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Article

Influence of Orientational Genesis on the Actuation of Monodomain Liquid Crystalline Elastomers

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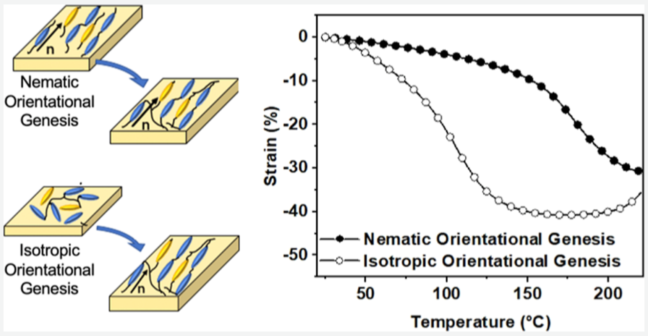
ABSTRACT: The macroscopic alignment of the nematic director within liquid crystalline elastomers (LCEs) amplifies the magnitude of the directional strain response. Theory predicts that the stimuli response of LCEs will be affected by the orientational genesis of cross-linking. We examine compositionally identical LCEs aligned by either mechanical or surface techniques. The two-step procedure to prepare LCEs by mechanical alignment first forms cross-links in a disordered state (e.g., isotropic orientational genesis), which thereafter are aligned by deformation during which polymerization (e.g., cross-linking) is completed. Comparatively, cross-linking within surface-aligned LCEs exclusively occurs within the ordered state (e.g., nematic orientational genesis). The orientational genesis of cross-linking in aligned LCEs, in compositionally identical samples, significantly affects the thermotropic and phototropic deformation of these materials. LCEs prepared by mechanical alignment (e.g., isotropic orientational genesis) have actuation temperatures that are as much as 75 °C lower than the analogous LCEs prepared by surface alignment (e.g., nematic orientational genesis). Likewise, the magnitude and rate of photoinduced strain generation in azobenzene-functionalized LCEs prepared by mechanical and surface alignment differ by a factor of 2 or greater.



INTRODUCTION

The enforced macroscopic alignment of liquid crystals is the foundation of the electro-optic response of these materials that has enabled their pervasive use in the display industry.[1] In these devices, the liquid crystal orientation is enforced by surface anchoring.[2] Surface anchoring relies on the minimization of energy based on interactions between alignment coatings and the liquid crystal mesogens. In order to minimize energy, the liquid crystals spontaneously organize, resulting in a macroscopic order to the system of molecules that can be subsequently altered by external stimuli to generate a functional response.

The anisotropy and order of liquid crystals are also retained in polymer networks. Here, we are interested in liquid crystalline elastomers (LCEs) which retain liquid crystallinity in lightly to moderately cross-linked polymer networks. When aligned, LCEs undergo large deformations if subject to thermal or optical stimuli[3,4] and are increasingly considered for the potential use as material actuators.[5,6] In this way, LCEs are material machines that transduce an energy input into a mechanical output.[7] In thermotropic liquid crystalline materials, heating induces a phase transition from the liquid crystalline (nematic) to the isotropic state. Similarly, photoinduced conformational changes of azobenzene[8] or other photochromic molecules[9] are able to trigger isothermal phase transitions (e.g., phototropic phase transitions) in both small molecules and polymeric materials.[10]

Phase transitions in small-molecule liquid crystalline systems are first order[11] and described by the Landau−de Gennes free energy.[12] The composition of the liquid crystalline mesogens strongly affects the strength of the intermolecular interactions (e.g., mesogen−mesogen interactions), which correspondingly affects the amount of energy (thermal or optical) necessary to induce a thermotropic or phototropic phase change in both small molecules[6] and polymer networks.[6,13,14] It has long been established that the phase behavior of LCEs deviate from that of small-molecule liquid crystals and exhibit supercritical, second-order phase transitions.[15] Recent literature reports detail approaches to adjust the nascent thermotropic response of LCEs by altering the aliphatic spacer length and pendant groups associated with chain extenders.[16,17] Recently, we have reported that LCEs prepared from a liquid crystalline monomer with a reduced intermolecular interaction enhances both thermotropic[13] and phototropic[14] actuation.

While recent reports document the contribution of mesogen−mesogen interactions to thermotropic and photo-

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tropic actuations of these materials, the polymer network topology also plays a considerable role in dictating the stimuli response.[18,19] In particular, the nature of cross-links in LCEs is predicted to heavily influence the ability of the organized polymer network to be disrupted by heat.[20−22] The theory predicts that the state of order in the liquid crystalline systems at the time of cross-linking will impact the measured nematic-to-isotropic transition temperature (T_{ni}).[23] The orientational genesis of cross-linking shifts T_{ni} largely due to the spontaneous strain imposed on the cross-links when mesogen−mesogen interactions are present in the nematic phase (i.e., nematic coupling). Prior experiments have demonstrated this behavior in both monodomain and polydomain networks.[24,25] Of particular interest are polydomain studies showing that although there is no long-range order, the nature of the cross-links within the microdomains impacts the properties of the elastomer.[26−28]

