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A pH-Responsive Liquid Crystal Hydrogel Actuator with Calcium-Induced Reprogrammable Shape Fixing

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ABSTRACT: Soft polymer actuators have myriad applications and have therefore gained considerable attention in recent years. However, it remains challenging to prepare soft actuators with predefined shapes. Here, a bilayer polymer actuator with a (re)programmable shape is prepared from a microporous anisotropic polypropylene scaffold and a thin, pH-responsive liquid crystalline network (LCN) layer. The hydrogen bonds between dimerized benzoic acid derivatives in the LCN can be disrupted by an alkaline treatment, resulting in a pH-responsive LCN hydrogel layer. The pH-responsive actuation is governed by both the anisotropic mechanical properties of the scaffold and the cross-link density of the LCN hydrogel. Ca²⁺ ions can be used to chemically cross-link the actuator resulting in an initial programmed shape. The shape fixing can be reversed by removing the Ca²⁺ ions with an ethylenediaminetetraacetic acid (EDTA) solution. The shape fixing can be performed locally, resulting in pH-responsive actuators with three-dimensional initial configurations of choice.

KEYWORDS: polyolefins, soft actuators, pH-responsive materials, reprogrammable, liquid crystal polymers, hydrogels, hydrogen bond

INTRODUCTION

Soft polymeric actuators have garnered much interest over the past decade due to their potential applications, including microfluidic devices, artificial muscles, and soft robotics. Various stimuli-responsive polymeric systems were developed, which change shape when exposed to light, electric or magnetic fields, humidity, pH, or temperature. More recently, examples of combined actuators and programmable shape-memory materials have been reported, enabling (re)programming and reuse of these materials.

Functionalyzed anisotropic polyolefins were used to fabricate soft actuators by either incorporation of responsive small organic molecules or a secondary responsive polymer network. Light-, humidity-, and temperature-responsive anisotropic polyolefin actuators have been reported. Expanding the types of stimuli and enabling shape reprogramming of the actuators may increase the range of applications for these types of soft polymer actuators.

In this work, a pH-responsive anisotropic microporous polypropylene (PP)-liquid crystalline network (LCN) composite bilayer actuator is synthesized, which can be locally fixed in a programmed shape, enabling programmed actuation. The thin LCN layer inside the PP scaffold is comprised of a dimerized benzoic acid monoacrylate derivative (I) and a diacrylate cross-linker (II), as depicted in Figure 1a. During base treatment, the hydrogen bonds (H-bonds) between benzoic acid moieties are disrupted and a hydrogel is formed (Figure 1b). This allows the LCN layer to swell primarily in the direction perpendicular to the molecular director, resulting in a pH-responsive shape deformation (Figure 1c). This shape deformation is highly dependent on the cross-link density. Calcium ions can be used to render the benzoic acids insensitive to changes in pH by binding two carboxylate salts.

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This cross-linking enables (local) shape fixing of the hydrogel and can be undone by removing the Ca²⁺ ions with an ethylenediaminetetraacetic acid (EDTA) solution. The directionality of the actuation is governed by both the scaffold as well as the cross-link density in the LC hydrogel. The cross-linker limits swelling perpendicular to the alignment director, promoting actuation along the alignment director. The anisotropy in the modulus of the PP scaffold makes deformation parallel to the fibrils more difficult, while promoting deformation perpendicular to the small fibrils (Figure S1).

