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Direct Ink Writing of a Light-Responsive Underwater Liquid Crystal Actuator with Atypical Temperature-Dependent Shape Changes

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In the recent years, light-responsive liquid crystal (LC) polymers have been studied as promising materials for the fabrication of untethered soft actuators. The underwater behavior of these advanced materials has, however, been rarely investigated. This paper reports on the fabrication of light-responsive amphibious LC actuators via direct ink writing (DIW). The actuators present two underwater deformation modes triggered by different stimuli. Temperature induces contraction/expansion and light induces bending/unbending. Unexpectedly, temperature can regulate the bending directionality, giving the material additional versatility to its deformation modes. These findings serve as a toolbox for the fabrication of light-responsive actuators via DIW that operate in air and underwater.

1. Introduction

Untethered liquid crystalline (LC) actuators are of increasing interest in many applications including microfluidics, biomaterial engineering, and soft robotics.[1] Typically, these actuators respond to external stimuli such as temperature,[2–5] humidity,[6,7] light,[8–11] or magnetic fields.[12,13] Among them, light is a versatile and promising platform to control the movement of these actuators in an easy and rapid manner.[14,15] Light-responsive LC actuators have been previously obtained by introducing azobenzene photoswitches.[16,17] Although considerable progress has been achieved in photoactuation in air,[8,9,18–20] there are few examples of LC actuators that are responsive underwater.[21,22] Additionally, it has been shown that by utilizing humidity, the light response of an LC film can be enabled or disabled.[19] Furthermore, temperature can enhance the extent of motion[23] or reverse the directionality of the light-driven bending motion.[24] These examples demonstrate the potential of combining different stimuli-responses in a single material to increase the versatility and control of actuation. Thereto, it is interesting to explore and design new LC precursors to obtain light-fueled actuators active underwater and investigate the effect of other stimuli, such as temperature, in their photoactuation.

For the fabrication of soft actuators, additive manufacturing (AM) is an attractive method.[25] AM has the ability to rapidly fabricate complex 3D objects at different length scales using a variety of materials.[26] In recent years, the direct ink writing (DIW) of liquid crystal elastomer (LCE) has emerged as a promising approach to fabricate soft actuators displaying distinct deformation modes.[2,27–35] Until now, most of these LCE-based actuators fabricated via DIW have shown reversible temperature-triggered shape changes, but no example shows light-triggered motion. It would be appealing to develop inks suitable for DIW equipment that can be used to fabricate light-responsive LCE actuators.

Herein, we developed an LCE-based ink for the fabrication of temperature- and light-responsive amphibious actuators via DIW. The ink was first tested on fibers drawn from droplets on a glass surface, as this method has some similarities with respect to the DIW process. Photoactuation of the fibers showed an atypical bending away from the light source motion. We determined that the underlying mechanism for this response is a smectic C (Sm C) to smectic A (Sm A) photoinduced phase transition. This same ink was then used to fabricate a light-fueled underwater LCE-based actuator via DIW. The planar aligned film contracted/expanded in response to temperature changes and bent away from the light source when illuminated at room temperature. Interestingly, when the film was photoactuated at ≈60 °C in water, it bent toward the light source. This temperature-dependent directionality of the light-triggered bending motion is the result of the different LC phases obtained.
at different temperatures. As a result, a temperature-controlled light-induced bending of the film is achieved.