While numerous studies have been undertaken to illustrate variations in LCE behavior as a function of the microdomain formation, there is limited extrapolation to macroscopic ordering, specifically when comparing LCE alignment methods. A critical step in the fabrication of LCEs is the alignment of mesogens to adopt a uniaxial (e.g., monodomain) orientation. Historically, alignment has been enforced by one of two methods. The first method utilizes a two-step polymerization process in which a lightly cross-linked network is first formed in the disordered state. A mechanical load is subsequently applied to induce long-range order, placing strain on the initially disordered cross-links. A second cross-linking step is initiated in the deformed (e.g., ordered) state to retain uniaxial orientation of the director in LCE. This approach was first employed in the preparation of uniaxially aligned LCE prepared by time-sequenced polymerizations in polysiloxanes and has since been extended to thiol-Michael addition chain extension reactions and subsequent photopolymerization of unconverted acrylate bonds in the polymer network.[29,30] Previous work details the importance of the strain imposed on the material and the effects of multistage cross-linking as related to the order−disorder transition.[31,32] Accordingly, the preparation of LCEs by this method necessitates a complex balance between cross-links formed in the disordered state (isotropic orientational genesis), those formed in the ordered state (nematic orientational genesis), and the mesogen−mesogen interactions contributing to nematic coupling in the LCE. A second approach, enabled by recent advances in materials chemistries, is to enforce the macroscopic alignment of LCEs by surface interaction.[33,34] In this method, liquid crystalline monomers are aligned by the interaction with surface treatment in a cell. Once aligned, an oligomerization step and subsequent photopolymerization of the monomers form the LCE, which largely retains the aligned state. The entirety of this reaction occurs in the nematic state and all cross-links originate from the ordered nematic phase (nematic orientational genesis).

The known relationship between the orientational genesis of a monodomain LCE during cross-linking and mesogen−mesogen interactions in LCEs provides opportunity to explore phase behavior effects as related to the approach of enforcing alignment on the LCE. Here, we fabricate compositionally identical LCEs independently by both surface and mechanical techniques. We explore three compositions that differentiate the extent of cross-links formed in each polymerization step. We subject these LCEs to thermomechanical and photomechanical characterization to show that both the coupling strength and orientational distribution of cross-links associated with the macroscopic alignment of the LCE affects phase behavior and actuation.

■ EXPERIMENTAL SECTION

Synthesis of Monodomain Azobenzene-Functionalized LCEs. Liquid crystalline elastomers (LCEs) containing azobenzene were synthesized by copolymerizing 4-(6-(acryloyloxy)hexyloxy)-phenyl-4-(6-(acryloyloxy)hexyloxy)benzoate (C6BAPE) (Synthon Chemical) and 1,4-bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]-2-methylbenzene (C6M) (Wilshire Technologies) in a 2:1 C6M/C6BAPE ratio with 15 wt % 4,4′-bis(9-(acryloyloxy)nonyloxy) azobenzene (ST04181) (Synthon Chemical). C6BAPE was used to lower the T_{ni} of the mixtures (compared to C6M) to further reduce temperatures for oligomerization in both the surface and mechanical alignment to ensure that the amine chain extenders did not evaporate. The liquid crystalline monomers were mixed with 1-hexylamine and diethylenetriamine in ratios of 0.75 amine/acrylate (1:1 hexylamine/diethylenetriamine by functional group) or 0.85 amine/acrylate (0.44:0.56 hexylamine/diethylenetriamine by functional group). A third composition was prepared with 1-octylamine and diethylenetriamine in a ratio of 0.75 amine/acrylate (1:1 octylamine/diethylenetriamine by functional group). A visible light photoinitiator (Omnirad 784, 2wt %) and co-initiator (benzoyl peroxide, 2:1 molar ratio of co-initiator/initiator) were added to all compositions. The monomer mixtures were heated to 150 °C and vortexed to ensure complete mixing. Thereafter, amine and initiators were added at 90 °C and vortexed until incorporated uniformly in the monomer mixture. To prepare samples by surface alignment, the mixtures were then drawn by capillary action into 50 μm thick alignment cells, fabricated by the antiparallel alignment of rubbed Elvamide-coated glass slides with a 50 μm glass spacer, at 95 °C (isotropic state) and cooled to 50 °C (nematic state). Mechanically aligned samples were prepared by placing between two unrubbed Elvamide-coated glass slides with a 50 μm Teflon spacer at 95 °C and cooling to 85 °C (isotropic state). The mixtures were held for 24 h at their respective temperature to facilitate the aza-Michael reaction. After 24 h, surface-aligned samples were photopolymerized in the alignment cells at the oligomerization temperature for 45 min (525 nm, 50 mW/cm^2) and were subsequently removed from the cells. Samples oligomerized in the isotropic state for the mechanical alignment were cooled to room temperature (nematic phase), removed from the glass slides, and cut into 2 mm wide strips. The strips were stretched to 150% of their original length to induce the liquid crystal alignment and were held for 5 min in the dark before photopolymerizing for 45 min in the stretched state (525 nm, 50 mW/cm^2). This value was selected to ensure the orientation of the liquid crystal mesogens to the loading axis. The measured thickness of samples, both mechanically and surface aligned, varied from 40−50 μm after final polymerization.

