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Humidity-Responsive Liquid Crystalline Polymer Actuators with an Asymmetry in the Molecular Trigger That Bend, Fold, and Curl

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S Supporting Information

ABSTRACT: We show a versatile method for the preparation of a variety of humidity-responsive actuators based on a single sheet of a hydrogen-bonded, uniaxially aligned liquid crystal polymer network. In this approach, the asymmetry in the molecular trigger in the anisotropic polymer film plays a dominant role leading to programmed deformation events. The material is locally treated with a potassium hydroxide solution to create the asymmetry in the responsiveness toward humidity, which allows to prepare actuators that bend, fold, or curl.

In nature, various examples exist of systems that show shape deformation as a response to environmental changes, such as humidity. For example, in plants bending deformations in the opening and closing of pine cones,¹ folding and unfolding of ice plant seed capsules,² opening of the morning glory flower,³ and helical curling deformation of *Bauhinia Variegata* seedpods⁴ take place as a result of changes in humidity. Such responsive bending, folding, and curling events in these hierarchically ordered materials are important for the functioning of natural systems. In materials science there is an ongoing interest in and demand for fabricating environmentally-responsive polymer materials that behave similarly to the systems found in nature.⁵ While light and temperature-responsive materials have often been reported, the fabrication of humidity-responsive materials remains less explored. Humidity-responsive actuators are interesting for many applications, such as power generators,⁶ smart textiles,⁷ artificial muscles,⁸ and sensors.⁹ Bending and curling can be mimicked using bilayers of materials with different swelling behavior^{3,4,7,8,10} or by subjecting only one side of a single-layer film to high humidity.¹¹ From an manufacturing point of view, it would be desirable to have a facile method to fabricate soft actuators from a single piece of polymer sheet that can be tailored to achieve bending, folding, or curling.⁶

Liquid crystal (LC) polymer actuators are a class of soft actuators which consist of a network of polymerized mesogenic molecules.¹² These materials are anisotropic, and the alignment of the molecules can be readily influenced to obtain specific properties. Upon decreasing their anisotropy through a stimulus,¹³ they will contract in the direction parallel to the alignment director and expand in all other directions. In planar aligned samples this leads to contraction and expansion of the materials in orthogonal directions. Single-layered actuators

based on this principle have been made to bend by exposing only one side of the film to the stimulus. Bending has also been obtained through introduction of asymmetry in the film as a gradual change in the alignment director through the thickness of the film, such as a twisted and splayed alignment. In addition, curling has been achieved by cutting a ribbon from a twisted nematic film at a 45° angle with the top or bottom director.¹⁴ Single-layer actuator films which deform as a response to changes in humidity have been prepared by immersion of a LC network with hydrogen-bonded carboxylic acid moieties in a basic solution to convert it to a hygroscopic polymer salt. These materials can take up water and swell mostly perpendicular to the alignment director.¹⁵ Like in previous examples, bending could be achieved in these materials by subjecting a film with planar alignment to high humidity on only one side, or by subjecting a film with a twisted or splayed alignment to a uniform humidity change. As such, humidity-responsive LC soft actuators have been reported based on asymmetry in the molecular orientation and/or a gradient in the humidity.

We now report on soft actuators that can be tailored to either bend, fold, or curl in response to changes in humidity, while being prepared from the same polymer sheet. In contrast to previous research, the shape deformation is not induced by asymmetry in either the stimulus or the alignment director, but as an asymmetry in the presence of the responsive molecular trigger in the material. This results in soft actuators that operate in a uniform humidity environment and without requiring a twisted or splayed alignment director. The asymmetry is achieved by locally treating a uniaxially aligned LC polymer sheet with a basic solution and convert it to a hygroscopic polymer salt. We have used this new and versatile method to prepare actuators that bend toward or away from a water surface, actuators that show complex humidity-responsive folding, and curling actuators with controlled handedness that unwind upon increasing the humidity of the environment.

