Video Article

# Preparation of Monodomain Liquid Crystal Elastomers and Liquid Crystal Elastomer Nanocomposites

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## Abstract

LCEs are shape-responsive materials with fully reversible shape change and potential applications in medicine, tissue engineering, artificial muscles, and as soft robots. Here, we demonstrate the preparation of shape-responsive liquid crystal elastomers (LCEs) and LCE nanocomposites along with characterization of their shape-responsiveness, mechanical properties, and microstructure. Two types of LCEs — polysiloxane-based and epoxy-based — are synthesized, aligned, and characterized. Polysiloxane-based LCEs are prepared through two crosslinking steps, the second under an applied load, resulting in monodomain LCEs. Polysiloxane LCE nanocomposites are prepared through the addition of conductive carbon black nanoparticles, both throughout the bulk of the LCE and to the LCE surface. Epoxy-based LCEs are prepared through a reversible esterification reaction. Epoxy-based LCEs are aligned through the application of a uniaxial load at elevated (160 °C) temperatures. Aligned LCEs and LCE nanocomposites are characterized with respect to reversible strain, mechanical stiffness, and liquid crystal ordering using a combination of imaging, two-dimensional X-ray diffraction measurements, differential scanning calorimetry, and dynamic mechanical analysis. LCEs and LCE nanocomposites can be stimulated with heat and/or electrical potential to controllably generate strains in cell culture media, and we demonstrate the application of LCEs as shape-responsive substrates for cell culture using a custom-made apparatus.

## Video Link

The video component of this article can be found at http://www.jove.com/video/53688/

## Introduction

Materials that can exhibit fast, reversible, and programmable shape changes are desirable for a number of emerging applications[1-9]. Shape-responsive stents can assist with wound healing and treatment[7]. Artificial robots can aid in exploration or in carrying out tasks in environments that are harmful or unsafe for humans[10]. Shape-responsive elastomers are desirable for use in active cell culture, in which cells are cultured in an active environment.[11-14] Other applications include packaging, sensing, and drug delivery.

Liquid crystal elastomers (LCE) are polymer networks with liquid crystal ordering[15-20]. LCEs are made by combining a flexible polymer network with liquid crystal molecules known as mesogens. The responsiveness of LCEs is derived from the coupling of liquid crystal order to strains in the polymeric network, and stimuli that influence the ordering of mesogens will generate network strains, and vice versa. In order to achieve large and reversible shape-changes in the absence of an external load, the mesogens must be aligned in a single direction in the LCE. A common practical challenge in working with LCEs is generating monodomain LCEs. Another challenge is generating shape changes in response to stimuli other than direct heating. This can be done through the addition of nanoparticles or dyes to LCE networks[21-28].

Here, we demonstrate the preparation of monodomain LCEs and LCE nanocomposites. First, we demonstrate the preparation of monodomain LCEs using the two-step method first reported by Kupfer *et al.*[29] This is still the most popular and well-known method for preparing monodomain LCEs, but achieving uniform alignment and consistency between samples can be challenging. We demonstrate an approach that can be easily implemented using standard lab equipment, including full details on sampling handling and preparation. Next, we show how conductive carbon black nanoparticles can be added to LCEs to produce conductive, electrically responsive LCEs. We then demonstrate the synthesis and alignment of epoxy-based LCEs. These materials exhibit exchangeable network bonds and can be aligned by heating to elevated temperatures and applying a uniform load. All LCEs are characterized through macroscopic sample imaging, X-ray diffraction measurements, and dynamic mechanical analysis. Finally, we demonstrate one potential application of LCEs as shape-responsive substrates for active cell culture.

