**Posters** Presenters can place their posters on the boards as early as 7AM Monday, and the posters can be displayed for the duration of the conference. The official poster session runs from 6 – 8 PM Monday, October 16.

A document that contains all poster abstracts is accessible through the ILCEC website [http://ilcec.blogs.rice.edu/](http://ilcec.blogs.rice.edu/)

2. JM Boothby, RS Kularatne, and TH Ware. “Controlled actuation in chromonic liquid crystal hydrogels”
3. H Kim, VV Naik, and TH Ware. “Tough, light responsive liquid crystal elastomers”
4. NP Godman, BA Kowalski, AD Auguste, and TJ White “Photopatternable Liquid Crystal Elastomers Prepared via Chain Transfer Agents”
5. CP Ambulo, JJ Burroughs, JM Boothby, H Kim, MR Shankar, and TH Ware “3D Printing Reversible Shape-Changing Elastomeric Structures”
6. MT Brannum, TJ White, GE Wnek, and LTJ Korley, “Shape and Color Tuning in Cholesteric Liquid Crystal Elastomers”
7. D Mistry, “New insights into the nature of semi-soft elasticity and ‘mechanical Fréedericksz transitions’ in LCEs”
8. D Mistry, “Mechanical behaviours of LCEs in complex geometries: Empirical equations and a negative order parameter”
9. J Lv, S Yan, B Xu, and Y Yu “High performance hierarchical photodeformable linear liquid crystal polymer”
10. OM Wani, H Zeng, P Wasylczyk, and A Priimagi “Programming deformation in soft actuators using laser (PICO®) projector”
12. Y Yao, “Hierarchical deformations in active, dynamic liquid crystalline elastomer (LCE) based microstructures”
Abstract – The unique capabilities of light activated covalent adaptable networks (CANs) enables spatial and temporal control over the covalent connectivity of photopolymerized networks. The unique control light affords makes CANs an attractive technology for use in stimuli responsive, shape changing polymer networks. We have implemented the CANs methodology via reversible addition fragmentation chain transfer (RAFT) in a liquid crystal elastomer (LCE) and demonstrated thermoreversible shape change programmed by RAFT bond exchange. The RAFT-LCE was programmed, using photo-generation of radical species that begins a cascade of RAFT reactions, into a desired shape, or in this case, programmed fold, through reorientation of the liquid crystal mesogens and network connectivity. The thermoreversibility of the order/disorder transition in RAFT-LCEs allows for disruption of the programmed shape at elevated temperatures and regeneration of the programmed shape at lower temperatures. We demonstrate programmable folding in RAFT-LCEs by initially straining the networks in the desired areas required for folding followed by selective or flood irradiation of the elastomer to induce bond exchange and stress relaxation. Varying amounts of light exposure, light intensity, and temperature allowed for continuous control of the programmed shape. Ultimately, we are left with a thermoreversibly shape-changing polymer, which can be programmed using a variety of conditions along with the spatial and temporal control of light. Furthermore, the programmed shape can be permanently erased while the polymer is at the elevated temperature enabling recyclable shape change as long as photoinitiator is present. Covalent adaptable liquid crystal elastomers provide a new and facile route for photo origami and other polymer shape changing applications.

References

In liquid crystalline polymer networks, shape change is directed by the local molecular order. This molecular ordering can be spatially patterned, resulting in monolithic materials that undergo complex shape change. However, liquid crystal polymer networks are typically hydrophobic and only respond to stimuli that would be incompatible with biological environments, such as high temperatures and organic solvents. Chromonic liquid crystals are a type of lyotropic liquid crystal which exhibits ordering in aqueous environments. Our group has recently shown that we can orient and crosslink chromonic hydrogels\(^1\). We now expand understanding of how chemistry affects polymer properties by incorporating hydrophilic acrylate and acrylamide comonomers with different functional side groups. In doing this, gels can be synthesized that undergo tunable, reversible shape change with the advantage of responding in different aqueous conditions. We present our work building on these initial results to control the amount of reversible shape change and increase the control over the molecular ordering. By controlling the crosslink density of the gel, we increase the volumetric shape change observed on heating from 25 °C to 70 °C from ~65% to ~450% (Figure 1). This shape change remains anisotropic despite the large volume change. Additionally, we utilize the patterning of surfaces to manipulate molecular orientation in these chromonic gels for control over the shape change. To evaluate these gels for potential biomedical devices, we also present results from biocompatibility studies.

