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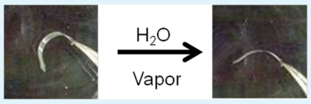
Humidity-Responsive Bilayer Actuators Based on a Liquid-Crystalline Polymer Network

Mian Dai,[†] Olivier T. Picot,[‡] Julien M. N. Verjans,[†] Laurens T. de Haan,[†] Albertus P. H. J. Schenning,*[,†] Ton Peijs,[‡] and Cees W. M. Bastiaansen*[,†,‡]

[†]Functional Organic Materials & Devices, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
[‡]School of Engineering and Materials Science, Queen Mary University of London, Mile End Road, London E1 4NS, U.K.

ABSTRACT: A humidity-responsive bilayer actuator has been developed that consists of an oriented polyamide-6 substrate and a liquid-crystalline polymer coating. The oriented substrate acts as an alignment layer for the liquid crystal. The liquid-crystalline polymer consists of a supramolecular network having hydrogen-bonded entities that, after activation with an alkaline solution, exhibit deformation in response to a change in humidity. The bending behavior of the bilayer actuator was analyzed, showing a large response to a change in the humidity.



KEYWORDS: *liquid-crystalline polymer network, bilayer actuator, humidity-responsive materials, supramolecular chemistry*

■ INTRODUCTION

In nature, many organisms are able to change their properties, such as their shapes, in response to the changes in the environment. For instance, pine cones respond to humidity and are open when dry, facilitating the release of the cone's seed, and closed when wet.[1] Stimuli-responsive polymers are a class of materials that can mimic these capabilities to change properties in response to a change in the environment.[2−10] For example, actuators have been reported that change shape upon a variety of external triggers. From an application point of view, an attractive approach to making stimuli-responsive polymer actuators is a bilayer system in which one layer is a stimuli-responsive coating and the other layer is a common polymeric substrate that gives mechanical strength. For example, to produce smart textiles, bilayer actuators would be appealing in which one layer is responsive to humidity and the other layer is a polyamide, a polymer commonly used in textiles.

Because humidity is variable in nature, humidity-responsive polymer actuators are receiving a lot of attention for personal comfort, health, and industrial and technological applications.[11] In the past, humidity-responsive hydrogels have been reported that exhibit an isotropic volume change.[12,13] Interestingly, these responsive polyelectrolytes have been integrated into bilayer actuators showing humidity-responsive bending resulting in a walking device.[14] Another class of interesting actuators are based on polymer liquid-crystalline (LC) networks. LC polymer actuators can easily exhibit complex anisotropic deformations, giving spiral ribbons, helicoids, and cone and anticone shapes.[15,16] Typically, the nature of these deformations is controlled by the alignment and molecular order of the LC units in all three dimensions in the polymer network.[17] Remarkably, humidity-responsive bilayer actuators based on LC polymers have never been reported previously, and only light-responsive bilayer actuators have been fabricated.[18]

Here we report on a humidity-responsive bilayer actuator that consists of an oriented polyamide-6 substrate and an aligned humidity-responsive LC polymer coating. The humidity-responsive LC polymer is based on a self-assembled supramolecular network consisting of covalent cross-links and hydrogen-bonded cross-links. Previously, this type of hydrogen-bonded LC network has shown a fast and reversible color response to changes in humidity,[19] while bending actuators have also been reported based on so-called twisted nematic films in which the polymer first was converted into a hydroscopic polymer salt.[20,21] In our bilayer actuator, stretched polyamide-6 was chosen as a second layer because this polymer is often used in textiles. Interestingly, the uniaxially oriented polyamide layer is able to align the LC polymer network.[22,23] A bilayer actuator that bends upon a change in the humidity could be fabricated. These results show that, in principle, it is possible to make more complex humidity-responsive actuators that are interesting for application in smart textiles.

