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Preparation of Liquid Crystal Networks for Macroscopic Oscillatory Motion Induced by Light

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Abstract

A strategy based on doped liquid crystalline networks is described to create mechanical self-sustained oscillations of plastic films under continuous light irradiation. The photo-excitation of dopants that can quickly dissipate light into heat, coupled with anisotropic thermal expansion and self-shadowing of the film, gives rise to the self-sustained deformation. The oscillations observed are influenced by the dimensions and the modulus of the film, and by the directionality and intensity of the light. The system developed offers applications in energy conversion and harvesting for soft-robotics and automated systems.

The general method described here consists of creating free-standing liquid crystalline films and characterizing the mechanical and thermal effects observed. The molecular alignment is achieved using alignment layers (rubbed polyimide), commonly used in the display manufacturing industry. To obtain actuators with large deformation, the mesogens are aligned and polymerized in a splay/bend configuration, *i.e.*, with the director of the liquid crystals (LCs) going gradually from planar to homeotropic through the film thickness. Upon irradiation, the mechanical and thermal oscillations obtained are monitored with a high-speed camera. The results are further quantified by image analysis using an image processing program.

Video Link

The video component of this article can be found at https://www.jove.com/video/56266/

Introduction

The search towards sustainable energy is an area of growing interest in response to the depletion of fossil energy and climate change. Methods to convert light energy into mechanical work are currently being investigated, such as photovoltaics to generate electricity, biomass to produce fuels, solar water splitting to produce oxygen and hydrogen. However, all these processes fueled by light require multiple steps before their energy production can run machines that perform work. Although these approaches offer a large panel of applications, they require production, storage and transport of intermediates (*e.g.*, electrical potential, chemical fuels). Hence, devices able to convert directly sunlight into macroscopic motion present advantages of simplification.

In the last decades, many examples of photo-actuators have been developed where polymers change shape upon irradiation[1,2,3]. However, in the large majority of these examples, continuous actuation requires turning the light on/off to switch from one state to the other. So far, only a limited number of photo-responsive materials working out-of-equilibrium has been described[4,5,6,7]. Systems based on liquid crystal networks (LCNs)[8,9,10,11,12,13] are also investigated because of their intrinsic anisotropy that allows for preprogramming the deformation in a controlled fashion[14]. Recently, it was reported that the photo-thermal effect induced by excitation of photo-stabilizers incorporated in LCN can generate oscillatory motion[15].

Here, the method to create LCN films that mechanically oscillate under continuous light irradiation is described. The conception of the films is detailed from the preparation of the cells to the characterization and the polymerization of the LC mixtures. The photo-actuation of the LCN films and the analysis of the motion are also reported. The LCNs are doped with molecules that can quickly dissipate light into heat within the network, which induces anisotropic thermal expansion and subsequent macroscopic deformation of the film. An interplay between self-shadowing, temperature variation and contraction/elongation of the material gives rise to the oscillatory motion[15]. The precise setup, including the orientation of the light and the sample to obtain this effect is highlighted in the protocol. The oscillation is characterized by its frequency and controlled by the properties of the LCN. To our knowledge, this is the first description of a method for the creation of LCN films that can self-oscillate, by a simple mechanism working with a broad range of dopants.

Protocol

NOTE: The overall procedure is detailed in **Figure 1**.

1. Preparation of Cells

1. Cleaning of glass plates
    1. Carefully clean 3 cm x 3 cm glass plates using soap and hot water to remove contaminations (**Figure 1A**).
    2. Place the glass plates in a beaker and cover with ethanol 99.5% (**Figure 1B**).
    3. Place the beaker in an ultrasonic bath for about 10 min.
    4. Carefully dry the glass plates with a tissue and blown air.
    5. Make sure that there is no trace of solvent, dust, or any type of contamination left on the plates.
       NOTE: The glass plates are now clean and should be manipulated with gloves.
    6. Place the glass plates in an UV-ozone photoreactor for 20 min in order to remove any organic residues. After the ozone treatment, the
       plates are ready for the coating step (**Figure 1C**).