**References**

Tough, light responsive liquid crystal elastomers

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Synthetic and processing approaches of responsive materials to integrate robust mechanical properties and shape morphing abilities are of intense interest. Liquid crystal elastomers (LCEs) are well-known reversible shape changing materials with large actuation strain. However, for practical engineering applications, LCEs are often limited by poor mechanical properties such as toughness, modulus, and actuation stress as compared to other engineering polymers and actuators. LCEs in many applications are also significantly restricted by the harsh stimuli needed to induce shape change, such as high temperatures. To overcome these limitations, we explore systems of LCEs that integrate robust mechanical properties and high work capacities by introducing crystallinity into LCEs. Notably, crystallized LCEs have elastic moduli two orders of magnitude higher and toughness five times higher than corresponding nematic elastomers. Also, these LCEs are capable of high load bearing during actuation, up to 1.3 MPa, and high work capacity, up to 730 kJ/m³. Finally, we will describe using stimuli, such as visible and UV light, to trigger the actuation of crystallized LCEs by functionalizing these materials with carbon nanotubes and azobenzene. We believe these synthetic and processing approaches could enable engineering applications of LCEs from implantable devices to smart electronics.
Photopatternable Liquid Crystal Elastomers Prepared via Chain Transfer Agents
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Recent advances in photopatterning techniques have allowed for the creation of designer polymer networks by preprogramming topological defects into a material before polymerization. These smart materials maintain the prescribed orientation and can reversibly change shape when triggered. One limiting factor in the advancement of programmable LCEs is the development of robust, chemical formulations that are quick and easy to fabricate, but are also conducive to previously developed photopatterning techniques. Specifically, we take advantage of the chain-transfer process that occurs during the polymerization of acrylates in the presence of thiols. This provides a straightforward method of synthesizing LCEs by decreasing the kinetic chain length in acrylate networks fabricated from reactive mesogens previously known to form glassy networks. The decrease in crosslink density, in conjunction with chain extension, contributes to an increase in elasticity without sacrificing the mechanical toughness of the films. The materials to be discussed exhibit mechanical properties similar to siloxane based LCEs, but do not require heavy metal catalysts and can be preprogrammed to give a desired shape change. The fabricated LCEs can undergo multiple reversible shape changes in response to heat, and the improvements to formulation techniques will also be discussed.
3D Printing Reversible Shape-Changing Elastomeric Structures
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Liquid crystal elastomers (LCEs) are stimuli-responsive polymers that undergo reversible shape-change in response to a variety of stimuli. By programming the molecular alignment of liquid crystal precursors before crosslinking, elastomers that undergo complex shape change can be fabricated. Alignment within LCEs has been previously accomplished through bulk mechanical straining, magnetic/electric fields, and surface treatments, but these techniques do not enable fabrication of 3D structures with locally controlled molecular alignment. Here we use additive manufacturing to spatially program molecular order in 3D, creating LCE structures capable of reversible shape-change. Specifically, we use direct-write printing followed by photopolymerization of liquid crystal oligomers to create these active structures. With the use of direct-write 3D printing, we exploit the ability to orient LC molecules with shear force to generate 3D structures with programmed molecular orientation. We use this new processing method to print morphing structures. For example, actuating structures with zero, positive, and negative Gaussian curvatures, each encoded with topological alignment patterns, can be achieved. By printing LCE structures with regions of both negative and positive Gaussian curvatures, we leverage the continuous actuation of the heat responsive material to design structures that undergo reversible snap-through actuation in ~5 ms once a critical temperature is reached. The snapping actuation of these complex 3D structures is similar to Venus Flytraps found in nature and man-made toy ‘poppers’. The 3D printed LCE snappers are also capable of generating work on loads ~20 times heavier than the weight of the snapper. This new manufacturing technique allows for simultaneous control of geometry and molecular order in active soft matter. We expect these smart structures can translate to applications in soft actuators, biomedical devices and tissue engineering scaffolds.
Biological systems employ anisotropy to enable selectivity in motion or to add functionality, such as structural color. Cholesteric liquid crystals (CLCs) are inherently and selectively reflective and can exhibit stimuli-induced changes in reflection color in compositions prepared with low-molar mass liquid crystals. Here, we explore on the ability to locally pattern the director orientation to yield materials that allow for both color and shape (topography) change in monolithic elements prepared from cholesteric liquid crystalline glassy films. The materials prepared in this examination are of the main-chain subclass, synthesized via photopolymerization, and optimized for performance from non-reactive chiral dopants. The mechanics of the deformation will be discussed. The ability to simultaneously and concurrently regulate the color as well as the direction of reflected light could open up interesting applications in textiles, optics, and sensing.
Photodeformable linear liquid crystal polymer with hierarchical superstructures

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Photodeformable liquid crystal polymer materials which show diverse light-induced irreversible shape change have wide promising applications ranging from organic actuator, robot, and sensor, to micro-mechanical system and microfluidic system[¹]. Most of photodeformable liquid crystal polymer materials are cross-linked liquid crystal polymers (CLCPs)[²], which combine versatile properties of both liquid crystal and the polymer network[³]. However, chemical crosslinking networks prevent melting and dissolving of CLCPs, which makes CLCPs incompatible with the traditional polymer processing methods. The poor processibilities of CLCPs severely restrict its practical application[⁴].

Here, we designed and synthesized a novel linear liquid crystal polymer (LLCP)[⁵], which has a long alkyl backbone containing double bonds and azobenzene moieties in side chains acting as both mesogens and photoresponsive groups. The flexible backbones and the azobenzene mesogens to self-assemble into a nano-scaled lamellar structure due to the molecular cooperation effect of liquid crystals. In addition, the long spacers provide enough free volume for the azobenzene mesogens to generate a highly ordered structure and undergo a fast photoresponse.

