

# From Robotics to Sensing: Liquid Crystalline Elastomers as Novel, Actuatable Materials

Mikayla Anderson

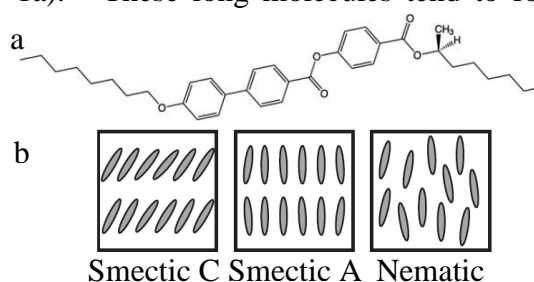
Literature Seminar

October 16, 2014

Friedrich Reinitzer discovered liquid crystals in 1888 when he observed the curious double melting points of cholesterol benzoate.<sup>1</sup> However, the utility of liquid crystals in display panels was not realized until the early 1970s.<sup>1</sup> Ever since then, liquid crystals have become ubiquitous in everyday devices such as display screens for televisions and cellular phones. Moreover, when incorporated into a polymer network liquid crystals exhibit remarkable qualities, including stimuli-responsive actuation and sensing capabilities.

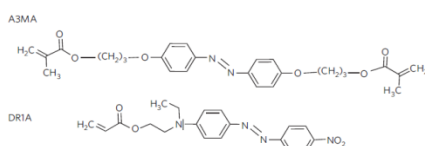
Liquid crystals are liquids with long-range order imparted by their molecular structure. Molecules that form liquid crystals, called mesogens, typically consist of a stiff, aromatic core and long, flexible chains (Figure 1a).<sup>1</sup> These long molecules tend to form anisotropic materials, which exist in three phases; smectic C, smectic A, and nematic (Figure 1b).<sup>2,3</sup>

Integrating liquid crystals into polymeric networks produces a new material with interesting characteristics, called a liquid crystalline elastomer (LCE). The self-aligning properties of the liquid crystals combined with the elastic properties of the polymer make them an attractive class of materials that can be applied in a diverse array of device designs.<sup>4-10</sup> In order to incorporate mesogens into a polymer network, they need to be chemically attached to the polymer backbone. They can either be incorporated into the polymer backbone (main-chain polymer) or attached via a spacer (side-chain polymer).<sup>2</sup> After attaching the mesogens, the network is aligned via mechanical stretching,<sup>2,10</sup> flow,<sup>6</sup> or electrical stimulation<sup>4</sup> and then cross-linked to sustain orientation of the mesogens. This synthesis ensures that there is a liquid crystalline monodomain, which is necessary for actuation.



**Figure 1:** (a) typical structure of a mesogen and (b) three phases of liquid crystals<sup>1,2</sup>

Typical stimulants for actuation include various nanoparticles or dyes. One common example for opto-mechanical actuation is an azobenzene dye. Under illumination, the dye undergoes a *cis-trans* isomerization.<sup>2,5</sup> This conformational change can be expanded into a macroscopic scale if the mesogens are aligned uniformly throughout the sample.

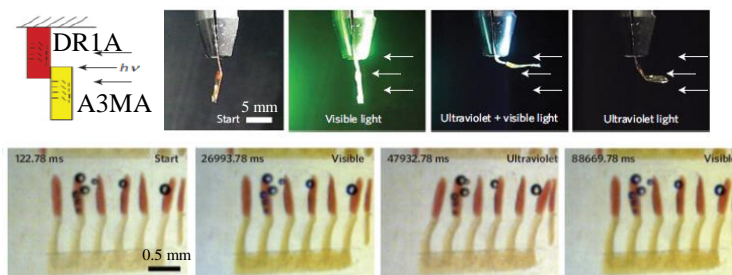


**Figure 2:** Azobenzene dyes<sup>5</sup>

azobenzene dyes (Figure 2) into the LCE to achieve dual bending modes.<sup>5</sup> They first fabricated two separate elastomer films with each dye in them to investigate the actuation.