 

## Protocol

# 1. Synthesis of Aligned Polysiloxane LCEs

1. Combine 166.23 mg of reactive mesogen (4-methoxyphenyl 4-(3-butenyloxy)benzoate), 40 mg of poly(hydromethylsiloxane), and 12.8 mg of crosslinker (1,4-di(10-undecenyloxybenzene)[30] with 0.6 ml of anhydrous toluene in a small vial (approximately 13 mm in diameter and 100 mm in length) charged with a stirring bar. Stir the solution at 35 °C for 25 min to dissolve.
2. In a separate vial, prepare a solution of 1 wt % dichloro(1,5-cyclooctadiene)-platinum(II) catalyst in dichloromethane. Add 30 µl of catalyst solution to the reagents from step 1.1 via pipette, stir to mix, and pour the solution into a custom-made (3 cm x 2 cm x 1 cm) rectangular polytetrafluoroethylene (PTFE) mold. Cover the mold loosely with a glass slide and place in heating oven at 60 °C for 30 min while shaking periodically to remove bubbles during the first 15 min.
3. Remove mold from heating oven and cool with liquid nitrogen by pouring liquid nitrogen into a small container and contacting the bottom of the PTFE mold with the liquid nitrogen for 2 sec.
    1. Once the mixture has cooled, carefully remove elastomer from mold using a metal spatula and place on top of a PTFE sheet. Trim the edges of the LCE using a razor blade and cut the LCE along its length into three equal sized pieces (approx. 2.7 cm length and 0.5 cm width).
4. Hang each piece by one end to a horizontal rod and attach 10 paperclips (4.4 g) to the other end of the LCE. Hold the LCE in place using tape, and add paperclips one at a time in 10 min increments. Hang the LCE for 7 days at RT, noting changes in length and uniformity. Discard any sample that tears or breaks. Remove samples and store at ambient.

# 2. Preparation of Electrically Responsive Polysiloxane LCE Nanocomposites

1. To prepare LCE nanocomposites with carbon black dispersed through the bulk of the sample, first repeat steps 1.1 - 1.4 above. Add 4.38 mg carbon black nanoparticles to the reaction solution containing reactive mesogen, crosslinker, and siloxane. Use a total of 5 paperclips instead of 10 for loading.
2. In order to add additional carbon black nanoparticles to the LCE surface, prepare 1% w/v solution of carbon black nanoparticles in toluene. Sonicate for 20 min to disperse nanoparticles and then pour the dispersion into a Petri dish. Immerse the LCEs from step 2.1 in the nanoparticle dispersion for 6 hr.
3. After 6 hr, use a pipette to withdraw the solution from the Petri dish and allow the elastomer to dry in air. Gently clean excess carbon particles on the surface using tape or a cotton swab.

# 3. Preparation of Reversible Epoxy-based LCEs

1. Mix 246.15 mg of 4,4'-diglycidyloxybiphenyl[31], 101 mg sebacic acid, 71.6 mg of hexadecanedioic acid, and 76 mg of carboxydecyl-terminated polydimethylsiloxane in a custom-made (3 cm x 2 cm x 1 cm) rectangular PTFE mold. Heat the samples by placing on a hotplate at 180 °C.
    1. Add 11.48 mg of (1,5,7-triazabicyclo[4.4.0] dec-5-ene) catalyst and stir using metal tweezers pre-heated to 180 °C. Continue reacting until the mixture forms a gel, after approximately 20 min, and stir periodically to remove bubbles generated by the reaction.
2. Remove the PTFE boat from the hotplate and allow to cool to RT. Use a razor blade to separate the elastomer from the PTFE mold.
3. Place two PTFE sheets in a polymer press at 180 °C. Place the elastomer from step 3.2 between the PTFE sheets and compress the sample to a thickness of 0.3 - 0.5 mm. Continue heating at 180 °C for 4 hr.
4. Remove the sample and cool to RT. Cut the sample into rectangular pieces (approximately 2.5 cm length and 0.5 cm width). Hang the sample at one end using polyimide tape inside a heating oven. Attach 12 paperclips (8.88 g) to the free end of the sample. Set the temperature of the heating oven to 165 °C O/N, or for 12 - 16 hr.
5. Remove the elastomer from the heating oven and note the change in length. Heat the sample to 80 °C on a hotplate to remove residual stress then cool back to RT.

