3D Printing of Liquid Crystal Elastomer Actuators

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3D PRINTING OF LIQUID CRYSTAL ELASTOMER ACTUATORS

A dissertation presented

by

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to

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In partial fulfillment of the requirements for the degree of Doctor of Philosophy in the subject of Engineering Sciences

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3D Printing of Liquid Crystal Elastomer Actuators

ABSTRACT

Soft robotics offer advantages over their rigid counterparts due to the intrinsic softness of their consisting materials, soft robotic matter. When equipped with programmable shape morphing and controllable function, soft robotics are best qualified for interaction with delicate objects, exploration of unknown terrains, and large, impact-resistant deformations. Towards this goal, new materials and fabrication methods are needed to create actuators with programmable shape-morphing behavior akin to human muscles. Liquid crystal elastomers (LCEs) are soft materials comprised of anisotropic liquid crystal mesogen molecules, which when aligned, give rise to reversible contraction with high energy density when heated above their nematic-to-isotropic transition temperature ($T_{NI}$). However, the ability to produce LCE actuators with programmed director alignment in arbitrary, bulk forms is a grand challenge.

The focus of my Ph.D. thesis is to create programmable LCE actuators through the integration of design, synthesis, and multi-material 3D printing methods. Towards this goal, solvent-free, oligomeric LCE inks were synthesized that incorporate rigid mesogens along their backbone as well as photopolymerizable groups at the chain ends. By varying the molecular composition of these oligomeric species, LCE inks with the appropriate viscoelastic response were designed for high operating temperature-direct ink writing (HOT-DIW), an extrusion-based 3D printing method. By tailoring polymer backbone and crosslinking chemistries of our LCE inks, their $T_{NI}$ could be varied from 92°C to 127°C after printing and UV cross-linking, and enable
custom thermal response. We further demonstrated that patterned LCEs with programmed director alignment along the print path were produced when printing in the nematic phase. These 3D LCEs exhibit large reversible contractility and high specific energy density. Our integrated approach allows for prescribed LCE alignment in arbitrary geometric motifs.

Building on this seminal advance, we created untethered soft robotic matter that repeatedly shape-morphs and self-propels in response to thermal stimuli through passive control. Specifically, we designed and printed active LCE hinges with orthogonal director alignment that interconnect rigid polymeric tiles. These hinges can be programmed as mountain or valley folds to produce reversible active origami structures. Moreover, in a single structure, we programmed hinges made of LCEs with disparate $T_{NI}$ to enable sequential folding and demonstrated untethered, reversible sequential folding in soft, active origami for the first time. We further demonstrated a self-compacting prism with a modular geometric locking mechanism capable of sequential folding with three temperature-specific, stable configurations. To enable the informed design of untethered robotic matter, LCE hinge bending angle and torque can be prescribed by geometry and LCE chemistry. We then exploited their exemplary performance by programming LCE hinges into the “rollbot”, an exemplar self-propelling structure with passive control. Specifically, we designed a pentagonal prism with low $T_{NI}$ LCE hinges and propellers with high $T_{NI}$ LCE hinges, informed by our torque and bending angle characterization, enabling reversible reconfiguration and self-propulsion across a heated surface.

To expand upon these capabilities, we developed a novel method of 3D printing aligned LCE filaments with embedded, coaxial liquid metal by co-extrusion of LCE and liquid metal through a core-shell nozzle. Our innervated LCE (iLCE) fibers are electrothermally heated well above $T_{NI}$ with programmable and predictable heat generation through the core of the filament,
which resulted in large, prescriptible contractile strains akin to those of our neat 3D printed LCEs. The iLCE fibers enable self-sensing of actuation through the resulting change of resistance with respect to actuation strain, where a change of resistance is directly predictable from strain. Moreover, our iLCEs exhibited reliable reversible actuation and considerable work output, which combined with self-sensing capabilities allows for closed loop control. Specifically, our actuators automatically reach target resistance and strain values rapidly and repeatedly despite large bias load perturbations. As a final demonstration, we patterned iLCEs with a spiral printpath to demonstrate programmable 3D shape morphing. Analogous to iLCE fibers, these spiral iLCEs were electrothermally heated, exhibited self-sensing, and were regulated with closed loop control.

In summary, we have developed a new platform for creating soft robotic matter through the design, synthesis, and assembly of LCE inks, which can be seamlessly integrated with structural, sensing, and functional materials. Our platform may be harnessed for applications including soft robotics, reconfigurable electronics, adaptable structures, and well beyond.
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CHAPTER 1
INTRODUCTION

Soft robotic matter is an emerging field that focuses on the design, synthesis, and assembly of stimuli-responsive, active materials (1–3). To date, considerable attention has been devoted to shape morphing materials that exhibit reversible actuation, sensing, and programmable control mechanisms (1, 2). Common actuation strategies such as pneumatic and dielectric elastomer actuators exhibit strong and high frequency actuation, respectively, but require rigid auxiliary equipment to function repeatedly (4–6). While shape memory polymers and hydrogels exhibit complex shape morphing, they lack reversibility and mechanical robustness, respectively (7–9). By contrast, liquid crystal elastomers (LCE) are promising candidates for soft robotic materials due to their intrinsically anisotropic, contractile, and reversible actuation with high energy density in response to heat (10, 11). However, their advantageous properties are only realized if the rigid mesogens within the LCEs are aligned (10, 11). To date, the strategies introduced to achieve this goal have been largely limited to either thin LCE films that are voxelated via command surfaces (12) or bulk LCEs that are uniaxially aligned under an applied mechanical load (13). However, we posit that 3D voxelated liquid crystal elastomers could be achieved by extrusion-based 3D printing. If successful, this approach would enable the rapid design and assembly of programmable soft robotic matter with intrinsic, reversible, and complex shape morphing capabilities and specific work exertion akin to human muscles.

To achieve this overarching goal, my Ph.D. thesis focuses on the design, synthesis, and characterization of LCEs in the form of soft, reversible, and contractile actuators with complex shape morphing capabilities that arise from programming their chemical composition, phase behavior, and voxelated architecture. Central to this goal is the development of main-chain LCE
inks with tunable nematic-to-isotropic transition temperature ($T_{NI}$) and viscoelastic properties that allow the nematic director to be deterministically aligned along the programmed print path. To demonstrate the power of our approach, we have created soft robotic matter capable of complex 2D-to-3D shape morphing behavior, muscle-like actuation, and sequentially folding origami structures, such as a rolling robot (i.e., a “rollbot”) that are passively controlled by heating. Finally, using core-shell 3D printing, we have created innervated LCEs composed of coaxial liquid metal core-LCE shell fibers and planar square spiral motifs with electrothermally (i.e., Joule heating) triggered shape morphing and actuation responses that are self-regulated via closed-feedback control.

1.1 DISSERTATION SCOPE

The first aim of my thesis is to synthesize main-chain LCE inks with different $T_{NI}$ values that are solvent-free, shear thinning, and rapidly photo-crosslinkable to allow for temperature-specific response and extrusion-based alignment. The second aim is to demonstrate that high temperature direct ink writing (HOT-DIW) enables programmable director alignment of these LCE inks along a prescribed print path. The third aim is to create untethered soft robotic matter in the form of origami-like architectures composed of LCE hinges that interconnect rigid polymeric tiles, which exhibit robotic functions including passively controlled sequential reconfiguration and self-propulsion. The last aim is the creation of innervated LCE fibers composed of a coaxial liquid metal core-LCE shell architecture that exhibit self-sensing feedback and self-regulating closed loop control.

The primary outcome of my thesis is the development of oligomeric, solvent-free LCE inks that enable 3D voxelated LCEs to be programmably printed via HOT-DIW. Our LCE inks and programming method realize LCE architectures in arbitrary geometric formfactors with minimal
dimensional constraints and temperature-specific actuation, where reversible shape morphing and heat response is prescribed by the printpath and ink chemistry, respectively. Accordingly, voxelated and thick bulk LCEs are fabricated that reversibly morph (2D-to-3D) and lift larger weights than previously reported. Next, our LCE inks with disparate $T_{NI}$ and structural ink are co-fabricated as active hinges to enable assembly of untethered soft robotic matter with prescribed sequences of reconfigurable forms and functions with passive control. As an exemplar of our platform, we design and demonstrate the untethered self-propulsion of the LCE “rollbot” across a heated surface. While our hinge-based LCE robotic matter facilitates untethered function, for greater control of predictable actuation in a variety of environments, we next embed heat stimulus on-board with soft electronics. Towards this goal, we co-extrude LCE and liquid metal through a custom core shell nozzle to fabricate coaxial innervated LCEs (iLCEs), where the liquid metal concurrently Joule heats and self-senses actuation. Our iLCE fibers exhibit highly programmable and predictable actuation. Moreover, actuation is auto-regulated with closed loop control to achieve a target actuation sequence in unidirectional and 3D shape morphing iLCEs.

1.1 DISSEMINATION ORGANIZATION

In Chapter 2, relevant literature on soft robotic matter is presented with a large emphasis on LCEs and their programming methods. In Chapter 3, the synthesis and 3D printing of our first LCE ink is reported as a new platform for programming shape morphing in arbitrary form factors. In Chapter 4, an integrated method for fabricating untethered soft robotic matter with passive control of shape morphing and self-propulsion is demonstrated. In Chapter 5, innervated LCEs with programmable actuation, self-sensing, and closed loop control are fabricated. Finally, the principal findings and conclusions of my Ph.D. work are provided in Chapter 6.
CHAPTER 2
LITERATURE REVIEW

2.1 MOTIVATION AND SCOPE

In this chapter, we will begin with an overview of the materials and fabrication approaches used to create soft robotic matter (1, 3, 14–19). Next, we will focus on a class of stimuli-responsive materials, known as liquid crystal elastomers (LCEs) which combine liquid crystalline (rigid) mesogens with highly extensible elastomeric networks. We will then introduce emerging strategies to pattern LCEs for use as soft shape-morphing architectures, actuators, and robotic matter.

2.2 SOFT ROBOTIC MATTER

Soft robotic matter is an emerging class of functional materials that both integrate as well as serve as soft actuators (1, 17, 19), soft sensors (1, 20), and materials control mechanisms (3, 20) (Fig. 2.1). Soft actuating materials convert energy to mechanical motion akin to human muscles. However, they require energy supplied by pneumatics, environmental stimuli (e.g., light), or resistive heating. Unlike shape-morphing structures composed of rigid materials (21–24), soft materials are more versatile and robust due to their inherent deformability (2, 17). However, the ability to creating soft robotic matter with programmable shape morphing capability in arbitrary form factors remains a challenge. As a foreshadow of subsequent chapters, a liquid crystal transition is illustrated as an example of hierarchically programmed, intrinsically soft actuation (Fig. 2.1).

Programmed actuation must be controlled and is generally achieved by addressing actuators through local power or stimuli modulation to achieve global function, where sensing components provide feedback on task performance or external environment. Addressable actuation
has been achieved largely through soft electronic communication (25–27), and more recently through varied response to external stimuli (28, 29), stored elastic energy (30), or soft logic (31–33). To date, these mechanisms have been harnessed to create soft robotic matter capable of locomotion, sequential folding, and untethered electronics-free motions.

Soft robotic materials with sensing capability are able to provide feedback, e.g., via a change in electrical resistance (34–38) or by passively converting external cues into specific responses (33, 39–41). While electronic signals provide precise information, such as when a sensorized soft gripper makes contact with an object (42, 43), transforming electronic signals into a desired output often requires a tethered interface to computer, power supply, and other electronics. Passive control of soft robotics via embedded intrinsic material logic provides an

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**Figure 2.1. Soft robotic matter.** (Left panel) Soft robotic matter is comprised of multiple functional, intercommunicating materials that give rise to shape morphing, sensing, and control. (Right panel) Programmable soft robotic matter is being developed for myriad applications, including delicate object manipulation, exploratory systems, and multifunctional reconfiguration.
avenue for functional autonomy. To date, passively controlled systems have relied on color change
driven by external pressure (33), antenna performance adjustment driven by temperature
dependent shape morphing (39, 40), and self-regulation driven by external light (41). However,
until recently (44), untethered fully soft, passively controlled locomotion had not been
demonstrated.

The design and integration of multiple soft robotic materials with minimal compromise in
form and function is a grand challenge. For example, traditional manufacturing methods, such as
molding and lamination, can limit both the number of materials and design complexity. The
resulting architectures also suffer from delamination at the interfaces between layered materials
(14, 45). Recently, 3D printing (3DP) has emerged as a promising avenue to overcome such
limitations. This additive manufacturing method, which enables multimaterial patterning across
length scales (2, 14, 45), has already been used to produce soft electronics, strain sensors, and
power sources (9, 46–48).

The inherent extensibility and adaptability of soft robotic matter is particularly suitable for
several functions, three of which are highlighted in Fig. 2.1. Because these materials have similar
stiffness and compliance to humans and other living organisms, they can be safely used for delicate
object manipulation (42, 49–54), wearable devices for health monitoring or assistive robotics (55,
56), and human/machine interfacing (2, 22). Secondly, with resilience to high loads, increased
degrees of freedom, and stimuli response, soft robots composed of these materials uniquely suited
for adaptive exploration, multipurpose task completion, and motility in unknown, confined, or
dynamic environments (2, 17, 25, 57–59). Lastly, soft structures enable extreme deformations that
can endure complex shape morphing into multiple forms, each tasked with a specific function for
task-specific reconfiguration (e.g., multimodal locomotion, graded mechanical properties) (25,
For multifunctional structures especially, self-folding origami with active hinges (i.e., active origami) are becoming ubiquitous due to their large deformations and ability to take on multiple forms in a single structure (60–63). Additionally, active origami with discrete hinges has simplified modeling and kinematic prediction methods, while maintaining the advantages of soft robotics (i.e., adaptability, stimuli response, and flexibility) (60–63).

To allow extensibility and adaptability, soft robotic matter is predominantly comprised of soft, functional materials whose stiffness is below ~1 GPa (2, 3, 17, 34, 51) (Fig. 2.2). This selection criteria enables infinite degrees of freedom during actuation, unlike discrete joints found in rigid robots (maximum of 6 degrees of freedom) (3, 64). Soft robotic matter relies on its shape morphing, and thus it is essential that actuating components are soft to allow resilience, compliance, and extensible shape morphing.

![Figure 2.2. Mechanical stiffness of biological and synthetic materials.](image)

Soft materials are defined as having a Young’s modulus of \( \leq 1 \) GPa. The stiffness of several materials widely used for shape-morphing and soft robotic matter are highlighted (top). Adapted from Ref. (17).

### 2.2.1 Soft actuators

Programmable, soft shape-morphing materials and their integration into complex 3D forms is a strong focus of soft robotic development. Actuating materials are selected based on their end use, as each have unique advantages and limitations. Important actuation performance and
selection criteria that impact function include actuation method (e.g., stimuli response for untethered function, electric response for precise movement), deformation mode, frequency, work density, strain, and auxiliary equipment (2, 17, 18).

Traditionally, soft actuation has been dominated by pneumatic systems (i.e., PneuNets or fluidic elastomer actuators (FEAs)) (Fig. 2.3Ai). These actuators are comprised of a network of embedded channels and cavities in inert, soft, silicone elastomers that can expand or contract with positive or negative pressure, akin to balloons, with large specific work (4, 42, 52, 65, 66). Several actuation motifs have been demonstrated in pneumatic systems with positive or negative pressure input, including contraction, expansion, bending, and torsional rotation (4, 42, 57, 65–68). Moreover, programmed networks of cavities in soft materials with disparate and programmed stiffness (Fig. 2.3Aii) have achieved programable actuation and locomotion modes (42, 51, 52, 58, 69), complex gaussian curvatures (68), and the first fully soft untethered soft robot (32) (Fig. 2.3Aii). However, soft robotic matter that rely on FEAs for shape morphing require bladder architectures that limit their geometry and function, as silicones are inert and not intrinsically shape morphing or muscle-like. However, FEA-based soft robotic matter must rely on bulky auxiliary equipment (pumps) (56, 57, 59), combustion reactions that limit actuation cycles (32, 70), and power sources (2, 51, 52, 60), which greatly limits their utility.

Dielectric elastomer actuators (DEAs) composed of silicone, acrylate, and polyurethane elastomers have been widely deployed as soft robotic matter. Simply put, DEAs are compliant capacitors with a soft elastomeric dielectric layer sandwiched between compliant electrodes that exhibit a small contraction and large expansion perpendicular and in-plane of electrodes, respectively. With inputted voltage, attraction of opposing charges drives contraction of the dielectric layer. DEAs generally outperform most other soft actuators in frequency, efficiency,
Figure 2.3. Soft Actuators. (A) (i) Scheme of FEA architecture and actuation. Adapted from Ref. (3). (ii) Image of FEAs unactuated and actuated (top), and integrated into a fully soft, untethered FEA soft robot. Adapted from Ref. (32). (iii) Geometries of FEAs with stiff external architectures (left) and corresponding actuated forms with increasing pressure (right). Adapted from Ref. (4). (B) (i) Multifunctional DEA with “on” segments indicated in inset. Adapted from Ref. (74). (ii) 3D printed interdigitated DEAs with addressable (top) and rotational actuation (bottom). Adapted from Ref. (6). (C) (i) Scheme of hydrogel shape change. (ii) Bioinspired 4D printed hydrogel as printed and swollen over time. Adapted from Ref. (7). (iii) Bistable hydrogel jumper while dry, activated, and after jumping when swollen. Adapted from Ref. (30). (D) (i) Scheme of SMP and common transition segment mechanisms. Adapted from Ref. (1). (ii) Sequentially folding origami employing SMP hinges with decreasing levels of absorption to light stimulus. Adapted from Ref. (28). (iii) Multi-material SMP actuator gripping hot screw. Adapted from Ref. (9). (iv) SMP swimmer propelling with bistable element in programmed, activating, and activated states (insets). Adapted from Ref. (90).
energy density, and strain (1, 2, 5), and while needing large power sources, have demonstrated robotic function such as swimming (71–74), and flying (75). Recent advancements to increase performance include distinct electrode geometries for multifunctional actuation (Fig. 2.3Bi) (74), liquid dielectric for increased contractile stroke (49, 76), incorporation with stiffer components for out-of-plane actuation (77, 78), and 3D printing of electrodes for high-throughput fabrication and increased modes of actuation (Fig. 2.3Bii) (6). Despite this progress, DEAs are limited in their shape, integration, and actuation motifs due to the need for particular sandwiched electrode architectures, a thin dielectric, and limited materials processability. Akin to FEA-based architectures, DEA-based soft robotic matter must be tethered to an external power source (2, 51, 52, 60).