Tensile Testing. Tensile experiments were conducted by dynamic mechanical analysis (RSA-G2, TA Instruments) on LCE strips cut parallel to the nematic director. The strain was applied at 5%/min. The moduli of the LCEs were taken in the linear regime in the stress−strain curve between 2 and 4% strain.

Differential Scanning Calorimetry. Phase transition temperatures for the monomers, oligomers, and polymers were measured using differential scanning calorimetry (Discovery DSC 2500, TA Instruments). Values are reported from the second heating cycles recorded at ramp rates of 5 °C/min.

Thermotropic and Phototropic Actuation. LCE strips (∼2 mm × 12 mm × 0.05 mm) were placed in tension (Discovery DMA 850, TA Instruments) at 0.001 N constant force. The thermomechanical strain response of the LCE was measured as the temperature was increased from 25 to 220 °C at 3 °C/min. The photomechanical strain response of the LCE was measured at room temperature upon exposure to UV light (365 nm, 50 mW/cm^2) for 3000 s. The UV light was turned on at 60 s.

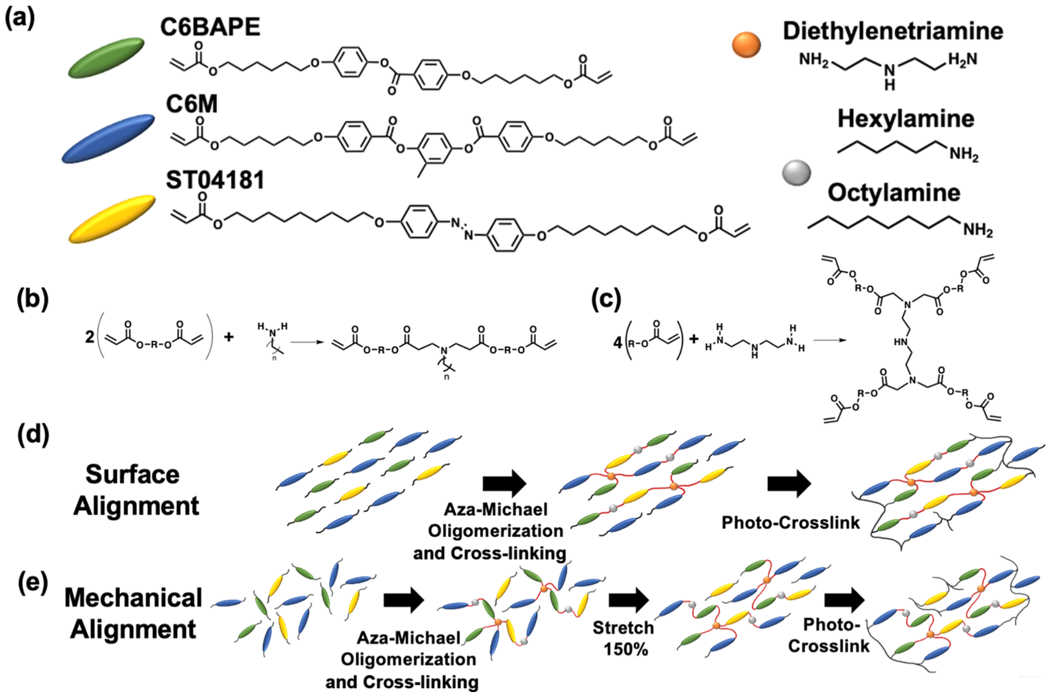

Figure 1. (a) Molecular structures for liquid crystalline diacrylates and amines used to prepare LCEs by (b) aza-Michael oligomerization and (c) aza-Michael cross-linking followed by acrylate photopolymerization after alignment is enforced by (d) surface interactions and (e) mechanical force. Mesogenic structures in (a) are represented by *R* in (b,c).

■ RESULTS AND DISCUSSION

Previous theoretical work details the correlation between the nematic-to-isotropic transition temperature (T_{ni}) and the state of order during cross-linking in liquid crystalline elastomers (LCEs).[23] Evident by the relationship between the order at the time of cross-linking ($S_{(x)}$) and at the T_{ni} ($S_{(0)}$), as exhibited in eq 1, LCEs cross-linked in an ordered state are expected to have an elevated transition temperature ($T_{\mathrm{ni}}^{(x)}$) in relation to that of the uncross-linked monomers (T_{ni}). Analogously, LCEs cross-linked in a disordered state will have a lower transition temperature. As discussed in this initial report, order established between the liquid crystalline mesogens is a balance of free energy invoked by straining of cross-links and mesogen−mesogen interactions giving rise to nematic coupling. Therefore, the relationship between T_{ni} and order is effectively an energy balance that can be experimentally isolated in LCEs by distinctive alignment genesis. Additionally, presented in eq 1 are variables that can be considered constant for a given composition; N_x is related to the number of cross-link constraints, k_{b} is the Boltzmann constant, T is the temperature, D represents constants related to nematic coupling, and A is a constant related to the Landau−de Gennes free energy. In LCEs prepared from identical compositions, the only variable changing is $S_{(x)}$.