2. Results and Discussion

2.1. Light-Responsive Ink for Direct Ink Writing

An LC-based ink for the fabrication of amphibious light responsive actuators via DIW equipment needs to fulfill two critical parameters: 1) shear thinning to achieve control over the molecular alignment during printing\cite{31,33} and 2) incorporation of a reactive azobenzene molecule as a crosslinker in order to get a photoresponse underwater\cite{22} preferably in the main chain oligomer since this enhances the extent of the photoactuation.\cite{36} Taking these requirements into account, we modified an already reported ink for fiber drawing\cite{23} by incorporating the azobenzene into the main chain LC oligomer (Scheme 1). The chemical composition for the oligomer consists of reactive mesogens 1,4-bis-[4-(6-acryloyloxyhexyloxy) benzoyloxy]-2-methylbenzene (1), photoresponsive moiety 4,4′-bis(6-acryloyloxyhexyloxy) azobenzene (2), and isotropic chain extender 3,6-dioxa-1,8-octanediithiol (3). The acrylate-terminated main chain LC oligomer was synthesized via a base-catalyzed thiol-Michael addition reaction with a slight excess of acrylate versus thiol. After chain extension, the 1H-NMR spectrum shows signals between 6.40–5.70 ppm (Figure S1, Supporting Information), implying the presence of acrylate end groups. As evidenced in the gel permeation chromatography (GPC) spectrum (Figure S2, Supporting Information), the characteristic absorption of trans-azobenzene peak at ≈365 nm and the absorption of the other moieties at ≈250 nm are at the same retention time, revealing that azobenzene molecules were indeed incorporated into the main chain oligomer. Based on GPC data, the weight average molecular weight was evaluated as ≈18 000 g mol$^{-1}$. Differential scanning calorimetry (DSC) traces and crossed polarized microscopy showed a smectic to nematic phase transition temperature ($T_{Sm/N}$) at ≈49 °C and a nematic to isotropic phase transition temperature ($T_{Ni/I}$) at 81 °C (Figure S3, Supporting Information).

Characterization of the photoactuation of the resulting LCE network was first performed by drawing fibers standing on a glass substrate using a previous reported procedure.\cite{23} This fiber drawing method has many similarities with DIW (vide infra) with respect to precursor rheology, polymer properties after UV curing, and response to light for actuation. The fibers had a diameter of ≈120 µm and a length of ≈9 mm. DSC traces of the fiber revealed a glass transition temperature ($T_g$) at approximately −16 °C and a broad $T_{Ni/I}$ centered at 74 °C (Figure S4, Supporting Information). The photoactuation of the fibers was investigated in air, at room temperature, and under the illumination of both UV (365 nm, 75 mW cm$^{-2}$) and visible (455 nm, 30 mW cm$^{-2}$) lights. Unexpectedly, when exposed to UV light, the fibers bent away from the light source (Figure 1; Movie S1, Supporting Information). A maximum bending angle of approximately −62° was achieved within 60 s of UV irradiation (Figure 1). Recovery to the unbent state was achieved by illuminating with visible light. These results show that here the effect of placing the azobenzene in the main chain oligomer does not only enhance the extent of the photoactuation at room temperature as previously reported,\cite{36} but it also reverses the bending direction. This bending motion away from the light was reversible for over 12 cycles of alternating UV and visible light with no signs of fatigue (Figure S5, Supporting Information).

LC actuators showing a directed motion away from the light source have been previously reported.\cite{24,37} In one case, fibers presenting side-chain azobenzene photoswitches bent away from the light source as a result of a free-volume generation from the cis-isomer at the illuminated surface.\cite{37} However, the current work employs the azobenzene as a crosslinker and this mechanism is therefore unlikely. In the other case, the uniaxial film that bent away from the light was the result of a photoinduced smectic (Sm) to nematic (N) transition that occurred at the illuminated surface.\cite{24} A similar mechanism could be
responsible for the heretofore observed actuation directed away from the light source. Therefore, the mesogenic phase of a fiber under different illumination conditions was investigated by 2D small-angle X-ray scattering (2D-SAXS). As shown in Figure 1, in the small angle region, we observed a typical Sm C pattern with four small lobes before irradiation. Upon illumination with UV light, the four diffraction arcs integrated into two diffraction arcs, revealing the formation of a Sm A phase. After light irradiation, the average layer spacing increased from 46.5 Å with a tilt angle of 13° to 48.5 Å with no tilt. Furthermore, the Sm C to Sm A phase transition was not visible in the temperature-dependent 2D-SAXS measurements (Figure S6, Supporting Information), indicating that the phase transition was induced by the cis-azobenzene population formed by UV light illumination. We calculated the fractional layer spacing increase and the length increase at the illuminated surface (see Supporting Information). These calculations reveal that the bending away from the light motion is the result of the light-induced Sm C to Sm A phase transition, which is macroscopically manifested by an anisotropic expansion at the illuminated surface.