# 4. Testing and Characterization of LCEs

1. Measure reversible strain by heating the samples on a hotplate to 120 °C and imaging with a camera. Note the initial sample length at RT, the sample length after heating to 120 °C, and the length after cooling back to RT. LCEs should contract by approximately 30% and return to their initial length on cooling. See example images shown in **Figure 1A** and **1B**.
2. Analyze phase transition temperature and glass transition by differential scanning calorimetry (DSC) by cutting a small piece from each LCE and scanning from 0 °C to 150 °C at a heating/cooling rate of 10 °C/min[32,33].
3. Quantify the degree of liquid crystal alignment by X-ray diffraction measurements. Place samples in an X-ray diffractometer with 2D imaging capabilities.[33] See example diffraction images shown in **Figure 2**.
   Note: The diffraction image should be anisotropic, reflecting the alignment of the LCE[33]. Polysiloxane LCEs are nematic and epoxy-based LCEs exhibit a smectic phase.
4. Measure stiffness of LCE and change in length and width using dynamic mechanical analysis (DMA). Record length and stiffness changes as a function of temperature for LCEs and as a function of electrical potential for the LCE nanocomposites.
    1. For thermo-mechanical measurements, use a razor blade to manually cut samples to dimensions of 2 cm x 0.3 cm and carefully fasten in between tension clamps. Apply a force of 1 mN to remove any slack.

1. Thermally equilibrate samples at 30 °C followed by heating and cooling cycles at 5 °C/min. Heat sample from 30 °C up to 120 °C. Changes in temperature produce changes in the length and width of the sample, which are recorded during the DMA measurement. See **Figure 3A** for thermomechanical measurements of an LCE sample.

2. For electromechanical measurements, manually cut LCE nanocomposite samples to dimensions of 2 cm x 0.3 cm and glue a copper wire at opposite ends of the LCE nanocomposites using a silver epoxy. Fasten the LCE nanocomposite using tension clamps with 1 mN tension.
    1. Apply an electrical potential through the copper wires at a voltage ranging from 0 - 60 V, a frequency of 60 Hz, and an on/off pulse duration ranging from 0.1 sec - 30 sec.
    2. Record shape changes in response to the electrical potential. Apply a fixed force of 1 mN to remove slack. The change in position of the clamps corresponds to shape changes in the sample. See **Figure 3B** for electromechanical measurements of an LCE nanocomposite sample.

## 5. Active Cell Culture through Electrical Stimulation of LCE Nanocomposites

1. Treat one surface of LCE nanocomposites under oxygen plasma for 30 sec. Spin cast 300 µl of a solution of polystyrene in toluene (1% w/v) at 3,300 rpm for 1 min on top of the plasma cleaned surface. Dry the elastomer under vacuum for 12 hr to remove toluene, and treat the polystyrene-coated surface of the LCE nanocomposite using oxygen plasma for 30 sec.
2. Place LCE nanocomposites in 70% ethanol solution for 30 min to sterilize the surface.
    1. Wash the LCE nanocomposite with phosphate buffered saline and transfer the LCE to a dry Petri dish with the polystyrene-coated side facing up. Coat the entire surface of the LCE by immersing in 5 ml of a rat tail collagen type I solution (50 µg/ml in 0.02 N acetic acid). Incubate the LCE nanocomposite at 37 °C and 5% $CO_2$ for at least 30 min.

3. Isolate neonatal rat ventricular cardiomyocytes and suspend in high-serum plating media as previously reported[11].
    1. Plate cells on top of LCE substrates described as above at a density of 100,000 - 600,000 cells/$cm^2$. Around 24 hr later, transfer the cells to low serum maintenance media (DMEM, 18.5% M199, 5% HS, 1% FBS and antibiotics). Allow cardiomyocytes to attach and proliferate on the surface of the LCE for 4 days.

