Programmed morphing of liquid crystal networks

Laurens T. de Haan, Albertus P.H.J. Schenning*, Dirk J. Broer*

Group Functional Organic Materials and Devices, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Den Dolech 2, 5600 MB Eindhoven, The Netherlands

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A promising candidate for the development of stimuli-responsive morphing materials are based on liquid crystal polymer networks. These anisotropic materials will contract along the alignment director and expand perpendicular to it when subjected to an anisotropy-reducing stimulus, such as heat. As the liquid crystals can be aligned prior to polymerization using various alignment techniques, it is possible to create networks with programmed, complex director profiles in three dimensions. This review shows the various designs that can be implemented and the complex morphing behavior that can be achieved in liquid crystal polymer networks.

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1. Introduction

Stimuli-responsive polymer materials, which respond to stimuli from the environment by changing their properties, are one of the focal points in materials science [1]. An important class of materials are those which reversibly change their shape upon exposure to a stimulus [2]. In particular, the ability to program a certain morphology into the material itself, which can be accessed at any time by applying the stimulus, would lead to materials that can be tailored to achieve a target actuation behavior without the need to assemble separate mechanical components. Applications for such materials could range from moving elements in microfluidic systems [3], such as shutters and flow controllers, to medical systems [4] and robotics [2c,5], where precisely controlled, complex movements are desired.

Promising candidates for the development of such materials are based on nematic liquid crystals. Liquid crystals possess a phase that has both anisotropic and fluid-like properties [6]. The material consist of rod-like molecules with orientational alignment that can be described by the alignment director $n$ and the order parameter $S$, where $S = \frac{1}{2} \cos^2 \theta - 1$, with $\theta (0 < \theta < \pi/2)$ being the angular deviation from $n$ (Fig. 1a) [7]. Liquid crystals typically have a multi-domain microstructure, but the alignment of the molecules can be controlled using various alignment techniques, such as electric fields, magnetic fields, or command surfaces, which allows excellent control over the molecular alignment even at macroscopic length scales.

When liquid crystals are equipped with polymerizable end groups, and a crosslinker is present, they can be polymerized into molecularly well-ordered polymer networks, commonly referred to as liquid crystal networks. UV initiated radical polymerization is usually the chosen polymerization technique, which can be performed on liquid crystals containing acrylate moieties. The polymer network formed retains the molecular alignment of the monomers [6,8]. By combining such reactive mesogens with alignment techniques, excellent control can be obtained over the molecular arrangement within the material, though the restrictions imposed by the alignment techniques often require the liquid crystal polymer networks to be prepared as thin films. In addition, the alignment techniques tend to work only on monomers and not polymers. Depending on its glass transition temperature, the network can either be an elastomer or a glass at room temperature, which have different mechanical properties. However, in both cases the films undergo a shape deformation upon changing the temperature. An increase in temperature lowers $S$ and therefore increases the average $\theta$. This manifests as a contraction $L_\parallel$ (with $\lambda < 1$) along the nematic director ($L_\parallel$) and an expansion $L_\perp$ perpendicular to it ($L_\perp$), where $\nu$ is the Poisson ratio that relates the responses of $L_\parallel$ and $L_\perp$ (Fig. 1b) [9]. In the presence of molecules that respond to other stimuli, the order parameter of the polymer network becomes susceptible to other triggers and the dimensions may change, for instance, upon contact with water or chemicals or by being exposed to light of a specific wavelength. The ability to change shape upon actuation by an external trigger makes these...
materials of interest for their use as actuator. The most popular liquid crystal actuators are those which contain mesogens based on azobenzene. This mesogen will undergo a trans-to-cis conformational change upon irradiation at 365 nm, which causes a deformation similar to heating. This allows for the preparation of UV-responsive films, which are desirable due to light being a well-controlled and versatile stimulus [10].

