Electrothermally Driven Dynamic Instability in Molecularly Ordered Liquid Crystalline Polymers

by

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Soft robots composed from compliant stimuli-responsive materials offer versatile actuation capabilities in small factors to unlock new pathways to program manipulation and motility. Integrating active and stimuli responsive materials as artificial muscles to power the drive mechanisms is particularly attractive. Here, we harness the work-dense responsiveness of molecularly ordered liquid crystalline elastomers (LCE), which can be powered using an array of stimuli, including heat and light. The work content of the LCE is directed by the patterned molecular order to interact with the geometry to drive mechanical non-linearities. Reversible actuation profiles that are impulsive in nature are demonstrated.

In this dissertation, we present a tape spring-like, transversely curved composite shell fabricated from liquid crystalline elastomer with uniaxial molecular order (monodomain), polyethylene terephthalate (PET) and an encapsulated electrode. We demonstrated ultra-fast snap through instability (∼ms) with ∼200mW electrical power inputs at low voltages (∼1V). This system is a latch mechanism. Before the occurrence of snap through motion, mechanical energy is built up in PET substrate (latched on), while remaining latent. Upon reaching the edge of the instability, the latch is spontaneously released, and an impulsive actuation is realized. The performance of these actuators against external loads is explored and approaches for modulating the latency are presented. This actuation was harnessed in sub-gram scale soft robotics, including water strider mimicking configurations and steerable robotics on a range of topographies.
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Preface

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1.0 Introduction

Soft robotics are smart systems that constructed by soft body with stimuli-responsive materials. Compared with rigid-body systems, soft robotics can actuate in multiple degree of freedom within constrained space by their flexibility and exhibit potentials to novel devices. Typically, the motion of soft actuators are produced by converting input energy into force generated from responsive materials. These materials can behave as machines in robotics or integrate with mechanisms based on their functionalities. Among all categories of smart materials, molecularly ordered liquid crystalline polymers are widely implemented into soft systems by their programmability and deformability. These materials exhibit long range orientational organization at molecule level and can generate anisotropic mechanical shape changes by an array of stimuli, such as light, heat, solvent or mechanical deformation. Particularly, soft liquid crystalline elastomers, a type of lightly cross-linked polymeric networks, can exhibit large amplitude reversible deformation as much as 400%. These materials possess highly ordered microstructures in which mesogenic molecules are orientationally aligned and can exhibit contractile strain along the nematic director, especially for unidirectionally aligned monodomain structural profile. By reversibility and programmability, liquid crystalline elastomers are preferably selected as stimuli-responsive material for soft robotics. These materials also exhibit potentials for fast responsive actuation driven at modest voltages (<5V) by Joule heat, compared with piezoelectric materials and dielectric elastomers and can be utilized as machines to produce large work content actuation. However, robotic systems constructed by soft liquid crystalline elastomers with mechanisms still remain to be designed and demonstrated.

The focus of this research is predominantly to achieve an electrothermally driven dynamic snap through instability by integrating monodomain liquid crystalline elastomer with latch mechanics. The basic idea is to encapsulate an conductive electrode between soft liquid crystalline elastomer (∼ MPa) and stiff polyethylene terephthalate (∼ GPa) with a natural transverse curvature. Ultrafast snap through actuation was firstly driven by a relatively small transverse curvature actuator with 150mW electrical power by 1.2V voltage. Contrac-
tile strain was produced along the axis of the curved shell by Joule heat, following by an expansion perpendicular to the nematic director, which gradually flattened the transverse curvature. Thermomechanical strain was initially accumulated in polyethylene terephthalate (PET) until reached a limit-point energy threshold. The energy built-up in the structure was finally released and worked as an impulse to induce the snap through motion at ms-time scales with maximal tip velocity at several 100mm/s. Comparison between small and large transverse curvature (same thickness for LCE) illustrated that the latch is geometric - the energy threshold for snap through will increase with larger transverse curvature, corresponding to longer latency time. Capacity of work generation was demonstrated between $10^{-7}$J to $10^{-5}$J by lifting against payloads (25mg, 50mg, 75mg...), with respect to $10^{-5}$J/s to $10^{-4}$J/s power generation for four different geometries. Particularly, the latency of actuation ($T_{\alpha}$) can be controlled by applying a pulsed electrical power, which will accelerate the snap through motion by preventing the actuator cooling to the ambient.

For dynamic characterization of this tape spring-like, transversely curved composite shell, an extensional bending mathematical model was used to analyze the strain energy of PET substrate during snap through motion by in situ observation of tip evolution. The strain energy was proved to release firstly and then increased gradually by an increment of longitudinal curvature. Magnitude of this released energy was illustrated to correlate with a dimensionless geometrical coupling parameter $\alpha$, which is proportional to square of the ratio between transverse curvature and thickness of the actuator. Geometry with large $\alpha$ value should overcome large energy threshold before snap through motion and release more strain energy, which demonstrated our hypothesis. Meanwhile, an underdamped second order oscillation was observed at the tip of actuator after snap through motion. A retardation between strain energy drop and maximal tip velocity implied the viscoelastic energy losses through polymeric networks. This basic curved platform was harnessed by an array of sub-gram scale functionalized soft robotics on various topographies.

The thesis is organized in five primary sections. The first chapter is literature review that provides a brief introduction of liquid crystalline polymers, including categories and alignment methods. Additionally, light/thermal response of liquid crystalline polymers and snap through instability are also briefly reviewed. The second chapter overviews my pre-
vious work for photomechanically snap through instability constructed by light-responsive polymeric materials in different geometries. The third chapter presents details about electrothermally driven snap through instability by shell like LCE/PET actuator. The fourth chapter discusses dynamic characterization for electrothermally driven snap through motion and practical applications in soft robotics. The final chapter describes the main conclusions and future work based on my current research.
Driven by requirement for daily life’s applications, functionalized polymeric materials are gradually developed to improve their advanced properties. Among these functionalized materials, molecularly ordered liquid crystalline polymers exhibit remarkable advantages, such as easy synthesized process, diversity in mechanical properties, reversibility and biocompatibility. These materials consist of basic molecules and flexible chain with anisotropy in polymeric networks and can be programmed by a range of external stimuli, such as light, heat, electrical and magnetic field. Mechanical work will be generated through these stimuli by different mechanisms, such as trans-cis isomerization under 365nm UV light irradiation or nematic-isotropic phase transition through thermal effect. Complex shape changes can also be induced by programming the spatial/hierarchical alignment of molecules in local regions of networks and these reversible mechanical deformations can be utilized into multiple potential applications, such as photomechanical devices, biological systems and flexible actuators for soft robotics based on their functionalities. This chapter aims at reviewing background (optical/thermal) for responsive liquid crystalline polymers and soft robotics constructed by stimuli-responsive materials, especially by molecularly ordered liquid crystalline polymers.

2.1 Molecularly Ordered Liquid Crystalline Polymers

Molecularly ordered liquid crystalline polymers are novel materials, which exhibit long range orientational or positional organization at the molecular level in liquid phase with rigid anisotropic mesogenic units incorporated into cross-linked polymeric networks[16]. The alignment of molecules can be exploited by multiple synthetic approaches, such as surface alignment by unidirectionally rubbing[38] and photoinduced reorientation[39, 40], external mechanical strain[41, 42], electric or magnetic field[43]. For cross-linked networks, the level of cross linking density manipulates the glass transition temperature ($T_g$), which will classify the material as glassy liquid crystalline polymers and soft liquid crystalline elastomers[44].
Furthermore, based on spatial alignment configuration in the networks, molecularly ordered liquid crystalline polymers can be classified into three main structural profiles: planar uniaxial monodomain[45], twisted nematic[46] and splayed nematic profiles[47].

2.1.1 Classification of Molecularly Ordered Liquid Crystalline Polymers

For monodomain structure, molecular is aligned in one direction uniformly through thickness of the thin film. Even though the aligned configuration is uniform for both glassy liquid crystalline polymers and soft liquid crystalline elastomers, mechanism for the response is different between these two materials. For soft liquid crystalline elastomers, a reversible contractile strain will generate along director through nematic-isotropic (N-I) phase transition by external stimuli, following by expansion perpendicular to the director with a constant volume[48]. The anisotropy of polymeric chains and backbones will be destroyed[49], which induces internal stresses (strains)[50] and governs macroscopic shape changes by phase transition. However, highly cross-linked glassy liquid crystalline polymers undergo a reduction of order parameter in polymeric network[13] by external stimuli, instead of nematic-isotropic phase transition. Expansion can be also induced perpendicular to the director. However, the volume of liquid crystalline network is varied by producing extra free volume in disordered network, which is demonstrated by a decrease of local density[51]. For twisted nematic structural profile, the alignment of rigid molecular spatially rotates from 0° to 90° in plane through the thickness of thin film and left hand/right hand twisted nematic geometry can be controlled by integrating chiral-dupont[52]. Typically, alignment on each surface is created by filling the material into a layer of grooved polyimide[53] or microchannels[54], which can be constructed by manually rubbing or lithography[55]. Similarly to uni-axial monodomain structure, contractile strain can also be induced along hierarchical (through thickness) director and spiralled shape changes will be generated by constructing a strip with an angle between principal axes and the director at two surfaces[56]. For splayed nematic structure, molecules are aligned along director on planar side, compared with a alignment perpendicular to the surface on homotropic side. Splayed nematic configuration is constructed by spatially rotate molecules from 0° to 90° from planar side to homotropic side through thickness.
Contractile strain will simultaneously produce on planar side, compared with expansion on hometropic side by external stimuli[41, 10]. Fig.1[1] shows the schematic of basic aligned profile for three different structures.

Figure 1: Aligned profile for (a) Monodomain (b) Twisted nematic (c) Splayed nematic molecularly ordered liquid crystalline polymer[1].

Molecularly ordered liquid crystalline polymers have been investigated for more than 100 years. In 1950, Kuhn discovered a reaction between polymeric networks and chemical solvent[57]. Friedrich Reinitzer found the intermediate in liquid crystalline phase and Flory figured out rigidity of segments in polymeric networks in 1956[58, 59]. De Gennes demonstrated the fundamental theory for liquid crystalline elastomers as early as 1969[60]. Based on the requirement of functional and structural applications[61], researchers have discovered and synthesized complex polymeric networks with a range of synthetic methods by different shapes of rigid mesogetic unit (rod-like and disk-like)[62]. The most common method is combining (meth)acrylate monomers with flexible chain by polymerization. Mechanical work is modulated by bonding monomers to different positions of backbone. Compared with side-chain polymeric networks, main-chain liquid crystalline polymers exhibit more distinct properties, such as their better thermal stability[63] and more strain production by external
stimuli[64]. Fig.2 shows the schematic when mesogenic units are bonded on main chain and side chain of backbone[2]. Furthermore, the mechanical properties of molecularly ordered liquid crystalline polymers can be improved by changing the structure of polymeric networks. For example, carbon atom on backbone of the networks can be replaced by polysiloxane through hydrosilylation of vinyl liquid crystalline monomers and silicone precursors, which forms a side-chain liquid crystalline elastomer and generates as much as 400% in plane strain by thermal effect[44, 65].

![Figure 2](image)

**Figure 2:** (a) Side chain, (b) Main chain molecularly ordered liquid crystalline polymers[2].

As functionalized materials, molecules of liquid crystalline polymers can be aligned in liquid phase and finally polymerized to form cross-linked networks. Based on cross-linking density and glass transition temperature of the polymeric network, molecularly ordered liquid crystalline polymers can be classified into two categories: glassy/cross-linked liquid crystalline polymers and soft liquid crystalline elastomers[3]. For glassy liquid crystalline polymers, these materials exhibit high glass transition temperature ($T_g = 60°\text{C} - 100°\text{C}$)[66] with highly cross-linked networks[67] and relatively high modulus (~GPa)[68] in stiff polymeric networks. Particularly, $T_g$ can be manipulated by varying the chemical structure of basic mesogenic unit[69] and degree of polymerization[70]. These materials have capacity of generating MPa-scale actuation stresses[71] with relatively small strain production (~10%)[53]. Compared with highly cross-linked liquid crystalline polymers, soft liquid crystalline elastomers exhibit low glassy transition temperature with relatively low modulus in order of MPa at ambient temperature and are widely applied into flexible devices[3]. Phase transition from nematic to isotropic can disorder the alignment of lightly cross-linked networks and
produce reversible elastic strain between 300% to 400% [64, 72, 73, 74], especially by heat. These functionalized materials are capable of generating huge specific work density [4, 75, 73] and have large potentials as artificial arms by their reversibility [76]. Moreover, the elastic network can undergo a rapid rate from isotropic to nematic phase during relaxation process by low cross-linking density and has potentials to construct repetitive soft robotics by this advantage [17, 2]. However, an irreversible 90° reorientation of molecules inside elastic network will occur [77, 78] when a strain is applied perpendicular to the director. This reorientation of molecules has been illustrated experimentally and theoretically [50, 73]. Fig.3[3] presents mechanical properties (elastic modulus, variation of order parameter by external stimuli and glass transition temperature) and schematic structure of (a) glassy liquid crystalline polymers and (b) soft liquid crystalline elastomers.

Figure 3: Mechanical properties of (a) glassy liquid crystalline polymers, (b) soft liquid crystalline elastomers [3].
2.1.2 Alignment Methods for Liquid Crystalline Polymers

For spatial alignment of polymeric networks, a number of approaches have been established to create specific structural organization in micro-sized domain[44]. The most versatile method is by surface alignment, which can be achieved by a range of methods, such as buffing technique, lithography or photoalignment. For example, Manfred Eich fabricated monodomain structural liquid crystalline polymers by constructing uniaxial grooves on thin polyimide layer. The polyimide layer was spinned coated on glass substrate and micro-sized grooves were fabricated by buffing technique[79]. The uniaxial alignment was achieved by filling melted materials through capillary action and same method was applied for light-responsive cantilever oscillators[11] and bending actuators[80]. Furthermore, by creating a glass cell that rubbing direction on Elvamide layers were orthogonal, a 90° twisted nematic structure can be achieved[12]. Same method was applied to create alignment on planar side of splayed nematic liquid crystalline polymers[14]. On the other hand, molecules can also be aligned by injecting into microchannels[81], which is typically fabricated by photolithography. For example, researchers photopatterned one-dimensional (1D) microchannels by photolithography and achieved 3D shape change by thermal effects[55]. Moreover, photoalignment is another advanced method for construction of hierarchical alignment for liquid crystalline networks[5]. Typically, photosensitive materials are integrated into polymeric networks and the alignment of molecules is manipulated by varying the polarization of linearly polarized light source[40]. For example, Taylor H. Ware et al synthesized spatially heterogeneous liquid crystalline elastomers and controlled the hierarchical alignment by varying polarization of 445nm laser on an optical patterning system[4].

