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Degree of Orientation in Liquid Crystalline Elastomers Defines the Magnitude and Rate of Actuation

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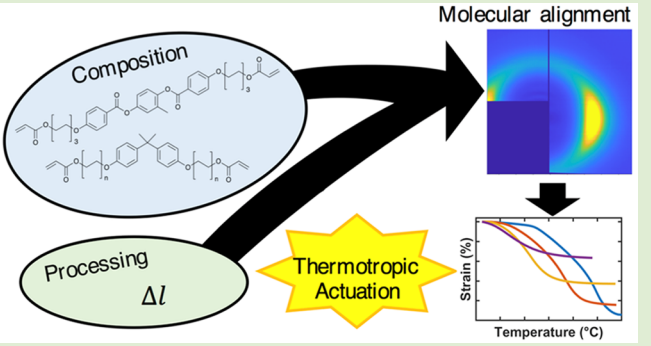
ABSTRACT: The anisotropy of liquid crystalline elastomers (LCEs) is derived from the interaction-facilitated orientation of the molecular constituents. Here, we correlate the thermomechanical response of a series of LCEs subjected to mechanical alignment to measurements of the Hermans orientation parameter. The LCEs were systematically prepared with varying concentrations of liquid crystalline mesogens, which affects the relative degree of achievable order. These compositions were subject to varying degrees of mechanical alignment to prepare LCEs with orientations that span a wide range of orientation parameters. The stimuli-response of the LCEs indicates that the liquid crystalline content defines the temperature of actuation, whereas the orientation parameter of the LCE is intricately correlated to both the total actuation strain of the LCE as well as the rate of thermomechanical response.



Liquid crystal elastomers (LCEs) are anisotropic, soft materials with distinctive mechanical[1,2] and optical[3,4] properties. The liquid crystallinity of LCEs is naturally thermotropic (e.g., the order of the materials depends on temperature).[5] The thermomechanical response of LCEs is directional when the liquid crystalline orientation is aligned.[5−7] Liquid crystallinity within LCEs is based on the organization of molecular units (e.g., mesogens) via intermolecular interactions between the typically aromatic units in the segment.[8] Aligned LCEs exhibit large and directional stimuli-response, associated with disruption of this orientational order.[5,9] Numerous reports detail thermotropic actuation of LCEs.[1,9−17]

The magnitude and rate of the stimuli-response are two critical performance metrics used to define the functional utility of these materials as actuators in applications such as soft robotics. Enabled by the facile preparation of LCEs via chain-extension reactions of liquid crystalline monomers (LCMs),[18] recent reports have examined the contribution of nonliquid crystalline (LC) comonomers as well as an adjustment to the mesogenic segment of the LCM to the magnitude and rate of stimuli-response. The inclusion of non-LC comonomers and use of LCMs with reduced intermolecular interactions have been shown to result in thermotropic actuation at lower temperatures.[19−21] While non-LC comonomers lead to a reduction in the rate of thermotropic actuation, LCMs with reduced intermolecular interactions produce higher rates of thermotropic actuation.[20,21] The origins of these trends have not been fully explored, in particular, with relation to how the molecular orientation of LCEs determines the thermotropic response.

Here, we are concerned with the association of orientational order and the magnitude and rate of stimuli-response. Therefore, characterizing orientational order is of critical importance to this work. The anisotropic alignment of liquid crystalline materials (both low molar mass and polymeric) has been observed through a number of different experimental methods, including X-ray scattering,[22−24] Raman spectroscopy,[25,26] FTIR spectroscopy,[27,28] and NMR.[29−31]

To explore the association of orientation and stimuli-response, we exploit the control afforded by mechanical alignment. Historically, the utilization of hydrosilylation reactions to prepare LCEs necessitated the use of mechanical alignment to realize so-called monodomain (or single crystal) LCEs.[6] While the original report of chain extension reactions utilized surface-enforced alignment, subsequent reports have detailed both aza-Michael and thiol-Michael addition reactions can be mechanically aligned with comparatively accessible chemistries.[7,14,32,33]

Toward this end, this study prepares LCEs with variation in composition (e.g., the degree of LC content) and magnitude of mechanical alignment. Mechanical alignment of LCEs is enforced by deformation of the material in a partially

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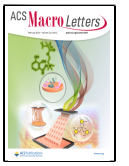