### 2.1. Direct Ink Writing of a Uniaxial Light-Responsive Polymer Film

The same LC-based ink was used for DIW to fabricate a uniaxial, light-responsive polymer film. The correlation between the alignment and the printing speed (2–13 mm s⁻¹) was investigated first (Figure S7, Supporting Information). The printing temperature was set to 40 °C and the nozzle diameter was 335 μm. Lines printed at speeds < 6 mm s⁻¹ displayed a non-variant brightness regardless of the orientation of the polarizer or analyzer, indicating different molecular orientations in the lines. Lines printed with speeds > 6 mm s⁻¹ were darker when parallel to the polarizer or analyzer than when at 45°. Such dark–bright states are associated with an oriented LCE along the axis of the printed line, that is, printing direction. This was further confirmed by a supplementary optical characterization using the dichroism from the azobenzene (Figure S8, Supporting Information). From this data, the optimal printing speed was set to 13 mm s⁻¹.

With the optimized printing parameters, we printed a single-layer film (5 × 20 mm) on top of a glass substrate coated with polyvinylpyrrolidone (PVP) acting as sacrificial layer (Figure 2). After photopolymerization at room temperature, the LCE-film between crossed polarizers was darker when the longitudinal axis of the film was parallel to the polarizer or analyzer than when the axis was at 45° (Figure 2). This clearly indicated that the molecular orientation was achieved and successfully fixed, that is, a planar LCE-film was fabricated via DIW. Using a contact profiling system, we determined the thickness of the film to be on average 78 μm. After optical and structural characterization, the film was detached from the glass substrate by dissolving the PVP layer to obtain a free-standing film. Finally, the DSC traces of the film showed a T of around 82 °C, a significantly broad T around 44 °C, and T at ~25 °C, which is similar to the fibers (Figure S9, Supporting Information).

### 2.2. Stimuli-Response of the Printed LCE-Film

#### 2.2.1. Characterization of the LCE-Film in Air

We first investigated the temperature-triggered response of the film using an oven. As previously reported for planar LCE-films, the film contracted along its long axis, parallel to the molecular director, and expanded perpendicular upon a temperature increase (Figure 2). When plotting the longitudinal shrinkage ratio (L/L₀) as a function of temperature, different stages of the response were observed (Figure 2). From 30 °C to ~40 °C, an increase of the film’s length occurred due to the anisotropic thermal expansion. Then, a first actuation region was observed from ~40 °C until ~60 °C in which the film contracted because of the Sm C to N phase transition. A second actuation occurred from ~60 °C to ~80 °C, in which the film’s length was
further reduced due to the N to isotropic (I) phase transition. The second one being steeper due to the reduced temperature range at which the N to I transition occurs as seen in the DSC traces (Figure S9, Supporting Information). At \( \approx 80 \) °C, the film was in its I phase and reached its maximum contraction, being around 50% of its initial length. From \( \approx 80 \) °C to 125 °C a slightly positive length increase was observed due to the thermal expansion of the network. When cooling to 30 °C the film recovered its initial length (Figure S10, Supporting Information). The reversible temperature-dependent anisotropic contraction/expansion further confirms a homogeneous planar alignment through the thickness of the film.