Another sophisticated method to align molecules is by external mechanical stretching[82]. This method was firstly discovered by Küpfer and Finkelmann in 1991[65] and works especially for soft liquid crystalline elastomers to get permanent uniform alignment. Basically, polymerization of the cross-linked networks is separated into two main steps. The first step is to create a weakly cross-linked network in oligomer state. Then the networks are deformed by external mechanical strain to obtain an uniform director orientation. The final step is to fully polymerize the stretched network to lock-in the anisotropy. In this way,
liquid crystalline elastomers can exhibit reversible deformations by nematic-isotropic phase transition. For example, Patrick Beyer et al synthesized a smectic main chain liquid crystalline elastomers (MC-LCE) by the same strategy and achieved reversible thermoactuation as much as 40%[45] and Antoni Sánchez-Ferrer et al constructed a microvalve for microfluidics by utilizing a nematic side-chain liquid crystalline elastomer[83], which was synthesized by the same two-step crosslinking step[84]. Particularly, the alignment of molecules can also be manipulated by external magnetic field before final photopolymerization. For example, Charles E. Hoyle et al synthesized an anisotropic liquid crystalline network by a low strength magnetic field (0.3T - 0.6T)[43] and Mohsen Tabrizi et al created voxelated patterning in a three-dimensional freeforms and aligned molecular anisotropy by 0.3T magnetic field[85].

2.1.3 Programmable Shape Change by Liquid Crystalline Polymers

Molecularly ordered liquid crystalline polymers, especially for soft liquid crystalline elastomers, can exhibit reversible and programmable actuation by an array of stimuli, such as light[86], heat[87, 88], solvent[89, 90], and mechanical work[53]. One of the most distinguishing features for liquid crystalline polymeric materials is the capacity to form heterogeneous mechanical responses in homogeneous composition. By manipulating local anisotropy of molecules, materials can undergo reversible spatially shape changes from 2D planar geometry to 3D or from 3D to 3D'. Typically, molecules can be aligned azimuthally (concentric circles) or radially and these patterns would be described as +1 topological defect[91]. 3D shape changes can be induced by macroscopic azimuthal contraction or radial expansion on flat film[92] and the organization of director profile can be achieved by a series of techniques, such as photoalignment and 3D printing.

For profiles created by photoalignment, photoaligned materials are always utilized for construction of desired director pattern. Typically, the local surface alignment is manipulated by polarization of external light source. By locally varying polarization of incident light, dyes in photoaligned materials will rotate and finally form a local surface alignment. For example, Taylor H. Ware et al synthesized a heterogeneous liquid crystalline elastomer with a local surface alignment by integrating azobenzene-based photoalignment materials[4]. They
firstly patterned an alignment layer by spinning coating azobenzene-based photoalignment materials in dimethylformamide (DMF) and illuminated with a 445nm laser. Azobenzene chromophore aligned normally to the polarization of 445nm laser after irradiation, which finally formed the objective pattern by varying the electric field vector of light. Glass cell with two surface aligned glass substrates was then constructed and liquid crystalline mixture was filled into this glass cell by capillary action. By this method, they finally created a liquid crystalline elastomer with 9 topological +1 defects in a flat film, which generated specific work capacity of 2.6J/kg and volumetric work capacity of 3.6kJ/m$^3$, as shown in Fig.4(a)[4]. In each defect, the director was aligned azimuthally around the center and shape of cone was induced by heating the flat film to 175°C. Same methods were applied to create programmable liquid crystalline elastomers with azimuthal director profile that generated 3D shape changes, including twisting ribbons and localized Gaussian curvature by Taylor H. Ware[93] and layered liquid crystal elastomer actuators that exhibited out-of-plane work capacity to nearly 20J/kg by Timothy J. White[73].

Another typical director profile created by photoalignment is radial alignment. For example, Laurens T. de Haan et al created a radial alignment layer by setting the polarization direction of a UV light parallel to the wedge of film, as shown in Fig.4(b)[5]. For construction of heterogeneous alignment layers, a glass cell with cinnamate-based linearly photopolymerizable (LPP) polymer spincoated on the surface of glass substrates was prepared. This glass cell was illuminated by a UV light, which produced alignment layers with director parallel to the polarization of light. Similarly to Taylor’s work[4, 93], a continuous variation of alignment was achieved by varying polarization of UV light source and using a photomask. Moreover, an IR-absorbing dye was integrated into this network, which is responsive to IR lamp irradiation. Flat film with radial alignment profile transformed into an anti-cone shape by contraction along in-plane radial director and expansion along the edge. The final actuation behavior is presented in Fig.4(b).

Additive manufacturing technique, such as 3D printing, is another mature method to program spatial director alignment for soft liquid crystalline elastomer. Typically, liquid crystalline polymeric inks are prepared and printed from a 3D printing nozzle, following by photo-polymerization through UV exposure. The alignment of mesogen is manipulated
Figure 4: Soft liquid crystalline elastomer film with +1 topological defect and actuation by external stimuli[4, 5].

by varying the direction of printing path. Reversible and programmable actuation can be achieved by designing the alignment profile. For example, Arda Kotikian et al designed a main-chain liquid crystalline elastomer with a reactive mesogen and amine linker via Michael addition[75]. This ink was printed by a high operating temperature writing machine at a temperature between $T_g$ and $T_{NI}$. To program a shape change from planar to 3D, a layered perpendicular meanders print path was designed and a reversible saddle 3D shape was achieved by heating the material above $T_{NI}$. Another typical example is a molecularly-engineered liquid crystalline elastomer actuator printed by Mohand O. Saed et al[94]. In this work, a nematic ink was formulated via thiol-acrylate Michael addition and was printed by a direct ink writing machine. Finally, a full cone formulation transferred from a +1 defect was achieved by azimuthal alignment profile.
2.2 Photo/Thermal Response of Molecularly Ordered Liquid Crystalline Polymers

Molecularly ordered liquid crystalline polymers are smart materials that exhibit long range anisotropy at molecule level. These materials will perform reversible shape change by an array of stimuli, especially by light and heat. As a contactless source, light can be spatially modulated by polarization, wavelength, intensity and is widely used to trigger responses for liquid crystalline polymers. For light responsive liquid crystalline network containing photochromic azobenzene mesogens, mechanical work will generate by converting energy from photoisomerization[95]. For thermal responsive liquid crystalline polymers, polymeric network will convert from a prolate spheroid to spherical profile during phase transition[16], which induces dimensional shape change. In this section, background for the response of light/thermal responsive liquid crystalline polymer is presented.

2.2.1 Light Responsive Liquid Crystalline Polymers

For light responsive crosslinked liquid crystalline polymers, photoinduced macroscopic deformation are always induced by incorporation of photochromic moieties (azobenzene derivatives) inside polymeric networks[96]. Generally, azobenzenes are stable in trans state with a rod-like shape. Under irradiation of 365nm UV light, trans isomer absorbs the energy and transfers to cis isomer on scale of picoseconds. Photoisomerization disorders the alignment of molecules and produces either a two-dimensional photoinduced contraction/expansion or three-dimensional bending/twisting deformation[97]. This photostrain is generated by shortening azobenzene derivative’s axis from 9Å to 5.5Å[98]. Meanwhile, bent cis isomer can also transfer back to trans isomer by visible light or thermal effect, following by a reversible deformation of liquid crystalline polymers [99]. Another typical mechanics to trigger responses for light responsive liquid crystalline polymers is called Weigert effect[100, 101, 102]. For photochromic moieties in both trans and cis state, the absorption spectra has a crossover around 440nm, which means that both trans and cis isomer can be activated by polarized light around this wavelength[103, 104]. When transition dipole moment of trans isomer
is parallel to the polarization of linearly polarized light, trans isomer is activated and rotates perpendicular to polarization of actinic light by repeating trans-cis-trans reorientation. After 90° reorientation, trans isomer becomes insensitive and suspends the photostrain production. Light will penetrate through larger thickness of liquid crystalline polymers with a less photostrain production by Weigert effect, compared with photoisomerization[102]. This trans-cis-trans reorientation are always induced by exposing 442nm (helium cadmium) or 457-514nm (multiline Argon-ion) laser[66]. Fig.5 shows transition between two states of azobenzene by photoisomerization and trans-cis-trans reorientation[6].

Figure 5: Photoisomerization and Weigert effect of photochromic derivatives[6].

For light responsive liquid crystalline polymers, a range of photo-responses can be exploited by trans-cis isomerization, such as bending[8], twisting[9] and oscillating[11]. The bending behavior was first discovered by Ikeda et al with polydomain liquid crystalline polymers[7]. In this work, a polydomain film was irradiated by a linearly polarized UV light (366nm) and the microdomain with azobenzene aligned parallel to the polarization preferably absorbed the energy of actinic light, which activating the film to bend towards light source along the electric vector by a absorption gradient through the thickness of film, as shown in Fig.6(a)[7]. For response of monodomain liquid crystalline film, photoisomerization results in a macroscopic contraction along director. The magnitude of deformation is manipulated by the penetration depth of incident light. Fig.6(b) shows a bending and unbending behavior of a crosslinked liquid crystalline polymer film under irradiation of 366nm UV and visible light[8]. For the response of twisted nematic structural profile, microscopically helical shape change can be achieved by varying the cutting direction between orientation of mid-plane alignment and long axis of film. For example, Fig.6(c) shows an isochoric winding actuation
for a spiral ribbon (offset angle is 45°) under irradiation of 365nm UV light[9]. For splayed nematic structure, photoisomerization enables contraction on planar side and expansion on homeotropic side. By this mechanics, a wave propagation was achieved by applying a 405nm laser on planar side of a strip constructed by a splayed nematic configuration[10]. Moreover, trans-cis-trans reorientation (Weigert effect) has also been widely utilized to create complex dynamic photomechanical responses. For example, Svetlana Serak et al achieved a high frequency oscillator (270Hz) by a monodomain azobenzene-functionalized liquid crystalline polymer[11]. This oscillation was driven by a 100mW laser with mixed wavelength (457, 488, 514nm), as shown in Fig.6(e).

Figure 6: (a) Reversible bending deformation for a polydomain LCP[7] (b) Reversible bending deformation for a monodomain LCP[8] (c) Twisting actuation for LCP in twisted nematic configuration[9] (d) Wave propagation for LCP in splayed nematic configuration[10] (e) High frequency oscillation by a monodomain LCP[11].
2.2.2 Thermal Responsive Liquid Crystalline Polymers

Molecularly ordered liquid crystalline polymers, including glassy liquid crystalline polymers and soft liquid crystalline elastomers, possess broadly advantages and exhibit large potentials for practical applications by their reversibility and programmability[49, 105]. For thermal responsive glassy liquid crystalline polymers, reversible mechanical shape changes are produced by a decrease of order parameter in polymeric network[12, 13] and dictated by director profile. For twisted nematic geometry, director rotates in plane from 0° to 90° through thickness and contractile strain will generate parallel to director by thermal effect. Three dimensional shape changes, such as coiling deformation can be observed by manipulating film geometry. Fig.7(a) shows a coiling shape change for a 15mm monolithic film with different width in twisted nematic geometry at 130°C[12]. Same spatially coiling actuation was also achieved by heating two combined monolithic films with different compositions, as shown in Fig.7(b)[13]. Compared with twisted nematic structure, the deformation of glassy liquid crystalline polymer in splayed nematic structure is relatively smooth and well programmed. Fig.7(c) and (d) show two-dimensional bending deformations with large amplitude by heating films from room to elevated temperature[14, 15].

Figure 7: Coiling deformation for (a) a 15mm twisted nematic film with different width at 130°C[12] (b) a combined twisted nematic monolithic film with two different compositions at 150°C[13] (c)(d) Large amplitude bending deformation for splayed nematic geometry[14, 15].
For soft liquid crystalline elastomers, large macroscopic anisotropic shape changes are normally produced due to their low modulus and cross-linking density. One of the most remarkable properties for this soft material is fully reversible large amplitude strain production (200%-300%) by order-disorder phase transition when heated to elevated temperature[106]. In polymeric network, flexible chain deforms into spherical geometry by external heat, inducing a contraction along the director. Network will recover to initial prolate geometry by cooling the temperature. Schematic of this phenomenon is shown in Fig.8(a)[16]. For thermomechanical response of soft liquid crystalline elastomers, molecules absorb external energy and transfer from nematic phase to isotropic phase by heating. Contractile strain is produced along the director during phase transition, with respect to an expansion perpendicular to the director by a constant volume(Fig.8(d)[18]). Fig.8(b)[2] shows phase change in polymeric networks by thermal effect. Reversible shape change of liquid crystalline elastomer enables the feasibility to lift weight and generates large specific work, as shown in Fig.8(c)[17].

Figure 8: (a) A unit cube of rubber in the isotropic (I) state and nematic (N) state[16] (b) Visualization of reversible shape change by N-I phase transition[2] (c) Weight lifting test for LCE film by thermal effect[17] (d) Strain production as a function of temperature for LCE with different applied stress[18]
2.3 Background of Flexible Actuators for Soft Robotics

Soft robotics have soft body that made out of flexible stimuli-responsive materials and are highly deformable. By integration of these stimuli-responsive materials, soft robotics enable conversion from external energy into force or motion and produce the desired shape changes with safe, comfortable human-machine interaction[107, 108]. Compared to rigid-body robots, these soft robotics can exhibit actuation in multiple degree of freedom in constrained space by their flexibility and have potentials to broad implementations, such as aerospace[109], medical implants[110] and automotive system[111]. For the construction of soft robotics, stimuli-responsive materials can behave as machines that harness input power to mechanical work[112], and can also be integrated with mechanics to magnify output for practical implementations, such as gripper[113], crawler[21], swimmer[114] and jumper[37]. In this section, soft robotics are presented by the sequence of shape memory alloys (SMA), piezoelectric materials, dielectric elastomers, ionic electroactive polymers and liquid crystalline polymers/elastomers.