4. Design and fabricate a custom vessel using a 3-D printer and using the schematic of the vessel shown in **Figure 4** using manufacturer's protocol.
    Note: The 3D printed vessel is a rectangular container with outer dimensions of 60 mm x 40 mm x 20 mm and inner dimensions of 50 mm x 30 mm x 15 mm. On two lateral surfaces, there are two sets of 5 mm holes used for inserting conductive carbon rods. Notches around the holes and up to the top edge of the container allow for placing a rectangular plastic piece (dimensions of 52.5 mm x 12 mm x 4 mm) across the vessel to hold the LCE in place at both ends. The distance between the holes is 3 mm on one side of the vessel, and notches are located around the holes as shown in **Figure 4**. This is designed to be compatible with the size of the LCE substrates described above. Conductive carbon rods are obtained through a commercial supplier as shown in the Materials Supplement.
    1. Insert carbon rods through the holes across the vessels and hold in place using medical grade silicone adhesive. Cure the adhesive O/N.

5. Transfer LCE nanocomposites with cardiomyocytes to a custom 3D-printed vessel filled with cell culture maintenance media and with parallel conductive carbon rods connected to an electric source. Place the LCE across the carbon rods and fix on one end to ensure electrical contact.
    1. Insert a rectangular plastic piece through the notches in the 3-D vessel to hold the LCE in place at one or both ends, but place this loosely over the LCE sample. Electrically stimulate LCE through the application of a 40 V AC electrical potential with a 5 sec on/off time for a total of 24 hr.

6. Stain the membrane of living cells using Calcein AM as described previously[11].
7. For nuclei staining, cover the cells with DAPI-containing mounting medium before imaging under an inverted fluorescent microscope. Use ImageJ to count the number of living cells and determine the angle of cell alignment using the best fit function.

## 6. Active Cell Culture with LCEs Using Direct Heating

1. Repeat steps 5.1 - 5.3 above using a pure LCE without carbon black nanoparticles added. This procedure is also described in detail in a prior publication.[11]
2. Transfer the LCE with cardiomyocytes to a Petri dish with cell culture maintenance media and a 0.5" x 2" Kapton resistive heater. Supply heat to the LCE by turning on the resistive heater with heating power of 12 W. Cycle on and off the heat with 5 sec intervals for at least 24 hr.

## Representative Results

Monodomain LCEs are shape-responsive due to coupling of network conformation with liquid crystal ordering. Heating LCEs results in a decrease in the liquid crystal order parameter, producing a contraction of the polymeric network along the primary alignment direction. This is easily visualized by placing an LCE on a hotplate, as shown in **Figure 1A** and **1B**. In heating up from RT, the LCE contracts along the length of the sample, and above the isotropic transition temperature the contraction is a maximum. The sample will also become optically clear above the isotropic transition temperature, while some haziness is observed for even perfectly aligned LCEs below the isotropization temperature. LCE nanocomposites will also exhibit shape-changes in response to heating, as shown in **Figure 1C** and **1D**. LCE nanocomposites can be heated either on a hotplate (not shown) or by applying an electrical potential across the sample. The sample will contract when the voltage is turned on. If little or no shape change is observed, this is likely a reflection of poor alignment of the liquid crystal director and the synthesis of the LCE should be repeated. As a check, the birefringence of pure LCE samples can be tested using a polarized optical microscope. Aligned samples should exhibit maximum birefringence when oriented at 45 degrees relative to crossed polararizers and should appear dark when oriented along or perpendicular to either the analyzer or polarizer.

Direct information on liquid crystal ordering can be obtained through X-ray diffraction[33]. As shown in **Figure 2**, an aligned LCE exhibits anisotropic liquid crystal diffraction peaks due to alignment of the mesogens. Peaks at wide angles are due to intermolecular spacing along the width of the molecule. In the case of epoxy-LCEs with smectic ordering, additional peaks are observed at low angles reflecting the smectic layer spacing. In all samples, the diffraction is anisotropic in the liquid crystal phase and disordered above the isotropization temperature. As shown in **Figure 2**, the siloxane LCE will exhibit nematic XRD peaks along the alignment direction while the epoxy-LCEs are main chain LCEs and exhibit wide-angle XRD peaks perpendicular to the alignment direction and low-angle peaks along the alignment direction corresponding to the smectic layer spacing.