### RESULTS AND DISCUSSION

**Fabrication and Characterization of the Composite Actuators.** The pH-responsive anisotropic microporous PP–LCN composite soft actuators were made by filling a thin LCN layer in the top side of the PP scaffold according to the method described in our previous work. A thin layer of the LC mixture, consisting of a dimerized benzoic acid derivative (I) and a diacrylate cross-linker (II), Figure 1a, is deposited on a glass slide with a sacrificial PVP layer. Subsequently, the PP scaffold is brought onto the molten LC mixture, upon which the LC mixture flows into the PP scaffold via capillary forces. Prior to photopolymerization, the LC-filled PP scaffold is exposed to a temperature treatment in which the LC mixture is brought into the smectic phase. The PP scaffold has anisotropic pores comprised of small fibrils and larger girders (Figure S1). In addition to the increased mechanical robustness, the geometric confinement of the pores aligns the mesogenic cores of the LC mixture parallel to the small fibrils during fabrication. Due to the stretching process by which the scaffold is made, the small fibrils are much stiffer than the girders, as measured by dynamic mechanical thermal analysis (DMA) (Figure S1). The storage modulus parallel to the fibrillar direction is approximately 3.5 times greater than that to the orthogonal direction. This makes deformation of the scaffold easier perpendicular to the fibrils, hence promoting actuation perpendicular to the fibrillar direction. Two ratios between molecules I and II (Figure 1a) were used to investigate the role of the degree of cross-linking in the LCN on the actuation. Samples with either a 40 wt % cross-linker and a 60 wt % benzoic acid derivative or a 10% cross-linker and a 90% benzoic acid derivative were made, hereafter referred to as 40% Cl and 10% Cl, respectively. Previous work has shown that single-layer LCN actuators based on 10% Cl swell mainly in the direction perpendicular to the molecular director upon converting the H-bonded carboxylic acids into the carboxylate, forming a water-absorbing polymer hydrogel salt. However, in the case of 40% Cl, no swelling was observed. Planar aligned LCN actuators typically have a modulus in the order of 3 to 4 GPa in the alignment direction, which is approximately two times greater than the modulus perpendicular to the molecular director.

After fabrication of the freestanding composite films, the layer thickness of the LCN in the scaffolds was determined by SEM imaging of cryogenically cut cross sections (Figure 1c and S2). Both samples are a bilayer with a 5 μm thick composite region comprised of both the LCN and scaffold and a region...
that consists only of the PP scaffold. There is no LCN layer on top of the scaffold, and defects in the LCN layer appear to be absent. The FT-IR spectrum shows a distinct $\text{C} = \text{O}$ stretching vibration at $1680 \text{ cm}^{-1}$ originating from the dimerized benzoic acids (Figure S3). Wide- and medium-angle X-ray scattering (WAXS and MAXS) reveal a lamellar spacing of $3.9 \text{ nm}$ perpendicular to the fibrillar direction and intermolecular stacking parallel to the fibrillar direction near $0.4 \text{ nm}$ for both the 10% Cl and 40% Cl samples (vide infra). Both features are characteristic of the formation of a smectic A (SmA) phase, in which the liquid crystals are aligned parallel to fibrils. However, for the 10% Cl sample, the layer spacing is more pronounced, suggesting a greater degree of order and/or alignment.

**pH-Triggered Actuation.** The pH-responsive shape changes of the anisotropic polymer actuators were investigated as a function of their alignment and cross-link density. Four actuators with two different cross-link densities (10% Cl and 40% Cl) were cut from larger sheets, both parallel and perpendicular to the fibrillar direction, to a size of $40 \times 5 \text{ mm}^2$. After a 0.1 M KOH solution treatment, a polymer K$^+$ salt was formed, accompanied by COO$^-$ stretching vibrations at $1540 \text{ cm}^{-1}$ and $1384 \text{ cm}^{-1}$ in the FT-IR spectrum (Figure S3). In Figure 2, an overlay is shown of the initial, H-bonded state and the final bent state in the polymer salt form. For samples cut parallel to the fibrillar direction, the initial state was always straight. The samples cut perpendicular, however, have a prebend of which the radius was not well defined. This might be due to the low modulus of the PP in this direction, in combination with the anisotropic polymerization-induced shrinkage and the difference in cross-link densities. In the case of the 40% Cl films, the sample cut parallel to the fibril direction had the largest deformation, which is surprising given that the scaffold is much stiffer in that direction, which should hinder actuation (vide infra). The sample cut perpendicular had almost no deformation, indicating that the composites made of 40% Cl have a preferential deformation direction parallel to the fibrillar direction. For 10% Cl, an inverse trend is observed compared to 40% Cl (Figure 2c,d). The sample cut parallel to the fibrils in the H-bonded state has a slight bend parallel to the fibrils, resulting in a “gutter”-like shape with the LCN layer on the inside. When submerged in the 0.1 M KOH solution, the film flattened out, indicating an expansion of the LCN perpendicular to the fibrillar direction has taken place, a transition that did not take place for the 40% Cl sample. When looking at the side of the sample in Figure 2c, only a minute actuation is recorded. The sample cut perpendicular to the fibrils in Figure 2d has a large prebend with the LCN layer on the inside of the curvature in the H-bonded state. When exposed to the 0.1 M KOH solution, a large deformation perpendicular to the fibrils occurs, similar to the sample cut parallel to the fibrillar direction. For 10% Cl, it appears that the swelling is perpendicular to the mesogenic alignment director, unlike the actuation behavior of 40% Cl.

