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The Contribution of Oligomerization Reaction Chemistry to the Thermomechanical Properties of Surface-Aligned Liquid Crystalline Elastomers

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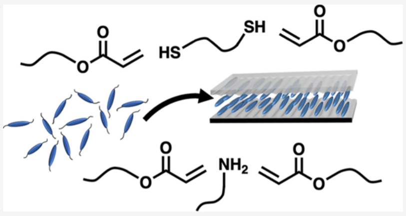

ABSTRACT: Liquid crystalline elastomers (LCEs) are stimulus-responsive materials that, when macroscopically aligned, undergo large, directional deformation amplified by the disruption of order within a polymer network. Recently, surface-enforced alignment has been used to prepare LCEs with spatial variation in the director orientation that enables the realization of complex 3-D shape transformation. Surface-enforced alignment is advantageous because it allows for high-resolution, nonlinear patterning of the nematic director within an LCE. When using surface alignment to enforce orientation within LCEs, multiple two-step reaction schemes have been commonly used, primarily aza-Michael oligomerization or thiol-Michael oligomerization with each addition reaction followed by photopolymerization of the residual acrylate-terminated oligomers. Here, LCEs were prepared by each polymerization technique with varied amine or thiol concentrations. The mechanical properties, thermomechanical response, reaction kinetics, and alignment were characterized and assessed for LCEs. This examination emphasizes the importance of the molecular weight between crosslinks over the reaction used to form the oligomer in determining the magnitude of the stimulus response of LCEs.

INTRODUCTION

Liquid crystalline elastomers (LCEs) are functional materials that uniquely combine the properties of both liquid crystalline molecules and polymer networks.[1,2] Liquid crystalline molecules are well known for their ability to form ordered phases that are disrupted upon the application of stimuli such as heat or light.[3,4] When combined with a polymer network, the order disruption causes the deformation of the polymer network connecting the liquid crystals. Notably, the introduction of a polymer network to a liquid crystalline system influences the properties of the material. For example, as detailed by Landau de Gennes theory, the first-order nature of phase transitions in small-molecule liquid crystals is altered by the introduction of a polymer network as a mechanical field.[5,6] Additionally, the crosslinking density affects the speed and magnitude of the deformation induced by the order disruption.[7,8] As evident by these examples, the design of LCEs for functional applications relies on thoughtful incorporation and control of polymer networks and their structure within liquid crystalline systems.

The selection of a synthetic strategy must also be paired with an alignment technique. Most commonly, LCEs are aligned by either mechanical or surface alignment.[9−14] Reactive components must be selected based on the requirements for the processing of each technique. While mechanical alignment has been studied extensively as a tool for fabricating LCEs with monodomain alignment, surface alignment offers the ability to program nonlinear nematic director profiles with high spatial resolution.[12] As such, surface alignment has recently been a topic of growing interest within the field of LCEs.

When using surface alignment to fabricate LCEs, two different acrylate-based two-step synthetic strategies are commonly employed. Historically, aza-Michael oligomerization has been the most common approach for generating acrylate-terminated oligomers in the polymer before crosslinking in an alignment cell.[12,15−19] In the aza-Michael reaction, a primary amine is typically combined with an excess of a diacrylate liquid crystalline monomer (LCM). The amine is mixed with an excess of acrylate, and the mixture is filled into an alignment cell, where it is allowed to oligomerize in the aligned nematic state. Following oligomerization, the acrylate-terminated oligomers are photopolymerized. The result is a crosslinked LCE possessing the alignment pattern prescribed by coatings on the glass slides used to fabricate the cell. In previous studies, the thermal and mechanical properties of these aza-Michael LCEs have been shown to be influenced by the molecular structure of the primary amine.[7,20]

Similar to the aza-Michael approach, thiol-Michael oligomerization has recently been shown to be amenable to surface alignment to allow the preparation of LCEs.[21] In this reaction, dithiol monomers are mixed with excess liquid crystalline diacrylate monomers, and a catalyst is added to facilitate thiol-

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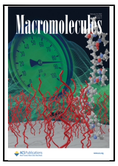