While the linear contraction and expansion behavior of liquid crystal actuator is interesting [11], their true potential lies in the generation of bending into three-dimensional shapes [12]. A common strategy to achieve bending is by using a bilayer consisting of a responsive liquid crystal network and a non-responsive polymer layer. Alternatively, bending can be achieved by exposing the material to an inhomogeneous stimulus. For example, when a UV-responsive material containing a UV absorbing dye is exposed to irradiation on one side, an intensity gradient will develop through the material. This causes a stronger deformation on one side, and bending takes place [13]. However, it would be more desirable to have access to single-layer, monolithic materials that undergo complex, 3-dimensional shape deformations without depending on the inhomogeneity of the stimulus, as this would greatly increase their versatility and the number of possible applications. To accomplish this, the morphology change has to be programmed into the molecular structure of the material itself, which is possible with liquid crystal networks. In the case of a uniaxially aligned film, $n$ is constant in all directions. When a homogeneous stimulus is used to actuate such a film, contraction and expansion do not lead to a bending deformation. However, by applying certain alignment techniques, films having a director variation in one or more directions can be prepared and more complex deformations can be achieved. This allows the development of programmable, complex shape deformation. The variation in director is often referred to as the director profile. To describe the director profile, a film can be pictured as a coordinate system, in which the $z$-axis run from $z = 0$ to $z = h$, where $h$ is the thickness of the film, and the $x$-$y$ plane is positioned parallel to the surface of the film (Fig. 1c).

To create liquid crystal polymer films with a non-uniform director profile in the $xy$ plane, an alignment technique that can facilitate the preparation of such alignments in the reactive mesogens is required. Polyimide layers are favored for the alignment of liquid crystals, but while advanced techniques for polyimide buffing are capable of generating non-uniform director profiles [14], the most versatile technique for the generation of complex director profiles is photoalignment [15]. To prepare photoaligned alignment layers, a photoresponsive material is irradiated with polarized UV light to cause a permanent or reversible chemical transformation. The molecules are more likely to absorb the light, and undergo the transformation, if the transition dipole moment is parallel to the electric vector of the polarized UV light. This creates anisotropy in the alignment layer, which can then be transferred to the reactive mesogens that come into contact with it. There are different photoalignment materials available. A popular class of materials are based on azobenzene. These material undergo a reversible trans to cis rearrangement when they absorb UV light, which causes the molecules to reorient. As the absorption is more efficient for molecules in which the transition dipole matches the polarization direction of the light, the alignment of the molecules is driven towards the direction perpendicular to the polarization direction, and anisotropy is created. Another class of alignment materials are the photopolymerizable polymers (LPP’s), which rely on a $[2+2]$ cycloaddition reaction between the photosensitive side groups of the polymer, which results in crosslinking of these groups [16].

Liquid crystal network actuators and morphing systems have been the topic of several reviews. These reviews often focus on systems that respond to one specific stimulus [10a,10g,17], or the applications of liquid crystal networks [4,9c,18]. In contrast, this review provides an overview of the methods that lead to complex morphology changes in liquid crystal polymer networks by controlling the director profile of the mesogenic units in three dimensions and without relying on an inhomogeneous stimulus or a bilayer system.

2. Alignment director variation through the thickness of the polymer film

2.1. Bending

A straightforward way to obtain bending deformations in liquid crystal networks is by utilizing the twisted and splayed nematic alignment profiles (Fig. 2). When a twisted or splayed alignment is present, there is a 90° change of the director along the $z$-axis. This causes expansion and contraction in the $xy$ plane at $z = 0$ to be different compared to the plane at $z = h$, and this mismatch in deformation causes bending. Therefore such films are suitable for the preparation of actuators that behave as cantilevers. The
actuators are somewhat similar in behavior to bilayer systems, except for the fact that instead of a sharp boundary between the layers, there is a gradual transition between the two sides of the film.