To shed more light on the actuation behavior, the dried polymer K$^+$ salt films (Figure 3) were further characterized by WAXS and MAXS. The 40% Cl polymer salt sample still has an isotropic ring near the lamellar spacing, while in the 10% Cl sample the diffraction patterns disappear. The transition to this “X-ray silent” morphology is linked to an amorphous morphology, in which most of the order is lost. These results show that the 40% Cl sample is able to partially maintain its order, while the 10% Cl loses the majority of its order when brought into the K$^+$ salt form. This contrast is most likely the result of the higher cross-link density in the 40% Cl sample, allowing it to maintain its lamellar morphology and limiting the expansion parallel to the fibrillar direction owing to the higher material stiffness. A simplified illustration of the described morphological changes is given in Figure 3i. Previous research showed that 10% Cl in the salt form can easily uptake water, resulting in swelling of the network and the formation of a hydrogel, explaining the actuation mechanism with the expanding LC layer on the outside of the bend. For 40% Cl, however, this is not possible because 40% Cl does not swell due to water uptake when brought into the salt form. A possible actuation mechanism for 40% Cl is either the increased volume due to the order–disorder transition or the uptake of K$^+$ ions. Previous studies revealed that networks comprised of 50% Cl were able to retain 21.7 wt % of K$^+$ ions when fully converted to the salt form. These results showed that the actuation of the LC hydrogel composite is a balance between anisotropy in the stiffness of the scaffold, anisotropy in swelling, the order–disorder transition, and K$^+$ uptake when switched between the H-bonded and K$^+$ salt forms.

The pH response of the actuator made from 10% Cl and cut perpendicular to the fibrils was investigated in more detail, as this actuator gave the largest response. Upon submerging of the H-bonded film into a 0.1 M KOH solution, the actuation occurs almost instantaneously (Video S1). To examine the actuation in more detail, a titration was performed with either an acid or a base at 10 s intervals. As shown in Figure 4, switching between the two states occurs over a quite narrow pH range. When titrating with a base, the actuation starts near pH = 10, and the largest deformation takes place between pH 11.1 and 12. The reverse process, in which titration is performed with an acid, shows a small hysteresis. The largest deformation takes place between pH 11.7 and 11, indicating that the reversible switching occurs in a relatively narrow pH range.
window, which is related to the pK_a of the benzoic acid group within the LCN hydrogel.¹⁷

**Shape Fixing with Ca^{2+} Ions.** To fix the shape of the pH-responsive actuators, calcium ions can be used to cross-link the composite actuator in the polymer salt state. Ca^{2+} can bind to two carboxylate units in the LCN, resulting in an initial programmed shape.¹⁸,³⁵ By submerging the sample in a 0.1 M CaCl_2 solution, the K^+ ions in the polymer salt actuator were exchanged with Ca^{2+} ions. This resulted in a shift of the COO\(^{-}\) vibration from 1384 to 1390 cm\(^{-1}\) in the FT-IR spectrum, as

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**Figure 3.** WAXS (top row) and MAXS (bottom row) spectra of both 10% Cl (a to d) and 40% Cl (e to h) composite actuators. The direction of the fibrils in the scaffold is depicted with a black arrow. A simplified illustration of the described morphology is given in (i) with molecules I and II in red and blue, respectively.