Differential scanning calorimetry (DSC) provides phase transitions in the LCEs[32]. Silicone based LCEs have a glass-transition temperature ($T_g$) well below RT and below the resolution of our DSC, but a clear peak is observed near 90 °C corresponding to the nematic-to-isotropic transition. A similar peak is observed in the LCE nanocomposites. In the case of the epoxy-based LCEs presented, a glass transition temperature near 20 °C is observed and a smectic-to-isotropic transition temperature near 60 °C. It is important to note that the glass and isotropic transition temperature can be modified by changing the composition of the elastomers and the linking group.

Dynamic mechanical analysis provides a quantitative measure of LCE shape change as a function of temperature and, in the case of LCE nanocomposites, as a function of applied voltage (**Figure 3**). The sample contracts with increasing temperature, up to the transition to the isotropic phase. In the case of a pulsed electrical voltage, LCE nanocomposites exhibit cyclic strain in phase with the electrical potential.

Active cell culture experiments are performed using a custom, 3-D printed vessel (**Figure 4**). The through-holes allow for placement of conductive carbon rods, and the vessel is filled with cell culture media. An example of cell attachment on an LCE nanocomposite surface is shown in **Figure 5** for a non-stimulated sample after 3 days of culturing. Cardiomyocytes show good attachment and viability.