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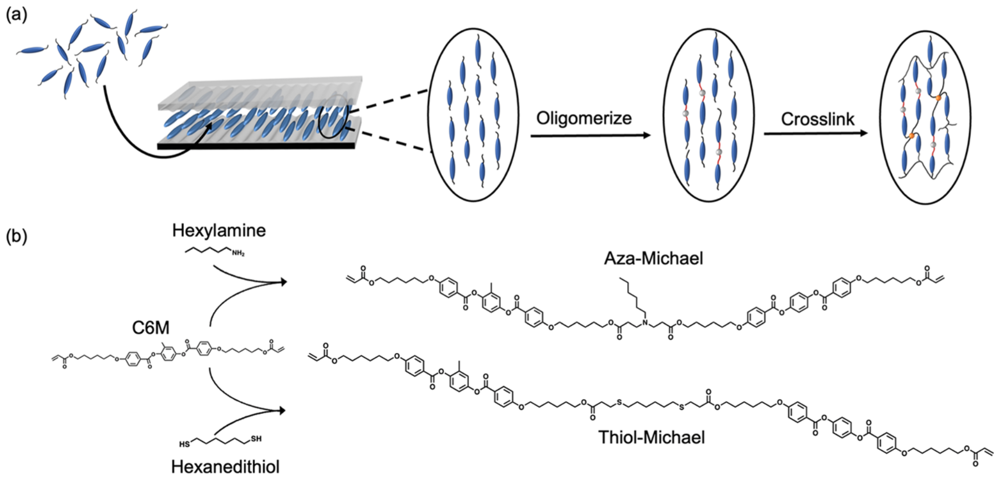

Figure 1. (a) Synthesis of an LCE subject to surface-enforced alignment via photopolymerization subsequent to chain extension reactions. (b) This work utilized the LCM C6M which was subjected to an aza-Michael addition reaction with hexylamine or thiol-Michael addition with HDT to form acrylate-terminated oligomers as illustrated.

Michael addition.[22] Again, the excess of acrylates is used to form acrylate-terminated oligomers that are photopolymerized once the thiol-Michael reaction is complete. Using thiol-Michael oligomers is desirable in LCEs because they offer more tunability than aza-Michael oligomers in the molecular weight or functional groups between crosslinks.[23,24] In aza-Michael oligomers, the primary amine always adds a single nitrogen between the two acrylate monomers, while the thiol-Michael reaction allows for many different lengths and chemical structures of the spacer that gets incorporated between the thiol end groups.

With the differences in comonomer contribution to the polymer network, it is expected that the two chemistries discussed will have differences in performance as functional materials. Here, surface-aligned LCEs were fabricated by aza-Michael or thiol-Michael oligomerization with subsequent photopolymerization of acrylate-terminated oligomers. An amine and thiol with nearly equivalent molecular weights, each with a six-carbon aliphatic group, were selected to allow direct comparisons between the materials as a function of comonomer concentration. The mechanical properties and stimulus response of LCEs prepared by these reactions are contrasted.

■ EXPERIMENTAL SECTION

Synthesis of LCEs. Elastomers were fabricated using a combination of 1,4-bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]-2-methylbenzene (C6M, Wilshire Technologies) with hexanedithiol (HDT, Sigma) or hexylamine (Sigma). All chemicals were used as received.

For materials using C6M and hexylamine, monomers were combined in molar ratios of 0.25:1, 0.5:1, and 0.75:1 amine/acrylate along with 1 wt % Omnirad 819 as a photoinitiator. C6M and the photoinitiator were heated to 150 °C and vortex-mixed before adding amine and subjecting the mixture to additional vortex mixing and heating at 90 °C. Melted mixtures were then capillary-filled into 30 μm alignment cells at 90 °C. Cells were moved to 65 °C immediately after filling and held at this temperature for 24 h to allow for the aza-Michael reaction to proceed before exposing them to 365 nm light (50 mW/cm^2) for 10 min. Polymer films were then removed from the alignment cells.