By contrast, active robotic matter exhibit intrinsic shape morphing and, thus, can harness power passively from ambient environmental stimuli (e.g., heat, light, and chemical gradients) (1). Thermally responsive materials can also be triggered via Joule heating, but this requires the integration of a conductive electrode network connected to an onboard or external power supply. To date, hydrogels, shape memory polymers (SMPs), and liquid crystal elastomers (LCEs) have been investigated as active soft materials. Hydrogel actuators absorb or desorb water to morph into complex, programmed architectures in response to stimuli such as heat (79, 80), electric field (81), light (82) or pH (83–85) (Fig. 2.3Di). Recent advancements in programmable hydrogel shape morphing include directional and positional swelling made possible by gradients in crosslinking (80, 86) or by inclusions of anisotropic fillers (7, 79). Furthermore, 4D printing of a novel hydrogel ink with anisotropic filler that aligns with DIW allowed bioinspired programming of complex curvatures and extreme shape morphing due to differential swelling (Fig. 2.3Dii) (7). While useful for physiological environments and interfacing with biology, hydrogel actuation is
generally weak and slow, and operation requires water submersion. However, functions such as gripping (53), walking (81), cargo transport (83), and jumping (30) have been reported for hydrogel actuators. Notably, recent work exploited elastic instability in hydrogel structures with directional swelling, where swelling of the hydrogel triggered a high-energy snap-buckling to enable exceptionally rapid jumping (Fig. 2.3Diii) (30). However, while capable of complex actuation, integration with other materials in specific architectures are necessary to provide quick or strong hydrogel actuation.

To achieve large deformations, strong muscle-like contractile actuation is generally necessary. Shape memory polymers (SMPs) have been widely employed for this task due to their large energy density and contractile strain. SMPs are manually deformed to a temporary form at temperatures above a physical transition temperature (e.g., glass transition temperature, $T_g$) or through secondary crosslinking mechanisms, cooled to ambient temperatures to lock-in the semi-permanent programmed form, and then actuated to their original, contracted form when heated directly, photothermally, or electrothermally (Fig. 2.3Ei) (1, 8, 28, 63, 87). Due to facile patterning methods, such as 3D printing, SMPs have been used as hinges in soft active origami to actuate flat sheets into permanent 3D forms (Fig. 2.3Eii)(28, 29, 62, 88, 89) as well as mechanical bistable elements to achieve propulsion due to their large force exertion (Fig. 2.3Eiv) (90). However, their actuation is not reversible and the lock-in step must be reprogrammed after every actuation, although it is possible to encode multiple temporary shapes with in response to different stimuli (Fig. 2.3Eii) with multiple transitions (Fig. 2.3Eiii) (9, 28, 91–93) or incorporate another bias actuator to reprogram the SMP when heated (88, 94). Recent strategies to actuate 3D structures utilize shape memory effects for permanently memorizing an operating form and a second materials mechanism
(e.g., thermal expansion) to reversibly actuate from the memorized form to an actuated form. However, these strategies are limited to specific architectures, such as yarns, textiles, and bilayer lattices (40, 95).

Like SMPs, LCEs exhibit intrinsic, strong, contractile actuation and like hydrogels, allow complex programming and shape morphing. Since LCEs are the primary focus of my Ph.D. thesis, a more detailed review of this class of active soft matter is provided in the next section.

2.3 LIQUID CRYSTAL ELASTOMER ACTUATORS

Soft robotic matter based on liquid crystal elastomers (LCEs) are of considerable interest due to their intrinsic and reversible contractility, large deformations, environmental stimuli response, and high energy density. These intrinsic properties offer several advantages over the other classes of materials described above (9, 65, 96). While liquid crystals and liquid crystal polymers are well studied over the past 100 years (1, 97), LCEs emerged in the 1990s based on an hypothesis by de Gennes in the 1970s (98). LCE actuators are largely of interest for use in soft robotics. However, programming LCE actuation requires an ability to specifically control their nematic director alignment. Hence, the development of LCE actuators requires simultaneous advances in materials design, synthesis, and processing methods that enable the desired actuation response, as discussed below.

2.3.1 Liquid crystals

LCEs are elastomers that are composed of rigid molecules, called mesogens (i.e., liquid crystals, LCs), that exhibit liquid crystalline mesophases. Mesogens are anisotropic molecules, either with prolate (calamitic) (Fig. 2.4) or oblate (disk) shape (10, 99–101). Liquid crystal (LC) mesophases were first discovered by Lehmann and Reinitzer in 1888, and posited as a “fourth state of matter”, since they flowed like liquid, yet exhibited birefringent optic properties like solid
Mesogens self-assemble into liquid crystal phases, with either orientational or positional order, arising from both steric and thermotropic effects \((10, 99)\). Some thermotropic mesophases are also commonly exhibited in LCEs, as shown in Figure 2.4. The critical temperature of the nematic to isotropic phase transition is denoted by \(T_{NI}\) (bottom).

**Figure 2.4. Representative liquid crystal phases.** Schemes of solid crystalline phase, liquid crystal mesophases, and isotropic phase exhibited by rigid LC mesogens. Smectic, nematic, and isotropic mesophases are commonly exhibited by liquid crystal polymers and elastomers. The critical temperature of the nematic to isotropic phase transition is denoted by \(T_{NI}\) (bottom).

crystals \((97)\). Mesogens self-assemble into liquid crystal phases, with either orientational or positional order, arising from both steric and thermotropic effects \((10, 99)\). Some thermotropic mesophases are also commonly exhibited in LCEs, as shown in Figure 2.4. The critical temperature \(T_{NI}\) denotes the transition temperature between liquid crystal nematic and liquid isotropic phases. Less commonly, cholesteric LC phases (chiral nematics) will also occur in LCEs, when chiral mesogens are incorporated that induce mesogen rotation with a characteristic pitch. This phenomenon gives rise to color-changing properties in response to heat or external fields \((102, 103)\).
2.3.2 Liquid crystal elastomers

Reactive rigid mesogens can be synthesized into liquid crystal polymers (LCP) that can be subsequently crosslinked into liquid crystal elastomers. Three types of LCEs exist: (1) side-on (2) end-on, and (3) main chain LCPs (Fig. 2.5A) ([10], [11]). Side-chain LCPs have mesogen pendants decorating a flexible polymer backbone, while main-chain LCPs have mesogens along their backbone, which normally alternate with a flexible spacer. LCEs are defined as loosely crosslinked LCPs. When crosslinked in an aligned state, a nematic LCE polymer will be held in an elongated configuration made energetically favorable by liquid crystal (rod-rod) interactions between the mesogens, unlike a typical spherical random-coil polymer configuration.

Figure 2.5. LCE precursor polymers. (A) Schemes of mesogen arrangement in liquid crystal polymer classes. (B) Elongated polymer configuration of an aligned representative unit of main-chain nematic LCE below $T_{NI}$ (left) and spherical polymer configuration above $T_{NI}$ (right). (C) Actuation of representative LCEs composed of different LC polymers, quantified as length ratio between nematic and isotropic phases. Adapted from Ref. ([II]).
When heated above their transition temperature, $T_{NI}$, nematic interactions are eliminated, and isotropic polymer configurational entropy (i.e., spherical random coil conformation) dominates, resulting in a reversible anisotropic contraction (Fig. 2.5B). This microscopic shape change translates into a macroscopic anisotropic actuation in the direction of alignment (i.e., director) as long as the LCE is initially crosslinked in an aligned, elongated configuration. This reversible shape change arises, since the crosslinks act as a shape memory mechanism that promotes the elastomer to reassume the elongated polymer state when cooled below $T_{NI}$ again (Fig. 2.5B) (10). LCEs produce from these three different LCP classes exhibit different actuation strains, with relatively larger actuation strains arising with increased coupling of mesogens to the polymer backbone (Fig. 2.5C). Consequently, when heated above $T_{NI}$, main chain LCEs exhibit larger actuation strains than side chain LCEs. Interestingly, LCEs produced from a combination of LCPs have also been reported to have extraordinary actuation strains (11).

2.3.3 LCE materials design

2.3.3.1 LCP and LCE synthetic routes

Several synthetic routes have been developed to generate LCEs, although certain chemistries are more conducive to specific LCP classes or fabrication methods (Fig. 2.6) (104, 105). Side-chain LCPs commonly consist of a flexible siloxane backbone that is decorated with vinyl or acrylate monofunctional mesogens via a heat-catalyzed reaction (Fig. 2.6A,B) (13). A multifunctional crosslinking mesogen or molecule is utilized to crosslink the LCP into an LCE. Multistep heat-activated synthetic routes with disparate reaction rates have been widely used to ensure full decoration of a polymer backbone (Fig. 2.6A) prior to full crosslinking (Fig. 2.6B), and to lengthen handling time of the LCE precursor (13). To leverage fabrication methods that require
low viscosity starting materials, mono- and bi-functional mesogens have been copolymerized and crosslinked in a single step to make side chain LCEs (106–108).

Figure 2.6. Common LCE chemistry schemes. (A) Chemistry scheme of platinum-catalyzed hydrosilylation with vinyl mesogens \((M)\) with fast reaction rate \((K_1)\), and (B) methacrylate analog with slower reaction rate \((K_2)\). (C) Scheme of platinum-catalyzed main-chain hydrosilylation with polydimethylsiloxane spacer. (D) Light-induced thiol-ene click chemistry for main-chain LCP polymerization. (E) Nucleophile \((\text{Nu})\) catalyzed thiol-acrylate click chemistry and (F) aza-Michael acrylate-amine addition for main-chain LCP polymerizations. Adapted from Ref. (105).

Main-chain LCE synthetic routes include chain growth of difunctional mesogens and difunctional spacers with a terminal, orthogonal crosslinking step (Fig. 2.6C-F). Orthogonal polymerization and crosslinking steps with heat- and photo-induced click chemistries respectively, have been a common and versatile method to synthesize main-chain LCEs in a one-pot approach (109–111). With growing interest in creating 3D LCE actuators for robotic applications, reactive mesogens based on acrylate or vinyl functional groups are becoming commercially available,
allowing both side-chain and main-chain LCEs to be synthesized with compatible chemistries (i.e., Click reactions) (Fig. 2.6D-F) (109, 110, 112).

2.3.3.2 Thermomechanical programming by materials design

Thermomechanical properties of LCEs including actuation temperature, actuation strain, and shape memory have been tuned through several materials design approaches.

Side-chain LCEs have generally exhibited lower actuation temperatures due to greater chain flexibility and decoupling of the mesogens from the polymer backbone (11). Recently, molecular and network characteristics of main-chain LCEs have been investigated to decrease their $T_{NI}$, and hence operating temperature range, while maintaining their large actuation strains. Research to date has focused on using commercially available mesogen monomers in thiol-ene, thiol-acrylate, and aza-Michael addition click chemistry with various crosslinking strategies to tailor their thermomechanical properties of main-chain LCEs.

While LCEs with different starting materials can be expected to behave uniquely, there are several overarching crosslinking and LCP design strategies that have been employed to modify $T_{NI}$ and their glass transition temperature, $T_g$. First, increasing crosslinking density has increased $T_{NI}$ of these LCEs due to larger network constraints, which has been demonstrated both in thiol-acrylate LCPs and aza-Michael addition LCPs crosslinked with thiol-ene or with acrylate polymerization (112–114). LCEs have been crosslinked by adding either tri- or tetra-functional isotropic crosslinkers to a main-chain LCP (115) or synthesizing main-chain LCP with crosslinking functional end groups (e.g. acrylates), where molecular weight of the LCPs dictate effective crosslink density (112). Moreover, crosslinking chemistries have been shown to effect $T_{NI}$ in LCE systems with similar crosslink density (113). Leveraging a trifunctional vinyl crosslinker to crosslink thiol-terminated LCPs resulted in a much lower and sharper actuation
temperature ranges than those with acrylate polymerization crosslinking. In the latter system, a more heterogeneous network arises due to lack of a uniform crosslinker functionality (113), consistent with other systems where $T_{NI}$ increases with crosslinker functionality (115).

By increasing spacer lengths between mesogens or adding alkyl side-chains to increase free volume, one can generate LCEs with lower $T_{NI}$ (110, 113, 116). Moreover, sufficient spacing between mesogens in LCPs has been shown to induce nano-segregation, which results in a smectic C phase or semi-crystallinity in main-chain LCEs (110). With increasing spacing length, stiffness will generally decrease until nano-segregation increases stiffness dramatically (110). However, to decrease $T_{NI}$ without inducing a smectic phase, nano-segregation, or semi-crystallinity, LCEs have been designed with a combination of spacer lengths between mesogens (113). By exploiting these molecular design trends, Ware and coworkers developed a LCE materials set based on thiol-acrylate LCPs with various thiol spacers and crosslinking chemistries that demonstrated an incredibly wide range of programmable $T_{NI}$ values from 28 ºC to 105 ºC (113). This tunability in $T_{NI}$ further increases versatility of LCEs for applications that require operation in ambient conditions.

Importantly, actuation strain is also tunable by materials design. Actuation magnitude will decrease with increased crosslinking, as the LCE stiffness and network constraint increase (113). Moreover, increasing crosslinker concentration has a greater effect on decreasing the magnitude of actuation above $T_{NI}$ than crosslinker functionality (115). Similarly, LCEs crosslinked with acrylate polymerization will exhibit lower actuation strains compared to controlled, thiol-ene crosslinked LCEs with tri-vinyl crosslinkers (113). While $T_{NI}$ is the critical temperature for actuation, $T_g$ is important for shape memory effects. Designing $T_g$ to be above ambient temperatures or designing a semicrystalline LCE enables shape memory (110, 112, 117), allowing
a deformed, heat treated shape to be stable at ambient conditions much like SMPs (110, 112). The $T_g$ of a given LCE increases with crosslink density across several systems (112, 114, 115) and also with decreasing spacing length (110).

2.3.3.3 Additional material functionality

The incorporation of functional moieties within LCEs enables multi-functionality. Apart from standard crosslinking with heat or light, additional dynamic crosslinking bonds in LCEs have been incorporated to allow stable reconfigured forms without a constant energy to maintain a deformed or actuated state. For these LCEs, dynamic chemical moieties have been incorporated to lock-in deformed or actuated forms by changing the crosslinking network with a variety of exchangeable bond chemistries and with stimuli either identical or orthogonal to actuating methods (118–122). Additionally, specialty LCE mesogens are selected to prescribe actuation and stimuli response. For example, to fabricate cholesteric color-changing LCEs, chiral mesogens have been incorporated either as side-chain pendants (102), or as main chain mesogens (103). For photoresponsive LCEs, photo-isomerizing azobenzene mesogens or photothermal nanoparticles have been incorporated in starting materials (104, 123). Below, the various stimuli responses of LCEs made possible by materials design will be discussed.

2.3.4 Stimuli responsive actuation

A major advantage of LCE actuators is their diverse stimuli response to on-board or external stimuli, such as heat, light, and chemical gradients. For example, LCEs with photothermal additives, such gold nanorods (AuNR) (124, 125), conjugated polymer nanoparticles (e.g. polyaniline) (126) or organic dyes (41, 127), and carbon nanoparticles (CNP) (128–130), enable internal heating (on-board) from external light sources, e.g., addressable photothermally actuated LCEs. Structured photomasks or focused lasers have enabled localized heating to achieve
multifunctional and addressable bending in photothermally actuated LCEs (Fig. 2.7A,B) (124, 130), where only regions exposed to light stimulus bend towards the light. Light-induced contraction has been demonstrated with photothermal LCE composites upon near-IR (nIR) light exposure in efforts to increase actuation versatility (126, 131, 132). Photothermally responsive LCEs can simultaneously functioned in robotic matter as sensor, actuator, and controller (41, 133). An artificial LCE iris with organic photothermal dyes exhibites self-regulated transmission through a decrease in aperture with increasing light intensity (Fig. 2.7C) (41). Additionally, carbon nanomaterials have been exploited to convert ambient sunlight to heat in LCE nanocomposites to

**Figure 2.7. Photothermally responsive LCEs.** (A) Reconfigurable LCE-gold nanoparticle composite film with director profile $n$ and programmable deformations based on light projection pattern (inset schemes, grey indicating light-exposed region). Adapted from Ref. (124). (B) A six-armed LCE-carbon nanotube composite with 24 different configurations depending on light exposure. Adapted from Ref. (130). (C) A self-regulating iris comprised of a photothermal dye-LCE composite (left) that decreases transmission with increasing irradiating light (right). Adapted from Ref. (41). (D) A self-regulating heliotropic solar panel with LCE nanocomposite actuators that bends towards sunlight (yellow arrows). Adapted from Ref. (133).
adjust solar panels without the need for auxiliary equipment (e.g. lasers) to achieve untethered self-regulating soft robotic matter (Fig. 2.7D)(133).

While photothermally responsive LCEs improve addressability and self-regulation of LCE structures, for low-temperature operation of LCE actuators, photoisomerizing molecules that undergo a trans-cis isomerization near-isothermally upon exposure to UV light have been employed. Azobenzene molecules are the most widely used photoisomers used in LCE. These molecules are aligned to the director in a trans isomer unless exposed to UV light, which isomerizes molecules to a cis configuration, inducing enough disorder to transition the nematic phase to isotropic, even in LCE films (Fig. 2.8A) (99). Generally, photoresponsive LCEs are not contractile since only surface azobenzene moieties make contact with light stimuli due to a short penetration depth, but nonetheless they have been used as bending actuators (41, 134, 135), twisting actuators (136–138), or cones (139). Moreover, polarized light can bend a single thin LCE film in various directions depending on light direction, exemplifying multifunctionality in light-fueled LCE structures (Fig. 2.8B)(134).

The cis-to-trans transition of azobenzenes can be slower than a desired actuator speed, requiring cycling UV light with heat or blue light to increase actuator frequency (99). However, to overcome this challenge, Bunning and coworkers have exploited the faster rearrangement of azobenzenes with polarized blue-green light (440-514 nm), to allow high frequency bending oscillation of LCE cantilevers fueled by continuous polarized light (Fig. 2.8C)(135, 140). Furthermore, in efforts to increase multifunctionality of light-responsive LCEs, Broer and coworkers demonstrated an array of artificial LCE cilia with two LCE materials with azobenzene moieties that respond either to visible or UV light (Fig. 2.8D)(141), that take one of four configurations depending on light conditions for use in micromechanical devices (141). Recent
advances in light-responsive LCEs include further chemical development of azobenzenes that are designed to undergo photoisomerization at different wavelengths to improve both diversity of stimuli and the addressability of multi-material patterned LCEs (28, 142).

Less common, but still noteworthy, is the actuation of LCEs with chemical gradients and swelling (Fig. 2.9). Swollen LCEs can lose their nematic order, and this transition to the isotropic phase shape morphs the LCE as expected with mesophase transitions. Hence, bending due to a change in humidity (Fig. 2.9A) (143) or direct solvent swelling to mimic heat-actuated forms

Figure 2.8. Photoresponsive LCEs. (A) (i) Scheme of trans isomer of azobenzene molecule incorporated in an elastomer and cis isomer when exposed to ultraviolet light. (ii) Scheme of nematic to isotropic transition of mesogens doped with azobenzene mesogens when exposed to UV light. Adapted from Ref. (99). (B) Azobenzene LCE film that bends to polarized light direction (white arrows). Adapted from Ref. (134). (C) Scheme of LCE cantilever oscillating reversibly (left) and still image of high-frequency actuating cantilever (right), actuating at 217 Hz, faster than the camera framerate. Adapted from Ref. (135). (D) Scheme of artificial cilia function utilizing two LCEs with disparate light response (red, yellow). (ii) LCE artificial cilia with various light conditions. Adapted from Ref. (141).
Figure 2.9. Chemoresponsive LCEs. (A) (i) Scheme of actuation mechanism with respect to humidity in an LCE film, (ii) image of free standing LCE film, and (iii) bending actuation of LCE film with humidity from human finger. Adapted from Ref. (143). (B) Dry LCE film that has a 2x1 array of azimuthally patterned director and films actuated into two cones in an isotropic solvated phase, demonstrated with three different solvents. Adapted from Ref. (12).