The humidity-responsive polymer films were prepared using the same liquid crystalline mixture containing hydrogen-bridged moieties as described before (Figure 1a).¹⁵ This material was given a planar, uniaxial alignment using a cell containing rubbed polyimide alignment layers. After photopolymerization, the film (thickness 18 μm) was retrieved from the cell and cut to the appropriate size (typically 3 × 20 mm). The planar alignment of the film was confirmed between

Received: May 31, 2014

Published: July 15, 2014

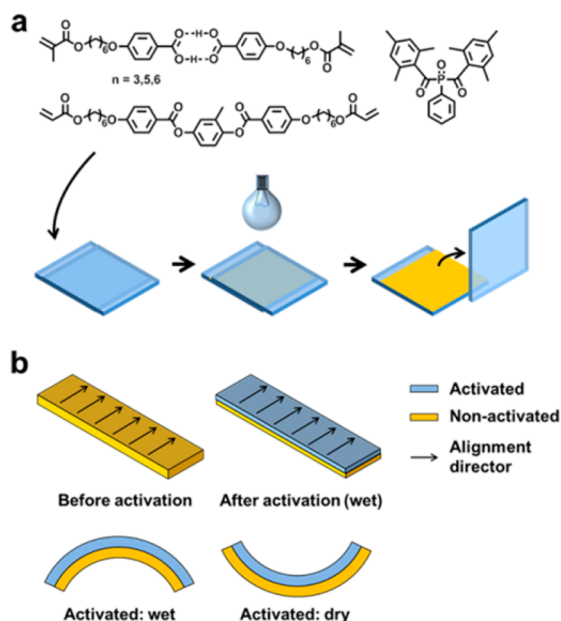


Figure 1. (a) Chemical composition of the LC hydrogen-bonded mixture and preparation procedure for making the LC films.¹⁴ (b) Schematic representation of the bending behavior of the ribbon with the alignment director perpendicular to the long axis, upon activation and when dried.

crossed polarizers (Figure S1). It should be noted that at this point the films do not yet respond to water. Initially, a water-responsive actuator with simple bending behavior was prepared by bringing only one side of the ribbon in contact with a 0.1 M KOH solution, followed by rinsing with water (Figure S2). The infrared spectrum, measured before base treatment, clearly showed the hydrogen bridges as a peak at 1682 cm^{-1} , which corresponds to the C=O stretching in hydrogen-bonded dimers. After base treatment and subsequent drying, this peak disappeared and two new peaks appeared at 1547 and 1395 cm^{-1} , resulting from antisymmetric and symmetric COO stretching, respectively. The spectrum measured at the nonexposed side remained unchanged (Figure S6).¹⁶

While the film was made wet, anisotropic swelling of the exposed side caused bending of the film toward the nonexposed side. When the ribbon was cut with the alignment director perpendicular to the long axis, bending along the long axis took place (Figure 1b). A ribbon in which the alignment was parallel to the long axis showed bending along the short axis while wet. This behavior is in good agreement with earlier observations that the swelling should take place predominantly perpendicular to the alignment director due to the anisotropic nature of the material¹⁴ and shows that the bending direction of such ribbons is strongly influenced by the alignment director of the mesogenic units. The expansion in the direction perpendicular to the alignment director was confirmed by thermo-mechanical analysis and was found to be 1.0%, which is in agreement with earlier results (Figure S3).¹⁵ Unexpectedly, when the film was dried, bending toward the base-treated side took place. This implies that the material, upon base exposure and subsequent drying, shrinks in comparison to the nonexposed side.¹⁷ The shrinkage is anisotropic and mainly takes place in the direction perpendicular to the alignment director. Although the mechanism for this shrinkage is unclear, it may be caused by increasing molecular order or by a more dense packing.¹⁸

To study the bending behavior in response to environmental humidity, the one-side base-exposed film with the alignment director perpendicular to the long axis (Figure 1b) was placed in a chamber in which the humidity is homogeneous and controllable. At high humidity (75%), the sample was straight, while at low humidity (15%) it was strongly bent toward the base-exposed side (Figure 2a) due to shrinkage caused by the