2. Coating of glass plates
    NOTE: Two sets of coated plates are prepared: one set with a planar alignment layer and the other with a homeotropic alignment. In a later
    stage, the cell will be composed of one planar glass plate and one homeotropic glass plate (**Figure 1D**).
    1. Air blow a glass plate and place it on the spin coater.
    2. Deposit the polyimide solution onto the glass plate to cover the entire surface (about 0.5 mL of solution).
    3. Spin coat the alignment layer according to the following conditions: Program 1: 5 s at 17 x g and acceleration of 11 x g/s; Program 2:
       40 s at 420 x g and acceleration of 17 x g/s.

3. Curing of the alignment layers
    1. Place the coated glass plates on a hot plate at 110 °C for 10 min in order to remove the majority of the solvent present in the alignment
       layer mixture (**Figure 1E**).
    2. Mark the glass plates (on the non-coated side) with distinctive signs to recognize the homeotropic and the planar alignment layers. A
       small arrow is usually helpful for the planar glass plate since it also indicates the rubbing direction described in a later stage (**Figure
       1F**).
    3. Once all the glass plates are coated, and the solvent is removed, place the glass plates in an oven at 180 °C for 1 h to cure the
       polyimide layer (**Figure 1G**).
       CAUTION: This step involves extremely hot temperatures; wear gloves, eyeglasses and appropriate personal protection.
    4. After baking the glass plates, let them cool down to room temperature.
       NOTE: To prevent any contamination between each step, it is recommended to place a protective foil over the glass plates.

4. Rubbing the planar alignment layer
    1. Rub the glass plates coated with the planar alignment layer in order to create (sub) microchannels in the layer that will guide the LC in
       one direction. To do so, place the glass plates with the coated side downwards on a velvet cloth. Apply a uniform and soft pressure with
       two fingers. Carefully drag the glass plate along the surface of the velvet cloth in a straight direction. Lift the glass plate and repeat the
       same operation three times (**Figure 1H**).
       NOTE: It is crucial to rub the plate in a single direction and only while going forward. Going back and forth in a straight direction will
       result in a poor alignment.

5. Gluing the cells
    1. Air blow the glass plates using the air blower.
    2. Prepare the adhesive by mixing a UV-curing glue with spacers (glass beads) having a well-defined diameter of 20 µm.
    3. Take a glass plate coated with a planar alignment layer and one glass plate coated with a homeotropic alignment layer. Place two tiny
       drops of glue at two adjacent corners of the planar glass. Then place two other drops of glue at about 5 mm from the two last corners
       (**Figure 1I**).
    4. Take the homeotropic glass plate and place it on top. Leave a gap of about 4 mm between the edges of the glass plates to provide
       enough space for the LC mixture. Make sure that the coated sides are facing each other.
    5. Cure the glue by placing the cell for 2 min under UV light.
       CAUTION: UV light is hazardous; wear gloves, eyeglasses and appropriate personal protection.

2. LC Mixture Preparation and Characterization

1. Components
    1. Weigh 97.5 mg of the LC diacrylate 1, 2.5 mg of photo-stabilizer and 1 mg of photoinitiator in a brown glass vial (**Figure 2**). Because of
       the sensitivity of the initiator, prevent UV light exposure to the mixture as best as possible.

2. Homogenous mixing of the powders
    NOTE: This step is performed in a chemical hood.
    1. Add 3 mL of dichloromethane (DCM) to the above components and shake until the solid is fully dissolved.
    2. Place the vial on a hot plate at 30 °C for 30 min and add a flow of argon to promote the quick evaporation of the DCM.
       NOTE: It is recommended to place the vial in vacuum to remove any residual trace of DCM.

