Smart Materials

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Engineering of Complex Order and the Macroscopic Deformation of Liquid Crystal Polymer Networks**

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In nature, the well-defined and precisely controlled structure of components on a molecular, supramolecular, and mesoscopic scale is crucial for the complex processes found in living organisms.[1] This hierarchical structuring has been a source of inspiration for materials scientists,[2–4] and has led to the field of functional supramolecular polymers.[5] However, it remains a challenge to program orientational and positional order on all length scales and in all three spatial dimensions in polymer materials. Herein, we demonstrate the straightforward engineering of complex order and macroscopic deformation of liquid crystal polymer networks that show well-defined deformation in three dimensions, through the use of patterned alignment layers in combination with polymerizable liquid crystals.[6,7] In liquid crystals, the molecular order is determined by the liquid crystalline phase, whereas at the mesoscopic level the 3D organization of the director can be controlled by alignment layers.[8] Photoalignment is an attractive method for the preparation of such alignment layers, and has previously been used to align liquid crystals, mainly for display applications. During this procedure, photosensitive materials are treated with linearly polarized light,[9–11] allowing straightforward complex patterning using photomasks (Figure 1 a).[12–15]

It has previously been shown that polymeric liquid crystalline materials can undergo mechanical deformation by an external stimulus owing to a reversible decrease in the anisotropy of the material.[16–18] Thus far, liquid crystalline networks have been used in which the molecular director only varies in one direction, that is, twisted nematic and splayed configurations that bend[19] or curl[20] after applying the stimulus. Recently, photoalignment of polymerizable liquid crystals has been used to prepare responsive shape-memory materials.[21] We now use this technique to prepare circularly patterned polymer networks, which respond to temperature increase with reversible, exotic shape deformations.[22,23] For the preparation of our alignment layers, we used a thin film of a cinnamate-based linearly photopolymerizable (LPP) polymer (Staralign 2100) spincoated onto glass substrates. To obtain an alignment cell, two substrates were glued together with a small (ca. 18 μm) gap between them. When irradiated

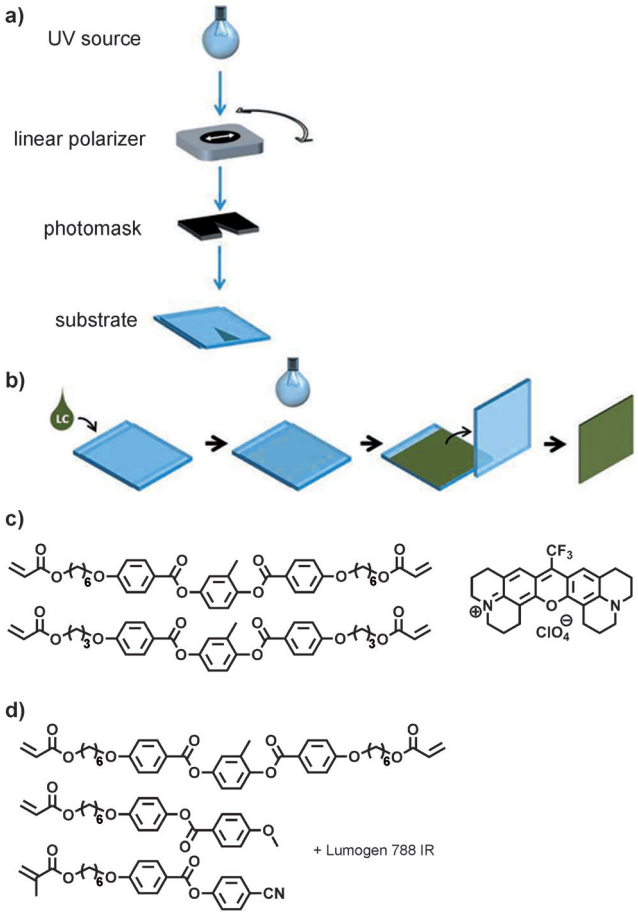

Figure 1. a) Setup for the preparation of patterned alignment cells. b) Procedure for making a patterned polymer liquid crystal (LC) network from a patterned alignment cell. c) Liquid crystal mixture for identification of the alignment director patterns. d) Liquid crystal mixture for the preparation of liquid crystal actuators.

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with linearly polarized UV light, the alignment material forms an alignment layer, with the alignment director oriented parallel to the direction of the UV light polarization. By slowly rotating the cell while irradiating through a photomask with a wedge-shaped opening, we prepared a series of different cells with a continuous change of the alignment direction throughout the LPP layer (Figure 1a).

