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Liquid Crystal Elastomer Based Novel Functional Materials

by

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Abstract

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Liquid crystal elastomers (LCEs) are fascinating materials in which the elasticity of polymer network is coupled to liquid crystalline (LC) order and exhibits rich behavior under various stimuli such as heat, light, electric and magnetic fields. Previous studies were helpful in understanding isolated properties of bulk LCEs under static conditions and large-strain deformation. In this thesis we focused on the development of new functional materials based on LCEs and gaining new insight into their mechanical properties under dynamic deformations. In chapter-2&3, LCE based buckling instability in thin films is discovered and found to be useful for nanoscale thin film metrology (down to 30nm). This overcomes the limitations of earlier known techniques that require clamping and mechanically straining of films and present challenges with small samples. For thick PS films (over 500nm), well-defined self-folding 3D dynamic structures (like lotus or helix) are achieved just by engineering film patterning on LCEs. The phenomena are quantitatively captured through FEM simulations and could be used to predict the film patterning on LCE to achieve desired 3D deformed structure. In chapter-4 a LCE based dynamic wrinkling instability is demonstrated by synthesizing an electrically conductive LCE nanocomposites (LCE-NCs) using a new two-step approach. LCE-NCs exhibit rapid (response times as fast as 0.6 s), large-amplitude (up to 30 %), and fully
reversible shape changes (stable to over 5000 cycles) under externally applied voltages (5 – 40V) via joule heating. Neonatal rat ventricular myocytes were cultured on LCE-NCs substrates, and good cell attachment and viability is observed. LCE-NCs provide a straightforward and scalable route to investigate cell response to a dynamically changing surface pattern. In chapter-5 a novel self-stiffening behavior in LCEs is discovered, a dramatic 90% increase in stiffness is observed under low-amplitude, repetitive (dynamic) compression. Such stiffening behavior is common in biological tissues but rare in synthetic elastomers. Combination of rheological measurements, optical microscopy, 2D-WAXD and FEM simulations, demonstrates dynamic stiffening is due to rotation of the nematic director under repetitive compression. The use of low-strain, repetitive compression represents a facile method to prepare uniformly aligned LCEs and finds applications in biocompatible, adaptive materials for tissue replacement.
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1 Review

1.1 A brief introduction to Liquid Crystal Elastomers

1.1.1 Liquid crystals
Liquid crystals (LCs) commonly serve as active components in both synthetic and biological materials. A useful definition of LCs is given by deGennes and Prost\(^1\): LCs have liquid-like order in at least one dimension, and they possess a degree of anisotropy in their mechanical, optical, and/or structural properties characteristic of some degree of order. Various types of molecules satisfy this definition. For example, amphiphilic molecules, such as surfactants in solution with a selective solvent, can form associated structures in which molecules are ordered in layers. Also, long, rigid molecules such as polypeptides, DNA, or viruses will display LC phases\(^1\) when highly concentrated in solution, due to steric interactions between highly anisotropic molecules. These types of LC phases that occur in solution, and whose phase behavior is strongly concentration dependent, are known as lyotropic LCs\(^1\). On the other hand, small organic molecules that exhibit LC ordering in the pure state are known as thermotropic LCs. Temperature as opposed to concentration (as in lyotropic LCs) determines the phase of thermotropic LCs. Ordering in thermotropic LCs arises both from steric effects and from intermolecular Van der Waals forces\(^2\). LC molecules and phases are oftentimes referred to as mesogens and mesophases, respectively.
LCs uniquely combine elastic properties characteristic of ordered materials along with fluidity and responsiveness to a variety of external stimuli. For example, an LC display is stable against shocks and temperature changes but responds quickly to modest electric fields, allowing for a fast and robust optical response. In the last twenty years, interest in LCs has blossomed as has their incorporation in a wide variety of materials. LCs have potential for a wide range of applications beyond displays. Potential applications include artificial muscles\textsuperscript{3,4}, tunable lasers\textsuperscript{5}, thin film transistors\textsuperscript{6}, responsive microfluidic elements\textsuperscript{7}, and self-assembled colloidal assemblies\textsuperscript{8}. However, the fluidity of LCs limits their use in active and responsive materials; oftentimes a rigid substrate is required to fix the director to a particular boundary condition, as in an LC display.

1.1.2 Liquid Crystals Elastomers

LCEs are crosslinked network of LC polymers. LC polymers comprises of LC molecules covalently attached to the polymer chain. LCPs have a highly anisotropic chain conformation that arises due to the coupling between liquid crystal ordering and polymer chain conformation. This anisotropy can be modulated via external stimulus and which in turn makes LCEs a highly responsive material that can react to electric or magnetic
fields, heat, or light by changing shape, color, and even size. If liquid crystals are the fourth state of matter, then liquid crystal elastomers (LCEs) represent a more robust form of the fourth state. LCEs are solids in the sense that they do not flow or fill a container, but yet they exhibit remarkable fluidity in the LC director, which defines the long-range orientation of LC molecules and can rotate in response to electric and magnetic fields, strains, and temperature changes. Due to their unique combination of rigidity and fluidity, LCEs have been proposed for a broad range of applications and responsive materials. Several recent examples include LCE “cilia” which can flex in response to light and heat, flexible strips that vibrate at a thousand times per second when irradiated with UV light, elastomers that can generate electricity when flexed, mechanical elastomeric strips that can perform work and rotate axles under illumination, and micron-sized actuators that can expand by over 100% with changes in temperature.

Furthermore, they have a reliable memory of where they began and will return to their initial state on removal of the external influence. These novel properties arise from the combination of LC order, polymer elasticity, and topological constraints or translational order of a crosslinked rubber. The first LCE was prepared in 1981, and later the method was improved so that aligned LCEs could be produced. Studies on these materials have led to a molecular model which can successfully explain most of the phenomena exhibited by these unique rubbers, in particular their ability to change shape and rotate the molecular orientational order in response to a variety of external stimuli. The story of LC-polymer materials is by no means complete, however. The LCEs produced by
Finkelmann and coworkers represent the first successful attempt at fabricating rubbery LC networks, and this initial success has inspired the search for new ways to combine LCs and polymers\textsuperscript{19,20}. More recently, photopolymerization has been utilized due to its versatility and compatibility with a variety of substrates and materials\textsuperscript{9,14,21,22}. Additionally, self-assembly methods have been used to provide better control over the structure of LCEs and LC gels\textsuperscript{23–26} as well as reversible crosslinking.

More recently, the potential of LCEs for making bio-inspired materials has been recognized\textsuperscript{27}, including work towards artificial muscles\textsuperscript{28} and responsive microstructured systems\textsuperscript{7,14}. This work is still in its infancy, and the potential for LCEs for applications is still unclear. In particular, we believe significant opportunity is available by studying LCEs with higher-order LC phases. The vast majority of the work with monodomain LCEs has focused on nematics, due in large part to challenges in preparing monodomain LCEs with higher order phases\textsuperscript{29}. Potential applications of chiral and smectic LCEs include tunable lasers, photonic materials, and elastomers with fast and reversible electromechanical response due to a macroscopic polarization in smectic C elastomers and a strong coupling between director orientation and deformations in the polymer network.
Figure 1.2: Demonstration of LCE response w.r.t various external stimuli. (a) LCE response towards thermal stimulus. The LCE reversibly contracts and expands with temperature changes. (b) Light driven plastic motor based on LCE. (c) Direction-controllable bending behavior of polydomain LC elastomer film upon irradiation of 366 nm with different polarization directions.

1.1.3 Classification of LCEs

LCEs can be classified as monodomain or polydomain based on the presence or absence of a global director. In a polydomain sample, there isn't any specific macroscopic order in the system (Figure 1.3b). In the micrometer size domains, LC molecules are all oriented in a specific direction, called a local director. Due to absence of positional order in the polydomain LCEs, this local director varies in space and assumes all possible orientations. But in case of monodomain LCEs, all the local directors will be oriented in the same direction. This globally preferred direction is referred to as the director and is denoted by unit vector $n$ (Figure 1.3a). The extent of alignment within a liquid crystal
sample is typically denoted by the order parameter, S, as defined by Figure 1.3e, where $\theta$ is the angle between long axis of molecule and the preferred direction, n. For isotropic samples, the value of S is zero, and for perfectly aligned samples it is 1. The specific alignment of molecules in one preferred direction in LCEs makes their physical properties such as refractive index, viscosity, diamagnetic susceptibility, directionally dependent.

![Figure 1.3: Schematic of (a) monodomain and (b) polydomain LCE. (c) and (d) are the experimental images of monodomain and polydomain LCEs. Monodomain LCE is perfectly transparent while polydomain is opaque. S ranges from -0.5 to 1.]

Another major classification-main-chain and side chain LCEs-is based on how the rodlike mesogens are attached to the backbone polymer chain. In main chain LCEs, mesogens are concatenated along the network backbone (Figure 1.4a). In side chain LCEs, mesogens are attached as pendant groups to the polymer chain via flexible spacer. Depending upon the orientation of mesogens with respect to the polymer chain, side-chain LCEs can be further classified into end-on and side-on LCEs (Figure 1.4 b,c). Conformational anisotropy of main chain LCEs is much greater due to the direct coupling...
between mesogens and backbone polymer chain. This generates more pronounced effect in macroscopic properties in comparison to the side chain types. But due to complex synthesis schemes of main chain LCEs, side chain LCEs are usually researched upon.

![Figure 1.4 Schematic representation of (a) main chain LCE (b) side-on side chain LCE and (c) end-on side chain LCE. (Adapted from 18).](image)

Mesogens can possess different types of ordering giving rise to different types of liquid crystalline phases\textsuperscript{18,19} such as nematic, smectic and cholesteric phases.

Nematic phase has no positional order only orientational order, i.e., the molecules all point in the same direction. The direction of molecules denoted by the symbol $n$ commonly referred as the ‘director’ (Figure 1.5a). The director $n$ is bidirectional that means the states $n$ and $-n$ are indistinguishable. All the smectic phases are layered structures that usually occur at slightly lower temperatures than nematic phases. There are many variations of smectic phases i.e. smectic A, smectic C and smectic C*. Each layer in smectic A is like a two dimensional liquid, and the long axis of the molecules is typically orthogonal to the layers (Figure 1.5b). Just like nematics, the state $n$ and $-n$ are equivalent. As with smectic A, the smectic C phase is layered, but the long axis of the molecules is not along the layers normal. Instead it makes an angle ($\theta$, Figure 1.5c). The
tilt angle is an order parameter of this phase and can vary from 0° to 45-50°. Smectic C* phases are smectic phases formed by chiral molecules. This added constraint of chirality causes a slight distortion of the Smectic C structure. Now the tilt direction precesses around the layer normal and forms a helical configuration. Cholesterics phases are sometimes also referred to as chiral nematic phases because they are similar to nematic phases in many regards (Figure 1.5d). Many derivatives of cholesterol exhibit this type of phase. They are generally formed by chiral molecules or by doping the nematic host matrix with chiral molecules. Adding chirality causes helical distortion in the system, which makes the director, n, rotate continuously in space in the shape of a helix with specific pitch. The magnitude of pitch in a cholesteric phase is a strong function of temperature.

Figure 1.5 Schematic illustrations of the different types of liquid crystal phases.

1.1.4 LCE shape responsiveness
Due to the strong coupling between nematic order and rubbery elasticity of polymer network, average molecular shape of LCE polymer chains is coupled to the orientational order of mesogens. Due to this LC polymer chains assume an ellipsoidal conformation in nematic phase while in isotropic phase they recover a random coil conformation\textsuperscript{33,34}. At the phase transition temperature, LC polymer chains undergo a shape transition from
ellipsoidal to spherical conformation (Figure 1.6). This is due to the dependence of LCE nematic order on temperature. In case of monodomain LCEs, where all the mesogens are oriented in the same direction, shape change of polymer chains collectively results in significant macroscopic shape change at phase transition temperature. Such macroscopic response is absent in polydomain LCEs due to the random director orientation. Since shape change effect originates due to the anisotropy of backbone polymer chain, main chain LCEs should exhibit the strongest shape change.

![Figure 1.6 Shape change of monodomain side chain-LCE triggered by thermal stimulus][66].

LCE actuation is generally specified by reporting the maximum force$^{35}$, maximum strain$^{35}$ or by the maximum working frequency. Among those maximum force and maximum strain are more common. Maximum strain a sample can generate is measured by heating the sample at a constant stress. Maximum force a sample can produce is measurements by heating the sample at constant strain.

1.1.5 LCE synthesis

A major breakthrough in the LCE synthesis took place in 1991, when Finkelmann$^{36}$ first successfully synthesized aligned nematic LCE via hydrosilylation reaction at
temperatures where the system exhibits a LC Phase. Later on, various schemes with different mesogens and backbone polymer chains have been proposed. Broadly LCE synthesis can be classified into four major pathways. First method is based on siloxane chemistry and is most commonly used. In this platinum catalyzed two-step process, mesogens and crosslinker molecules are partially attached to the linear polysiloxane chain\textsuperscript{37}. Partially crosslinked LC network is then mechanically stretched at room temperature for 2-3 weeks to complete the crosslinking reaction. Stretching is required to induce chain anisotropy to achieve monodomain LCEs. This method could be used to synthesize end-on\textsuperscript{36}, side-on\textsuperscript{38,39} and main chain LCEs\textsuperscript{40}. In second method, liquid crystal polymer with functional groups is initially synthesized. The crosslinking reaction is then initiated by mixing the functionalized LCP with multifunctional crosslinker\textsuperscript{24}. Typically used for methacrylate and polyacrylate based LCEs. In third method, LCP functionalized with crosslinkable groups is initially synthesized followed by thermal or photo induced crosslinking reaction\textsuperscript{41}. Fourth method is a one pot synthesis approach where LC monomer, radical initiator and crosslinker are all reacted together\textsuperscript{40}. For my research, we used the siloxane-based approach to synthesize LCEs. This approach is relatively easy to implement and allows easy exchange of different mesogenic side groups without making significant changes in the system.

For most applications monodomain LCEs are required. LCEs can be easily prepared without any external force or bias during synthesis, but the resulting elastomer is polydomain, with only local alignment of the LC director but no uniform alignment macroscopically. The synthesis of uniformly aligned LCEs is difficult and only reliably
achieved for nematic elastomers (although a few examples of chiral\textsuperscript{5} and smectic\textsuperscript{42} LCEs have been reported).

### 1.2 Buckling instability in thin films

Instability phenomena in thin films can give rise to well-defined, periodic topological features on surfaces. Examples of this type of phenomena include the aging human skin and the surface of dried fruit and have led to many technological applications in the fields of flexible electronics\textsuperscript{43–48}, thin film metrology\textsuperscript{49}, and micro/nano-fabrication\textsuperscript{50}. Traditional techniques (scanning probe microscopy (SPM)\textsuperscript{51}, nanoindentation\textsuperscript{52–54}) are limited either in their accuracy or ability to process a large number of samples. On the other hand, the measurement of thin films modulus can be carried out with high accuracy and throughput by observing a surface wrinkling instability\textsuperscript{55}. In particular, stretching a system composed of stiff film on top of flexible substrate can lead to the formation of wrinkling patterns that can display rich surface morphologies and ordering at multiple length scales.

A distinct advantage of the surface wrinkling phenomena is the flexibility it brings in the types of materials (Figure 1.7c) that could be tested such as metal films\textsuperscript{50,56}, polymer brushes\textsuperscript{57,58}, polymer nanocomposites\textsuperscript{59}, carbon nanotubes\textsuperscript{60} etc. The ability to generate well-defined micron scale topological patterns over large areas has applications in various fields including nanoparticle assembly\textsuperscript{61,62}, wettability\textsuperscript{63}, adhesions\textsuperscript{64} etc. Surface wetting properties are dependent on its chemistry and roughness\textsuperscript{65–67}. Butterfly wings and lotus leaves are the prime examples of the effect of surface roughness on wettability. It
has been demonstrated that the stretching induced wrinkling instability can control surface roughness and hence wettability\(^{63}\) and adhesion\(^{64}\) properties of surfaces.