3. Observation under Polarized Optical Microscope (POM) for phase transition determination
   1. Once the mixture is fully dry, place a small amount (± 10 mg) between two glass plates coated with the planar alignment layer.
      NOTE: In order to characterize the phases properly, it is recommended to use unrubbed planar glass plates.
   2. Place the slides in a POM equipped with a hot stage. Heat up the cell until the image turns black (using crossed polarizers) indicating the isotropic phase.
   3. Slowly cool down the hot plate and note the transition temperatures. For the mixture described above, the isotropic to nematic transition is at 103 °C and the nematic to smectic transition occurs at 86 °C (**Figure 3A**).

3. Film Preparation

1. Filling of the cells (**Figure 1J**)
   1. Place the cell on a hot plate with the homeotropic side upwards. Set the temperature to 110 °C (isotropic phase) to facilitate the filling of the cell because the fluid is less viscous than in the nematic phase.
   2. Place part of the solid mixture on the edge of the cell.
   3. The solid melts and the liquid mixture flows by capillarity in the cell. Add more mixture at the edge until the cell is filled.

2. Cooling to the nematic phase and polymerization (**Figure 1K**)
   1. Once the cell is filled, slowly cool it down (5 °C/min) to 90 °C to be in the nematic phase.
   2. As soon as the film is at the right temperature, polymerize the mixture by placing it under UV light at 90 °C for 30 min.
      CAUTION: UV light is hazardous, it is advised to perform the polymerization in a protected environment.
   3. A post-baking step is recommended to ensure the full polymerization of the network. Place the cell on a hot plate at 130 °C for about 10 min and let it slowly cool down to room temperature.

3. Opening of the cell and cutting of the sample
   1. To open the cell, put a razor blade at one edge and push it in between the two glass plates. The cell opens at once (**Figure 1L**).
   2. To peel off the film, lift a small corner with a razor blade. If needed, the glass plate can be placed in hot water to facilitate the removal of the film (**Figure 1M**).
   3. Remove the film from the water and gently peel it.
   4. Cut a stripe along the molecular director (rubbing direction of the planar side) of the film having the following dimensions: 4 mm x 2.5 cm (**Figure 1N**).

4. Self-oscillation Observation

1. Setup in the lab
   1. Clamp the sample using a self-closing tweezer in such a way that 1.7 cm of the film is free to move.
   2. Hold the sample vertically and direct the light emitting diode (LED) beam (400 mW/cm^2) perpendicular to the sample. Typically, the light is about 20 cm away from the sample. The light should reach the top of the film, below the tweezer (**Figure 4**). The oscillations obtained are recorded with a high-speed camera (150 frames/s) and analyzed with an image processing program.

2. Setup with direct sunlight
   1. Proceed as described above in steps 4.1.1 but instead of using the LED light, focus the sunlight on top of the film with a lens.

3. Measurement of the thermal effect
   1. Measure the temperature variation in the oscillating sample using a thermal camera[15] (40 frames/s).

Representative Results

The success of the protocol is the observation of the oscillatory motion of the film under light irradiation. Oscillations are large and no misleading result can be seen. Moreover, the oscillations are stable over time (timescale of hours) and little fatigue was observed.