$$T_{\mathrm{ni}}^{(x)} = T_{\mathrm{ni}} + 4N_x k_{\mathrm{B}} T \frac{D}{A}\left(S_{(x)}{}^{2} - \frac{1}{2}S_{(0)}{}^{2}\right) \qquad (1)$$

The compositions examined here are based on the liquid crystalline monomers C6M, C6BAPE, and ST04181 (Figure 1a). As detailed in prior reports, a facile approach to preparing LCEs amenable to the surface-enforced alignment involves the use of the aza-Michael reaction between amines and acrylate. Upon heating a mixture with a stoichiometric acrylate excess, the reaction of the amines and the acrylates produced acrylate end-capped oligomeric precursors (Figure 1b). The inclusion of the multifunctional amine DETA is a route to introduce cross-linking in this state (Figure 1c). While the aza-Michael addition can potentially occur at both the primary and secondary amines of DETA, spectroscopic analysis indicates that the secondary amine is minimally reactive compared to the chain extension via primary amines. Subsequent to the aza-Michael addition reaction, the alignment of the nematic director was enforced by either surface interaction (Figure 1d) or mechanical force (Figure 1e), and acrylate cross-links were formed in both aligned states by photopolymerization. The alignment of the LCEs was uniaxial (monodomain) with an orientation parameter in the range of 0.23−0.28 (POM images in Figure S1, representative WAXS in Figure S2).

Three compositions of materials were prepared to illustrate differences in the LCE stimuli-response, relating to eq 1. A baseline composition consisted of hexylamine as a chain extender and an amine/acrylate ratio of 0.75:1 with 1:1 chain extending/cross-linking amine (6S75 and 6M75). A second composition consisted of hexylamine as a chain extender and an amine/acrylate ratio of 0.85:1 (6S85 and 6M85). This composition maintains the concentration of chain-extending amine consistent with the baseline composition but increases the number of amine cross-links in the first cross-linking step and, therefore, is a route to alter N_x. The third composition utilized octylamine as a chain extender and an amine/acrylate ratio of 0.75 (8S75 and 8M85). This composition parallels the cross-linking steps of the first composition but increases the pendant chain length for amine in a route to indirectly modify the intermolecular interactions between mesogens in the polymer network. For nomenclature, we refer to samples by the alkyl chain length of the chain extending amine (6 or 8), the alignment method (surface—S, mechanical—M), and the concentration of amine (75 or 85).

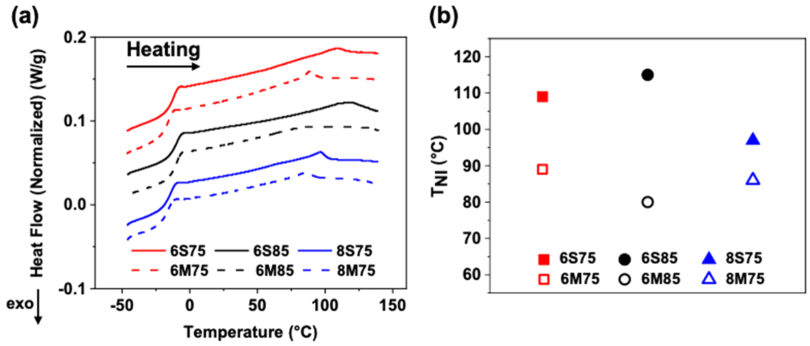

Figure 2. (a) DSC thermograms for partially polymerized LCEs after the first cross-linking step when subject to the surface (solid lines) or mechanical alignment (dashed lines). (b) T_{ni} after the first cross-linking step plotted as a function of composition in order of increasing T_{ni} as measured by DSC.

Table 1. Material Properties for Surface (*S*) and Mechanically (*M*) Aligned LCEs Containing Hexylamine (6) or Octylamine (8), with DETA in Ratios of 0.75:1 (75) or 0.85:1 (85) Amine/Acrylate[a]

	first cross-linking			second cross-linking					
composition	$T_{g,1}$[b] (°C)	$T_{ni,1}$[c] (°C)	gel fraction$_1$	$T_{g,2}$[b] (°C)	$T_{ni,2}$[c] (°C)	gel fraction$_2$	modulus$_2$[d] (MPa)	M_c[e] (g/mol)	S[f]
6S75	−13	109	0.74	−3	178	0.93	34 ± 5	101	0.26
6M75	−14	89	0.73	−4	141	0.96	33 ± 4	104	0.28
6S85	−11	115	0.76	−4	178	0.93	32 ± 6	113	0.23
6M85	−11	80	0.75	−4	107	0.94	34 ± 8	118	0.24
8S75	−17	97	0.72	−8	173	0.94	27 ± 4	100	0.23
8M75	−17	86	0.73	−8	111	0.93	25 ± 2	108	0.25

[a] Properties measured after first cross-linking step denoted by subscript 1 and after second cross-linking step denoted by subscript 2. [b] Measured using midpoint of second cycle DSC heating curve. [c] Calculated as maximum magnitude of first derivative of thermomechanical strain curves. [d] Measured parallel to nematic director of the LCE after second cross-linking in linear stress−strain region (2−4%). [e] M_c calculated using the density of films and storage modulus at 100 °C measured using DMA after second cross-linking (Figure S6, eq S1, Table S1). [f] Herman's orientation parameter calculated from WAXS data.