To study the photoactuation, the printed LCE-film was clamped and hung on a stand as shown in Figure S11, Supporting Information. The film bent away from the light source as previously observed in the fibers (Figure 3; Movie S2, Supporting Information). Surprisingly, the response was obtained at lower light intensities; one order of magnitude smaller. We characterized the photoactuation by tracking the film’s endpoint displacement under different light intensities and over time (Figure 3). Increasing the light intensity increased the maximum bending angle until a plateau was reached. The maximum bending angle was attained after 5 min of 365 nm light (1.1 mW cm\(^{-2}\)) illumination. We recorded the film’s surface temperature with a high-speed thermal camera (Figure S12, Supporting Information). No significant increase on temperature was observed during photoactuation, which indicates that the bending motion is mostly governed by photomechanical effects. When the light was turned off, the film remained in the bent state due to the long lifetime of the cis-azobenzene moieties at room temperature.[22] Hence, different metastable bending angles could be obtained at different low light intensities (Figure S13, Supporting Information). Reversion to the initial shape, through 455 nm light (0.8 mW cm\(^{-2}\)) irradiation, took around 1 min. It is worth mentioning that when the film was exposed from the other side, it still bent away from the light source. The actuation rate of the film was slower than the photoactuation in the fiber. We speculate that the difference arises from the different geometries, objects sizes, and the lower light intensity used to actuate the film. Finally, the reversibility of
the photoactuation is demonstrated in Figure 3 in which after 10 cycles of alternating UV and visible light the film showed no signs of fatigue, similar to that previously observed for the fibers (Figure S5, Supporting Information). These results show that the printed LCE-film displays two different responses triggered by two distinct stimuli: light induces bending/unbending and temperature induces contraction/expansion.

2.2.2. Temperature-Dependent Photoactuation in Water

The underwater photoactuation was first studied by placing the hanging film in water at 20 °C, at which the polymer is in its Sm C phase (Figure 4; Figure S11, Supporting Information). Upon illumination with a 365 nm light (1.1 mW cm\(^{-2}\)), the film bent away from the light source (Figure 4; Movie S3, Supporting Information). When the light was turned off, the film remained mostly bent, and slightly returned to its initial shape. Only when illuminated with 455 nm illumination (0.8 mW cm\(^{-2}\)) did the film bend back to its initial state. The photoresponse in water at 20 °C showed a similar motion as in air while having a larger amplitude of actuation. If the thermal contribution to the back isomerization of the azobenzene moieties (cis–trans) is absent, as water acts as a heat sink, this might result in an overall higher cis-isomer population, hence in a larger actuation upon irradiation underwater in comparison with air.[22,38,39] Drag forces in water were not observed to have a negative influence on the actuation amplitude.

Furthermore, we investigated the photoresponse of the polymer network in its N phase by heating the water to 60 °C. Upon illumination with 365 nm light the film bent toward the light (Figure 4). After turning the light off, the film slowly returned to its initial state unlike in the experiment at 20 °C where the film remained stationary. In this case, the elevated temperature most likely reduces the lifetime of the cis-isomers. This reveals that it is difficult to keep the metastable state at higher temperature. Upon exposing the film to a 455 nm light, the film recovered faster to the unbent state. Figure S14 and Movie S4, Supporting Information, show a second actuation cycle at 60 °C in which a reduced time period between the illumination with 365 and 455 nm lights was used. In this second cycle, the photo-induced back isomerization is faster than the thermally induced one. In contrast to what occurs at room temperature (vide supra), at 60 °C the LCE-film is in its N phase and so isomerization of the azobenzene led to an increase of disorder in the network resulting in a contraction along the molecular axis and expansion perpendicular in the illuminated surface resulting in a bending motion toward the light motion.[40] It should be noted that the temperature-dependent photoactuation was also observed for the drawn fibers showing that the atypical response is related to the light responsive ink (Figure S15, Supporting Information).

The temperature-dependent photoactuation of the film was further tracked by cooling the water from 60 to 20 °C while maintaining a constant UV light illumination (Figure 4). At 60 °C, the film bent toward the light source. While decreasing the temperature from 60 °C to ≈47 °C, the film maintained a constant deformation. Upon further cooling from ≈47 to 30 °C, the LCE network underwent a gradual phase transition from...
Figure 4. Temperature-dependent photoactuation of the printed LCE-film in water. a) Schematic representation and side-on images of the film during actuation as a response of two different stimuli: light and temperature. Temperature changes the LC phase of the film, from Sm C to nematic or vice versa. In the Sm C phase at low temperature, the film bends away from the light source. At high temperatures, in the nematic phase, the film bends toward the light source. Also, at elevated temperature the presence of convection flow, from right to left (as seen in Movie S4, Supporting Information), changes slightly the initial shape of the film. b) Bending angle as a function of irradiation time for a film at 20 °C (left) and 60 °C (right). The bending angle is defined in the inset in Figure 3. c) Photoactuation of the film in water at various temperatures while under continual 365 nm light exposure. In this case the starting position is set as the zero for the bent state, as shown in the left inset drawing. The other two schemes show the bend of the film at different temperatures with respect to the starting position. For both (b) and (c), the purple and blue regions indicate, respectively, the illumination with a 365 nm light (1.1 mW cm$^{-2}$) and 455 nm light (0.8 mW cm$^{-2}$).
with 478 was performed to evaluate the number average molecular weight (Mn) of 40 000 g mol⁻¹. Brucker Advance III HD spectrometer with chloroform as solvent. GPC index (PDI) of oligomers. Shimadzu apparatus was used for the GPC measurements using and the reference was polystyrene (PS) with an average Mn of 350 000 g mol⁻¹.