2.3.1 Shape Memory Alloys

Shape memory alloy (SMA) is a metal alloy that deforms at low temperature and can recover to original shape by heating. The most typical example for shape memory alloy is nickel-titanium (NiTi) alloy, which behaves rapid deformation rate and high ductility at high temperature[115, 116]. To induce macroscopic shape change of NiTi alloys, materials are typically subjected to a mechanical stress at twinned Martensite phase in low temperature, following by a crystallographic transition to austenite phase by heating, shown in Fig.9(a)[19]. Based on these advantages, NiTi alloys are widely applied to construct soft robotics. For example, Xiaonan Huang et al achieved a highly dynamic shape memory alloys soft actuator driven by 7.4V[20]. This soft actuator can switch between actuated and unactuated state within 3s by high thermal conductivity of elastomeric tapes and actuate by utilizing mismatch of the strain between prestretched and unstretched thermal elastomeric layers. This tethered jumping actuator can jump over an obstacle of ∼10mm (Fig.9(b)[20]).
Another example is a steering meshworm created from soft braided meshtube and NiTi coils, shown in Fig.9(c)[21]. This steering mesh worn can rotate $10^\circ$ within 30s by dominating contracted length of shape memory alloy spring. The same idea was implemented into a soft robot arm constructed by shape memory alloy (SMA) springs in a specific arrangement with a flexible braided sleeve, which is inspired from Octopus vulgaris arm[22]. This soft robot arm enable potential capacity for grasping objects with different weights, shown in Fig.9(d)[22].

Figure 9: (a) Crystallographic microstructural changes in shape memory alloys during phase transition between low and high temperature[19] (b) A tethered jumper fabricated by NiTi shape memory alloys[20] (c) Steering movement of a meshworm achieved by NiTi shape memory alloys[21] (d) Grasping actuation by soft robotics constructed by shape memory alloy muscles[22]
2.3.2 Piezoelectric Materials

Piezoelectric materials, such as quartz, BaTiO$_3$ and synthesized ceramics, are capable of releasing electric charge by external stress and generating stress by applying electric field. This special property of piezoelectric materials is defined as piezoelectric effect (shown in Fig.10(a)[23]), which is widely utilized for construction of soft actuator by large power density and scalability[117]. Among piezoelectric materials, piezoelectric ceramic is the most common objective by a relatively high value of piezoelectric charge ratio (d), which is the ratio between generated charge and applied stress and represents for the energy conversion efficiency[118]. Piezoelectric actuation can be induced by generating tensile or compressive stress of piezoelectric ceramic by electric field, but is limited by its high stiffness[119]. Another typical material is piezoelectric polymers, which exhibits smaller elastic modulus and piezoelectric charge ratio (d).

Typically, the energy efficiency and power generation of piezoelectric configurations can be improved by modifying electrode pattern, poling and stress direction[119]. By utilizing piezoelectric responses with the design of geometry in objective system, soft robotics can be achieved by piezoelectric effect. For example, Audelia G. Dharmawan et al presented a novel legged piezoelectric miniature robot, shown in Fig.10(b)[24]. This single unimorph actuator can realize steerable movement by applying different frequency of voltage to different leg’s positions. A controllable speed was also achieved by manipulating the magnitude of applied voltage. In another instance, Yichuan Wu et al built a soft robotic based on a curved unimorph piezoelectric structure[25]. This soft robotics exhibited the fastest speed of movement among published artificial insect scale robotics (20bl/s) and mimicked the locomotion of insects, such as climbing inclines and carrying weights as shown in Fig.10(c)[25].

However, the above examples are both tens of mg and only actuate on land. To overcome the limitation of work space, Noah T. Jafferis et al demonstrated an untethered insect-sized flapping-wing microscale aerial vehicle (90mg). The flapping actuation of wings were manipulated and driven by piezoelectric actuators, as shown in Fig.10(d)[26]. Most importantly, the efficiency of this system is comparable with insects in nature and the basic structure is only powered by 110 - 120mW. This actuator sets a milestone in field of insect-scale flying.
vehicles, with a 70mg extra payload capacity. The achievement described here illustrates the feasibility of a tethered flight vehicle powered under low voltage by carrying on-board power supply.

![Image](image_url)

Figure 10: (a) Production of tensile/compressive strain by applying external electric field for piezoelectric materials[23] (b) A steerable legged robot constructed by a unimorph actuator and legs[24] (c) Soft robotics constructed by piezoelectric PVDF carries a load that is 6 times than own body weight[25] (d) A untethered flight driven by a pair of piezoelectric actuators[26]

2.3.3 Dielectric Elastomers

Dielectric elastomers are one of subclassifications from electroactive polymers, that can generate stimuli-induced electromechanical responses by applied voltage (kV). DC field can be applied across the thickness of dielectric elastomers by coating conductive electrodes (carbon nanotube[120], graphite[121]) on surface. Under electric field, Maxwell stress gener-
ates through elastomeric network and dielectric elastomer will expend in orthogonal vector. Bending actuation will also be induced by fixing surface from one side of elastic layer, as shown in Fig.11(a)[27]. Working as a compliant capacitor, this stimuli-responsive material has been widely incorporated into soft robotics system and implemented in plenty of configurations, such as crawling oscillators[122], soft jellyfish[123] and micropump[124]. One typical example is a high speed dielectric elastomer actuator-based system (v > 1bl/s), constructed by multilayers. As shown in Fig.11(b)[28], a bug combined with four multilayer legs (elastomer, electrode, carbon fiber stiffener) actuated at 1.5Hz under relatively low voltage. This multilayer fabrication eliminates the requirement for prestretch and rigid segments. Another example is a 190 mg autonomous untethered soft robotics driven by \( \sim 450\text{V} \). The speed of this unloaded dielectric robotics can reach as much as 30mm/s and can navigate a designed path with three independent legs, as shown in Fig.11(c)[29]. The movement of leg was achieved by triggering low voltage dielectric elastomer under AC driving signal.

Figure 11: (a) Planar and bending actuation of dielectric elastomer film under DC field[27] (b) A steerable four legged soft robotics constructed by multilayer dielectric elastomer[28] (c) Navigation of untethered dielectric elastomer soft robotics in a designed path[29]
2.3.4 Ionic Electroactive Polymers

Ionic electroactive polymers are another distinct stimuli-responsive materials that are inherently sensitive to external electric field. Accordingly, ionic electroactive polymers exhibit low voltage requirement (few volts) for actuation, compared with piezoelectric materials and dielectric elastomer[125]. Electromechanical strain is induced by movement of ions when applied to electric field, which consequently leads to a bending deformation[30]. However, some limitations exist in the implementations of ionic electroactive polymers, such as slow response time and low energy efficiency. Nevertheless, this material is still widely utilized for soft robotics, especially for bending cantilever that generates large force and electromechanical strain in low voltage (4V)[31]. This bending configuration can be integrated to electric system and realizes advanced actuation, such as a biomimetic jellyfish robotics shown in Fig.12(c)[32]. In a word, these materials are widely applied into biomedical field by their low density and high toughness, and exhibit huge potentials to construct soft robotics by large strain production under relatively low electric field.

Figure 12: (a) Deformation of ionic electroactive polymers in electric field[30] (b) Actuation of a 12 layers IPMC cantilever lifting a 124g weight by 4V DC voltage[31] (c) Jellyfish soft robotics constructed by IPMC[32]
2.3.5 Liquid Crystalline Polymers/Elastomers

Liquid crystalline polymers are cross-linked networks that exhibit long range orientational organization in molecular level. Mesogenic units show anisotropy in liquid phase and can be aligned preferentially in same direction, defined as nematic director\(^{[126]}\). Stimuli-responsive mechanical work can be generated by integrating azobenzene moieties or by thermal effect and the magnitude of work generation is typically controlled by cross-linking density of the polymeric network. Large reversible macroscopic shape change can be observed by liquid crystalline elastomers, which are light cross-linked liquid crystalline polymers. Spontaneous uniaxial contraction (\(\sim 300\%\) thermomechanical strain\(^{[74]}\)) can be produced along director by nematic-isotropic phase transition under heat. By their reversibility and elasticity, liquid crystalline polymers are widely utilized for widespread applications, especially for soft robotics with biomimetic locomotion, such as worm-like crawler\(^{[127]}\) or swimmer\(^{[50]}\).

The recent studies indicate that LCE can be easily powered by electrical potential and can realize complex shape change and diversiform locomotions. The most common method to electrically power liquid crystalline elastomers is by integrating conductive pattern into the soft body. One typically example is an electrically powered bilayer “Janus” soft robot constructed by LCN and polyimide\(^{[33]}\). This “Janus” soft robot can achieve complex locomotion(Fig.13(a)), such as self-locking gripping and crawling by body contraction and expansion. Joule heat was produced by the encapsulating conductive heating wire between liquid crystalline elastomer and kapton film. This “Janus” soft robot can achieve a total 25mm horizontal displacement within 90s. Another typical example is an LCE-based tubular actuator with multiple actuation modes controlled by low voltages. Thermomechanically deformation has been realized by combining soft liquid crystalline elastomers with stiffer substrate, as shown in Fig.13(b)\(^{[34]}\). Joule heat was also produced by integrating a conductive wire with LCE. Self-regulated untethered crawler was demonstrated by integrating power supply on-board. This untethered soft robotics can generate 40mm horizontal displacement within 1200s by triggering a pair of diagonal tubular actuators. Moreover, a fully soft robot which can sense the environment and exhibits locomotion like an inchworm was illustrated by using carbon-black-doped liquid-crystal elastomer (LCE-CB) nanocomposite,
as shown in Fig.13(c)[35]. Complex shape program can be achieved by partially heating the active materials with independently addressable heaters. This soft actuator produced a 12mm forward locomotion distance within 350s.

Figure 13: (a) Locomotion of a wave-like walker constructed by sandwiching a conductive heating wire between LCE and kapton film[33] (b) Locomotion of untethered soft tubular actuator by Joule heat[34] (c) Crawling locomotion of an inchworm soft actuator[35]

2.4 Ultra-fast Snap Through Instabilities

Snap through motion is a mechanical instability, where elastic structures typically transfer from one equilibrium state to another by ultrafast speed (ms)[128]. This rapid motion can be exploited by storing and releasing elastic energy between equilibrium state and is widely observed in nature, such as rapid closure of Venus flytrap leaf[129] and hummingbird’s beak during attempted insect capture[130]. Snap through instability has been commonly employed in plenty of applications, including a locomotion of jumping robotic[131, 132, 133], passive control of microfluidics[134] and ventricular assist device[135].
Researchers have theoretically and experimentally investigated snap through instability by designing the structure of objective system and apply this dynamic instability to deploy activating actuators by a range of smart materials. For example, Christoph Keplinger et al demonstrated a snap through instability by mounting a soft dielectric membrane (expansion strain $\sim 1692\%$) on a chamber of a suitable volume and applying a voltage to trigger the snap without causing electrical breakdown[136, 137]. Scott Scharfenberg et al observed a snap through instability from graphene layers by AFM when these materials changed from closely conforming to corrugated metallic substrate in order to remain nearly flat to the substrate[138]. Seung-Won Kim et al created a bio-mimetic flytrap robot and achieved a rapid snap through motion by embedding shape memory alloy springs into a laminated carbon fiber reinforced prepreg (CFRP) structure[113].

Ultra-fast snap through motion can be efficiently induced by exploiting the geometry of system. These configurations will transfer from one stable position to a remote stable equilibrium position by breaking local stability from external loads. The loads can be generated by external stimuli, such as light[139], heat[140, 141], electric[136] or magnetic fields[142]. Simple buckled arch configuration is one typical example that is widely utilized in mechanical system and applied as energy harvesting devices. This configuration offers plenty of advantages, such as simple construction process, precise positioning control and potentials for rapid motion between two equilibrium states. Snap-bucking can be realized by deforming the structure quasistatically to elastic instability with external energy absorption. This rapid motion (ms) typically transfers between two stable states and attracts interest of researchers to develop practical applications. For example, Amir Alipour Skandani et al fabricated a simple buckled arch actuator by clamping both ends (clamped-clamped) and achieved a bistable snap through actuation by irradiating polarized 375nm UV laser on an azobenzene-functionalized polyimide[143]. Michael Gomez et al investigated a critical slowing down of snap through by rotating one end of single buckled configuration at an angle[144]. Sano and Wada et al designed a buckled beam with one hinged end and changed the bi-stable structure into a monostable configuration by snap through motion[145].

Even though soft robotics exhibits high deformability and can generate more degree of freedom, compared with rigid body. These soft machines still exhibit some drawbacks,
such as slow locomotion speed and low manipulation strength. In order to create high performance actuation, snap through instability has been widely applied to fully explore the ability of soft robotics. For example, Yichao Tang et al achieved a soft pneumatic actuator with a tunable bistable spine mechanism and utilized snap-through bistability to amplify the actuation speed and motion (Fig.14(a))[36]. Another typical example is a bio-inspired jumping robotics that utilized the snap through impulsive mechanism triggered by shape memory alloys, as shown in Fig.14(b)[37].

Figure 14: (a) Spine-inspired high-speed and high-force soft robotics with spine mechanism triggered by snap through instability[36] (b) Water strider jumping from water by snap through instability[37]
3.0 Photomechanical Instabilities in Light-responsive Polymeric Materials

Snap through motion is a dynamic instability that has been commonly employed in plenty of practical applications, such as a locomotion of jumping robotic[131], passive control of microfluidics[134] and ventricular assist device[135]. Both post-buckled and shell like geometry can generate snap through motion and this elastic instability has been widely implemented in daily life, such as a popping and jumping toys[132, 133]. These configurations will transfer from one stable position to another remote stable position by breaking local stability from external loads. The loads can be generated by external stimuli, such as light[139], heat[140, 141], electric[136] or magnetic fields[142].

For light-responsive polymeric networks, mechanical strain is produced by trans-cis isomerization, which distracts the alignment in the network. In azo-polymeric networks, azobenzene aligned parallel to the polarization of linearly polarized light source will preferably absorb energy and generate photomechanical strain in the network[98]. Contraction/expansion generated by photoisomerization depends on the principle axis of molecular orientation[146]. For example, in splayed nematic aligned profile, contraction will accumulate on the planar side and expansion will generate on the hometropic side. In this chapter, we review some results from previous work about photomechanical instability driven by light-responsive polymeric materials. First of all, the snap through motion was induced by a simple buckled arch and we also achieved a tuned photomechanical switch constructed from a laterally constrained arch by utilizing a polarized 375nm UV laser. Reversible and cycled actuation was demonstrated by this elastic bifurcated arch. The time to trigger the snap through motion was investigated as a function of end displacement ratio and irradiation position. Second of all, a shell like structure was constructed by using high modulus liquid crystalline polymers in splayed nematic aligned profile and a high torque-dense rotary actuator was finally achieved (1~10 N.m/kg at ∼100 rad/s angular velocity) by snap through motion. This snap through motion was harnessed for an array of implementations, such as lifters and grabbers.
3.1 Tuned Photomechanical Switching of Buckled Arches

3.1.1 Introduction

Contactless actuation of polymers can be triggered by external stimuli, especially by light. Transducing light power into mechanical work has attracted significant attention for remote control of polymers embedded with photochromic moieties to realize complex shape changes. Considering the geometry to induce snap through motion, a standard arch configuration exhibits many distinct advantages, such as precise, discrete positioning and reversibility between two stable geometries. Most importantly, equilibrium stability can be held by buckled arch configuration without external energy input or load. Here, we firstly demonstrated an ultrafast snap through behavior (∼ms) by a simple buckled arch. We investigated the latency time ($T_{cr}$) to trigger the snap through motion as a function of the irradiation position and end displacement ratio. A tuned photomechanical switch was finally achieved by adding a laterally constrained pin in this elastic system.