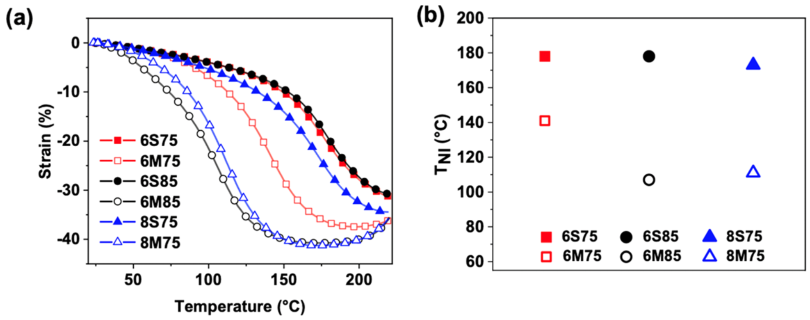

Figure 3. (a) Thermomechanical strain generated from fully polymerized LCEs prepared by surface alignment (closed symbols) and mechanical alignment (open symbols). Samples were held at 0.0005 N constant force as the temperature was ramped at 3 °C/min from 35 to 220 °C. (b) T_{ni} of the fully polymerized LCEs are plotted as a function of composition.

In order to determine the effect of the alignment genesis on the phase behavior and stimuli-response of these LCEs, we will consider the amine and acrylate cross-linking steps separately. In one set of materials, which ultimately used mechanical loading to align mesogens in the LCE, the amine cross-linking step was carried out in the unaligned isotropic phase, creating cross-links within a disordered liquid crystal system. In the second set of materials, which exploited the surface alignment techniques for aligning mesogens in the LCE, this step was carried out in the nematic phase. Accordingly, the amine cross-links originated within an ordered state as dictated by surface-enforced alignment. In traditional syntheses of LCEs by surface alignment, this first polymerization generally involves only chain extension (e.g., pure oligomerization via a primary amine). Here, we introduce amine cross-linking to allow us to compare the materials across the two alignment methods.

Figure 2 illustrates the difference in liquid crystalline properties of the materials after the first cross-linking step. LCE prepared by surface alignment materials exhibited higher T_{ni} than those formed during mechanical alignment for all three compositions. From eq 1, although these cross-linked oligomers are compositionally identical, the T_{ni} is suppressed by cross-linking in the disordered state (mechanical alignment, order parameter 0.00) and elevated by cross-linking in the ordered state (surface alignment, order parameter 0.23). The LCE 6S85 exhibits a higher T_{ni} than 6S75 (and analogously 6M85 lower than 6M75 T_{ni}) due to the contributions to N_x in this first amine cross-linking step. Both 8S75 and 8M75 had T_{ni} values lower than that of their 6S75 and 6M75 counterparts.

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This behavior relates to the impact of intermolecular interactions between mesogens imposing spontaneous strain on the system. With a longer aliphatic tail on the amine chain extenders, mesogen−mesogen interactions are weakened, leading to lower energy inputs required for phase transitions and illustrating that both nematic coupling strength as well as elastic free energy of cross-links need to be considered in the optimization of the LCE phase response. Control experiments confirm that the compositionally-equivalent materials maintain similar T_g values and gel fractions within pairs of materials (Table 1), confirming that the considerable differences in T_{ni} reported here originate from the genesis of cross-linking.

Following the first amine cross-linking step, both networks undergo photoinitiated free-radical acrylate polymerization. As detailed by Verwey and Warner, this second cross-linking step can be analyzed in an analogous fashion to the first cross-linking step, taking imposed strains and energies to be relative to the state of the relaxed system in the current condition.[31] The phase behavior of the LCE after acrylate cross-linking is illustrated in Figure 3. Thermomechanical strain generation (e.g., thermotropic actuation) is shown as a function of temperature in Figure 3a (negligible material degradation after 170 °C, see Figure S3). The corresponding variation in T_{ni}, calculated from the inflection point of the thermomechanical response curves, is summarized in Figure 3b. In this step, N_x for acrylate cross-links is identical within compositional pairs, and cross-linking occurs in an ordered state in both alignment methods, leading to an increase in T_{ni} in relation to their respective values following the first cross-linking step. In addition to the multistage effects being sequentially relative, initial disordered cross-links have been strained in mechanically aligned samples as opposed to all cross-links remaining unstrained in the ordered nematic state for surface alignment. This approach leads to greater separation of the T_{ni} for the two sets of samples for all compositions. Introducing more amine cross-links in the first step lowers the mechanically aligned T_{ni} from 141 °C (6M75) to 107 °C (6M85) as more cross-links are strained in the second step and less acrylate cross-links remain to reinforce nematic order. No change is seen between the T_{ni} of LCEs 6S75 and 6S85 because all cross-links were formed in the aligned nematic state in either case. Incorporating a longer chain amine (8M75 and 8S75) results in lowering of both T_{ni} values compared to 6S75 and 6S85 due to mesogen−mesogen interactions being weakened and easier disruption of order.

