



A Rewritable, Reprogrammable, Dual Light-Responsive Polymer Actuator

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Abstract: We report on the fabrication of a rewritable and reprogrammable dual-photoresponsive liquid crystalline-based actuator containing an azomerocyanine dye that can be locally converted into the hydroxyazopyridinium form by acid treatment. Each dye absorbs at a different wavelength giving access to programmable actuators, the folding of which can be controlled by using different colors of light. The acidic patterning is reversible and allows the erasing and rewriting of patterns in the polymer film, giving access to reusable, adjustable soft actuators.

The controlled actuation of soft matter is an emerging field in materials science, and many examples of these stimuli responsive adaptive polymers have been reported in the past decade.^[1–3] Among these, folding, often related to origami art, has attracted considerable interest.^[4–8] An appealing feature of folding is the ability to deform a 2D object into a chosen 3D structure in response to a stimulus. Common strategies for obtaining folded structures are based on differences in chemical composition and the use of bilayers.^[5,6,9–12] Recently,

the printing of a responsive ink on a non-responsive pre-strained polymer sheet was described allowing sequential and localized folding.^[13] So far, however, rewritable and reprogrammable folding polymer sheets have been rarely reported. Only very recently, reprogrammable 3D shape-memory Nafion sheets for origami and reconfigurable molding have been developed.^[14]

For creating bending and folding within a single material while operating in a dry environment, liquid crystal networks (LCNs), which consist of polymerized mesogenic molecules, are appealing. LCNs give the ability to orient the reactive mesogens in three dimensions using alignment layers, for example. LCNs that contain a change in orientation of the mesogens over the thickness of the film, that is, splay or twist alignments, are able to bend in response to a change in the order parameter induced by a stimulus such as temperature, humidity, or light.^[15–17] Folding can be obtained by patterning the polymer film using patterned alignment layers,^[18] patterned photopolymerization of various mesophases,^[19] and/or by a gradient formed during polymerization.^[20] However, the fabrication of soft actuators based on LCNs capable of folding has been rarely described. A humidity responsive actuator based on a single sheet of a hydrogen-bonded, uniaxially aligned LCN has been described. Folding was obtained by locally treating the polymer film with a potassium hydroxide solution to create an asymmetry in the responsiveness towards humidity.^[21] Photo-induced asymmetric bending has been achieved using LCNs containing two photoresponsive dyes to create artificial cilia modularly driven by different colors of light,^[22,23] while a dual-layer-based LCN actuator has been reported that bends or twists through modulation of the color of light.^[24] However, the patterning methods are limited to simple designs, and complex patterns are difficult to achieve.

Herein, we report on a rewritable and reprogrammable single polymer film that can generate various shapes upon light irradiation of different colors. The LCN film contains a pH-sensitive azomerocyanine (**1-AM**) dye that can be locally converted to the hydroxyazopyridinium (**1-HAP**) form by an acid (Figure 1). This facile patterning of the dyes gives access to an actuator the folding of which can be programmed. The actuation is reversible and instantaneous and the shape deformation depends on the type of pattern and the wavelength of the light stimulus. The reversibility of the acid patterning makes it possible to fabricate rewritable and reprogrammable patterns on a single polymer actuator film.

To achieve patterning and actuation within an LCN film, a pH- and light-responsive azomerocyanine dye (**1-AM**) was used.^[25] Upon acidification, this purple colored **AM** dye is

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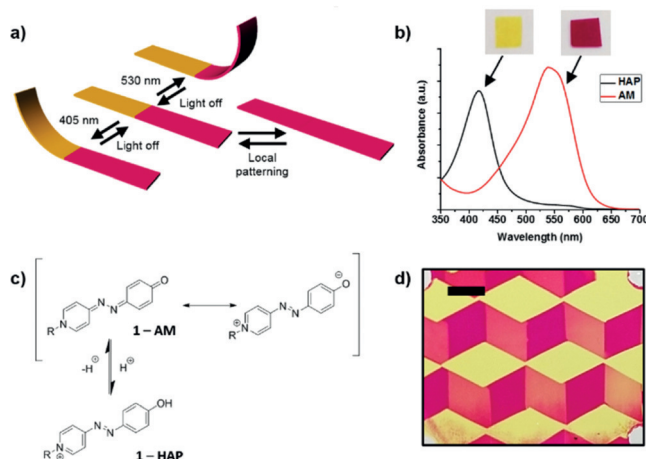


Figure 1. a) Schematic of the reprogrammable and rewritable polymer actuator. The yellow regions contain **1-HAP** and the magenta regions contain **1-AM**. b) Absorption spectra of the splay-aligned LCN polymer film before (**1-AM**) and after (**1-HAP**) acid treatment. Insets: The polymer film before and after acid treatment. c) Molecular changes upon acid and base treatment of **1-AM**. d) Example of a pattern achieved with exposure to acidic vapor of a splay-aligned **1-AM** LCN polymer film. Scale bar = 5 mm.