(Fig. 2.9B) (12, 144) have been reported. Additionally, pH responsive LCE shape change has been achieved by synthesizing hydrogen-bonded mesogens that dissociate into non-mesogenic moieties at high pH (145). Lastly, swelling an LCE with an anisotropic solvent or ionic liquid have enabled LCE actuation via reorientation of the LCE director in response to an electric field (146, 147) with decreased field requirements for director reorientation. Both swollen LCE gels and chiral smectic LCEs or LCE-CNT composites have been actuated with an electric field (i.e., electrostriction (148, 149) or an electroclinic effect (150)) with minor strains demonstrated.

2.3.5 Programming LCE alignment

LCE actuation is only achievable if LCEs are sufficiently crosslinked in an aligned configuration. Therefore, several researcher have focused on developing alignment methods to program LCE architectures. Mechanically aligned LCEs were first realized by Küpfer and Finkelmann in the 1990s (13), which generated excitement about exploring their use as artificial muscles thereafter (151, 152) motivated further developments of programming methods and materials. Below, alignment quantification and approaches to program LCEs are discussed.
2.3.5.1 Director

Long-range alignment of mesogens in LCE’s is critical and essential to achieve anisotropic actuation, anisotropic mechanical response, and distinctive optical properties (10, 153). A quantitative measure of long-range alignment is described with the scalar order parameter, $S$ (below).

\[
S = \langle \frac{3}{2} \cos^2 \theta - \frac{1}{2} \rangle
\]

The scalar order parameter, $S$, measures the average deviation of mesogens, $\theta$, from the target, bulk direction of orientation (i.e. the director), where $S=1$ corresponds to a hypothetical perfect alignment (i.e. crystalline) and $S=0$ corresponds to perfect isotropy (i.e. liquid) (99). Aligned nematic phases generally have a scalar order parameter of roughly 0.3-0.8 (101). Greater spontaneous shape change above $T_{NI}$ is achieved with greater chain anisotropy, which for main-chain nematic elastomers scales directly with the order parameter (99). Negative order parameters have recently been demonstrated experimentally with a unique processing method of in-plane isotropic stretching of a shell (i.e. balloon). Here, all mesogens are perpendicular to the director (i.e., mesogens are randomly tangent to the shell surface), where force tangent to biaxial expansion is the director (154).

Absent alignment methods, LCP and LCEs are polydomain. Characteristic domain size is generally on the order of a couple microns for LCPs as a result of a competition between the random field effect, which favors small domains with a penalty for long-range order, and Frank elasticity, which favors large domains with a penalty for domain boundaries. Within a given domain, all mesogens have short-range, local order in a single direction (Fig. 2.10A inset). Characteristic domain size of an LCP increases with temperature until $T_{NI}$, where domain size is zero (99, 155). We note that in LC’s, domain size increases and self-assembles with time in addition
to temperature, whereas in LCPs, domain sizes are stable over moderate timescales due to higher viscosity and decreased mobility (155).

2.3.5.2 Mechanical alignment

The first actuating LCE was realized by Küpfer and Finkelmann, with an alignment method now deemed the “Finkelmann method” or “mechanical alignment”, which is still widely used (13,

![Image 1](image1.png)

**Figure 2.10. Mechanical alignment of LCEs.** (A) Scheme of polydomain partially-crosslinked LCE (left), where colors depict different domains with local mesogen orientation annotated with arrows. Scheme of stretched partially crosslinked LCE, where domains have rotated and stretched to the direction of stress (right). Inspired by Ref. (156). (B) (i) Polydomain sample with high scattering and (ii) monodomain sample that is optically transparent when strained and aligned. Adapted from Ref. (99). (iii) Three region stress-strain plot of polydomain LCE transitioning to monodomain (left) and corresponding order parameter as a function of stress (right). Region I, II, and III correspond to domain distortion, domain rotation, and strain stiffening. Adapted from Ref. (10). (C) Image sequence of mechanically-aligned LCE lifting a 10g weight with 75% strain in response to heat. Adapted from (13).
This method imposes an applied stress, while heating a polydomain LCE sample in the nematic phase to drive domain rotation, elongation, and, ultimately, coalescence (Fig. 2.10A) (13, 109, 156). Above a threshold stress, $\sigma_{\text{threshold}}$, domain rotation occurs resulting in domain alignment along the stress direction (Fig 2.10B). Domain rotation is a zero-energy process and results in a plateau in the stress-strain curve characteristic of LCE soft elasticity (10, 157, 158). When mechanically aligned as a monodomain, LCEs exhibit extreme deformations when cycled above and below their $T_{NI}$ (Fig 2.10C) (13). Mechanical alignment enables fabrication of unidirectionally aligned LCEs up to cm’s in length in the form of 3D hollow tubes (25, 110, 159), balloons (154), and fibers (141, 160, 161). However, this approach does not allow the director field to be spatially varied.

2.3.5.3 Command surfaces

Like those found in liquid crystal displays (LCDs) (10), command surfaces have also programmed 2D LCE films. Command surfaces have historically been rubbed polymer surfaces (e.g., polyimide or polyvinyl alcohol rubbed with velvet or felt) which sandwich and align mesogens primarily due to surface interactions arising from microgrooves and polymer alignment (97, 112). Recently, command surface resolution and directionality have been improved to increase shape morphing capabilities and versatility by using substrates with absorbed conjugated organic dyes, which have been demonstrated to align small molecule mesogens (112) (Fig. 2.11A). These dye layers command either homogenous or homeotropic alignment of mesogens by way of mesogen-dye surface interactions (10, 106, 123, 162) (Fig. 2.11A, left) and unidentical command surfaces can further program splay or twist orientations, respectively (Fig. 2.11A, right) to program bending-mode actuations (141, 162, 163).
Photopatterning of dyes allows remarkable pixilation or voxelation of LCEs (12, 164).

High resolution, photo-aligned, voxelated command surfaces (50x 50 um, 100um thick voxels) were recently pioneered by White and coworkers, exemplified with a comparison of a prescribed

**Figure 2.11. Command surface alignment of LCEs.** (A) Schematics of adsorbed dye configurations and resulting mesogen alignment (left). Schematics of 2D mesogen alignment when sandwiched between homogeneous and/or homeotropic command surfaces (right). Reproduced from Ref.’s (123) (162). (B) (i) Projection lithography setup that transfers a (ii) high-resolution image to a command surface to program LCEs. (iii) POM micrograph of photo-programmed LCE (1 x 1 cm) to replicate high-resolution image (ii). Adapted from Ref. (165). (C) (i) POM micrograph of a command surface aligned LCE film (left) with a 3x3 array of azimuthally programmed director, and scheme of mesogen arrangement in repeat unit (right). (ii) LCE film in ambient conditions (25 °C) and actuated above $T_{NI}$ (175 °C). Adapted from Ref. (12). (D) (i) Scheme of inscribed surface with parallel mesogen alignment. (ii) Scheme of inversely designed face with actuated gaussian curvatures dictated by angle between top and bottom inscribed surfaces, and image of actuated LCE film with overlaid prediction. Adapted from Ref. (167).
image and an identical POM micrograph of an LCE aligned by command surface (Fig 2.11B) (12, 165). In conjunction with a novel LCE precursor material to increase actuation strain, White and coworkers used a photoaligned command surface to program a 3x3 array of azimuthally rotating director in an LCE film that actuates into a cone array above $T_{NI}$, with each cone exhibiting an enormous stroke (Fig 2.11C) (12). As only low viscosity LCE precursors can be aligned by surface interactions, only densely crosslinked liquid crystal networks (LCNs) were previously fabricated with command surfaces in a combined acrylate polymerization and crosslinking route, resulting in minimal actuation due to a high degree of crosslinking (106, 162). A typical LCN phase transition through $T_{NI}$ results in a change of order parameter $\sim$5%, only a fraction of that for LCEs, ($\sim >$ 90%) (10). To overcome this challenge, White and coworkers designed main-chain click chemistries (12, 114) that can both be aligned with a command surface as short oligomers and continue thermal polymerization in their aligned state, prior to a terminal orthogonal photocrosslinking step (12).

Microscopically inscribed surfaces are another method for programming complex director fields in LCE films. These surfaces are produced by using direct laser writing to pattern non-unidirectional grooved surfaces in 2D (166, 167), where inscribed channels have sufficiently small pitch ($\sim$ 1µm (167)) to align LC materials (167, 168). This method has resulted in complex shape morphing LCE films, including programmed Gaussian curvatures with exemplary predictability and inverse design (Fig. 2.11D) (167). While command surface alignment methods allow both complexity and voxelation of the LCE director, the resulting LCEs are limited to thin films (maximum of $\sim$100 µm) due to surface-mesogen interactions (167).
2.3.5.4 Field alignment

Magnetic fields have recently been used to program director alignment (Fig. 2.12A) (169) by exploiting the anisotropic magnetic susceptibility of rigid mesogens. This approach is most suitable for side-on or end-on LCEs. For example, Aizenberg and co-worker created LCE micropillar arrays with magnetically aligned directors prior to crosslinking (Fig. 2.12B)(170). In this approach, LCEs have utilized chain extending or single step polymerization and crosslinking steps

![Diagram of field alignment](image)

**Figure 2.12. Magnetic field alignment of LCEs.** (A) Scheme of magnetic rearrangement of mesogens with respect to magnetic field H. Adapted from Ref. (169). (B)(i) Images of magnetically aligned pillar array of LCEs, (ii) detached pillars at low temperature, and (iii) actuated above T_{NI}. Adapted from Ref. (170). (C) (i) Scheme of microfabricated LCE honeycomb repeat unit and image of LCE honeycomb structure at ambient conditions (bottom). (ii-iv) LCE crosslinked with different magnet configuration and resulting director orientation (top) and resulting actuation above T_{NI} (bottom). The unactuated honeycomb repeat unit is overlaid with white outline. Adapted from Ref. (172).
(with mono- and bi-functional mesogens) to produce low viscosity starting materials (i.e., monomer mesogens) that enable mold-filling and alignment with lower, accessible magnetic fields \((107, 108)\). Recently, microfabricated architectures like microplate arrays, honeycomb structures, and artificial irises have been programmed with uniform or non-uniform fields to produce complex shape morphing LCEs \((171, 172)\). For example, honeycomb structures are crosslinked with one of three different director orientations dictated by magnetic field placement, to program three different actuated forms (Fig. 2.12C). Shape change has been modeled with magnetically and command surface aligned LCEs especially, due to the existence of interesting, non-unidirectional programming. Buckling origami \((173, 174)\) and Gaussian curvature \((167, 175–177)\) have been modeled or inversely designed to inform director profiles in LCEs to morph into a prescribed actuated form. While this method does allow one to generate 3D LCEs, magnetically aligned actuators are currently limited to micro-architected materials.

Lastly, LC fibers has been aligned under laminar flow within microfluidic devices \((178)(179)\). The carrier fluid imparts a shear stress that aligns the LCE director along the flow direction during wet spinning \((179)\) (Fig. 2.13A). Similar strategies have also been used to fabricate and align 3D LCE microparticles in large batches that have an anisotropic shape change when heated above \(T_{NI}\) (Fig. 2.13B)\((180)\). Less commonly, electric fields have also been reported to align LCEs in the form of electrospun fibers \((181, 182)\).
2.3.5.5 Programming 3D LCEs

Thick LCE actuators exert greater forces (183, 184) and possess better structural integrity under self- and applied loading conditions, and thus are of interest for soft robotics and mechanical logic. To fabricate 3D LCEs with programmed actuation, researchers have used stereolithography coupled with a rotating magnetic field (Fig. 2.14A) (185). The system reorients a magnet to align a layer, selectively crosslinks pixels that require this specific alignment, and then repeats the process in a layerwise manner to produce 3D LCEs with arbitrary director alignment (Fig. 2.14Ai). Another method to achieve this goal combines command surfaces and repeated lamination generate 3D LCEs (Fig. 2.14B)(184). These laminated thick films maintain their expected shape
morphing above $T_M$ with little to no change in stroke with added layers (Fig. 2.14B), with 4-layer actuators exerting almost 10x the specific work of their single film analogs ($\perp$). However, these methods of fabricating 3D LCEs produce glassy materials with limited actuation, or with limitations in varying 3D director through the thickness.

My PhD thesis explores the design and fabrication of 3D LCEs by direct ink writing (DIW), an extrusion-based 3D printing method. As described in Chapter 3, my research has shown that it
is possible to generate programmed 3D LCE actuators by inducing director alignment along the print path (183, 186, 187). Building on this advance, my research has also demonstrated LCE inks with varied stimuli response (113) as well as their seamless integration into multimaterial, untethered soft robotic matter (44).

2.4 CONCLUSIONS

Soft robotic matter are starting to realize their full potential as adaptive exploratory robots, multifunctional reconfiguring structures, and delicate object manipulators, but still require greater actuator development and versatility. Towards these goals, LCEs are emerging as a promising actuator option due to their intrinsically contractile, high energy density actuation, and their inherent responsivity to both environmentally- and electronically-delivered stimuli. While several strategies to program and integrate LCEs with other functional materials have been established, existing programming methods limit form, multi-material integration, and function of LCE actuators. The development of LCE materials and additive programming methods that are parallel to soft robotic materials assembly methods will allow meaningful and controllable actuation without compromising formfactor or internal architecture within soft robotic systems.
CHAPTER 3

3D PRINTING OF LIQUID CRYSTAL ELASTOMERIC ACTUATORS WITH SPATIALLY PROGRAMMED NEMATIC ORDER

This chapter has been adapted from the following publication:


3.1 INTRODUCTION

Liquid crystal elastomers (LCEs) are soft materials capable of large, reversible shape changes, which may find potential application as artificial muscles (188, 189), soft robots (190, 191), and dynamic functional architectures (192–196). Two important approaches have emerged for synthesizing LCEs; one involves the incorporation of mesogens as side chains in siloxane elastomers (197), while the other integrates mesogens within the main chains via chain-extending reactions (198). Both types of LCEs undergo a large contraction along the direction of the nematic director, i.e., parallel to the direction of mesogen alignment, when heated above their nematic-isotropic temperature ($T_{NI}$) (197–199), swelled by solvent (198, 200) or exposed to light to induce cis-trans conformational changes in the case of light-responsive mesogens (201, 202).

To date, the alignment of LCEs has been primarily achieved in thin films (thickness < 100 μm) via molecular interactions with command surfaces (199–202), mechanical stretching (197, 203, 204), or applied magnetic fields (205–207). Although thicker LCEs can be produced with the latter approaches, they typically possess uniaxially aligned directors. Recently, both LCE thin films (198) and 3D structures (208) have been fabricated with programmable control over their director orientation. Using an optical patterning system, White and co-workers (198) created voxelated command surfaces composed of azobenzene-based photoalignment materials,
whose orientation is defined with high spatial precision (minimum area ~0.01 mm$^2$) through control of the electric field vector of the linearly polarized light. Using a two-step synthesis method, they produced LCEs composed of a poly(b-amino ester) network. First, low viscosity precursors are aligned on the patterned command surface, and then the monomers undergo chain extension reactions to form main-chain nematic macromers that are subsequently cross-linked. Their voxelated LCE thin films exhibit large shape changes and specific work. Quite recently, Ware and co-workers designed a LCE ink based on this chemistry and reported the 4D printing of shape-morphing LCE architectures in both planar and 3D motifs, including those with opposing negative and positive Gaussian curvatures that exhibit reversible snap-through transitions (208).

Here, we report the design and additive manufacturing of LCE actuators (LCEAs) with spatially programmed nematic order in arbitrary form factors. Unlike soft actuators based on shape memory polymers, elastomeric matrices with embedded pneumatic channels, or electroactive polymers that require mechanical pre-programming, external pressure sources (209), or large voltages (210), respectively, LCE actuators (LCEAs) exhibit large, reversible, and repeatable contraction with high specific work capacity (211, 212). We use high operating temperature direct ink writing (HOT-DIW) (213) to align the mesogen domains within oligomeric LCE inks along the printing direction. Upon printing and UV curing, we characterize the order parameter, actuation strain, and specific work of these programmably aligned LCEs. To demonstrate the versatility of HOT-DIW, we created shape-morphing LCEA architectures that undergo reversible planar-to-3D and 3D-to-3D’ transformations on demand as well as 3D LCEAs (~1 mm thick) capable of lifting 233% more weight than other LCE actuators reported to date (214).
3.2 EXPERIMENTAL METHODS

3.2.1 LCE ink preparation and characterization

An oligomeric LCE ink is prepared using a modified one-pot synthesis based on a catalyst-free aza-Michael addition chemistry, which has been reported previously (199). As-received 1,4-Bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]-2-methylbenzene (Synthon, 97%, 2g), n-butylamine (Sigma-Aldrich, 99.5%), and Irgacure 651 (I651, BASF) are added to a 25mL round bottom flask in 1:1 molar ratio and 2 wt%, respectively. The mixture is heated to 110°C, above the melting point of the mesogen and the $T_{NI}$ of the resulting LCE and stirred vigorously. The reaction is shielded from fluorescent light, and the clear, yellow product is quenched in ice after 18 h. To determine phase transitions of interest, differential scanning calorimetry is performed on the ink. The LCE ink is sealed in an aluminum hermetic pan and is heated to 120°C to erase any thermal history, cooled to -50°C, then heated to 200°C, all at a rate of 10°C min$^{-1}$ (Q200; TA Instruments). The rheological properties of the LCE ink are characterized using a controlled stress rheometer (Discovery HR-3 Hybrid Rheometer; TA Instruments) equipped with 20 mm steel Peltier plate geometry and 0.750 mm gap. Prior to testing, the ink is brought to $T_{NI}$ to erase the thermal history. Oscillatory tests are conducted by sweeping shear stress at 1 Hz frequency.

3.2.2 HOT DIW of LCE ink

The HOT-DIW printhead is a modified version of a customized design reported previously (Fig. 3.1) (213). Briefly, it is comprised of a steel barrel surrounded by a heater coil (FM Keefe Company Inc., 62H36A5X-1128) with temperature readout by thermocouple (K-type) at the tip of the stainless steel 250 μm nozzle (TecDia Inc., ARQ-S-2535) and internal temperature readout by thermocouple (K-type) to prevent heating the barrel above the $T_{NI}$ while printing. The temperature of the nozzle is set to the print temperature of 50°C and maintained with a temperature controller.
HOT-DIW is performed with a custom 3-axis motion control stage (Aerotech Inc.) that deposits ink via pressure-driven extrusion with an Ultimus V pressure box (Nordson EFD) according to programmed G-code (Mecode). LCEAs are printed on pre-cleaned glass substrates secured to a leveled multi-axis stage (ThorLabs). Each batch of ink (~2 g) is manually consolidated into large pellets and loaded into the barrel at room temperature. The temperature is increased above \( T_{NI} \), then cooled at \(~10^\circ\text{C} \text{ min}^{-1} \) rate until the nozzle temperature reaches that of the prescribed printing temperature.