Similar to the material properties measured after the first cross-linking step, the T_g, elastic modulus, cross-link density, and gel fractions for each pair of materials are consistent with one another, eliminating potential contributions from the polymer network viscoelasticity. However, the differences in the results generated from the tensile testing of these materials beyond the linear elastic region (Figure 4) are an indication of the difference in the nature of the cross-links formed via each alignment method. All compositions have nearly the same elastic modulus values, specifically in each compositional pair, measured in the 2−4% strain region. Samples with longer aliphatic chain amines (8S75 and 8M75) have slightly lower modulus values as expected, given the results of the previous work,[17] and display tensile curves shifted to lower stress values at any given strain compared to materials formed with the shorter aliphatic chain amine (6S75 and 6M75).[17] Once out of the elastic region, mechanically aligned samples have little to no rubbery elastic behavior because the amine cross-links are already strained in addition to the LC mesogens being ordered. Surface-aligned samples exhibit some rubbery elastic behavior because amine cross-links are initially unstrained and can be deformed by stretching the sample. By increasing the amount of cross-linking amine, this effect is exacerbated, as evident by the more dramatic rubbery elastic behavior in 6S85 compared to 6S75, because the amine cross-links are longer than the acrylate cross-links and can therefore be stretched more. There is a clear indication of higher trapped strain and energy in the case of mechanical alignment, which would ultimately lead to mechanically aligned LCEs having lower T_{ni}.

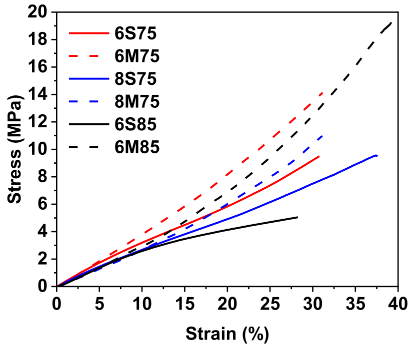

Figure 4. Tensile curves for surface aligned (solid lines) and mechanically aligned (dashed lines) LCEs measured parallel to the nematic director.

The effect of the alignment method on phase behavior is also apparent in phototropic actuation of these azobenzene-functionalized LCEs. Figure 5a plots the photoinduced strain measured in the LCEs as a function of the time exposed to UV light (365 nm, 50 mW/cm^2). The maximum photoinduced strain values are plotted as a function of composition in Figure 5b. These trends mirror the associated thermotropic actuation response. Specifically, surface-aligned samples achieve lower photomechanical strains due to cross-links and nematic coupling from mesogen−mesogen interactions both resisting order disruption caused by the isomerization of azobenzene. Increasing the number of amine cross-links in the first step again enhances the association of stimuli and order disruption for LCE 6M85, as more disordered amine cross-links are naturally opposing the order within the LCE and fewer acrylate cross-links are reinforcing it. This outcome is in agreement with previous analysis showing a correlation between the photomechanical response and proximity to T_{ni} as well as comparisons between isomerization-driven and thermally driven disruption of order.[10] No change is seen in the surface-aligned strain generation between 6S75 and 6S85 because all cross-links were formed in the aligned nematic state. Incorporating a longer chain amine (8M75 and 8S75) results in increased strain generation in both cases due to nematic coupling by mesogen−mesogen interactions being weakened and allowing for easier disruption of order as a result of azobenzene isomerization.

The correlation between thermotropic and phototropic responses is illustrated in Figure 6. Here, the maximum phototropic strain is plotted as a function of T_{ni} for each composition. This correlation agrees with the previous studies on the relationship between the phototropic response and the proximity to T_{ni} in which the phototropic response increases in magnitude as the experimental temperature approaches the thermotropic transition temperature.[10] Because the phototropic experiments were performed at ambient temperatures,

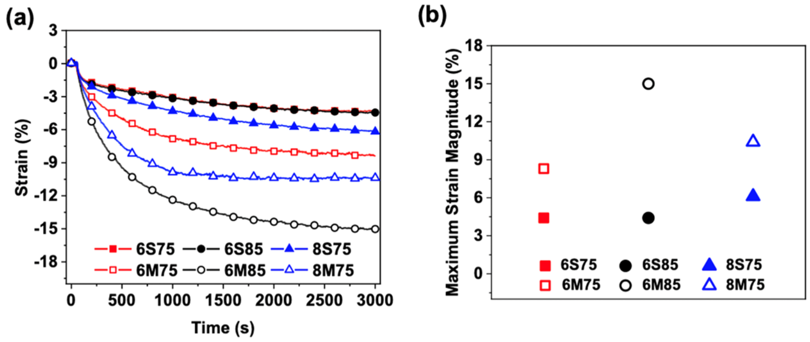

Figure 5. (a) Photomechanical response of LCEs prepared by surface alignment (closed symbols) or mechanical alignment (open symbols). Samples were held at 0.0005 N constant force and exposed to UV light (365 nm, 50 mW/cm^2). (b) Maximum photoinduced strain value is plotted as a function of composition.