For materials using C6M and HDT, monomers were combined in molar ratios of 0.25:1, 0.5:1, and 0.75:1 thiol/acrylate along with 1 wt % Omnirad 819 as a photoinitiator. Monomers were heated to 150 °C and vortex-mixed before adding dibenzylamine (1 mol %) and diethylenetriamine (0.4 mol %) as catalysts and subjecting the mixture to additional vortex mixing. The mixture was then capillary-filled into a 30 μm alignment cell at 90 °C. The cell was moved to 65 °C immediately after filling and held at this temperature for 2 h; then, the temperature was increased to 80 °C for 22 h to allow for the thiol-Michael reaction to proceed in the nematic state. After the 24 h oligomerization, materials were exposed to 365 nm light (50 mW/cm^2) for 10 min while remaining at 80 °C to crosslink the materials via homopolymerization of excess acrylates.

Polarized Optical Microscopy. Polarized optical micrographs were captured using a Nikon polarizing microscope.

Real-Time Fourier Transform Infrared Spectroscopy. Real-time Fourier transform infrared (RT-FTIR) spectroscopy was performed using a Nicolet iS50 and a custom heating accessory. Before measurement, monomeric mixtures were melted and prepared as described previously but without a photoinitiator included. A sample of each melted mixture was sandwiched between NaCl salt plates and placed on the heating stage at 90 °C. Absorption spectra were collected every 1 min for 20 h. Changes in the area of acrylate (800−820 cm^{-1}) peaks were monitored, and conversion was calculated using the difference between the initial peak area and peak area at each time point.

Differential Scanning Calorimetry. T_g of each LCE was measured using differential scanning calorimetry (Discovery DSC 2500, TA Instruments). Data are reported from the second heating cycles performed at a ramp rate of 5 °C/min.

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

Wide Angle X-ray Scattering. Static wide-angle X-ray scattering (WAXS) experiments were performed on beamline 11-BM Complex Materials Scattering at the National Synchrotron Light Source II at Brookhaven National Laboratory. Patterns were acquired on samples using 13.5 keV energy and 10 s exposures. Data reduction and order parameter calculations were performed in Igor using the Nika analytical package and through a custom script in MATLAB, respectively.

Thermomechanical Actuation. LCEs were cut into strips (~2 mm × 12 mm × 0.03 mm) along the aligned axis and placed in tension (Discovery DMA 850, TA Instruments) at a 0.005 N constant force. Thermomechanical strain response was measured as the temperature was increased from 25 to 250 °C at 5 °C/min.

■ RESULTS AND DISCUSSION

The preparation of LCEs subject to surface-enforced alignment was first realized via an aza-Michael addition reaction of diacrylate LCMs.[12] Subsequent reports detailed the utilization of a similar approach, utilizing the thiol-Michael addition of diacrylate LCM, which initially was only amenable to mechanical alignment. A recent report details the preparation of LCEs via the thiol-Michael addition reaction that is compatible with alignment via surface anchoring.[21] Enabled by this report, this work prepares surface-aligned LCEs with these two synthetic approaches (Figure 1a) to elucidate the influence of these distinctive reactions on stimulus response and mechanical properties. Compositions were first subjected to either aza-Michael or thiol-Michael oligomerization (Figure 1b) to prepare acrylate-terminated oligomers which were subsequently crosslinked by photopolymerization. In LCEs prepared by aza-Michael addition ($\mathrm{LCE_{AM}}$), a canonical liquid crystalline diacrylate (C6M) was mixed with a primary aliphatic amine (hexylamine) in ratios of 0.25:1, 0.5:1, and 0.75:1 amine/acrylate (by reactive site). The monomer mixtures were filled into 30 μm alignment cells in the isotropic state and cooled to the nematic state to induce monodomain alignment. The surface-aligned monomers were oligomerized via aza-Michael addition for 24 h before the acrylate-terminated oligomers were photopolymerized. In LCEs formed by thiol-Michael reactions ($\mathrm{LCE_{TM}}$), C6M was mixed with an aliphatic dithiol (HDT) in ratios of 0.25:1, 0.5:1, and 0.75:1 thiol/acrylate (by the reactive site). The thiol-Michael addition reaction was catalyzed by the addition of amines (triethylamine and diethylene triamine).[21] The monomer mixtures were filled into 30 μm alignment cells in the isotropic state and cooled to the nematic state to induce monodomain alignment. The aligned monomers were oligomerized via thiol-Michael addition for 24 h before the acrylate-terminated oligomers were photopolymerized.