The general procedure for inducing wrinkling instability is to deposit a thin film on top of a soft substrate (e.g. PDMS), and strain the bilayer using a mechanical device (Figure 1.7). This approach typically suffers from large sample size, mechanical constraints at the clamped ends and difficult to implement. We envisioned that replacing the PDMS substrate with a stimuli-responsive liquid crystal elastomer would simplify the method and provide new methods for inducing surface buckling.

![Diagram](image.png)

Figure 1.7 Schematic depiction of a mechanical device built for straining Polystyrene laminated Polydimethylsiloxane bilayer system and an optical image of thickness gradient in PS film and corresponding wrinkling wavelength\(^{55}\) (b) anisotropic wetting behavior on wrinkled surface\(^{63}\) (c) wide variety of materials have been characterized via wrinkling instability\(^{55}\) and (d) nanoparticle assemblies using wrinkling pattern\(^{61}\).
In this dissertation we describe our successful implementation of reversible surface wrinkling in response to a variety of external stimuli, including temperature, UV light and electric or magnetic fields by using liquid crystal elastomers (LCEs) as flexible substrates. We demonstrate that surface wrinkling can be induced with moderate temperature changes, and the wavelength of the wrinkles provides a quantitative measure of the polymer thin film modulus. Furthermore, the reversible shape-change properties of LCEs enable ‘erasing’ and ‘re-orienting’ surface wrinkles in a single bilayer sample, and depositing a thick poly(styrene) film on top of an LCE results in a sample which reversibly curls with temperature. This bypasses the need for mechanical clamping and stretching and enables new applications for assembly. We find that the wrinkling instability in LCEs can be used to measure the moduli of thin polymer films and that the orientation of wrinkling pattern can be controlled using LCEs just by changing the temperature. Recent studies\textsuperscript{61,62} have shown that particle assemblies with excellent short and long-range order can be generated utilizing wrinkling instability technique (Figure 1.7d). The LCE-based wrinkling instability reported here potentially gives further control over the particle assemblies by reversibly switching their macroscopic arrangement by external stimuli (heat, light, electric or magnetic fields).

1.3 Shape responsive polymers for cell culture
Muscular cell sheet holds promise for the tissue regenerative medicine such as corneal surface reconstruction, myocardial tissue regeneration, Type-I diabetes treatment. Recent investigations into the use of muscular cell sheets have demonstrated the feasibility of layering sheets of muscle cells over a human heart for recovery of heart function\textsuperscript{68,69}. 
This technology could transform the way surgeons and cardiologist treat heart failure and lead to regenerative therapies that cure heart failure without the need for a transplant. For clinically relevant cell sheet function, cardiac myocytes must be able to generate force sufficient to significantly aid heart contraction, and they should conduct depolarization waves at speeds comparable to the native myocardium to avoid the possibility of generating arrhythmias. Studies have shown that random monolayer distributions of cardiomyocytes result in force generation and conduction speeds of the depolarization wave that are much lower than in native tissues. However, systems that align cardiomyocytes and allow for rhythmic mechanical conditioning result in much higher forces and wave conduction speeds. Current challenge is fabrication of suitable substrates for cell culture that can exhibit time-varying deformation.

Structural organization within these cell sheets is critical to achieve desired tissue function and is mostly governed by scaffold design, mutual interaction between cells and other environmental factors. Through a process known generally as mechanotransduction, cells convert physical cues to biochemical signals essential to cellular development and function. Traditionally used bio-scaffolds for cell and tissue growth lacks the nanoscale morphological features of the organs they are to replace. This limits their performance. Recent developments have shown the ability to engineer biomaterials with tunable mechanical properties and topographies. This provide a means to investigate cell-matrix interactions and potentially actively direct the growth and development of engineered tissues.
A combination of equibiaxial stretching devices and patterned substrates have been previously implemented to study cardiomyocyte response to mechanical stresses. A wide range of topographies is developed but special attention is given to results on groove-ridge topographies. As an alternative to mechanical stretching devices, shape-responsive materials potentially provide a scalable and more easily implemented technique to control substrate strain and stress. Poly(N-isopropylacrylamide) (PIPAAm) has been used in laminar tissue engineering and apply biaxial stretching to encapsulated cells by taking advantage of the material’s lower critical solution temperature (LCST) at 32 °C. Effect of changing substrate modulus on cell culture have also been studied using UV-induced crosslink degradation. Recently shape memory polymers (SMP) based substrates were developed to study the effect of changing surface topography during cell culture. Quantitative observations were made of cell alignment on SMP based substrate undergoing thermally triggered topological transformation during cell culture. These studies have contributed substantially to our fundamental understanding of cell-matrix interactions. But most of these studies were performed using static or quasi-static substrate, thereby limiting our ability to tune or program substrate topography or mechanical properties during cell culture.

In this dissertation, we report the preparation of shape-responsive substrates based on liquid crystal elastomers (LCEs) that reversibly contract and expand in response to an electrical potential. We demonstrate that these siloxane-based elastomers provide an easily implemented and versatile approach to generate shape-responsive substrates for cell culture. We show that LCE based dynamic substrates can achieve fast cycle times.
(0.1 – 1 Hz) with strains up to 20%. The strain response is applicable in cell culture media, and cells (neonatal cardiomyocytes) plated on the LCEs remain viable after several days of electromechanical stimulation. Neonatal myocytes show improved alignment when cultured on shape-responsive substrates compared with static flat or patterned surfaces. These materials potentially provide a straightforward and scalable route to aligned cell sheets and enable investigation of cell response to a dynamically changing surface pattern. These LCE substrates may also be useful for the development of cardiac tissue grafts with improved cardiomyocyte alignment.

1.4 Self-stiffening materials

Biological tissue have the remarkable ability to increase in stiffness when subjected to external stress, a response generally termed ‘functional adaptation’. For example, collagenous tissue such as bone, skin, and ligaments exhibit directional strengthening due to the presence of protein fibers that can align under external stress. Well-known examples include bone remodeling and strengthening through a process which involves changes in bone mass and porosity, and muscle development, tumor growth, and blood vessel structure are all affected by mechanical stresses. This adaptive behavior is essential to the longevity and versatility of biological tissues. The development of synthetic elastomers with a similar response to external stress may be beneficial to tissue implants, cartilage, load bearing structures or for the development of model synthetic systems. Similar effect in terms of strain or work hardening has been observed for metals where movements in dislocations in crystal structure influences their stiffness. In work hardening, mechanical strain causes creation and movements of dislocations in the
crystal structure, which prevents further mechanical deformation and thereby increasing the material strength.

Unlike biological tissue, synthetic rubbers lack internal structure that can reorganize in response to external forces. Conventionally, under repeated mechanical stress synthetic materials undergo microstructural damages causing various failure mechanisms such as delamination, cracking, fracture. As per Mullins effect, polymer networks exhibit softening when subjected to cyclic strain\textsuperscript{104,105}. While the Mullins effect is not fully understood, it has been seen in crystallizable rubbers or rubbers with added fillers and has also been observed in biological tissue\textsuperscript{106,107}. Several physical interpretations\textsuperscript{105} were proposed to explain the Mullins effect such as bond rupture, chain rupture, molecules slipping, filler rupture, chain disentanglement etc. Recently, stiffening behavior was reported for bundled actin networks under cyclic shear\textsuperscript{108}. This was observed at higher crosslink densities and attributed to the physical nature of the network, which allowed reorganization of the network constituents, resulting in hardening after cyclic shear\textsuperscript{108}. By contrast, an unexpected stiffening response was recently reported for a composite system made up of a poly(dimethyl siloxane) elastomers and a dense, aligned array of carbon nanotubes\textsuperscript{104,109}. The presence of carbon nanotubes was found to be necessary to self-stiffening. Recent studies have also reported work hardening in all polymer system but at higher strain values such as interpenetrating polymer network hydrogels\textsuperscript{110} and poly(dimethyl siloxane) network at low temperatures\textsuperscript{111}.

Herein, we report self-stiffening in pure elastomers; specifically, polydomain liquid crystal elastomers (LCEs) in response to repetitive compressive stress. We demonstrate
this response for a series of LCEs and attribute the increase stiffness to macroscopic ordering of the nematic liquid crystal (LC) director. As mentioned before LCEs exhibit the phenomenon of ‘soft elasticity’ due to the additional internal degrees of freedom of network anisotropy and long-range ordering. Soft elasticity enables LCEs to accommodate large strains with little resistance\textsuperscript{18,112,113}. LCEs are homogeneous materials on macroscopic length scales but are comprised of various molecular constituents. Under cyclic loading, the transition from the polydomain to monodomain state can to some extent be understood as the motion/rotation of these separate constituents, but more accurately it represents a collective motion of side-groups, crosslinker, and polymer network segments.

In the case of polydomain LCEs, the nematic director is globally disordered and mechanical strains or external electric or magnetic field can be used to uniformly align the nematic director\textsuperscript{20,114–116}, but this typically requires large strains (> 50%) or external electric or magnetic fields. The use of low-strain, repetitive compression represents a facile method to prepare uniformly aligned LCEs, which are typically prepared by applying large tensile strains or external fields during material synthesis\textsuperscript{117–122}.

The novelty of the present work is the discovery of dynamic stiffening in a synthetic, homogeneous polymeric network with liquid crystalline order. Additionally, the presence of liquid crystal order enables quantitative characterization of side-group and network chain orientation before and after deformation, establishing a direct connection between stiffening and network chain conformation. The observed dynamic stiffening in polysiloxane LCEs may be useful for the development of self-healing materials and
biocompatible, adaptive materials for tissue replacement. Previous works have focused on the properties of LCEs under large-strain deformation, but our findings indicate rich behavior at previously overlooked low-strain, dynamic deformations.

1.5 Research Motivations

Past studies on LCEs have mostly focused on understanding isolated properties of bulk LCEs under static conditions and large-strain deformation. My thesis is focused on the development of new functional materials based on LCEs and gaining new insight into the mechanical properties under dynamic deformations.

In chapter-2, LCE based buckling instability in thin film is demonstrated. Instability phenomena in thin films can give rise to well-defined, periodic topological features on surfaces and have led to technological applications in the fields of flexible electronics, thin film metrology, and micro/nano-fabrication. Thermally responsive LCEs allow buckling instability in nanoscale polymer films and can be used to measure modulus of nanoscale polymer films, down to 20 nm. Furthermore, the surface wrinkle orientation can be controlled using different preparation methods and reoriented in a single sample with temperature changes only. This overcomes the limitations of earlier known techniques that require clamping and mechanically straining films, which can introduce errors and present challenges with small samples. In Chapter-3 we demonstrate that well-defined self-folding 3D dynamic structures can be achieved in case of thick PS films (over 500 nm). By simply engineering film patterning on LCEs complex shapes like lotus or helix are possible. The phenomena are captured through finite element simulations, in
quantitative agreement with experiments and could be used to predict the film patterning on LCE to achieve desired 3D deformed shape.

In chapter-4, a new two-step approach of synthesizing electrically responsive LCEs via adding nanoparticles both before and after crosslinking is demonstrated. Electrically conductive liquid crystal elastomer nanocomposites (LCE-NCs) exhibit rapid (response times as fast at 0.6 s), large-amplitude (contraction by up to 30 %), and fully reversible shape changes (stable to over 5000 cycles) under externally applied voltages (5 – 40 V). LCE-NCs have robust mechanical, electrical and thermal properties; and exhibit a robust electromechanical response in air and cell culture media via joule heating. LCE-NCs provides a biocompatible electrically responsive dynamic scaffold for cell culture capable of mimicking the native cell growth conditions. Neonatal rat ventricular myocytes were cultured on LCE-NCs substrates, and good cell attachment and viability both with and without electrical stimulation is observed. Under voltage stimulation cells align in the direction of contraction/elongation of the substrate. LCE-NCs therefore represent versatile shape-responsive materials operable in biological media, and the work presented provides a general approach to LCE-NCs with a fast and reversible mechanical response to external stimuli. These materials potentially provide a straightforward and scalable route to aligned cell sheets and enable investigation of cell response to a dynamically changing surface pattern. The fully reversible and fast LCE-NCs response may also be of interest for applications including implantable materials, regenerative therapies, drug delivery, and packaging.
In chapter-5, a novel self-stiffening behavior in LCEs under dynamic deformation is discovered. While biological materials have the capacity to repair and strengthen in response to external stress, for example bone remodeling and strengthening, this is typically lacking in synthetic materials. Polydomain nematic liquid crystal elastomers (LCEs) exhibits increase in stiffness by up to 90% when subjected to a low-amplitude (5%), repetitive (dynamic) compression. Combination of rheological measurements, polarizing optical microscopy, 2-D X-ray diffraction and finite element modeling simulations, demonstrates dynamic stiffening is due to rotation of the nematic director under repetitive compression. While previous work has reported strain-induced realignment of the nematic director, the use of a low-strain, repetitive deformation represents a novel and easily implementable method to uniformly align LCEs. Furthermore, the observed dynamic stiffening in LCEs may be useful for the development of self-healing materials and biocompatible, adaptive materials for tissue replacement. Additionally, the use of low-strain, repetitive compression represents a facile method to prepare uniformly aligned LCEs, which are typically prepared by applying large tensile strains or external fields during material synthesis. Previous work has focused on the properties of LCEs under large-strain deformation, but our findings indicate rich behavior at previously overlooked low-strain, dynamic deformations.
2 Liquid Crystal Elastomers based Buckling Instability in Thin Films

The work described in this chapter was a collaborative work with Prof. Dr. Paul Luchette, Prof. Peter Palffy-Muhoray and Prof. Biswal.

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2.1 Abstract

Past studies on LCEs have mostly focused on understanding isolated properties of bulk LCEs, but relatively little is known about LCEs in micro- and nano-structured environments. Here, we will demonstrate that LCEs can be used to generate structured surfaces via reversible surface wrinkling and measure mechanical properties of polymeric thin films. A thin polymer film deposited on top of a shape-responsive LCE exhibits a reversible, periodic surface wrinkling pattern in response to temperature changes. The orientation of the wrinkles depends on the orientation of the nematic director and the temperature at which the bilayer is prepared, and the wrinkles can be re-oriented in a single sample by heating or cooling the sample above or below the preparation temperature. We show that this bilayer system can be used to measure the modulus of nanoscale thin poly(styrene) films deposited on the LCE. This system provides a simple method for measuring the mechanical properties of thin polymer films without the need for clamping and mechanical stretching and provides a new approach to generate reversible, microstructured surfaces.
2.2 Introduction

Periodic surface structures lead to novel properties and functionality. Some well-known examples from nature include structural colors in hummingbird feathers\(^{123}\), butterfly wings\(^{124}\) as well as the self-cleaning properties of the lotus leaf\(^{425}\) and have led to many technological applications in the fields of flexible electronics\(^{43,44,46,126–128}\), thin film metrology\(^{49}\), and micro/nano-fabrication\(^{50}\). Surface wrinkles have been used for over two decades to measure the forces generated by cells moving across a surface\(^{129–131}\), and more recent work has taken advantage of mechanically-induced surface wrinkling patterns to characterize the mechanical properties of nanoscale thin films\(^{49,55}\). The measurement of mechanical properties of thin polymer films is critical for a variety of applications including optics, data storage, microelectronics, and bioengineering etc. Additionally, superhydrophobic surfaces\(^{132}\) and surfaces with reversible wettability can be fabricated by controlling the surface topography.