3.1.2 Materials and Experimental Setup

Photomechanical materials used here are polyimides embedded with azobenzene derivatives (AzoPI) and the chemical structure of azo-polyimides is shown in Fig.15. During isomerization under the irradiation of 375 nm UV laser, the rod-like trans molecule contracts to form cis isomer in bent state, which produces macroscopic deformation. A photostrain gradient will accumulate in the polymeric network when the light penetrates through the thin film. The bent cis molecule will finally transfer back to trans state by visible light ($\lambda > 540$nm) or by thermal effect.

AzoPI thin film (15µm) was cut from bulk material sheet by 1mm wide. This strip was clamped at both ends and kept straight on a linear stage with micrometer, as shown in Fig.16. The original length in unbuckled state is represented by $L_0$. For a simple buckled structure (Fig.16(a)), $L_0 = 20$mm. For a bifurcated structure (Fig.16(b)) with external rigid constraint, $L_0 = 56$mm. The diameter of constrained pin in the middle of the setup is 0.7mm. The objective end displacement of the elastic system was modified by rotating the
micrometer. The final length of the strip was characterized by \( L \), and the end displacement ratio was calculated by \( \frac{L}{L_0} \). The actinic light source is a polarized 375nm UV laser, with an intensity of 100mW/cm\(^2\) measuring by Thorlabs S302C thermal power sensor. The light induced snap through instability was recorded by Aven Mighty Scope camera with a 7 frames/s rate. A 150W fiber optic illuminator with a halogen bulb (Cole Parmer) was utilized to remove the residual photostrain in polymeric networks. Images were characterized by ImageJ software and the variation of curvature was recorded by a custom code written in MATLAB.

Figure 16: Experimental stage for (a) simple buckled structure (b) bifurcated structure before and after compression. Scale bar is 5mm
3.1.3 Results and Discussion

For non-constrained simple buckled arch, the strip was clamped at both ends and buckled up by constructing an end displacement at one side. Polarized 375nm UV laser was irradiated in the middle of the arch to trigger the ultra-fast snap through motion. Fig.17(a) shows the schematics of polymeric network in buckled state. When the strip is buckled up, expansion occurs on the surface of strip with a contractile strain at the bottom. By irradiation of UV laser on the surface, photoisomerization will gradually reduce the original expansive strain and induce the snap through motion. To observe the snap through motion, we tracked curvature variation during the irradiation process. In Fig.17(b), snap through occurs at the point when the geometry undergoes a discrete jump from the edge of instability to the second stable position.

Figure 17: (a) Schematic of snap through motion for a simple buckled arch configuration (b) Relationship between curvature variation as a function of irradiation time, scale bar is 2mm
To investigated the effect of light source, snap through instability was triggered by three different irradiated positions. Fig.18(b) presents $T_{cr}$ as a function of irradiated positions and end displacement ratio. As shown in Fig.18, it was easier to induce the snap through instability when UV laser was closed to the clamped end. This configuration exhibited symmetric behavior for light focused on left and right sides of the arch. Stationary simulations of this non-constrained arch has been done by Dr. M.L. Smith from Hope college, using COMSOL and the simulated results matched the qualitative behavior of these experiments when light was in position B and C, along with experimental results from other glassy liquid crystalline polymers under development. From the above experimental results, we can conclude that: 1) The latency time ($T_{cr}$) to trigger the snap through motion will increase as the arch is buckled more severely. 2) It is easier to trigger snap through motion when light focuses on the left and right side of midpoint symmetrically. This single buckled arch can be implemented into some practical applications, such as mechanical energy harvesting devices.

Figure 18: (a) Complete cycle for snap through motion by unidirectional irradiation at different positions for a structure with 0.995 end displacement ratio, scale bar is 2mm (b) Latency time ($T_{cr}$) as a function of irradiated positions and end displacement ratio
In order to achieve cycled and reversible snap through motion, a constrained bifurcated arch was constructed by adding a lateral constrained pin in the elastic system. As shown in Fig. 19, the 375nm UV laser was firstly irradiated on the left side of the bifurcated arch. Photostrain gradient in the polymeric network transferred the geometry to the edge of instability. The accumulated energy will release within $\sim 10$ ms and transfer the left side from upwards to downwards state. Visible light (>500 nm) was applied to remove residual photostrain for half an hour. Then the UV laser was positioned on the right side to induce the snap through motion and transfer the geometry back to the original configuration. The completed cycle can be actuated repetitively for more than 10 cycles.

Figure 19: (a) Evolution of the constrained bifurcated arch during a complete cycle of snap through actuation, scale bar is 5mm (b) Complete photoresponsive snap through actuation by unidirectional irradiation ($L/L_0 = 0.975$)
Similarly to the simple buckled arch, the time to trigger snap through motion for bifurcated structure was investigated as a function of irradiated position and end displacement ratio. As shown in Fig. 20, when laser is in the middle of the left portion (A) and near the cylindrical pin (B), the latency time \( T_{cr} \) increases with a decrease end displacement ratio. Meanwhile, it is harder to trigger snap through motion at position B than A, which is opposite to the tendency of simple buckled structure. Furthermore, the latency time increases with the increasing end displacement ratio in position C, which is opposite to the tendency in position A and B. For a large end displacement ratio \( (L/L_0 = 0.99) \), it is easy to observe that \( T_{cr}(C) < T_{cr}(A) < T_{cr}(B) \). This experimental result exhibits the same trend compared with simulation by Dr. Matthew. This bifurcated arch has huge potentials to impact energy harvesters, sensors and soft robotics applications for further investigations. This work has been published in Smart Materials and Structures in 2019 with collaboration by Dr. Matt Smith from Hope College.

Figure 20: Latency time \( (T_{cr}) \) to trigger snap through motion as a function of irradiated position and end displacement ratio on left side for a bifurcated arch
3.2 High Torque-dense Photomechanical Actuation by Splayed Nematic Azo-Functionalized Liquid Crystalline Polymers

3.2.1 Introduction

Light responsive mechanical actuators are widely implemented into industrial fields by contactless and remote operation. However, the photomechanical work potential is still challenged to achieve high-performance actuation, such as jumpers, hoppers and high-speed crawlers. To fully explore the behavior of photomechanical actuations, liquid crystalline polymers integrated with azobenzene are widely chosen as active materials to convert the photo-energy into photomechanical response by programming the nematic alignment profile.

Here, a shell like curved actuator was fabricated by utilizing splayed nematic liquid crystalline polymers. A hinge-like, high torque-dense actuation was achieved by non-linear snap through instability. By confining the boundary conditions, an ultrafast photomechanical actuation with $\sim 4 \text{N.m/kg}$ torque density was demonstrated. Furthermore, by varying the confined transverse curvature of the shell like structure, hierarchical strain distribution was observed at the crease from experimental results. This high torque-dense actuator was finally harnessed for some mechanical applications powered by UV light, such as levers, lifters and grabbers.

3.2.2 Materials and Experimental Setup

The splayed nematic azobenzene-functionalized liquid crystal polymers (ALCP) was synthesized by copolymerizing a mixture composited from 89.1wt% of RM34C, 9.9wt% of 8c azobenzene and 1wt% of photoinitator (I-784). To construct the splayed nematic molecular orientation, a glass side was spin-coated with Elvamide (Dupont 8023R) and rubbed by velvet to create micro-sized grooves. Another glass slide was spin-coated with polyimide (Nissan Chemical SE5661) to induce homeotropic alignment. These two glasses were bonded together by epoxy adhesive mixed with 50$\mu$m silica spacer. The mixture was heated at 120°C and then filled into the prepared glass cell. The temperature was then decreased to 70°C to reach the nematic phase. For polymerization, the nematic network was first polymerized by
10 min with a small intensity, following by 50 min fully polymerization at high intensity by using a Edmund MI-150 high-intensity illuminator equipped with a cut off filter ($\lambda \geq 420\text{nm}$, 35mW/cm$^2$). Fig.21 shows (a) the POM images for high modulus splayed ALCP under a pair of cross polarizer with $0^\circ$ and $45^\circ$ corresponding to the polarizer and (b) morphology of cross section by SEM.

**Figure 21:** (a) Polarized optical microscopy (POM) images of high modulus splayed nematic ALCP under cross polarizers which the planar alignment is $0^\circ$ and $45^\circ$ corresponding to the polarizer (b) SEM image for cross section of ALCP. The red line indicates the alignment of director through the thickness

The optical setup applied here is an OmniCure AC450 Curing LED lamp systems with 365nm wavelength. The concave side (homeotropic) of curved sample was faced to the UV light source, holding by a tweezer. The intensity of this unpolarized UV light is 500 mW/cm$^2$. In order to record the deformation of actuator during irradiation, two Mighty Scope 1.3M USB Digital Microscope (200x magnification, 7 frames/s) were set to track both side and
bottom view of the actuator. The high-speed images was captured by PHANTOM V2511 High Speed Video Camera (1000 fps). A Wide-area 3D Measurement System VR-3000 Series was utilized to scan the configuration before and after the snap through instability.

### 3.2.3 Results and Discussion

For the construction of the shell like actuator, a rectangular film (10mm×6mm) was excised from the fundamental sheet (50µm). A Cu wire (D = 300µm) was glued on planar oriented side along the longer boundary (W = 10mm) and the alignment of director was parallel to the shorter boundary (L = 6mm). Cylinder with a diameter (D = 7.4mm) was first utilized to manually form the curved shell like geometry. Unpolarized UV light (365nm, I = 500mW/cm²) was applied to irradiate on the homeotropic side. During irradiation, this curved actuator deformed away from the light source by expansion on the homeotropic side. Photostrain gradient was formed within 10's of µm through the thickness of the polymeric network. Within 1.8s, the boundary of the curved actuator bent away from the light source by trans-cis isomerization on homeotropic side. The strain energy in this elastic system gradually increased and accumulated energy was finally released with a rapid speed after reaching an energy threshold and lead the ultra-fast snap through actuation due to the interplay between the pre-biased boundary condition and the photostrain gradient. This ultra-fast snap through motion occurred within 16ms. The continuous irradiation separated this geometry into two oppositely curved regions. To investigate the influence of transverse curvature, the diameter of cylinder was varied from 7.4mm to 4.4mm. A more curved shell like actuator was constructed by the same method. Point-like defects symmetrically emerged at the corner of the formatted crease by actuator with larger transverse curvature. Here, we conclude that the strain distribution at the crease strongly depended on the pre-bias curvature imposed at the boundary of ALCP and was characterized by the geometry of the rotary actuator.

For the calculation of torque density, a 8.5mg weight was glued to the curved 3.6mg splayed nematic ALCP film (10mm× 6mm × 50µm), connected by a 1.86mg rod. The corner of rectangular film was excised to maximize the work density (L_c = 3mm). During
irradiation, the weight and rod will rotate around point A. The torque generation can be calculated by:

\[ \tau = I \alpha \]  

(3.1)

Where I is the moment of inertia, \( \alpha \) is angular acceleration during the ultrafast rotation. The moment of inertia can be calculated by:

\[ I = \sum mr^2 = m_1 r_1^2 + \frac{m_2 r_2^3}{3} + m_3 r_3^2 \]  

(3.2)

\( m_1 \) is the weight of payload (8.5mg), \( m_2 \) is the weight of rod (1.86mg), \( m_3 \) is the weight of ALCP film which rotates around A (0.53mg). For the value of \( r \), \( r_1 \) is 10mm, \( r_2 \) is 10mm, \( r_3 \) is 1mm. An Image tracking software TRACKER was used to track the angular acceleration \( \alpha \) (14100/s^2). Then the torque generated by this rotary actuator was 14.63 \times 10^{-6} \text{N.m} \) and the torque density is calculated by:

\[ \bar{\tau} = \frac{\tau}{M} \]  

(3.3)

In this experiment, the maximum angular velocity is 73 rad/sec and torque density is 4N.m/kg. This result locates in the reasonable range between 1N.m/kg and 10N.m/kg, simulated by Dr. Mahnoush Babaei from Carnegie Mellon University and the ultrafast snap through motion occurred within 40ms. For our current rotary actuator, the torque density is comparable against some other electromechanical systems, such as hydraulic systems (torque density is between 10N.m/kg to 120N.m/kg with angular velocity between 0.4rad/s to 100rad/s) and pneumatic systems (torque density is between 1N.m/kg to 40N.m/kg, with angular velocity between 5rad/s to 450rad/s).
4.0 Electrothermally Driven Snap Through Instabilities by Monodomain Liquid Crystalline Elastomer

4.1 Introduction

In this chapter, a bilayer soft actuator was presented by combining soft monodomain liquid crystalline elastomer (LCE) with latch mechanism. Material was synthesized by thiol-acrylate Michael addition reaction. Monodomain profile of molecules was achieved by mechanical stretching with a final frozen-in by polymerization. Transversely curved composite shells constructed by monodomain liquid crystal elastomer (LCE) and polyethylene terephthalate (PET) with encapsulated electrodes presented millisecond-scale actuation with ∼200mW electrical power inputs at low voltages (∼1V). The actuation profiles were proved to be functions of the geometry and the electrical pulse patterns. First of all, by varying the transverse curvature and thickness of LCE, work content can reach between $10^{-7}$J to $10^{-5}$J and power density can reach as much as 5kW/m$^3$. Second of all, the latency of actuation can be reduced by powering the actuators with a electrical power pulse. This electrical power pattern allows the geometry reset to the native state, but prevents it cooling to the ambient before subsequent actuation cycles.