The system is held at this temperature (typically 50°C) for \(~30 \text{ min} \) prior to printing to allow the system to reach a steady state operating condition. As the ink is extruded, it is exposed to UV light (Omnicure, S2000) at an intensity of \(~12 \text{ mW cm}^{-2} \) (Fig. 3.1). After printing, LCEAs are exposed to higher intensity UV \((~31 \text{ mW cm}^{-2}) \) for 20 min (10 min for the top and bottom sides) to ensure uniform crosslinking. Printed LCEAs that are thicker than two filamentary layers are exposed to UV light every 2 layers for 400s \((~31 \text{ mW cm}^{-2}) \).

*Figure 3.1. High operating temperature-direct ink writing (HOT-DIW) of LCEAs. Images of (left) HOT-DIW setup and (right) LCEA ink printing.*
3.2.3 LCE actuator characterization

X-ray measurements are performed on a SAXSLAB system with a Rigaku 002 microfocus X-ray source (CuK$_{\alpha_1}$ = 1.5409Å) with sample to detector (PILATUS 300K, Dectris) distance of 109.1 mm for 15 min with Osmic staggered parabolic multilayer optics to focus the beam crossover at the second pinhole. It contains two sets of JJ X-ray 4 jaw collimation slits that are 0.9mm. WAXS samples consisted of one-layer LCEAs printed as unidirectional strips. Their order parameter is calculated from the WAXS data using Eq. 1 by numerically integration (MATLAB function trapz):

\[ S = \bar{P}_2 = 1 - N^{-1} \frac{1}{2} \int_0^\pi I(\theta) \left[ \sin^2 \theta + \sin \theta \cos \theta \log \frac{1 + \sin \theta}{\cos \theta} \right] d\theta; \quad (1) \]

where \( N = \int_0^\pi I(\theta) d\theta \) (215).

Printed LCE architectures are photographed using a camera (Canon 5D Mark III) between crossed polarizers (ThorLabs) keeping imaging conditions constant for both positions of crossed polarizers. Micrographs of unidirectional LCE samples are obtained using an inverted microscope equipped with crossed polarizers (Axio Observer, Zeiss).

Cyclic actuation measurements are performed on a custom 3-axis motion control stage. Printed LCEAs are placed on a thin silicone oil layer on top of an anodized aluminum stage and lowered onto and raised off of a hotplate such that their temperature is alternated between room temperature (held for 210 sec) and 105°C (for 180 sec), respectively (Fig. 3.2). Photographs of these LCEA samples are taken throughout this process (Canon EOS 5D Mark III) at a frequency of 0.1 Hz. An in-house MATLAB image analysis script is used to determine the dimensions of the actuated samples. To demonstrate their ability to lift weight, mass standards (Spectrum Chemicals) are attached to printed LCEAs with a binder clip (1.19g) and heated with a heat gun (Milwaukee,
MHT3300). To demonstrate their ability to reversibly change shape, printed LCEAs are heated using a hot plate (IKA RET basic) and imaged during this process. The saddle LCEA is actuated on hot plate held at 90°C, while the spiral, conical array, and mesh LCEAs are actuated on hot plate held at 95°C. Note, the spiral actuation is aided by a heat gun that is held above the actuator. All actuators are lubricated with silicone oil to prevent adhesion to the substrate prior to actuation.

3.3 RESULTS AND DISCUSSION

3.3.1 Ink characterization

The alignment of liquid crystalline domains during HOT-DIW is dependent on the LCE ink composition, rheology, and printing parameters. To maximize their potential actuation strain, we designed a photopolymerizable, solvent-free, main-chain LCE ink (198). Specifically, this ink is produced by creating oligomers from a reactive mesogen and amine linker via aza-Michael addition (Fig. 3.3A) (198, 199). Reactive acrylate end groups ensure that the 3D printed LCEAs form crosslinks upon UV exposure, which is essential for retaining the programmed director alignment imposed by the printing process prior to ink relaxation. Solvent-free LCE inks not only enable elongation of liquid crystal polymer chains at lower shear rates and molecular weight than
their solvent-based counterparts (216), they avoid the volumetric changes and residual stresses that arise from solvent loss during drying.

We printed the oligomeric LCE ink at elevated temperatures between $T_g$ and $T_{NI}$ using HOT-DIW (Fig.s 3.1 and 3.3B), i.e., between -22°C and 95°C, respectively, as determined by differential scanning calorimetry (Fig. 3.4A). This large temperature range provides a broad window for 3D printing LCEAs with programmed director alignment (217). As temperature is increased in the nematic state, the LCE viscosity decreases dramatically from 25°C to 80°C and concomitantly, it becomes less shear thinning. In the isotropic state (120°C), the LCE ink is Newtonian fluid with a viscosity that is roughly two orders of magnitude lower than the value measured at room temperature (Fig. 3.4B). To enable HOT-DIW patterning of high fidelity

**Figure 3.3.** LCE ink design and printing. (A) One-pot synthesis of the photopolymerizable LCE ink that includes a spacer (yellow chain), mesogen (R), and photoinitiator. (B) Schematic illustration of HOT-DIW of the LCE ink, where (i) shows the disordered LCE ink morphology inside the heated barrel, (ii) ordered morphology that emerges due to induced director alignment within the nozzle, and (iii) resulting ordered morphology in printed and crosslinked LCE filaments.
architectures, the LCE ink must possess a strong shear thinning response. We therefore selected a
printing temperature of 50°C, where the LCE ink also exhibits a viscoelastic response that
facilitates its shape retention during the printing process (Fig. 3.4C). The as-printed LCE features
are exposed to UV light to induce cross-links between reactive end groups, which preserve the
programmed director alignment within the printed LCEA architectures.

3.3.2 Spatial programming of nematic order

To demonstrate spatial control over director alignment during HOT-DIW, we first printed
an LCEA bilayer composed of an H-shaped layer (top, 100 μm) and a square-shaped layer (bottom,
100 μm) patterned on a glass substrate (12 x 12 mm) using a nozzle diameter of 250 μm and a print
speed of 4 mm s\(^{-1}\) at 50°C (Fig. 3.5). The H-shaped layer consists of an array of LCE filaments
printed in a meanderline pattern using a 90° (from horizontal) print path, while the square layer is
printed using a diagonal (45° from horizontal) print path. Using polarized optical microscopy, one
clearly observes the spatial control of the director along the direction of print path, i.e., only the

![Figure 3.4. LCE ink characterization.](image)

(A) DSC data for the LCE ink, which shows the measured glass transition temperature, \(T_g\), and the nematic-to-isotropic transition, \(T_{NI}\). (B) Log-log plot of LCE ink viscosity as a function of shear rate measured at room temperature (25°C) the optimal printing temperature (50°C), and below (80°C) and above (120°C) \(T_{NI}\). (C) Log-log plot of the shear storage, \(G'\), and loss, \(G''\), moduli as a function of shear stress for the LCE ink measured at 50°C at 1 Hz.
H-shaped layer is bright when the cross-polarizers are oriented at 45°/135° (Fig. 3.5A, top), while only the square layer is bright (Fig. 3.5A, bottom) when they are oriented at 0°/90°.

To determine the effect of temperature on director alignment, we printed samples (125 μm height) both below (50°C) and above (105°C) $T_N$ using a 250 μm nozzle and printing speeds between 2-10 mm/s. Note, different applied pressures are used to ensure that the printed filament

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**Figure 3.5. Spatial programming of the director.** (A) Polarized optical microscopy (POM) images of a printed LCE structure composed of an underlying square layer printed using a diagonal meander and a top layer composed of an orthogonally printed “H”-shape taken using rotated polarizers (scale bar = 2.5 mm). Polarizer and analyzer directions are indicated as double arrows. (B) Plot of intensity as a function azimuthal angle for LCE samples printed at 50°C and 105°C at 10 mm s$^{-1}$ (top) and their corresponding order parameters (bottom). (C) Plot of intensity as a function of azimuthal angle of LCE samples printed at 50°C at varying speed (top) and their corresponding order parameters (bottom).
Figure 3.6. Printed LCEA alignment. (A) Polarized optical microscopy (POM) images of LCEAs printed at different speeds and temperature (scale bars = 0.250 mm). (B) Representative WAXS patterns for printed LCEAs produced using vertically oriented meanderline pattern.
width (100 μm width x 125 μm height) is approximately the same in all cases. LCE samples printed at 50°C had significantly better director alignment along the print path, i.e. a higher order parameter (Fig. 3.5B, see also Fig. 3.6) than samples printed at 105°C. The LCE ink is subjected to both shear and extensional flow during the HOT-DIW process, (218) which induces alignment of their mesogenic domains (217, 219). As expected, the order parameter of LCEA samples printed at 50°C increases with print speed due to enhanced director alignment (Fig. 3.5C).

3.3.3 LCE actuator performance

To investigate their actuation performance, we printed LCEA unidirectional bilayers (15 x 3 x 0.25 mm) using a nozzle diameter of 250 μm, average print speed of 4.8 mm s⁻¹ and a meanderline horizontal print path. The printed LCEA bilayers are then cycled twenty times between ~ 26°C and 105°C (Fig. 3.7A). For these experimental conditions, we measured an average repeatable actuation contraction of -43.6±6.7% along the print direction and an average expansion of 29.8±5.9% normal to that direction (Fig. 3.7B). We note that these LCEAs can be

![Figure 3.7. Printed LCE actuators.](image)

**Figure 3.7. Printed LCE actuators.** (A) Images of printed (left) and actuated (right) LCEAs fabricated using a unidirectional print path (scale bar = 5 mm). (B) Their measured strain in the direction perpendicular and parallel to the print path upon cycling the LCEAs above and below $T_{NI}$, red and blue, respectively.
successfully cycled up to 100 times (Fig. 3.8). Full actuation of these printed LCEA occurs in approximately 180 s, while relaxation back to their original dimensions requires 210 s given our heating/cooling experimental setup (Fig. 3.9). Hence, a conservative estimate of the cycle time required to “reversibly switch” these printed LCEAs is approximately 390 s for the thermal cycling conditions used. We note that longer cooling times are needed due to the lack of active cooling.

Figure 3.8. Cyclic actuation of printed LCEAs. (A) Experimental set-up for cyclic testing of LCEA actuation. (A) The average actuation measured in the directions perpendicular and parallel to the LCEA print path (total cycles = 20). (B) The measured strain in the direction perpendicular and parallel to the print path for 3D printed LCEA bilayers when cycled above and below $T_{NI}$ (total cycles = 100).

Figure 3.9. Time response of LCEAs when thermally cycled above and below $T_{NI}$. One exemplary actuation cycle taken from cyclic actuation experiments, with strain measured in the directions perpendicular and parallel to the LCEA print path. Dashed line corresponds to original dimensions (i.e. 0% strain). Conservative time response of full actuation and return to original dimensions is approximately 390 sec.
Next, we printed thick LCEAs (1mm thick) and explored their ability to contract when tethered to different weights to demonstrate use in load bearing actuation applications including as soft robotic actuators (Fig. 3.10A). These thick actuators were printed using a nozzle diameter of 250 μm, average print speed of 3.7 mm s\(^{-1}\) and a meanderline print path. In these weight-lifting experiments, strain is calculated using the unloaded LCEA length (Fig. 3.10A, left) as the initial length, rather than the elongated length when loaded below \(T_{NI}\) (Fig. 3.10A, middle), and its final length after the loaded LCEA is heated above \(T_{NI}\) (Fig. 3.10A, right). Importantly, these thick LCEAs can lift roughly 1000 times their own weight of 106±1.5 mg. With increased weight loading, the actuation strain for the LCEAs decreases and the actuator work increases, with a maximum energy density of 39 J kg\(^{-1}\) (Fig. 3.10B). Since they are not composed of a single domain, the LCEAs can elongate upon heating or with large bias loads to a more ordered state \((220)(221)\) prior to contraction (Movie 3). If the contraction does not surpass the original length, the actuation strain is noted as a positive value, work is negative, and labeled in red in Fig. 3.10B. Upon cooling, the unloaded LCE actuators return to within 11% of their initial length. To impart larger contractile strains at even larger bias stress for a given structure, one can simply print thicker actuators. Based on the stress-strain measurements reported from loading actuators with large weights (Fig 3.10), these printed LCEAs exhibit an elastic modulus of 3.1 ± 0.3 MPa at room temperature when loaded along the print direction.
3.3.4 LCE actuator programmability and scalability

As a final demonstration, we printed LCEAs with spatially programmed directors that are capable of complex, reversible shape transformations. First, to program shape change into a cone with positive Gaussian curvature, LCEAs (of diameter 10 mm) are printed using a nozzle diameter of 250 μm and print speed of 4.5 mm s⁻¹ with four layers (0.4 mm thick) each of which is based on equivalent Archimedean spiral print paths (Fig. 3.11A). Using this type of print path (222), the

Figure 3.10. Printed LCE Actuators. (A) Image sequence obtained for a LCEA (1 mm thick) printed using a unidirectional print path lifting a 20g weight, which shows the LCEA in the unloaded (left) and loaded states with the 20g weight (middle) at $T < T_{NI}$, and the actuated state when $T > T_{NI}$ (right) (scale bar = 10 mm). (B) Specific work (work normalized by actuator mass) and actuation strain of LCEAs lifting different weights. Red highlights the weight range over which the average LCEA does not contract in positive ($x$) direction.
LCEA transforms into a cone with a maximum height of 6.5mm when heated above $T_{NI}$, which corresponds to a 1628% stroke out-of-plane. As expected, the LCEA recovers its original dimensions and shape upon cooling (Fig. 3.12A). We also printed LCEAs capable of morphing into shapes with negative Gaussian curvature with 5 mm s$^{-1}$ print speed (Fig. 3.11B). In these four-layer LCEAs (0.4 mm thick), the top and bottom pairs of layers are printed using perpendicularly oriented, in-filled meanders. Upon heating, this LCEA morphs into a saddle form. However, due to residual stresses introduced during inline UV crosslinking, it does not return to its original flat conformation upon cooling, but rather snaps into an inverted saddle configuration (Fig. 3.12B). When heated again, it snaps back into the programmed saddle configuration, and alternating actuation between both configurations is observed upon thermal cycling. Hence, after the initial actuation, this LCEA exhibits a repeatable 3D-to-3D' shape transformation. Both disks with spiral (Fig. 3.11A) or perpendicular meander (Fig. 3.11B) print paths start with similar dimensions, but undergo drastically different shape changes above $T_{NI}$, showcasing the ability of HOT-DIW to pattern a given formfactor while separately programming shape change.

HOT-DIW of LCEAS also provides a means to produce large area actuators, showcased by using two different repeat units to produce 5x5 arrays that actuate with in-plane (Fig 3.11C) or out-of-plane deformations (Fig 3.11D). We created in-plane mechanical metamaterials in the form of printed LCEA meshes with a strut width of 0.86 mm and thickness of 0.5 mm (Fig. 3.11C), which shrinks isotropically ~18% in-plane (i.e., both horizontally and vertically) and recovers to their initial dimensions upon cooling to room temperature (Fig. 3.12C). Lastly, we printed a larger LCEA (2.5 cm x 2.5 cm) capable of out-of-plane shape change (Fig. 3.11D) using a print path that consists of a square spiral array. This LCEA morphs out-of-plane into an array of cones with a
maximum height of 1.92 mm upon heating to 95°C, returning to its near-initial conformation upon cooling (Fig. 3.12D).

Figure 3.11. Programmable shape morphing LCEAs. (A, B) Images of disc-shaped LCEAs (~0.4 mm thick) printed using layered spiral (A, top) and layered perpendicular meanders (B, top) print paths (scale bars = 1 mm). Upon heating above $T_{NI}$, these LCEAs morph into a cone (A, bottom) and saddle (B, bottom) shape, respectively (scale bars are 1 mm). Top-down images of mesh-shaped LCEAs (~0.5 mm thick) after printing (C, left) and shrinking into an isotropic form (C, right) upon heating above $T_{NI}$ (scale bars = 5 mm). (D) Top view (upper row) and side view (lower row) of a LCEA sheet after printing (left) and morphing (right) into a conical array upon heating above $T_{NI}$ (scale bars = 5 mm).
In summary, we have demonstrated the ability to create LCEAs with programmed director alignment by HOT-DIW. By controlling the ink composition, rheology, and printing parameters, LCEAs were fabricated in multilayered structures with arbitrary thickness and overall dimensions. These LCEAs exhibited large contractions when heated above their nematic-to-isotropic phase transition, which enabled their exceptional actuation performance with a maximum energy density of 39 J kg\(^{-1}\) and complex shape-morphing capabilities, including both 2D-to-3D and 3D-to-3D’ transformations. Additive manufacturing of LCEA architectures opens new avenues for creating artificial muscles, soft robotics, and other dynamic functional structures based on these materials.

Figure 3.12. Optical images of printed LCEAs after actuating above \(T_{NI}\) and returning to room temperature, for representative architectures: (A) spiral disk, (B) saddle disk, (C) mesh, and (D) conical array (scale bar = 5 mm).

3.4 CONCLUSIONS

In summary, we have demonstrated the ability to create LCEAs with programmed director alignment by HOT-DIW. By controlling the ink composition, rheology, and printing parameters, LCEAs were fabricated in multilayered structures with arbitrary thickness and overall dimensions. These LCEAs exhibited large contractions when heated above their nematic-to-isotropic phase transition, which enabled their exceptional actuation performance with a maximum energy density of 39 J kg\(^{-1}\) and complex shape-morphing capabilities, including both 2D-to-3D and 3D-to-3D’ transformations. Additive manufacturing of LCEA architectures opens new avenues for creating artificial muscles, soft robotics, and other dynamic functional structures based on these materials.
CHAPTER 4

3D PRINTED LIQUID CRYSTAL ELASTOMER SOFT ROBOTIC MATTER WITH PASSIVE CONTROL OF UNTETHERED SHAPE MORPHING AND PROPULSION

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A. Kotikian*, C. McMahan*, E. C. Davidson, J. M. Muhammad, R. D. Weeks, C. Daraio, J. A. Lewis
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4.1 INTRODUCTION

Soft robots are versatile in ways that rigid systems are not. Their compliant nature allows them to safely interact with living organisms (223, 224) and fragile objects (224, 225). They can perform complex motions as a result of simple actuation inputs (226–228), conform to arbitrary geometries (229), perform multi-gait propulsion (58), morph into different shapes (58, 230), and withstand large deformation or impact without damage (231). However, challenges associated with the integration of untethered, fully soft actuation modalities currently limits their broader utilization. To date, soft robots have primarily relied on pneumatic networks embedded within elastomeric matrices for actuation and propulsion (58, 224, 228, 232). Yet most pneumatically actuated soft robots must be tethered to rigid power and control systems to generate sufficient forces for locomotion (228, 233). Recently, active materials that self-actuate in response to environmental stimuli have been explored as an alternative for soft robots. These materials are compelling options to achieve shape-change and locomotion in response to external stimuli such as temperature, light, and chemical gradients (234–238), as well as to stimuli from other elements embedded in their structural frame, such as electric fields and current (227, 239–241). However, active materials still require advancements to overcome several limitations. For example,
electroactive actuators must be tethered to rigid power sources (240, 241), shape-memory polymers require manual reprogramming (88, 238, 242), bilayer strips made of materials that undergo differential growth are volumetrically expensive (239, 243, 244), and hydrogel-based actuators need pairing with pneumatic systems to produce large forces quickly (223, 245).