Among others, the quality of the splay alignment is of importance for the accomplishment of the self-sustained actuation (**Figure 5A**). The gradient in molecular orientation throughout the thickness of the film induces a contraction/expansion at the planar/homeotropic sides of the film upon actuation[16,17,18]. This asymmetric response enhances the macroscopic motion. The failure of the experiment (absence of bending, small deformation or odd bending) can be explained by a poor LC alignment. First, the film should be transparent. (**Figure 5B**). To verify the correct splay alignment in a simple step, the film attached to the glass substrate is observed between crossed polarizers above a diffused white light source(**Figure 5C-E**). By rotating the film between the cross polarizers from 0° to 45° in the xy plane, the film should sharply change brightness. By pivoting the film out of the plane around the molecular director, the film should change color from black (in plane) to white (out of plane) while viewing from the top. Similar verification steps can be done prior to polymerization by observing the cell through a polarizer on top of the hot plate covered with an aluminum foil. Moreover, when the film is cut in strips, it presents a natural curvature with the center of the curve in the homeotropic side. This is due to the residual stress originating from the polymerization at an elevated temperature, where the expansions of the two sides of the film have opposite signs (**Figure 6A**). In case the alignment is not successful, the method to prepare the polyimide layers should be reconsidered. The production of those cells is crucial to obtain well-aligned films. The most critical step is the rubbing: a too strong pressure on the plate will remove partially the polyimide layer and result in a very poor command layer for alignment. At room temperature the film is in the glass state (**Figure 3B**). If the film is soft and/or tacky, it means that the polymerization is not completed, most probably because the irradiation time is too short or the initiator is degraded. The mixture of LC mesogens should be homogeneous and dry before the filling of the cell, because the presence of solvent might influence the phase behavior of the LC mixture. The LC mixture should be aligned prior to polymerization. Precautions should be taken to avoid thermal polymerization during the process of alignment by going through the steps rapidly and not heating the sample above 130 °C for a prolonged time. Filling the cell just above the clearing point is sufficient (110 °C).