converted to the yellow colored **HAP** derivative.^[25–27] Both dyes are photo-responsive upon light irradiation at the proper wavelength and exhibit excellent stability over time.^[28] The light induced *trans*–*cis* isomerization of azobenzene and photothermal effects will reduce the order in the LCN leading to anisotropic shape changes.^[29]

In this study, a photopolymerizable analogue of **1-AM** was synthesized and mixed with an LC host (see the Supporting Information). This monomer mixture gives a nematic phase at relatively low temperatures, which facilitates sample preparation, that is, cell filling and photopolymerization under moderate conditions. After polymerization, a purple colored splay-aligned LCN film containing 1.5 wt% of **1-AM** is obtained. Splay-aligned films were prepared because they are known to bend owing to the opposite expansion/contraction at the top and the bottom of the film upon lowering the order parameter.^[15]

When the polymeric film is exposed to trifluoroacetic acid (TFA) vapor for about 30–60 s and placed on a hotplate at 100 °C for about 10 s to promote the protonation, a color change from purple to yellow is observed indicating the conversion from **1-AM** to **1-HAP** (Figure 1).^[25] UV/Vis spectroscopy (Figure 1 b) shows a blue shift of the absorption band from 550 nm to 405 nm and indicates the full conversion of **1-AM** to **1-HAP** as the absorption band at 550 nm has almost disappeared. The use of TFA as acid vapor yields a stable yellow film at room temperature, and the film recovers to its initial state only when soaked in a basic aqueous solution of NH_4OH . It should be noted that when different acids are used the degree of protonation can be tuned (see the Supporting Information).

In order to fabricate a patterned film containing photo-responsive **1-AM** or **1-HAP** dyes, a **1-AM** polymer film was locally exposed to acidic vapor. This was achieved by placing

a polydimethylsiloxane (PDMS) mask on top of the film. The mask locally covers the sample, and subsequently the negative of the mask is exposed to TFA vapor. This method gives considerable freedom of design and complex patterns can be made in a few seconds (Figures 1 d). To obtain a high resolution between the exposed and non-exposed areas, a good contact between the PDMS mask and the film must be ensured to prevent diffusion of the condensed acid at the interface. Furthermore, quick protonation upon heating limits the lateral diffusion of the acid within the film. Other patterns can be easily achieved using different masks.

The orthogonal responsive behavior of the two dyes was investigated by using visible light of 405 and 530 nm as the stimulus (Figure 1 a). First, the **1-AM** containing polymer film was clamped at one side and exposed to light. The splay-aligned film bends strongly (50°) when exposed to 530 nm and bends to a lesser extent when exposed to 405 nm (20°), for an intensity as high as 185 mW cm^{-2} (Figure 2). Bending always

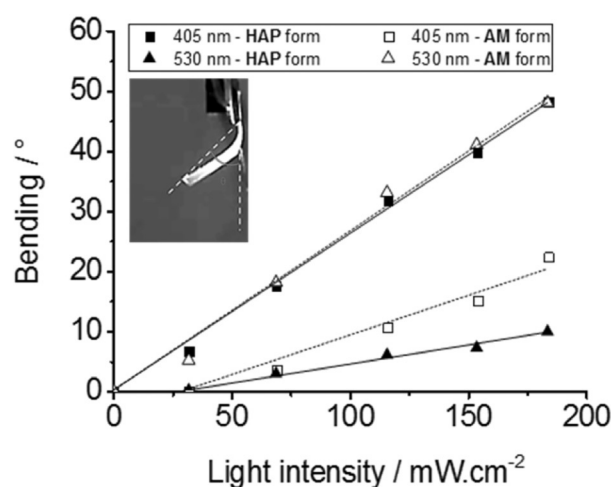


Figure 2. Selective bending of the film before (**1-AM**) and after (**1-HAP**) acid treatment as a function of light intensity. Each film is exposed to both light of wavelengths, 405 nm and 530 nm. Inset: Method used to calculate the bending angle.

occurs in such a way that the planar-aligned side is inside, regardless of which side of the polymer is exposed. This shows that the bending is determined by the splay alignment in the polymer film. A similar but opposite behavior is observed when the acid treated film (**HAP** form) is exposed to the same wavelengths; for the 530 nm light, the film hardly bends (10°) whereas it bends to a higher extent (50°) in the same direction as for the 405 nm light, using similar intensities (Figure 2). These results show that **1-AM** films predominantly respond to 530 nm light while **1-HAP** films respond to 405 nm light. A complete orthogonal light response is not obtained as both films absorb light at 405 and 530 nm (Figure 1 b). It should be noted that upon switching off the light, all films unbend immediately^[28] and that all experiments were performed with a single polymer film.