The cells were filled with a mixture of polymerizable liquid crystals by capillary action, and after heating the liquid crystalline samples to the nematic phase, photopolymerization was carried out to obtain a polymer film in which the alignment direction of the liquid crystals was frozen (Figure 1b). We used two different nematic liquid crystal mixtures. One mixture consists of two mesogens, which are combined in a 1:1 ratio to reduce the clearing point and to allow curing at room temperature (Figure 1c).[7,19d,24] The mixture contains a blue dichroic dye (Rhodamine 700) that allows the determination of alignment direction in the resulting polymer network when it is placed between parallel polarizers. The second mixture consists mostly of mesogens with a single acrylate group, as the low crosslink density of the resulting film allows a strong shape deformation response upon heating.[25] This mixture contains an IR-absorbing dye (Lumogen 788 IR) to obtain an actuator that can be heated by applying IR irradiation (Figure 1d). To both mixtures, a radical initiator (Irgacure 184 or Irgacure 819, respectively) is added to allow photopolymerization.

We first focused on making liquid crystal polymer films with continuous, circular liquid crystal director profiles. The alignment layers were prepared by slowly rotating cells containing the LLP layers while exposing them to linearly polarized UV light through the wedge-shaped photomask (Figure 1a). Different patterns could be prepared by polarizing the UV light in different directions. When the polarization direction was set perpendicular to the long axis of the wedge, azimuthal alignment layers were obtained. Setting the polarization direction of the UV light parallel to the wedge created radial alignment layers, and a polarization direction set at an angle of 45° to the wedge produced spiral alignment layers. The cells were then filled with the mixture containing the dichroic dye (Figure 1b,c) and photopolymerized at room temperature in the nematic phase. The resulting films were then placed between polarizers and studied. Between crossed polarizers, the azimuthal, spiral, and radial films showed no light transmission in the areas where the mesogenic units are positioned either parallel or perpendicular to the polarization direction of the incoming polarized light; however, the transmission gradually increased towards the intermediate areas where the long molecular axis is at a 45° angle (Figure 2a). This manifested as a dark fan-shaped area in a bright field. Between parallel polarizers, the areas where the liquid crystals are aligned parallel to the polarization direction appeared in a deeper shade of blue compared with those aligned in a different direction (Figure 2a). This coloration is caused by the blue dichroic dye, which aligns with the liquid crystals and shows more absorption when it is aligned parallel to the polarization direction of the incoming light. Blue regions are observed at different areas in the polymer films, proving that azimuthal-, radial-, and spiral-aligned director

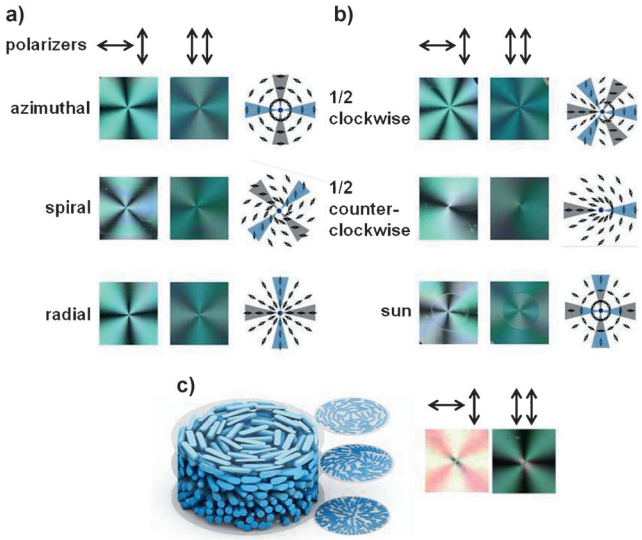

Figure 2. Liquid crystal crosslinked polymer films with circular alignment patterns. The gray triangles in the illustrations of the alignment patterns indicate non-transmissive areas in the crossed polarizer setup. The blue triangles indicate areas with no transmission between crossed polarizers, and with blue transmission between parallel polarizers. a) Films with azimuthal, spiral, and radial alignments viewed between crossed polarizers and parallel polarizers. b) More complex films, aligned using UV light with a rotating polarization direction; the substrate was always rotated counterclockwise. The bottom film was prepared using a rotating substrate in combination with the use of circular masks. c) Illustration of the circular twisted nematic alignment, and the resulting film between perpendicular and parallel polarizers.

profiles have been created. As expected, the black fan-shaped sections are stationary when the samples are rotated (Supporting Information, Movie 1).

To further explore our method, we also prepared more complex circular patterns without rotational symmetry. This was done by continuously rotating the polarization direction of the UV light during the rotation of the cell. Two patterns were created with the polarization direction rotating at half the speed of the substrate rotation. In one case, the polarization direction and substrate were rotating in the same direction, and in the other case they were rotating in opposite directions. The resulting polymer films made by using these cells showed the expected features under crossed and parallel polarizers (Figure 2b). As expected, in contrast to the azimuthal, spiral, and radial films, the black fan-shaped sections in these asymmetric samples are rotating (Supporting Information, Movie 1).