The mechanical and thermal oscillations registered by the high-speed camera confirm the success of the presented protocol (**Figure 7; Video 1**). When the film is clamped at one end, leaving 1.7 cm free to move and irradiated at the planar side with focused light, it unbends towards the flat state in the direction of the light (**Figure 6B**). The hinge is located at the position of the focus point of the light (**Figure 4**). The film should move smoothly, perpendicular to the clamp and not on the side. Then the film starts to move continuously with oscillations of frequency 7.6 Hz ± 5% and amplitude 30 ° ± 10% for a film of dimensions 1.7 cm x 0.4 cm x 20 μm. The thermal oscillations measured with the thermal camera present the same frequency (7.4 Hz ± 5%), with a slight phase delay due to the inertia of the film. This frequency f is governed by the dimensions and the modulus of the film[15]. The amplitude of the oscillations varies with the light intensity and will be influenced by the setup, and in particular, the positioning of the focus point of the light on the sample. The mechanism of oscillation is as follows: 1) the curled film is irradiated with focused light, the dopant absorbs the light and converts it into heat, the film warms up at its hinge and unbends in the direction pre-defined by the LC alignment; 2) the tip shadows the hinge of the film, which induces a decrease of its temperature and its subsequent unbending by relaxation; 3) the hinge is again under irradiation, warms up and the film bends[15]. The repetition of these successive steps gives rise to the oscillations. The key factors in observing this phenomenon are the photo-thermal effect and the self-shadowing of the film, controlled by the intensity and the position of the focused light (**Figure 4**). For instance, a slightly tilted lamp will induce a complete curling of the sample. Moreover, too low of a light intensity does not give large bending because the temperature at the hinge is insufficient, while too high of a light intensity on the hinge will induce overshooting (**Figure 6C**, 180 ° bending of the film). Another requirement for the success of the experiment is to place the setup in an environment protected from wind to avoid perturbation.
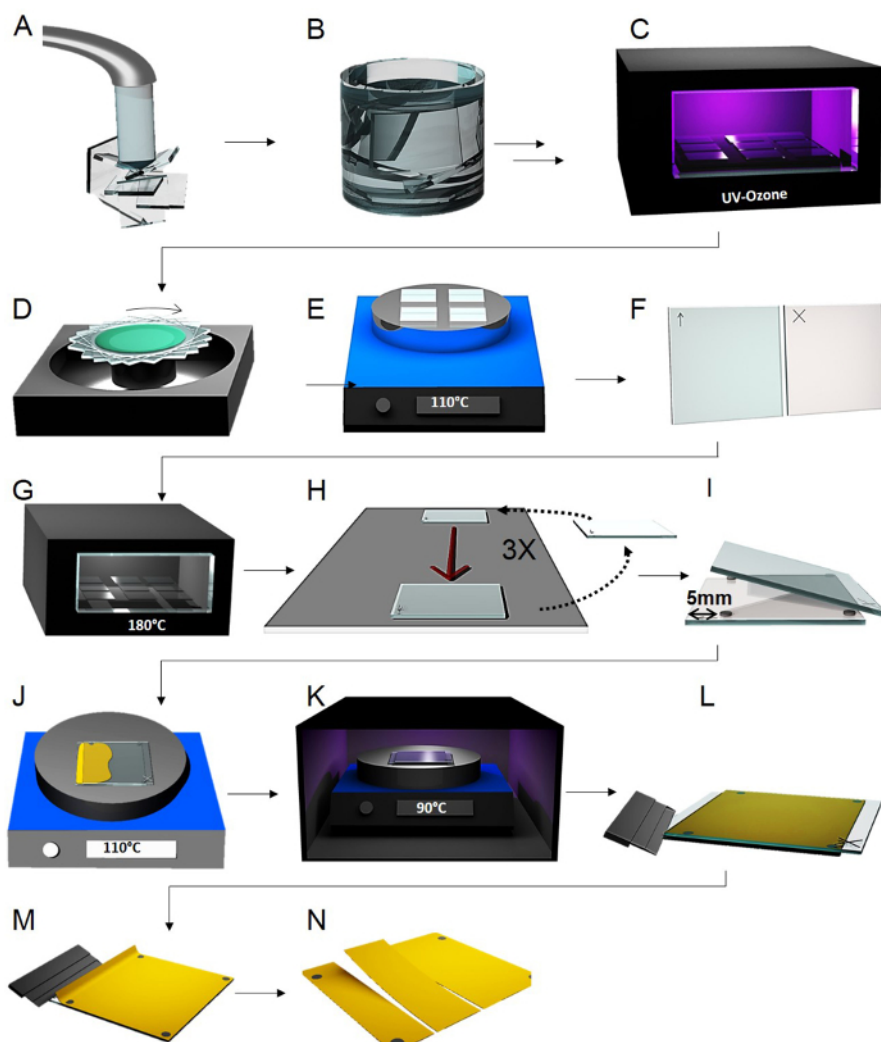
Figure 1. **The Overall Procedure to Obtain the Splay Aligned LCN in 14 Steps (From A-N).** Steps **A-C**: cleaning of the glass plates; steps **D-G**: coating of the glass plates to create planar or homeotropic alignment layers; step **H**: rubbing of the glass plates using a velvet cloth; step **I**: gluing the plates to form the cell; step **J**: filling the cell with the LC mixture and alignment in the nematic phase; step **K**: photo-polymerizing under UV light; steps **L-N**: opening of the cell and cutting of the film to obtain a strip. Please click here to view a larger version of this figure.
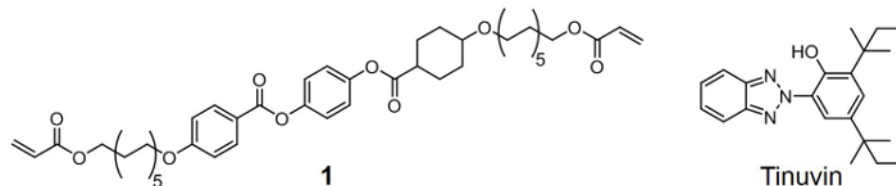