The creation of untethered, soft robots that perform complex tasks is difficult. For example, pneumatically actuated soft robots typically undergo large deformations across their entire structural frame (58, 231). Predicting the kinematics of these systems is not straightforward, since nonlinear elastic models that satisfy a diverse set of boundary conditions are required. These challenges are compounded when the implementation of control systems is desired. Origami-based strategies offer a compelling alternative for designing soft robots that exhibit large shape changes through a reduced set of predictable motions. One can greatly simplify the design space by localizing deformations to creases within the robotic structure, e.g., using actuating hinges connected to planar facets. Recently, reconfigurable robots with rigid on-board power sources and electronic controls have been constructed by this method (246–249).

Soft robots may also benefit from hinge-based actuation, in which compliant, energy dense actuators are placed at creases, while stiffer structural elements serve as planar facets (250). Folding patterns can be modelled and predicted geometrically using existing mathematical tools (251–253). The design and implementation of controls in origami-based untethered systems can be achieved solely through the constitutive response of the actuating hinges, while locomotive gaits can be encoded within their frames via programmable folding sequences. While controlled folding sequences have been realized in rigid and hybrid (soft/rigid) systems (246, 254), fully soft systems implemented to date are typically irreversible (88, 238, 255), geometrically constrained (256) or tethered to rigid power sources (239, 257). New advances are needed to generate
untethered soft robots that exhibit repeatable actuation (258), self-morphing (245) and self-propulsion in response to external stimuli (259).

Liquid crystal elastomers (LCEs) have recently emerged as a promising class of soft active matter, since they generate large, powerful, and repeatable deformations upon heating above their nematic-to-isotropic transition temperature ($T_{NI}$) (260, 261). The direction of contractile strain (director) can be programmed by aligning rigid mesogens during fabrication (260, 261). In addition to thermal stimuli, LCEs that respond to electric (262), light (107, 263), or chemical stimuli (234, 264) have been synthesized. However, despite their remarkable behavior, LCEs have not been widely integrated within untethered robotic structures due to fabrication challenges that relegate them to simple unidirectional actuators (260) or voxelated thin films (~50 µm thick) (264, 265). These LCEs are either too compliant to support large loads or lack the capability to output large torques in compact, untethered arrangements (174, 239, 266, 267). Moreover, attempts to achieve LCE-based untethered locomotion limits actuators to very small sizes, a reliance on structured light, and a lack of integrability with other functional components (235–237, 268). Recently, voxelated LCEs have been produced in thick film geometries (~1 mm thick) via 3D printing (269–271). These 3D LCEs actuate reversibly and exhibit large work capacities. However, facile fabrication methods that enable LCE actuators with programmed director alignment to be combined with soft structural materials have not yet been demonstrated in a single-step process.

In this chapter, we focus on creating untethered, soft robotic matter that can reversibly shape-morph and propel itself in response to thermal stimuli. Specifically, we printed LCE hinges that interconnect structural polymeric tiles to produce active architectures that exhibit large, repeatable deformations. Using this method, the folding orientation, hinge angles, and actuator geometry are fully programmable. By incorporating LCEs with two different $T_{NI}$, we created soft
robotic matter that exhibits sequential folding and unfolding in response to different temperatures. Through an integrated design and manufacturing method, we demonstrated simple embodiments of origami-inspired soft robots, whose shape morphing and self-propulsion are passively controlled both thermally and temporally via the constitutive response of the printed matter. As a proof-of-concept, we produced an origami-based architecture that can assume three different stable geometrical configurations, depending on its history of temperature exposure. Next, we characterized the mechanical response of the active hinges, which generate a torque capable of folding and lifting printed objects that are more than two orders of magnitude heavier than the hinges themselves. Finally, we exploited their torque response to create a printed (flat) structure that reconfigures to a pentagonal prism and propels itself by rolling on a hot surface, which we refer to as a “rollbot.”

4.2 EXPERIMENTAL METHODS

4.2.1 Ink formulations and characterization

Both LCE inks are synthesized in one-pot approaches to decrease processing steps and to provide large batches of ink necessary for 3D printing (Fig. 4.1). The LCE ink with lower \( T_{NI} \) (\( L_{NI} \)) is synthesized by a previously reported thiol-acrylate “click” reaction (270). As-received 2,2’-(ethylenedioxy)diethanethiol (Sigma-Aldrich), 1,4-Bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]-2-methylbenzene (Wilshire Technologies, Inc.), 1,4-bis-[4-(3-acryloyloxypropypropyloxy) benzoyloxy]-2-methylbenzene (Matrix Scientific), and (1,3,5-triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)- trione (Sigma-Aldrich) in mole ratio 1.0:0.6:0.2:0.133, and 1 wt% triethylamine (Sigma-Aldrich), 2 wt% butylated hydroxytoluene (Fisher Scientific), and 1.5 wt% Irgacure 651 (BASF) are melted and mixed in an amber scintillation vial with a heat gun (Milwaukee, MHT3300) and vortex for approximately 5 min. The reaction is subsequently
heated and stirred for 3 hrs at 65 °C in an oil bath. The LCE ink with higher $T_{NI}$ ($H_{NI}$) is synthesized by a previously reported aza-Michael addition method (269). As-received 1,4-Bis-[4-(6-acryloyloxyhexyloxy) benzoyloxy]-2-methylbenzene and n-butyl amine (Sigma-Aldrich) in 1.1:1 mole ratio, 0.2 wt% butylated hydroxytoluene, and 2 wt% Irgacure 651 are added to a 25 mL round bottom flask fitted with a condenser. The reaction is stirred at 105 °C for 18 hrs while shielded from ambient fluorescent light.

![Figure 4.1. Ink schemes.](image)

(A) Ink scheme of $LT_{NI}$ ink. Two mesogens with different spacings (n=3,6), a dithiol chain extender, and a tri-vinyl crosslinker are combined with catalyst triethylamine (TEA), inhibitor (BHT) and photoinitiator (PI). (B) Ink scheme of $HT_{NI}$ ink. One mesogen (m=6) and primary amine chain extender are combined with inhibitor (BHT) and photoinitiator (PI).

The structural tile ink is prepared by mixing Ebecryl 8413 resin (Allnex) and pentaerythritol tetraacrylate (TCI Chemicals) in a 1:1 weight ratio with 10 wt% fumed silica (EH-5, Cabot), and 4 wt% Irgacure 651. Irgacure 651 is added as a solution in dichloromethane (Sigma-Aldrich) at a concentration of 750 mg/mL. After each reagent is added, the ink is mixed in a SpeedMixer (FlakTek, Inc.) for approximately 3 min. The solvent is evaporated before printing. Best results for printing are yielded when the structural ink is shielded from light and used within
two weeks of preparation. An Instron tensile testing machine is used to measure the stiffness of dogbone-shaped structural tiles.

The respective $T_{NI}$ of each oligomeric LCE ink is determined by differential scanning calorimetry (DSC) measurements (TA Q200 calorimeter). Un-crosslinked LCE ink samples (10-15 mg each) are hermetically sealed inside TZero aluminum pans. Samples are analyzed via a heat-cool-heat cycle between -50 °C and 150 °C with ramp rates of 10 °C/min to clear the thermal history on the first heating ramp, and to access both the glass transition temperatures and nematic-to-isotropic transition temperatures of the inks. Samples are held isothermally for one minute at both the high and low temperatures. Data from the second heating ramp is analyzed to determine their $T_g$ and $T_{NI}$ values.

The rheological properties of inks are measured using a controlled-stress rheometer (Discovery HR-3 Hybrid Rheometer; TA Instruments) equipped with a 20 mm peltier plate geometry with 250 µm gap. Prior to each test, LCE inks are brought to 100 °C, then to testing temperature for 300s to erase structural history of the inks during the loading process. During the viscometry measurements, shear rate is swept from 0.001 s$^{-1}$ to 1000 s$^{-1}$. During the oscillatory measurements, stress is swept from 0.01 Pa to 1000 Pa at 1 Hz. The rheological properties of the elastomeric ink used to pattern the structural tiles are measured using a 40 mm cone geometry under ambient conditions. During the viscometry measurements, the ink viscosity is measured as the shear rate is increased from 0.0001 s$^{-1}$ to 10,000 s$^{-1}$. During the oscillatory measurements, its storage and loss moduli are determined by carrying out stress sweeps from 0.0001 Pa to 10000 Pa at 1 Hz.

Alignment of printed LCE samples is characterized by X-ray scattering measurements on a SAXSLAB system with a Rigaku 002 microfocus X-ray source ($\lambda = 1.5409$ Å) with a sample to
detector (PILATUS 300 K) distance of 109 mm to capture the mesogen-mesogen correlations at q ~ 1.5 Å\(^{-1}\). WAXS samples consist of two-layer printed LCE unidirectional strips (200-250 µm thick). Samples are exposed for 300 seconds. Data reduction is performed using the Nika Macro for Igor Pro. The Herman’s orientational order parameter \( \langle P_2 \rangle \) is calculated by extracting the intensity of the mesogen scattering peak as a function of azimuthal angle, masking low-intensity regions due to the beamstop and gaps in the PILATUS 300K detector, and then using a custom MATLAB script. The order parameters of printed \( LT_{NI} \) and \( HT_{NI} \) LCEs are 0.1707 and 0.2688, respectively.

Unbiased linear actuation of unidirectional LCE as a function of temperature is determined by increasing temperature at 4 °C/min with a programmable heating stage (Instec, modified HCS302) on 20 x 5 x 0.375 mm unidirectional samples from 25 °C to 150 °C. The stage is covered in a thin layer of silicone oil to enhance heat transfer and reduce friction. Images are collected from above every 15 s via a Canon EOS Rebel T2i camera with a Canon 100 mm macro lens and dimensions are analyzed via ImageJ.

4.2.2 Fabrication and operation of programmable soft matter

LCE hinges are printed using a customized HOT-DIW printhead (operating at T < 100 °C). The printhead is comprised of a machined copper block that is designed to couple to a Nordson 3 cc high pressure adapter (Nordson EFD). For heating control, an RTD sensor in the block (Omega) monitors the temperature adjacent to the nozzle, two 100 W ¼ x 2 in cartridge heaters (Omega) in the copper block provide heating, and a Teflon mounting block provides insulation. Feedback control is provided via an Omega platinum series single zone temperature controller. The LCE inks are loaded into a custom SS 3cc syringe with a 250 µm nozzle (TecDia, Inc.). \( LT_{NI} \) and \( HT_{NI} \) inks are printed at 26°C and 50-55°C and at print speeds of 25 mm/s and 28 mm/s, respectively.
Both are printed at a print height of 0.125 mm, filament spacing of 0.125 mm, and a pressure of 455 psi using a 3 cc high pressure adapter controlled with a pressure box (Ultimus V, Nordson EFD). On-the-fly UV curing (Omnicure S2000) is carried out at 20,000 µW/cm\(^2\) for the \(LT_{NI}\) LCE ink and 8000 µW/cm\(^2\) for the \(HT_{NI}\) LCE ink. Structural tiles are printed by extruding the ink through a 410 µm tapered nozzle (Nordson EFD), at an average speed of 30 mm/s, print height of 0.25 mm, filament spacing of 0.2 mm and pressure of 60 psi (Ultimus V, Nordson EFD). Structural tiles are printed to connect LCE hinges after all LCE components are completed. Inks are printed using our multi-material 3D printer (customized ABG 10000, Aerotech Inc) and G-Code (MeCode). All samples except the shape-morphing element and self-propelling structure are printed on an untreated glass slide (VWR). The triangulated polyhedron and the self-propelling structure are printed on a sacrificial polyvinyl alcohol (Sigma-Aldrich, 99% hydrolyzed) coated glass substrate. After printing, all samples are crosslinked upon exposure to UV light (6,000 µW/cm\(^2\)) for approximately 15 min per side.

The triangulated polyhedron, which can assume three different geometrical configurations, is fully printed in a single step in a flat configuration. The 3D configuration is achieved by bonding the edges of outlying LCE hinges to structural tiles with the structural ink and UV crosslinking. All hinges in the structure are 0.5 mm thick and 6 mm wide. The triangulated polyhedron is actuated in two steps. First, it is placed in an oven at 100 °C to actuate the \(LT_{NI}\) LCE hinges. Next, it is placed in an oven at 155°C to actuate the \(HT_{NI}\) LCE hinges.

The self-propelling structure is printed with \(LT_{NI}\) LCE hinges that are 0.75 mm thick and 4 mm wide and \(HT_{NI}\) LCE hinges that are 0.5 mm thick and 2 mm wide. The last HT\(_{NI}\) LCE hinge that propels the structure at the open vertex of the pentagonal prism is 0.5 mm thick and 4 mm wide. The self-propelling structure is tested on a substrate with sand-covered silicone adhesive.
(Rutland). The substrate is heated with a hotplate to have a surface temperature of approximately 200°C. To provide a heated and convective environment, a space heater (Sunbeam) is placed 4” in away and set at 27 °C. To ensure a thin boundary layer of heat at sand surface, a fan is used. Both the convective heater and fan are aligned to be parallel to the self-propelling structure.

4.2.3 Characterization of programmable soft matter

Images of actuated origami samples that demonstrate programmed mountain and valley folds are taken in an oil bath of temperature 125°C acquired from above. The hinge used to demonstrate large torque capabilities is heated with a heat gun (Milwaukee, MHT3300) until the sample is optically clear, indicating full actuation. All unbiased folding angle measurements are conducted by printing one stiff panel longer than the other to fit in an acrylic holder perpendicular to the panel face. Hinges are printed as mountain folds unless otherwise specified. The hinges are inverted into an oil bath of the temperature of measurement and imaged from above with a camera (Canon EOS 5D Mark III). For repeatable bending measurements, hinges are alternated between room temperature and a hot oil bath. For $LT_{NI}$ and $HT_{NI}$ LCE hinges, the oil bath is at 120°C and 150°C, respectively. Images are taken after 30 s in the hot oil bath and after 2 min at room temperature. Images of a sequential folding structure with one $LT_{NI}$ and one $HT_{NI}$ hinge are taken from above as samples are heated from room temperature to 150 °C in an oil bath and cooled passively to room temperature again. Edges of all hinges analyzed for bending angle are colored black with permanent marker (Sharpie) to enhance contrast for image analysis (MATLAB). All images analyzed for bending angle are taken using a Canon EOS 5D Mark III camera from above.

To measure their torque output, one of the LCE hinges’ structural panels is fixed to a rotary stage that is used to control hinge angle (Fig. 4.2). The second panel is attached to a thin string 10 mm away from the edge of the LCE. The string, with negligible bending stiffness, is axially stiff
and is fixed to a force sensor at the other end. A linear stage is used in conjunction with the near-inextensible string for fine tuning the target hinge angle, ensuring that the force vector being measured by the sensor is normal to the second hinge panel and to the sensor plate. The actuators are heated using a 24W metal ceramic heater (Thorlabs, Inc.), causing them to bend away from the sensor until reaching the target hinge angle. At this target angle, the string experiences axial forces, which are measured by a Mettler Toledo XS205 scale. The measured force plateaus with the completion of the nematic-to-isotropic phase transition. Torque cycling experiments are carried out at a 0° hinge angle by turning the heater off upon reaching full actuation.

![Figure 4.2. Torque measurement experimental setup.](image)

Torque of the LCE hinges can be measured (left) as a function of angle $\theta$ by rotating a rotary stage (right). The force sensor is attached to the hinge at the end of the panel, approximately 1 cm from the edge of the LCE component, which is in contact with a thin heater. A linear stage is used to ensure that the hinge tile attached to the force sensor is parallel to the sensor surface. Scale bars are 1 cm.
4.3 RESULTS AND DISCUSSION

4.3.1 Printing active hinges and structural tiles

The active hinges and structural tiles used for soft robotic matter are fabricated as shown in Figure 4.3. The hinges are composed of LCE bilayers that exhibit orthogonally programmed nematic order, which interconnect each structural tile. All inks are formulated with the desired viscoelastic behavior needed to facilitate direct ink writing (Fig. 4.4) (272). For extrusion through small nozzles, hinge materials are printed at a temperature at which they are shear thinning (Fig. 4.4). The LCE inks are solidified with in situ photocrosslinking and do not require a yield stress (Fig. 4.4). The structural tile ink is shear thinning and requires a yield stress to maintain its printed form upon extrusion as it is only crosslinked after the structure is printed (Fig. 4.4).

Two oligomeric LCE inks are synthesized with low and high $T_{NI}$ values of 24°C and 94°C and are referred to as $LT_{NI}$ and $HT_{NI}$ inks, respectively. Such differences arise due to disparities in their backbone flexibility and crosslinking chemistry (Fig. 4.5). The $LT_{NI}$ ink is composed of a thiol-terminated liquid crystalline oligomer and tri-vinyl functionalized crosslinker (270), while

![Figure 4.3. 3D printing of active hinges.](image-url)
the $HT_{NI}$ ink is composed of an acrylate-terminated liquid crystalline oligomer analogous to previously reported inks composed of main-chain mesogens (264, 269, 271, 273) (Fig 4.1). To ensure strong adhesion between the printed hinges and tiles, the structural ink used for printing the structural tiles is composed of a photopolymerizable diacrylate resin and an acrylate crosslinker that chemically binds to the reactive LCE groups. Chemical adhesion between LCE hinges and structural tiles is necessary to withstand large actuation strains at the hinge interface. The ink

**Figure 4.4. LCE and structural polymer ink rheology.** (A) Apparent viscosity as a function of shear rate for $LT_{NI}$ and $HT_{NI}$ LCE inks at printing temperature 26°C and 55°C, respectively. (B) Storage ($G'$) and loss ($G''$) moduli as a function of shear stress at 1 Hz for $LT_{NI}$ and $HT_{NI}$ LCE inks at the respective printing temperatures of 26°C and 55°C. (C) Apparent viscosity as a function of shear rate for the structural polymer ink under ambient conditions. (D) Storage ($G'$) and loss ($G''$) moduli as a function of shear stress at 1 Hz for the structural polymer ink under ambient conditions.
rheology is modified by adding fumed silica to achieve the desired yield stress and a shear thinning behavior needed for printing (Fig. 4.4).

The LCE inks are printed using high operating temperature direct ink writing (HOT-DIW) (269). To facilitate director alignment during printing, the $LT_{NI}$ ink is printed at 26°C, while the $HT_{NI}$ ink is printed at 50-55°C (Fig. 4.4) (269). Ink crosslinking is photo-initiated immediately upon printing to lock-in the programmed director alignment along the print path, and confirmed by WAXS (Fig. 4.6). After printing and cross-linking, the low $T_{NI}$ LCE structures become fully isotropic at 92 °C, while high $T_{NI}$ LCE structures do so at 127°C (269, 271) enabling these structures to sequentially actuate in response to thermal stimuli (Fig. 4.7). We note that LCE actuation can occur over a wide temperature range (270). Unidirectionally printed $HT_{NI}$ LCE films (0.375 mm thick) exhibit a repeated contraction of -49.8 ± 0.9% along the printing direction and an expansion of 41.7 ± 5.7% perpendicular to that direction, while the $LT_{NI}$ LCEs exhibit respective values -31.1 ± 0.6 and 21.5 ± 0.6% (Fig. 4.7). The structural tiles are printed under ambient conditions via DIW. The placement of each structural tile induces a bending axis that is parallel to

![Differential scanning calorimetry curves for the LCE inks.](image)

**Figure 4.5. Differential scanning calorimetry curves for the LCE inks.** The $LT_{NI}$ and $HT_{NI}$ values are approximately 24°C and 94°C, respectively, for the two oligomeric LCE inks. [Note: The $T_g$ and smectic-to-nematic transition temperature ($T_{SN}$) for the $HT_{NI}$ ink are approximately -20 °C and 20 °C, respectively.]
Figure 4.6. LCE alignment. 2D wide angle X-Ray scattering patterns of unidirectional printed (A) $LT_{NI}$ and (B) $HT_{NI}$ LCEs. (C) Normalized intensity as a function of azimuthal angle. (D) Normalized radial intensity as a function of the momentum transfer vector $q = (4\pi/\lambda) \sin \theta$.