For twisted films, at $z = 0$ contraction along the $x$-axis and expansion along the $y$-axis takes place, while the opposite happens at $z = h$. This leads to an anticlastic deformation with negative Gaussian curvature (Fig. 2a) [19]. However, such curvature leads to stretches due to the curvature in the $x$ direction working against the curvature in the $y$ direction and vice versa. When these stretches become sufficiently large, suppression of one of the principal curvatures becomes more favorable, which leads to cantilever-like bending behavior. The strains at which suppression takes place depend on the sample dimensions, but for the dimensions of a typical experimental sample, a saddle shape is rarely observed. The direction in which bending is suppressed is the direction with the lowest curvature, since that curvature is easier to undo. Therefore, a long ribbon bends along its long axis while suppressing the bending along the short axis [20]. In addition, some out-of-plane twisting deformation can be expected, due to the chirality of the twisted nematic alignment (vide infra) [21], and this has also been observed in practice [22]. These predictions do not take into account any outside influences. For example, in clamped samples often formation of kinks can occur near the clamp, and such effects can make the deformation of cantilevers with this alignment profile unpredictable and hard to control [22]. A better controlled bending deformation can be achieved in films with splayed alignment [22]. In these films, bending will only be in one direction (no Gaussian curvature), and therefore there is no anticlastic deformation (Fig. 2b). The bending direction of the cantilever is solely determined by the alignment director on the planar side, as it always bends in the same direction as the alignment director, independent of sample dimensions. As there is no cost for anticlastic suppression to achieve cantilever-like deformation, bending of these actuators is more efficient. The bending is also less effected by clamping, if the clamp is placed at the edge of the film that doesn’t bend, which allows better controlled deformations.

Twisted and splayed actuators can find applications in interesting devices. For example, small, inkjet-printed, light responsive actuators with splayed alignment were prepared that mimic the movements of cilia found in microorganisms. A liquid crystal mixture was inkjet-printed from dichloroethane. The splay alignment was induced using a single rubbed polyimide layer that induced a homeotropic alignment with an 80° pretilt angle on one side of the film, and a surfactant was added to the liquid crystal mixture to induce planar alignment on the other side (Fig. 3a and b). This resulted in splayed alignment with a uniform director on the planar side due to the pretilt angle. In a special case the structures consisted of two domains: One domain contained the azobenzene derivative A3MA, which undergoes a trans-to-cis isomerization when irradiated at 358 nm, while the other domain contained the azobenzene derivative DR1A, which undergoes this transition at 490 nm (Fig. 3b). This allowed independent actuation of the domains with light of different wavelengths, to induce asymmetric motion with a different forward and backward stroke, which should be capable of creating flow in liquids (Fig. 3c and d). Such flow generation could be useful in microfluidic systems [23].

By using hydrogen-bridged liquid crystal networks (nOBA), twisted and splayed actuators were produced that respond to water vapor (Fig. 4a). After polymerization, water is not yet capable of penetrating the network, but when the film is treated with a basic solution (usually KOH) the internal hydrogen bonds are broken and a hygroscopic salt is formed. When water is absorbed the network swells, the order parameter is reduced and the anisotropic deformation results in stronger expansion perpendicular to the alignment director. In this way, actuators that respond to humidity have been prepared (Fig. 4b). As different solvents have different swelling capability with respect to the network, they will also respond to solvent polarity upon immersion (Fig. 4c). The activation with basic solution will be reversed in an acidic solution, which causes the actuator to respond to solution pH (Fig. 4d). All these films were pre-bent after polymerization due to intrinsic stresses, which explains why they were not flat in the non-swollen state [24].
Curl-shaped and helicoidal deformation can be achieved by cutting ribbons from a 90° twisted nematic network in such a way that the alignment director at the surface makes a 45° angle with the short axis of the ribbon. Like twisted nematic actuators that bend, the coiling deformation is caused by a mismatch in contraction and expansion in the xy plane at \( z = 0 \) and at \( z = h \). The angle \( \theta \) between the long axis of the ribbon and the alignment director in the xy plane at \( z = 0 \) determines the handedness of the resulting coil; when the angle is positive (clockwise from the long axis), the coil will be right-handed, and when it is negative (counterclockwise from the long axis), the coil will be left-handed (Fig. 5). There is also a small influence of the twist handedness on the formation of the coils [21], which will be discussed below.