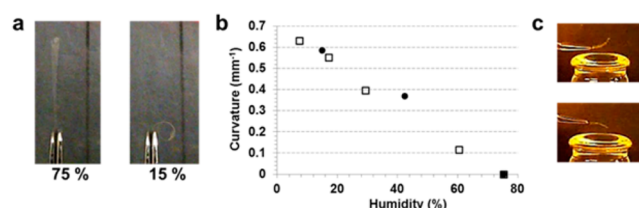


Figure 2. Actuation behavior of a one-side base treated planar aligned LC polymer film. (a) Actuation in a controlled humidity chamber. (b) Curvature ($1/r$) of the film as a function of humidity. Squares indicate data points which were obtained while increasing the humidity, and circles indicate decreasing humidity. The error in the data points is $\sim 10\%$. (c) Bending of the film when facing the water surface with the base-treated side (top) or the nontreated side (bottom).

evaporation of water from the base-treated side. When the bending curvature ($1/r$) was plotted against the relative humidity (Figure 2b), a linear relationship was observed. The curvature was found to range from 0 mm^{-1} at high humidity to 0.6 mm^{-1} at low humidity. We were unable to increase the humidity to a point where bending toward the untreated side took place ($>75\%$), as was observed when the actuator was rinsed with water after the preparation process. To investigate the response to a humidity gradient, the film was brought close to a water surface. As expected, bending toward the water surface took place when the untreated side was facing the water (Figure 2c, Movie S1), and the curvature increased when the distance to the water surface was decreased. When the film was flipped, it was bending away from the water. This shows that the direction of the bending is determined by the asymmetry in the responsive molecular trigger in the polymer film and not by the presence of the humidity gradient.

Next, we induced complex folding in our polymer films by selective base treatment of specific areas on the film's surface (Figure 3). An actuator with three folds in an alternating pattern was prepared. To do so, the outer parts on one side of the film were first exposed to the base, then the film was rinsed in water and dried, and a second exposure was carried out on

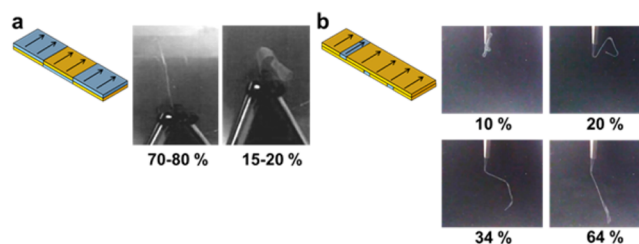


Figure 3. Folded actuators, which are prepared through selective activation of the film. (a) A ribbon in which the outer parts are exposed to an alkaline solution on one side, and the center part on the other side (blue regions), actuated in a humidity chamber. (b) A ribbon with three narrow hygroscopic polymer salt bands (blue parts), actuated in the humidity chamber by increasing the humidity. Arrows indicate the molecular director in the polymer films.

the center part of the film on the other side (Figure 3a). The actuation of this film was tested in the humidity chamber. The film displayed an accordion shape in a dry environment (15%), while at high humidity (75%) a straight polymer film was again obtained, which is similar to the actuator with only one base-treated domain. To demonstrate that sharp, hinge-like folding could also be induced, three narrow parts of the film were base-treated. A ribbon with three hinges, two on one side of the film and one on the other side, was prepared (Figure 3b) and investigated in the humidity chamber. At low humidity, sharply bent hinges were observed having three folds, and the actuator was fully contracted. Again, at high humidity (75%) the actuator was nearly straight.