Figure 2. **Chemical Structures of the Components Used.** Please click here to view a larger version of this figure.
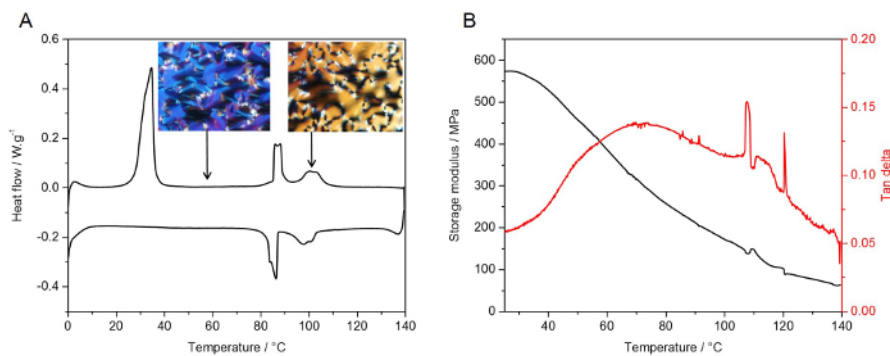
Figure 3. **Thermal Characterization of the Monomer Mixture and Polymer Film. A)** Differential scanning calorimetry (DSC) of the mixture prior to polymerization to determine the phase transitions. Insets: POM pictures, scale bars: 100 µm. **B)** Dynamic mechanical thermal analysis (DMTA) measurement of the polymeric film. Please click here to view a larger version of this figure.
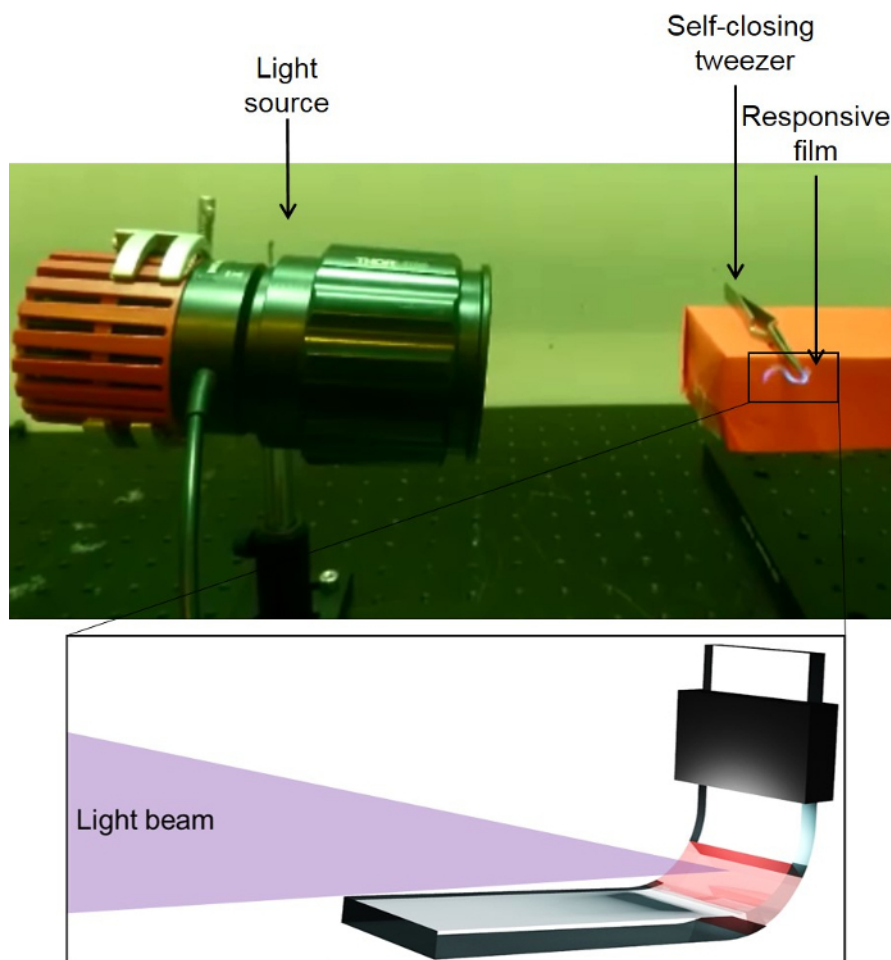