■ EXPERIMENTAL SECTION

Materials. The monomers *n*OBA (*n* = 3, 5, and 6) were obtained from SYNTHON Chemicals (Germany) and mixed in the weight ratio of 1:1:1 to generate a low crystallization temperature and a broad temperature range in which the mixture exhibits a nematic phase.[24] The mesogen C6M was obtained from Merck (Germany) and used as a covalent cross-linker for mechanical stability. The photoinitiator Irgacure 819 was obtained from CIBA Specialty Chemicals (Germany). The LC mixture contains 86 wt % *n*OBA, 12 wt % C6M, and 2 wt % Irgacure 819 (see Figure 1). The LC mixture exhibits a nematic phase between 56 and 95 °C, which is close to the results shown in the literature.[24] The uniaxially stretched PA-6 films (thicknesses = 15 and 25 μm) were obtained from Goodfellow (U.K.).

Fabrication of a Humidity-Responsive Bilayer System. The LC mixture was mixed with the solvent xylene in weight ratio of 1: 5 at 100 °C and sprayed with an airbrush onto the surface of stretched PA-6 film to form a thin uniform coating. After spraying, the sample was heated at 110 °C to evaporate the solvent. Then the sample was

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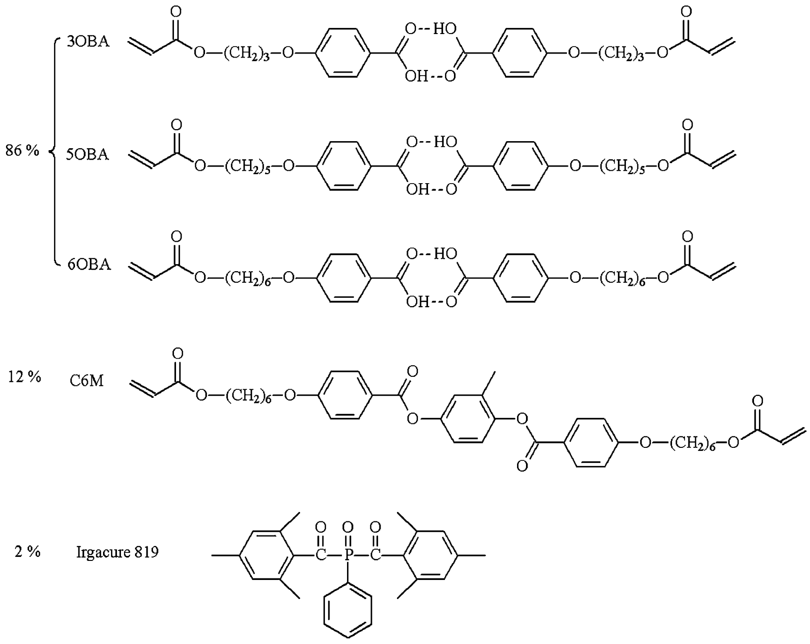

Figure 1. Chemical structures of the components of the LC mixture.

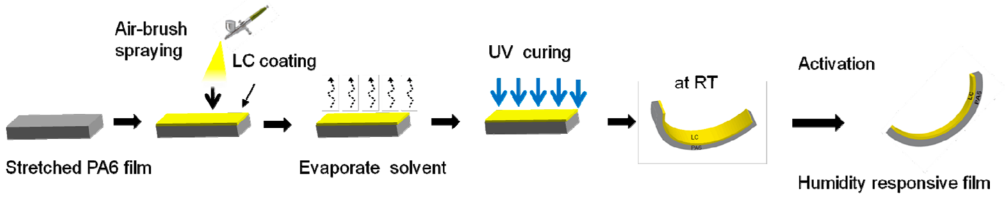

Figure 2. Schematic representation of the fabrication process of the humidity-responsive bilayer polymer actuator.

cooled down and polymerized using a UV Exfo mercury lamp at 85 °C in the nematic phase of the mixture. After cooling to room temperature, the sample was treated with a 0.1 M NaOH solution for 25 s to break the hydrogen bonds. After that, the bilayer film was simply dried using a tissue. Finally, a humidity-responsive bilayer system was obtained. The whole procedure is shown in Figure 2.

To characterize the pure LC coating, the LC coating with the substrate was glued to a glass slide, and then the PA-6 substrate was peeled off; consequently, a LC coating on a glass slide was obtained.