Here, we report surface wrinkling in liquid crystal elastomers (LCEs), which exhibit large, spontaneous shape changes in response to temperature. LCEs are rubbery polymeric networks with long-range orientational and/or positional order\(^{18,20}\). Crosslinking of a poly(methylhydrosiloxane) (PHMS) polymer functionalized with liquid crystal molecules, also known as mesogens, results in a rubbery network with anisotropic mechanical properties and stimuli-responsive behaviour. In particular, LCEs can change shape reversibly in response to light\(^{13,133,134}\), temperature\(^{21,28}\), and electric fields\(^{135–139}\). Shape-changes in monodomain LCEs, which have a uniformly aligned liquid crystal (LC) director, can range from 10 % to 400 % of the initial LCE size.
We envisioned that LCEs could be used to generate reversible, periodic, and oriented surface patterns in response to modest temperature changes. Surface wrinkles induced by temperature changes have been reported using a poly(dimethylsiloxane) (PDMS) and shape-memory polymers, but LCEs offer fully reversible shape-changes. Other approaches for inducing surface wrinkling in elastomers include mechanical strain and osmotic stresses from solvent swelling.

Herein, we show that LCEs provide a reliable substrate for generating reversible surface wrinkles. Surface wrinkling can be induced in LCE-poly(styrene) (PS) bilayers by both increasing and decreasing temperature, and wrinkles can be re-oriented in a single sample by heating or cooling above the temperature at which the bilayer was prepared. Furthermore, surface wrinkles in LCEs can be used to measure the moduli of nanoscale thin PS films, down to a thickness of 30 nm. Finally, deposition of a micrometer-thick PS film on top of the LCE gives an elastomer which reversibly curls over a small (30-50 °C) temperature range.

2.3 Experimental

2.3.1 Monodomain LCE synthesis

The synthesis of monodomain LCEs was carried out by the two-step Finkelmann method. Briefly, LC (mesogen) monomer (207.5 mg, 0.696 mmol), diacrylate crosslinker 1,4-di(10-undecenyloxy)benzene (16.0 mg, 0.0387 mmol) and polymethylhydrosiloxane (34 mg, 0.774 mmol of repeat unit (Si-H), $M_w=2300$ g/mol) (Figure 2.1) are dissolved in 0.4 mL toluene along with 30 mL of a 1wt % solution of platinum catalyst dichloro(1,5-cyclooctadiene)platinum(II) in dichloromethane. Partial
crosslinking is achieved by heating the reaction mixture at 60°C for 1 hour. Next, the partially crosslinked elastomer is hung vertically, stretched by applying a load, and annealed at room temperature for several days. This results in uniform orientation of director along the stretching direction. For this study, LCEs with 10% crosslinking density were used. Thermal responsive behaviour of all the LCE samples was measured using optical microscopy equipped with heating stage before employing them for making LCE bilayers.

![Chemical structure and synthesis process]

**Figure 2.1:** The 2-step synthesis of polysiloxane based side-chain monodomain LCE

### 2.3.2 PS-LCE bilayer synthesis

PS-LCE bilayers were prepared by transferring a PS film onto LCE surface via a film transfer technique, similar to a technique previously described. Briefly, nanoscale PS films were prepared by spin-casting a 0.25 - 3 wt % PS solution ($M_w = 271$ kg/mol, polydispersity=1.02, Polymer Standards Service-USA Inc) onto a silicon substrate cleaned by UV-ozone treatment. To transfer the PS film to the LCE substrate, the LCE was gently placed on top of the PS film, and good contact between the LCE and PS film
was visually confirmed followed by immersed immersion in water at a fixed temperature for 10 hours, and then peeled off and dried under vacuum. Due to infiltration of water into the interface between PS film and Si wafer hydrophilic surface, the PS film detaches from the Si surface and is gradually gets transferred from the wafer onto the LCE. This method can be used to prepare LCE-PS bilayers with different PS film thicknesses and at different preparation temperatures.

![Figure 2.2: Schematic depiction of synthesis of LCE-PS bilayer via film transfer technique.](image)

### 2.4 Characterization of LCEs

Polarized optical microscopy (POM) measurements (Axioplan2, POM, SEA, Rice University) were carried out to check for the uniform alignment of mesogens in as synthesized LCEs. As shown in Figure 2.3, sample appears dark when the nematic director is parallel to one of the crossed polarizers and brightest when the director is oriented at a 45\(^\circ\) angle to the polarizers. Quantitative measurements of the extent of mesogen alignment were carried using 2D-WAXS measurements (Figure 2.4).
Figure 2.3: Optical microscope images of LCE between crossed polarizers with nematic director (a) 0°, parallel and (b) 45°, w.r.t polarizer or analyzer. Scale bar represent 50 µm. n and c represent orientation of nematic director and crossed polarizers respectively.

Figure 2.4 (a) 2D X-ray diffraction of monodomain nematic LCE. Data was acquired using a Rigaku Raxis-IV++ equipped with an incident beam monochromator, pinhole collimation (0.3 mm) and Cu X-ray tube (λ = 1.54 Å). The sample to detector distance was 100 mm. (b) Plot of intensity versus 2θ (°) for a 2D X-ray diffraction measurement of the monodomain sample of 5CB.

2.4.1 Mechanical characterization of LCEs

Mechanical properties of LCEs were determined via the stress-strain measurements performed using dynamic mechanical analyzer (DMA-Q800) (Figure 2.5). All the measurements were performed at a constant temperature of 30°C. Figure 2.5 shows that for initial strains (< 3%) the stress is almost negligible which is due to some initial slacking present after loading LCE in DMA-Q800. Hence detected force remains nearly constant until the LCE becomes taut. Elastic modulus of LCE determined by the slope of the stress-strain curve in the linear regime (neglecting data for strains < 3%) is ~0.24MPa.
Figure 2.5: Stress-Strain measurements of a LCE in a direction parallel to the nematic director.

2.4.2 Reversible Thermo-mechanical response in LCEs
Monodomain LCEs spontaneously change shape as a function of temperature due to the temperature dependent order parameter of the LC mesogens, and the shape change is fully reversible on both heating and cooling the sample. Variation of temperature, especially across the nematic-isotropic transition temperature \( T_{NI} \), leads to large changes in the nematic order parameter of LCEs. This increase or decrease in the nematic order drives a spontaneous elongation parallel or perpendicular to the director respectively. The degree of shape change both parallel and perpendicular to the nematic director for the LCEs was measured as a function of temperature using POM and a home-built heating stage (Figure). The temperature dependent shape change is completely reversible.
Figure 2.6 Shape change of LCE (10% crosslinking density) with temperature. $L_\parallel$: normalized LCE dimension parallel to director; $L_\perp$: normalized LCE dimension perpendicular to director. Normalization was done w.r.t corresponding isotropic lengths. The inset images show the shape change monitored at 35 and 90 °C under crossed polarizers. Scale bars represent 80 µm.

2.5 Result and Discussions

2.5.1 LCE based wrinkling instability

Bilayers composed of a thin polymeric film on top of a thick and deformable PDMS substrate exhibit surface wrinkling patterns in response to mechanical deformation. The patterns result from the in-plane compressive strain at the substrate/film interface and represent a compromise between the energy required to bend the stiff film and deform the PDMS substrate. We envisioned that spontaneous shape-changes in LCEs in response to external stimuli (heat) could be used to generate the in-plane compressible strain needed to induce wrinkling instability. To test this, uniformly aligned, side-chain nematic LCEs were prepared by the two-step crosslinking method. To test whether
Surface wrinkling could be induced with temperature changes in LCE bilayers, we prepared two PS-LCE bilayer samples, both with a 30 nm PS film and a 0.36 mm-thick LCE. The first sample was prepared by film transfer at 30 °C and the second at 60 °C. Surface wrinkling in both of these samples was monitored using optical microscopy equipped with a home-built heat stage. As shown in Figure 2.7, the sample prepared at 30 °C is uniform at room temperature but exhibits surface wrinkling when the temperature is increased to 40 °C. As the temperature increases, the LC order parameter decreases and the LCE spontaneously deforms, with contraction along the director (and dilation in the perpendicular directions) resulting in surface wrinkles above a critical strain (approximately 5%, achieved at 40 °C). Conversely, for the sample prepared at 60 °C, surface wrinkles oriented parallel to the nematic director appear upon cooling the sample. The LC order parameter increases as the temperature is decreased, resulting in a spontaneous elongational strain in the direction parallel to the global nematic director (and compressive stress normal to the director). For both cases, the wavelength of the surface wrinkles is independent of temperature above the critical strain.
As shown in Figure 2.8, the orientation of wrinkling pattern is set by the temperature at which PS is deposited via film transfer technique. When PS film transfer is carried out at temperatures below room temperature, 5-6 °C, the LCE order parameter decreases on heating back to room temperature and the sample contracts along the director. Conversely, when film transfer is carried out at elevated temperatures, the nematic order parameter increases on cooling down to room temperature, resulting in a uniaxial extension of the LCE along the director and wrinkles parallel to the director.
Figure 2.8: Schematic for the preparation of LCE-PS bilayers at two different temperatures and optical microscopy images for resulting surface wrinkles at 30°C. Wrinkling wavelength and PS film thickness are approximately 3 µm and 30 nm, respectively, for the samples shown, and the scale bar is 20µm.

2.5.2 Reorientation of wrinkling pattern
While previous work has demonstrated temperature-induced surface wrinkling, LCE bilayers uniquely enable the reversible reorientation of wrinkles with temperature in a single sample. As shown in Figure 2.9a, an LCE-PS bilayer (35 nm PS and 0.36 mm LCE) prepared at 50 °C is uniform at 50 °C but exhibits surface wrinkles parallel to the nematic director if the sample is cooled below the preparation temperature. Conversely, if the sample is heated above the preparation temperature (to 60 °C) surface wrinkles appears oriented perpendicular to the nematic director. This response is fully reversible with temperature.
Figure 2.9 Optical microscopy images of the top surface of a PS-LCE bilayer (a) prepared at 50 °C (scale bars: 5 µm) and (b) prepared at 30 °C (scale bars: 10 µm). In (a), wrinkles are re-oriented in a single sample by heating or cooling past the preparation temperature. In (b), wrinkles are reoriented by heating to the Tg of PS, annealing the sample, and then cooling. n represents the orientation of LCE nematic director.

While relatively small temperature changes (20-30 °C) below the glass-transition temperature $T_g$ of the PS film give reversible surface wrinkling patterns, larger temperature changes over a range that exceeds the $T_g$ of the PS film can also be used to erase and re-orient surface wrinkles. To demonstrate this, a 50 nm PS thin film was transferred onto the LCE substrate at 30 °C and subsequently heated to the $T_g$ (~105 °C) of the PS film (Figure 2.9b). Surface wrinkles oriented perpendicular to the nematic director appear at temperatures below the $T_g$, but upon annealing the sample near the $T_g$.
of PS, surface wrinkles are ‘erased’ due to viscoelastic flow of the PS film. The surface becomes uniform after annealing for approximately 30 minutes, and on subsequent cooling surface wrinkles reappear oriented parallel to the nematic director.

One drawback of this technique is that large temperature variations are associated with large strains that can cause cracking or delamination of the PS films (Figure 2.10). Directional switching studies of wrinkling pattern orientation were performed with changing temperature by the magnitude of ~75 °C. This is significantly higher and introduces great strains in the system (~50%), which can lead to other phenomena such as cracking, delamination in PS film. Cracking of coatings under high strains has been reported previously \(^{147-151}\). It was shown that width of cracks is strongly dependent on the thickness of coating and applied stress. The formation of cracks in the top PS film makes the LCE based wrinkling instability reversible only for small strain values (<5 %). The cracking phenomena could be avoided by selecting the polymers with lower \(T_g\) values (for example poly (methacrylate)\(^{152}\)) or tuning the \(T_{NI}\) of LCEs.
Figure 2.10: (a) Schematic and optical microscope images of various phenomena that occurs in nanoscale thin PS films on the LCE substrate under high strains (b) cracking (c) delamination and (d) both.

2.5.3 Mathematical model
Surface wrinkles in bilayer samples are a type of Euler buckling instability where the stiff, thin film (PS in the present study) is in contact with a softer and thicker substrate; compressive stress leads to more favorable short wavelength displacements in-comparison to simple bowing. In this section we briefly review the buckling instability theory of a stiff film on top of a compliant substrate, which has been previously described. Both film and the substrate are assumed to be linear elastic solids, and it is assumed that no slipping occurs at the interface between the film and the substrate. The film thickness \( h \) is significantly smaller than the thickness of the substrate whereas the modulus of the thin films is significantly greater than that of the substrate. When the system undergoes a small elastic deformation characterized by applying compressive strain \( \varepsilon \), the film/substrate bilayer is uniformly compressed and the surface remains flat below a critical value for the strain. Above a critical value, the film and substrate surface buckle, forming a wrinkling pattern (Figure 2.11). This buckling instability represents a compromise between the energy required to bend the stiff upper film and to deform the softer underlying substrate.
Figure 2.11: Schematic illustration of a wrinkling instability for a stiff thin film on top of a compliant substrate.

Surface wrinkling instability can be analyzed using Euler-Bernoulli beam-bending equation\textsuperscript{154} and introducing an additional term to account for the applied force for stretching:

\[
E_f I \frac{d^4 z}{dx^4} + F \frac{d^2 z}{dx^2} + k z = 0 \quad (1)
\]

Where \( E_f = E_f / (1 - \nu_f)^2 \) is the film plane-strain modulus with \( E_f \) Young’s modulus and \( \nu_f \) for Poisson’s ratio, \( I \) is the moment of inertia, which is equal to \( \frac{wh^3}{12} \) for a film of width \( w \) and thickness \( h \). \( F \) is the applied force, and \( k \) is the Winkler’s modulus\textsuperscript{153}. Assuming a sinusoidal profile for the buckling gives:

\[
z(x) = A \sin(2\pi x/\lambda) \quad (2)
\]

Where \( A \) and \( \lambda \) are the amplitude and wavelength of the wrinkling pattern. Substitution of Equation 2 in Equation 1 yields

\[
F = 4E_f I \left( \frac{\pi}{\lambda} \right)^2 + E_s w \frac{\pi}{\lambda}^{-1} \quad (3)
\]

Where \( E_s = E_s / (1 - \nu_s)^2 \) is the substrate plane-strain modulus with \( E_s \) Young’s modulus and \( \nu_s \) for Poisson’s ratio. According to Equation 3, there exists a particular value of \( \lambda \) at which \( F \) is minimized (\( F_c \)). For a film/substrate bilayer under a compressive strain \( e \), the surface remains flat for values of \( F \) lower than \( F_c \), when \( F \) exceeds \( F_c \) the system undergoes a wrinkling instability. Minimization of Equation 3 with respect to \( \lambda \) yields
\[ \lambda = 2\pi h \left( \frac{E_f}{3E_s} \right)^{1/3} \] (4)

Equation 4 and Equation 3 could be used to calculate the critical force \( (F_c) \), stress \( (\sigma_c) \) and strain \( (\varepsilon_c) \) required to induce wrinkling instability.

\[ \sigma_c = \left( \frac{9}{64} E_s^2 \frac{E_f}{E_s} \right)^{1/3}; \quad \varepsilon_c = \frac{1}{4} \left( \frac{3E_s}{E_f} \right)^{2/3}; \quad A = h \sqrt{\frac{\varepsilon - \varepsilon_c}{\varepsilon_c}} \] (5)

An expression for the wrinkling amplitude is derived by assuming that the release of tensile strain in the system, upon onset of the instability, is equal to the difference between the applied strain and the strain needed to induce the instability. Equation 4 and Equation 5 provides simple expressions for the wavelength of the instability, the critical strain at which the wrinkling instability first appears, and the amplitude of the instability as a function of the strain. This analysis of the surface wrinkling instability has been widely applied to thin films on laminated polymeric substrates, especially PDMS, and agrees well with experimental data.