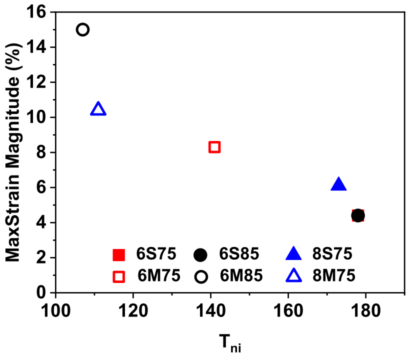

Figure 6. Maximum photomechanical strain as a function of T_{ni} for each LCE prepared by surface alignment (closed symbols) or mechanical alignment (open symbols).

the correlation is exhibited here as the increasing phototropic strain generation with decreasing T_{ni}. The strong correlation between the two stimuli responses emphasizes the importance of considering the balance between nematic coupling between mesogens and cross-linking states associated with LCE alignment methods as discussed hereto when employing LCEs as both thermotropic and phototropic functional materials.

■ CONCLUSIONS

Thermotropic and phototropic disruptions of the order in monodomain liquid crystalline elastomers (LCEs) is heavily influenced by the orientational genesis of cross-links associated with the method of alignment. Mechanical alignment prepares monodomain LCE that originate from isotropic cross-links, which reduce T_{ni} and increase the magnitude of the photoinduced strain. Surface alignment, in which cross-linking occurs in the nematic phase, comparatively increases the T_{ni} of LCE and lowers the magnitude of the photomechanical strain.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.1c00437.

POM, WAXS, TGA, monomer DSC, M_c calculation data, and film images (PDF)

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Author Contributions

The manuscript was written through contributions of all the authors. All the authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Kirsch, P.; Bremer, M. Nematic Liquid Crystals for Active Matrix Displays: Molecular Design and Synthesis. *Angew. Chem., Int. Ed.* **2000**, *39*, 4216−4235.

(2) Creagh, L. T.; Kmetz, A. R. Mechanism of Surface Alignment in Nematic Liquid Crystals. *Mol. Cryst. Liq. Cryst.* **1973**, *24*, 59−68.

(3) White, T. J.; Broer, D. J. Programmable and Adaptive Mechanics with Liquid Crystal Polymer Networks and Elastomers. *Nat. Mater.* **2015**, *14*, 1087−1098.

(4) Hogan, P. M.; Tajbakhsh, A. R.; Terentjev, E. M. Uv Manipulation of Order and Macroscopic Shape in Nematic Elastomers. *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **2002**, *65*, 10.

(5) Goodby, J. W. Phase Transitions: General and Fundamental Aspects. *Handbook of Liquid Crystals*; Wiley, 2014; pp 1−18.

(6) Goodby, J. W.; Davis, E. J.; Mandle, R. J.; Cowling, S. J. Chemical Structure and Mesogenic Properties. *Handbook of Liquid Crystals*; Wiley, 2014.

(7) McCracken, J. M.; Donovan, B. R.; White, T. J. Materials as Machines. *Adv. Mater.* **2020**, *32*, 1906564.

(8) Ikeda, T.; Tsutsumi, O. Optical Switching and Image Storage by Means of Azobenzene Liquid-Crystal Films. *Science* **1995**, *268*, 1873−1875.

(9) Kosa, T.; Sukhomlinova, L.; Su, L.; Taheri, B.; White, T. J.; Bunning, T. J. Light-Induced Liquid Crystallinity. *Nature* **2012**, *485*, 347−349.

(10) Finkelmann, H.; Nishikawa, E.; Pereira, G. G.; Warner, M. A New Opto-Mechanical Effect in Solids. *Phys. Rev. Lett.* **2001**, *87*, 015501.

(11) Gramsbergen, E. F.; Longa, L.; de Jeu, W. H. Landau Theory of the Nematic-Isotropic Phase Transition. *Phys. Rep.* **1986**, *135*, 195−257.

(12) Lebar, A.; Cordoyiannis, G.; Kutnjak, Z.; Zalar, B. The Isotropic-to-Nematic Conversion in Liquid Crystalline Elastomers. *Liquid Crystal Elastomers: Materials and Applications*; Springer, 2010.

(13) McCracken, J. M.; Donovan, B. R.; Lynch, K. M.; White, T. J. Molecular Engineering of Mesogenic Constituents Within Liquid Crystalline Elastomers to Sharpen Thermotropic Actuation. *Adv. Funct. Mater.* **2021**, 2100564.

(14) Hebner, T. S.; Bowman, C. N.; White, T. J. The Contribution of Intermolecular Forces to Phototropic Actuation of Liquid Crystalline Elastomers. *Polym. Chem.* **2021**, *12*, 1581−1587.