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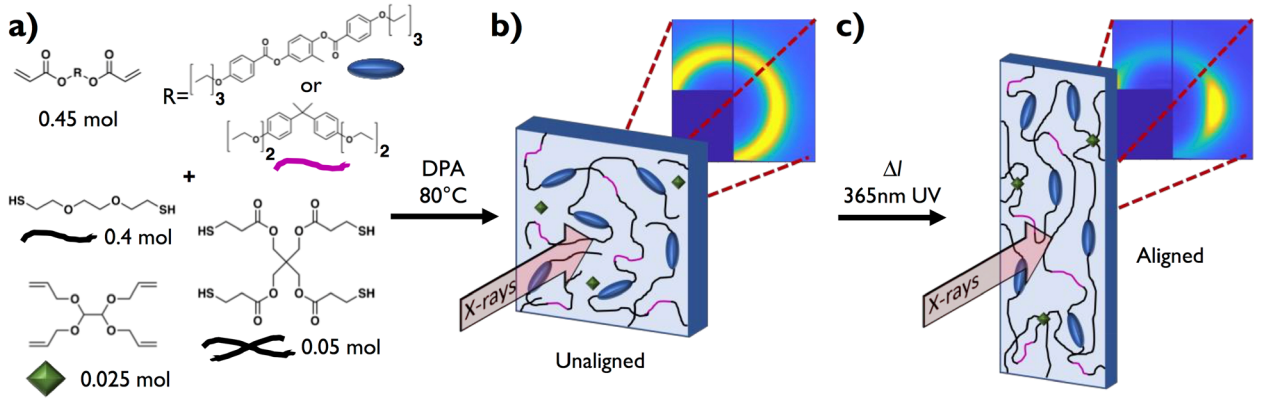

Figure 1. (a) Liquid-crystalline and non-liquid-crystalline diacrylate monomers are reacted with an excess of thiol groups through a base-catalyzed thiol-Michael addition reaction. (b) After the thiol-Michael reaction, the pre-polymers have no macroscopic alignment (WAXS pattern inset). (c) LCEs are aligned by mechanical deformation (WAXS pattern inset), which is arrested by completing the polymerization with UV light exposure.

polymerized state. Upon loading, the mesogens align to the deformation axis, analogous to the reorientation of the liquid crystalline director in LCE to load in the soft elastic regime.[34] It has been well established that the maximum ordering in LC networks occurs at the end of the "soft elastic plateau", characterized by the onset of strain hardening in stress−strain diagrams.[19,35,36]

On the other hand, the relationship between nematic ordering and the concentration of LC content is not well documented.

Theories based on mean-field approximations, such as the Maier−Saupe theorem, predict a linear dependence of orientational order of nematic mesophases on the number of liquid crystalline molecules.[37−39] These theories, however, were not specifically developed for LC networks and have well-known shortcomings.[40,41]

Experimentally, several recent studies have utilized reductions in LC content to tailor the phase behavior of LCEs and lower their actuation temperatures for use in a wide variety of applications, including biomedical devices.[19,39,42] It is notable these reductions in actuation temperature are accompanied by considerable reductions in actuation strain, which is an undesirable result for most LCE applications. Elastomers prepared with sufficiently reduced LC content will in fact present no liquid crystalline phase until mechanical strain is introduced.[43] This indicates decreased LC content leads to a more readily thermally induced order−disorder transition until a point where no LC phase is present at ambient temperature. While these studies provide clues as to the level of ordering in these elastomers, there has been no quantification of molecular ordering to accompany LCE actuation data. Effects of mesogen orientation on actuation are of considerable interest to tailor LCEs for temperature-specific applications while preserving suitable actuation performance.[44]

This examination utilizes a two-step reaction in which diacrylate monomers are subject to thiol-Michael addition and followed with subsequent photopolymerization of residual thiol and ene moieties.[21,45,46] To control the degree of liquid crystallinity in the LCE, we prepared compositions by mixing the canonical LCM 1,4-bis-[4-(6-acryloyloxy-hexyloxy)-benzoyloxy]-2-methylbenzene (C6M) with the non-LCM bisphenol A ethoxylate diacrylate (BPAEDA). This comonomer was selected due to the similarity in molecular weight and aromatic content. These diacrylate comonomers were mixed with the dithiol 2,2′-(ethylenedioxy)diethanethiol (EDDT) and the tetrathiol pentaerythritol tetrakis(3-mercaptopropionate (PETMP). The secondary thiol−ene reaction was facilitated by the inclusion of the tetraene glyoxal bis(diallyl acetal) (GDA), which does not participate in the thiol-Michael addition reaction and undergoes minimal homopolymerization. The mass of each reagent is included in Table S1.