4.2 Experiment

4.2.1 Synthesis of Monodomain Liquid Crystalline Elastomer

Thiol-acrylate reaction was used to create oligomerized LCE precursors, where mechanical deformation is used to induce uniaxial (monodomain) order, which are then frozen-in by polymerization[147]. Mesogenic mixtures containing main-chain diacrylate-based monomers such as 1,4-bis-[4-(6-acryloxyhexyloxy) benzoyloxy]-2 methylbenzene (RM82) in combination of di-thiol chain extenders (e.g. EDDT; 2,2-(ethylenedioxy)diethanethiol) enable
work-dense Joule-heated artificial muscles[148]. Here, liquid crystal elastomers (LCEs) were synthesized via a thiol-acrylate Michael addition reaction. LCE networks were prepared by RM82 (diacylate liquid crystalline monomer), EDDT thiol spacer for the first network and vinyl cross linker for the second network. The basic structure for these three monomers is shown in Fig. 25. For the preparation of monomer mixture, 1.2 mol EDDT thiol chain extender (Sigma-Aldrich Corp.) was added to 1 mol liquid crystalline monomer RM82 (Wilshire Technologies Inc.) and heated at 120°C to melt the sample. A rotary mixer was applied to uniformly mix the melted sample for a few seconds. After that 0.3 mols vinyl cross-linker TATATO (Sigma-Aldrich Corp.), 2 wt.% of thermal initiator BHT (Sigma-Aldrich Corp.), 2 wt.% of the photo-initiator I-369 (Ciba Specialty Chemicals Inc.) and 2 drops of trimethylamine Et3N (TCI Chemicals) were mixed and heated at 120°C for melting. This final liquid mixture was then ready to fill into a prepared glass cell.

![Chemical structures](image)

Figure 22: (a) Diacylate liquid crystal monomer RM82 (b) EDDT thiol spacer (c) Vinyl cross linker.

For construction of a glass cell, the glass substrates were firstly sonicated for 20 minutes in a 2% water solution of Alconox cleaner, following by rinsing thoroughly through de-ionized water. After that, the glass substrates were sonicated in isopropanol (IPA) for
20 minutes and then dried. A layer of Ease Release 200 (Smooth-On Inc.) was sprayed on the surface of glass for easy removal after fabrication. Spacers of suitable thickness determined by the desired LCE thickness were put along the boundary of glass to control the thickness of liquid crystalline elastomer thin film. Liquid monomer mixture was poured on the surface of glass and the second cleaned glass substrate was then covered and pressed over the mixture. A pair of binding clips was applied at the boundary of the glass to bound the glass cell. The final mixture was then kept at 80°C to form oligomerization for 30 minutes, following by a photopolymerization in isotropic state with 50mW/cm² 365nm UV light (Omni cure, Lumen Dynamics) on each side for 60 seconds. After photo-polymerization, the cell was split open and the film was recovered and cut into 1cm (length) by 1.5cm (width) sheet. This thin film was subsequently mounted on a fine translation stage and stretched to about 1.65 times along the length. The stretching of the film caused the rod-like RM82 LC monomers to align in the stretching direction, inducing an internal director at a finite order parameter. By mechanically maintaining the strain, the film was then photo-polymerized at room temperature with 365nm UV light at an intensity of 50mW/cm² for 10 minutes to “freeze” in the ordered alignment. Fig.23 shows the aligned film and POM images under cross polarizers which director is 0° and 45° with respect to the polarizer.

Figure 23: (a) Monodomain liquid crystalline elastomer after photo-polymerization (b) Polarized optical microscopy images (POM) for uniaxial monodomain liquid crystalline elastomer in which the planar alignment orientation is 0° and 45° corresponding to the polarizer. n illustrates the direction of the director.
4.2.2 Fabrication of Curved Shell LCE/PET Actuator

A curved, tranversely shell like bilayer actuator was constructed by combining LCE, polyethylene terephthalate (PET) film and an encapsulated electrode. The construction of conductive electrode for external Joule heat supplement was achieved by microfabrication. First, a 23µm clear Polyester film (McMASTER-CARR, storage modulus at room temperature = 1.71GPa) was adhered to a squared Si wafer with a double-sided tape. A bilayer photoresist (LOR-5B and S1805) was then spin-coated on the surface of the PET film. The details for the bilayer coating recipe are as follows:

1) Spin coat LOR-5B: 600rpm for 10s + 4000rpm for 1min + 600rpm for 10s
2) Bake sample for 15min at 110°C and blow cold
3) Spin coat S1805: 600rpm for 10s + 4000rpm for 1min + 600rpm for 10s
4) Bake sample for 5min at 115°C and blow cold
5) Put the sample in a wafer box and cover it with Aluminum foil (avoid any light exposure)

After spin coating the photoresist, a U shape pattern was created using Heidelberg Direct Write Lithography system (MLA100). This lithography system automatically detected the perimeter of the sample and used a digital mask to sequentially expose smaller pattern fields to yield the U shape design by a wavelength of 365nm light with intensity 70mJ/cm². The dimension for U shape pattern is shown in Fig.24(a).

A diluted 351 developer solution (volume ratio to water is 1:4) was prepared to remove the bilayer photoresist in the patterned region. The sample was put into the 351 developer solution for 90s, then blow-dried and finally immersed into DI water for 30s. After blow-drying with N₂, the sample was cleaned in AZ400K solution for 45s and then DI water for 30s. After development, Plassys Electron Beam (e-beam) Evaporator MEB550S was used to sputter a 2nm Titanium layer with rate 0.02nm/s and a 30nm Silver layer with rate 0.05nm/s. The final resistance for the conductive pattern is 10Ω and stable for every construction. After sputtering with the e-beam evaporator, the sample was then put into the PG remover (Kayaku Advanced Materials), which removed the bilayer resist overnight. The sample was dried by N₂ and rinsed in IPA for 1min. The PG remover will separate PET
and double side tape by chemical reaction, leaving a flat PET substrate with conductive electrode. Fig. 24(b) illustrates the process for creating the conductive, Joule heating U-shape electrode.

![Image](image_url)

Figure 24: (a) Dimensions for conductive electrode on PET substrate (b) Schematic for construction of conductive electrode (2nm Ti + 30nm Ag) by microfabrication.

For the construction of LCE/PET tape spring actuators, the PET sample with the electrode was wrapped on a metal bar (D = 10mm, 11mm, 16mm) and held with tape. Heat treatment at 120°C for 15 minutes thermoformed the PET into a shell. A layer of diluted, high-temperature silicone sealant (LOCTITE SI 5154, McMASTER-CARR) (0.2g silicone sealant + 1.8g chloroform, 1ml) was spin coated on the surface of the electrode for 5s at 500rpm, followed by 30s at 5000rpm. Then, a monodomain LCE film was placed on
a glass substrate. The curved PET containing the glue was pressed on the LCE film and air bubbles were removed by rolling a cylinder. The nematic director of the monodomain LCE was aligned along the axis of the PET shell. For electrical connectors, a copper sheet was first polished and glued to kapton. Then two 1mm lines (1mm gap) were marked on copper by permanent marker and electrolytic etched in FeCl$_3$ solution by 2h. The copper was washed by methanol and this copper/kapton flexible connector was soldered to wires and connected to actuator by pure silver epoxy electrically conductive adhesive (ConductiveX). Fig.25 presents the flowchart of the fabrication process.

Figure 25: Flow chart for the fabrication of curved shell LCE/PET actuator encapsulating a Joule heating electrode.

4.2.3 Multispectral Imaging/Characterization Test-bed

The composite LCE/PET actuator was set on an experimental setup capable of powering it with electrical pulses, while enabling its imaging in infrared and the visible spectrum. An GW INSTEK GPS-4303 4CH system and Arduino UNO REV3 microcontroller were
integrated to the circuit to generate periodical power pulses. In situ current value was obtained from a current sensor. To observe the snap through motion, Mighty Scope 1.3M USB Digital Microscope cameras (200x magnification with 7 frames/s) were set from front and side views and a FLIR 325A Infrared camera was positioned to monitor the actuator temperature in the infrared. The details during snap through motion was characterized using a Phantom Ultrahigh-Speed camera V2511 (1000 fps). The characterization test-bed is shown in Fig.26.

Figure 26: Multispectral Imaging/Characterization test-bed.

4.3 Result and Discussion

Dynamic Mechanical Analysis (DMA) measurement for monodomain liquid crystalline elastomers was firstly performed by using a Perkin Elmer 8000 system with the loading applied along the molecular director. LCE film was cut into a 20mm × 5mm rectangle (long axis along nematic director) and mounted with 0.1N of pre-stretching force. An oscillatory
force was applied at 1Hz to stretch LCE film along nematic director and the temperature was swept from -30°C to 100°C. The storage modulus of LCE is (2.9 ± 0.2)MPa at room temperature and glass transition temperature is (-3.5 ± 0.6)°C. Thermomechanical response of the monodomain samples was also benchmarked by in situ tracking the strain variation along the director. 40µm sample was heated on a hotplate, where the temperature was varied from the ambient to 90°C. Shape change was observed and recorded by Mighty Scope 1.3M USB Digital Microscope (200x magnification with 7 frames/s). In situ images were analyzed and the thermomechanical strain ($\varepsilon$) was measured as a function of the temperature. $\varepsilon = (L_T - L_0)/L_0$, where $L_0$ is initial length before heating and $L_T$ is the length at the corresponding temperature. The length was measured along the director as a function of time by using a open-source video analysis and modeling software named TRACKER. The nascent thermomechanical response of the LCE is illustrated in Fig.27(a). Strain-temperature characterization of samples revealed an inflection point corresponding to the greatest rate of strain production at 53°C – the nematic-isotropic transition temperature ($T_{NI}$)[149]. Heating the LCE to temperatures in excess of ($T_{NI}$) elicited a contractile strain (38 ± 2%).

In a composite actuator, the snap through motion is harnessed with the nematic director aligned along the axis of the shell as illustrated in Fig.27(b). The first actuator was fabricated with 70µm LCE and 23µm PET substrate. The transverse curvature is $\kappa_0 = 0.08\text{mm}^{-1}$ and the total length of the PET shell is 15.5mm. The LCE in the prior flat state is 10mm × 10mm, which coincides with the location of the U-shaped electrode underneath it. While, the LCE covers the entire width of the PET, 4mm of the PET extends in length beyond the LCE film. The actuator was heated for 4s and relaxed for 20s in one cycle. Triggering the actuator with 150mW of electrical power at an input voltage of 1.2V leads to a progressive accumulation of the strain energy supplied by the U-shaped electrode. As shown from the side view by high speed camera in Fig.27(c), the principal axis of the curvature was everted to that longitudinal to the actuator after being powered for 3.5s. The mechanical impulse was generated over 20ms. Images of the actuator along its axis (end view; n is into the plane) in Fig.27(c) illustrates how the tensile strains produced normal to the n in the LCE work to reduce the native $\kappa_0$. This occurs, while the contractile strains along n produce the bending strains to evert the curvature. The shape evolution of the free edge of the actuator
was highlighted using a red dashed line, in the end view. Fig.27(d) illustrates the infrared thermograph of the actuator at the onset of the snap through. The mean temperature on the surface of LCE during heating and cooling is also shown, where the accumulation of the thermal energy from Joule heating occurred. Thermomechanical strains are generated in response to this heating. This reversible actuation was performed to 100 actuation cycles, without any perceivable degradation of performance.

Figure 27: (a) Thermomechanical response of the LCE illustrating contractile strain as a function of temperature, measured along the nematic director n. Scale bar is 2mm (b) The LCE is composited with a PET substrate with a sandwiched U-shaped electrode. The PET substrate is characterized by a native curvature that the actuation of the LCE seeks to evert (c) Side view high speed in situ image sequence and end view image sequence for snap through motion within 20ms. Scale bar is 2mm (d) Mean temperature (averaged over sample area) profile on the surface of actuator during heating and relaxation for one cycle.
To demonstrate the effect of transverse curvature, actuators (70µm LCE/23µm PET substrate) with two different transverse curvatures ($\kappa_0 = 0.08\text{mm}^{-1}$ and $\kappa_0 = 0.15\text{mm}^{-1}$) were powered for 4s and 7s respectively and powered off for 20s in one cycle ($V_{\text{actuator}} = 1.2\text{V}$, $P = 150\text{mW}$). To illustrate the feasibility of snap through motion, each actuator was triggered for 15 cycles. IR images during snap through for two transverse curvatures are shown in Fig.28(a). The max temperature reaches 71.7°C on smaller curved actuator ($\kappa_0 = 0.08\text{mm}^{-1}$) when snap through happens, which is approximately 20°C lower than that for larger curved actuator ($\kappa_0 = 0.15\text{mm}^{-1}$). Fig.28(b) shows the mean temperature profile during heating and relaxation process. For actuator with $0.15\text{mm}^{-1}$ transverse curvature, displacement generated at the tip is $(4.13\pm0.28)\text{mm}$, compared to $(2.19\pm0.10)\text{mm}$ for actuator with $0.08\text{mm}^{-1}$ transverse curvature (Fig.28(c)). The latency time to trigger snap through motion is $(3.45\pm0.21)s$ for actuator with $0.08\text{mm}^{-1}$ transverse curvature, compared to $(5.88\pm0.35)s$ for actuator with $0.15\text{mm}^{-1}$ transverse curvature (Fig.28(d)).

Figure 28: (a) Snap through motion and corresponding infrared thermography for actuator with two transverse curvatures (scale bar is 2mm) (b) Mean temperature profile on the surface of actuator during heating and relaxation for one cycle (c) Displacement generated at the tip of actuators and (d) Latency time before snap through for 15 actuation cycles.
This actuation is enabled by a geometric latch – the native, transverse curvature latches the actuator, while it accumulates the strain energy. Upon reaching a threshold, it spontaneously releases, and the impulse is generated. The magnitude of the transverse curvature is a design variable. In Fig.27(b) and (c), the transverse curvature is $0.08 \text{mm}^{-1}$. Larger the curvature, the longer the latch persists, during which the strain energy is accumulated before snap through motion. The latency of actuation is higher when the curvature increases. To investigate the dynamics of ultrafast snap through motion, PHANTOM V2511 high speed video camera was utilized to record the actuation at 1000fps.