2.5.4 LCE based wrinkling instability as a metrological tool

Accurate measurement of the mechanical properties of thin polymer films is important for a number of technological applications including coatings, optical reflectors and filters, dielectric stacks and lithographic resists. Methods available to measure mechanical properties of thin films include scanning probe microscopy (SPM) and nanoindentation, but discrepancies of up to 70% have been reported in nanoindentation measurements of polymeric materials. For SPM measurements, uncertainty in the tip size and contact area compromise accuracy, and the method is inherently low-throughput. By contrast, surface wrinkling is a widely applicable,
accurate, and simple method for measuring mechanical properties of thin polymeric films. Problems associated with indentation techniques such as indentation depth, creep, and unloading rate do not interfere with measurements based on surface wrinkling.

The relationship in Equation 4 forms the basis of the technique known as strain-induced elastic buckling instability for mechanical measurements (SIEBIMM) and enables calculation of the thin film modulus via measurement of the wavelength of surface wrinkles and the modulus of the deformable substrate. This method has been used to characterize the properties of a variety of materials, including metal films, polymer brushes, polymer nanocomposites, carbon nanotubes, among others.

Here, we will apply SIEBIMM to measure the modulus of the nanoscale PS films and to test whether the relationship between the surface wrinkle wavelength and film modulus follows Equation 4. As described before, the elastic modulus of the LCE substrate was measured with a dynamic mechanical analyzer (DMA-Q800) and found to be 0.24 MPa. Using the same LCE sample, we tested PS film thicknesses ranging in thickness from 30 nm up to 400 nm (Fig 5). Samples were prepared at room temperature and heated to 40 °C to create surface wrinkles, and the wavelength of surface wrinkles was measured with an optical microscope. As shown in Figure 2.12 and Figure 2.13, the wavelength increases linearly with PS film thickness and varies from 2 mm up to 40 mm over this PS film thickness range. By applying Equation 4, we find that for film thicknesses greater than 100 nm, the measured modulus (Figure 2.14) is in good quantitative agreement with the bulk PS modulus of 3.5 GPa. At film thicknesses below 50 nm, we observe a
drop in the film modulus, similar to what has been previously observed in SIEBIMM measurements\textsuperscript{163,170}. These data indicate that LCEs are reliable substrates for measurement of polymer moduli via SIEBIMM without the need for clamping and mechanically straining the sample.

Figure 2.12 Optical microscopy images showing wrinkling patterns of PS-LCE bilayers with varying PS film thicknesses, measured by spectroscopic ellipsometry and indicated by the number at the top of each image. Scale bar represent 10µm.
Figure 2.13 Dependence of wrinkling wavelength on the PS film thickness for PS-LCE bilayer system. Thickness measurements of PS film were within error of 1%. The data points and error bars were evaluated by repeating each measurement six times.
Above a critical thickness of the PS film (for a particular LCE thickness), surface wrinkling is no longer favored. Instead, due to the elongational anisotropy of the PS and LCE films, PS-LCE bilayers exhibit reversible curling. This was observed for a bilayer sample prepared at room temperature with a 986 nm-thick PS film and 0.36 mm-thick LCE. While initially flat at room temperature, the bilayer reversibly curls over a temperature range of 30-80 °C, near the nematic-to-isotropic transition temperature ($T_{NI}$) of the LCE (see Figure 2.15 and video in supporting information). The LCE curling phenomenon is found to be very reversible (Figure 2.16), with only slight hysteresis is observed after subjecting the sample to several heating and cooling cycles. This response
analogous to the bending and twisting of elastomers by non-homogeneous swelling\textsuperscript{171} and the reversible curling in metallic bilayer strips\textsuperscript{154,172–175}, where the curvature of bilayer is proportional to the difference in elongation of the two layers. This has a potential implication as a thermo responsive self-folding capsules in biomedical applications. An advantage of the PS-LCE bilayer system is the large strains that are achieved over a temperature range of approximately 30-50 °C. The performance is comparable to those demonstrated in dielectric elastomer actuators (strains up to 300% have been reported by applying an electric field of 420 MVm\textsuperscript{-1})\textsuperscript{176,177} but can be achieved with temperature changes instead of external voltages. More detailed investigation of self-folding in LCEs is described in chapter-3.

Figure 2.15 Images of PS-LCE bilayer reversibly curling with temperature. PS film and LCE substrate were 986 nm and 0.36 mm in thickness, respectively.
Figure 2.16 Curvature of PS-LCE bilayer as a function of number of heating (30-80 °C) and cooling (80-30 °C) cycles. PS film and LCE substrate were 986 nm and 0.36 mm in thickness, respectively. Curvature was measured by taking images of the LCE sample during heating and cooling cycles and processing the images using ImageJ 1.440.

2.6 Conclusions

In summary, we have demonstrated that LCEs can be used to generate reversible, periodic surface patterns. Surface wrinkles spontaneously develop with temperature changes due to the temperature dependent shape of the LCE substrate, and the orientation of the surface wrinkles is either parallel or perpendicular to the nematic director, depending on the sample preparation conditions and direction of temperature change. Surface wrinkles can be reoriented in a single sample by heating and cooling beyond the sample preparation temperature. LCEs can be used as a metrology tool to accurately measure the moduli of nanoscale polymer films via SIEBIMM, and above a critical thickness ratio of PS film to LCE substrate the PS-LCE bilayer exhibits reversible curling with temperature.
3 Shape Responsive Liquid Crystal Elastomer Bilayers

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3.1 Abstract

Monodomain liquid crystal elastomers (LCEs) are shape-responsive materials, but shape changes are typically limited to simple uniaxial extensions or contractions. In chapter-2 we demonstrated LCEs could be used to generate structured surfaces via reversible surface wrinkling and measure mechanical properties of polymeric thin films. Here, we demonstrate that complex surface patterns and shape changes, including patterned wrinkles, helical twisting, and reversible folding, can be achieved in LCE-polystyrene (PS) bilayers. LCE-PS bilayer shape changes are achieved in response to simple temperature changes and can be controlled through various material parameters including overall aspect ratio and LCE and polystyrene film thicknesses. Deposition of a patterned PS film on top of an LCE enables the preparation of an elastomer that reversibly twists and a folding leaf-like elastomer, which opens and closes in response to temperature changes. The phenomena are captured through finite element simulations, in quantitative agreement with experiments.
3.2 Introduction

Natural systems that can fold or change shape in response to environmental changes are well-known, and synthetic materials that behave similarly are desirable for applications including optics\textsuperscript{178,179}, three dimensional (3D) biological scaffolds\textsuperscript{180–182}, particle alignment\textsuperscript{183}, responsive surfaces\textsuperscript{184,185} and controlled release and encapsulation of drugs, particles and cells\textsuperscript{186–188}, among other applications. Synthetic self-folding materials have been demonstrated through the use of homogeneous bilayers\textsuperscript{189–191}, comprised of one active and one passive layer. Folding is triggered by a shape-transition in the active layer, which leads to folding due to restricted motion by the passive layer. Previous studies explored pH-responsive\textsuperscript{192}, thermoresponsive\textsuperscript{172,174,193}, solvent responsive\textsuperscript{194,195} and electrically sensitive active layers\textsuperscript{196}, and patterning of an active layer on passive layers provides more complex shape changes\textsuperscript{194,195}. Solvent swelling is typically used since it can provide large, reversible volume changes\textsuperscript{197}.

In this study, we demonstrate versatile self-folding behaviour in elastomeric bilayers in response to temperature changes. The phenomenon is based on monodomain nematic liquid crystal elastomers (LCEs), which have a uniformly aligned nematic director and undergo spontaneous uniaxial shape changes with variations in temperature. This enables the preparation of reversible self-folding elastomeric materials, and with patterning of a passive layer on the active LCE, more complex, 3D shape changes can be achieved. While shape-memory polymers enable
complex 3D shape changes, LCEs offer the advantage of full reversibility and significant shape and texture changes near room temperature. Self-folding films have also been demonstrated in photolithography patterned polymer-multilayer films driven by residual stresses present\textsuperscript{181,198}, and LCEs offer the possibility to control the magnitude of these stresses through the temperature-dependent shape of the LCE.

Previous work with monodomain LCEs have demonstrated uniaxial extensions and contractions with temperature changes, and work with liquid crystal films has led to more complex deformations \textsuperscript{199–207} achieved by 3D patterning of the liquid crystal director in planar, twisted nematic, homeotropic, and splay geometries. Here, we demonstrate a straightforward approach using monodomain LCE coated with a thin PS top film, which we refer to as an LCE-PS bilayer. In recent work, we studied reversible wrinkling and folding in LCE-PS bilayers\textsuperscript{208}. Here we show that this relatively simple system enables a rich response beyond reversible folding through variation of several system parameters: the thickness ratio of PS to LCE, the overall aspect ratio of the bilayer, the relative stiffness of the top film and LCE, bilayer preparation temperature, and patterning of the top passive film. Finite element method (FEM) simulations can predict the self-folding behaviour of LCE bilayers and are in quantitative agreement with experimental observations.

\textbf{3.3 Experimental}
3.3.1 LCE synthesis
Monodomain LCEs were prepared via 2-step Finkelmann method\textsuperscript{209} as described in chapter-2.

3.3.2 LCE-PS bilayer synthesis via Film Transfer Technique
PS-LCE bilayers were prepared via film transfer technique as described in chapter-2.

3.4 Result and Discussions
Monodomain LCEs spontaneously change shape as a function of temperature\textsuperscript{21,210}, and the shape change is fully reversible on both heating and cooling over several cycles, as shown in Figure 3.2. In the self-folding materials studied below, film transfer is carried out near room temperature. Residual stresses are present after film transfer due to unintended strains and deformations during deposition. Earlier investigations have shown that residual stresses can cause debonding\textsuperscript{211,212} and cracks in the film\textsuperscript{213,214}. To reduce the effect of residual stresses, all LCE-PS bilayer samples are annealed for 2 hours above the $T_g$ of PS before measurement. The PS film thickness was measured by spectroscopic ellipsometry (Accurion, GmbH, Germany) for thin PS films and by UV-Vis for thicker films (thickness > 1µm)\textsuperscript{215}.
Figure 3.2: Change in the LCE dimensions parallel ($L_\parallel$) and perpendicular ($L_\perp$) to the nematic director for several heating and cooling cycles (bottom). $L_\parallel$ and $L_\perp$ are normalized with respect to their values at 30°C. Length changes of monodomain LCEs were measured using DMA-Q800 at a heating and cooling rate of 5°C/min.

In previous study (chapter-2), we have demonstrated that LCEs can be used to generate reversible, periodic surface patterns. Surface wrinkles spontaneously develop with temperature changes due to the temperature dependent shape of the LCE substrate, and can be used as a metrology tool to accurately measure the moduli of nanoscale polymer films via SIEBIMM. Above a critical thickness of the PS film (for a particular LCE thickness), surface wrinkling is no longer favored. Instead, due to the elongational anisotropy of the PS and LCE films, PS-LCE bilayers exhibit reversible curling. This was observed for a bilayer sample prepared at room temperature with a 986 nm-thick PS film and 0.36 mm-thick LCE. While initially flat at room temperature, the bilayer reversibly curls over a temperature range of 30-
80 °C, near the nematic-to-isotropic transition temperature ($T_{NI}$) of the LCE (see Figure 2.15 and video in supporting information). The LCE curling phenomenon is found to be very reversible, with only slight hysteresis is observed after subjecting the sample to several heating and cooling cycles. This response analogous to the bending and twisting of elastomers by non-homogeneous swelling\textsuperscript{171} and the reversible curling in metallic bilayer strips\textsuperscript{154,172–175}, where the curvature of bilayer is proportional to the difference in elongation of the two layers. This has a potential implication as a thermo responsive self-folding capsules in biomedical applications. An advantage of the PS-LCE bilayer system is the large strains that are achieved over a temperature range of approximately 30-50 °C. The performance is comparable to those demonstrated in dielectric elastomer actuators (strains up to 300% have been reported by applying an electric field of 420 MVm\textsuperscript{-1})\textsuperscript{176,177} but can be achieved with temperature changes instead of external voltages.

By varying PS film thickness, we can induce folding in PS-LCE bilayers, as shown in Figure 3.3. At low film thicknesses (< 500 nm) surface wrinkling is observed\textsuperscript{208}. As the PS film thickness increases, the periodic wrinkles increase in wavelength until they are completely suppressed in favor of bilayer folding. The curvature of the self-folded structure first increases with increasing PS film thickness and then decreases as the passive PS film suppresses any deformation, shown in Figure 3.3 for PS film thicknesses in the range of 0.65 mm – 10 mm.
3.4.1 Theoretical Model

The surface wrinkling instability phenomena is a result of Euler structural instability$^{216}$ and can be quantitatively described using the Euler-Bernoulli beam-bending equation$^{217-219}$. Briefly, the surface wrinkling instability represents a compromise balancing the energy for deformation of both the thin PS film and soft LCE substrate while satisfying no-slip boundary conditions at the interface. As the PS film thickness increases, the energy for a wrinkling deformation increases and eventually is suppressed in favor of folding. LCE-PS bilayer folding can be quantitatively described using beam bending theory$^{154}$. FEM simulations were
performed using COMSOL Multiphysics 4.2 simulation package to predict self-folding behavior in LCE bilayers. The LCE substrate and thin polymer film are assumed to be linear elastic solids with no slipping at the bilayer interface. To reproduce the experimental conditions, the temperature of the bottom surface of the LCE is increased from 298 K ($T_{\text{ref}}$) to 349 K (the nematic-to-isotropic transition $T_{NI}$) in the simulations. All other surfaces are open to ambient conditions, resulting in a small temperature gradient across the sample. The thermal conductivity of poly(dimethylsiloxane) is used in the calculations, and the LCE thickness is 500 mm in the simulations. LCEs were modeled as having different thermal expansion coefficients in different directions relative to the nematic director:

$$\alpha_x = \frac{1}{T_{NI} - T_{\text{ref}}} \left( \frac{\Delta L_x}{L_x} - 1 \right); \quad \alpha_y = \frac{1}{T_{NI} - T_{\text{ref}}} \left( \frac{\Delta L_y}{L_y} - 1 \right); \quad \alpha_z = \frac{1}{T_{NI} - T_{\text{ref}}} \left( \frac{\Delta L_z}{L_z} - 1 \right)$$

where $\Delta L_x$, $\Delta L_y$ and $\Delta L_z$ represents the change in dimensions of the LCE as temperature increases from $T_{\text{ref}}$ to $T_{NI}$. Dimension changes along the length and width ($\Delta L_x$ and $\Delta L_y$) of LCEs were measured by temperature-controlled optical microscopy using a Zeiss microscope equipped with THMS 600 hot plate, and the value of $\Delta L_z$ is calculated assuming volume conservation\textsuperscript{18}. We used a value of $7.10^{-5} \text{ K}^{-1}$ for the thermal expansion coefficient of PS\textsuperscript{220}.

### 3.4.2 Effect of film thickness on LCE bilayer deformation

FEM simulations capture the self-folding response and the dependence of curvature on film thickness. As shown in Figure 3.4, the curvature predicted by FEM is in quantitative agreement with experimental observations for 5 different samples. Curvature decreases with PS film thickness above 2 mm, and for much thicker films the folding is almost completely suppressed. Note that FEM simulations ignore the effects of gravity. Experimentally, we found that folding was completely suppressed for LCE-PS bilayers with very thick PS films (> 10 mm), as shown in Figure 3.3. Videos showing the unfolding of an LCE-PS bilayer and
snapshots of FEM simulations of LCE-PS bilayer folding are provided in the supporting information.