To explore the contribution of LC content, a series of samples were prepared with a range of mixtures of C6M and BPAEDA. The overall LC content of the material was determined by the concentration of C6M, where a material with an LC content of 0.5 has a network composed of 50% C6M by mass. The molar ratio of functional groups was held constant to ensure the materials retain similar network architecture upon polymerization. These and other materials examined here were first subject to a base-catalyzed thiol-Michael addition reaction step to produce unaligned, lightly cross-linked pre-polymers with excess thiol groups (Figure 1b). The mesostructure of the pre-polymers was strongly dependent on the concentration of C6M, where at high concentrations these materials were polydomain nematic and at low concentrations they were isotropic (Figure S2). The pre-polymers were cut into rectangular strips and stretched to different lengths (strain from 0% to 300%). Upon deformation, all samples exhibit birefringence (Figure S3). The samples were then held at this length and exposed to 365 nm UV light (75 mW cm^{-2} for 10 min) at ambient temperature to lock in the alignment via thiol−ene reaction between the thiol-terminated macromers and the tetraene (Figure 1c, Supporting Information, S4). Wide-angle X-ray scattering (WAXS) patterns for an exemplar pre-polymer and aligned LCE are illustrated in Figure 1b,c.

The materials were subject to thermal analysis via differential scanning calorimetry (DSC) to confirm the nematic−isotropic transition temperature (T_{NI}) shifts to lower temperatures as the concentration of C6M is reduced. Below 0.36 LC content, the elastomeric material does not exhibit a liquid crystalline phase transition (Figure S5). Next, we examined the thermomechanical response of the materials subject to isostress tension and heating. Here, we analyze materials subject to 300% strain during second-stage polymerization (actuation data for all samples included in Figure S6). As evident in Figure 2a, decreasing the concentration of C6M considerably reduces the thermotropic actuation temperature of these materials. For example, an LCE prepared with 0.74 LC

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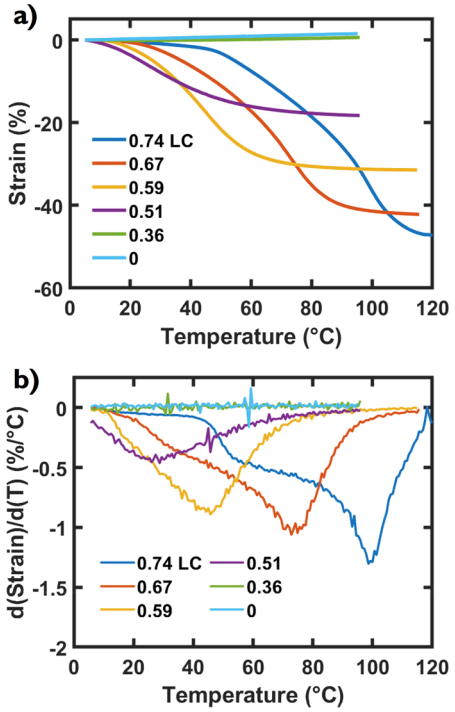

Figure 2. Thermomechanical response of LCEs prepared with 0−74% liquid crystalline monomer measured as (a) strain and (b) derivative of strain−temperature response as a function of temperature.

content has a maximal response at 100 °C that shifts to 25 °C for the 0.51 LC content LCE. Notably, the magnitude of the strain response of LCE is reduced from −40% to −20% as the C6M concentration is decreased. Absent of order, the elastomers prepared with 0.36 LC content and 0 LC content expand and exhibit a <1% strain. These results agree well with other contemporary reports exploring the role of non-LC content.[19,45]

The LC concentration in the materials also affects the rate of thermomechanical response. This is evident in Figure 2b, where the derivative of the strain−temperature response of the materials is plotted against temperature. By reducing C6M concentration, the maximum rate of thermotropic response decreases from 1.3% $°C^{1-}$ for the 0.74 LC sample to 0.5% $°C^{1-}$ for the 0.51 LC sample. Notably, recent reports utilizing distinctive LCMs to reduce the strength of the mesogen−mesogen interaction to shift the thermomechanical response to lower temperatures retain a large magnitude and high rate of actuation.[20,21]

From this basis, we now consider the role of the magnitude of strain on the orientational order of the materials and the influence on the corresponding thermotropic response. Figure 3a presents data from tensile tests performed on the unaligned pre-polymers. These exemplar samples illustrate the influence of C6M concentration on the stress−strain response. The difference between the tensile response of the 0.74, 0.67, and 0.59 LC samples may be related to the proximity of the material from the T_{NI} in these experiments in ambient conditions. Despite the differences in the evolution of the stress−strain response, all materials proceed to a strain-hardening regime by 100% strain, which is indicative of the completion of the director orientation. It is important to note that changing temperature has a strong effect on the tensile behaviors of LCEs and would therefore be expected to affect the molecular ordering in these materials, particularly at low strains.[47]