Finally, humidity-sensitive curling actuators were prepared. In this experiment, a ribbon was cut from a planar aligned polymer film in such a way that the nematic director made a -45° angle with the long axis of the film (Figure 4a). After one-

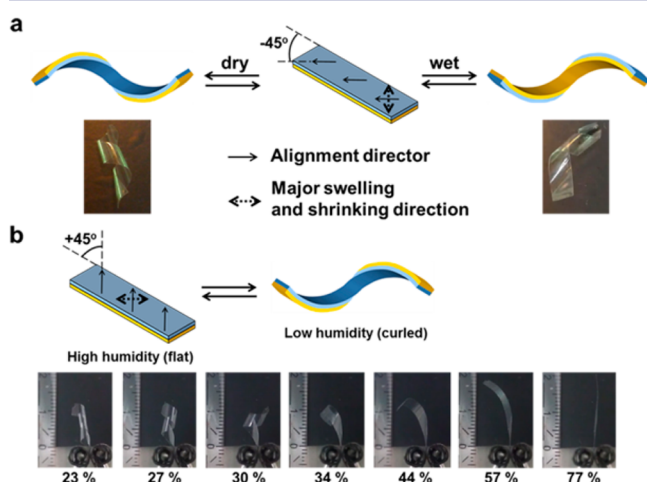


Figure 4. Curling actuators prepared by one-side base exposure of LC films (blue area). (a) Ribbon with the molecular director at a -45° angle with respect to the long axis of the film, and the resulting curling behavior after activation in KOH solution, both in the wet and dry state. (b) Curling and uncurling of the $+45^\circ$ actuator at high and low humidity, respectively. The behavior of this actuator is also shown in the humidity chamber with increasing humidity.

side exposure, the ribbon adopted a right-handed curl shape while wet, with the base-treated side on the outside. When the ribbon was dried, the handedness of the curl reversed to left handed, with the base-treated side on the inside. As seen before, the polymer salt side swells when wet in comparison to the untreated, nonresponsive side, and this swelling predominantly takes place perpendicular to the molecular director. Since the nematic director makes a -45° angle with the long axis of the film this will lead to right-handed curling in which the polymer salt side is on the outside (Figure 4a). In the dry state, shrinkage dominates perpendicular to the molecular director, causing the helix to reverse its handedness. When a strip was cut in which the nematic director was at a $+45^\circ$ angle with the long axis of the film, the resulting curl was left-handed when wet and right-handed when dry (Figure 4b), which shows that the handedness in these humidity-responsive curling actuators is fully directed by the orientation of the molecular director with respect to the long axis of the film. This ribbon was investigated in a humidity chamber (Figure 4b). At low humidity, the ribbon was tightly curled. When the humidity was increased, the ribbon started to uncurl. At high humidity it was

straight, similar to the bending and folding actuators showing the reproducibility of the humidity response. It should be noted that this kind of deformation requires anisotropic deformation and would not be possible with materials that swell or shrink isotropically (Figure S4 and S5).

In conclusion, we have developed a new, facile, and versatile method for the preparation of polymer actuators based on LCs that can be tailored to bend, fold, or curl as a response to changes in humidity. In this material the deformation is fully controlled by the asymmetry in the responsive molecular trigger present in the polymer film. By locally exposing a monolithic, uniaxially aligned hydrogen-bonded polymer film to an alkaline solution, hygroscopic regions are obtained on one side of the film. Anisotropic swelling and shrinkage was observed on the polymer salt side, which caused a strong bending deformation of the ribbons. Folding deformation was achieved by patterned base treatment, and curling deformation could be achieved when the alignment director of the mesogenic units was put at a -45° or $+45^\circ$ angle with the long axis of the ribbon, in which the handedness was controlled by the molecular director.

Our approach provides a new method for the preparation of stimuli-responsive actuators from a single polymer sheet. In this novel principle the asymmetry in the molecular trigger in the anisotropic polymer film plays a dominant role leading to programmed deformation events in a versatile fashion. This method can in principle be extended to other types of triggers such as photochromic molecules and chemical compositions to tune the material response as well as anisotropically ordered hydrogels and lyotropic LCs. In the future, even more complex deformation may be achieved using inkjet printing techniques for the local base treatment and using photoalignment to prepare complex three-dimensional director patterns.^{13c-f}

■ ASSOCIATED CONTENT

Supporting Information

Materials and methods with detailed analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to The Netherlands Organization for Scientific Research (NWO, VICI grant) for funding this research.

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- (17) Experiments have been performed in which the relation between bending direction and both alignment direction and film dimensions was investigated (see SI).
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