It was shown, both experimentally and through finite-elements simulations, that cutting ribbons with \( \theta = \pm 45° \) can lead to the formation of both helicoids and curls. In this research, a mixture of a polymerizable, achiral mesogen (A-6OCB), a nonreactive LC (6OCB), a nonreactive left-handed chiral dopant (S-811), plus 7% of crosslinker (HDDA), was polymerized between rubbed polyimide (6OCB), a nonreactive left-handed chiral dopant (S-811), plus 7% of crosslinker (HDDA), was polymerized between rubbed polyimide alignment layers with orthogonal alignment directors to create a polymer network with a 90° left-handed twist (Fig. 6a). Upon removal of the nonreactive components, anisotropic shrinkage caused the deformation into a chiral shape. Ribbons were cut from this film with \( \theta \) being 45° or -45°, which were called S- and L-geometry, respectively. The length and thickness of the ribbons were kept constant while the width was varied. It was found that narrow ribbons with a small width/thickness ratio twist around a straight central line to form helicoids with negative Gaussian curvature and no bending (Fig. 6b and c), while wide films with a large width/thickness ratio will bend to form curls with small Gaussian curvature and strong bending (Fig. 6d and e). The dependence of the shape on the sample dimensions is caused by the competition between bending energy cost and in-plane elastic energy cost: Narrow films are easier to be stretched than to be bended, which leads to helicoid formation, while wide films are easier to be bended than to be stretched, and form coils. Furthermore, it was found that the shapes uncurl upon raising the temperature, go through a flat state (at temperature \( T_{\text{flat}} \)), and then curl into the opposite handedness (Fig. 6b–c). The pitch was plotted as a function of temperature, and was shown to fit well with the theoretical predictions of the shape deformations (Fig. 6f and g). It was also predicted that at temperatures near \( T_{\text{flat}} \), the wide ribs should transition into a helicoid shape, but this could not be verified in the experiments [25].

The deformation of the same ribbons, in which \( \theta \) was of a different value than 45° or -45°, which was termed X-geometry, was also studied. Only the narrow ribbons with small width/thickness ratios were considered in this study. Interestingly, it was found that when \( \theta \) was not ±45°, the formation of helicoids is not possible and only coils are observed. In other words, only S- and L-geometry can produce helicoids. Simulations showed that for ribbons with a small \( \theta \) (between 3° and 9°), small variations in \( \theta \) strongly influenced the pitch, but did not influence the diameter of the coil. It was also shown that upon gradually increasing \( \theta \) from 5° to 45°, the shape gradually changes from a coil into a helicoid (Fig. 7a). Finally, simulations showed that at \( \theta = 0 \), the ribbon still has a non-zero pitch (Fig. 7b). This is in agreement with the earlier observation that such ribbons tend to twist out of plane instead of showing unidirectional bending (as discussed in paragraph 2.1), and the effect is indeed caused by the chirality of the director twist. However, the effect is very weak and can be cancelled out by having \( \theta \) deviate a few degrees from 0. In this case, achiral bending can be obtained [21].
Fig. 4. Liquid crystal films based on twisted and splayed alignment that deform upon water swelling. a) Composition of the reactive liquid crystals used to make the network. b) Base-treated films that deform based on humidity, at high (85%) and low (15%) relative humidity. The films were treated with KOH for various periods of time (0–20 s) prior to the experiment. Copyright Institute of Electrical and Electronics Engineers c) The base-treated liquid crystal film shows different bending behavior in different solvents, in this case water and acetone. Copyright Wiley–VCH d) The activated film de-swells when the pH is lowered. Copyright Institute of Electrical and Electronics Engineers.

Fig. 5. Coil formation in ribbons made from twisted nematic films upon lowering the order (helicoids not shown). a) When the angle $\theta$ between the long axis of the ribbon and the nematic director at $z = 0$ is positive, a right-handed coil is formed. b) When $\theta$ is negative, a left-handed coil is formed.
UV-driven coiling actuators have also been prepared by adding azobenzene-based mesogens to the liquid crystal networks. Ribbons cut at a 45°/C14 angle from a densely crosslinked network with twisted nematic alignment displayed UV-driven deformation (Fig. 8a) [26]. In a different research, curling deformations of UV-responsive, azobenzene-containing films with twisted and splayed alignment were compared. However, the UV light that was used as the stimulus was polarized, and the irradiation was carried out on one side of the film, which created an intensity gradient over the thickness of the film. Therefore, the stimulus was not homogeneous [27]. UV-responsive curling actuators with a right-handed domain, a left-handed domain, and a straight domain have been prepared by adjusting the cutting method, and have been shown to be able to do work by moving the uncurled part up and down upon switching between UV and visible light (Fig. 8b) [28].