While prior studies have utilized each of these approaches to prepare LCEs, no prior study has directly contrasted the oligomerization, polymerization, polymer structure, and resulting stimulus-responsive behavior of LCEs prepared by these distinctive reactions. The LCEs prepared by these reactions are largely predicated on the specifics of the disparate chain extension reactions. Accordingly, the oligomerization kinetics of C6M via aza-Michael and thiol-Michael addition were examined using RT-FTIR spectroscopy. As seen in Figure 2, at similar stoichiometric ratios, the aza-Michael oligomerization resulted in increasingly lower acrylate conversion than the thiol-Michael oligomerization as amine and thiol concentrations were increased. The observed difference in conversion is attributed to the lower relative reactivity of a secondary amine due to steric hindrance, which is formed by the aliphatic amine monomer once it reacts the first time with an acrylate monomer.[25] The kinetic data in Figure 2 indicates a reduction in the reaction rate for the aza-Michael reaction within the first few minutes of oligomerization as a result of primary amines being converted to the less-reactive secondary amines.

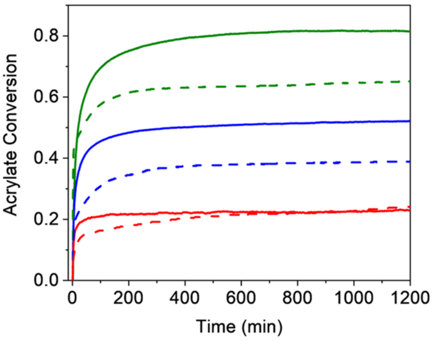

Figure 2. Conversion of acrylates when subject to aza-Michael (dashed) and thiol-Michael (solid) addition reactions at amine/acrylate or thiol/acrylate concentrations of 0.25:1 (red), 0.5:1 (blue), and 0.75:1 (green).

The comparison of kinetic data during Michael addition informs the subsequent formation of LCEs from the acrylate-terminated oligomers prepared by chain extension. As per Figure 2, at equivalent ratios of either thiol/acrylate or amine/acrylate, the mixture of oligomers prepared via the aza-Michael reaction had a higher concentration of excess acrylate available for crosslinking in the photopolymerization step than the thiol-Michael mixture. Accordingly, the higher excess acrylate content in aza-Michael materials resulted in a comparatively higher crosslink density in the final LCE. Additionally, since aza-Michael adds only a single nitrogen between acrylates while thiol-Michael inserts the entirety of the dithiol monomer between the acrylates, the acrylates were separated by shorter spacers in the aza-Michael addition than the thiol-Michael addition, even though the overall molecular weights of the oligomers were comparable. Since these oligomers define the spacing between crosslinks, crosslink density would be expected to decrease significantly when the thiol concentration was increased in the thiol-Michael reaction. Comparatively, increasing amine concentration in the aza-Michael reaction would also decrease crosslink density but not to the extent of the thiol-Michael system. The expected differences in crosslink densities were verified by using Carother's equation[26] to calculate the theoretical degree of polymerization in each composition, assuming that the linear oligomer formed in the Michael reaction correlated with the molecular weight between crosslinks. These calculations are detailed in the Supporting Information. The resulting molecular weights between crosslinks are shown in Table 1 for each composition. These calculations verify that oligomers prepared via thiol-Michael have a comparatively higher molecular weight between crosslinks for a given stoichiometric ratio. The oligomers produced in the two different Michael addition reactions were not able to be directly compared by experimental techniques due to the differences in compatibility across characterization techniques. However, the representative GPC and MALDI data (Figure S1) validate the calculated molecular weight range and trends presented in Table 1.