![Diagram](image)

**Figure 3.4:** Comparison of simulations and experimental results for the curvature values of the deformed LCE-PS bilayers as a function of PS film thickness. Points correspond to experimental measurements and the line shows FEM simulation predictions. The LCE thickness is 0.48 mm in the experiments and 0.5 mm in the simulations. LCE bilayer aspect ratio is 3. Snapshots of FEM simulations are shown.

The aspect ratio of the LCE bilayer is also important for the shape response, (Figure 3.5) as has been reported for other self-folding materials\(^2\). For bilayer aspect ratios \(L_||/L_\perp\) greater than 1, the bilayer folds along the nematic director, with increasing curvature for higher aspect ratios. For aspect ratios less than one, the film folds primarily along an axis perpendicular to the nematic director but also along the director, resulting in a saddle-like shape, as shown in Figure 3.5. This reflects the presence of two orthogonal stresses in the LCE bilayers: tensile stress along the director and compressive stress perpendicular to director.
Figure 3.5: Comparison of simulations and experiments for the curvature values of the deformed LCE-PS bilayers as a function of bilayer aspect ratio. Filled and unfilled circles represent experiment and simulation data points, respectively. The LCE thickness is 0.48 mm in the experiments and 0.5 mm in the simulations. PS film thickness is 1.2 µm.

3.4.3 Effect of film stiffness on LCE bilayer deformation

Previous studies have shown that the stiffness of the film deposited on top of the soft elastomer is relatively unimportant to the folding response\textsuperscript{154}. Finite element modeling simulations performed here also predicted the same. For several orders of magnitude changes in the film modulus, relatively modest changes to the curvature are predicted. Experimentally, we tested folding in LCE-PS and LCE-poly(3-hexylthiophene) (LCE-P3HT) bilayers. The stiffness of P3HT is approximately 1.3 GPa,\textsuperscript{222} compared with 3.5 GPa for PS. The elastic modulus of the LCE substrate was measured to be 0.24 MPa.
3.4.4 Complex shapes via LCE bilayers

Complex 3D shape changes can be achieved by patterning the PS film on top of the LCE. Depositing a patterned top film constrains the shape-change in a particular direction, allowing for curling in opposite directions or twisting with controlled chirality. As shown in Figure 3.7, relatively simple surface patterns can give controlled curling and twisting. An ‘S-shape’ is achieved by coating half of the elastomer on opposite sides with a thin PS or Au film. A twisted elastomer is achieved by depositing a film of PS diagonally across the LCE, and a 4-arm folding elastomer is created by coating each arm on either the top or bottom surface with a PS film. Note that the LCE is a monodomain, and the nematic director is aligned parallel to the long axis of two arms and perpendicular to the long axis of two arms. These patterned LCEs were tested experimentally and in FEM simulations. Experiments were carried out with both LCE-gold and LCE-PS bilayers. The former were straightforward to pattern using a
Denton Desk V Sputter system and covering a desired portion of LCE during deposition. Prior to depositing gold on LCE, a very thin layer of chromium (5 nm) was deposited to ensure good adhesion of the metal film. The thickness of the gold film deposited was 80 nm.

FEM simulations demonstrate that curling to form an S-shape, twisting, and closing of a 4-armed LCE structure can be achieved through patterned LCE-PS and LCE-Au bilayers. For each sample, the final curvature is affected by the thickness ratio and aspect ratio of the bilayers.

As shown in Figure 3.7, controlled curling and twisting was achieved experimentally in patterned LCE bilayers. Four-armed curling was achieved in both LCE-gold (LCE-Au) and LCE-PS bilayers. The latter gave a larger degree of curling on heating and a better match to FEM simulations, likely due to the large modulus of gold. Although FEM simulations and measurements indicate the top film modulus has a relatively modest effect, very stiff films can suppress shape changes (see ESI). A video demonstrating the folding of the four-armed elastomer leaf is provided in the ESI.
3.4.5 Complex shapes via LCE bilayers at low temperature

As-prepared LCE bilayer samples are flat at room temperature and folded at elevated temperature, but the temperature dependence of the folding can be easily reversed in LCE-PS bilayer samples through thermal or solvent annealing, as shown in Figure 3.8. Films heated above the $T_{NI}$ initially fold or wrinkle, but on annealing above the PS glass-transition temperature $T_g$ (105 °C), folding or wrinkling is erased due to relaxation of the PS film. On cooling back to room temperature, the PS film becomes glassy and the LCE deforms below the $T_{NI}$ resulting in a folded sample at room temperature. The temperature dependence below $T_{NI}$ of the resulting curling is opposite that of the initially prepared sample, and the final deformation is fixed at room temperature. To recover the initial response – flat at room temperature and folded at elevated temperature – the same sample can be solvent annealed at room temperature. Solvent annealing (dichloromethane) swells the PS film, resulting in
relaxation of the bilayer and recovery of the undeformed bilayer sample. Subsequent heating results in folding or wrinkling as in the initially prepared sample. Thus, LCE-bilayers enable fully reversible folding and a tunable temperature dependence of the shape.

![Image of LCE-PS bilayer behavior](image)

Figure 3.8: Behavior of LCE-PS bilayers at temperatures below $T_g$ and after annealing above $T_g$.  

### 3.5 Conclusions

We demonstrated a straightforward method for achieving 3D temperature dependent shape changes in LCE bilayers. Homogeneous LCE-PS bilayers spontaneously curl at elevated temperature, with a curvature dependent on the thickness ratio of the PS and LCE layers and the overall sample aspect ratio. Patterned samples show more complex 3D shape changes, including controlled curling and twisting. As-prepared samples are undeformed at room temperature and folded at elevated temperatures, but the temperature dependence can be reversed by thermal annealing above the $T_g$ of the PS top film. Thus, the shape-response of LCE-PS bilayers is fully reversible and easily controlled through patterning, annealing, and variation of material parameters.
4 Electromechanically Responsive Liquid Crystal Elastomer Nanocomposites for Active Cell Culture

We acknowledge the support from Tomi Adetiba and Dr. Jeffery Jacot for designing and conducting the cell culture studies on LCE nanocomposites. In addition, Xianyu Li for conducting the XPS studies, Prof. Pulickel M. Ajayan for helpful discussion and providing the DMA-Q800 instrument to perform mechanical studies on LCE nanocomposites.

4.1 Abstract

Shape-responsive materials that respond quickly and reversibly to stimuli other than temperature changes are desirable for biomedical applications. To date, work has focused primarily on shape-memory polymers, which exhibit a one-way shape response. In this chapter a LCE based dynamic wrinkling instability is demonstrated by synthesizing an electrically conductive LCE nanocomposites (LCE-NCs) using a new two-step approach. Here, we demonstrate that electrically conductive liquid crystal elastomer nanocomposites (LCE-NCs) exhibit rapid (response times as fast at 0.6 s), large-amplitude (contraction by up to 30 %), and fully reversible shape changes (stable to over 5000 cycles) under externally applied voltages (5 – 40 V). LCE-NCs are prepared by adding conductive carbon black nanoparticles before and after crosslinking, and LCE-NCs exhibit a robust electromechanical response in air and cell culture media. Neonatal rat ventricular myocytes cultured on electrically-stimulated LCE-NCs exhibit enhanced elongation and alignment along the primary direction of strain. LCE-NCs represent versatile shape-responsive materials operable in biological media, and the work presented provides a general approach to LCE-NCs with a fast and reversible mechanical response to external stimuli.
4.2 Introduction

Shape-responsive materials have been developed for a broad range of applications including tissue engineering, endovascular devices for stroke treatment, active cell culture, antifouling, and microfluidics, among others. For biomedical applications, there is a need for materials that are responsive to stimuli other than temperature changes in the surroundings. To give a few examples, biocompatible shape-responsive materials can be implemented as surgical stents for simplifying tying and untying knots or placing sutures. Light responsive, reactive polymer systems can be used as reversible adhesives to bond and de-bond surfaces controllably with light exposure. Responsive polymeric surfaces are of interest for active cell culture, where in a changing surface topography or substrate stiffness triggered by an external stimulus can lead to a change in cellular growth and alignment.

Polymer nanocomposites that bring together a polymer network with functional nanoparticles are responsive to stimuli including electricity, magnetic fields, and light. Work with responsive polymer nanocomposites to date has largely focused on shape-memory polymers for the responsive polymer network, but a drawback of shape-memory polymers is their one-way shape response, with some exceptions. Other examples of shape-responsive materials include reactive polymer networks, supramolecular polymers, liquid crystal elastomers, dielectric elastomers and the introduction of nanoparticles into these responsive polymers enables enhancement of modulus and the triggering of a stimuli response through indirect heating, such as through the application of an electric field or magnetic field. To date, a material that exhibits a fast and fully reversible shape change operable in biological media has not been reported.

Among these various shape-responsive materials, polysiloxane-based liquid crystal elastomers (LCEs) are distinguished by a large-amplitude and fully reversible shape change.
Polysiloxane LCE nanocomposites (LCE-NCs) can exhibit a fast shape-response response to various external stimuli including electrical currents\textsuperscript{231,232}, alternating magnetic fields\textsuperscript{233,234}, or light\textsuperscript{235,236}. However, LCEs and LCE-NCs have not been incorporated in living systems due to several technical challenges. First, nematic-to-isotropic transition temperatures in LCEs are typically 70 °C or higher. Second, electrically-responsive LCE-NCs reported are unstable to cycling the electromechanical response quickly degrades. Finally, it is unclear whether LCEs or LCE-NCs are biocompatible and can be implanted or interfaced with living systems.

Here, we report conductive LCE-NCs that have a rapid and stable electromechanical shape response and can be used as responsive substrates for dynamic cell culture. LCE-NCs are prepared by introducing conductive carbon black nanoparticles both before and after crosslinking. The resulting LCE nanocomposites are electrically responsive and capable of rapid (response times as fast at 0.6 s), large-amplitude (contraction by up to 30 %), and fully reversible shape changes in response to applied voltages (5 – 40 V). In contrast to other LCE-NCs and shape-responsive materials studied, the electromechanical response is fully reversible (up to 5000 cycles tested) and operable in cell culture media with negligible heating of the surroundings. To demonstrate the biomedical application of LCE-NCs, we utilize conductive LCE-NCs as responsive substrates to culture neonatal rat ventricular myocytes (NRVM). Contractile properties of cardiac tissues is known to be related to cellular alignment\textsuperscript{237}, and substrates that can improve myocyte elongation and alignment are of interest for regenerative therapies. We find that NRVM remain viable on both stimulated and static LCE-NC substrates, and NRVM cultured on responsive substrates exhibit dramatically improved alignment and cell elongation.

### 4.3 Experimental

#### 4.3.1 LCE nanocomposites (LCE-NCs) synthesis
LCE nanocomposites are synthesized by introducing carbon black nanoparticles within LCE matrix via two-step method. First, carbon black nanoparticles are blended with the reactive mixture (vinyl terminated mesogen monomer + divinyl crosslinker + polyhydromethylsiloxane + toluene) before crosslinking. The first-step of crosslinking was performed in a mold along with a slow rocking motion. This creates a slight agitation during crosslinking reaction to prevent the precipitation of nanoparticles. During crosslinking, the elastomer is uniaxially stretched to induce uniform alignment of the nematic liquid crystal director. Alignment is confirmed by polarized optical microscopy, wide angle X-ray scattering and by the reversible shape-change of the LCE with temperature.

Second, additional carbon black nanoparticles are introduced through solvent swelling in a chloroform dispersion of carbon black nanoparticles (7 mg/mL). This results in infiltration of carbon black nanoparticles into the surface of the sample and a higher carbon black content along the sample edges. Choice of solvent is based on the LCE solubility. Solvents like methanol and hexanes are poor solvents for LCE network, resulting in no or very less penetration of nanoparticles within the network. On the other hand, dichloromethane is an extremely good solvent and it basically tears apart the LCE network. We found toluene to be an appropriate solvent. In toluene, LCE expands reasonably (~400%) causing nanoparticles to penetrate few micrometers inside the rubbery network and thereby decreasing the resistivity of the resulting composite. Afterwards, air drying the sample leaves behind a micrometer thick conductive layer of nanoparticles on the LCE surface (Figure 4.1).

As control studies, monodomain LCEs\textsuperscript{17} and conductive LCEs\textsuperscript{238} via immersion approach were also synthesized as reported previously.
4.3.2 LCE nanocomposites characterization

A series of aligned LCE-NCs were prepared using this two-step approach with varying amounts of nanoparticle added before crosslinking, followed by surface infiltration of additional carbon black through solvent swelling. As shown in Figure 4.3, the thermo-mechanical strain decreases with increasing amount of nanoparticles added before crosslinking. Pure LCEs and LCE-NC 0% (surface infiltration only) exhibit roughly 35% length contraction with heating while LCE-NC 6% exhibits a maximum contraction of 15%. The weakened thermo-mechanical response of LCE nanocomposites could be due to poor alignment (low order parameter) of LC polymer chains. 2D-Wide angle X-ray diffraction measurements reveal that that the liquid crystal order parameter decreases with increased nanoparticle content (Figure 4.3). The addition of nanoparticles also increases the LCE modulus, from a value of 1.1 kN for pure LCEs to 8.1 kN for 20 wt % nanoparticles added.

Based on differential scanning calorimetry measurements, thermal phase transition behavior of LCE composites is found similar to that of the neat LCEs with a little shift of about few degrees in nematic-isotropic transition temperatures. We found that for LCE composite with low nanoparticles concentration (≤2 wt%) shift in $T_{NI}$ is few degrees on the lower side compared to neat LCE. But for concentration higher than 2wt%, $T_{NI}$ tends to be few degrees higher than that for neat LCE. Earlier studies have also shown the dependence of mesophase transition behavior of LCE composites on the nanoparticles concentration.
Figure 4.2: Thermo-mechanical response in LCE nanocomposites. Strain measurements along the nematic director were carried out using a dynamic mechanical analyzer (DMA-Q800) at a heating rate of 5°C/min. The number shown for each sample gives the wt % nanoparticles added before crosslinking. LCE-I, LCE-D and LCE-NC represents LCEs with nanoparticles added before, after and the both before and after crosslinking respectively.
4.4 Results and Discussions

4.4.1 LCE-NCs electromechanical response under steady voltage

The electromechanical response of LCE-NCs under a steady voltage was recorded under a pulsed electrical potential applied by a Myopacer pulse generator (Figure 4.4). Voltage and frequency parameters of applied field were varied from 40V to 10V and 90Hz to 10Hz respectively. Quantitative measurements of sample contraction and elongation in air were carried out using a DMA-Q800. Figure 4.4 shows the electromechanical response of LCE-NC with varying nanoparticles concentration as a function of applied voltage at 90hz frequency. At higher voltages (40V), maximum obtainable strain values are quantitatively comparable to the thermo-mechanical strain in these LCE composites at temperatures close to $T_{NI}$, which implies heat generation due to joule heating effect at 40V is enough to raise the LCE composite temperature above, or close to $T_{NI}$. Similar to voltage, frequency of applied signal...
also has a significant effect on the magnitude of electromechanical response in LCE composites.

Figure 4.4: Electromechanical response of LCE nanocomposites with varying nanoparticles concentration as a function of applied voltage at 90Hz and 10ms pulse width. Contraction of LCE composite along the nematic director was recorded using DMA-Q800. Electric field was applied using Myopacer.