3. Conclusions

In conclusion, we have developed an LC oligomeric ink for the fabrication of amphiphilic light-fueled actuators via DIW. Remarkably, the light-triggered bending directionality can be regulated by temperature. When illuminated at room temperature, the LCE actuators undergo a light-induced phase transition from Sm C to Sm A that results in a motion directed away from the light source. Whereas when illuminated at elevated temperatures (>45 °C), the same actuator acts toward the light source. These results show a new approach to control the photoinduced deformations in printed actuators and serve as an attractive method for the fabrication and design of light-fueled 3D actuators through additive manufacturing that operates both in air and underwater.

4. Experimental Section

Materials: 1,4-Bis-[4-(6-acryloyloxyhexyloxy)] benzoxloyoxy]-2-methylbenzene (1, RM82) was purchased from Merck. 4,4‘-Bis(acryloyloxyhexyloxy) azobenzene (2, A6A) was purchased from Synthon. 3,6-Dioxo-1,8-octanediol (3), DODT and 1,8-diazacycloundecene (DBU) were obtained from Sigma-Aldrich. Base catalyst triethylamine (TEA) was obtained from Acros. Photoinitiator Irgacure 819, was purchased from Ciba. Polyvinylpyrrolidone with an average molecular weight of 40 000 g mol⁻¹ was purchased from Sigma-Aldrich. Solvent, dichloromethane (DCM) was obtained from Biosolve.

Characterization: 1H NMR spectra were collected on a 400 MHz Bruker Advance III HD spectrometer with chloroform as solvent. GPC was performed to evaluate the number average molecular weight (Mn), weight average molecular weight (Mw), and polydispersity index (PDI) of oligomers. Shimadzu apparatus was used for the GPC measurements using and the reference was polystyrene (PS) with an average Mn of 350 000 g mol⁻¹.

DSC measurements were employed to determine the transition temperature of oligomers and fibers in a TA Instruments DSC Q1000. 2D-SAXS measurements were conducted on a Ganesha lab instrument with a GeniX-Cu ultralow divergence source producing X-ray photons equipped with a wavelength of 1.54 Å and a flux of 1 × 10¹⁰ photons s⁻¹. A Pilatus 300 K silicon pixel detector with 478 × 478 pixels, each 172 µm² in size was utilized to collect scattering patterns. All microscopy images were taken from a Leica DM 2700M equipped with two polarizers that were operated either standing or hanging, were placed at 21.0 cm distance from collimated UV light (365 nm, Thorlabs M365LS2) and visible light (455 nm, Thorlabs M455LS-C2). A controller (ThorLabs DC4104) was used to tune the intensity of the lights. All objects were illuminated with the 455 nm light before performing the photoactuation to ensure that all azobenzene molecules were in the trans-isomer. A camera (Nikon D7200, Olympus OM-D E-M10 Mk III) was used to record the light-driven deformation. The temperature of the surface of the film was controlled using a Gobi camera from Xenics. Underwater actuation was conducted inside a transparent container with flat sides that was filled with water either at 20 °C or at 60 °C (Figure S11, Supporting Information). The temperature of the water was controlled using a digital thermometer.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.
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Conflict of Interest

The authors declare no conflict of interest.

Keywords

4D printing, amphibious, direct ink writing, light-responsive polymers, liquid crystal actuators

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