Figure 4. **Picture of the Setup Showing the LED on the Left Side, and the Oscillating Film Clamped to the Tweezer in Front of the Light.** The inset shows the schematic representation of the bended film and the localized light illumination. The red area corresponds to the warm hinge mentioned in the text. Please click here to view a larger version of this figure.
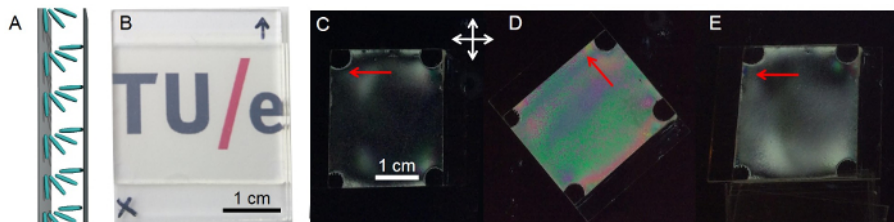
Figure 5. **A**) Schematic representation of the splay alignment. **B**) Picture of the glass cell in front of the TU/e logo showing the transparency and the absence of color of the film. The arrow indicates the rubbing direction of the planar glass plate. **C-E**) Pictures of the film taken between crossed polarizers showing the characteristics of the splay alignment (**Picture D**: rotation of 45 ° in the XY plane, **Picture E**: pivoting out of the xy plane). The molecular director of the alignment is indicated by the red arrow. Scale bar: 1 cm. Please click here to view a larger version of this figure.
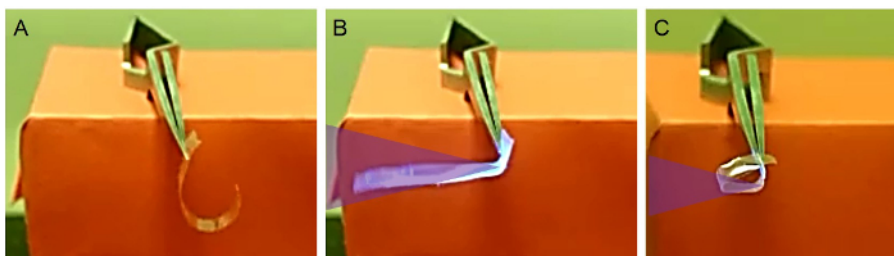