4.4.2 Response time scales of electromechanical response in LCE-NCs
Response time of electromechanical behavior in LCE composites depends both on nanoparticles concentration and parameters of the applied electric field. Characteristics time scales (relaxation time, activation time) of the electromechanical response are shown in Figure 4.5. Activation time refers to the time duration when field is turned ON and LCE reaches within 1% of the final equilibrium strain value. Relaxation time indicates the time
period when field is turned OFF and LCE recovers back within 1% of its initial dimension. Figure 4.5a shows the activation time in LCE composites as a function of nanoparticles concentration and applied voltage. At all voltages, activation time is inversely proportional to the nanoparticles concentration. Low activation time is due to the increased conductivity of LCE-DI composites with increasing nanoparticles concentration. On the other hand relaxation time of LCE composites is solely a function of nanoparticles concentration (Figure 4.5). At a given voltage, relaxation time decreases with increasing nanoparticles concentration that is due to the increase in thermal conductivity and elastic modulus of LCEs with increasing concentration of nanoparticles. Frequency dependence of both activation and relaxation time is similar to the voltage.
Figure 4.5: Characteristic time scales of electromechanical response of LCE-NC composites with varying nanoparticles concentrations prepared via combination approach. (a) Activation and (b) relaxation time as a function of applied voltage at 90Hz and 10ms pulse width. Contraction of LCE composite along the nematic director was recorded using DMA-Q800. Electric field was applied using Myopacer.

4.4.3 Reversible electromechanical response in LCE-NCs

The reversible electromechanical response of LCE-NCs was recorded under a pulsed electrical potential applied by a Myopacer pulse generator in series with a time relay circuit (Figure 4.6a). Quantitative measurements of sample contraction and elongation in air were carried out using a DMA-Q800. As a representative example, in Figure 4.6b we show the electromechanical response of LCE-NC2% to a 40 V AC signal (60 Hz) with a 10.5 s pulse duration (10.5 s on and off times). LCE-NC 2% exhibits reversible contraction and elongation, in phase with the applied electrical potential. The sample contracts when the voltage is turned on and returns to its original length when the voltage is turned off. The strain amplitude is approximately 20 % and is completely reversible for the duration of the
experiment, 16 h or greater than 5000 cycles (Figure 4.6c). Movies of the LCE-NC shape response are provided in the Supporting Information.

**Figure 4.6:** Reversible electromechanical response in LCE-NC 2%. A schematic for our experimental set-up is shown on the top-left along with a photograph of the sample used in this experiment. (b) Overlay of electromechanical response in LCE-NC and the applied square wave signal with 10.5 s on and off times. (c) Shape response of LCE-NC2% composite along the nematic director under applied electric field of 40V, 60Hz and 10.5 s on/off times for about 18 hours. Strain measurements were carried out using a dynamic mechanical analyzer (DMA-Q800). Zoomed in snippets at different times shows electrically responsive LCE-NCs are stable to the cycling electromechanical response for large periods.

The amplitude and speed of the shape response can be tuned by varying the pulse duration, the applied voltage, and the nanoparticles concentration, as shown in Figure 4.7a-c. The strain amplitude is greater for larger pulse durations (Figure 4.7a), larger applied voltages (Figure 4.7b), and higher nanoparticles concentrations (Figure 4.7c). Under all of these conditions, the timescales for contraction and elongation are equal to the pulse duration.
The two-step approach to preparing LCE-NCs is important for achieving a reversible electromechanical response capable of multiple cycles. Previous work with LCE-NCs prepared through surface infiltration of carbon black found the electromechanical response degraded quickly. Conversely, LCE-NCs prepared through carbon black added before crosslinking only (without solvent swelling and surface infiltration) have much higher resistivities and poor electromechanical responses (Table 4-1). Thus, the surface infiltration step is important for achieving a high-conductivity, percolating conductive carbon black network near the sample edges, while the uniform carbon black dispersion is essential for stability and full electromechanical reversibility. As a result of this heterogeneous structure, LCE-NCs are electrically conductive only near the sample edges. Samples studied are cut from large rectangular pieces, and as a result opposite faces are not connected by percolating conductive pathways.
Table 4-1: Characterization of LCE nanocomposites with nanoparticles added only before crosslinking.

Thermo-mechanical strain is measured by heating sample above nematic-isotropic transition temperature. For electromechanical strain measurements a 20V, 60 Hz AC signal is used. Values in the parenthesis correspond to LCE composites with carbon black nanoparticles added both before and after the crosslinking. Shape change in LCE composite along the nematic director was recorded using DMA-Q800.

4.4.4 Discussion on electromechanical response in LCE-NCs

The shape-responsiveness of LCE-NCs can be attributed to Joule heating of the samples. When the electrical potential is turned on, the passage of an electrical current results in resistive heating, with power equal to $V^2/R$, where $V$ is the magnitude of the applied voltage and $R$ the sample resistivity. Resistive heating reduces the liquid crystal order parameter and induces spontaneous contractions in LCE along the nematic director, as shown in Figure 2.6. As a result, greater strain amplitudes are observed at higher applied voltages and higher nanoparticles concentrations (corresponding to samples with lower resistivity $R$). The strain amplitude is also dependent on the pulse period since longer pulse durations result in greater bulk temperature changes in LCE-NCs. Temperature variations in the sample can be quantitatively described through finite element modeling simulations. These simulations apply 3-D energy conservation equations assuming Joule heating through conductive pathways, heat dissipation at sample edges, and a length-independent thermal and electrical conductivity. Since electrical leads are connected to one side of the LCE-NC, heat is generated only on one surface of the elastomer. Experimental values are available for most
material parameters, and the heat transfer coefficient was found by comparison to experimental IR measurements of LCE-NCs in air. As shown in the Figure 4.9, reasonable agreement is found between the model and experimental measurements except at extreme voltages (10v and 40v). This could be attributed to the significant changes in resistivity\(^ {239} \) and surface area of LCE composite with voltage due to resistive heating.

Figure 4.8: (a) IR imaging of resistive heating in LCE nanocomposites as a function of applied voltage. Camera frames were taken after the sample temperature reached a steady state.
Figure 4.9: Comparison between thermal imaging using IR measurements (in air) and finite element modeling predictions of temperature variation in LCE-NC sample. For FEM simulations, it is assumed that sample has uniform density, thermal conductivity, heat capacity, and uniform joule heating only at the bottom surface. Heat transfer coefficient value is obtained by fitting experimentally measured surface temperature (based on IR studies) and FEM predictions.

4.5 Cell culture on LCE-NCs

Stimuli-responsive 2-D substrates with active topographies and mechanical properties enable the study of cellular response to an actively changing environment. A combination of equibiaxial stretching devices and patterned substrates have been previously implemented to study cardiomyocyte response to mechanical stresses. As an alternative to mechanical stretching devices, LCE-NCs potentially provide a scalable and more easily...
implementable technique to control substrate strain. Here, we show that surface modified LCE-NCs are biocompatible, allow for cell growth and are applicable as stimuli-responsive 2D substrates for cell growth.

### 4.5.1 Surface modification of LCE-NCs

Polysiloxane elastomers are low surface-energy materials, and thus surface modification was necessary to improve cell adhesion. Samples were coated with different protein coatings i.e. sure rat tail collagen type 1, Laminin and fibronectin to enhance the cell adhesion. Prior to protein coating samples were treated with UV ozone treatment for 30mins or oxygen plasma treated for 5seconds to increase the hydrophilic nature of the samples to allow for greater protein attachment. The viability was compared across the various ECM proteins and surface treatments to determine the ideal coating and treatment for optimum cell viability. Rat tail collagen type 1 was found to give the highest cell growth and viability (Figure 4.10).

![Figure 4.10: Statistical analysis of cell viability as a function of LCE surface treatment and extracellular matrix (ECM) protein coating](image_url)
The surface modification gives rise to a wrinkling instability when the sample contracts (Chapter 1). Micrographs from optical microscopy observations of the LCE-NC surface are provided in Figure 4.11 along with a movie in real-time recorded while observing the surface of LCE-NC with a microscopy under the application of a voltage (Supporting Information). Surface wrinkles appear only during sample contraction (voltage on) and are oriented perpendicular to the axis of contraction.

Figure 4.11: Dynamic reversible surface patterns in LCE-NC composites. (a) Schematic depiction of achieving dynamic wrinkling instability in Au-LCE-NC bilayer. Movie file of dynamic surface wrinkling in LCE-NC composites is included in the supplementary information.

4.5.2 Cell culture on passive substrates
Sprague Dawley Neonatal Rat Ventricular Myocyte (NRVM) were cultured on PDMS and LCE-NCS. PDMS and unstimulated LCE-NCS were studied as controls to test cell viability
and attachment. LCE-NCs with a smooth top surface and aligned wrinkled top surface were studied. These were prepared by coating the top surface with gold at elevated and at room temperature, respectively. PDMS substrates were used to generate random wrinkles using previously reported methods\textsuperscript{50}. As shown, we observe cell attachment in each case, with improved cell elongation and alignment on LCE-NC with aligned wrinkles. Optimal cell alignment was found at a surface wrinkle wavelength of 4 mm (figure), consistent with previous reports studying cell alignment on wrinkled surfaces\textsuperscript{241}.

![Figure 4.12: Fluorescent optical microscopy measurements of cell culture on passive substrates with (b) flat, (c) random and (d) aligned wrinkling morphology. The cells were obtained from neonate (1 day old) Sprague-Dawley rat ventricular cardiomyocyte.](image)

4.5.3 Cell culture on reversible LCE-NCs substrates

The experimental set-up for cell culture on electrically stimulated substrates is shown in Figure. LCE-NCs are placed on top of conductive carbon rods connected to a Myopacer pulse generator via a time relay. Sides of LCEs were cleaved to make sure percolating pathways do not connect the top and bottom faces of the LCE-NCs, and therefore resistive heating only occurs on the bottom surface in contact with the electrodes. This is necessary to make sure cells don't experience any electric field while LCEs were stimulated. NRVM were first cultured for 1 day under static conditions to ensure cell adhesion before initiating shape
response. After 24 h, a 40 V AC pulsed electrical signal was applied continuously for 72 h. Samples were subjected to a 0.6 s pulse duration, corresponding to a 3 % electromechanical strain. As shown in Figure 4.13a, a significant improvement in cell alignment along the primary direction of contraction/elongation is observed. As an important control, cell culture was carried out under similar conditions but with both ends of the LCE-NC mechanically fixed to prevent contraction/elongation (Figure 4.13b). Under this control experiment, even with electrical stimulation, no cell alignment is observed. Thus, we conclude mechanical contraction/elongation is responsible for cell alignment in these experiments. Preliminary experiments provides the proof of concept that dynamic strain can lead to better-aligned cell sheets in comparison to passive substrates. More detailed characterization of cell alignment is needed to quantify extent of cell alignment as a function of frequency and amplitude of dynamic strain.

Figure 4.13: Fluorescent optical microscopy measurements of cell culture on electrically stimulated LCE-NC composites (a) with and (b) without electromechanical response. The cells were obtained from neonate (1 day old) Sprague-Dawley rat ventricular cardiomyocyte.

4.6 Conclusion

In summary, we have shown that liquid crystal elastomer nanocomposites (LCE-NCs) exhibit a fast and reversible electromechanical response, and we demonstrate the use of shape-responsive LCE-NCs in active cell culture for the growth of aligned neonatal cardiomyocyte
cell sheets. LCE nanocomposites are prepared using a two-step method that involves dispersing conductive carbon black before crosslinking, applying a load during crosslinking, and subsequent surface infiltration of additional carbon black through solvent swelling. The resulting LCE nanocomposites are electrically responsive and capable of rapid (response times as fast at 0.6 s), large-amplitude (contraction by up to 30 %), and fully reversible shape changes in response to applied voltages (5 – 40 V). In contrast to other LCE-NCs and shape-responsive materials studied, the electromechanical response is fully reversible (up to 5000 cycles tested) and operable in cell culture media with negligible heating of the surroundings. Our approach to conductive LCE-NC can be used to generate similar responsive LCEs responsive to other stimuli, such as magnetic fields or light. Neonatal rat ventricular myocytes were cultured on LCE-NCs substrates, and we observe good attachment and viability both with and without electrical stimulation. Under voltage stimulation cells align in the direction of contraction/elongation of the substrate. LCE-NCs therefore represent versatile shape-responsive materials operable in biological media, and the work presented provides a general approach to LCE-NCs with a fast and reversible mechanical response to external stimuli. While here we only demonstrated the applicability of LCE-NCs to active cell culture, the fully reversible and fast response may also be of interest for applications including implantable materials, regenerative therapies, drug delivery, and packaging.
5 Dynamic Self-Stiffening in Liquid Crystal Elastomers

The work described in this chapter was a collaborative work with Prof. Ajayan. We also thank Prof. Patra for the insightful discussions and Richard Crouse for assistance with 2DWAXD studies.

Part of this work is published in Nature communications, 4, 1739 (2013).

In this study we report a self-stiffening response in polydomain LCEs when subjected to repetitive dynamic compression. Previous work has focused on the properties of LCEs under large-strain deformation, but our findings indicate rich behavior at previously overlooked low-strain, dynamic deformations. Additionally, the use of low-strain, repetitive compression represents a facile method to prepare uniformly aligned LCEs, which are typically prepared by applying large tensile strains or external fields during material synthesis.

5.1 Abstract

Biological tissues have the remarkable ability to remodel and repair in response to disease, injury, and mechanical stresses. Synthetic materials lack the complexity of biological tissues, and man-made materials which respond to external stresses through a permanent increase in stiffness are uncommon. Here, we report that polydomain nematic liquid crystal elastomers increase in stiffness by up to 90% when subjected to a low-amplitude (5%), repetitive (dynamic) compression. Elastomer stiffening is influenced by liquid crystal content, the presence of a nematic liquid crystal phase and the use of a
dynamic as opposed to static deformation. Through rheological and X-ray diffraction measurements, stiffening can be attributed to a nematic director which rotates in response to dynamic compression. Stiffening under dynamic compression has not been previously observed in liquid crystal elastomers and may be useful for the development of self-healing materials or for the development of biocompatible, adaptive materials for tissue replacement.

5.2 Introduction

Biological tissues have the remarkable ability to remodel and repair in response to disease, injury, and mechanical stresses\textsuperscript{242–244}. Well-known examples include bone remodeling and strengthening through a process which involves changes in bone mass and porosity,\textsuperscript{98} and muscle development, tumor growth, and blood vessel structure are all affected by mechanical stresses\textsuperscript{99–101}. Synthetic materials lack the complexity of biological tissues, and man-made materials which respond to external stresses through a permanent increase in stiffness are uncommon\textsuperscript{104,109}. Here, we report that polydomain nematic liquid crystal elastomers (LCEs) increase in stiffness by up to 90\% when subjected to a low-amplitude (5\%), repetitive (dynamic) compression. Such self-stiffening is uncharacteristic of synthetic rubbers\textsuperscript{104,105} but arises in polydomain LCEs due to the presence of a mobile nematic director that re-orient in response to external stresses. The observed dynamic stiffening in polysiloxane LCEs may be useful for the development of self-healing materials and biocompatible, adaptive materials for tissue replacement. Additionally, the use of low-strain, repetitive compression represents a facile method to prepare uniformly aligned LCEs, which are typically prepared by
applying large tensile strains or external fields during material synthesis\textsuperscript{117-122}. Previous work has focused on the properties of LCEs under large-strain deformation, but our findings indicate rich behavior at previously overlooked low-strain, dynamic deformations.