After photopolymerization, both the LCEs fabricated by aza-Michael ($\mathrm{LCE_{AM}}$) and thiol-Michael ($\mathrm{LCE_{TM}}$) reactions retained monodomain alignment as evident in the polarized optical micrographs in Figure 3a,b. WAXS diffraction patterns taken from these LCEs are presented in Figure 3c,d and confirm nematic alignment with orientation parameters spanning 0.39−0.47 (Table 1). Thus, while the resulting $\mathrm{LCE_{AM}}$ and $\mathrm{LCE_{TM}}$ materials may differ for a given stoichiometric ratio in the molecular weight between crosslinks, these materials retain effectively equivalent orientation from surface-enforced alignment. It should also be noted that the value of the order parameter for the C6M control sample is considerably lower than that of the $\mathrm{LCE_{AM}}$ and $\mathrm{LCE_{TM}}$ samples, likely due to shrinkage stress during the photopolymerization of the oriented monomers.[14]

The differences in molecular weight between crosslinks in $\mathrm{LCE_{AM}}$ and $\mathrm{LCE_{TM}}$ were then correlated with the mechanical properties of the materials. The stress−strain curves for the LCEs are presented in Figure 4a,b, and the elastic moduli both

Table 1. Material Properties for Surface-Aligned LCEs Fabricated by either Aza-Michael or Thiol-Michael Oligomerization and Crosslinking of Acrylate-Terminated Oligomers

	aza-Michael			thiol-Michael			C6M
composition	0.25:1	0.5:1	0.75:1	0.25:1	0.5:1	0.75:1	0:1
average MW between crosslinks[a] (g/mol)	850	950	1400	900	1500	3100	670
strain magnitude at 250 °C[b] (%)	9	11	28	9	24	47	6
max strain rate[c] (%/°C)	0.1	0.2	0.3	0.1	0.5	0.5	0.04
parallel modulus[d] (MPa)	890 ± 90	540 ± 140	66 ± 8	780 ± 190	160 ± 30	17 ± 9	1760 ± 30
perpendicular modulus[d] (MPa)	250 ± 70	160 ± 10	21 ± 5	190 ± 20	40 ± 5	6 ± 1	945 ± 130
orientation parameter[e]	0.47	0.41	0.42	0.39	0.45	0.47	0.26
T_g[f] (°C)	42	21	2.5	35	13	−3.7	45

[a] Calculated as average molecular weight after step-growth oligomerization using Carother's equation.[26] Experimental RT-FTIR monitoring of acrylate consumption during oligomerization was used for conversion and the average molecular weight of respective main-chain monomer components was used as the molecular weight of a repeat unit. [b] Reported magnitude of contraction from thermomechanical strain generation (0.005 N constant force, 5 °C/min heating). [c] Calculated as a maximum derivative of thermomechanical strain generation (0.005 N constant force, 5 °C/min heating 25−225 °C). [d] Tensile pull 5%/min, modulus calculated in the linear strain regime (2−4%). [e] Herman's orientation parameter, calculated from WAXS diffraction data. [f] Reported value from the midpoint in the second DSC heating cycle (5 °C/min).