As shown in Fig.29(a), snap through motion occurred within 20ms for actuator with $\kappa_0 = 0.08 \text{mm}^{-1}$ transverse curvature, compared with 12ms for actuator with $0.15 \text{mm}^{-1}$ transverse curvature. To investigate details during snap through motion, image tracking software Tracker was used to track the displacement $\delta$ (mm), velocity (mm/s) and angular velocity (rad/s) at the tip. An automatic tracking mode was applied for characterization during snap through motion. Fig.29(b)-(d) shows the comparison for actuators with different transverse curvatures. Firstly, high speed tracking of the tip displacement during actuation revealed an underdamped second-order dynamics. The actuator presented oscillations after the impulsive actuation, which was dynamically damped by the surrounding air and the intrinsic viscoelasticity of the material. For $\kappa_0 = 0.15 \text{mm}^{-1}$, 5.13mm deflection was observed at the tip. Maximal velocity at the tip reached 830mm/s, with a corresponding angular velocity at 186rad/s. For $\kappa_0 = 0.08 \text{mm}^{-1}$, deflection at the tip was 2.54mm, with maximal velocity 327mm/s and maximal angular velocity 59rad/s at the tip. Both of these two curved actuator behaved a damping oscillation after the snap-through motion.

As discussed before, transverse curvature latches the strain energy accumulated in PET substrate. Actuator with large transverse curvature requires more latency time to absorb energy and overcome a larger energy barrier to induce snap through motion, with respect to a higher mean temperature profile on the surface of LCE and a more powerful actuation. This conclusion was proved by a comparison of deflection and velocity variation during snap through motion. The accumulated strain energy released by PET substrate during snap through motion is also strongly related to the energy input, which is dominated by transverse curvature. Here, the thickness of LCE was kept uniform to eliminate the effect of
active material. However, the work content of this bilayer actuator is not only related to the prebiased curvature, but also correlated to the thickness of geometry during heating process.

![Figure 29: (a) High speed images of ultrafast snap through motion for actuators with two different curvatures (scale bar is 2mm) (b) Deflection (c) Tip velocity (d) Tip angular velocity as a function of time during damping oscillation.](image)

The work and power generation of the actuator against an external load was studied by applying a range of weights to the tip of the actuator. The masses of triangle-shaped copper sheets were varied (m=25mg, 50 mg, 75 mg, 100 mg...) to benchmark the actuation against their weight (Fig.30(a)). When electrically powered, the actuator performs work against gravity during snap through motion, as shown in Fig.30(b). By varying the payload that
resists the snap through motion, the displacement and the peak velocity of actuation were measured using video analysis and modeling software TRACKER on the acquired videos.

Figure 30: (a) Schematic for a transversely curved shell like actuator with a triangle-shaped copper payload (b) Time-series of snap through motion for actuator constructed by 100µm LCE with 23µm PET substrate. The transverse curvature for this actuator is 0.1mm\(^{-1}\) and the payload at the tip is 48mg. The snap through motion occurs within 50ms by lifting the load for (4.03±0.26)mm with 185mW electrical power (scale bar is 2mm) (c) The force-displacement characteristics of the actuators is benchmarked against opposing loads. The work content of the actuation is benchmarked as a function of the geometry (d) The force-velocity characteristics are illustrated to measure the power output by the actuators.

The geometry of the actuator was also varied to explore the effect of the thickness of the LCE ranging from 70µm (\(\kappa_0 = 0.08\text{mm}^{-1}\)), 100µm (\(\kappa_0 = 0.1\text{ and } 0.12\text{mm}^{-1}\)) and 160µm (\(\kappa_0 = 0.15\text{mm}^{-1}\)). The native curvature for the various LCE thicknesses is noted in parentheses. For each actuator, snap through motion was triggered for 15 cycles to demonstrate the
stability. Fig.30(c) shows the relationship between force (N) and displacement (\(\delta\): mm) at the tip during snap through motion (i.e., Force-Displacement characteristic of the actuator). The range of work content is between \(10^{-7}\)J and \(10^{-5}\)J. The average electrical power input for the 70\(\mu\)m\(\kappa_0 = 0.08\) mm\(^{-1}\), 100\(\mu\)m\(\kappa_0 = 0.1\) mm\(^{-1}\), 100\(\mu\)m\(\kappa_0 = 0.12\) mm\(^{-1}\) and 160\(\mu\)m\(\kappa_0 = 0.15\) mm\(^{-1}\) samples is 160mW, 170mW, 180mW, 190mW, respectively. The \(T_{cr}\) values are \((3.5\pm0.2)s\), \((1.6\pm0.1)s\), \((3.8\pm0.1)s\) and \((7.7\pm0.4)s\), for each case in the absence of a load at the tip. The composite actuators typically weigh \(\sim20\) mg. Meanwhile, using the aforementioned characterization platforms, maximal velocity was characterized as a function of payload for different geometries. As shown in Fig.30(d), the peak power generated during ultrafast snap through motion can reach as much as \(10^{-4}\)J/s.

The approach to the mechanical instability is determined by the time required to heat the actuator from the ambient to generate the desired mechanical work content. The latency of the actuation (\(T_{cr}\)) is limited by this. An alternate strategy to enable faster actuation cycles emerges using pulsed Joule heating. The idea is to power the actuator in pulses to first progressively heat it to enable it to undergo snap through motion. A sample composed from 70\(\mu\)m LCE and 23\(\mu\)m PET with \(\kappa_0 = 0.08\) mm\(^{-1}\) with 20mg payload was subjected to electrical pulses with a peak power of 180mW for 1.5s with 2s intervals (Fig.31(b)). The sample’s temperature increased during the 1.5s and cooled down over 2s. Over 7 pulses of this energy, the peak temperature increased from the ambient to achieve a steady state, following which the snap through instability was observed (Fig.31(c)). However, after the snap through motion, when the actuator was allowed to cool down for 2s, it returned to its native state. But the average temperature remained above the ambient as revealed using infrared thermography. Then, when the actuator was again provided a heating pulse over 1.5s, its temperature again increased, but from a value above the ambient because it was not given the time to cool down entirely. Heating the actuator in this manner reduces the latency of the actuation to 0.6s from 1.2s, if it was otherwise powered continuously from the ambient temperature in each actuation cycle. Note, that the latency is defined as the time to trigger snap through after the electrical pulse has been triggered for a given cycle. However, this comes at a cost. The first snap through motion that was triggered after the 7 pulses of electrical power generated a maximum displacement of \(\sim5.3\)mm within 65ms. However, the
subsequent snap through motion that occurred with each pulse generated a displacement of \(\sim 1.9\text{mm}\) (Fig.31(d)) within 30ms. Details of snap through motion between the first cycle and the following cycles are compared in Fig.31(a).

Figure 31: (a) Experimental comparison for faster snap through motion (1.5s heat/2s relax) between first and the following cycle (scale bar is 2mm) (b) Pulsed electrical power for latency time modulation of the snap through motion (c) Mean temperature profile on the surface of LCE by electrical pulses, red spots represent the temperature when snap through occurs (d) Displacement at the tip of actuator during snap through motion between the first and following cycle.
4.4 Summary

In this chapter, a tape spring-like, transversely curved composite shell composed of monodomain liquid crystalline elastomer, polyethylene terephthalate (PET) and an encapsulated electrode was developed. An ultra-fast snap through instability (∼ms) with ∼200mW electrical power inputs at low voltages (∼1V) by a geometric latch mechanisms was demonstrated. Before the occurrence of snap through motion, mechanical energy was latched on and built up in PET substrate while the curved structure remained latent. The latency time ($T_{cr}$) to trigger snap through motion is strongly correlated with transverse curvature and the thickness of active materials. Contractile strains along the director produced bending strains by Joule heat, which induced tensile strains normal to the director to flatten the transverse curvature. An energy threshold was eventually reached and the accumulated strain energy built up in PET substrate was finally released via snap through at ms-time scales. The thin film actuators enabled work generation up to $10^{-5}$J and impulsive power up to $10^{-4}$J/s by powering against opposing payloads with different geometrical profiles. The latency time of actuation ($T_{cr}$) was also reduced by heating the actuator with pulsed electrical power. This heating mode fastened the time to trigger the snap through motion, with a work content cost that represents by a decrease of displacement at the tip.
5.0 Dynamic Characterization and Implementations for Curved Shell Like LCE/PET Soft Robotics

5.1 Introduction

Transversely shell like structure is a typical tape-spring geometry that is straight in longitudinal direction with a transverse cross section. This structure can be extended and coiled between two bistable configurations and was firstly discovered by Daton Lovett[150]. By bistability during the folding deformation, this geometry has attracted attentions for researchers by its potentials in the field of deployable structures[151]. The folding behavior has been proved highly nonlinear and directionally dependent[152], both by experiment and computational models. Comparing the bistable tape-spring structure and our bilayer curved actuator, our design eschewed bistability. When the power is off after snap through motion, the actuator spontaneously resets to its native state. However, the energy variation during snap through is comparable to the coiling deformation when the shell like structure is folded.

In this chapter, an extensional bending model that was used for bistable cylindrical shells was applied to characterize the strain energy ($U_{\text{total}}$) by in situ observation of the geometric evolution. The strain energy ($U_{\text{total}}$) was illustrated to be released at the beginning of snap through actuation, following by an increment with the progressive bending deformation. The released energy and energy barrier to trigger snap through motion was demonstrated proportional to a dimensionless geometrical coupling parameter $\alpha$, which related to the dimension and geometry of our actuator. Meanwhile, a retardation between drop in strain energy and maximum tip velocity was also discovered. The maximal bending energy and impulsive power calculated from the image analysis were comparable with the maximal value of the work/power generation by actuators with different geometries, which proved the accuracy of this extensional bending model. The snap through actuation was also implemented in sub-gram scale soft robotics, including water strider mimicking configurations and steerable robotics on different topographies. Motility of this tethered robotics demonstrated feasibility towards untethered microbotics using on-board power source.
5.2 Dynamic Characterization for Curved LCE/PET Actuator

5.2.1 Calculation of Bending Energy

To characterize dynamic behavior of this curved bilayer actuator, displacement at the tip was tracked by analysis and tracking tool TRACKER. As shown in Fig.32(a), the actuator (70µm LCE/23µm PET substrate, $\kappa_0 = 0.08\text{mm}^{-1}$) behaves as a damped harmonic oscillator and ultrafast snap through motion occurs within 20ms after generation of impulse. Gaussian overshoot occurs before termination of vibration and a geometry-dependent maximal point of velocity was observed at 11ms (marked as a red spot in Fig.32(b)).

An extensional bending model was applied here to characterize the variation of total strain energy ($U_{total}$) in PET substrate. In situ observation of the geometric evolution allows for harnessing the extensional bending model that was used to model bistable cylindrical shells [153]. Generally, the energy of the curved shell is composed of the bending energy ($U_b$) and stretching energy ($U_s$), which can be expressed by the following equations[153, 154]:

\[
U_b = \frac{1}{2} k^T D k, U_s = \frac{1}{2} \varepsilon^T A \varepsilon
\]  

(5.1)
k and $\varepsilon$ are the curvature and strain of the mid-plane, D and A are bending and stretching stiffness defined by the so-called ABD matrix[155]. Total strain energy of a shell ($U_{\text{total}}$) is equal to the sum of bending energy ($U_b$) and stretching energy ($U_s$)[154]. For our bilayer actuator, the strain energy ($U_{\text{total}}$) contained in the $\sim2$ GPa modulus PET substrate was calculated as a function of time. The stretching energy of PET substrate is neglected during snap through motion (no strain production along mid-surface)[36]. Characterizing the geometry of the actuator allowed a measurement of the curvatures along the length of the actuator so that the total strain energy ($U_{\text{total}}$) can be approximately expressed by the bending energy ($U_b$) in the following equation[156]:

$$U_{\text{total}} \approx U_b = \frac{1}{2} \beta R [D_{11} \kappa_x^2 + 2 D_{12} \kappa_x (\kappa_y - \frac{1}{R}) + D_{22} (\kappa_y - \frac{1}{R})^2] L$$ (5.2)

R is the transverse radius of PET substrate, $\beta$ is the angle subtended by cross section and L is the total length. For our actuator, $\beta R = 10$mm. $\kappa_x$ (mm$^{-1}$) and $\kappa_y$ (mm$^{-1}$) are longitudinal and transverse curvature for PET substrate. Since the deformation of PET substrate (total length L $\approx 15$mm) is not uniform during snap-through motion, longitudinal curvature $\kappa_x$ and transverse curvature $\kappa_y$ was tracked as a function of position (mm) and time (ms) by Newton-Cotes formulas. For polyethylene terephthalate (isotropic material), D$_{11}$, D$_{12}$, D$_{22}$ value are calculated from the following D matrix:

$$D_{ij} = \frac{h^3}{12} \begin{pmatrix} E & vE & 0 \\ \frac{vE}{1-v^2} & E & 0 \\ 0 & 0 & G \end{pmatrix}$$

Where h is the thickness of PET (23$\mu$m), E is the storage modulus and G is shear modulus, corresponding to the temperature of PET substrate when snap through occurs. For curved shell like bilayer actuator, the mean temperature profile on the surface of PET is correlated to the transverse curvature and thickness of LCE. Therefore, D$_{ij}$ was calculated as a function of temperature and geometry of actuator. Poisson ratio $v$ is 0.43 for PET. Fig.33 shows the dynamic mechanical analysis (DMA) characterization for PET substrate. The temperature was swept from 25°C to 150°C and the glass transition temperature is shown at 120°C.
Figure 33: (a) Storage modulus (b) tan δ value for polyethylene terephthalate (PET) as a function of temperature.