Upon curing, the printed tiles exhibit a stiffness of $766 \pm 41$ N/m.

Figure 4.7. Actuation response of unidirectional printed LCEs. The measured contractile and expansion strain observed perpendicular and parallel to the print direction, respectively, as a function of temperature for unidirectional aligned LCE actuators printed from $LT_{NI}$ and $HT_{NI}$ inks [Note: Sample dimensions are approximately $20$ mm x $5$ mm x $0.375$ mm.]
MPa, which provides the structural integrity to prevent collapse of the printed architectures under self- and applied loading conditions.

To achieve controlled bending, each LCE hinge is fabricated in a “bilayer” design, in which the bottom half is composed of multiple layers printed along the same direction and the top half is composed of multiple layers printed in the orthogonal direction (Fig. 4.3, left). A spontaneous strain mismatch causes each hinge to bend when heated above their actuation temperature. We chose an orthogonal bilayer design because the spontaneous strains in each layer favor a single bending direction around a given axis. Consequently, greater curvatures are achieved compared to bilayer hinges composed of a top LCE layer and a bottom inactive layer (266, 267). The folding orientation of each LCE hinge is defined by the print path. The bilayer (bottom/top) orientation relative to the printing direction determines whether they exhibit mountain (0°/90°) or valley (90°/0°) folds (Fig. 4.8A). Because self-folding is reversible, the printed structures can be repeatedly actuated by cycling above and below their respective actuation temperatures. To demonstrate this, we printed both mountain and valley hinges in a simple structure composed of two LCE hinges that interconnect three structural tiles, as shown in Fig. 4.8A (center), which repeatedly folds and unfolds without manual intervention. By varying the specific arrangement of active hinges and structural tiles, we can realize more complex self-folding structures, including the square twist unit cell shown in Fig. 4.8B. In both cases, the architectures contain hinges printed using a single LCE ink (HTNI). Below, we demonstrate the broad versatility that arises from the integration of multiple LCE hinges of different TNI values with structural tiles.
Sequential self-folding is essential for untethered origami-inspired structures, as this capability enables collision prevention during shape-morphing and locomotive gaits with multiple degrees of freedom triggered by distinct stimuli (250, 255). By printing LCE inks with different actuation temperatures, we can create soft robotic matter with programmable sequential folding upon heating (Fig. 4.9A). The unbiased bending angle (where hinges do not bear a load) increases with temperature for both $LT_{NI}$ and $HT_{NI}$ LCE hinges. From direct observations, we find that both the onset and completion of folding for the $LT_{NI}$ LCE hinges occurs at significantly lower

**Figure 4.8. 3D printing of soft robotic matter.** (A) The LCE hinges are printed in the form of $0^\circ/90^\circ$ and $90^\circ/0^\circ$ bilayers, which bend into mountain and valley folds, respectively, when actuated above $T_{NI}$. A simple structure composed of two hinges, with mountain and valley folds, that interconnect three structural tiles is shown as-printed (middle, top) and as-actuated (middle, bottom). (B) A more complex, square-twist reconfigurable structure is printed (left) and actuated at 125 °C (right). The hinges that form the central square and the four hinges that point toward the center of the structure (left) are mountain folds, the others are valley folds. All scale bars are 1 cm.

**4.3.2 Programmed sequential folding**

Sequential self-folding is essential for untethered origami-inspired structures, as this capability enables collision prevention during shape-morphing and locomotive gaits with multiple degrees of freedom triggered by distinct stimuli (250, 255). By printing LCE inks with different actuation temperatures, we can create soft robotic matter with programmable sequential folding upon heating (Fig. 4.9A). The unbiased bending angle (where hinges do not bear a load) increases with temperature for both $LT_{NI}$ and $HT_{NI}$ LCE hinges. From direct observations, we find that both the onset and completion of folding for the $LT_{NI}$ LCE hinges occurs at significantly lower
Figure 4.9. Untethered, sequential, and reversible folding of active hinges. (A) Chemical composition of the $LT_{NI}$ (blue) and $HT_{NI}$ (orange) oligomeric LCE inks (where $n=3$ and 6, and $m=6$ in the molecular structures). (B) Bending angle $\theta$ as a function of temperature for $LT_{NI}$ and $HT_{NI}$ LCE hinges with length of 10 mm, width of 4 mm, and thickness of 0.25 mm. (C) A printed structure composed of $LT_{NI}$ and $HT_{NI}$ LCE hinges with mountain folds that interconnect three structural tiles, which undergoes sequential actuation when heated (left to center) and cooled (center to right). The scale bar is 1 cm. (D) Bending angle $\theta$ as a function of thickness, $h$, for $LT_{NI}$ and $HT_{NI}$ LCE hinges of fixed length of 10 mm and width of 3 mm. Their bending angle decreases with thickness. Other bilayer systems display inverse proportionality between curvature and thickness (275–277). We plot this relationship, where $c$ is a constant, for comparison. Both hinges exhibit a maximum bending angle of 180°, where panels contact one another. (E) Bending angle $\theta$ as a function of hinge width, $w$, for $LT_{NI}$ and $HT_{NI}$ LCE hinges of fixed length of 10 mm and thickness of 0.5 mm.
temperatures, relative to their \( HT_{NI} \) counterparts (Fig 4.9B). Specifically, the \( LT_{NI} \) LCE hinges begin to fold below 40°C, while the onset of folding occurs near 60°C for \( HT_{NI} \) LCE hinges.

We note that due to residual stress from crosslinking in the isotropic phase (274), thin \( LT_{NI} \) LCE hinges possess a negative bending angle under ambient conditions (Fig. 4.10). While both types of hinges can achieve a 180° folding angle, their temperature response depends strongly on their composition and overall dimensions (Figs. 4.10-4.11). Leveraging these capabilities, we printed a simple structure that integrates both \( LT_{NI} \) and \( HT_{NI} \) LCE mountain hinges, which interconnect three structural tiles and sequentially actuate when heated (Fig. 4.9C). As expected, the \( LT_{NI} \) LCE hinge folds completely before the \( HT_{NI} \) LCE hinge actuates. The structure unfolds in reverse upon cooling to room temperature, i.e., the \( HT_{NI} \) LCE hinge unfolds to its flat configuration first, followed by the \( LT_{NI} \) LCE hinge. This demonstration highlights our ability to create soft robotic matter with reversible programmed sequential folding in untethered motifs.

**Figure 4.10. Bending angle as a function of temperature.** Bending angles \( \theta \) of (A) \( LT_{NI} \) and (B) \( HT_{NI} \) LCE hinges (0.25 mm thick) with varying width \( (w=1-4 \text{ mm}) \) as a function of temperature. Due to residual stress in printed \( LT_{NI} \) LCE hinges, their measured bending angle is negative at low temperatures.
Folding temperatures are programmed by the LCE chemistry and hinge angles are prescribed geometrically by the printing process. We define the hinge length and width as the in-plane geometric parameters in the directions parallel and perpendicular to the folding axis, respectively. The hinge thickness is defined in the surface normal direction and is varied in discrete increments of 0.25 mm, which corresponds to twice the print height used during HOT-DIW. By varying the number of printed layers, we produce hinges with thicknesses between 0.25 mm (1 layer in each direction) and 1 mm (4 layers in each direction). The spontaneous curvature that the actuators assume at temperatures above $T_{NI}$ scales with inverse hinge thickness (Fig. 4.9D), akin to other bilayer systems (275–277). $HT_{NI}$ LCE hinges can exhibit greater unbiased folding angles compared to $LT_{NI}$ LCE hinges of identical geometry (Fig. 4.11) because the strain differential between the directions parallel and perpendicular to alignment is greater for the former than the latter. Curvature scales with the strain differential across layers (275, 276). For a given hinge thickness, the folding angle increases proportionally with the hinge width (Fig 4.9E), as the curvature remains constant when their width is varied. Since our additive manufacturing approach

**Figure 4.11. Bending angle as a function of hinge dimensions.** Bending angles of LCE hinges of varying thickness ($h$) and width ($w$), when actuated above their $T_{NI}$. Hinge angles $\theta$ are measured at 120°C and 150°C for the $LT_{NI}$ and $HT_{NI}$ LCE hinges, respectively. Maximum bending angle is 180° due to panel collision.
is both scalable and flexible, there is no limit on the hinge thickness or geometry. However, near the edges of the LCE where the nozzle changes direction in a semicircular arc, the director is not aligned in the direction of the rest of the LCE layer. This misalignment imposes a minimum hinge width that must exceed two nozzle diameters (0.25 mm).

We note that the minimum film width also increases with hinge thickness, since the misalignment radius increases for LCE layers printed on themselves compared to on the underlying glass substrate (i.e., first layer). This misalignment effect causes hinges printed as valley folds to have marginally smaller bending angles compared to those with mountain folds, since their top layer is parallel to hinge width, which is a smaller in-plane geometric parameter than hinge length (Fig. 4.12). The printed LCE hinges can bend repeatedly without bias weight and their maximum folding angle remains constant over multiple heating and cooling cycles (Fig. 4.13). Their repeatable actuation is an essential feature for untethered soft robotic applications that operate without manual intervention.

![Figure 4.12. Valley fold bending angles.](image)

Printed LCE hinges (0.25 mm thick) of varying width w exhibit valley folds with smaller bending angles \( \theta \) than their mountain fold counterparts.
We next demonstrate that soft robotic matter can be designed and printed with geometric locking mechanisms. As one example, we created the triangulated polyhedron shown in Figure 4.14, which is based on a well-known origami design (278). The structure is printed in a planar layout (Fig. 4.14A) before manually joining the edges (Fig. 4.14B) to create an open polyhedron that is stable at room temperature (Fig. 4.14C). The top and bottom sections of the polyhedron are identical, except for that different LCE inks are used to print their respective hinges. Specifically, the top section contains $LT_{NI}$ LCE hinges that facilitate folding into a compacted form when heated above 95°C. The bottom section contains $HT_{NI}$ LCE hinges that remain unfolded when the top layer actuates (Fig. 4.14D), yet compact when heated above 155°C (Fig. 4.14E). An environment temperature that is well above the $T_{NI}$ of both materials is used to accelerate the folding process. All hinges are constructed with a 6 mm width and 0.5 mm thickness to ensure 180° folding angles upon actuation.

**Figure 4.13. Repeatable hinge folding.** Bending angles $\theta$ of $LT_{NI}$ and $HT_{NI}$ LCE hinges (0.25 mm thick and 2 mm wide) when cycled above and below $T_{NI}$. 
This geometry is stable after each intermediate folding stage even if the structure is returned to room temperature (Fig. 4.15). This behavior is similar to what is observed in paper-origami structures that lock in intermediate folding states due to bending of the facets between two flat-faceted states (278, 279). Guest and Pellegrino (278) provide a good overview of these multi-stable geometries and their kinematics. The observed behavior (Fig. 4.14-4.15) for these printed structures suggest that a variety of multi-stable architectures can be created by our approach.
4.3.3 Programmed untethered self-propulsion

Untethered self-propulsion is a requirement for autonomous and pre-programmed robotic systems that navigate large distances in uncertain environments (242). This poses challenges, especially given that untethered operation often requires onboard power and control systems that add mass to the robot (245, 280). LCE bilayers offer a promising option for these tasks, because they are energy-dense and are capable of performing multiple loading and unloading cycles in response to external stimuli. However, due to the inherently soft nature of LCE hinges, large external moments induce bending and lead to actuated hinge angles that are different from the unloaded hinge measurements (Fig. 4.9).

As an example, a printed $LT_{NI}$ LCE hinge achieves a 79° bending angle when unbiased (Fig. 4.16A), but when a 10 g mass is suspended 1 cm away from the hinge at room temperature, it deflects to -72° due to its compliance. When heated above $T_{NI}$, the hinge bends by 55° and the mass is lifted 6.5 mm (Fig. 4.16B), corresponding to a work output of approximately 0.06 mJ. This actuation is remarkable for a soft actuator with dimensions 10 mm x 3 mm x 1 mm. It corresponds to an energy density of 29.3 J/kg when accounting for the combined mass (22 mg) of the LCE.
hinge and structural panels, which is in good agreement with our previous chapter (269). Indeed, the mass of the lifted object is more than 450 times greater than the hinge mass.

**Figure 4.16. Torque capacity of printed active hinges.** (A) $LT_{NI}$ LCE hinge (10 mm x 4 mm x 1 mm) folds to a 75° bending angle while unbiased. (B) When a 10 g mass is suspended 1 cm away from the LCE hinge at room temperature, it deflects to -72°. The mass is lifted by approximately 1 cm when actuated above $T_{NI}$. (C) Exerted torque as a function of hinge folding angle, $\theta$, as defined by the inset. Hinge composition and thickness $h$ are the primary factors that affect torque output. (D) LCE hinges (5 mm x 3 mm x 0.5 mm) undergo multiple actuation cycles with negligible changes in the torque output. All scale bars are 1 cm.

We quantified the torque output of LCE bilayer hinges to further explore their suitability for reconfigurable and propulsive soft robots. Both types of LCE hinges are tested in different geometries. For a given thickness, $LT_{NI}$ LCE hinges output more torque than their $HT_{NI}$ counterparts (Fig. 4.16C). Torque increases with hinge thickness for both LCE chemistries, but diminishes with increasing folding angle (Fig. 4.17). Consequently, heavier self-assembling and self-propelling structures will require hinges that are capable of greater torque outputs, as hinges will only fold until there is an equilibrium between external moments and their curvature-
dependent torque capacity. Torque output remains constant over multiple heating and cooling cycles (Fig. 4.16D), which is essential for repeatable propulsion in untethered robots. We notice an asymmetry in the torque produced by the actuators when heated compared to the relatively lower restoration torque exerted by hinges during cooling. This asymmetry is a disadvantage for applications that require large torque outputs in both rotational directions, but leads to energy savings in deployable structures that require a permanent post-actuated configuration, such as the

Figure 4.17. Torque measurements for hinges of varied dimensions. $h$ indicates hinge thickness in mm, $w$ indicates hinge width in mm, and $\theta$ is the folding angle.
printed structure shown in Figure 4.14, which remains locked in a post-actuated configuration rather than unfolding under ambient conditions.

We exploited the large torque output by the printed LCE hinges to achieve passive control of self-assembly and propulsion in a rolling architecture (i.e., rollbot) (Figure 4.18). The entire structure is printed flat with a total mass of 1.67 g. The structural frame is composed of two outer rails that use $LT_{NI}$ LCE hinges to morph from a flat state (Fig. 4.18A) to a pentagonal prism with edge lengths of 15 mm (Fig. 4.18B). These rails are connected by bridges that hold propelling $HT_{NI}$ LCE hinges. A hot plate held at an average surface temperature of 200°C and a convective environment that sustains the ambient temperature at 45°C are used to passively induce the desired assembly and rolling motion. Under these conditions, the $LT_{NI}$ LCE hinges actuate to a $\sim 72^\circ$ hinge angle and remain folded throughout the rolling process due to the modest difference between their $T_{NI}$ and the ambient temperature even away from the hot plate. The actuated $LT_{NI}$ hinges provide enough torque to keep the structure in the pentagonal shape during rolling, so that a locking mechanism is not necessary.

A free body analysis is used to determine the torque requirements for shape reconfiguration and propulsion (Fig. 4.19). To transform into a pentagonal prism, the $LT_{NI}$ LCE hinges must have a minimum torque output of 9.9 mN-cm at a $0^\circ$ hinge angle (flat configuration) and a sustained torque of 0.3 mN-cm when fully folded (Fig. 4.20). Given these torque and angle requirements, we printed $LT_{NI}$ LCE hinges with a width of 4 mm and a thickness of 0.75 mm. In the assembled 3D configuration, the $HT_{NI}$ LCE hinges actuate when in contact with the hot plate, rolling the structure over the adjacent vertex and onto the next hinge, which carries out the same action. Propelling the structure over vertices requires a $36^\circ$ tipping angle, and the corresponding torque needed to initiate this action is 6.9 mN-cm exerted by the hinge (Fig. 4.20). To realize this, we
printed $HT_{Ni}$ LCE hinges that are 2 mm wide and 0.50 mm thick as propelling actuators. These hinges are also printed with a 4 mm offset from the tipping vertex to provide mechanical advantage. Due to this offset, $HT_{Ni}$ LCE hinges must fold by 63°. A greater hinge angle is needed...
Figure 4.19. Free body diagrams of self-propelling rollbot. (A) Moment diagrams for calculating the torque at the \( LT_{NI} \) LCE hinge (b) that requires the greatest torque for self-reconfiguration into a pentagonal prism. Here, \( m \) is the mass of each panel, \( g \) is gravitational acceleration, \( L \) is the length of each panel. (B) Moment diagrams for calculating the torque requirements of \( HT_{NI} \) LCE hinges that induce self-propulsion. Here, \( M \) is the entire mass of the structure, \( \epsilon \) is the offset of the center of mass C.M. from the tipping point, \( l \) is the length of the propelling plate, \( \delta \) is the offset of the hinge from the tipping vertex, \( \phi \). A no-friction assumption is taken for the contact between the structure and the ground. Only forces that affect a torque about the tipping point are shown for clarity in the image.
for tipping over an open vertex, so 4 mm $HT_{NI}$ LCE hinges are used for propulsion over a small gap. Both $LT_{NI}$ and $HT_{NI}$ LCE hinge dimensions are chosen based on the torque measurements described above, and a pentagonal frame is selected to showcase the torque capabilities of LCE hinges (rolling over vertices requires large torque outputs). Because these hinges unfold away from the hot surface, their repeated actuation is possible. This allows temperature gradient-driven propulsion to continue even after the structure completes a full roll without a need for manual reprogramming, traveling ~12 cm in 95 s (Fig. 4.18C). This simple concept can be expanded upon to passively control soft robotic matter, and ultimately, robots with more sophisticated reversible functions and locomotive gaits.

**Figure 4.20. Torque requirements of hinges for self-propelling rollbot.** (A) Torque required from $LT_{NI}$ LCE hinges for self-assembly into a pentagon as a function of folding angle $\theta$. (B) Torque required from $HT_{NI}$ LCE hinges as a function hinge angle for self-propulsion. The required moment is zero at the tipping point. A 63° hinge angle induces a 36° tipping angle about the vertex.