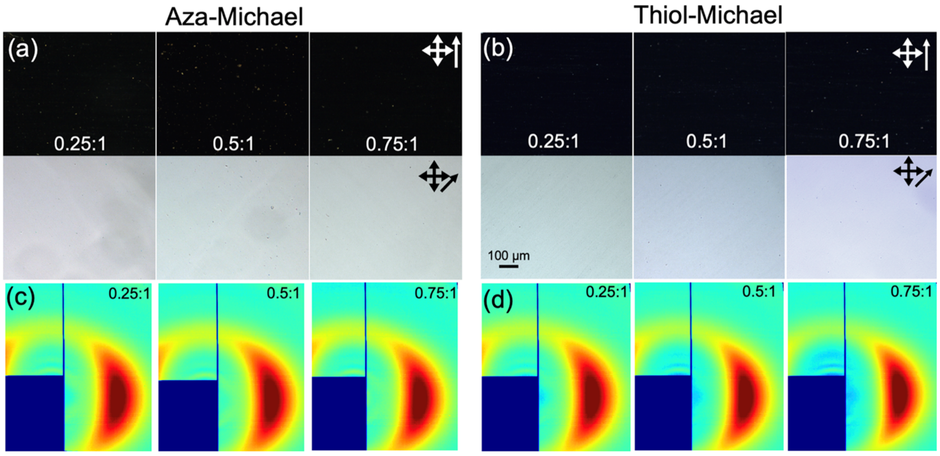

Figure 3. Monodomain alignment is enforced by surface anchoring evident in the birefringence of the polarized optical micrographs of LCEs fabricated by (a) aza-Michael or (b) thiol-Michael addition and subsequent crosslinking of acrylate-terminated oligomers. The magnitude of the orientational order is quantified by WAXS diffraction patterns in (c) LCE_{AM} and (d) LCE_{TM}.

parallel and perpendicular to the nematic director are summarized in Table 1. The relationships between elastic moduli and molecular weight between crosslinks are illustrated in Figure 4c,d. Notably, LCE_{AM} and LCE_{TM} had similar tensile behavior when the concentration of thiol or amine was relatively low (0.25:1). However, the mechanical properties of these materials deviated as the thiol or amine concentration increased. LCE_{TM} was consistently softer than LCE_{AM}. The comparatively reduced modulus for LCE_{TM} was expected and attributed to the lower crosslink density of these materials. Although these studies were primarily focused on comparing the LCE_{TM} and LCE_{AM} materials, it should also be noted that, as discussed in prior work,[20] the aliphatic amine tail impacts thermomechanical properties within the LCE_{AM} series and likely contributes to properties based on amine concentration.

Finally, the thermomechanical actuation of both the LCE_{AM} and LCE_{TM} samples was assessed. At low thiol or amine concentrations, the maximum strain rate and the magnitude of strain generated at 225 °C were comparable for both LCE chemistries (Figure 5a and Table 1). As the thiol or amine concentrations increased, the LCE_{TM} generated the most strain with the fastest maximum strain rate compared to the analogous compositions of LCE_{AM} (Table 1). Accordingly, from this comparison of LCE_{AM} and LCE_{TM}, it is clear that there is a direct relationship between the magnitude of actuation strain and the average molecular weight between crosslinks. This correlation is starkly evident in Figure 5b.

A key takeaway from this examination is that the magnitude of thermomechanical actuation is intrinsically coupled to the molecular weight between crosslinks. In these particular materials, the oligomerization via thiol-Michael addition produces larger concentrations of higher molecular weight oligomers which resultingly produces LCE with lower crosslink density. Therefore, the thiol-Michael approach offers greater tunability in programing actuation response in LCEs. However, it should also be noted that compared to the aza-Michael approach, the preparation of LCEs utilizing surface-enforced alignment and thiol-Michael oligomerization is commonly problematic. In a prior unreported study, we observed phase separation (Figure S2) or crystallization (Figure S3) in thiol−acrylate mixtures during the thiol-Michael oligomerization. Therefore, when selecting the chemistry for preparing surface-aligned LCEs, both feasibility from a synthetic viewpoint and the desired functional properties in the resulting LCE, particularly the molecular weight between crosslinks, need to be considered.

