figure 2

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The azo-LCE compositions were prepared with +1 azimuthal defects subsumed in the center of square films of $5 \times 5 \text{ mm}^2$ with 50 µm thickness. a) Illustration of the director profile described by a of +1 azimuthal defect. b) A representative photograph of a +1 azimuthal defect within an azo-LCE taken between cross polarizers. c-f) The five azo-LCE films were placed on a white surface and subjected to 365 nm irradiation of 100 mW cm⁻² for 15 min. Photographs were taken to measure the relative deflection of the materials c) during exposure, d) 5 s after exposure, e) 2 min after exposure, and f) after 532 nm exposure (\approx 50 mW cm⁻² for 10 min).

Plainly evident in the images in Figure $\underline{2}$, the optimum photomechanical response can be achieved when the azo-LCEs has the largest concentration of azobenzene and the highest molecular weight between crosslinks (the lowest crosslink density). Additional photographs of the films and details of the amplitude of the height change with respect to their original thickness (50 µm) are shown in Figure S3 (Supporting Information).

Arrays of defects can be blueprinted into the films as well (**Figure 3**). Here, a sample prepared from composition 3 is prepared in an alignment cell designed to yield a 3 × 3 array of +1 azimuthal defects. After preparation, some residual stress and undulation is apparent upon cooling to room temperature. Upon irradiation with 365 nm light, the sample deflects. In a recent examination of thermal responses, the deflection of the cones exhibits up/down symmetry (meaning the film is equally likely to choose to deflect up or down upon heating).<u>41</u>

Here, because of the directional nature of the light exposure, the cones in nearly all instances deflect upward. Irradiation with longer wavelength (532 nm) light restores the film approximately to the initial condition. Other director profiles represented by other topological charge strengths including +1 radial and -1 were prepared of composition identical to sample 3 and irradiated as shown in Figure <u>3</u>b,c. While the birefringence of the materials taken between cross polarizers in Figure <u>3</u>a-c are indistinguishable (four brushes), their resulting shape change upon 365 nm irradiation are markedly different dictated by the distinct differences in the director profiles (inset to Figure <u>3</u>b,c).

Figure 3

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a) A 3 × 3 array of +1 azimuthal defects is prepared in an azo-LCE (composition 3). Upon irradiation with 365 nm light, nine conical domes emerge from the film. The cones are metastable after removal of the UV light before being returned to the flat state by irradiation with 532 nm light. Both single (1 × 1) and arrays (2 × 2 or 3 × 3) of topological patterns are prepared with either b) a +1 radial defect or c) a -1 defect upon irradiation with 365 nm light. Inset: photographs of a single film (5 × 5 mm²) between cross polarizers, and illustrations of the corresponding director profile of the b) +1 and c) -1 director profiles in the azo-LCE.

Light allows remote as well as spatial control of the mechanical response of the elastic sheets prepared from these materials. This is illustrated in **Figure 4**. Here a 1 × 3 array of a +1 azimuthal defect is prepared once again in composition 3. The deflection of each cone can be selected by localizing the UV irradiation to selected locations within the monolithic film. The photoinduced deformation can be restored to the initial position by irradiation with 532 nm irradiation. Subsequent exposures can repeat or select another area of the film to deform by localized UV irradiation.

Figure 4

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A 1 × 3 array of +1 azimuthal defects is prepared in azo-LCE (composition 3). Localizing the UV irradiation selectively actuates the conical domes in the film. Subsequent exposure to 532 nm light restores the film to the original flat state.

2.3 Interplay between Photogenerated Strain and Mechanical Properties of the Materials

Hereto, we have focused on all optical deformation and recovery of topography within sheets composed from the azo-LCE films. To further elucidate the differences in the photochemical response of the materials, the samples were investigated with UV-vis spectroscopy. Samples were prepared from compositions 1–5 in the polydomain orientation inside LC cells with \approx 5 µm thickness. As in Figures 3 and 4, the materials were irradiated with 365 nm light at 50 mW cm⁻² for 10 min. Irradiation with 365 nm quickly causes a decrease in absorption corresponding to the $n-\pi^*$ band of *cis* isomer (451 nm). The absorption spectra for samples prepared from compositions 1–5 is plotted in **Figure 5**. The PSS of the azo-LCEs examined here is reached within a few minutes at these thicknesses. The isomerization degree at the PSS is estimated using the Equation 1

where, A_0 is the absorbance at λ_{max} before UV irradiation, and A_t is the absorbance at the same wavelength at the PSS.47, 48 It should be noted that RM82 has negligible absorbance in this portion of the spectrum. For samples prepared from compositions 1–3, the isomerization degree from *trans* to *cis* isomer at the PSS remains relatively low (less than 30%). By contrast, the isomerization degree of the PSS gradually increases when the materials become glassier by increasing crosslink density (compositions 4 and 5).

Figure 5

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UV-vis spectra of the a-d) azo-LCEs and e) azo-LCN before and after (at the photostationary state, PSS) UV exposure (365 nm and 50 mW cm⁻²): a) composition 1, b) composition 2, c) composition 3, d) composition 4, and e) composition 5. The isomerization degree at the PSS is inset into each panel.