In order to further ensure the mechanical properties of the LLCP, the LLCP with high molecular weight was prepared by ring-opening metathesis polymerization (ROMP). Its molecular weight is at least one order larger than common photodeformable liquid crystal polymers. The results of differential scanning calorimetry (DSC) and polarizing optical microscope (POM) measurement show that the LLCP is a smectic liquid crystal polymer. The results of one dimensional X ray scattering (1D-SAXS), transmission electron microscope (TEM), one dimensional wide-angle X ray diffraction (1D-WAXD) and two-dimensional wide-angle X ray diffraction (2D-WAXD) indicate that LLCP self-assemble into a composite lamellar structure at nano-scale. The LLCP can be both melt by heating and dissolved in organic solvents, so it is compatible with traditional polymer processing methods, which will strongly promote the development and application of liquid crystal polymer materials in the field of entirely light-driven soft actuators.

References

Programming deformation in soft actuators using laser (PICO®) projector

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Liquid crystal elastomers and polymer networks (LCPs) have emerged as promising materials for fabrication of soft actuators.¹ Their deformation mode is dictated by the director distribution of the constituent liquid-crystal molecules within the polymer network, which makes it critical to develop means for precise control over the molecular alignment. Photoalignment technique has proven to be very useful in patterning complex director orientations into liquid-crystalline materials and is being actively pursued in the context of LCPs.² Herein, we present our recent results on photopatterning in monolithic LCP films, using a low-cost, commercially available laser (PICO®) projector. Photoalignment and photopatterning is achieved by spatially controlling light polarization. Without any complex optical modifications, projector is capable of programming a minimum feature size of 50 µm to an overall area of 25x14 mm. We use this projector to engineer shape changes in LC actuators, and several complex deformations are demonstrated. By obviating the need for expensive light source and complex optics, this projector enables scalable, low-cost photopatterning with relatively high throughput and can be used as an easy alternative for photopatterning of LCPs. Thereby, it widens the scope of shape-programmable liquid-crystalline polymers and actuators, rendering their fabrication more versatile.

References

Modeling of mechanical wave generation in a photoactive polymer ribbon

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We model mechanical wave generation in a light-driven photoactive nematic liquid crystal elastomer (LCE) ribbon, via non-linear finite element simulations. We study a liquid crystal network doped with azoderivatives that rapidly isomerize under UV illumination, with half-life of order 1 second. This work was carried out in collaboration with Anne Hélène Gelebart and Dirk Broer and coworkers[1] who fabricated/characterized these polymer materials. We consider a ribbon-shaped sample with homeotropic anchoring on one surface and planar anchoring, along the ribbon’s long axis, on the opposite surface. The sample is clamped along its short edges and illuminated at a selected angle. In our model, we treat this splayed director field as fixed in the sample’s body frame. Mechanical actuation is modeled via a Hamiltonian [2,3]:

$$H = \frac{1}{2} \sum_t V^t C_{ijkl} \varepsilon^t_{ij} \varepsilon^t_{kl} - \alpha \sum_t V^t \varepsilon^t_{ij} (S^t - S^0) \frac{1}{2} \left( 3 n_i^t n_j^t - \delta_{ij} \right) + \frac{1}{2} \sum_p m_p v_p^2$$

The first term is the elastic strain energy summed over elements $t$, where $\varepsilon_{ij}$ is the Green-Lagrange strain and $C_{ijkl}$ is a tensor of elastic constants. The second term is the potential energy due to coupling of strain and nematic order with a coupling coefficient $\alpha$. Here $S^t$ is the instantaneous nematic scalar order parameter in element $t$, and $S^0$ is the value in the fully relaxed nematic state; and $n_i^t$ is the local nematic director. The last term represents kinetic energy using the lumped mass approximation, with mass $m_p$ and instantaneous velocity $v_p$ of each node $p$.

The effective force on each node is calculated as the derivative of the total potential energy with respect to node displacement. To model photoactuation, we consider incoming light as a plane wave and use a simplified ray tracing algorithm to determine what parts of the sample are illuminated and what parts are in shadow. The local scalar order parameter $S$ in each element evolves as a function of time according to its exposure to light, using a simplified kinetic model of the azoderivate’s trans-cis isomerization/relaxation. Thus the local order parameter decreases in illuminated voxels and relaxes back to the equilibrium value in shadowed voxels. Attenuation of light through the thickness of the sample is also considered.

The model demonstrates generation and motion of photoactive mechanical waves driven by self-shadowing behavior, demonstrating the mechanism driving wave generation in Gelebart’s experimental system. We find the directionality of wave propagation is determined by the orientation of the polymer film (homeotropic side up vs planar side up) by means of the induced curvature upon illumination and discuss the similarities and differences between the two orientations. Self-shadowing causes asymmetric actuation of the ribbon, resulting in internal stresses that are unbalanced between the front and back sides of the wave crest, thus determining the direction of wave propagation. We also describe how the ribbon "resets" to generate the next wave crest after a full period of motion. Lastly, we discuss the significance and potential applications of this photoactuated oscillation for light-driven autonomous robotics.

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