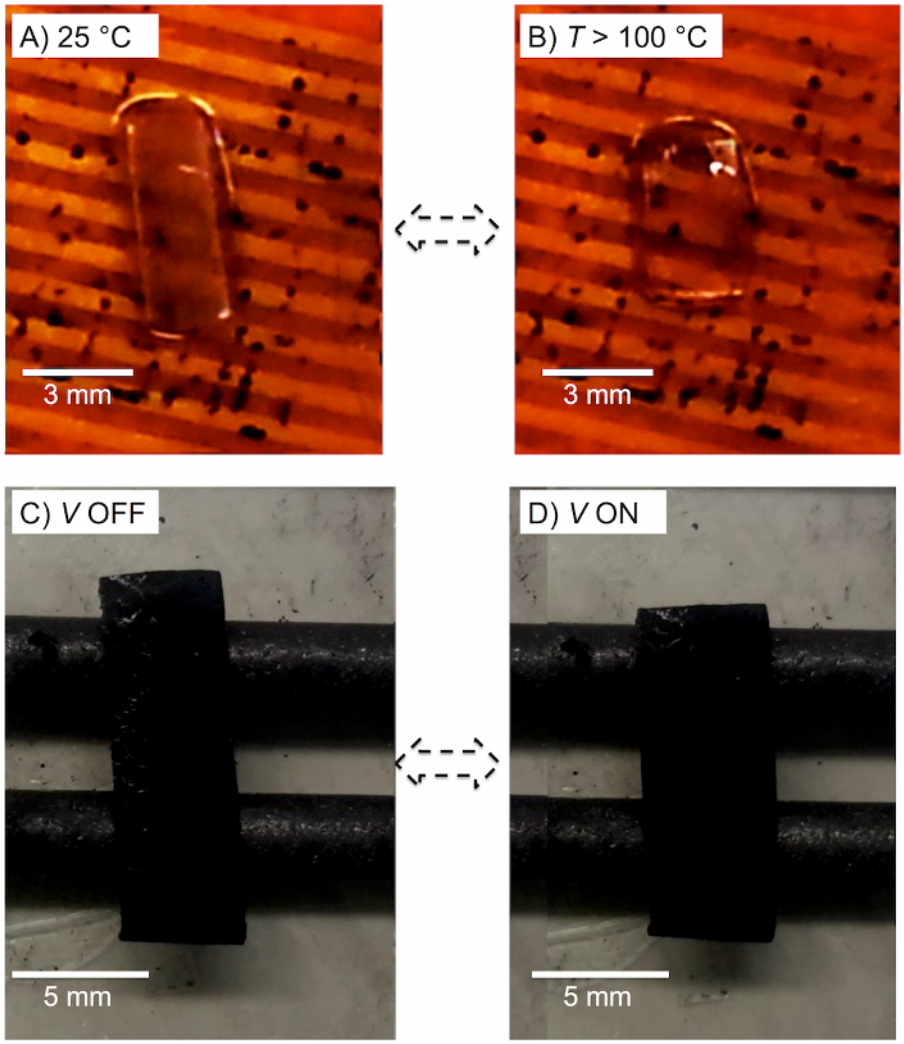


**Figure 1. Shape-response of LCEs and LCE Nanocomposites.** LCEs contract and elongate reversibly when heated from RT (**A**) to above the nematic-to-isotropic transition temperature, roughly 80 °C (**B**). LCE nanocomposites contract on the application of an electrical potential (**C** and **D**). The voltage applied is a 40 V AC signal. Please click here to view a larger version of this figure.

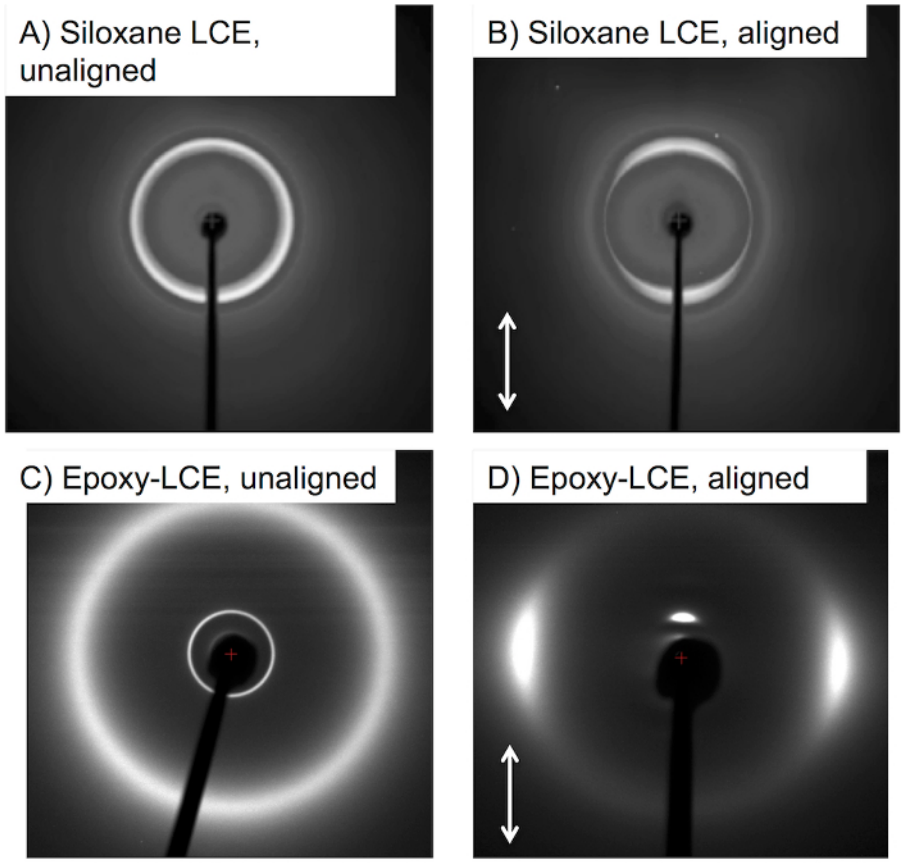


**Figure 2. 2-D X-ray diffraction from aligned LCEs.** Aligned LCEs exhibit anisotropic diffraction patterns due to liquid crystal alignment. The alignment direction is in the vertical direction as indicated by the white arrow in frames (**B** and **D**). Please click here to view a larger version of this figure.