3. Alignment director variation in the xy plane of the polymer film

3.1. Continuous circular patterns

Liquid crystal films that deform into 3-dimensional shapes can be prepared using continuous, circular director profiles. These profiles are based on disclinations, which are the topological defects that occur naturally in planar aligned nematic liquid crystals without a preferred orientation, and can be observed as the centers of the brushes in a Schlieren texture when the material is analyzed using polarized optical microscopy [29]. They are described as singularities around which the alignment director varies continuously. The strength m of the disclination is defined as the number of times the director rotates when the singularity is circumnavigated once [30], with the sign depending on whether the rotation is in the same direction as the circumnavigation (+) or in the opposite direction (−). For example an azimuthal (concentric circles) or radial (spokes) pattern would be described as a +1 pattern, as the alignment director makes one full rotation when the disclination is circumnavigated once (Fig. 9a−c).

Fig. 6. a) Liquid crystal mixture used to make coil and helicoid ribbons. A-6OCB is a reactive mesogen, 6OCB is a nonreactive mesogen, HDDA is a crosslinker, S-811 is a nonreactive chiral dopant. b) Helicoids formed by narrow ribbons (thickness 35.2 μm, width 0.23 mm) with a negative θ (L-geometry). c) Helicoids formed by narrow ribbons (thickness 35.2 μm, width 0.22 mm) with a positive θ (S-geometry). d) Coils formed by wide ribbons (thickness 35.2 μm, width 0.76 mm) with a negative θ (L-geometry). e) Coils formed by wide ribbons (thickness 35.2 μm, width 0.83 mm) with a positive θ (S-geometry). f) Plot of the inverse twist pitch (pL) of the helicoids as a function of temperature, T/TNI, where T is current temperature and TNI is the nematic to isotropic transition point. A left-handed twist pitch is defined as positive and a right handed twist pitch as negative. The lines indicate theoretical predictions. g) Plot of the inverse pitch (pH) and inverse diameter (d) of the coils as a function of temperature. A left-handed twist pitch is defined as positive and a right handed twist pitch as negative. The open symbols represent the pitch and the filled symbols represent the diameter. The lines indicate theoretical predictions. Copyright National Academy of Sciences.

Fig. 7. Simulations of the effect of the angle θ on the shape of narrow ribbons at T = TNI, where TNI is the nematic to isotropic temperature. a) A series of ribbons with increasing θ. At low values, a coiling ribbon is observed, which slowly transitions into a helicoid upon approaching θ = 45°. b) Chirality reversal of the ribbons at values of θ around zero. At θ = 0, the ribbon still has a chiral shape. The open ring shape lies around θ = −2.5°. Copyright American Physical Society.
There have been theoretical predictions on the deformation of films with an alignment based on a $+1$ disclination. When disk-shaped piece of liquid crystal polymer film with an azimuthal director profile, described as $C = 2\pi r$, is heated, it adopts a new circumference $C' = \lambda C$ and a new radius $r' = \lambda^{-1} r$ due to anisotropic deformations. Because $0 < \lambda < 1$ and $r > 0$, we know that $C' < 2\pi r'$, which means that the circumference has become too small to accommodate the radius but is still a circle. This can only be solved by a deformation out of the plane of the film to form a cone shape. The circumference of the base of this cone equals $C'$, and the radius of the base equals $r'\sin\phi$, where $\phi$ is the cone opening angle (Fig. 10). The Gaussian curvature of the shape is positive and concentrated at the tip, where the singularity is located. In the case of a disk with radial alignment, $C' = \lambda^{-1} C$ and $r' = \lambda r$, so $C' > 2\pi r'$ which means that the circumference is too large for the radius. This can be solved by buckling of the circumference into a sinusoidal wave, which is positioned on a sphere with radius $r'$. This will generate an “anticone” shape with a source of negative Gaussian curvature located at the center (Fig. 10). At higher strains, the number of buckles can increase, leading to a more crumpled anticone [31].