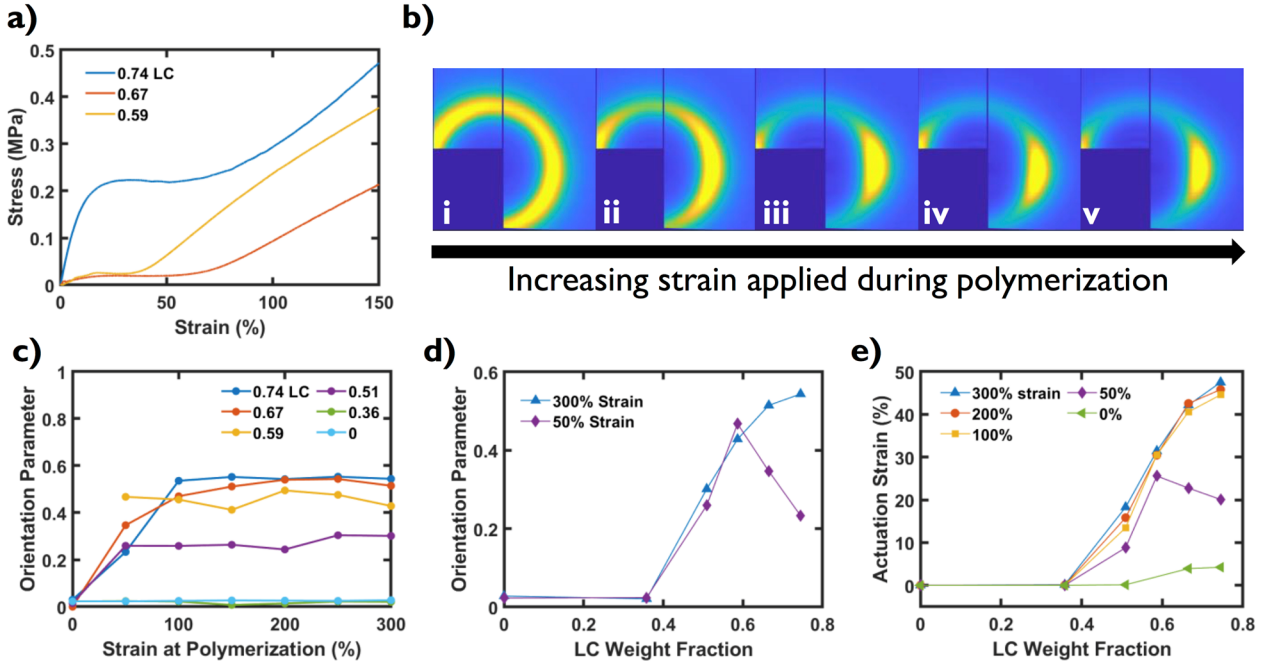

Figure 3. (a) Tensile tests of elastomers show the soft elastic plateau corresponding to mesogen alignment ends before 100% strain. (b) WAXS patterns from 0.67 LC elastomers polymerized at (i) 0% strain, (ii) 50% strain, (iii) 100% strain, (iv) 200% strain, and (v) 300% strain. (c) Herman's orientation parameter of elastomers as a function of the strain applied to the material during polymerization. The data point for 0.59 LC sample at 0% is excluded due to sample damage during experimentation. (d) Orientation parameter as a function of LC content for samples polymerized at two values of strain. (e) Above 100% strain during polymerization, there is no significant difference in the actuation strain of LCE polymerized with increasing strain.

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Figure 3b presents WAXS patterns for an illustrative LCE composition based on 0.67 LC content. The pattern in Figure 3b-i is obtained from an LCE that is not subject to mechanical alignment and polymerized via a thiol−ene reaction. This pattern is essentially isotropic and indicates the material does not have a macroscopic orientation. Subsequent patterns in Figure 3b-ii−v are taken from materials subjected to 50%, 100%, 200%, and 300% strain during mechanical alignment. With samples subjected to higher values of strain, a greater degree of ordering is apparent in the WAXS patterns, as evident by the nematic arc narrowing in azimuthal angle.[48] Evident from the patterns in Figure 3b and presented in Figure 3c, the orientational order of this material plateaus at around 100% strain (Figure 3b-iii). WAXS patterns for all samples are included in Figure S7.

The intercoupling between C6M concentration, magnitude of strain during mechanical programming, and corresponding orientation are summarized in Figure 3c. Hermans' orientation parameter was calculated for all samples (Supporting Information, S8). The orientation parameter of LCE samples exhibiting thermomechanical response all increase with strain before plateauing. In the 0.74 and 0.67 LC samples, the maximum value of the orientation parameter is reached at 100% and 150% strain, respectively, while the 0.59 and 0.51 LC samples reach their maximum orientation parameter at 50% strain (the 0.59 LC sample polymerized at 0% strain was not included as this sample was damaged during experimentation). From this data it is clear samples with very low LC content (0.36 and 0 LC) do not have a high enough concentration of liquid crystalline mesogens in the network to retain an aligned mesophase.