### 4.4 CONCLUSIONS

In this chapter, we have demonstrated a design and additive manufacturing method for integrating LCE bilayer actuators that respond to different thermal stimuli with structural panels to produce passively-controlled, shape morphing and self-propelling structures. Using this
approach, programmable hinges can be produced from different LCEs that actuate in response to thermal stimuli. To demonstrate the utility of these actuators, we incorporated programmable hinges into origami structures with programmed mountain and valley folds, reversible untethered sequential folding structures, and the passively-controlled “rollbot”.

To advance this platform, several challenges remain to be addressed. In thin and wide hinges especially, the orthogonal orientation of these bilayer hinges induces significant anticlastic bending (i.e., saddle-like surfaces), which reduces their bending energy (174). Even so, torque outputs are large enough for lifting objects that are significantly heavier than the hinges themselves and, importantly, for self-propulsion. Additionally, passively controlling soft robotic matter such as the rollbot requires a specific thermal environment which can limit use to laboratory-engineered settings rather than unexplored natural environments. In the future, LCEs with sharp phase transitions will enable predicted function in uncertain environments that deviate from an ideal target thermal environment. We envision that given the modular nature of these inks, it would be relatively straightforward to incorporate LCEs that respond to other stimuli (e.g., light, pH, humidity) within these printed architectures. Through the introduction of multiple stimuli-responsive actuators and more complex folding sequences, we can further expand the functionality of untethered soft robotic systems capable of task-specific reconfiguration and locomotion.
CHAPTER 5

INNERVATED, SELF-SENSING LIQUID CRYSTAL ELASTOMER ACTUATORS WITH CLOSED LOOP CONTROL

This chapter has been adapted from the following submitted manuscript:


5.1 INTRODUCTION

Liquid crystal elastomers (LCEs) are soft active materials that are being widely developed for soft robotics (14, 105, 281–283), actuators (1, 11, 17, 284), and shape shifting architectures (40, 285, 286). LCEs are composed of a crosslinked polymer network that contains rigid mesogens that actuate in response to heating above their nematic-to-isotropic transition temperature ($T_{NI}$) (12, 13), exposure to light (124, 127, 134), or chemical gradients (12, 144, 145). When their mesogen alignment is programmed along a specified direction, known as the director, these active materials exhibit large, reversible, and anisotropic contraction with high energy density parallel to the director (10). Initial methods to program director alignment have been limited to thin films (12, 167) and 1D motifs (13), including bulk LCEs with mechanically induced alignment (13, 109). Recently, extrusion-based 3D printing has been used to induce director alignment along the printpath enabling 3D LCEs to be fabricated with programmed shape-morphing behavior, actuation response, and seamless integration with other materials (44, 113, 183, 287). While shape-morphing behavior has largely been achieved using light-responsive LCEs (124, 127, 163), thermally responsive LCEs may be optimal actuators due to their ability to contract in response to embedded stimuli and provide sensory feedback.
Coupling LCEs with resistive elements that enable Joule heating on demand has already been exploited for locomotion (25–27), gripping (25, 288), and color change (289, 290). However, heating elements are typically laminated onto unidirectionally aligned LCE films in bilayer motifs (26, 27) limiting their shape, actuation mode, and function. Recently, gold serpentine-(25, 291), carbon nanoparticle-(292), and liquid metal-(111, 290, 293, 294) based heating elements have been incorporated within LCEs to induce actuation upon internally heating these composites above their \( T_{NI} \). The intrinsically soft nature of eutectic gallium indium liquid metal (LM) elements (295–297) makes this approach particularly useful for omnidirectional shape shifting, resistive self-sensing, and closed loop control strategies. Unfortunately, it is challenging to integrate LM within LCE actuators. One emerging strategy is to incorporate LM emulsions with LCEs via printing (111, 294) or spray-coating (293). However, sintered, emulsion-based LCE-LMs with complex director alignment lack the self-sensing necessary for closed loop control(298) and self-sensing, while spray coated LM-LCEs have only been demonstrated in the form of unidirectional actuators, whose thin LM traces are prone to electrical failure due to electromigration at the high currents required for Joule heating (293).

In this chapter, we report the programmable assembly of innervated LCE actuators (iLCEs) with prescribed contractile actuation, self-sensing, and closed loop control via core-shell 3D printing. This extrusion-based direct ink writing method enables coaxial filamentary features composed of pure LM core surrounded by an LCE shell, whose director is aligned along the print path. Next, we program, measure, and model the thermal response of iLCE fiber-type actuators during Joule heating, including quantifying the concomitant changes in fiber length and resistance that arise during simultaneous heating and self-sensing. Due to their reversible, high-energy actuation and their resistive-based sensory feedback, we then show that iLCEs can be regulated
with closed loop control even when perturbed with large bias loads. Finally, we fabricate iLCE architectures capable of programmed, self-sensing 3D shape change with closed loop control.

5.2 EXPERIMENTAL METHODS

5.2.1 Ink preparation and characterization

The LCE ink is prepared using an aza-Michael addition method, which we reported previously (44). A 1.1:1 molar ratio of 1,4-bis-[4-(6-acryloyloxy-hexyloxy)benzoyloxy]-2-methylbenzene (Wilshire Technologies Inc.) and n-butylamine (Sigma-Aldrich), 0.2 wt% butylated hydroxy toluene (Fisher Scientific), and 2 wt% Irgacure 651 (BASF) are combined, stirred, and heated at 105 °C for 18 h in the absence of light. The ink is transferred to a custom stainless steel barrel and degassed in a vacuum oven (VWR) overnight prior to printing. A liquid metal (LM) ink composed of eutectic gallium indium (5N Plus) is used as-received.

Thermal conductivity ($k$) is measured with a thermal conductivity analyzer (CTi, C-Therm) on printed LCE in a temperature test chamber (TJR-A-F4T, Tenney) (Fig. 5.1). To reach thermal equilibrium between measurements, the test chamber is held at target temperatures for 10 min, with measurements taken every 60 s. The coefficient of thermal expansion ($CTE$) is measured via a dilatometer (DiL, C-Therm) both parallel and perpendicular to the director of printed LCEs with approximate dimensions of 5x5x2 mm$^3$ with a heating rate of 2 °C min$^{-1}$. The data is processed using the ASTM E0229-17 standard (Fig. 5.1). Mechanical testing is conducted on printed LCE perpendicular bilayers with approximate dimension of 30x5x0.4 mm$^3$ (Instron 5566, 100 N load cell). The mechanical deformation is modeled by the 5-parameters hyperplastic Mooney-Rivlin Model (299), where appropriate parameters for the mechanical model are determined by optimization via the Levenberg-Marquardt method (Fig. 5.1).
5.2.2 Fabrication of iLCEs

Core-shell nozzles are first produced using stereolithography (Perfactory Aureus, Envisiontec) and subsequently coated with 1H,1H,2H,2H-perfluorooctyltriethoxysilane (FOTS, Oakwood Chemical) to minimize crosslinking with the LCE ink. The nozzle dimensions are provided in Fig. 5.2. The LCE ink is extruded through the outer shell of the coaxial nozzle by applying pressure (Ultimus V, Nordson EFD). A polyimide flexible heater (McMaster-Carr) was wrapped around the nozzle to maintain a constant temperature of 25 °C. The LM ink is extruded through the inner core of the nozzle using a syringe pump (PHD Ultra, Harvard Apparatus). During

Figure 5.1. Thermal characterization of LCE. (a) Strain of 3D printed LCE sample in directions parallel and perpendicular to the director with respect to temperature. (b) Thermal conductivity of 3D printed LCE in direction perpendicular to the director sample with respect to temperature. (c) Experimental and modeled stress of a printed LCE as a function of applied stretch of perpendicular LCE bilayer.
printing, the core-shell printhead is tilted 20° from the vertical axis to improve printability of innervated LM (core)-LCE (shell) architectures, referred to as iLCEs. iLCE cross-sections are ellipsoidal, with initial major and minor diameters of 1.34 ± 0.12 mm x 0.93 ± 0.08 mm and 0.702 ± 0.04 mm x 0.571 ± 0.05 mm for the LCE shell and LM core, respectively.

Figure 5.2. Core-shell nozzle specifications. [Note: Dimensions are to scale (mm).]

iLCEs are printed in the form of 1D coaxial fibers and 2D-to-3D shape morphing structures using a custom-built, three-axis motion controlled stage (Aerotech Inc.) equipped with on-the-fly UV crosslinking at ~8 mW cm⁻² intensity (Omicure, S2000). iLCEs fibers and spiral-based planar structure are printed on a polyvinyl alcohol (80% hydrolized, Aldrich)-coated glass substrates or pre-cleaned glass substrates (VWR), respectively, to allow release from the substrate without deformation. Spiral iLCEs are printed on a rotary stage (Aerotech Inc.), since the tilted nozzle prevents extrusion in both positive and negative x-directions. iLCE fibers are typically printed by extruding the LCE ink at an applied pressure of 3.6 MPa and the LM ink at a flow rate of 0.0197 mL min⁻¹ with a print speed of 2 mm s⁻¹ and a print height of 0.25 mm. Spiral iLCEs are printed with a 1.7 mm center-to-center spacing between filaments using under the same conditions, except
at a reduced print speed of $0.85 \text{ mm s}^{-1}$. At the start and end of each printed iLCE, the LCE ink is over-extruded by reducing the print speed by a factor of 2 as the nozzle is translated for 5 mm in the desired direction. After printing, the iLCEs are fully crosslinked by an additional UV exposure step of $\geq 30 \text{ min}$ in duration on each side (S2000, Omnicure; $\sim 5 \text{ mW cm}^{-2}$).

As a final step, a 23 AWG copper wire (Diji-Key Corp.) is mechanically filed, inserted in the iLCEs, connected to their LM core, and sealed with an adhesive (NOA 68, Norland Inc.) that promotes bonding upon crosslinking with UV light (S2000, Omnicure; minimum 300 s). A 28 AWG compliant lead wire (Diji-Key Corp.) of roughly 10 cm length is then soldered onto one end of iLCE fibers as to not affect LCE $L/L_0$ and $R/R_0$ (Fig. 5.3). Spiral iLCEs do not require a lead wire. During their 2D-to-3D shape morphing, these architectures are imaged on a layer of black craft sand (Just Artifacts) on super-cushioning polyurethane foam (McMaster-Carr) to minimize friction, adhesion, and thermal diffusion with the substrate upon cooling.

**Figure 5.3. iLCE fiber testing setup.** (a) Electrical testing circuit used for iLCE fibers and spiral architectures, including voltage-reading multimeter, current source, iLCE, and compliant lead wire. [Note: Compliant lead wires were used only for iLCE fibers.] (b) Testing setup for image capture and minimal interreference in shape change of iLCE fiber.
5.2.3 Electrothermal testing of iLCEs

To electrothermally (Joule) heat and measure the resistance of iLCE actuators, programmed current is provided via a power supply (2230G-30-6, Keithley) and voltage is measured at 1 s intervals using a multimeter (34405A, Agilent) (Fig. 5.3). The power source and multimeter are controlled in parallel by a custom MATLAB script. The resistance $R$ is normalized by the initial resistance $R_0$ of the iLCE (RM3544-01, HIOKI) to determine the normalized resistance, $R/R_0$. The length $L$ is normalized to initial length $L_0$ (in pixels) to determine the normalized length, $L/L_0$. Power input, which is normalized by total interfacial area between the LM (core) and LCE (shell), is calculated from the initial resistance, LM length between leads, and elliptical cross-sectional area, where major and minor diameters are estimated from imaging the top and side of the printed core-shell filament (SteREO Discovery V20 Microscope, Zeiss). Power input of spiral iLCEs is normalized by total interfacial area estimated from initial resistance (RM3544-01, HIOKI) and assuming a circular LM cross-section to account for disparities in cross-sectional area of LM along the edges and corners of the spiral.

All electrothermal tests on iLCE fibers are repeated with identical current profiles on the leads replicated without the fiber, which included the compliant lead wire and copper connection lead of the same lengths. Measured resistance of the leads is subtracted from the total resistance to obtain the resistance of neat iLCE. All current profiles for iLCE fibers included a current ramp up in increments of 0.5 A with each increment held for 5 s up to the peak current corresponding to the chosen power input ($on$), held for 60 s, then ramped down identically, and held at 0.5 A for 60 s unless otherwise noted. Cycling is also conducted with these ramps and with peak current values held for 30 s. For iLCE fibers, an $off$ state corresponds to 0.5 A to measure the $off$ resistance without significant heat input. Similarly, for spiral iLCEs, an $off$ state is at 0.1 A. Spiral iLCEs are
tested with 0.1A per 1s ramps, and cycled 4x with current holds of 60 s and 120 s at the \textit{on} and \textit{off} states, respectively. Peak \textit{on} currents 2.813 A and 4.873 A are applied for 5 mW mm\(^{-2}\) and 15 mW mm\(^{-2}\) power inputs, respectively.

5.2.4 Modeling and characterization of iLCE actuation

The 3D thermal-mechanical model consists of a transient study with solid mechanics and heat transfer modules (Comsol Multiphysics), where the geometry of the device is based on the average dimensions of our iLCE fiber. The heat source for the model is set as joule heating through the core of the iLCEs. Heat losses are assumed to occur by natural convection and a correlation for thin vertical cylinders is implemented to determinate the Nusselt number of the heated surface across space and time \((300)\). Values for LM thermal conductivity \((k = 26.4 \text{ W m}^{-1} \text{ k}^{-1})\), specific heat \((c_p = 333.75 \text{ J kg}^{-1} \text{ K}^{-1})\), density \((d = 6,250 \text{ kg m}^{-3})\), resistivity \((\rho = 2.79 \times 10^{-7} \Omega \text{ m})\), and coefficient of thermal expansion \((\text{CTE} = 32.97 \times 10^{-6} \text{ K}^{-1})\) and LCE specific heat \((c_p = 1000 \text{ J kg}^{-1} \text{ K}^{-1})\) and density \((d = 1,200 \text{ kg m}^{-3})\) are estimated from the literature \((111, 301, 302)\).

Images used to measure length are captured (EOS Rebel T2i, Canon) every 5 s for iLCE fibers and every 1s for spiral iLCEs and analyzed using image analysis software (Fiji) and a custom Python script. The iLCE actuators used for thermal imaging are first spray painted with a thin coat of graphite paint (Bonderite L-GP G Acheson) to prevent errors in surface temperature measurement arising from the nematic to isotropic phase transition. Thermal imaging is carried out using an IR camera (SC5000, FLIR) and their temperature is calculated (Altair) using an emissivity of 0.95.

Average values of normalized resistance, normalized length, and work for each printed iLCE fiber tested are averaged over the second half of peak current input (e.g., for a peak hold of 60 s, the measured values at 30-60 s would be averaged). Bias load is applied to the actuators by
adding paperclips to the bottom of the actuator. Weight-lifting experiments are conducted starting at low power then increasing to high power for each load and actuating at 35 mW mm\(^{-2}\) without weight between loads to erase thermal history. Specific work was calculated with respect to the average mass of LCE (35 mg ± 2 mg), estimated from the cross-sectional dimensions across 50 mm of fiber and taking the density of LCE as 1.08 g mL\(^{-1}\). The average height of spiral iLCEs is acquired at the end of the peak current time for on and off states.

5.2.5 Closed loop control of iLCEs

The PID closed loop control is implemented using a custom script (Python 2.7) to program electrical current and measure the voltage drop across iLCEs (E36233a, Keysight) (Fig. 5.4). The target \(R/R_0\) is inputted in the control script and the target \(L/L_0\) is estimated given target \(R/R_0\) and our electrothermal actuation characterization. The sampling rate of the loop is set to be 1000 Hz, which is 4 orders of magnitude faster than the thermal response of the iLCE. PID gains are

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**Figure 5.4. Closed loop control flow chart.** Flow chart for closed loop control of iLCE fiber actuation, which includes a PID controller and power source, where red indicates current input and blue indicates resistance measurement. The system measures the instantaneous resistance \((R_i(t))\) at time \(t\), and calculates the error, \((e(t))\), with respect to the target resistance \((R(t))\) set point. The sum of the three errors \((\Sigma)\) is then used by the controller to tune the current \((u(t))\) so that the system reaches the desired target resistance.
estimated using the system identification toolbox (MATLAB). For iLCE fibers, the PID gains (K_p, K_d, K_i) are found to be 22, 21, and 0.9 respectively. For the spiral iLCEs, the PID gains (K_p, K_d, K_i) are found to be 2.5, 2, and 0.001 respectively. The target step lengths of iLCE fibers and spiral architecture were 20 s and 60 s, respectively. Images used to measure length of the control response are captured (Nikon D850) every 2 s for iLCE fibers and every 1 s for spiral iLCEs and analyzed for length using image analysis software (After Effects, Adobe) and custom python script.

5.3 RESULTS AND DISCUSSION

5.3.1 iLCE design and fabrication

To fabricate iLCEs, we co-extrude pure LM and a main-chain LCE ink developed previously (44, 183, 287) through a core-shell nozzle mounted on a custom-built, direct ink writing platform. Because alignment of the LCE director to a prescribed printpath requires sufficient shear and extension during extrusion, the nozzle shell is retracted relative to the core (303, 304) and the nozzle is tilted 20° from vertical to create a coaxial LCE (shell)-LM (core) fiber (Fig. 5.5, 5.6a). These iLCEs are printed within the nematic phase at 25°C and subjected to UV curing immediately upon exiting the core-shell nozzle to preserve the prescribed director alignment and the uniformity

Figure 5.5. Optical image of iLCE filament (scale bar = 500 μm).
of LM deposition (44, 183, 296, 304). The LCE ink is over-extruded at the beginning and end of the iLCE printing process to locally disrupt director alignment in those regions thereby facilitating connection to electrical leads with minimal actuation at each end as well as sealing the LM to prevent auto-evacuation. When heated above $T_{NI}$, iLCEs contract in their designated print direction with correlated self-sensing (Fig. 5.6). Since their actuation response is gradual, we define a $T_{NI}$ of 127 °C as the temperature at which maximum LCE actuation is first observed (44). When iLCE fibers are electrothermally heated above $T_{NI}$ via Joule heating, they exhibit a pronounced actuation response (Fig. 5.6c).

**Figure 5.6. Innervated LM-LCE fibers.** (a) Schematic illustration of core-shell 3D printing of iLCE fibers composed of a liquid metal (LM) core surrounded by a liquid crystal elastomer (LCE) shell, whose director is aligned along the printpath. (b) Schematic illustration of iLCE actuation when cycled above and below the LCE nematic-to-isotropic transition temperature, $T_{NI}$. (c) Images of an iLCE fiber before (left) and after (right) electrothermally (Joule) heating above $T_{NI}$ (scale bar = 5 mm).
5.3.2 Electrothermal programming of iLCE actuation and self-sensing

We can control the actuation behavior of iLCEs by modulating the Joule heating power (Fig. 5.7). Notably, these iLCEs exhibit uniaxial contractile strains comparable to pure 3D printed LCEs reported in our previous work (44) (Fig. 5.7a). We normalize the power input by the initial interfacial area associated with the LM core and LCE shell regions between connection leads to enable direct comparison between printed iLCEs, where power input reflects the current input and initial resistance. We then characterized the surface temperature of the iLCE fibers at discrete power inputs (Fig. 5.7b, 5.8a). As expected, the center of the iLCE fibers exhibits the highest temperature, which increases with power input up to a maximum value of 178.7 °C ± 4.4% at 40 mW mm\(^{-2}\). Importantly, core-shell printing allows iLCE fibers to be produced with relatively large LM cross-sections relative to other patterning methods, enabling high average current and low maximum voltage inputs (i.e., 9.28 A ± 5.5% at 0.5315 V ± 6.5%) and consequently elevated heat generation at attainable maximum current densities of 29.6 A mm\(^{-2}\) ± 3.3% (40 mW mm\(^{-2}\)) without electrical failure (Fig. 5.8b).