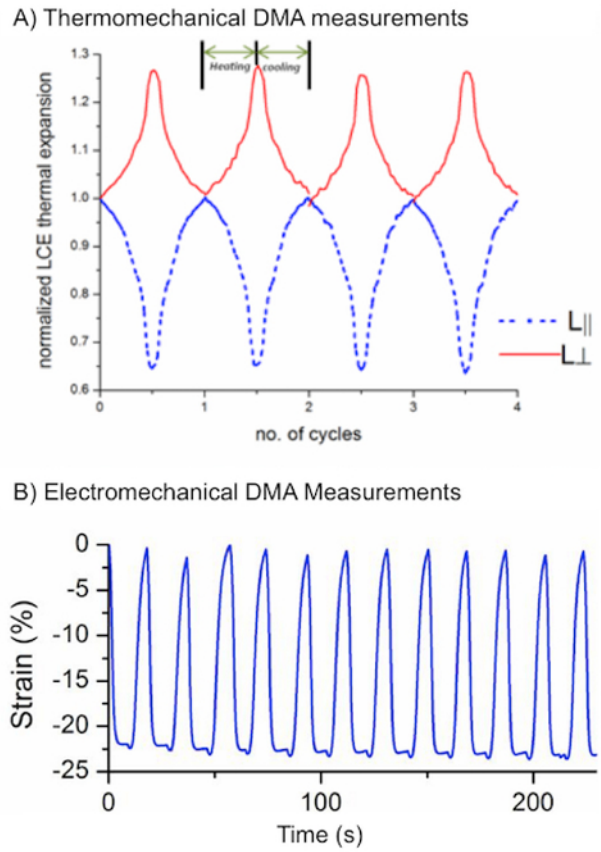


**Figure 3. Dynamic Mechanical Analysis (DMA) of shape-responsiveness in LCEs.** (**A**) thermomechanical measurements of a siloxane LCE for 4 heating and cooling cycles. The maximum contraction is 35% along the sample length. (**B**) Electromechanical strain measured in an LCE nanocomposite with a 40 V AC electrical potential turned on and off every 15 sec. Please click here to view a larger version of this figure.

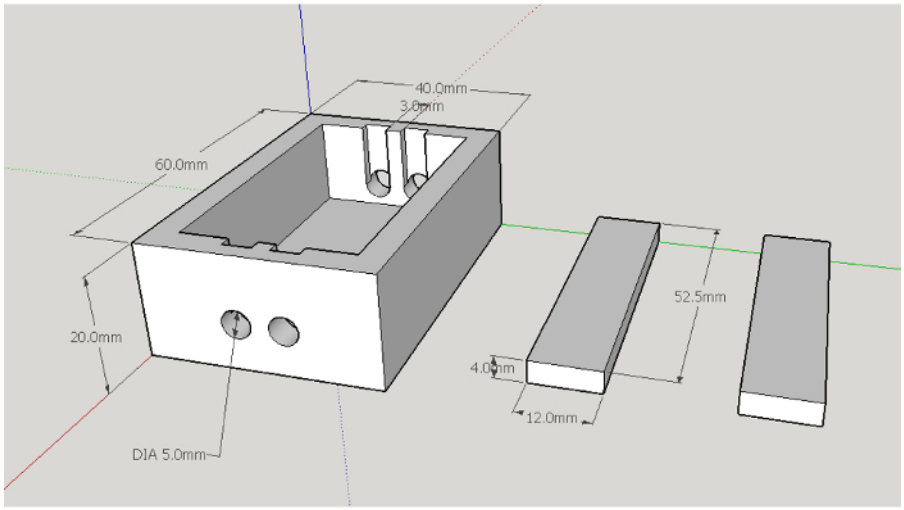


**Figure 4. Schematic of custom vessel for active cell culture.** Through holes allow for insertion of conductive carbon rods, which are secured and sealed at the edges using a silicone, bio-grade adhesive. The two plates are used to secure the LCE on one or both ends. Please click here to view a larger version of this figure.