As shown in Figure 3, the A3MA film responds strongly to ultraviolet light while the DR1A film is responsive to visible light. The authors then use an inkjet printer to fabricate the final devices, providing a means of fabrication that is both cheap and simple. The resulting structures show

One example of an opto-mechanical actuator, developed by Van Oosten, et al., integrates two

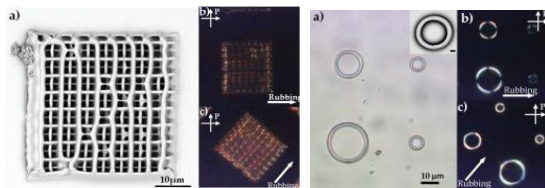


**Figure 3:** Actuation of (a) separate dye films glued together and (b) printed films<sup>5</sup>

promising actuation properties when illuminated under both visible and ultra-violet light (Figure 3), and have the potential to be used as pumps or mixers in microfluidic devices. Their integration into microfluidic devices is still primitive, however, due to their slow actuation. In order for their value to be realized in these devices, the authors suggest that motion of a few hertz will provide adequate fluid manipulation.<sup>5</sup>

Many successful LCEs are prepared as films, which are simple to fabricate for initial investigations of actuation properties. Zeng, et al. developed a technique to fabricate LCEs with complex structures via direct laser writing (DLW).<sup>7</sup> DLW is used to fabricate 3D structures with sub-micrometer resolution by polymerizing a photo-sensitive material with a tightly focused laser beam. The authors utilize this polymerization as the last step in the synthesis of opto-mechanical LCEs.

The authors were able to fabricate the various structures that can be seen in Figure 4. There is some swelling observed that is due to the solvent used, which increases with each



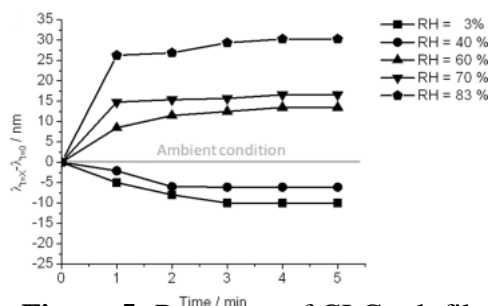
**Figure 4:** DLW written LCE structures: 3D woodpile (left) and rings with various diameters (right)<sup>7</sup>

additional layer and alters the original, desired dimensions of the structure. Swelling will be important to control in future applications, especially if these structures are to be used in microphotronics. Their application in microphotronics is particularly interesting as photonic responses to structural periodicity could be tuned quite easily

with DLW. However, the authors do not demonstrate an ability to deform the LCE structures for opto-mechanical applications even though they claim to have maintained mesogen molecular orientation. Overall, the authors present a unique technique to fabricate intricate 3D structures of LCEs that maintain their structural integrity as well as mesogen orientation.

Finally, LCEs can be useful for more than actuation. For example, Herzer, et al. developed a strategy to use LCEs as humidity sensors for possible applications in food packaging.<sup>8</sup> The group's previous work with hydrogen-bonded (H-bonded) LCEs prompted their development of a colorimetric humidity sensor.<sup>9</sup> The H-bonded system included mesogens that contained carboxyl groups as the basis for H-bonding. With an increase in pH, H-bonds are broken and the ions from the alkaline solution are dispersed throughout the polymer network, creating a hygroscopic polymer salt film. Upon exposure to water, the salt film swells significantly and results in a macroscopic shape deformation.<sup>8,9</sup>

The authors used this strategy and incorporated these H-bonded mesogens into a cholesteric liquid crystal (CLC) polymer network. CLCs are chiral nematic liquid crystals



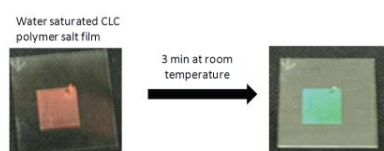
**Figure 5:** Response of CLC salt film to various RH conditions. A change in SRB was measured (y-axis) vs. time<sup>8</sup>

where the axis of the director (determines mesogen orientation) varies throughout the layers.<sup>2,8</sup> The helical pitch refers to the periodic variation of the director and can change dramatically upon swelling or contraction of the film. The pitch also determines the selective reflection band (SRB) of the CLC,<sup>3,8</sup> so swelling of the CLC film will result in an overall color change.

The authors utilized this attribute of CLCs to achieve the desired optical humidity sensors by first preparing a thin film of the CLC mixture, then submerging the film in KOH to produce a hygroscopic salt film. When tested under various relative humidity (RH) conditions, the films responded quickly and red-shifted within 2 minutes (Figure 5). This red-shift is due to

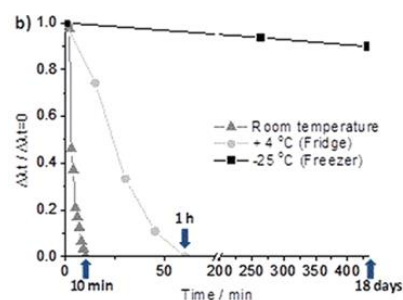
swelling of the film, which subsequently increases the helical pitch. At a RH of 3%, a blue-shift is observed and can be explained through a contraction of the film. Films were fabricated in ambient conditions, however, an ambient RH was not reported. If ambient RH is assumed to be 50%, any RH below this would result in a contraction of the film and a blue-shift would be observed.