Humidity Response of the Activated Bilayer Polymer Actuator. To investigate the humidity-responsive deformation of the bilayer polymer actuators in a spatially homogeneous humid air environment, a homemade humidity chamber was utilized, which is basically made up by a plastic container (~25 cm × 40 cm). The plastic container has two openings equipped with two tubes that are connected to dried and humid nitrogen, respectively. To obtain humid nitrogen, a special cylindrical glassware (diameter = ~10 cm; height = ~20 cm) was made that contains water. The glassware is enclosed to prevent water evaporation. There are two interconnected bubblers inside the glassware and incorporated into the same piece of the glassware. The two bubblers are filled with water through which we pass nitrogen. As the nitrogen is fed through, it becomes more humid and is sent into the container. By adjusting the input volume of the dried and humid nitrogen, respectively, we can create a spatially homogeneous humid nitrogen environment in the container. The samples are placed inside this humidity chamber to study their deformations in response to the relative humidity (RH). The images of the samples under different RH values were taken using a camera and used to measure the bending radii of the samples.[25,26] For determination of the bending radius, the middle part of the bilayer film was used to avoid end effects. In the middle part, the bending is homogeneous. The RH is measured with a humidity/temperature sensor (Vaisala).

Characterization. The optical anisotropy of the pure LC coating was examined by polarized optical microscopy (POM) between two crossed polarizers prior to activation.

Fourier transform infrared (FTIR) spectra were measured by a Bio-Rad FTS 6000 spectrometer. The absorbance spectra of the LC coating on the sample were recorded respectively before and after activation in the alkaline solution. Attenuated total reflectance (ATR) IR spectra were measured with a Varian 670 IR spectrometer with a slide-on ATR accessory, where a germanium crystal was used. The penetration depth was <0.5 μm. For the determination of the dichroic ratio, the sample was positioned with the stretching direction parallel and perpendicular to the polarization direction of the IR beam to obtain polarized ATR spectra.

The measurement of the thickness of the LC coating was carried out using a FEI Quanta 3D scanning electron microscope. To prevent charging in the electron beam, a thin gold layer was coated on the cross section of the bilayer film by vapor deposition.

■ RESULTS AND DISCUSSION

To produce a humidity-responsive bilayer film, a thin layer (~4 μm) of the LC mixture is spray-coated on the surface of the uniaxially stretched PA-6 film and then polymerized in the nematic phase at 85 °C using a UV Exfo mercury lamp. After polymerization and cooling to room temperature, a prebent film with a curvature $1/r$ is obtained in which the PA-6 substrate is always on the outside of the curvature. Probably, this bending of the film originates from the polymerization shrinkage of the LC network in combination with an increased order at room temperature. Previously, a similar behavior was observed in single-layer polymer films with a rotating director profile that were fabricated at elevated temperature and cooled to room temperature.[24,27] The film is subsequently dipped in a NaOH solution for activation and dried, and again a prebent bilayer polymer is obtained (see Figure 3).

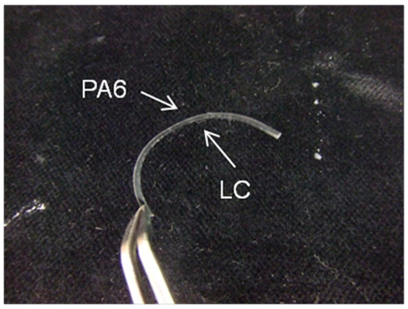

Figure 3. Image of a bent bilayer polymer containing a 25-μm-thick PA-6 layer and a 4 μm LC polymer salt at ambient conditions at room temperature.

The response of the activated bilayer polymer actuator to a gradient in humidity (or water vapor) is shown in Figure 4. It is found that this bilayer actuator exhibits less bending as it bends toward the side of the PA-6 substrate within seconds. The actuator is not bending away form the water, suggesting that the humidity gradient does not play a dominant role in the bending behavior.[21] The bending curvature is not homogeneous, which might be due to end effects, for example, due to the clamp.