(15) Lebar, A.; Kutnjak, Z.; Žumer, S.; Finkelmann, H.; Sánchez-Ferrer, A.; Zalar, B. Evidence of Supercritical Behavior in Liquid Single Crystal Elastomers. *Phys. Rev. Lett.* **2005**, *94*, 197801.

(16) Broer, D. J.; Mol, G. N.; Challa, G. In-situ Photopolymerization of Oriented Liquid-crystalline Acrylates, 5.. Influence of the Alkylene Spacer on the Properties of the Mesogenic Monomers and the Formation and Properties of Oriented Polymer Networks. *Makromol. Chem.* **1991**, *192*, 59−74.

(17) Yoon, H.-H.; Kim, D.-Y.; Jeong, K.-U.; Ahn, S.-k. Surface Aligned Main-Chain Liquid Crystalline Elastomers: Tailored Properties by the Choice of Amine Chain Extenders. *Macromolecules* **2018**, *51*, 1141−1149.

(18) Warner, M.; Terentjev, E. *Liquid Crystal Elastomers*; Oxford University Press: New York, 2003.

(19) Talroze, R. V.; Zubarev, E. R.; Kuptsov, S. A.; Merekalov, A. S.; Yuranova, T. I.; Plate', N. A.; Finkelmann, H. Liquid Crystal Acrylate-Based Networks: Polymer Backbone-LC Order Interaction. *React. Funct. Polym.* **1999**, *41*, 1−11.

(20) Hanus, K.-H.; Pechhold, W.; Soergel, F.; Stoll, B.; Zentel, R. Phase Behavior and Elastic Properties of a Slightly Crosslinked Liquid Crystalline Main-Chain Polymer. *Colloid Polym. Sci.* **1990**, *268*, 222−229.

(21) Lee, Y.; Choi, S.; Kang, B.-G.; Ahn, S.-k. Effect of Isomeric Amine Chain Extenders and Crosslink Density on the Properties of Liquid Crystal Elastomers. *Materials* **2020**, *13*, 3094.

(22) Davis, F. J. Liquid-Crystalline Elastomers. *J. Mater. Chem.* **1993**, *3*, 551.

(23) Warner, M.; Gelling, K. P.; Vilgis, T. A. Theory of Nematic Networks. *J. Chem. Phys.* **1988**, *88*, 4008−4013.

(24) Küupfer, J.; Finkelmann, H. Liquid Crystal Elastomers: Influence of the Orientational Distribution of the Crosslinks on the Phase Behaviour and Reorientation Processes. *Macromol. Chem. Phys.* **1994**, *195*, 1353−1367.

(25) Symons, A. J.; Davis, F. J.; Mitchell, G. R. Liquid Crystal Elastomers: Interaction between the Network and Smectic Ordering. *Liq. Cryst.* **1993**, *14*, 853−860.

(26) Davis, F. J.; Mitchell, G. R. Liquid Crystal Elastomers: Controlled Crosslinking in the Liquid Crystal Phase. *Polymer* **1996**, *37*, 1345−1351.

(27) Traugutt, N. A.; Volpe, R. H.; Bollinger, M. S.; Saed, M. O.; Torbati, A. H.; Yu, K.; Dadivanyan, N.; Yakacki, C. M. Liquid-Crystal Order during Synthesis Affects Main-Chain Liquid-Crystal Elastomer Behavior. *Soft Matter* **2017**, *13*, 7013−7025.

(28) Urayama, K.; Kohmon, E.; Kojima, M.; Takigawa, T. Polydomain-Monodomain Transition of Randomly Disordered Nematic Elastomers with Different Cross-Linking Histories. *Macromolecules* **2009**, *42*, 4084−4089.

(29) Küpfer, J.; Finkelmann, H. Nematic Liquid Single Crystal Elastomers. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 717−726.

(30) Yakacki, C. M.; Saed, M.; Nair, D. P.; Gong, T.; Reed, S. M.; Bowman, C. N. Tailorable and Programmable Liquid-Crystalline Elastomers Using a Two-Stage Thiol-Acrylate Reaction. *RSC Adv.* **2015**, *5*, 18997−19001.

(31) Verwey, G. C.; Warner, M. Multistage Cross-Linking of Nematic Networks. *Macromolecules* **1995**, *28*, 4299.

(32) Lee, J.; Guo, Y.; Choi, Y.-J.; Jung, S.; Seol, D.; Choi, S.; Kim, J.-H.; Kim, Y.; Jeong, K.-U.; Ahn, S.-k. Mechanically Programmed 2D and 3D Liquid Crystal Elastomers at Macro- A Nd Microscale: Via Two-Step Photocrosslinking. *Soft Matter* **2020**, *16*, 2695−2705.

(33) Broer, D. J.; Boven, J.; Mol, G. N.; Challa, G. In-Situ Photopolymerization of Oriented Liquid-Crystalline Acrylates. III: Oriented Polymer Networks from a Mesogenic Diacrylate. *Makromol. Chem.* **1989**, *190*, 2255−2268.

(34) Ware, T. H.; McConney, M. E.; Wie, J. J.; Tondiglia, V. P.; White, T. J. Voxelated Liquid Crystal Elastomers. *Science* **2015**, *347*, 982.