To predict its thermal behavior, we modeled the thermal response across the cross-sectional area and length of the iLCE fibers. Given their architecture, we expect minimal temperature gradient through the cross-section of LCE (Fig. 5.7c) and a moderate heat gradient along the length of the fiber (Fig. 5.9). The modeled surface temperature is in good agreement to experimental maximum surface temperature (Fig. 5.7d). Resistance decreases with heat due to the change in geometry of the actuator, with a plateau in normalized resistance \(R/R_0\) above 25 mW mm\(^{-2}\), also corresponding to the power at which the entire iLCE fiber is expected to be above its \(T_{NI}\) (127 °C) (Fig. 5.7d, 5.9).
Figure 5.7. Electrothermal actuation of iLCE fibers. (a,b) Optical and corresponding thermal images of representative iLCE fibers actuated with discrete power inputs ranging from 1 - 40 mW mm\(^{-2}\), which increase from left to right, as labeled (scale bar = 5 mm). (c) Thermal model of the temperature across the iLCE fiber (cross-section) at these discrete power inputs, where inner and outer black outlines indicate initial dimensions of LM and LCE, respectively. (d) Measured surface temperature, surface temperature extracted from thermal model, and average \(R/R_0\) of iLCEs at these discrete power inputs. (e) \(L/L_0\) and \(R/R_0\) with respect to time of a representative iLCE at these discrete power inputs. (f) Average \(L/L_0\), average \(R/R_0\), and theoretical \(R/R_0\) modeled with Ohm’s law with resistivity temperature correction for discrete power inputs. [Note: Error bars indicate standard deviations.]
Figure 5.8. Time-dependence of electrothermal actuation of iLCE fibers. (a) Current profiles, corresponding maximum surface temperatures, and $R/R_0$ with respect to time for a representative iLCE actuated at several power inputs. (b) Average $L/L_0$ and $R/R_0$ for iLCEs actuated at 40 mW mm$^{-2}$ for 30 min followed by 3 min at off current (0.5 A) without current ramps. (c) Current profiles, $L/L_0$, and $R/R_0$ with respect to time for a representative iLCE actuated at several power inputs. (d) Average $L/L_0$ and $R/R_0$ of iLCEs actuated at 40 mW mm$^{-2}$ for 1 min followed by 1 min at off current (0.5 A) without current ramps. [Note: Lines denote average values, while shaded regions or error bars indicate standard deviations.]
Figure 5.9. Thermal gradient of iLCE fibers. (a - i) Thermal model and expected shape change of fiber iLCEs along cross-sectional area of fiber center (left) and along length (i.e., director direction) (right) actuated with discrete power inputs (1 - 40 mW mm\(^2\)). Initial dimensions of length and of cross-sectional area of the LCE and LM are outlined in black to illustrate expected shape change parallel and perpendicular to print direction. [Note: iLCE cross-sections are ellipsoidal, with initial major and minor diameters of 1.34 ± 0.12 mm by 0.93 ± 0.08 mm and 0.702 ± 0.04 mm by 0.571 ± 0.05 mm for the LCE shell and LM core, respectively. Scale bars indicate the minimum and maximum temperatures for each power input.]
Next, we investigated the programmable shape change and predictable self-sensing performance of these iLCE fibers. As expected, their actuation at different power inputs shows that $R/R_0$ is closely correlated with normalized length ($L/L_0$) during Joule heating (Fig. 5.7e) and also with cooling (Fig. 5.8c). Hence, changes in $L/L_0$ and $R/R_0$ are dependently programmable with power input (Fig. 5.7f), i.e., greater contractile strain results in greater decrease in resistance. Since resistance depends on both geometry and temperature, it can be predicted taking the temperature generated and strain of iLCEs at discrete power inputs (Eq. 5.1), accounting for both the change in geometry and temperature, where $\alpha$ is the temperature coefficient of resistivity.

$$\frac{R}{R_0} = [1 + \alpha(T - T_0)] \left(\frac{L}{L_0}\right)^2$$  \hspace{1cm} (5.1)

To achieve more reliable changes in $L/L_0$ and $R/R_0$, current is ramped up and down. However, these iLCEs can be rapidly actuated by applying a step input power of 40 mW mm$^{-2}$, in which over 90% of their maximum contractile strain is attained within 10 s (Fig. 5.8d).

### 5.3.3 iLCE actuator performance

To characterize actuator performance, we explored iLCE actuation strain repeatability and work output. When cycled between on and off states 25 times, iLCEs exhibit average $L/L_0 = 0.79 \pm 0.5\%$ and $R/R_0 = 0.68 \pm 0.7\%$ or $L/L_0 = 0.49 \pm 0.1\%$ and $R/R_0 = 0.35 \pm 0.9\%$ for low (i.e., 10 mW mm$^{-2}$) and high power (i.e., 40 mW mm$^{-2}$) on states, respectively (Fig. 5.10). Notably, iLCEs demonstrate repeatable programming of $L/L_0$ and resulting $R/R_0$ at both partial and full actuation, which are closely correlated throughout the duration of the power profile used (Fig. 5.10).
Figure 5.10. Repeatable and reversible actuation of iLCEs. (a) Scheme of reversible iLCE actuation (left) and plot of measured $L/L_0$ and $R/R_0$ when cycled at low (10 mW mm$^{-2}$) and high (40 mW mm$^{-2}$) power inputs (right). (b) $L/L_0$ and $R/R_0$ with respect to time of a representative iLCE cycled at low and (c) high power, 10 and 40 mW mm$^{-2}$, respectively. (d) Average $L/L_0$ and $R/R_0$ over 25 cycles, where black represents the off state and colors represents the on state. [Note: Error bars indicate standard deviations.]
Next, we electrothermally heated iLCEs at several power inputs and bias loads in weight-lifting experiments. Akin to unstressed iLCE experiments, increasing power input results in larger strains, but decreases with larger bias loads (Fig. 5.11). Work exertion increases with both power input and bias load (Fig. 5.11). We find that 30 mW mm\(^{-2}\) power and 7.5g bias load are the maximum power and loading conditions that these iLCEs can reliably lift. Upon heating, LCE actuators increase in length prior to contracting with sufficient bias loads, as observed for other LCEs that are not monodomain (Fig. 5.12)\(^{183}\)(221). If total contraction results in length greater than the initial unbiased length (\(L_0\)), it is defined as an extension (i.e., \(L/L_0 > 1\)) and negative work output. Overall, iLCEs lift bias loads over 200x their own LCE weight, with maximum specific work (40.7 J kg\(^{-1}\) ± 9.1%) comparable to previous work (44). To further increase the work output of iLCEs, LCE cross-sectional area can be increased either by printing bundled iLCE fibers or patterning pure LCEs alongside these fiber(s) via multimaterial 3D printing.

![Figure 5.11. Performance of iLCE fiber actuators.](image)

**Figure 5.11. Performance of iLCE fiber actuators.** Scheme of iLCEs lifting weight (left) and plot of measured \(L/L_0\) and specific work (work by LCE mass) when lifting different weights at discrete power inputs (right). [Note: Error bars indicate standard deviations.]
Figure 5.12. Current profile, change in $L/L_0$, and sensing of a representative iLCE with applied bias loads. The sharp increase in $R/R_0$ of the iLCE at 35 mW mm$^{-2}$ when loaded with 7.5 g indicates sample failure. [Note: Two out of four tested samples never failed, one failed after testing at 30 mW mm$^{-2}$ with 7.5 g bias load, and one failed at 35 mW mm$^{-2}$ (shown here) with 7.5 g bias load.]
5.3.4 Closed loop control of iLCEs

Given that iLCEs are able to reversibly actuate with self-sensing capabilities and exert substantial work, we explored regulating actuation with closed loop control (Fig. 5.13). Specifically, a control system is programmed with a target $R/R_0$ that autoregulates iLCE resistance feedback to reach the target over time, even with bias stress perturbations (Fig. 5.13a). We designate a target resistance square wave with two targets $R/R_0 = 0.90$ and $R/R_0 = 0.65$ for 20 s.

Figure 5.13. Closed loop control of iLCE fiber actuation. (a) Optical images of a representative iLCE fiber with self-adjusting actuation under several loading conditions (scale bar = 10 mm). (b) Self-adjusting current profile (top) and change in resistance and length (bottom) as a function of time for iLCE fibers that are perturbed with bias loads, while reaching target values of resistance (black, dashed) and corresponding length (red, dashed). [Note: Lines denote average values, while shaded regions or error bars indicate standard deviations.]
each, corresponding to target contractile strains of approximately 5% and 23%, respectively. The current rapidly self-adjusts without manual intervention such that the $R/R_0$ values of the iLCEs lie within the target resistance curve with 3.1% and 4.5% overshoot and undershoot, respectively. Importantly, our iLCE actuators are capable of tracking self-sensing actuation while rejecting disturbances up to 4.2 grams (> 115x the LCE weight) within 20 s (Fig. 5.4, 5.13b).

5.3.5 3D shape morphing iLCEs with closed loop control

As a final demonstration, we fabricated iLCE spirals with 2D director patterning via 3D printing to achieve a programmable out-of-plane shape change (Fig. 5.14). Specifically, we patterned the iLCE with a square spiral printpath, which is expected to actuate into a cone when heated above $T_{NI}$ (12)(183). Like its fiber actuator counterparts, spiral iLCEs are repeatedly actuated via Joule heating and output a corresponding change in resistance. At low power input (5 mW mm$^{-2}$), a fraction of the iLCE actuates and forms a partial cone, corresponding to a maximum height of 8.77 mm ± 1.9% with corresponding $R/R_0$ of 0.63 ± 2.0% (Fig. 5.14). At higher power input (15 mW mm$^{-2}$) almost the entire structure is above $T_{NI}$ and actuates into a full cone with a maximum height of 12.29 mm ± 1.6% and corresponding $R/R_0$ of 0.35 ± 1.5% (Fig. 5.14). We note that the frequency of cycling current is slow to allow cooling of the large structure, with cycles 1-4 shown in Fig. 5.15. With sufficient time to cool, the spiral iLCEs return to a flat shape and within 5% of the initial $R/R_0$. The reversible and large change in resistance corresponding to the change in height enables closed loop control of 3D shape change (Fig. 5.14, 5.15). Here, we program a target resistance curve with 60 s intervals at $R/R_0 = 0.8$ and $R/R_0 = 0.6$ and the iLCE spiral actuates to these targets both with and without a bias load (4.7 g). Longer time intervals relative to those of iLCE fibers are necessary due to the scale of the iLCE spiral and ensuing
timescale of heat dissipation. This capability could be deployed to create reconfigurable iLCE-based antennae with closed loop control in the future, and, hence, tunable RF properties (40).

Figure 5.14. 3D actuation of iLCE spiral architectures with closed loop control. (a) Side-view images of a printed iLCE when cycled between off (0 mW mm$^{-2}$, left) and on (5 mW mm$^{-2}$, right) power input. [A top-view image of the printed iLCE spiral architecture (off state) is shown in the inset.] (b) Average height and resistance profile of printed iLCE spiral architectures cycled at a power input of 5 mW mm$^{-2}$. (c) Side-view images of a printed iLCE when cycled between off (0 mW mm$^{-2}$, left) and on (15 mW mm$^{-2}$, right) power input. (d) Average height and resistance profile as a function of time for printed iLCE spiral architectures cycled at 15 mW mm$^{-2}$ power. [Note: The plots do not include the first cycle.] (e) Image sequence of a printed iLCE spiral architecture and (f) resistance profile of actuation as a function of time with closed loop control (bottom), where the target resistance is shown as a dashed line. (scale bars = 5 mm). [Note: Lines denote average values, while shaded regions or error bars indicate standard deviations.]
Figure 5.15. Actuation and control of iLCE spiral architectures. (a) Full cycle with respect to time of iLCE spiral architectures actuated 4x at 5 mW mm$^{-2}$ and (b) at 15 mW mm$^{-2}$ power. (c) Current profile and corresponding resistance profile of a closed loop controlled iLCE spiral, where target resistance is dashed. [Note: Lines denote average values, while shaded regions or error bars indicate standard deviations.]
5.4 CONCLUSIONS

In summary, we have fabricated innervated LCEs with programmable actuation, self-sensing, and closed loop control via core-shell 3D printing. Importantly, our approach enables pure liquid metal cores to be directly embedded within LCE-based coaxial fibers. We demonstrated that these iLCE fibers exhibit prescribed and predictable thermal responses, strain, and self-sensing upon Joule heating, with strains of nearly 50% when heated above their nematic-to-isotropic transition temperature. Programmability, repeatability, magnitude of sensing signal, and large work output enabled closed loop control of printed 1D iLCE fibers and 2D-to-3D shape-morphing architectures, respectively. With further development, iLCE architectures in arbitrary designs could be printed and controlled in a closed loop system for use in intelligent soft robotics, reconfigurable soft electronics, and RF devices.
CHAPTER 6

CONCLUSIONS

My Ph.D. research focused on creating programmable liquid crystal elastomers via 3D printing with an emphasis on the synthesis, assembly, and characterization of shape morphing architectures and actuators, which are either passively or actively controlled. Specifically, two oligomeric, main-chain LCEs were synthesized with different nematic-to-isotropic transition temperatures (high and low \( T_{NI} \)). These materials were formulated into solvent-free, photopolymerizable inks with the requisite viscoelastic behavior needed for high operating temperature direct ink writing (HOT-DIW). Using this extrusion-based 3D printing method, LCEs could be fabricated with programmed director alignment along the printpath in nearly arbitrary motifs. To highlight this capability, 3D LCEs were produced that exhibited programmable and reversible shape morphing (2D-to-3D) behavior as well as bulk actuators capable of lifting nearly 1000x their own weight upon heating above \( T_{NI} \). Next, by co-printing high and low \( T_{NI} \) LCE hinges that connected rigid polymer panels, both sequentially folding origami and untethered soft robotic matter were produced and passively controlled by thermally heating above their respective \( T_{NI} \) values. As a final example, innervated LCE (iLCEs) fibers composed of an LCE shell that surrounds a liquid metal core were produced by core-shell 3D printing. These multifunctional actuators exhibit large contractile strains when electrothermally (Joule) heated above \( T_{NI} \). The actuation response of these self-sensing iLCEs can be programmably defined via closed loop control. The principal conclusions of my Ph.D. research are summarized below.

1. **Design of LCE inks for high operating temperature direct ink writing (HOT-DIW)**

Using a thiol-acrylate “click” reaction and an aza-Michael addition, oligomeric, main-chain LCE inks with \( T_{NI} \) values of 24 and 94 °C, respectively, were synthesized. These solvent-free
inks exhibit the desired viscoelastic response needed to facilitate director alignment under shear flow during HOT-DIW. Specifically, our LCE inks are printed at temperatures within their nematic phase, at which the inks exhibit a strong shear thinning behavior. To lock in their microstructure upon exiting the nozzle, these inks are rapidly photopolymerized through the incorporation of trifunctional vinyl crosslinkers for the thiol-acrylate ink and acrylate reactive end groups for the aza-Michael ink.

2. Programming LCE alignment via HOT-DIW

Using HOT-DIW, 3D LCEs with programmed director alignment were produced by printing oligomeric LCE inks at elevated temperatures within the nematic phase. Printing at higher speed increased alignment of the director to the printpath, with a maximum order parameter of 0.3816 ± 0.02. These 3D LCEs exhibit large, reversible contractility along the alignment direction as well as high specific work when actuated under load, corresponding to a maximum energy density of 39 J/kg. Using this fabrication method, one can deterministically define their local director alignment in arbitrary geometric motifs. As a simple demonstration, two LCEs with the same initial dimensions (thick discs), but differing print paths were generated, which exhibited either positive (i.e., cone) or negative (i.e., saddle) gaussian curvatures upon heating above their $T_{NI}$. Multiple LCE architectures with in-plane or out-of-plane transformations were designed, printed, and passively controlled via thermally heating.

3. Sequential folding origami via programmable LCE hinges

Bilayer hinges in both mountain and valley folds were fabricated by HOT-DIW of low and high $T_{NI}$ LCE inks, which interconnect rigid polymeric panels. This technique affords control over the bending direction, orientation, bending angle, and torque, as needed to create sequentially folding origami structures. The LCE hinges were programmed to bend up to 180°
at temperatures above $T_{NI}$, with energy density up to 29 J/kg when lifting greater than 450 times their mass. Their bending angle was predominantly determined by the bilayer geometry, while their torque was determined by their chemistry and thickness. As exemplars, several origami structures were produced including a reversible structure with parallel mountain and valley folds, and a square twist structure that remains in a stable, flat-folded state after it has been actuated at temperatures above $T_{NI}$.

4. **Untethered, self-propelling soft robotic matter enabled by sequential folding**

Untethered soft robotic matter was designed and fabricated by co-printing with LCE hinges with low and high $T_{NI}$ values that interconnect rigid polymeric tiles. These hinges are programmed to sequentially fold with increasing temperature to embody task-specific configurations, including a simple origami structure and a self-compacting 3D prism. Using this technique, self-propelling soft robotic matter, named the “rollbot”, was produced, which exploited the large torque and disparate temperature responses of these two types of LCE hinges to reconfigure into a pentagonal prism and self-propel itself across a hot surface. These structures were passively controlled and exhibited programmed shape-morphing sequences in response to their external environment without user interference.

5. **Innervated LCE actuators via core shell printing**

Innervated LCE (iLCE) actuators in the form of coaxial fibers and planar spiral motifs were fabricated by coextrusion of LCE (shell) and liquid metal (core) inks through a core-shell printhead integrated with HOT-DIW. The liquid metal core functions as an electrically resistive element that enables electrothermal (Joule) heating of the LCE shell to drive fiber actuation and as a sensor to provide piezoresistive feedback on changes in geometry and temperature. These iLCEs were generated without electrical failure and contractile actuation
was realized in both 1D and 3D morphing structures, which were capable of withstanding heating to 179 °C.

Electrothermal heat generation was modeled and controlled in these iLCEs, such that the desired change in length of coaxial fiber actuators is deterministically defined by the input power used. Akin to pure 3D LCE actuators, these iLCEs exhibit comparable and substantial maximum reversible contraction (52%) and work output (40.7 J/kg). Lastly, both 1D fiber and square spiral iLCEs demonstrated self-sensing capabilities upon shape-morphing either uniaxially or in 2D-to-3D motifs.

6. **Closed loop control of iLCEs**

Due to their large work output, strong piezoresistive signal, and reversibility, iLCEs can be controlled with closed loop control. iLCE power input was auto-regulated to reach target normalized resistance and strain with low error and rapid speed. In the future, this comprehensive control mechanism for LCE systems would benefit intelligent soft robotics, reconfigurable soft electronics, and RF devices.

In summary, my Ph.D. thesis opens new avenues for the programmable fabrication of 3D LCEs that may find potential use in soft robotics, adaptable structures, and reconfigurable electronics.
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