Photoalignment has been used to prepare liquid crystal polymer films with these director profiles. By applying photoalignment to a rotating substrate, polymer networks with azimuthal and radial patterns could be prepared. The polymer films contained an IR absorbing dye, which allowed heating of the samples through IR irradiation. As expected, these networks deformed into cones and saddles, respectively, upon heating (Fig. 11a–c) [32]. By continuously rotating the polarization direction during the photoalignment procedure, director profiles based on higher order topological defects were also prepared [32a,33]. In one study, networks containing azobenzene-based mesogens were prepared with alignment structures based on disclinations ranging from strength $+2/5$.

![Fig. 8. a) Light-responsive coiling actuator based on a densely crosslinked network. Copyright Royal Society of Chemistry. b) Coiling actuator with a left-handed domain, a straight domain, and a right-handed domain. Upon irradiation with UV or visible light, one of the coiling domains contracts and the other expands. The liquid crystal mixture used is shown in Fig. 6a. Copyright Nature Publishing Group.](image)

![Fig. 9. Examples of disclinations, and the corresponding picture between crossed polarizers. a) $m = +1$ azimuthal disclination. b) $m = +1$ radial disclination. c) $m = +1/2$ disclination. Copyright Wiley–VCH.](image)

![Fig. 10. Shape deformation of films with an $m = +1$ disclination pattern upon heating. A film with an azimuthal pattern will contract along the radius and expand along the circumference to form a cone with a base radius $r'\sin\phi$, where $\phi$ is the cone opening angle. A film with a radial pattern will form an anticone shape with a buckled circumference. Copyright Royal Society.](image)
to $-2/5$, and their actuation behavior upon UV irradiation was systematically studied (Fig. 11d). It was found that the negatively charged disclinations produced deformations with a number of equally spaced valleys localized to the areas where the director points towards the singularity, the number of such areas ($V$) depending on the disclination strength according to $V = 2|m| + 2$. Similarly, the positively charged defects with $m > 2$ produced a number of tear-shaped dimples ($T$) equal to $T = 2m - 2$. Additionally, an $m = 10$ and an $m = -10$ disclination were also produced, which resulted in a deformation with 18 tear-shaped nodes and 22 valleys, respectively. Finally, arrays of defects were patterned on a single film and successfully actuated.

3.2. Discrete patterns

Discrete patterns can also be used to obtain complex shape deformation in liquid crystal polymer films. Such patterns consist of multiple domains, with varying alignment directors between the domains, which are joined by discontinuous boundaries. To avoid incompatibility between the domains, the deformations on both sides of the boundary have to match, which can be accomplished by having the angle between the boundary and the alignment director be the same on both sides. This is referred to as rank-1 connectedness. Keeping this rule in mind, it is possible to design a director profile and predict the change in shape upon actuation. It has been shown that this kind of blueprinting can be accomplished using a “vocabulary” consisting of six different types of triangular domains. The first two types are triangles which are an angular section from a $+1$ disclination (azimuthal or radial), the second two types have the alignment director running parallel or perpendicular to one of the edges, and the third two types have a rank-1 connected border bisecting the triangle (Fig. 12a). Upon actuation, the base angle $\theta$ of the wedge will change. When multiple wedges are joined in such a way that the base angles form a closed circle, the change in $\theta$ will

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**Fig. 11.** Liquid crystal polymer films with alignment profiles based on disclinations. a) Reactive liquid crystals used to make the films with azimuthal and radial alignment. b) Alignment and deformation behavior of a film with azimuthal alignment. Upon heating through IR irradiation, a cone shape is observed. c) Upward bending angle $\theta$ plotted against the distance between the sample and the IR lamp. The angle becomes larger when the distance is decreased due to an increase in temperature in the sample. d) Alignment and deformation behavior of a film with radial alignment. Upon heating through IR irradiation, an anti-cone shape ($n = -2$) is observed. e) Reactive liquid crystals used to make UV-responsive films. f) Deformation behavior of a series of films with alignment profiles based on disclinations with various values of $m$, containing azobenzene moieties to allow UV actuation. From left to right: Disclination strength $m$, schematic representation of the alignment profile, film as observed between crossed polarizers, deformation upon UV irradiation, and an illustration of the deformation. Copyright Wiley-VHC.