To demonstrate the power of our method, two polymer films with even higher complexity were prepared. In the first case, a structure was made in two steps with an azimuthal alignment on the inner circle and a radial alignment on the outer circle, which we have termed the "sun alignment" (Figure 2b). The alignment of the resulting film was verified between crossed and parallel polarizers, and showed the expected properties (Figure 2b). As a second example, an alignment cell was constructed from two glass substrates, one having a radial alignment layer and the other one an azimuthal alignment layer. The resulting polymer film

obtained from this cell possessed a liquid crystal configuration with a gradual transition from azimuthal to radial through the thickness of the film, which can be described as a circular twisted nematic alignment, and showed the expected features between parallel and crossed polarizers (Figure 2c).

To show the functionality of our materials, we investigated the actuation behavior of freestanding films upon heating by IR irradiation. To this end, new films were prepared using the second liquid crystal mixture (Figure 1d). In this case, photopolymerization was carried out at elevated temperature in the nematic phase to obtain a polymer film. The actuation behavior of the azimuthal and radial films upon heating was investigated. A piece of polymer film was cut in a circular shape from the azimuthal actuator around the center, followed by irradiation with an IR lamp while holding it in place with a suction gripper at the center. Prior to heating, the actuator was only slightly bent (Figure 3a). Upon switching on the lamp, deformation was observed into a conical shape within seconds, with the cone apex located at the center and pointing downward (Figure 3a, and Supporting Information, Movie 2). When the lamp was switched off, the film returned to its original shape. When the distance between the lamp and the actuator was varied, the upward bending angle changed accordingly (Figure 3b), which demonstrates that the degree of deformation depends on the intensity of IR irradiation. The actuation experiment was repeated for the actuator with a radial alignment pattern. When the IR lamp was switched on, the film deformed into an anti-cone shape (Figure 3c). The degree of actuation could be varied by changing the distance from the IR source. These findings are in agreement with theoretical models for the mechanical responses of disclinations in nematic crosslinked networks.[26,27] In the case of an azimuthal alignment pattern, a reduction of the liquid crystal order upon temperature increase leads to compression along the azimuthal direction and an expansion along the radial direction (Figure 3a). These stresses cannot be accommodated within the sheet plane, causing deformation of the flat sheet out of the plane into a cone. In the case of a radial alignment pattern, the opposite deformations take place (Figure 3c). This results in an anti-cone, which is recognizable as a saddle shape.

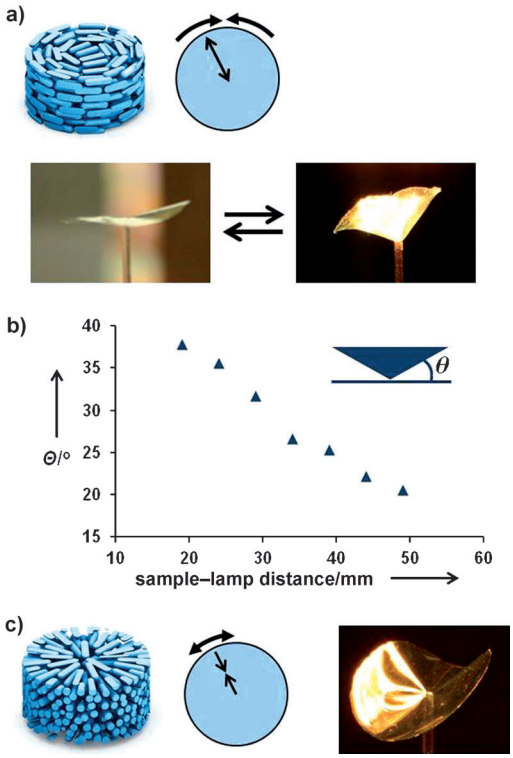

Figure 3. Actuation of films with azimuthal and radial alignments. a) Actuation behavior of an azimuthal polymer film upon heating with an IR lamp. b) Angle of upward bend versus the distance between the sample and the lamp. c) Actuation behavior of a radial polymer film. The arrows along the radius and the azimuth indicate the direction of deformation.

In conclusion, our results show that patterned alignment layers can be used to align polymerizable liquid crystals and prepare freestanding polymer films with complex order. The materials shown here comprise only a small number of the possible hierarchical structures that can be designed and prepared, and we expect that by using different mask sizes and patterns the possible dimensions and shapes can be greatly expanded. We have demonstrated that our polymer films can function as actuators that reversibly deform into cone or saddle shapes that are often seen in the complex and directed movement of living organisms. We can expand the range of possible applications by looking at different shapes, and we are currently investigating the deformation behavior of the other patterns described in this work. Additionally, we could use materials that respond to different stimuli, and the composition of the liquid crystal mixtures could be varied in order to change other properties of the material, leading to new and powerful methods for the fabrication of polymer materials with a complex order having novel optical, mechanical, and electronic properties.

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