**Figure 4.** (a) Titration curve of the displacement of an actuator of 10% Cl cut perpendicular to the fibrils. Actuation when titrated with a base (b) and an acid (c). Scale bar = 1 cm.
illustrated with the shift from the dotted to the dashed line in Figure S3. This process can be reversed by submerging the sample in an 0.1 M KOH solution saturated with EDTA, which led to the return of the COO$^-_{170}$ vibration from 1390 to 1384 cm$^{-1}$, indicating the reversible binding of Ca$^{2+}$ ions.

After forming the K$^+$ polymer salt, a physical molding procedure was used to locally expose the sample to Ca$^{2+}$ ions. As shown in Figure 5a, by placing the sample in a “zig-zag”-shaped mold (i), which was not completely connected leaving holes for exposure, horizontal areas are not exposed to the Ca$^{2+}$ ions, whereas the vertical regions are exposed. An actuator, made from 10% Cl cut perpendicular to the fibrils direction, was first brought into the K$^+$ salt form. The sample was then placed into the “zig-zag” mold and submerged in a CaCl$_2$ solution yielding a fixed “zig-zag” pattern as the final programmed shape (ii). Reprogramming was demonstrated by programming and reprogramming left- and right-handed curls, as shown in Figure 5b. The initial H-bonded, flat shape (i) was brought into the K$^+$ salt form. By wrapping the sample around a cylinder and submerging it into a CaCl$_2$ solution, a left-handed curled film was produced (ii). The shape was reprogrammed by first removing the Ca$^{2+}$ ions with a saturated EDTA solution and subsequently wrapping the film around the same cylinder in a right-handed manner. Fixing the shape by exposing the film to Ca$^{2+}$ ions resulted in a film with a right-handed curl (iii).

**pH-Responsive Actuator with Programmable Shape Fixing.** By submerging the “zig-zag” mold only partially in a CaCl$_2$ solution, a shape can be programmed with two separate regions, that is, a pH-responsive region, which was not submerged, highlighted in blue, and a patterned fixed region with alternating exposed and non-exposed areas, highlighted in alternating blue and red in Figure 6a. When changing the pH from acidic to alkaline, the large blue area actuates as expected while the alternating region also bends, however, with non-actuating sections in between, as shown in Figure 6b. The programmed shape can be removed and brought back into the H-bonded state by first removing the Ca$^{2+}$ ions with EDTA and subsequently decreasing the pH of the solution, resulting in an actuator with a typical prebend, as shown in Figures 6c and 2d.

**CONCLUSIONS**

In this work, a reprogrammable, pH-responsive actuator has been made comprised of an anisotropic, microporous PP scaffold and a LCN hydrogel layer showing a large deformation in a narrow pH window. The anisotropic modulus of the PP and anisotropic swelling of the LCN hydrogel determine the actuation direction of the composite film. By locally exposing the actuator to Ca$^{2+}$ ions, chemical cross-links can be made, resulting in predefined shapes.

With our method, complex programmable deformations in soft actuators are possible. Furthermore, both the layer thickness and the chemical composition of the LCN can be altered to optimize the actuation properties further. A microporous anisotropic scaffold can also be used as a platform...
for other stimuli-responsive polymers, such as fortifying hydrogels, which have a limited mechanical strength.36

### MATERIALS AND METHODS

**Materials.** 4-((6-(Acryloyloxy)hexyl)oxy)benzoic acid (molecule I) was received from Ambeed Inc. (USA), 4-((4-((6-(acryloyloxy)-hexyl)oxy)phen氧)carbonyl)phenyl 4-((6-(acryloyloxy)hexyl)benzoate (molecule II) was supplied by Synthon Chemicals. Tetrahydrofuran (THF) and ethanol were purchased from Acros chemicals. Irgacure 819 was purchased from Ciba. The PP scaffold, CelGard2500, was purchased from Celgard, USA. Polyvinylpyrrolidone (Mw 1,300,000 kg/mol), KOH, EDTA, and HCl were purchased from Sigma-Aldrich.