Irradiation with UV light results in conversion of azobenzene from the *trans* to *cis* conformation.49 The reverse process occurs by thermal relaxation or by irradiation of visible light. Evident in Figure 5, as the T_g of the azo-LCE decreases the isomerization degree at the PSS also decreases. The population of a large concentration of *cis* isomers in the PSS is related to a variety of factors including light source (wavelength) and intensity, concentration, thickness of material, and material properties. Since the major driving force of optical deformation of azo-LCEs is the decrease in the nematic order during photoisomerization (with some contribution from the accompanying temperature change), it would be reasonable to expect that the

concentration of *cis* isomer generated in a PSS would bring a larger deformation of azo-LCEs. Evident in Figure 2, samples prepared from formulation 3, the most elastomeric sample, show the largest deformation in spite of the lowest isomerization degree (13% from UV–vis) produced upon 365 nm irradiation. On the other hand, samples prepared from formulation 5,the highly crosslinked sample, show much smaller deformation but the highest extent of isomerization (54%). Based on the results of photochemical and characterization of the photomechanical response, we speculate that the largest reduction in nematic order of azo-LCEs does not necessarily occur in the sample generating the largest amount of *cis* isomer. Instead, the largest decrease in nematic order inducing the largest deformation of azo-LCEs by UV light occurs at samples for the lowest crosslink density. In this way, the photoinduced shape transformation of the azo-LCEs is an interplay between the magnitude of photogenerated strain and the mechanical properties of the material.

The mechanical properties of the azo-LCEs examined here are dictated by a number of factors most importantly the crosslink density, yielding materials with glass transition temperatures ranging from -3 to 26 °C. UV light irradiation of the monomer in solution completely converts the material to the *cis* isomer. However, embedding the chromophore by covalently bonding it into the polymer network dramatically reduces the isomerization degree to as low as 13%. Prior examinations have explored the degree of isomerization (reported as *cis* isomer concentration) in azo-LCN (glasses) with either main chain or side chain connectivity with values ranging from 7% to 82%.50 Statistically it can be expected that the azobenzene chromophores are more prevalent in the main chain of the polymer networks but could also reside in the crosslinking sites. The chemistry employed here allows for the direct correlation of the thermomechanical properties of the material to the photochemistry occurring within the material. This complements and extends our prior investigation which examined the photomechanical response of a material as a function of temperature.<u>51</u> In the prior examination, the material composition was maintained but the network mobility (e.g., the viscoelastic properties) was regulated by temperature. Somewhat unexpectedly, we reported a decrease in photomechanical response (visualized as bending of a cantilever) at temperatures exceeding the glass transition of the material. However, we were not able to delineate whether the material properties or the temperature dependence of the *cis-trans* isomerization dictated the photomechanical response. It is clear from Figure 5 that the ability of azobenzene to sustain and remain in the *cis* isomeric form within the polymer networks examined here is strongly influenced by the viscoelastic properties of the material (generally described by T_{g}). As the mobility of the polymer network is increased, the probability for thermal back relaxation of the *cis* isomer to the *trans* form substantially increases.

2.4 Kinetic Mismatch between Photochemistry and Mechanical Response

We conclude this examination by contrasting the mechanical relaxation of the materials (represented by measuring the angle of the cone to a normal as a function of time) to the thermal *cis-trans* isomerization (monitored by UV–vis spectroscopy) for the azo-LCE samples at various crosslink densities (samples prepared from compositions 3–5) as shown in Figure 6. It should be noted that the deflection and relaxation of the cone can be correlated to strain per Modes<u>46</u> and the angle is used here as a visual representation of strain in this geometry. Interestingly, the expected correlation of the photochemistry and mechanical response is not observed. The *cis* isomer in the sample 3 containing loosely crosslinked networks recovers the stable *trans* isomer within 2.2 h but the mechanical relaxation in the dark occurs over 51 h (Figure <u>6</u>a). The mechanical relaxation of the material prepared from the formulation 5 (more densely crosslinked network) restores earlier than the recovery of *trans* isomer (Figure <u>6</u>c). The azo-LCE prepared from formulation 4 has fairly close agreement between the relaxation kinetics between photochemistry and mechanical. These conflicting results imply that in the dark, the photochemistry is decoupled from the mechanical relaxation. Since the concentrations of azobenzene among these materials are comparable, these results indicate that crosslink density has divergent influence on the relaxation kinetics for the photochemical and mechanical response. A recent report details a similar finding for azo-LCN materials with $T_{\rm g}$ above room temperature.30

Figure 6

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Comparison of the *cis-trans* thermal relaxation of materials prepared from compositions 3–5 and the mechanical recovery of the flat state: a) composition 3, b) composition 4, and c) composition 5.