The deformation of the bilayer polymer actuator (15 μm PA-6 and 4 μm LC coating; one end is fixed, and the other end is free-standing) was investigated in more detail in a homemade humidity chamber in a spatially homogeneous humid air environment. The curvature of the bilayer film at equilibrium as a function of the RH shows a high curvature κ equal to $1/r$ (r is the bending radius) at low RH and is bent with the PA-6 substrate on the outside of the curvature (Figure 5a). Upon increasing RH, the curvature decreases and the bilayer film bends less, resulting in a flatter bilayer actuator. To estimate the reproducibility, we cycled a number of times between low and high RH (Figure 5a). The results indicate that the bending motion is reversible and repeatable.

The influence of the substrate thickness on the bending behavior of the bilayer film was also studied (Figure 5b). A comparison was made between a bilayer film I (25 μm PA-6 and 4 μm LC coating) and a bilayer film II (15 μm PA-6 and 4 μm LC coating). For reference purposes, the response of a pure single PA-6 film III to the RH was also studied. It is found that the pure single PA-6 film III does not respond to variations in humidity in a bending-mode deformation (Figure 5b). The bilayer films I and II both show a bending-mode deformation under humid conditions, and the bending curvature of the bilayer film I is smaller than that of the bilayer film II. Of course, this is to be expected because the bending moment of the PA-6 substrate increases substantially with increasing thickness.[25]

To determine the bending mechanism of this humidity-responsive bilayer actuator, the alignment of the pure LC coating was first investigated. POM images recorded between two crossed linear polarizers (see Figure 6) show that when the LC coating is positioned with the stretching direction (of the PA-6 substrate) parallel/perpendicular to the polarizer axes, a homogeneous dark state is observed. When the LC coating is oriented with the stretching direction at approximately 45° to the polarizer axes, a bright state is observed. This indicates that the LC mesogens are well-aligned, and a monodomain LC coating is obtained.

The optical anisotropy in the surface region of the pure LC coating prior to activation was also examined by polarized ATR IR spectrometry. It has been reported that polarized ATR can be used to study the molecular orientation near the surface of the polymer films.[28,29] The polarized ATR spectrum shows a band at 1729 $\mathrm{cm^{-1}}$, which is assigned to the stretching vibration of carbonyl groups attached to the polymer backbone and shows no anisotropy in the spectra (Figure 7). The band at 1682 $\mathrm{cm^{-1}}$ originates from the asymmetric stretching vibration of the carbonyl groups of the hydrogen bonded dimer. The bands at 1255 and 1165 $\mathrm{cm^{-1}}$ are due to the C−O−C asymmetric stretching vibration. The bands associated with the stretching vibrations of the benzene rings occur at 1606, 1580, 1511, and 1422 $\mathrm{cm^{-1}}$, which are usually used to determine the orientation of the mesogens.[28,29] Regarding the intensity at 1729 $\mathrm{cm^{-1}}$ as the same in each spectrum, it is clearly indicated that the bottom surface of the LC coating, which is attached to the substrate and was removed from the substrate, has a high dichroism around 1606 $\mathrm{cm^{-1}}$, which originates from the stretching vibration of benzene rings. The dichroic ratio D can be calculated from the polarized ATR spectra by the relation[28]

$$D = \frac{A_{\parallel}}{A_{\perp}} \tag{1}$$

where $A_{\parallel}$ and $A_{\perp}$ are the ATR spectra in absorbance for the sample positioned with the stretching direction parallel and perpendicular to the polarization direction of the IR beam, respectively. The dichroic ratio of the bottom surface is ~5.6. On the other hand, the top layer of the LC coating shows a relatively low dichroism at 1606 $\mathrm{cm^{-1}}$, and the average dichroic ratio D is ~2.8. This indicates that a splay-like alignment (see Figure 9a), with bottom surface having parallel alignment and the top surface having close to homeotropic alignment with a tilt of the LC, was obtained on the PA-6 substrate.