For calculation of the bending energy during snap through motion, curved PET substrate was separated equally by 15 spots and the distance between each spot (ΔL) is 1mm (Fig.34(a)). Longitudinal curvature κ_x and transverse curvature κ_y were calculated for each ΔL and the accumulated energy in each was also calculated. For example, in the region between spot 1 and 2, the total bending energy during snap through motion can be calculated by the following equation:

\[
U_b(2) = \frac{1}{2} \beta R \{ D_{11} \kappa_{x(12)}^2(t) + 2D_{12} \kappa_{x(12)}(t)[(\kappa_{y(12)}(t) - \frac{1}{R}] + D_{22} [\kappa_{y(12)}(t) - \frac{1}{R}]^2 \}\Delta L \quad (5.3)
\]

Where κ_{x(12)}(t) and κ_{y(12)}(t) are longitudinal and transverse curvature in the region between spot 1 and 2 as a function of time during snap through motion. The longitudinal curvature κ_x(t) for four geometries in our experiments was measured by a custom code written by MATLAB (Fig.34(b)). For the measurement of transverse curvature κ_y(t), the chord length (L_0) from side view image was tracked by software TRACKER. Tracking the displacement of the edge of the shell, as it evolves (or flattens) during the actuation can be
used to measure the transverse curvature ($\kappa_y = \frac{1}{R}$). It can be shown that for the transverse width is 10mm, the transverse curvature $\kappa_y$ can be calculated by the following equation:

$$ \cos\left(\frac{10}{2R}\right) \times R + L_0 = R $$

(5.4)

![Figure 34: (a) Shell like actuator separated by 15 regions spaced $\Delta L$ (1mm) apart, scale bar is 2mm. (b) Longitudinal curvature as a function of time during snap through motion for four geometries.](image)

For parameters in D matrix, $D_{11}$, $D_{12}$ and $D_{22}$ were related to storage modulus ($E'$) of PET substrate, with respect to the temperature when ultrafast snap through occurred. Table.1 presents the value for mean temperature of actuator, storage modulus ($E$) and D value at onset of snap through for four geometries. Finally, the total bending energy for the whole curved PET substrate was calculated using Newton-Cotes formulas:

$$ U_{b(\text{total})}(t) = \sum_{i=1}^{15} U_{b(i)}(t) $$

(5.5)

By utilizing this extensional bending model, the dynamic of actuator constructed by 70$\mu$m LCE and 23$\mu$m PET substrate ($\kappa_0 = 0.08\text{mm}^{-1}$) was firstly characterized. As shown in Fig.35(a), within the first 7ms, the total bending energy drops from $1.9 \times 10^{-7}$J (point A) to $1.6 \times 10^{-7}$J (point B) and the average power to release the energy is $4 \times 10^{-6}$J/s. It is noteworthy that the drop in the bending energy that occurs at 7ms leads the maximum tip velocity, which occurs at 11ms (Fig.32). The retardation is likely a consequence of

59
Table 1: Value of mean temperature on actuator, storage modulus and D value at onset of snap through for 4 geometries

<table>
<thead>
<tr>
<th></th>
<th>$G_1$</th>
<th>$G_2$</th>
<th>$G_3$</th>
<th>$G_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean temperature ($^\circ$C)</td>
<td>37.9 ± 0.51</td>
<td>34.3 ± 0.50</td>
<td>42.5 ± 0.33</td>
<td>39.7 ± 0.33</td>
</tr>
<tr>
<td>Storage modulus (GPa)</td>
<td>1.67</td>
<td>1.68</td>
<td>1.65</td>
<td>1.66</td>
</tr>
<tr>
<td>$D_{11}$ (J)</td>
<td>2.07E-06</td>
<td>2.09E-06</td>
<td>2.05E-06</td>
<td>2.06E-06</td>
</tr>
<tr>
<td>$D_{12}$ (J)</td>
<td>8.91E-07</td>
<td>9.00E-07</td>
<td>8.83E-07</td>
<td>8.88E-07</td>
</tr>
<tr>
<td>$D_{22}$ (J)</td>
<td>2.07E-06</td>
<td>2.09E-06</td>
<td>2.09E-06</td>
<td>2.06E-06</td>
</tr>
</tbody>
</table>

the inertia (even in the absence of an external load) and the viscoelastic losses. Following this drop, the bending energy increases with the progressive increase in the longitudinal curvature $\kappa_x$. The eversion of the curvature is complete and the snap through is complete at C. The bending energy at this point is $1.1 \times 10^{-6}$J. Compared with work content in weight lifting test, the maximum work generation of this actuator (extremal point of the Force-Displacement in Fig.30(c)) is $6.73 \times 10^{-7}$J, which is comparable to the final bending energy. This characterization is repeated for high-speed images obtained from the various geometries explored in Fig.33. For each of these in Fig.35(b), the maximal bending energy calculated from the image analysis is comparable and closely correlated with the maximal value of the work generated (extremal point of the force-displacement in Fig.30(c)) for all four geometries in our test. On the other hand, the power to release the bending energy is defined by the following equation:

$$P = \frac{\Delta E_{\text{release}}}{t_{\text{release}}}$$  \hspace{1cm} (5.6)

Where $\Delta E_{\text{release}}$ is the released bending energy (J) during snap through motion, $t_{\text{release}}$ is defined as the time internal (ms) when the bending energy drops. As shown in Fig.35(c), the value of power when the bending energy was released is in the same order compared with the maximum power by lifting a payload during snap through motion. From the analytical calculation and experimental result, we can conclude here that the work content of curved
bilayer actuator during snap through motion is mainly transformed from the released energy at the beginning of snap through motion, which is closely correlated to the geometry of the actuator.

Figure 35: (a) Measurement of the bending energy by tracking the transverse curvature of the actuator reveals a drop after 7ms, which precedes the highest tip velocity of the actuator that occurs at 11ms. Scale bar in figure is 2mm (b) The maximum bending energy measured using the image analysis at the end of the snap through correlates with the maximal work-content measured from the force-displacement profiles (c) The power for released bending energy during snap through is proved in the same order with the maximal FV measured from force-velocity profiles.
5.2.2 Mechanism Analysis of Snap Through as a Function of Geometry

To investigate the mechanism of rapid snap through motion for our bilayer actuator, a dimensionless geometrical coupling parameter $\alpha$ was defined based on the following equation[113], which encapsulates the coupling between bending and stretching and defines the energy barrier to be overcome for driving the snap through motion:

$$\alpha = \frac{L^4 \kappa^2}{h^2} \quad (5.7)$$

Where $L$ is the length (mm) and $h$ the total thickness ($\mu$m) of the actuator, $\kappa$ is the transverse curvature ($mm^{-1}$). It has already been demonstrated that $\alpha$ value quantifies the coupling between bending and stretching deformation when snap through motion occurs[157]. A larger $\alpha$ value represents that it is harder to stretch the mid-plane to trigger snap through motion, with respect to a larger energy barrier to overcome. It is also implies that the greater $\alpha$ value, the more energy built up and released from the snap through motion, corresponding to a more rapid velocity. To illustrate the potential relationship between $\alpha$ value and energy barrier for our curved shell like bilayer actuator, $\alpha$ value was calculated for actuators with different dimensions and geometries, as shown in Table.2.

### Table 2: Value of $\alpha$ and latency time for actuator with different geometries

<table>
<thead>
<tr>
<th></th>
<th>L(mm)</th>
<th>h(\mu m)</th>
<th>$\kappa(\text{mm}^{-1})$</th>
<th>$\alpha$</th>
<th>$T_{cr}$(s)</th>
<th>P(mW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>10</td>
<td>93</td>
<td>0.08</td>
<td>$7.40 \times 10^3$</td>
<td>3.5</td>
<td>150</td>
</tr>
<tr>
<td>G2</td>
<td>10</td>
<td>123</td>
<td>0.10</td>
<td>$6.61 \times 10^3$</td>
<td>1.6</td>
<td>170</td>
</tr>
<tr>
<td>G3</td>
<td>10</td>
<td>123</td>
<td>0.12</td>
<td>$9.52 \times 10^3$</td>
<td>3.8</td>
<td>180</td>
</tr>
<tr>
<td>G4</td>
<td>10</td>
<td>183</td>
<td>0.15</td>
<td>$6.72 \times 10^3$</td>
<td>7.7</td>
<td>190</td>
</tr>
<tr>
<td>G5</td>
<td>10</td>
<td>183</td>
<td>0.22</td>
<td>$14.45 \times 10^3$</td>
<td>10.0</td>
<td>200</td>
</tr>
</tbody>
</table>

To represent the energy barrier to overcome before snap through motion, the value of energy input (J) was firstly calculated by multiplying the power with latency time ($T_{cr}$) to induce snap through motion. The relationship between input energy and $\alpha$ value is presented in Fig.36(a). As shown in Fig.36(a), the input energy increased with an increment of $\alpha$ value,
which implied a higher energy barrier to overcome to trigger the rapid snap through motion. A same positive trend was also found in the relationship between latency time ($T_{cr}$) and $\alpha$ value, as shown in Fig.36(b). Moreover, the speed of snapping ($\omega_{max}$) and released bending energy was also plotted as a function of geometrical parameter $\alpha$, as shown in Fig.36(c)-(d). Here, we can conclude that for our curved bilayer actuator, the geometry with a large $\alpha$ value will release more bending energy and snap more rapidly than that with small $\alpha$ value.

Figure 36: (a) A clear positive correlation was proved between input energy and dimensionless geometrical coupling parameter $\alpha$ for actuator with different geometries (b) The latency time to trigger the rapid snap through motion (c) Maximum angular velocity (d) Released bending energy during snapping was plotted against $\alpha$. 
5.3 Motility For Tethered Curved LCE/PET Soft Robotics

In previous chapter, monodomain liquid crystalline elastomer in the tape-spring unimorph configuration was proved to be utilized as active material to flat prebiased transverse curvature by strain production along aligned director through Joule heat. By utilizing snap through actuation as an impulse, an articulated array of LCE/PET tape spring actuators can be designed as hopping legs. This rapid motion can be harnessed as a sub-gram scale directional-controlled microrobotic.

Here, a steerable microrobotic configuration was firstly designed to harness the response of the LCE/PET actuators to power motility on surfaces characterized by relatively low friction, where the snap through motion leads to the actuator’s tip (and foot) slipping past the surface. Fig.37(a) shows the schematic of this directional-controlled microrobotic. A pair of simple transverse curved (tape spring) actuator (160µm LCE/23µm PET, $\kappa_0 = 0.16\text{mm}^{-1}$) was set on a PET platform (15mm × 10mm × 23µm), with a L-shape foot fabricated from copper (50µm) attached at the tip of actuator. The total weight of this microrobotic is $\sim 140\text{mg}$. For motility of this steerable microrobotic, the basic idea is to enable the snap through motion to create an oppositely curved structure, while enabling the impulse to lift the entire robot. In doing so, the actuator everts its curvature and allows the L-shaped foot to present its sharp edge to the surface.

Fig.37(b) illustrates the high-speed sequence of images showing the snap through motion on the surface of a table, where the foot rapidly slips past the surface. The actuator then adopts a bent shape. Turning off the power to the actuator leads it to relax to the native shape, starting from this configuration. This allows the entire body to translate along the surface while remaining pinned at the foot where snap through is triggered. In this configuration, the role of the snap through is to allow the robot to achieve purchase on an otherwise smooth surface and achieve motility during the relaxation of the actuator, when the power is turned off.

As shown in Fig.37(c), by heating the actuator on the left side for 15s under 180mW, the microrobotic achieve a motility over 11mm after first heating cycle. The robot with the two actuators is capable of a bidirectional motion. By heating the left actuator for 20
cycles, a total 100mm horizontal displacement was achieved to the right, with a total 70mm
displacement to the left when heating the right actuator for 20 cycles. The displacement in
each heating cycle on both side is shown in Fig.37(d).

![Figure 37](image)

Figure 37: (a) Schematic for a steerable microrobotic composed of two snap-through legs and
a judiciously designed L-shaped foot (b) Time-sequenced high speed images of snap through
actuation of the left leg, scale bar is 10mm (c) Motility of microrobotic to the right side by
heating left actuator for 15s under 180mW, scale bar is 10mm (d) Horizontal displacement
within 20 heating cycles on both side of actuator.

Another typical strategy to achieve motility is to fully take advantage of the impulsive
snap through actuation by the LCE/PET tape spring actuators. One instantiation was
in a water strider that floats on the surface of water by virtue of its weight. The snap
through actuation was used to power a paddle that broke through the surface tension during
a downward stroke and powered the advance of the water strider. As shown in Fig.38(a), a curved actuator (160µm LCE/23µm PET, $\kappa_0 = 0.17\text{mm}^{-1}$) was set on a “four-leg” PET platform with a paddle made by polyester at the tip of the configuration. The leg of PET platform was bent and wetted on the surface of water, which enabled the entire structure ($W \approx 120\text{mg}$) to float on the surface of water, similarly to the design of a jumped water strider [37]. As shown in Fig.38(b), powering the actuator with 185mW for 20s generated the expected snap through actuation that plunged the paddle into the water, breaking through the surface tension. The water strider advanced around 13mm during the snap through actuation. After powering off, the actuator spontaneously reset but triggered negligible backlash during the reverse stroke. Successive actuation cycles enable the water strider to propel itself on the surface of water in discrete jumps. The robustness characteristics of this actuator was demonstrate by repetitive actuation for 5 cycles.

Furthermore, motility on loose sand was also achieved. During heating process, the tip of heated actuator will dig into soft surface of loose sand and drag the whole body by friction, while another actuator will block the movement of whole system during relaxation. Compared with microrobotic on flat tough surface, the “L-shape” copper tips were changed to a normal rectangular configuration with a 50 µm Cu sheet to avoid high friction, as shown in Fig.38(c). The microrobotic ($W \approx 135\text{mg}$) hopped towards right for 2.23mm by heating the right side actuator within 15s powered by 185mW. This experiment demonstrated the feasibility of using snap through motion as an impulse to trigger directional controlled locomotion. To increase the efficiency of movement, motility on an arbitrary surface[158] was demonstrated using a two-legged actuator composed of two LCE/PET actuators (160µm LCE/23µm PET, $\kappa_0 = 0.17\text{mm}^{-1}$) that are each equipped with a foot at their ends. The idea is to achieve bi-directional motion by harnessing the snap through actuation on sand with an arbitrary, wavy topography. Fig.38(d) illustrates the movement generated when the actuator on the right was powered. To trigger movement of the microrobotic to right, the actuator at right side was heated by 216mW for 12s and the snap through resulted in the copper foot digging into the sand, transferring the impulse to the entire structure, which jumped to the right by 9mm. The relaxation of actuator reset to its native state. Actuation over multiple cycles were pursued to enable the robotic structure to advance to the right for
38mm within 6 heating/cooling cycles. This microrobotic can also be triggered backwards by heating another actuator. The same actuator was also triggered in a incline and behaved as a hopper by snap-through motion.