LCEs are comprised of a crosslinked network of flexible polymer chains with liquid crystalline order (Fig. 1a)\textsuperscript{16,18}. Polydomain LCEs were prepared by coupling liquid crystal mesogens to poly(hydrogenmethylsiloxane) (PHMS) (Figure 5.2), as has been previously reported.\textsuperscript{17} The resulting materials are rubbery ($T_g \approx -30 \, ^\circ C$), nematic networks with no global orientation of the nematic director (polydomain). Nematic order fundamentally alters the response of LCEs to external stresses. Network chains in LCEs are locally anisotropic and assume an ellipsoidal conformation, in contrast to the spherical random coil conformation of conventional isotropic rubbers. LCEs exhibit ‘soft elasticity’ which is exemplified by large-strain deformations with little resistance\textsuperscript{18,112,245}. Herein, we examine the behavior of polydomain LCEs under a repetitive, compressive deformation at low strains (5\%). We find a significant increase in stiffness after extended compression and, through a combination of dynamic mechanical testing (DMA), 2-dimensional wide-angle X-ray diffraction (2DWAXD), and polarized optical microscopy (POM) can attribute microstructure changes to a mobile nematic director which re-orient in response to dynamic stresses.

### 5.3 Methods

#### 5.3.1 Materials
Toluene, Pt-catalyst ((dichloro (1, 5-cyclooctadiene) platinum (II)), allylbromide, butanol, 11-bromo-1-undecene, sodium hydride (60% dispersion in mineral oil), hydroquinone, magnesium sulfate, PHMS (poly (hydromethylsiloxane)) \((M_w=1700-3200\text{ g/mole})\), ethyl acetate, 4-hydroxyl-4′-cyano biphenyl, sodium hydroxide, tetrahydrofuran (THF), diethyl ether, dimethyl formamide (DMF), 6-bromo-1- hexanol, benzene, methanol, and potassium carbonate were purchased from commercial suppliers and used as received. The crosslinker (1,4-di(10-undecenyloxy)benzene) was synthesized as described previously.\(^{246}\) 4-(1-Hexanol oxy)-4′-cyano biphenyl and mesogenic side-group were prepared as described below.

5.3.1.1 **Preparation of 4-(1-hexanol oxy)-4′-cyano biphenyl (3)**

4-hydroxyl-4′-cyano biphenyl (1, 7mmol, 1.36g), 6-bromo-1-hexanol (2, 10mmol, 1.83 g), and \(\text{K}_2\text{CO}_3\) (14mmol, 1.934g) were dissolved in 25 ml DMF and heated to 90 °C for 20 hours. The reaction was then quenched by adding water and filtering to collect a white precipitate. The precipitate was then dried under vacuum and recrystallized in benzene to obtain the desired product. \(^1\text{H} \text{NMR (400 MHz, CDCl}_3\), \(\delta\text{ (ppm): 7.8-7.6 (m, 4H) 7.54-7.50 (d, 2H), 7.0-6.9 (d, 2H), 4.20 (t, 2H), 3.36 (t, 2H), 1.8 (m, 2H), 1.7 (m, 2H), 1.40 (m, 4H).}}\)

5.3.1.2 **Preparation of Mesogenic Side-Group (4)**

3 (6 mmol, 1.77g) was slowly added to a solution of sodium hydride (12.5mmol, 0.3g) in 30 ml diethyl ether/ DMF (10:1). The reaction mixture was stirred under nitrogen atmosphere for 1 hour before cooling to 0 °C and adding a solution of allyl bromide (1.2 g, 10 mmol) in 5 ml diethyl ether dropwise. The reaction was allowed to proceed...
overnight before adding brine to quench the reaction. The layers were separated and the organic layer was washed with 1N HCl and water. The product was concentrated under reduced pressure and purified by column chromatography (silica gel, eluent: ethyl acetate/ hexanes 1:9 v/v). $^1$H NMR (400 MHz, CDCl3), $\delta$ (ppm): 7.7-7.5 (m, 6H), 7.0-7.1 (d, 2H), 5.8 (m, 1H), 5.0 (d, 2H), 4.2 (t, 2H), 4.0 (d, 2H), 3.4 (t, 2H), 1.8-1.4 (m, 8H).

![Chemical reaction diagram]

Figure 5.1 Synthetic scheme for the preparation of cyanobiphenyl mesogenic side-group (4)

5.3.1.3 Polydomain LCE synthesis

Polydomain LCE samples were synthesized in the isotropic phase as described previously. Briefly, mesogenic side-group (4), 4-(1-hexanol oxy)-4′-cyano biphenyl crosslinker and PHMS (poly (hydromethylsiloxane)) were dissolved in toluene along with the Pt catalyst, and the reaction was allowed to proceed at 70 °C for 3 days. Elastomers were then swollen in dichloromethane for several days to wash out the unreacted materials and nonreactive solvent. By gradually increasing the methanol content of swelling solvent, elastomers were deswollen and then air-dried before testing. To investigate the role of mesogen content on mechanical properties, a systematic series of polydomain LCEs (LCE90, LCE80, LCE60, LCE40 and LCE20) were prepared with mesogen content ranging from 90 to 20 mol % relative to the Si-H bonds in the PHMS
polymer (Figure 5.2). Poly(dimethyl siloxane) (PDMS) was also studied for comparison to the LCEs. PDMS is chemically and mechanically similar to the LCEs studied, but with no mesogen content.

Figure 5.2 Schematic for the synthesis of a polydomain LCE. A representative LCE sample is shown on the right-hand side, and dynamic mechanical testing was carried out on LCEs with dimensions of 1.5 mm x 1.5 mm x 1 mm.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mesogen Content (^a) (mole %)</th>
<th>Crosslinker Content (^a) (mole %)</th>
<th>(T_{NI} ) (^b) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCE90</td>
<td>90</td>
<td>10</td>
<td>67</td>
</tr>
<tr>
<td>LCE80</td>
<td>80</td>
<td>20</td>
<td>55</td>
</tr>
<tr>
<td>LCE60</td>
<td>60</td>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td>LCE40</td>
<td>40</td>
<td>40</td>
<td>N/A</td>
</tr>
<tr>
<td>LCE20</td>
<td>20</td>
<td>40</td>
<td>N/A</td>
</tr>
<tr>
<td>PDMS</td>
<td>NA</td>
<td>0.493(^e)</td>
<td>NA</td>
</tr>
</tbody>
</table>

Table 5-1 Characteristics of LCEs and PDMS. \(^a\)relative to molar content of Si-H in PHMS. \(^b\)measured by DSC; where no value is listed, no measureable \(T_{NI}\) was found down to 0 °C. \(^e\)degree of crosslinking\(^{247}\) \(\text{nm}^{-3}\)

5.3.2 Dynamic mechanical analysis
For the DMA studies, the samples were razor cut to dimensions of 1.5 mm x 1.5 mm x 1 mm. All sample dimensions were measured using DMA and verified with a digital caliper. Dynamic Mechanical Testing was carried out in compression mode as illustrated in Figure 5.3 using TA Instruments Q800 DMA at a 5% strain amplitude, 5 Hz frequency and at a preload of 0.01N. All the tests were conducted isothermally at 45°C, except where otherwise noted.

![Figure 5.3](image)

Figure 5.3 (a) Schematic depiction of the LCE sample placed between two plates for dynamic compression (b) actual image of the experimental setup. (c) Plot of the time-dependent strain applied during dynamic compression measurements. A frequency of 5 Hz is used for all measurements in the present study.

5.4 Results

5.4.1 Dynamic stiffening in polydomain LCEs

Generally, materials under repeated stress display signs of microstructural damages known as fatigue and ultimately cause cracking, fracture etc. Conventional approach to avoid this failure risk is by strengthening the materials by reinforcing it with fillers and healing agents. Naturally occurring materials such as bone and actin bundles exhibits a different mechanical response towards cyclic or repeated loading known as ‘self-stiffening’. Bone responds to repeated mechanical loading by increasing its density.
and structure remodeling to adapt to loading. This phenomenon also known as ‘wolf’s law’ reduces the risk of fracture. We observed a similar mechanical response in polydomain LCEs towards cyclic loading.

To observe LCEs response towards cyclic loading, polydomain LCEs with different mesogen content (Table 5-1) were prepared and placed between two compressions plates in a DMA-Q800 (as mentioned before). Under 16 h of repetitive, compressive loading (5 Hz, 5 % strain), LCE90 exhibits a 90 % increase in stiffness (Figure 5.4). Interestingly, the increasing stiffness gradually reaches a plateau. This can be attributed to the saturation of micro-structural changes within the LCE polymer matrix and will be discussed in a later section. The strain amplitude is maintained at 5 % for the duration of the experiment. The temperature was the lowest that DMA can maintain without using liquid nitrogen. Remarkably, the final stiffness of LCE90 surpasses the initial values of other LCEs studied despite the lower crosslink density of LCE90 (Table 5-1).

Dynamic mechanical testing of all LCEs prepared shows that mesogen content is correlated with increased stiffness, in particular for the series of samples where the crosslink density is held constant (LCE20, LCE40, and LCE60) (Figure 5.4). LCE60 and LCE80 exhibit a similar, although less pronounced, stiffening response compared with LCE90. The stiffness increase under 5 % compressive loading is 63 % and 33 % for LCE80 and LCE60, respectively. LCE20 and LCE40, both with no nematic phase exhibit a stiffness increase of only 14%. Finally, PDMS exhibits a stiffness increase of only 1.4 %.
Figure 5.4 Change in stiffness (%) versus time for a series of LCEs varying in mesogen content and PDMS under dynamic compressive strain. The extent of stiffening is correlated with LCE mesogen content. The LCE is dynamically compressed between two flat plates at 5 Hz, 45 °C, a pre-load of 0.01N, and a 5 % strain amplitude using a DMA Q800.

Furthermore, stiffening is only observed under dynamic, compressive stress. To stress the importance of having dynamic loading for self-stiffening, LCEs were subjected to static load tests. An extended static compression test with an applied stress greater than the maximum stress applied during dynamic compression (70 kPa) and a strain of 6 % resulted in only a modest (~10 %) stiffness increase (see Figure 5.5). Thus, consistent with previous reports\textsuperscript{120,121}, a static deformation at low strain (<10 %) does not result in significant changes to the microstructure of the LCE. To further eliminate the possibility of further crosslinking within LCE, an additional control experiment, samples held at 45 °C for at least 16 h in the DMA without compression show no stiffness increase.
The presence of nematic order is essential to the stiffening response in LCEs (Figure 5.5). As shown in Figure 5.5, LCE90 exhibits a modest increase in stiffness when dynamically compressed in the isotropic phase at 80 °C (~ 15 %, similar to LCE20 and LCE40) while stiffness increases by more than 80 % when the same measurement is carried out in the nematic phase at 45 °C. This same trend is observed for all nematic LCEs (Figure 5.5).

5.4.2 Microstructural changes in LCE under dynamic load

Next I focused on understanding the self-stiffening mechanism in polydomain LCEs by analyzing the morphological changes before and after cyclic loading. Control comparison experiments (Figure 5.6) provide strong evidence that LCEs are undergoing structural
changes under repetitive compressive loading. Microstructure changes in polydomain LCEs were analyzed by 2DWAXD. X-ray scattering measurements were performed using a Rigaku Raxis-IV++ equipped with an incident beam monochromator, pinhole collimation (0.3 mm) and Cu X-ray tube (\(\lambda = 1.54 \text{ Å}\)). The sample to detector distance was 100 mm. Before compressive deformation, all LCEs exhibit an isotropic scattering peak characteristic of a polydomain, nematic LCE (Figure 5.6b). In the experimental configuration used for this study, scattering peaks corresponding to mesogen spacing along the molecular width are clearly resolved, enabling quantification of orientational ordering of the mesogenic side-groups. After dynamic compression, a clear anisotropy emerges in LCE90, LCE80, and LCE60 (see Figure 5.6c). Anisotropic scattering is only observed in the \(x-z\) and \(y-z\) planes, but the scattering pattern in the \(x-y\) plane remains isotropic. This indicates that the nematic director in these samples rotates away from the \(z\)-axis (compressive direction) to lie primarily in the \(x-y\) plane but remains globally disordered in the \(x-y\) plane, resulting in an oblate LC orientation after dynamic compression.
Figure 5.6 2D-WAXS analysis of LCEs after dynamic compression. (a) Schematic of geometry during dynamic compression experiment and (b) 2D WAXD pattern of unstressed, polydomain LCE90. All LCEs exhibit similar 2D WAXD patterns before dynamic compression. (c) 2D WAXD patterns of LCEs with varying mesogenic content subjected to compressive dynamic load (5 Hz, 5 % strain) for at least 16 hours. The patterns are shown for three independent LCE faces (x-z plane, x-y plane, and y-z plane), and the arrow on the bottom right hand side indicates the direction of compression. The anisotropic scattering pattern observed for the x-z and y-z planes indicates that the LCE nematic director rotates away from the z-axis (compressive direction) to lie primarily in the x-y plane, but the nematic director remains disordered in the x-y plane. d, Macroscopic alignment parameter $S$ for dynamically stressed LCEs extracted from model fit of 2D WAXD pattern. The order parameter $S$ is defined with respect to the x-y plane. The order parameter for the x-z and y-z planes is an average of the order parameters measured in each plane.

The reorientation of the LC side-groups was also observed qualitatively through polarizing optical microscopy (POM); global reorientation of the nematic director away
from the z-axis is consistent with reduced light transmission through the x-z and y-z faces when crossed polarizers are aligned with the axis of compression (Figure 5.7).

![Diagram of compression experiment](image)

**Figure 5.7 POM analysis of LCEs after dynamic compression.** (a) Schematic of dynamic compression experiment. b, Polarizing optical microscopy images of dynamically stressed LCE90 along three different faces. The absence of birefringence in the x-z and y-z faces when crossed polarizers are oriented parallel to the compression direction (z-axis) indicates reorientation of the nematic director perpendicular to the z-axis. All scale bars represent 0.1 mm.

### 5.4.3 Effect of strain amplitude and frequency on LCEs self-stiffening

Dynamics of self-stiffening in LCEs depends on the strain amplitude and frequency of repetitive dynamic load. LCEs are comprised of various molecular constituents such as mesogens, polymer chains and crosslinker molecules, as shown schematically on Figure 5.2. During compression, some of these constituents respond very quickly – such as the rotation of the LC side-groups - while other constituents may require a longer time to respond – such as different polymeric segments or the crosslinked polymer network. LCE self stiffening phenomena or the transition from the polydomain to monodomain state can
to some extent be understood as the motion/rotation of these separate constituents, but more accurately it represents a collective motion of side-groups, crosslinker, and polymer network segments. We probe LCE response to dynamic load at different frequencies and observe increase in stiffness is directly proportional to the frequency. Even at low frequency (1Hz), LCEs exhibit self-stiffening behavior but to a lower extent compared at high frequency (Table 5-2). Similarly a systematic series of test were conducted on LCEs at different strain amplitudes. Interestingly, we found no change in stiffness when LCEs were subjected to low amplitude dynamic load (1.25%). This implies self-stiffening response in LCEs is nonlinear phenomena. Stiffening phenomena in LCEs is only observed for strain values greater than approximately 2%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Frequency (Hz)</th>
<th>Strain amplitude (%)</th>
<th>Change in Stiffness°</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCE90</td>
<td>5</td>
<td>1.25</td>
<td>439</td>
</tr>
<tr>
<td>LCE90</td>
<td>5</td>
<td>2.5</td>
<td>676</td>
</tr>
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<td>5</td>
<td>3</td>
<td>1100</td>
</tr>
<tr>
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<tr>
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<td>5</td>
<td>5</td>
<td>4893</td>
</tr>
<tr>
<td>LCE90</td>
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<td>5</td>
<td>3700</td>
</tr>
<tr>
<td>LCE90</td>
<td>10</td>
<td>5</td>
<td>5267</td>
</tr>
</tbody>
</table>

Table 5-2 Self-stiffening in polydomain LCEs under repetitive compressive dynamic load as a function of strain amplitude and frequency at 45°C.