Generally, when the materials are prepared with mechanical alignment of 100% strain or more, the magnitude of the orientation parameter is defined by the concentration of C6M. However, samples prepared with mechanical alignment of 50% strain have a complex dependence (Figure 3d). At this condition, the maximal orientational order is seen in the sample with 0.59 LC content. Increasing the LC content to 0.67 or 0.74 actually results in a reduction in orientational order. We emphasize this dependence as it is a byproduct of the stress−strain behavior of the pre-polymer, evident in Figure 3a. At 0.59 LC content, the pre-polymer has moved into the strain-hardening regime, whereas the pre-polymers with 0.67 or 0.74 LC content are still in the soft plateau region (e.g., mesogens have not been completely reoriented).

Finally, we contrast the thermomechanical response of these materials as a function of C6M concentration and as a function of the magnitude of strain applied during mechanical alignment (Figure 3e). Generally, the magnitude of the actuation increases with the concentration of C6M, as well as with the magnitude of strain during alignment. However, we want to highlight two points of particular interest. First, a maximum is evident in the magnitude of actuation strain at an intermediate concentration for samples prepared with 50% strain during mechanical alignment. Informed by the similar trend in Figure 3d, the orientational order of the LCE has a stronger effect on the actuation strain than the LC concentration of the material. Second, above 100% strain during mechanical alignment, the dominant contributor is the concentration of C6M and the resulting influence on the relative degree of orientational order in the material. The data for the rate of actuation shows the same trends as the actuation strain data (Figure S9).

We conclude this work by emphasizing the coupling of orientational order and thermomechanical response in LCEs by plotting the magnitude of actuation strain (Figure 4a) and

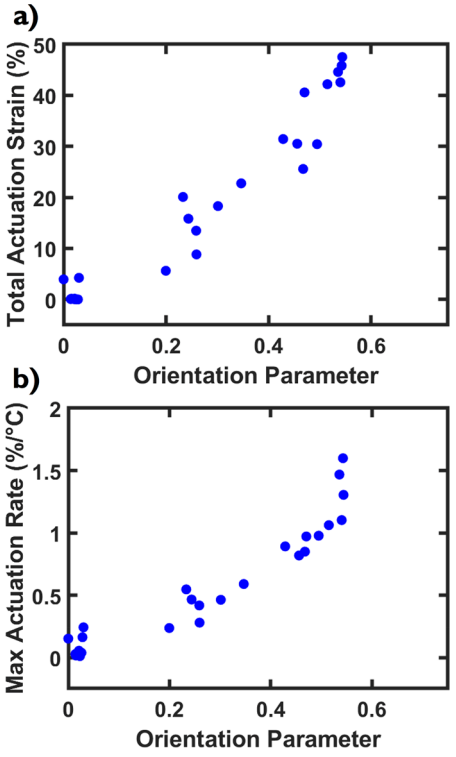

Figure 4. Actuation (a) strain and (b) rate of elastomers as a function of the orientation parameter as determined by WAXS.

thermotropic actuation rate (Figure 4b) as a function of the measured orientation parameter for all materials analyzed in Figure 3. The linear association between total actuation strain and orientation parameter is a result of the coupling between the LC ordering and the polymer network and has been seen in a number of LCE systems.[49] It is notable that the rate of thermomechanical actuation is also linearly related to the orientation parameter, which suggests this metric is also determined by the degree of coupling between the network and the LC order. While these may be intuitive associations, it is important to appreciate the orientation of an LCE can be affected by the relative concentration of LC units in the material and the processing conditions (e.g., degree of strain in mechanical alignment or the shear rate in direct ink write printing).

The orientation parameter of LCE networks generally has little impact on the actuation temperature. This is evident in Figure 5, which plots the temperature at which the maximum rate of actuation occurs for all samples (with total actuation strain greater than 0.5%) against the orientation parameter. Rather, the actuation temperature is defined largely by the composition itself. This mirrors prior reports that demonstrate that diluting the LC content shifts the actuation temperature to lower temperatures. However, within a given composition, while the degree of orientation strongly affects the magnitude and rate of thermomechanical response, the degree of orientation does not affect the temperature at which actuation occurs.