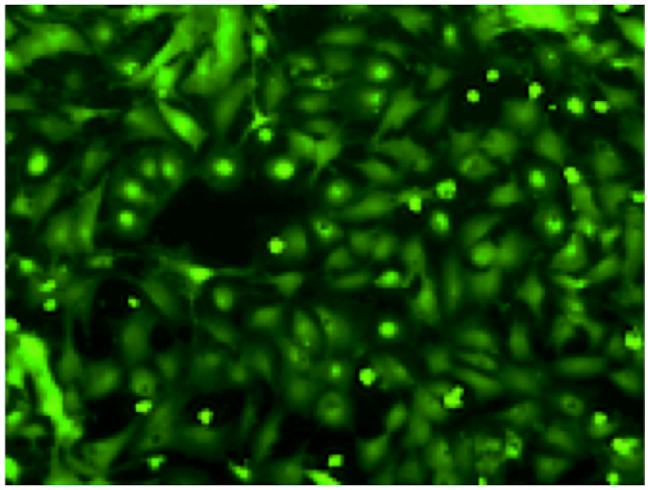

**Figure 5. Fluorescence analysis of cardiomyocytes on an LCE nanocomposite surface.** Cells are stained with Calcein AM, and live cells appear green. Please click here to view a larger version of this figure.

## Discussion

In order to produce monodomain LCEs, the LCEs need to be uniaxially loaded during crosslinking. This is challenging in practice because the LCE is loaded when it is only partially crosslinked, and therefore is not mechanically robust and can easily break or tear. The procedure described above (steps 1.1 - 1.4) can produce monodomain LCEs consistently. One critical step is the removal of the LCE from the PTFE mold for loading at the appropriate time. If the LCE is removed too quickly, it will easily break or tear. On the other hand, waiting too long before loading results in poor alignment of the final LCE. Another important step is the loading of the LCEs. Loading too much weight or loading the weight too quickly can result in the sample breaking or falling. While the protocol gave a specific load for aligning an LCE, the load can be adjusted for larger or thicker LCE samples. An important limitation of the procedure is the continuous, large-scale production of aligned LCEs. Each LCE substrate is aligned by hanging and loading.

LCE nanocomposites are produced by introducing conductive carbon black nanoparticles in two separate steps. This is important for achieving materials that are conductive and exhibit a stable electro-mechanical response for several days of continuous electrical stimulation. Prior work explored only surface infiltration of carbon black nanoparticles, but this produced LCE nanocomposites with an electromechanical response that degraded quickly.[21] LCE nanocomposites are prepared and aligned similarly to the pure LCEs, but are more delicate than the pure LCEs due to a lower network content. A reduced load is used in the preparation of LCE nanocomposites.

In the case of epoxy-based LCEs, alignment is more straightforward. At elevated temperatures, epoxy-LCEs exhibit reversible network crosslinking. Thus, the network synthesis and alignment can be carried out in separate steps. If done properly, the LCE will be significantly longer along the loading direction after alignment. The alignment in these materials can also be erased by heating the samples above 160 °C, and the materials can be re-shaped or re-aligned by applying a load at 160 °C or higher temperatures.

Implementation of LCEs for active cell culture presents a number of practical challenges. First, the LCEs must be sterilized. This is typically done using ethanol or exposing the sample to UV light. The surface of the LCEs is of low surface-energy, and therefore the LCE surface has to be modified to promote cellular attachment. One approach presented here is to deposit a thin layer of polystyrene by spin casting followed by rat tail collagen I. UV-ozone treatment is used to promote adhesion between the layers and remove organic contaminants. A common problem is ensuring uniformity of the top LCE surface in the case of the LCE nanocomposites. The surface becomes significantly rougher during the preparation of LCE nanocomposites. The surface can be cleaned by immersing in solvents to remove adhered nanoparticle and gently rubbing the surface with a spatula or cotton swab. Scotch tape is also an effective method to remove carbon black aggregates on the surface but has been found to be detrimental to cellular attachment and proliferation.

Liquid crystal elastomers are unique in that they exhibit a fully reversible shape response to a variety of external stimuli. One potential application is for dynamic cell culture, and the fabrication of 3-D LCE constructs[34] or electrospun fibers[35,36] could extend this work to scaffolds for cellular growth and engineering. LCEs also have applications in sensing, responsive surfaces,[37] and robotics.

## Disclosures

The authors have nothing to disclose.

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