Interestingly, much larger bending can be observed when exposed to higher intensities; and, at values above 300 mW cm^{-2} , the film starts to oscillate in the same way as

previously reported.^[29] Temperature measurements reveal that when the polymer films are exposed to wavelengths of light at which the films absorb, the temperature significantly increases (see the Supporting Information). This suggests that photothermal processes are the dominant factor in the deformation response similar as earlier reported.^[29]

The patterning method and orthogonal light responsive can be used to create complex deformation patterns such as localized and wavelength dependent folding. To explore this, films (2.5 cm × 0.4 cm) with a striped pattern were fabricated by using the facile local acid treatment method (see above). Polymer films comprising 3 stripes of 405 nm HAP-responsive regions and 4 stripes of 530 nm AM-responsive regions were made (Figure 3). When exposed to 405 nm light, only the HAP regions (yellow) bend while the purple parts remain straight. Upon switching off the light, the film unbends within seconds and returns to the flat state. When this film is exposed to 530 nm only the purple areas bend, leading to a folded polymer. The intensity of the light dictates the bending angle and therefore also influences the final shape.

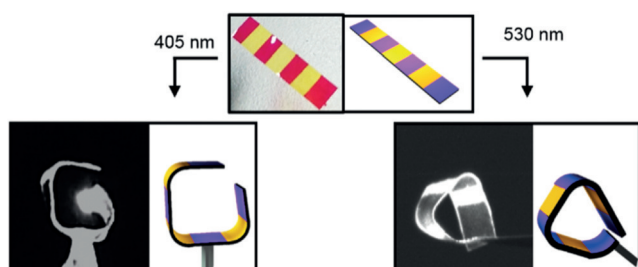


Figure 3. Specific bending of a patterned film. The same film is exposed with 405 nm (left) and 530 nm (right) light. The film specifically bends at the yellow region when exposed to 405 nm and at the magenta region when exposed with 530 nm. When switching off the light, the film unbends to the flat state. At the right of each image a schematic of the patterned film and its bending behavior is shown.

The influence of the width of the active part was also studied and appears to be of importance. When the lines are too narrow, the film barely bends. For example, for a stripe of 4 mm width and 25 mm length, a minimum of 1 mm active material was needed to obtain large bending. Those results are in line with earlier reported experimental and theoretical results for similar hinge-based actuation systems.^[6]

To investigate if rewritable and reprogrammable actuators can be fabricated, an AM-1 polymer film was patterned with acid and erased with base (Figure 4). Upon patterning with acid, a polymer film was obtained having three unexposed areas and two acid-treated areas. When exposed to 405 nm light, the polymer folds into a U-shape because of the strong bending of the yellow parts. The pattern can be erased by soaking the film in an aqueous solution of NH₄OH at 80 °C for 30 s, and a new pattern can be created by following the same procedure as described above (Figure 4). When an acid-treated line is programmed along the molecular axis, the film bends homogeneously and tend to roll up over the full length (Figure 4). Using TFA as acid, up to four rewriting cycles could be performed with a single film.

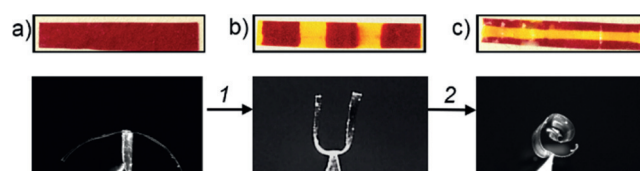


Figure 4. a) AM-1 splay-aligned polymer with the planar side at the top. b) The same film locally patterned with acid vapors (top) and exposed to 405 nm. The film bends specifically at the yellow areas (bottom). c) The same film placed in NH₄OH to erase the pattern and patterned again with acid vapor yielding differently patterned film (top) showing different bending behavior upon exposure to 405 nm (bottom).

In conclusion, we have shown that it is possible to fabricate reusable and reprogrammable photoresponsive polymer actuators by a facile method. Upon incorporation of a pH-sensitive photochromic azo dye in a liquid crystalline network, a variety of patterned polymer films can be obtained by a simple acid treatment. These polymers give access to programmable dual photoresponsive actuators, the folding of which can be controlled by different colors of light. The acidic patterning is reversible and allows to erasing and rewriting new patterns in the polymer film, giving access to re-useable, adjustable soft actuators. This approach can be used to fabricate rewritable actuators that curl or twist by using trigger molecules having two stable states. Preliminary experiments show that by combining two photoresponsive dyes having pH-dependent stable states, a plurality of patterns can be created with an increasing degree of complexity (see the Supporting Information).

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Conflict of interest

The authors declare no conflict of interest.

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