Figure 38: (a) Schematic for a 120mg water strider constructed by a curved bilayer actuator with a paddle (b) Snap through actuation powers a paddle that propels the microrobotic (13mm) along the surface of water, scale bar is 10mm (c) Schematic for a 135mg steerable microrobotic with a pair of curved bilayer actuator (d) Snap through motion powers a 9mm leap on loose, arbitrarily structured sand, scale bar is 10mm.
5.4 Summary

In this chapter, dynamic characterization was presented by an extensional bending model that was used to model bistable cylindrical shells. The tip displacement revealed an underdamped second order oscillation after snap through motion, which was caused by the surrounding air and the intrinsic viscoelasticity of material. Millisecond-scale tracking of the evolution of the geometry of the PET shell during the actuation illustrated a drop in the bending energy during the snap through that preceded the achievement of the highest tip velocity by a few milliseconds. The energy barrier before snap through and the drop of bending energy during snap through were demonstrated clearly correlated to a dimensionless geometrical coupling parameter $\alpha$, which was controlled by the dimension and geometry of our actuator. The maximum bending energy and impulsive power calculated from the image analysis were comparable to the extremum value of the work/power generation by actuator with different geometries, which proved the accuracy of our extensional bending model. Understanding the trade-space of this actuation enabled the fabrication of robotic prototypes that demonstrated motility on water and on land. The light weight of the actuators enabled their utilization in a prototypical water strider that floats on the surface of water via surface tension, while using the snap through to power a paddle to power motility. Actuation on soft sand and hard surface is demonstrated in prototypes equipped with feet-like structures to optimize the interaction of the snap through actuation with various substrates.
## 6.0 Conclusion and Future Work

In this thesis, monodomain soft liquid crystalline elastomer was firstly synthesized via thiol-acrylate Michael addition reaction. Monodomain profile was achieved by mechanical external stretching. Mol ratio between EDDT thiol extender and host mesogen RM82 was controlled by 1.2, which elicited \(~40\%\) contractile strain along director by thermal effect. For the construction of transversely shell like bilayer actuator, a U-shape conductive electrode (2nm Ti/30nm Ag, \(R = 10\Omega\)) was encapsulated between monodomain liquid crystalline elastomer (70\(\mu\)m, 100\(\mu\)m and 160\(\mu\)m) and 23\(\mu\)m polyethylene terephthalate (PET). A millisecond-scale rapid snap through motion was demonstrated with \(~200\mW\) electrical power inputs at low voltages (\(~1\mathrm{V}\)) by a geometric latch mechanisms. The latch was proved to be geometric - the energy barrier for snap through and the released energy are encoded by transverse curvature and the thickness of actuator. Meanwhile, the robustness of actuation was performed by 100 repetitive cycles without any degradation of performance. The work content of our curved actuator is between \(10^{-7}\)J to \(10^{-5}\)J by varying the transverse curvature (0.08mm\(^{-1}\) to 0.15mm\(^{-1}\)) and the thickness of elastomer (70\(\mu\)m to 160\(\mu\)m), with respect to a power as much as \(10^{-4}\)J/s. Furthermore, the actuator revealed an underdamped second order oscillation after snap through motion, which was induced by the intrinsic viscoelasticity of material. The actuation profile was proved not only related to the geometry, but also the electrical pulse pattern. A pulsed Joule heat pattern (1.5s heat/2s relaxation) was applied to trigger a faster snap through actuation, with a sacrifice of deflection at the tip.

For dynamic characterization during snap through motion, an extensional bending model was utilized by in situ tracking the geometric evolution with Newton-Cotes method. The bending energy was illustrated to decrease then increase with an increment of longitudinal curvature. The characterized final bending energy was comparable to maximum work generation for each geometry, which implies an energy transition during snap through. Most importantly, a dimensionless parameter \(\alpha\), which correlated to the geometry and dimension of actuator, was proved to have a positive correlation with the energy barrier and released bending energy. A higher \(\alpha\) value implies that the actuator should overcome a higher energy
barrier to induce snapping, corresponding to a larger latency time ($T_{cr}$) and input energy before snap through. We also conclude that the actuator will snap fast by releasing more bending energy, when the geometry exhibits a large $\alpha$ value. Finally, this actuation was harnessed in sub-gram scale soft robotics, including a water-strider mimicking configuration and a steerable microrobotic that navigate on multiple topographies.

To further investigating the implementations of snap through motion by our transversely shell like bilayer actuator, my future work includes the following three sections.

6.1 Self-regulated Untethered Soft Bilayer Actuator

A self-regulated untethered soft bilayer actuator is proposed here. The specific work includes the following steps:

1) Sensing the variation of resistance during snap through for shell like actuator. In prior work, we have already thermally triggered snap through actuation by glassy splayed nematic liquid crystalline polymers. 2nm Titanium and 30nm Silver were sputtered on planar side of splayed nematic liquid crystalline polymers by e beam evaporator. It has been proved that the resistance of conductive actuator decreased during snap through motion by variation of geometry. For our current shell like actuator, the transverse curvature will be flattened before snap through, which induces a variation of resistance. In the process of snap through motion, the actuator will transfer from flat state to a bending state. The variation of resistance is negligible and NPN transistor can not sense the variation of current to disconnect the circuit. To sense the feedback, a mechanical switch can be integrated into the circuit of the electric system. The resistance of this mechanical switch ($R_s$) should be sensitive to the variation of dimension, such as the length and width of actuator. When the transverse curvature is fattened before snap through motion, the mechanical switch will be stretched, which induces a dramatic increment of resistance. Then the circuit will be disconnected by NPN transistor, following by a spontaneous relaxation of this bilayer actuator. The actuator will reset to original geometry again, with respect to a decrease of resistance from mechanical switch. By this self-regulated mode, we expect to sense the obvious variation of resistance in the circuit.
2) Integrating commercial LiP battery (3.7V) on soft actuator to achieve untethered actuation. The final step to create the self-regulated actuator is to integrate a on-board battery. In prior work, we have demonstrated feasibility of a LiP battery to induce snap through for our actuator. The dimension of this commercial LiP battery is 2mm (thickness) \times 15mm (length) \times 15mm (width) and weight is between 430mg to 500mg. This commercial battery is proposed to set at the tail of the actuator. After snap through occurs, the mechanical-gated transistor will receive signal feedback and switch off by sensing the variation of current in whole circuit. The final objective is to achieve an untethered self-regulated soft microrobotic, which can be powered in low voltage(\sim3.7V).

![Image](image.png)

Figure 39: (a) Commercial LiP battery (3.7V) (b) Schematic for untethered soft robotics with battery onboard

6.2 Steerable Microrobotics in Multiple Working Atmospheres

Considering the adaptability of our current bilayer actuator, we also plan to trigger the locomotion of a steerable soft robotics in some other working atmospheres, such as water or high-temperature limited space. For our current soft robotics, the average power input is \sim200mW and applied voltage is \sim1.2V. The snap through instability was induced in air
with a heat capacity \( (C_p) \) of 1.012\( \text{J/(g}\cdot\text{K}) \). Compared with air at room temperature, the heat capacity \( (C_p) \) of pure water exhibits a larger value, which is 4.217\( \text{J/(g}\cdot\text{K}) \). In another word, the Joule heat generated from our U-shape electrode will diffuse more rapidly through the water, which will finally lead a lower energy efficiency comparing the actuation in air. The steady mean temperature on LCE will be lower, which brings challenges to trigger the snap through instability.

For the active material in our bilayer actuator, EDDT1.2 exhibits a nematic-isotropic transition temperature \( (T_{NI}) \) at 53\( ^\circ\)C, with a temperature broadness \( (\Delta T) \) as much as 14\( ^\circ\)C. To demonstrate the feasibility of snap through actuation in water, a new soft liquid crystalline elastomer was synthesized by varying the thiol structure to decrease the \( T_{NI} \) and temperature broadness \( (\Delta T) \). The thiol spacer was varied from EDDT to GDMP and mol ratio between thiol spacer and host mosegon RM82 was changed from 1.2 to 1.0. This material was also synthesized via thiol-acrylate Michael addition reaction. The basic structure for diacrylate liquid crystal monomer, thiol spacer and Vinyl cross linker is shown in Fig.40.

![Chemical structures](image)

Figure 40: (a) LC monomer RM82 (b) GDMP thiol spacer (c) Vinyl cross linker
For thermomechanical strain characterization, a 40µm GDMP1.0 film was set on a hot-plate, similarly to the test of EDDT1.2. This thin film was heated from ambient temperature to 90°C, as shown in Fig.41(b). The maximum final strain production is (43 ± 2)% with 47°C nematic-isotropic transition temperature. Comparing the thermomechanical strain result with EDDT1.2 (Fig.41(a)), GDMP1.0 exhibits a lower $T_{NI}$ with relatively large strain production. Furthermore, the temperature broadness ($\Delta T$) of GDMP1.0 is more narrow than EDDT1.2, with a value of 6°C. From the above result, GDMP1.0 can be applied as an objective active material for the actuator working in water.

![Figure 41: Strain generation as a function of temperature for (a) EDDT1.2 (b) GDMP1.0](image)

To achieve a steerable microrobotics in water, the process can be separated into the following two steps:

1) Demonstration of snap through instability for a bilayer curved actuator in water. In this pre-test, a bilayer actuator is proposed to be constructed by 100µm GDMP1.0 and 23µm PET substrate with a reasonable transverse curvature ($\kappa_0$ is between 0.1mm$^{-1}$ and 0.2mm$^{-1}$). The power for energy input is set between 200mW to 500mW and the applied voltage is controlled between 1.5V to 2.5V. IR camera is also set on top of this bilayer actuator to record the temperature variation during the heating and cooling process. The weight lifting test is also planned to investigate the work generation for a actuator in water.
2) Directional-controlled soft swimmer in water. After the demonstration of snap through instability in water, a steerable soft robotics is proposed here to realize directional-controlled swimming actuation in water. As presented in Fig.42(b), a pair of bilayer actuator is bonded with a conductive pattern on a PET body by epoxy conductive adhesive. To trigger the actuation of these two actuators, a proposed 2.4V voltage is applied on the conductive system. By snap through instability in the water, this soft robotics will swim forwards. To control the direction of this movement, external voltage can be applied between A/C or B/C to selectively trigger the left/right actuator. In this mode, a left/right side actuation will be achieved.

![Diagram of water](image)

**Figure 42:** Strain generation as a function of temperature for (a) EDDT1.2 (b) GDMP1.0

To trigger snap through instability in a high-temperature space, we have already illustrate the feasibility to trigger a faster snap through motion by pulsed Joule heat. Here, a thermomechanical strain will firstly accumulate in the active material by high temperature condition. In order to avoid the actuation before heating, a larger transverse curvature will be formed. The proposed transverse curvature is set as a function of surrounding temperature. A same steerable actuator will be constructed after proving the snap through motion in different temperatures.
6.3 Light Responsive Self-regulated Actuator by Snap Through Instability

For soft liquid crystalline elastomer, this material can produce large mechanical strain by external stimuli, such as light and heat. Particularly, light is a contactless source that can be modulated by light intensity, polarization and wavelength. For light-responsive liquid crystalline elastomer, photochromic moisty is typically integrated into the polymeric network. Photomechanical strain is generated by photoisomerization, which will distract the alignment of molecules. Here, a self-regulated light-responsive transversely shell like actuator is proposed to realize locomotion by snap through instability.

For the synthesis of active material, 0.3g RM82 and 0.075g BDMT thiol spacer are first integrated with 0.022g 6c azobenzene. This mixture is mixed on hotplate at 110°C. Then 0.06g Vinyl cross linker and 0.005g I-789 photoinitiator are added into the mixture and heated at 110°C. This final mixture is filled into a glass cell constructed with specific thickness of spacer. This glass cell is left on the hotplate for 3h, following by a 5min photopolymerization on both sides by green light. Then the material is cut and stretched by 100% mechanical strain. Finally this network is fully polymerized by green light for 20min. The basic structure for RM82, Vinyl cross linker and thiol spacer is shown in Fig.43.

Figure 43: (a) LC monomer RM82 (b) BDMT thiol spacer (c) Vinyl cross linker
Before the construction of light-responsive bilayer actuator, we first test the photomechanical strain production by applying a 21.35mg weight at the end of a 75µm thin film (5mm × 10mm). Fig.44(a) presents the schematic of a linear actuator. A 365nm UV light is irradiated on the surface of thin film for 15s with 150mW/cm$^2$ intensity. After that, the elastic network is fully relaxed for 5min under visible light. This linear photomechanical actuation is triggered for 4 cycles to illustrate the stability of actuation. For strain characterization, in each cycle, three different regions are selected. The value of strain production is tracked by a image tracking software and the final average strain production curve is plotted by a custom code constructed from IGOR. As shown in Fig.43(b), our current soft liquid crystalline elastomer can generate as much as 30% of photomechanical strain. This result illustrates the feasibility to construct a light responsive bug by snap through instability.

Figure 44: (a) Schematic of a linear actuator by lifting a 21.35mg load (b) Photomechanical strain production curve as a function of time for 4 actuation cycles

Similarly to our thermo-responsive actuator, we also investigate the work/power generation during the snap through motion. As shown in Fig.45, the work content for our current light-responsive curved actuator can reach as much as $6.25 \times 10^{-5}$J, with a peak power gen-
eration as much as $3.56 \times 10^{-4}$ J/s. By tracking the tip deflection and angular acceleration during the snap through motion, the torque density of our current actuator can reach as much as $4$ N.m/kg.

**Figure 45:** (a) Force(N) vs $\delta$(m) as a function of transverse curvature (b) Force(N) vs $V$(m/s) as a function of transverse curvature

After demonstrating a soft light-responsive liquid crystalline elastomer that can produce $\sim 30\%$ photomechanical strain and a transversely curved shell like bilayer actuator that can generate as much as $\sim 6 \times 10^{-5}$ J work with $\sim 3 \times 10^{-4}$ J/s power impulse, a self-regulated actuator is proposed here by utilizing snap through instability. Before the construction of self-regulated actuator, we first demonstrate a hopper which will jump forwards on a slippery surface by snap through instability, as shown in Fig.46(a). This actuator is constructed by a $90 \mu$m LCE with $23 \mu$m PET substrate. A pair of rectangular copper is attached on tip of both side to increase the friction during actuation. Powering under $250$ mW/cm$^2$ UV light, the transverse curvature will be flattened firstly by expansion generated perpendicular to the director and the principle axis will finally bend along the longitudinal direction after snap through motion, as shown for red dashed line in Fig.46(a). This snap through motion is trigger for more than 5 cycles to illustrate the stability. We finally propose a self-regulated light-responsive bug by integrating an umbrella onboard. As shown in Fig.46(b), UV light
will irradiate on LCE and induce the snap through motion, similarly as the result we discuss before. After snap-through, the umbrella will be dragged forwards by the bending of PET and finally block the actinic light. By the shadow created after snap through motion, LCE will relax rapidly, following by a geometrical transformation from bent state to original configuration. In this mode, we can achieve a automatic light-responsive bug that can produce locomotion by self-regulation.

Figure 46: (a) Snap through actuation of a bilayer soft actuator powered under 250mW/cm$^2$ UV light (b) A proposed self-regulated bug by integration of an umbrella.
Appendix

Publications

A.1 Journal Publications


A.2 Conference Presentations


Bibliography