5.4.4 Coupling between LCE deformation and nematic director orientation
The dynamic mechanical analysis measurements together with WAXD patterns for stressed and unstressed LCEs establish a clear connection between stiffening and reorientation of the nematic LC director. In LCEs, network chain conformation is coupled
to the nematic director orientation. Therefore, the observed re-orientation of the mesogenic side-groups perpendicular to the compressive axis reflects a reorientation of the LCE network chains (Figure 5.8b). The strain lines corresponding to a linear, compressive deformation were calculated by performing finite element modeling (FEM) simulations using COMSOL Multiphysics 4.2 simulation package. Simulation results predict elongational strains in the plane perpendicular to the compressive axis. This elongational strain is expected to preferentially align the ellipsoidal LCE network chains in the $x$-$y$ plane and, due to coupling between the LC side-group and polymer backbone, result in the observed reorientation of the nematic director. 2DWAXD images indicate reorientation of the LC side-groups in the $x$-$y$ plane, consistent with a preferential orientation of the LC side-groups parallel to the polymer backbone.

Figure 5.8: a, Finite element modeling (FEM) simulation showing stress lines as a result of compression. FEM simulations were performed out using COMSOL Multiphysics 4.2 simulation package. b, Reorientation of prolate LC polymer chains under compressive strain.
The 2DWAXD data also enable calculation of a macroscopic alignment parameter 
\[ S = \left( \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right), \]
averaged over the entire sample where \( \theta \) is the angle between the local 
director orientation and the \( x-y \) plane\(^{251,252} \). The increase in macroscopic alignment is directly correlated with mesogen content, as shown in Figure 5.4. Furthermore, the coupling between mesogen side-group orientation and polymer orientation results in macroscopic changes to sample dimensions. As shown in the Table 5-3, dimensional changes up to 8.3% along compression (measure along \( z \)-axis) and 7.7% along \( x \) and \( y \)-axes are recorded, consistent with the coupling of macroscopic shape and global director orientation.

### Table 5-3 Stiffness and dimensional changes in LCEs before and after dynamic compression

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial Stiffness(^a) (N/m)</th>
<th>Final Stiffness(^b) (N/m)</th>
<th>Change in Stiffness(^c)</th>
<th>Before Compression</th>
<th>After Compression</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Length (mm)</td>
<td>Width (mm)</td>
<td>Height (mm)</td>
<td>Length (mm)</td>
<td>Width (mm)</td>
</tr>
<tr>
<td>LCE90</td>
<td>5308</td>
<td>10201</td>
<td>89</td>
<td>1.39</td>
<td>1.58</td>
</tr>
<tr>
<td>LCE80</td>
<td>5493</td>
<td>8960</td>
<td>63</td>
<td>1.57</td>
<td>1.47</td>
</tr>
<tr>
<td>LCE60</td>
<td>7521</td>
<td>10005</td>
<td>33</td>
<td>1.52</td>
<td>1.47</td>
</tr>
<tr>
<td>LCE40</td>
<td>6708</td>
<td>7358</td>
<td>14</td>
<td>1.43</td>
<td>1.56</td>
</tr>
<tr>
<td>LCE20</td>
<td>6471</td>
<td>7388</td>
<td>14</td>
<td>1.52</td>
<td>1.46</td>
</tr>
<tr>
<td>PDMS</td>
<td>4090</td>
<td>4145</td>
<td>1.4</td>
<td>1.456</td>
<td>1.589</td>
</tr>
</tbody>
</table>

Sample dimensions were measured using DMA and verified with a digital caliper. Each dimension is measured independently and accurate to within ± 0.02 mm. Percentage values give the dimensional change relative to the dimensions before stress is applied. \(^a\)measured at 5% strain. \(^b\)measured at 5% strain after ~17 hours of continuous dynamic compression.

#### 5.4.5 Relaxation of LCE self-stiffening

Since the stiffening response arises due to a director reorientation, stiffening is fully reversible. An ideal LCE sample with no entanglements and no compositional disorder would deform softly under compression and have no resistance to deformation. In real systems, resistance to deformation is observed, and the system undergoes non-ideal deformations (chain stretching, entanglements), which can increase the free energy of the
final state. By analyzing the relaxation of the network after compressive stiffening, we can learn about the stability of the final state. To analyze relaxation of the aligned elastomer two separate studies were carried out. In first study, a dynamically compressed LCE was allowed to sit at room temperature for long period of time (months). In second study, after dynamic compression LCE is thermally annealed at temperature above the $T_{NI}$. Both samples were subjected to the same compressive alignment, and analyzed periodically over the course of several months for softening and loss of alignment via dynamic mechanical analysis and 2DWAXD. For LCE kept at room temperature, three months later the stiffness returns to its initial value and the director orientation is polydomain (Figure 5.9). For a dynamically stressed sample annealed above the $T_N$, relaxation kinetics was extremely fast, within 4 hours LCE stiffness returns to its initial value with mesogens back in random orientation (Figure 5.10). Figure 5.11 shows the stress-strain relationship comparison between the unstressed, dynamically stressed, thermally annealed and 3 months relaxed LCE.

**Figure 5.9** 2DWAXS analysis of a dynamically stressed LCE90 as a function of relaxation time at room temperature (~25°C). The sample was subjected to 1000 min dynamic compression at 5% strain, 5Hz and 45°C.
Figure 5.10 2DWAXS analysis of a dynamically stressed LCE90 sample before and after thermally annealing. The sample was thermally annealed above $T_{NI}$ for 4 hours after 1000 min dynamic compression at 5% strain, 5Hz and 45°C.

Figure 5.11: a, Stress-strain plots for LCE90 subjected to different mechanical loading and thermal histories. The dynamically stressed sample is tested immediately after 1000 min dynamic compression. This sample is observed to recover its initial stress-strain behavior after relaxing at room temperature for 3 months or after annealing above the $T_{NI}$ for 4 hours. All stress-strain profiles are recorded along the compression axis.

5.4.6 Theoretical understanding of LCEs self-stiffening
The stiffening response can be understood within the theoretical framework of nematic rubber elasticity\textsuperscript{18}. Warner et al. showed that for nematic LCEs, the free energy density satisfies the following equation: 

$$F_{el} = \frac{1}{2} \mu \text{Tr} \left( \bar{\lambda} \cdot \bar{\lambda}^T \cdot \bar{l}^{-1} \cdot \bar{l}^{-1} \right),$$

where $\mu$ is the rubber elastic modulus, $\bar{\lambda}$ is strain and $\bar{l}$ is the network step-length tensor that describes the local (generally anisotropic) chain conformation. This theory assumes Gaussian, phantom network chains and the absence of quenched disorder. A consequence of this free energy expression is that strains $\bar{\lambda}$ of the form $\bar{\lambda} = \bar{l}^{1/2} \cdot \bar{W}_\alpha \cdot \bar{l}^{-1/2}$, where $\bar{W}_\alpha$ is an arbitrary rotation by an angle $\alpha$, come with no increase to the elastic free energy. Thus, for this type of strain, the LCE deforms ‘softly’ with no resistance. This result only applies to the ideal case, but real elastomers more commonly exhibit semi-soft elasticity, with some resistance to deformation below a threshold stress value. An example of this for a polydomain LCE under uniaxial strain is shown in Figure 5.12; the elastomer exhibits, after a strain threshold, a pronounced plateau in the stress. This stress plateau is a direct result of ‘soft elasticity’ and is associated with nematic director rotations. At higher strains, the nematic director is fully aligned, and director reorientations can no longer accommodate further strain, resulting in a stress increase. This particular example reflects the behavior of LCEs under large (> 10\%) uniaxial strains but similar behavior is observed in the present study for LCEs under compression. In initially unstressed samples, a ‘soft’ elastic response is observed. The softness or reduced stiffness is a result of a globally disordered nematic director that can accommodate deformations through rotation. However, extended dynamic compression results in a reorientation of the nematic director and a corresponding increase in stiffness. Similar to the behavior of
LCEs under uniaxial tension, reorientation of the nematic director is associated with an increased resistance to deformation.

Figure 5.12 Stress-Strain relationship of polydomain LCE under uniaxial tension (data reproduced with permission from Clarke et al.253).
A comparison of deformed and undeformed LCEs shows that the measured stiffness increase is a distinctly nonlinear phenomenon. As shown in Figure 5.13, there is no difference in stiffness between stressed and unstressed samples for strain values less than 1%. Thus, as expected, at low compressive strains LCEs behave linearly, and the slope of the stress-strain curve simply reflects the equilibrium Young’s modulus. Differences between stressed and unstressed LCEs are only observed for strain values greater than approximately 2%. This threshold value may reflect “semi-softness” in LCEs which arises due to polymer chain length polydispersities, compositional fluctuations, and other network non-idealities.

Strain-stiffening in LCEs contrasts with the irreversible softening of polymeric networks under cyclic strain, a phenomenon known as the Mullins effect\textsuperscript{104,105}. While the Mullins effect is not fully understood, it has been seen in crystallizable rubbers or rubbers with added fillers and has also been observed in biological tissue\textsuperscript{106,107}. Recently, stiffening behavior was reported for bundled actin networks under cyclic shear\textsuperscript{108}. This was observed at higher crosslink densities and attributed to the physical nature of the network, which allowed reorganization of the network constituents, resulting in hardening after cyclic shear\textsuperscript{108}. This contrasts with the dynamic stiffening reported here in covalent LCE networks. The novelty of the present work is the discovery of dynamic stiffening in a synthetic, homogeneous polymeric network with liquid crystalline order. Additionally, the presence of liquid crystal order enables quantitative characterization of side-group
and network chain orientation before and after deformation, establishing a direct connection between stiffening and network chain conformation.

5.5 Conclusions

In summary, we report LCE self-stiffening in response to dynamic, compressive loading. The stiffening behavior observed here is for a permanent network at low strains, and can be attributed to a mobile nematic director. Director reorientation and alignment at low strains and dynamic compression has not been previously reported in LCEs and suggest underlying network relaxation modes at 5 Hz which govern the response. LCEs, which increase in stiffness, may be useful for the development of self-healing materials or for the development of biocompatible, adaptive materials for tissue replacement. Dynamic compression is a straightforward method for preparing uniformly aligned nematic LCEs, and may be applicable to higher-order liquid crystal phases, including chiral nematics and smectics. Other repetitive deformations (e.g. uniaxial tension, shear) at low strain values may lead to similar director reorientations in LCEs and will be the focus of future work.
6 Conclusions and Future Outlook

Liquid crystal elastomers (LCEs) are fascinating materials and have been the topic of research interest for last couple of decades. Unique macroscopic shape responsive property of LCEs makes them desirable in the field of actuators, sensors, microfluidics, robotics etc. Various types of LCEs were studied with special emphasis on nematic LCEs both in polydomain and monodomain state. LCEs are based on polymeric materials and therefore can be incorporated into bio-inspired structures via established directed assembly methods, including both top-down and bottom up self-assembly techniques. In this dissertation, we focused on the development of new functional materials based on LCEs and gaining insight into the mechanical properties under dynamic deformations. We demonstrated LCEs could induce buckling instability in thin films to create well-defined, periodic topological features on surfaces and have applications in thin film metrology. LCEs based bilayers could also exhibit self-folding 3D dynamic structures like lotus or helix and finite element simulations could be used to predict the film patterning on LCE to achieve desired 3D deformed shape. We also report a new two-step approach of synthesizing electrically responsive LCEs via adding nanoparticles both before and after crosslinking. LCE-NCs have robust mechanical, electrical and thermal properties; and exhibit rapid and reversible shape and topography changes in response to modest voltages. LCE-NCs provides a biocompatible electrically responsive dynamic scaffold for cell culture and enable investigation of cell-matrix interactions to a dynamically changing surface pattern. Furthermore, we report a novel self-stiffening behavior in LCEs under low amplitude dynamic deformation, which finds applications in biocompatible adaptive materials for tissue replacement. We hypothesized stiffening
behavior is due to rotation of the nematic director under repetitive compression which is evident in rheological and 2-D X-ray diffraction studies. The use of low-strain, repetitive compression represents a facile method to prepare uniformly aligned LCEs, which are typically prepared by applying large tensile strains or external fields during material synthesis. Previous work has focused on the properties of LCEs under large-strain deformation, but our findings indicate rich behavior at previously overlooked low-strain, dynamic deformations.

In chapter-4, we demonstrated electrically responsive LCE nanocomposites could act as dynamic scaffold for cell culture. Besides electric field, magnetic field could also be employed to stimulate LCEs nanocomposites and represents more simplified approach to remotely trigger LCE response in a cell culture media. Since cells grow best on porous sponge-like surfaces, LCE based responsive aligned fiber mats could also be developed via electrospinning technique for enhancing cell growth. Below are some preliminary studies in this direction. Figure 6.1 shows the scanning electron microscopy images of LCP fiber mats before and after crosslinking. The crosslinking of LCP fiber network is achieved by adding a bifunctional photoactive molecule in the electrospinning solution and post processing under UV exposure. Next step would be to collect the fibers on a rotating drum collector to achieve global alignment of fibers in the LCP fiber mat sample. The LCP fiber mat sample with all the fibers aligned unidirectionally is necessary to achieve macroscopic shape responsive.
While monodomain nematic LCEs have been widely studied and incorporated into functional materials, higher order LC elastomers are difficult to align and study in the monodomain state. Only a handful of reports of aligned chiral nematic LCEs\textsuperscript{14}, smectic LCEs\textsuperscript{15}, and recently chiral smectic LCEs\textsuperscript{40,47} have been reported. Chiral nematic LCEs contain only long-range orientational ordering, with an orientation follows a helix, with a wavelength that is on the order of the wavelength of light. The first report involving alignment of chiral nematic LCEs\textsuperscript{48} took advantage of a compressive deformation of a swelled LCE, but the method gives imperfect alignment and is difficult to reproduce in practice. In contrast to nematic and chiral nematic LCEs, no reliable method exists to prepare smectic LCEs. Commonly, polydomain smectic LCEs are prepared followed by high-strain uniaxial stretching.\textsuperscript{15,49-50} While this does provide some alignment in limited regions of the sample, this also leads to tearing of the materials.\textsuperscript{19} LCEs with chiral or smectic ordering have significant potential for use in applications such as lasing, electromechanical devices, flexoelectric devices, and memory storage. We believe that

Figure 6.1 Scanning electron microscopy images of (a) liquid crystal polymer fibers and (b) crosslinked liquid crystal polymer fiber network.
higher order LCEs can be aligned using repetitive dynamic compression and might be useful for advanced functional applications. Dynamic compression may be much easier to apply and take advantage of in practice, and based on the results for nematic LCEs (chapter-5) may give significantly improved alignment. Alignment could be easily tracked by following both changes in stiffness and orientational ordering of the side-groups with 2DWAXS. This has not been explored previously and represents a more facile route to prepare uniformly aligned LCEs.

Phase behavior of a liquid crystal elastomer shows a marked dependence upon the history of sample preparation. Urayama group\textsuperscript{122} has shown that LCEs prepared by isotropic genesis, crosslinking the mesogenic molecules at high temperature isotopic state and cooling back into nematic state, undergoes polydomain-monodomain phase transition at a much smaller critical stress compared to LCEs prepared by crosslinking in nematic state (nematic genesis). Nematic genesis LCE requires much larger energy for the formation of monodomain state in comparison to isotropic genesis LCE. In chapter-5, we demonstrated polydomain LCEs prepared via isotropic genesis exhibits self-stiffening behavior when subjected to a low-amplitude repetitive (dynamic) compression. Based on rheological and X-ray diffraction measurements, self-stiffening phenomena in LCEs could be attributed to a nematic director which rotates in response to dynamic compression. We believe investigating behavior of nematic genesis LCEs under repetitive dynamic deformations will provide more insight in to the formation of monodomain LCE and LCE behavior in general under repetitive compression.
7 References


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