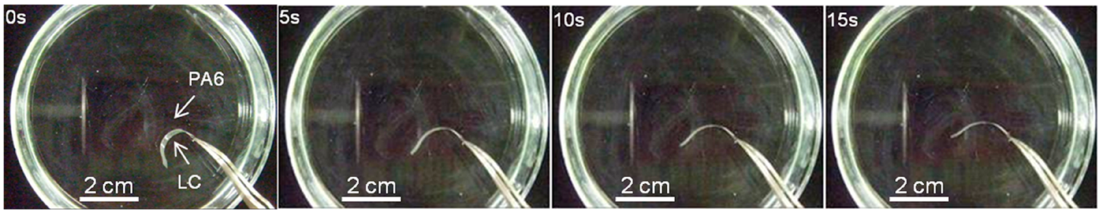

Figure 4. Humidity-responsive behavior of the activated bilayer actuator (25 μm PA-6 substrate and 4 μm LC coating) after exposure to water vapor.

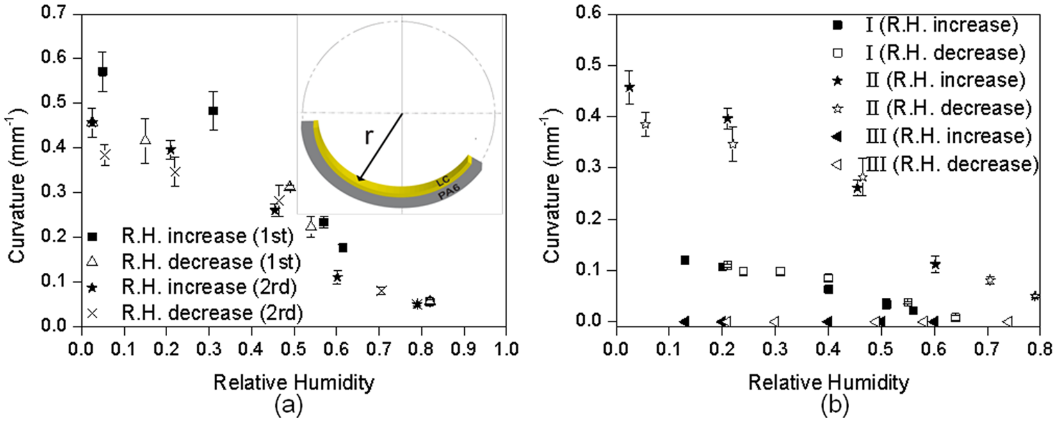

Figure 5. (a) Curvature of a bilayer film (15 μm PA-6 substrate and 4 μm LC coating) as a function of the RH. The experiment was done twice. The RH was first increased and then decreased to investigate the corresponding responsive behavior of the bilayer film. The inset illustrates the bending radius *r* defined for the bilayer film. (b) Curvature of the bilayer films (I and II) as a function of the RH in the second running. The bilayer film I is a 25 μm PA-6 and 4 μm LC coating. The bilayer film II is a 15 μm PA-6 and 4 μm LC coating. Film III is a pure PA-6 film of 25 μm thickness.

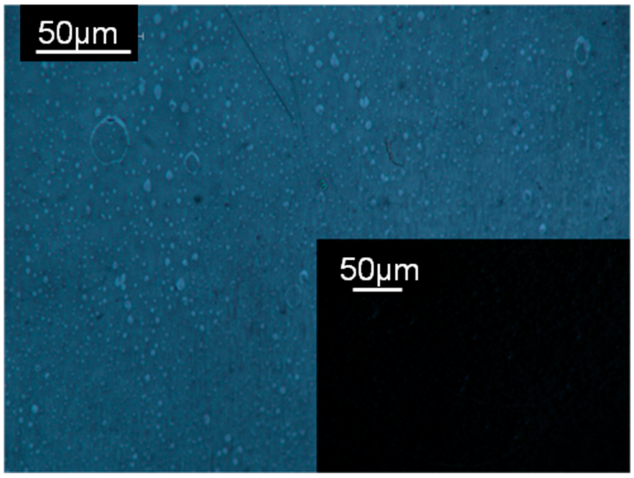

Figure 6. POM image of the LC coating between crossed polarizers with the stretching direction of the sample oriented at approximately 45° to the polarizer axes. The inset is a POM image of the LC coating between crossed polarizers with the stretching direction of the sample parallel or perpendicular to the polarizer axes.