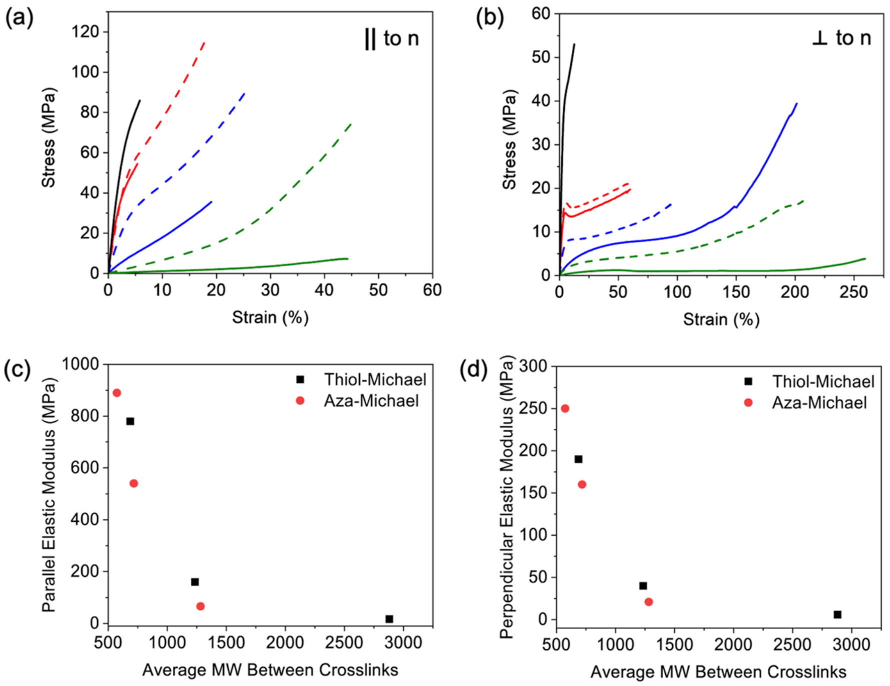

Figure 4. Stress−strain curves for LCEs fabricated by aza-Michael (dashed) and thiol-Michael (solid) addition reactions using amine/acrylate or thiol/acrylate ratios of 0:1 (black), 0.25:1 (red), 0.5:1 (blue), and 0.75:1 (green). Acrylate-terminated oligomers were crosslinked and the LCEs were pulled in tension at 5%/min in the directions (a) parallel and (b) perpendicular to the nematic director. Resulting elastic moduli are correlated with the average molecular weight between crosslinks for both (c) parallel and (d) perpendicular measurements.

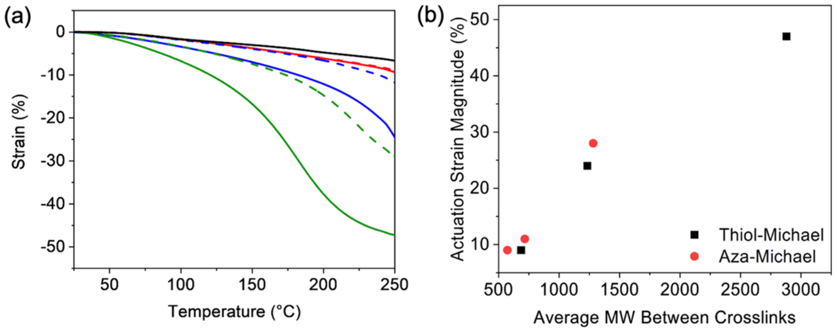

Figure 5. (a) Thermomechanical response (0.005 N constant force, 5 °C/min) of LCEs fabricated by aza-Michael (dashed) and thiol-Michael (solid) addition reactions using amine/acrylate or thiol/acrylate ratios of 0:1 (black), 0.25:1 (red), 0.5:1 (blue), and 0.75:1 (green). (b) Maximum actuation strain magnitude as a function of calculated average molecular weight between crosslinks.

■ CONCLUSIONS

This study details the differences in the material properties and stimulus response of LCEs prepared from two common acrylate-based two-step polymerization reactions. The difference in stimulus response is rooted in the differences in the oligomerization reaction and resulting differences in the formed polymer network. Thiol-Michael oligomerization followed by acrylate photopolymerization offered a greater range of material property tunability as compared to aza-Michael oligomerization. However, it should be appreciated that many compositions of acrylate and thiols exhibit crystallization or phase separation, which in our experience is rarely observed in aza-Michael reactions of diacrylate LCMs.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.2c02371.

Description of average molecular weight calculation, GPC and MALDI data, and optical micrographs (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All 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) White, T. J.; Broer, D. J. Programmable and Adaptive Mechanics with Liquid Crystal Polymer Networks and Elastomers. *Nat. Mater.* **2015**, *14*, 1087−1098.

(2) Warner, M.; Terentjev, E. *Liquid Crystal Elastomers*, International Series of Monographs on Physics; Oxford University Press: New York, 2003.