3 Conclusion

Here we have demonstrated photoresponsive and reversible shape change in thin elastic sheets prepared from azo-LCE. The order of the azo-LCEs examined here decreases upon generation of *cis* isomers by UV irradiation, which leads to macroscopic shape changes. The irradiation of longer wavelength (532 nm) regenerates *trans* isomers, and the initial shape can be restored. Such reversible shape evolution can be programmed and is dictated by the topology of the nematic director imprinted into the azo-LCE written by photoalignment. Wirelessly powered and locally selective actuation of azo-LCEs are also demonstrated through light activation. Structure-property-performance relationships are developed correlating the magnitude of the photomechanical response to the crosslink density and azobenzene concentration. Unlike previously documented reconfigurable LCEs largely limited to direct heating, the shape and actuation strain of elastic sheet in this study can be remotely controlled

in a precise manner, which may expand their applications in self-folding devices in aerospace and biomedicine.

4 Experimental Section

Materials: 1,4-Bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]-2-methylbenzene (RM82) was purchased from Synthon Chemicals. *N*-Butylamine (95%) was purchased from Sigma-Aldrich. The photoinitiator Irgacure 784 (I-784) was donated by Ciba (now BASF). 4,4'-bis[6-(acryloyloxy)hexyloxy]azobenzene (2Azo) and photoalignment material (PAAD 22) were purchased from Beam Co. All materials were used as received unless otherwise noted.

Instrumentation: The LC mixtures and LC oligomers were examined by a Nikon POM equipped with a thermal stage (Mettler Toledo). The nematic to isotropic transition temperatures (T_{ni}) reported were determined on cooling. Thermal transition temperatures (e.g., glass transition temperatures, T_g) of polymerized films were characterized by TA instruments Q1000 differential scanning calorimeter (DSC). Each sample was heated to 200 °C then cooled to -50 °C and heated again to 200 °C under nitrogen at a rate of 10 °C min⁻¹. The glass transition temperatures were determined from the second heating cycle. Absorption spectra were collected on a Cary 5000 UV-vis–NIR spectrometer. 5 µm thick samples were used for the UV-vis absorption measurements. EXFO Omnicure S1000 (λ = 365 nm) was used to induce *trans-cis* photoisomerization of azo-LCE samples. Proton nuclear magnetic resonance spectra were recorded at 300 MHz on a Bruker AVANCE 300 spectrometer with CDCl₃ as solvent.

Photoactuation Procedure: Free standing azo-LCEs harvested from the LC cell were placed on the flat surface followed by irradiating with 365 nm (EXFO Omnicure S1000, 50–100 mW cm⁻²) at ambient temperature. UV irradiation caused conformational change of azobenzene at the molecular level, which brought disruption of nematic order of azo-LCEs through cooperative motional effect between azobenzene and nematic monomer. As a result, topographical changes of azo-LCEs from 2D to 3D shapes occurred according to nematic director profiles written by photoalignment. The initial flat shapes of azo-LCEs were restored by irradiating with 532 nm (Ar⁺ laser, 50 mW cm⁻²) for 10–15 min or by storing in dark (thermal relaxation) at room temperature for several hours.

Synthesis of Azobenzene-Functionalized Liquid Crystalline Elastomers: The monomer mixtures detailed in Table <u>1</u> were designed to prepare azo-LCE samples with varying azobenzene concentration with similar crosslink densities as well as isolate the role of crosslink density at fixed azobenzene concentration. The photoinitiator was added at 3 wt% of the total monomer concentration. The mixture was heated to the isotropic state and vigorously vortexed for homogeneous mixing. The polymerizations were performed in a two-step reaction procedure. The mixture was filled into a liquid crystal cell at ≈80 °C by capillary action and then placed in an

oven about 18 h at 75 °C, during which the chain extension of LC monomer proceeds through aza-Michael addition reaction between acrylate and amine. Afterward, the sample was exposed to 532 nm laser light (\approx 100 mW cm⁻²) for 2 h at about 75 °C for photopolymerization of diacrylate.

Fabrication of Liquid Crystal Cells: The alignment layer of the liquid crystal cells was prepared by using Elvamide or the photoalignment dye (PAAD 22). Glass substrates were cleaned by sonication using acetone and isopropanol, followed by plasma cleaning process. Then, Elvamide solution (0.125 wt% in methanol) was spin coated onto plasma cleaned glass substrates. The two glass substrates were glued together using a mixture of optical adhesive (Norland) and 5 µm silica spacers, followed by curing under 365 nm lamp for 10 min. For photoalignment, a PAAD 22 solution (0.33 wt% in DMF) was spin coated onto the plasma cleaned glass followed by baking at 100 °C for 10 min to remove residual solvent. The detail of photoalignment procedure has been explained in our previous publication.<u>41</u> After patterning, the two glass slides were glued together using a mixture of two-part epoxy adhesive and 50 µm silica spacers to set the desired thickness. The LC cells were filled with monomer mixtures by capillary action.

Gel Fraction Analyses: To evaluate degree of crosslinking of azo-LCEs, gel fraction analyses were performed by extracting uncross-linked portion of materials. The azo-LCE films were immersed in chloroform at room temperature at least 48 h without stirring. Gel fraction values (*G*) of azo-LCEs were determined by the ratio of initial mass before extraction to dried mass after extraction.

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