The capability of the films to perform as humidity sensors provoked the authors to test them as temperature sensors as well. Polymer salt films were soaked in water until they appeared red in color and then dried at various temperatures while their SRB was monitored with time (Figure 6). The films at room temperature were observed to dry (via color change) within 10 minutes, films at  $-4^{\circ}\text{C}$  dried within 1 hour, and films in a freezer at  $-25^{\circ}\text{C}$  were not observed to dry or change color over the time span of 18 days. While these temperatures are fairly dispersed, the experiment demonstrates the ability of the sensors to detect when frozen food has gotten warm and possibly spoiled. Sensors were also printed to establish their commercial viability. These were printed on both glass and triacetyl cellulose (TAC) substrates, as TAC can be used for



**Figure 7:** Printed CLC salt film dried at room temperature<sup>8</sup>

bulk commercial processing. While printed films exhibit a higher density of defects, a quicker response time is observed (Figure 7). This has been attributed to a faster drying of water through these defects.<sup>8</sup> Liquid crystal elastomers are a diverse set of materials that can be used for various actuation and sensing applications. The few essential materials necessary for fabrication enables a high degree of versatility when selecting both the polymer network and the mesogens to use. For instance, chiral nematic mesogens were used for their unique optical properties in the sensor application while azobenzene-derivate mesogens were used for the printed artificial cilia. While there is still work to be done, these results are promising for the future of LCEs, especially in applications such as microfluidics and sensing.



**Figure 6:** Response of CLC salt film to various temperatures. A change in SRB was measured (y-axis) vs. time<sup>8</sup>

These were printed on both glass and triacetyl cellulose (TAC) substrates, as TAC can be used for bulk commercial processing. While printed films exhibit a higher density of defects, a quicker response time is observed (Figure 7). This has been attributed to a faster drying of water through these defects.<sup>8</sup>

1. Lagerwall, J.P.F.; Scalia, G. A New Era for Liquid Crystal Research: Applications of Liquid Crystals in Soft Matter Nano-, Bio-, and Microtechnology. *Curr. Appl. Phys.* **2012**, *12*, 1387-1412.
2. Ohm, C.; Brehmer, M.; Zentel, R. Liquid Crystalline Elastomers as Actuators and Sensors. *Adv. Mater.* **2010**, *22*, 3366–3387.
3. Xie, P.; Zhang, R. Liquid Crystal Elastomers, Networks and Gels: Advanced Smart Materials. *J. Mater. Chem.* **2005**, *15*, 2529-2550.
4. Lehmann, W.; et al. Giant Lateral Electrostriction in Ferroelectric Liquid-Crystalline Elastomers. *Nature* **2001**, *410*, 447-450.
5. Van Oosten, C. L.; Bastiaansen, C. W. M.; Broer, D. J. Printed Artificial Cilia from Liquid-Crystal Network Actuators Modularly Driven by Light. *Nat. Mater.* **2009**, *8*, 677-682.
6. Ohm, C.; Serra, C.; Zentel, R. A Continuous Flow Synthesis of Micrometer-Sized Actuators from Liquid Crystalline Elastomers. *Adv. Mater.* **2009**, *21*, 4859-4862.
7. Zeng, H.; et al. High-Resolution 3D Direct Laser Writing for Liquid-Crystalline Elastomer Microstructures. *Adv. Mater.* **2014**, *26*, 2319-2322.
8. Herzer, N.; et al. Printable Optical Sensors Based on H-Bonded Supramolecular Cholesteric Liquid Crystal Networks. *J. Am. Chem. Soc.* **2012**, *134*, 7608-7611.
9. Harris, K. D.; Bastiaansen, C. W. M.; Lub, J.; Broer, D. J. Self-Assembled Polymer Films for Controlled Agent-Driven Motion. *Nano Lett.*, **2005**, *5*, 1857-1860.
10. Yamada, M.; et al. Photomobile Polymer Materials – Various Three-Dimensional Movements. *J. Mater. Chem.*, **2009**, *19*, 60-62.