**Fig. 12.** a) The six different triangular building blocks from which morphing films with discrete alignment profiles can be constructed. Copyright SPIE. b) Four wedges are joined together to form a pattern similar to the azimuthal pattern shown earlier. When smoothening is not taken into account, this film is expected to deform into a pyramidal shape, but smoothening will cause the film to resemble a cone instead. Copyright American Physical Society.
create either an angular surplus or deficiency, and shape deformation in the third dimension will occur (Fig. 12b). This is similar to the deformation of the films with a circular pattern as described in the previous paragraph. The sharp boundaries are not expected to induce sharp folds, as the curvature will be delocalized over the surface to reduce bend energy, smoothening the surface. However, if more disclinations are present, this smoothening will cause incompatibilities and will be suppressed to some extent [34].

Several blueprint designs have been proposed. For example, two domains with perpendicular alignment directors, which would normally be incompatible, could be joined by a zigzag line of alternating points of positive and negative disclinations. At low strains, such a film could deform by having one domain crumple to accommodate to the deformation of the other domain. However, at higher strains it is more likely that the buckling gets divided over the entire surface. A likely solution is a shape with faceted cylindrical shells joined by an expanding midsection (Fig. 13a) [34b]. A different example is a film with a pyramidal pattern (as in Fig. 12b), but with a single \( \pm 1/2 \) disclination pair located halfway on one of the rank-1 connected boundaries. This film is expected to deform into a pyramid with a spiraling, crumpled moat around it (Fig. 13b) [34a]. Finally, a complex director profile based on a director blueprint was designed to prepare a film with apertures which could be opened and closed by applying heat. The profile consisted of two \( +1/2 \) disclination, with a \( -1 \) disclination directly in between. A slit was cut between the two \( +1/2 \) disclinations. Due to the presence of the slit, the contraction along the radius of the \( +1/2 \) defects no longer causes deformation into a cone shape, but instead the slit is opened. The profile can be tiled in a single film to allow multiple slits to be present, resembling a sieve in which the pores can be opened and closed by heat (Fig. 13c). This film was prepared in practice, and it was shown that the slits reversibly open when the film is floating on a hot water bath (Fig. 13d) [35].

Fig. 13. Deformation of films with discrete alignment patterns featuring discontinuous boundaries. a) Two domains with orthogonal alignment directors are joined by a boundary with disclinations of positive (blue) and negative (red) strength. The actuated shape is expected to have a crumpled and a flat domain at low strains, and to resemble two faceted cylindrical shells joined by an expanding midsection at high strains. Copyright SPIE. b) A pattern with a \( +1 \) disclination at the center and a \( \pm 1/2 \) disclination halfway one of the boundaries. This pattern is expected to result in a pyramid with a spiraling moat. Copyright American Physical Society. c) A pattern with \( -1/2 \) and \( +1/2 \) disclinations joined by slits, which are expected to open when the temperature is increased. Copyright The Royal Society. d) A film having the aperture-bearing director profile. It is floating on a water bath, which is heated to induce actuation. On the right, a close-up of a closed slit (top) and the same slit after opening (bottom) is shown. Copyright The Royal Society.

Fig. 14. Actuation behavior of a film with “radimuthal” alignment. a) Schematic representation of the alignment profile, including cross sections at \( z = 0, z = 0.5h \), and \( z = h \). b) An angular section of the film, with the alignment directors and the preferred bending direction. c) Division of a circular film into four and five sections. The areas that are not joined, and can therefore bend, are shown in gray. d) Internal energy of the system (U) as a function of the number of sections (m). The energy minimizes at \( m = 4 \). e) Preferred shape deformation of a film with radimuthal alignment upon heating, both as a drawing and as shown in practice. The liquid crystal used are shown in Fig. 10a. Copyright Royal Society.
4. Alignment director variation in 3 dimensions of a polymer film