**Fabrication of the Composite Soft Actuators.** Two LC mixtures were made consisting of either 60 wt % monoacrylate (I) and 40 wt % diacrylate (II) (40% Cl) or 90 wt % monoacrylate I and 10 wt % diacrylate II (10% Cl), with the addition of 1 wt % photoinitiator and 0.1 wt % inhibitor. The LC mixture was dissolved in THF (20 wt %) and subsequently bar-coated with a wet film thickness of 6 μm onto a PVP-coated glass substrate. After evaporating THF, the PP scaffold was rolled onto the molten LC layer. After application of the PP scaffold, the sample was cooled inside a temperature-controlled chamber at 1 °C/min from 115 to 75 °C. The sample was then photopolymerized with UV light for 15 min with a light intensity of 15 mW/cm² in an inert atmosphere. Finally, the sample was removed from the sacrificial layer by submerging it in lukewarm water.

**DMA Analysis.** DMA measurements of the scaffold were performed on a TA Instruments Q800 series dynamic mechanical thermal analyzer. The sample with a width of 5.3 mm was measured at an oscillation displacement of 25 μm, a frequency of 1 Hz, and a preload force of 0.01 N. The sample was heated between 0 and 110 °C at a rate of 5 °C/min.

**Scanning Electron Microscopy.** SEM analysis was performed on a Quanta FEG 3D SEM (FEI) in secondary electron mode, with a beam current of 5 kV. Cross sections of the samples were prepared by submerging the sample into ethanol and freezing the wetted sample in LN₂. Subsequently, the sample was cut with a scalpel inside the LN₂ parallel to the fibril direction.

**X-ray Scattering.** MAXS/WAXS experiments were performed on a Ganesha lab instrument equipped with a Genix-Cu ultralow divergence source producing X-ray photons with a wavelength of 1.54 Å and 1 × 10⁴ photons per second. Diffraction patterns were collected on a Pilatus 300 K silicon pixel detector with 487 × 619 pixels of 172 μm².

**Infrared Spectroscopy.** Fourier transfer infrared (FT-IR) spectra were measured on a Varian 670-IR spectrometer equipped with a golden gate setup in attenuated total reflection mode.

**Actuation and Titration Experiments.** Samples were cut perpendicular and parallel to the fibril directions at a size of 5 × 40 mm². Samples were clamped by tweezers and set at a fixed height relative to the camera. The actuator was fully submerged in a glass box of approximately 400 mL with 0.1 M KOH solution while a camera was recording at an interval of 15 s. During the titration experiment, the film was submerged in a 0.1 M HCl solution. Subsequently, a 2 M KOH solution was added using a syringe pump at a rate of 15 mL/h. Titration toward low pH was performed by titrating with a 2 M HCl solution with the same rate. Image analysis was performed with ImageJ software.

**Shape Fixing.** A sample with a size of 40 × 5 mm² was cut with the long axis of the sample perpendicular to the small fibrils from 10% Cl. The sample was wrapped around a glass cylinder at an angle of 45° and fixed at the end with two small pieces of the parafilm. Finally, the sample was submerged in a 0.1 M KOH solution to break the hydrogen bonds. Subsequently, the sample was submerged in a 0.1 M CaCl₂ solution for 15 min. The sample was removed from the solution and released from the glass cylinder. To remove the programmed shape, the sample was submerged in a 0.1 M KOH solution saturated with EDTA for 15 min.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsapm.1c01686.

- Actuation of the 10% Cl LCN-PP actuator in the hydrogen-bonded state submerged in a 0.1 M KOH solution (MP4)
- DMA analysis of the microporous PP; SEM analysis of the composite film; and FT-IR data (PDF)

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**Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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