To check whether the hydrogen bonds in the LC network are completely broken after activation with NaOH, both sides of the LC coating, i.e., the top and bottom surface, were investigated by reflection FTIR measurement. The FTIR spectra (see Figure 8) indicate that, after activation, the absorption peak at 1682 cm^{-1} for the top surface has completely disappeared, which indicates that the hydrogen bonds are completely broken.[20] However, for the bottom surface, the absorption peak at 1682 cm^{-1} still exists, which means that hydrogen bonds in the LC network are not completely eliminated. This is probably due to the diffusion limitations of the alkaline solution in the bottom surface of the LC network. In other words, it is assumed that the PA-6 substrate restricts diffusion of the alkaline solution into the LC coating, and a sodium salt gradient is generated.[30]

On the basis of these data, the bending motion of the humidity-responsive bilayer actuator could be due to several parameters (see Figure 9), such as the large expansion of the LC network, the splay alignment of the LC network, and the sodium salt gradient in the LC network. When the humidity increases, the LC polymer layer exhibits a large expansion,

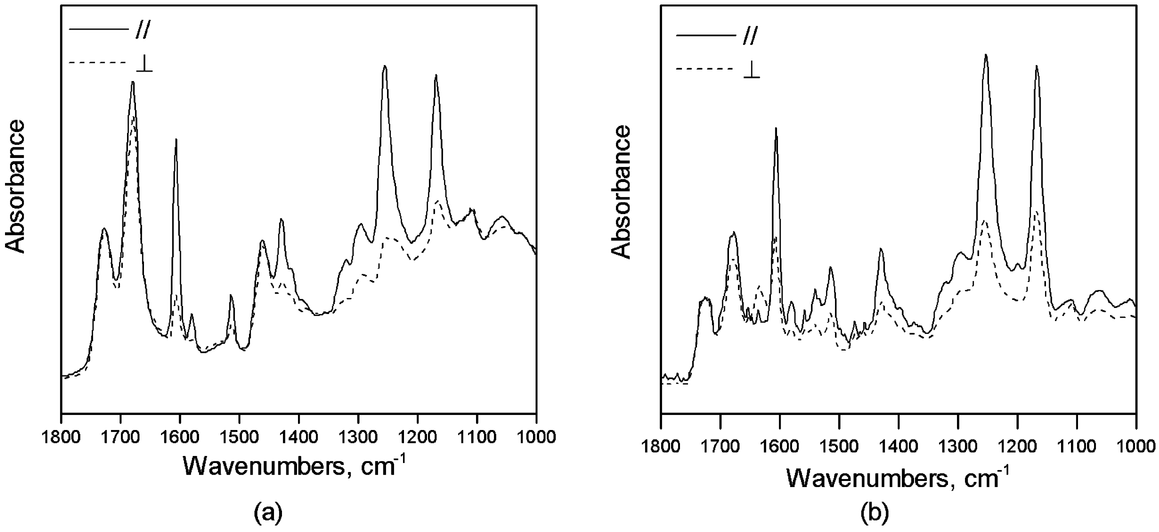

Figure 7. Polarized ATR spectra of the LC coating: (a) bottom surface of the LC coating attached to the substrate; (b) top surface of the LC coating exposed to air.

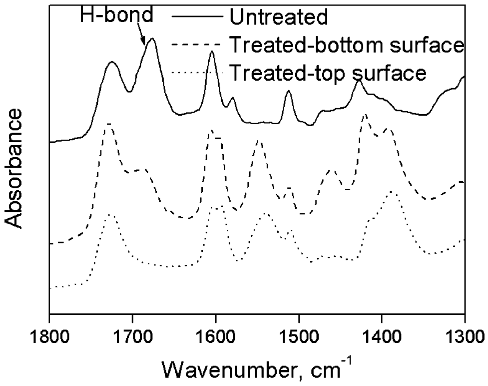

Figure 8. FTIR spectra of the LC coating before and after treatment in a NaOH solution. Here, the top surface is the surface of the LC coating exposed to air and the bottom surface is the surface of the LC coating attached to the substrate.