Figure 6. **A**) Picture of the film clamped with a tweezer showing a natural curvature with the center of the curve in the homeotropic side. **B**) Picture of the film going to a flat state upon photo-irradiation (365 nm, 0.52 W/cm^2). **C**) Picture of a film irradiated with too high of a light intensity showing a bending at 180 °. Please click here to view a larger version of this figure.
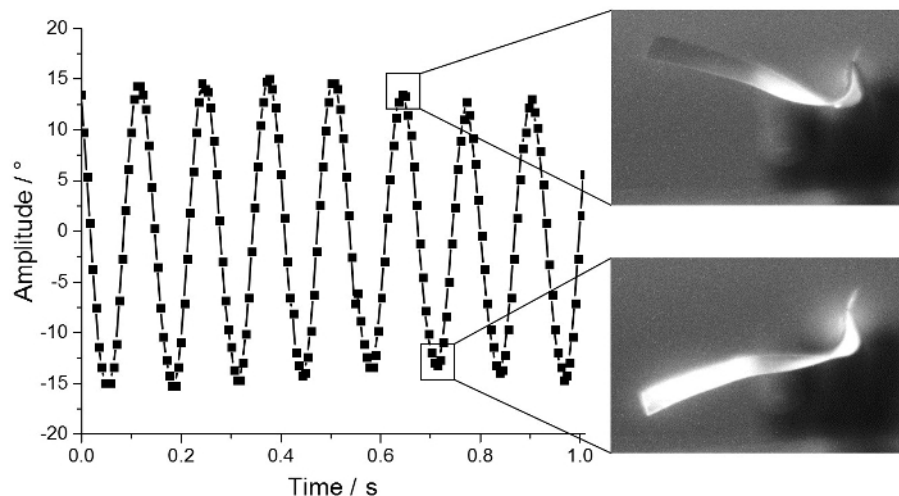
Figure 7. **Mechanical Oscillations of the Tip of the Film Over Time During Irradiation with UV Light (LED 365 nm, 0.52 W/cm^2)**. Insets: Screenshots of the moving film recorded with the high-speed camera. The film geometry is 1.7 cm (length) x 0.4 cm (width) x 20 µm (thick). Please click here to view a larger version of this figure.
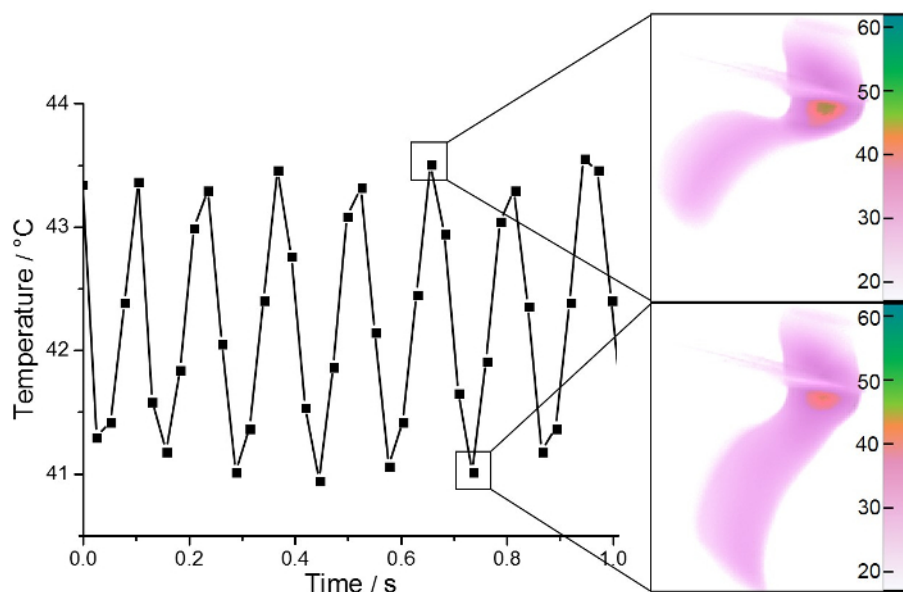
Figure 8. Thermal Oscillations of the Exposed Area (Hinge) Over Time During Irradiation with UV Light (LED 365 nm, 0.52 W/cm^2). Insets: Screenshots of the oscillating film with the temperature profile registered with the thermal camera showing the changes of temperature at the hinge. The film geometry is 1.7 cm (length) x 0.4 cm (width) x 20 μm (thick). Please click here to view a larger version of this figure.

Discussion

The results described here are comparable with the previous study[15] on a LC diacrylate with a spacer of 6 carbons. It shows that the method to obtain oscillation can be applied to films with different mechanical properties[16].

The preparation of a photo-thermal responsive LCN is reported. There are a few steps in the described protocol that are critical, such as the rubbing of the planar alignment layers and the preparation of the cell. Indeed, the success of the protocol relies on the high quality of the LC splay alignment, which also limits the application to thin films.

Previously, many examples of photo-actuators based on LCNs that contain a large quantity of photo-switches have been reported[11,12,13,19]. The main advantages of the method developed here are the limited quantity of dopants needed to observe the actuation (< 5 wt%) and the broad choice of dopants available.[15] These results expand the range of potential applications. Moreover, the power of this protocol is the ability to vary the frequency and the amplitude of the oscillation by changing the modulus of the film with a different matrix composition, the dimensions of the stripe and the light intensity.

This methodology can be readily extended to fabricate a broad range of LC materials for automated systems. The protocol described herein paves the way to the development of non-equilibrium systems for soft-robotics and automated materials.

Disclosures

The authors have no conflict of interest.

Acknowledgements

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