In conclusion, we synthesized a series of LCEs where the composition and processing conditions were varied to give a

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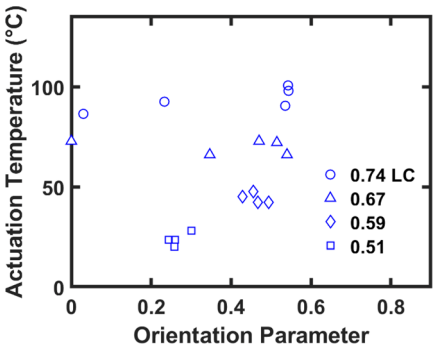

Figure 5. Actuation temperature of LCEs as a function of orientation parameter.

range of actuation responses. Decreasing the LC content of the network is associated with a drastic decrease in actuation temperature, actuation strain, and actuation rate. Changing the LC content of the network also affects the extent of the soft elastic regime in these materials, which in turn dictates the amount of strain needed to induce maximum alignment. Overall, it was found the orientation parameter of LCE networks is the key determinant of their total actuation strain and rate of shape change. These findings should be applicable for any number of applications where LCEs are being designed for use as artificial muscles.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.2c00754.

Experimental procedures, Hermans' Orientation parameter calculation, and supplementary data (PDF)

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Notes

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■ REFERENCES

(1) Thomsen, D. L.; Keller, P.; Naciri, J.; Pink, R.; Jeon, H.; Shenoy, D.; Ratna, B. R. Liquid Crystal Elastomers with Mechanical Properties of a Muscle. *Macromolecules* **2001**, *34* (17), 5868−5875.

(2) Roberts, P. M. S.; Mitchell, G. R.; Davis, F. J.; Pople, J. A. Mechanical Switching and Soft Elasticity in Liquid Crystal Elastomers. *Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals* **1997**, *299* (1), 181−186.

(3) Hisano, K.; Kimura, S.; Ku, K.; Shigeyama, T.; Akamatsu, N.; Shishido, A.; Tsutsumi, O. Mechano-Optical Sensors Fabricated with Multilayered Liquid Crystal Elastomers Exhibiting Tunable Deformation Recovery. *Adv. Funct Materials* **2021**, *31* (40), 2104702.

(4) Xie, P.; Zhang, R. Liquid Crystal Elastomers, Networks and Gels: Advanced Smart Materials. *J. Mater. Chem.* **2005**, *15* (26), 2529.

(5) Jiang, H.; Li, C.; Huang, X. Actuators Based on Liquid Crystalline Elastomer Materials. *Nanoscale* **2013**, *5* (12), 5225.

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

(7) Ware, T. H.; McConney, M. E.; Wie, J. J.; Tondiglia, V. P.; White, T. J. Voxelated Liquid Crystal Elastomers. *Science* **2015**, *347* (6225), 982−984.

(8) Ula, S. W.; Traugutt, N. A.; Volpe, R. H.; Patel, R. R.; Yu, K.; Yakacki, C. M. Liquid Crystal Elastomers: An Introduction and