(3) Demus, D. 100 Years Liquid Crystal Chemistry. *Mol. Cryst. Liq. Cryst. Incorporating Nonlinear Opt.* **1988**, *165*, 45−84.

(4) Goodby, J. W.; Davis, E. J.; Mandle, R. J.; Cowling, S. J. Chemical Structure and Mesogenic Properties. *Handbook of Liquid Crystals*; Wiley-VCH, 2014; pp 1−30.

(5) 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; pp 147−185.

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

(7) 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.

(8) Saed, M. O.; Torbati, A. H.; Starr, C. A.; Visvanathan, R.; Clark, N. A.; Yakacki, C. M. Thiol-Acrylate Main-Chain Liquid-Crystalline Elastomers with Tunable Thermomechanical Properties and Actuation Strain. *J. Polym. Sci., Part B: Polym. Phys.* **2017**, *55*, 157−168.

(9) 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*, 23.

(10) Hebner, T. S.; Bowman, C. N.; White, T. J. Influence of Orientational Genesis on the Actuation of Monodomain Liquid Crystalline Elastomers. *Macromolecules* **2021**, *54*, 4023−4029.

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

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

(13) Broer, D. J.; Finkelmann, H.; Kondo, K. In-Situ Photopolymerization of an Oriented Liquid-Crystalline Acrylate. *Die Makromolekulare Chemie* **1988**, *189*, 185−194.

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

(15) Kuenstler, A. S.; Chen, Y.; Bui, P.; Kim, H.; DeSimone, A.; Jin, L.; Hayward, R. C.; Kuenstler, A. S.; Bui, P.; Kim, H.; Hayward, R. C.; Chen, Y.; Jin, L.; DeSimone MathLab, A.; DeSimone, A. Blueprinting Photothermal Shape-Morphing of Liquid Crystal Elastomers. *Adv. Mater.* **2020**, *32*, 2000609.

(16) Ahn, S.; Ware, T. H.; Lee, K. M.; Tondiglia, V. P.; White, T. J. Photoinduced Topographical Feature Development in Blueprinted Azobenzene-Functionalized Liquid Crystalline Elastomers. *Adv. Funct. Mater.* **2016**, *26*, 5819−5826.

(17) 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.

(18) Auguste, A. D.; Ward, J. W.; Hardin, J. O.; Kowalski, B. A.; Guin, T. C.; Berrigan, J. D.; White, T. J.; Auguste, A. D.; Ward, J. W.; Hardin, J. O.; Kowalski, B. A.; Berrigan, J. D.; White, T. J.; Guin, T. C. Enabling and Localizing Omnidirectional Nonlinear Deformation in Liquid Crystalline Elastomers. *Adv. Mater.* **2018**, *30*, 1802438.

(19) Ware, T. H.; Biggins, J. S.; Shick, A. F.; Warner, M.; White, T. J. Localized Soft Elasticity in Liquid Crystal Elastomers. *Nat. Commun.* **2016**, *7*, 10781.

(20) 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.

(21) Hebner, T. S.; Kirkpatrick, B. E.; Anseth, K. S.; Bowman, C. N.; White, T. J. Surface-Enforced Alignment of Reprogrammable Liquid Crystalline Elastomers. *Adv. Sci.* **2022**, *9*, 2204003.

(22) Nair, D. P.; Podgórski, M.; Chatani, S.; Gong, T.; Xi, W.; Fenoli, C. R.; Bowman, C. N. The Thiol-Michael Addition Click Reaction: A Powerful and Widely Used Tool in Materials Chemistry. *Chem. Mater.* **2013**, *26*, 724−744.

(23) 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.

(24) 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*, 7537−7547.

(25) Desmet, G. B.; D'hooge, D. R.; Omurtag, P. S.; Espeel, P.; Marin, G. B.; Du Prez, F. E.; Reyniers, M. F. Quantitative First-Principles Kinetic Modeling of the Aza-Michael Addition to Acrylates in Polar Aprotic Solvents. *J. Org. Chem.* **2016**, *81*, 12291−12302.

(26) Lodge, T. P.; Hiemenz, P. C. *Polymer Chemistry*, 3rd ed.; CRC Press, 2020.