Patterning in all three spatial dimensions could also be achieved using photoalignment. By combining an azimuthal substrate with a radial substrate, an alignment cell could be created with both a circular director variation in the xy plane and a 90° twist along the z direction, termed the “radimuthal” alignment (Fig. 14a) [32a]. When actuated, the film experiences forces similar to the twisted nematic films discussed earlier and deforms into a 3-dimensional shape with lower stress. However, suppression of the negative Gaussian curvature by bending in a single direction is not possible in this system due to geometric constraints. This can be envisioned by dividing the film into a number of angular sections that behave as twisted nematic actuators and fold towards the side with radial alignment (Fig. 14b). However, due to these domains being joined together, bending can only take place in the outer areas of the domains. The film therefore deforms into a polygon with curled edges and a flat center. The number of domains, and as such the number of edges of the polygon, is determined by a tradeoff between the total amount of bending surface and the deviation from the preferred bending direction. When the number of domains is small, more surface area is allowed to bend to release the stress, but as the domains are larger the bending direction close to the borders of the domains deviates more strongly from the preferred bending direction (Fig. 14c). The optimal shape can be found by minimizing the internal energy of the system (Fig. 14d), and was found to have four domains, which corresponds to a square shape. The film was also prepared in reality, and indeed showed the expected square shape (Fig. 14e) [36].

Shape-memory materials with alternating bend and straight domains were prepared by combining a substrate with a uniaxial alignment layer with a photoaligned alignment layer with domains with orthogonal alignment directions. In this way a cell with alternating twisted nematic and uniaxial domains was created. Upon heating, in a ribbon with this director profile the twisted nematic domains showed bending, while the uniaxial domains remained flat (Fig. 15a) [37]. By combining two photoaligned substrates, a network with orthogonal twisted domains was prepared. When a ribbon cut from this film was heated, the domains were bending in opposite directions, with a final shape resembling the folding of an accordion (the musical instrument). Such a shape deformation allows large end-to-end displacement with only small strains: The film can contract along almost its entire length while λ is only in the order of a few percent (Fig. 15b). As is often observed in twisted nematic actuators, an out of plane twisting was present in the actuation behavior of these films, which can again be explained by the small effect of the chiral twist in the molecular alignment (as explained in paragraph 2.2). A similar alignment profile was also prepared, consisting of a chessboard pattern with squares with orthogonal alignment directors. When this film was heated up, it deformed into a strongly dented shape (Fig. 15c). The deformations were all confirmed using a finite elements analysis [38].

5. Conclusion and Outlook

In summary, the combination of polymerizable liquid crystals with advanced alignment techniques allows for the preparation of morphing systems in which the molecular buildup, and therefore the shape, can be precisely controlled. An appreciable number of different examples of advanced morphology designs achieved through controlling the director profile of liquid crystal polymer networks have been shown. Many of the theoretically predicted designs have not yet been shown in practice, which means that there is still plenty of room for more experiments. In addition,
actuators that respond to different stimuli could be prepared. For example, actuators with complex director profiles that respond to chemical stimuli have hardly been reported.

Besides trying new designs and shapes, an important next step in this area of research should be to start working towards applications for these materials. With the ability to generate any kind of shape morphology by controlling the molecular buildup of a material, tailor made components for advanced devices can be designed and produced. However, to realize this in the future, more insight is still required. For instance, the ability of these complex morphing films to do physical work is only rarely addressed. If these systems are to find applications in microfluidics and robotics, better materials properties are needed. The chemistry of the materials could be further optimized to suit the potential applications, both by using new types of reactive mesogens and by blending the liquid crystals with other materials such as a carbon nanotubes [39], and as interpenetrating networks with other polymers.

A different direction towards applications would be to look for functions in which the focus lies not on the ability of the material to do work, but on the precisely controlled, complex shapes that can be achieved. For example, applications could be found as stimuli-responsive lenses, where only the shape and not the materials properties are important. Materials that deform irreversibly, on the other hand, could be used to craft static components with complex shapes for use in various microsystems. It is also possible to move away from thin films, and work has already been done in the field of responsive coatings [40], as well as molding of liquid crystal networks to create 3-dimensional objects with complex alignment director profiles [41]. Other techniques that could be combined with liquid crystal networks are inkjet printing and 3D printing, lithography, and holography. As recently discussed such techniques can also be used as a novel method to achieve morphing in polymer films by a programmed asymmetry in the molecular trigger [42].

References