Review of Emerging Technologies. *Liquid Crystals Reviews* **2018**, *6* (1), 78−107.
(9) Li, M.-H.; Keller, P. Artificial Muscles Based on Liquid Crystal Elastomers. *Philos. Trans. R. Soc. A* **2006**, *364* (1847), 2763−2777.
(10) Ambulo, C. P.; Burroughs, J. J.; Boothby, J. M.; Kim, H.; Shankar, M. R.; Ware, T. H. Four-Dimensional Printing of Liquid Crystal Elastomers. *ACS Appl. Mater. Interfaces* **2017**, *9* (42), 37332−37339.
(11) Kotikian, A.; Truby, R. L.; Boley, J. W.; White, T. J.; Lewis, J. A. 3D Printing of Liquid Crystal Elastomeric Actuators with Spatially Programed Nematic Order. *Adv. Mater.* **2018**, *30* (10), 1706164.
(12) López-Valdeolivas, M.; Liu, D.; Broer, D. J.; Sánchez-Somolinos, C. 4D Printed Actuators with Soft-Robotic Functions. *Macromol. Rapid Commun.* **2018**, *39* (5), 1700710.
(13) Kotikian, A.; Morales, J. M.; Lu, A.; Mueller, J.; Davidson, Z. S.; Boley, J. W.; Lewis, J. A. Innervated, Self-Sensing Liquid Crystal Elastomer Actuators with Closed Loop Control. *Adv. Mater.* **2021**, *33* (27), 2101814.
(14) Hebner, T. S.; Bowman, C. N.; White, T. J. Influence of Orientational Genesis on the Actuation of Monodomain Liquid Crystalline Elastomers. *Macromolecules* **2021**, *54* (9), 4023−4029.
(15) Saed, M. O.; Volpe, R. H.; Traugutt, N. A.; Visvanathan, R.; Clark, N. A.; Yakacki, C. M. High Strain Actuation Liquid Crystal Elastomers via Modulation of Mesophase Structure. *Soft Matter* **2017**, *13* (41), 7537−7547.
(16) Roach, D. J.; Yuan, C.; Kuang, X.; Li, V. C.-F.; Blake, P.; Romero, M. L.; Hammel, I.; Yu, K.; Qi, H. J. Long Liquid Crystal Elastomer Fibers with Large Reversible Actuation Strains for Smart Textiles and Artificial Muscles. *ACS Appl. Mater. Interfaces* **2019**, *11* (21), 19514−19521.
(17) Xu, Y.; Dupont, R. L.; Yao, Y.; Zhang, M.; Fang, J.-C.; Wang, X. Random Liquid Crystalline Copolymers Consisting of Prolate and Oblate Liquid Crystal Monomers. *Macromolecules* **2021**, *54* (12), 5376−5387.
(18) Herbert, K. M.; Fowler, H. E.; McCracken, J. M.; Schlafmann, K. R.; Koch, J. A.; White, T. J. Synthesis and Alignment of Liquid Crystalline Elastomers. *Nat. Rev. Mater.* **2022**, *7* (1), 23−38.
(19) Shaha, R. K.; Torbati, A. H.; Frick, C. P. Body-temperature Shape-shifting Liquid Crystal Elastomers. *J. Appl. Polym. Sci.* **2021**, *138*, 50136.
(20) 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**, *31* (16), 2100564.
(21) Bauman, G. E.; McCracken, J. M.; White, T. J. Actuation of Liquid Crystalline Elastomers at or Below Ambient Temperature. *Angew. Chem. Int. Ed* **2022**, DOI: 10.1002/anie.202202577.
(22) Merkel, D. R.; Traugutt, N. A.; Visvanathan, R.; Yakacki, C. M.; Frick, C. P. Thermomechanical Properties of Monodomain Nematic Main-Chain Liquid Crystal Elastomers. *Soft Matter* **2018**, *14* (29), 6024−6036.
(23) Sims, M. T.; Abbott, L. C.; Richardson, R. M.; Goodby, J. W.; Moore, J. N. Considerations in the Determination of Orientational Order Parameters from X-Ray Scattering Experiments. *Liq. Cryst.* **2019**, *46* (1), 11−24.
(24) Agra-Kooijman, D. M.; Kumar, S. X-ray Scattering Investigations of Liquid Crystals. In *Handbook of Liquid Crystals*; Goodby, J. W., Tschierske, C., Raynes, P., Gleeson, H., Kato, T., Collings, P. J., Eds.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2014; pp 1−38. DOI: 10.1002/9783527671403.hlc014.
(25) Southern, C. D.; Gleeson, H. F. Using the Full Raman Depolarisation in the Determination of the Order Parameters in Liquid Crystal Systems. *Eur. Phys. J. E* **2007**, *24* (2), 119−127.
(26) Zhang, Z.; Panov, V. P.; Nagaraj, M.; Mandle, R. J.; Goodby, J. W.; Luckhurst, G. R.; Jones, J. C.; Gleeson, H. F. Raman Scattering Studies of Order Parameters in Liquid Crystalline Dimers Exhibiting the Nematic and Twist-Bend Nematic Phases. *J. Mater. Chem. C* **2015**, *3* (38), 10007−10016.
(27) Urayama, K.; Mashita, R.; Kobayashi, I.; Takigawa, T. Stretching-Induced Director Rotation in Thin Films of Liquid Crystal Elastomers with Homeotropic Alignment. *Macromolecules* **2007**, *40* (21), 7665−7670.
(28) Fukunaga, A.; Urayama, K.; Koelsch, P.; Takigawa, T. Electrically Driven Director-Rotation of Swollen Nematic Elastomers as Revealed by Polarized Fourier Transform Infrared Spectroscopy. *Phys. Rev. E* **2009**, *79* (5), 051702.