which leads to a reduction in strain mismatch and thus the unbending of the bilayer actuator. Previous work indicates that LC polymer networks exhibit an anisotropic expansion under humid conditions, which has a smaller macroscopic expansion parallel to the director and a larger macroscopic expansion perpendicular to the director.[20,21,24] Because of the director rotation profile in the splay-aligned LC network, mismatches of (in-plane) expansion at the two surfaces (top and bottom) of the LC polymer layer force bending deformation toward the bottom surface of the LC polymer layer, which contributes to the unbending of the bilayer actuator because the bilayer actuator is prebent. Meanwhile, the sodium salt gradient in the LC network also results in a larger expansion at the top surface and a smaller (or even no) expansion at the bottom surface of the LC polymer network, which is beneficial to the unbending deformation of the bilayer actuator as well. All of these parameters contribute to the unbending of the bilayer actuator. Therefore, we are not able to determine the exact or dominant mechanism of deformation of the bilayer polymer. We tried to remove the LC polymer layer from the bilayer to obtain a free-standing film that could be analyzed in detail. Unfortunately, we did not succeed because the films were too thin.

■ CONCLUSIONS

We have demonstrated a humidity-responsive bilayer polymer actuator that consists of an oriented PA-6 substrate and a splay-aligned hydrogen-bonded LC coating. A facile method, i.e., spray coating, was utilized to fabricate this bilayer actuator, which can be easily combined with other processing technologies. After hydrogen bonds are broken, the bilayer film acts as a humidity actuator that responds to the humidity changes with a bending-mode deformation in a fast, reversible, and repeatable manner. At high humidity, the actuator is straight, while at low humidity, the polymer bends. Interestingly, this bending behavior is different from that of polyelectrolyte bilayer actuators, which bend more if the humidity is increased.[14] It is possible to produce other stimuli-responsive bilayer actuators by using different LC mixtures that respond to light, temperature, etc. Furthermore, more complex deformations are possible by controlling the alignment of the LC polymers and creating patterned structures. For example, larger deformations of the bilayer film, such as curling deformation, can be created by using a chiral nematic configuration of the LC network.[16]

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: C.W.M.Bastiaansen@tue.nl (C.W.M.B.), A.P.H.J. Schenning@tue.nl (A.P.H.J.S.).

Notes

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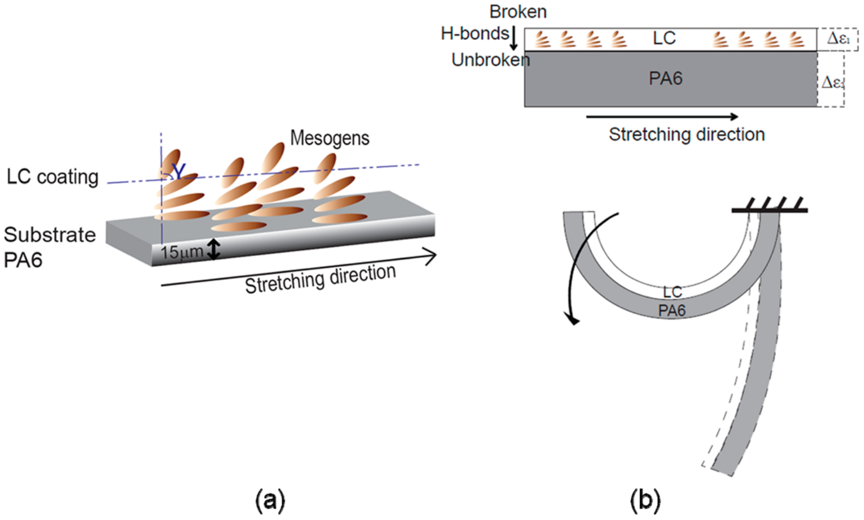

Figure 9. (a) Schematic illustration of the splay-like-aligned LC coating on the PA-6 substrate. (b) Schematic representation of a humidity-responsive bilayer film. The LC coating shows splay-like alignment and has a hydrogen bond gradient from top to bottom in the network. Under the humid conditions, the LC coating has a larger expansion ($\Delta\varepsilon_1$) compared to the expansion ($\Delta\varepsilon_2$) of the PA-6 substrate. The bilayer film exhibits less bending.

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