(29) Knapkiewicz, M.; Rachocki, A.; Bielejewski, M.; Sebastião, P. J. NMR Studies of Molecular Ordering and Molecular Dynamics in a Chiral Liquid Crystal with the Sm C α * Phase. *Phys. Rev. E* **2020**, *101* (5), 052708.
(30) Mann, S. K.; Devgan, M. K.; Franks, W. T.; Huband, S.; Chan, C. L.; Griffith, J.; Pugh, D.; Brooks, N. J.; Welton, T.; Pham, T. N.; McQueen, L. L.; Lewandowski, J. R.; Brown, S. P. MAS NMR Investigation of Molecular Order in an Ionic Liquid Crystal. *J. Phys. Chem. B* **2020**, *124* (24), 4975−4988.
(31) Barker, P. B.; van der Est, A. J.; Burnell, E. E.; Patey, G. N.; de Lange, C. A.; Snijders, J. G. NMR of Deuterium in Liquid Crystal Mixtures. *Chem. Phys. Lett.* **1984**, *107* (4−5), 426−430.
(32) McConney, M. E.; Martinez, A.; Tondiglia, V. P.; Lee, K. M.; Langley, D.; Smalyukh, I. I.; White, T. J. Topography from Topology: Photoinduced Surface Features Generated in Liquid Crystal Polymer Networks. *Adv. Mater.* **2013**, *25* (41), 5880−5885.
(33) 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* (25), 18997−19001.
(34) Warner, M.; Terentjev, E. M. Liquid Crystal Elastomers, Reprinted. *International series of monographs on physics*; Clarendon Press: Oxford, 2009.
(35) Terentjev, E. M. Liquid-Crystalline Elastomers. *J. Phys.: Condens. Matter* **1999**, *11* (24), R239−R257.
(36) Dey, S.; Agra-Kooijman, D.; Ren, W.; McMullan, P.; Griffin, A.; Kumar, S. Soft Elasticity in Main Chain Liquid Crystal Elastomers. *Crystals* **2013**, *3* (2), 363−390.
(37) Luckhurst, G. R.; Zannoni, C. Why Is the Maier−Saupe Theory of Nematic Liquid Crystals so Successful? *Nature* **1977**, *267* (5610), 412−414.
(38) Humphries, R. L.; James, P. G.; Luckhurst, G. R. Molecular Field Treatment of Nematic Liquid Crystals. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 1031.
(39) Barnes, M.; Cetinkaya, S.; Ajnsztajn, A.; Verduzco, R. Understanding the Effect of Liquid Crystal Content on the Phase Behavior and Mechanical Properties of Liquid Crystal Elastomers. *Soft Matter* **2022**, *18* (27), 5074−5081.
(40) Schultz, T. D. On the Validity of the Maier-Saupe Theroy of the Nematic Transition. *Mol. Cryst. Liq. Cryst.* **1971**, *14* (1−2), 147−164.
(41) Wulf, A. Difficulties with the Maier−Saupe Theory of Liquid Crystals. *J. Chem. Phys.* **1976**, *64* (1), 104−109.
(42) Niu, H.; Wang, Y.; Wang, J.; Yang, W.; Dong, Y.; Bi, M.; Zhang, J.; Xu, J.; Bi, S.; Wang, B.; Gao, Y.; Li, C.; Zhang, J. Reducing the Actuation Threshold by Incorporating a Nonliquid Crystal Chain into a Liquid Crystal Elastomer. *RSC Adv.* **2018**, *8* (9), 4857−4866.
(43) Donovan, B. R.; Fowler, H. E.; Matavulj, V. M.; White, T. J. Mechanotropic Elastomers. *Angew. Chem., Int. Ed.* **2019**, *58* (39), 13744−13748.
(44) Ambulo, C. P.; Tasmim, S.; Wang, S.; Abdelrahman, M. K.; Zimmern, P. E.; Ware, T. H. Processing Advances in Liquid Crystal Elastomers Provide a Path to Biomedical Applications. *J. Appl. Phys.* **2020**, *128* (14), 140901.
(45) Saed, M. O.; Ambulo, C. P.; Kim, H.; De, R.; Raval, V.; Searles, K.; Siddiqui, D. A.; Cue, J. M. O.; Stefan, M. C.; Shankar, M. R.; Ware, T. H. Molecularly-Engineered, 4D-Printed Liquid Crystal Elastomer Actuators. *Adv. Funct. Mater.* **2019**, *29* (3), 1806412.
(46) Saed, M. O.; Terentjev, E. M. Siloxane Crosslinks with Dynamic Bond Exchange Enable Shape Programming in Liquid-Crystalline Elastomers. *Sci. Rep* **2020**, *10* (1), 6609.

https://doi.org/10.1021/acsmacrolett.2c00754
ACS Macro Lett. 2023, 12, 248−254

(47) Clarke, S. M.; Terentjev, E. M.; Kundler, I.; Finkelmann, H. Texture Evolution during the Polydomain-Monodomain Transition in Nematic Elastomers. *Macromolecules* **1998**, *31* (15), 4862−4872.
(48) DeLongchamp, D. M.; Kline, R. J.; Fischer, D. A.; Richter, L. J.; Toney, M. F. Molecular Characterization of Organic Electronic Films. *Adv. Mater.* **2011**, *23* (3), 319−337.
(49) Krause, S.; Zander, F.; Bergmann, G.; Brandt, H.; Wertmer, H.; Finkelmann, H. Nematic Main-Chain Elastomers: Coupling and Orientational Behavior. *Comptes Rendus Chimie* **2009**, *12* (1−2), 85−104.

https://doi.org/10.1021/acsmacrolett.2c00754
ACS Macro Lett. 2023, 12, 248−254