Liquid Crystals

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Photo-Switchable Surface Topologies in Chiral Nematic Coatings**

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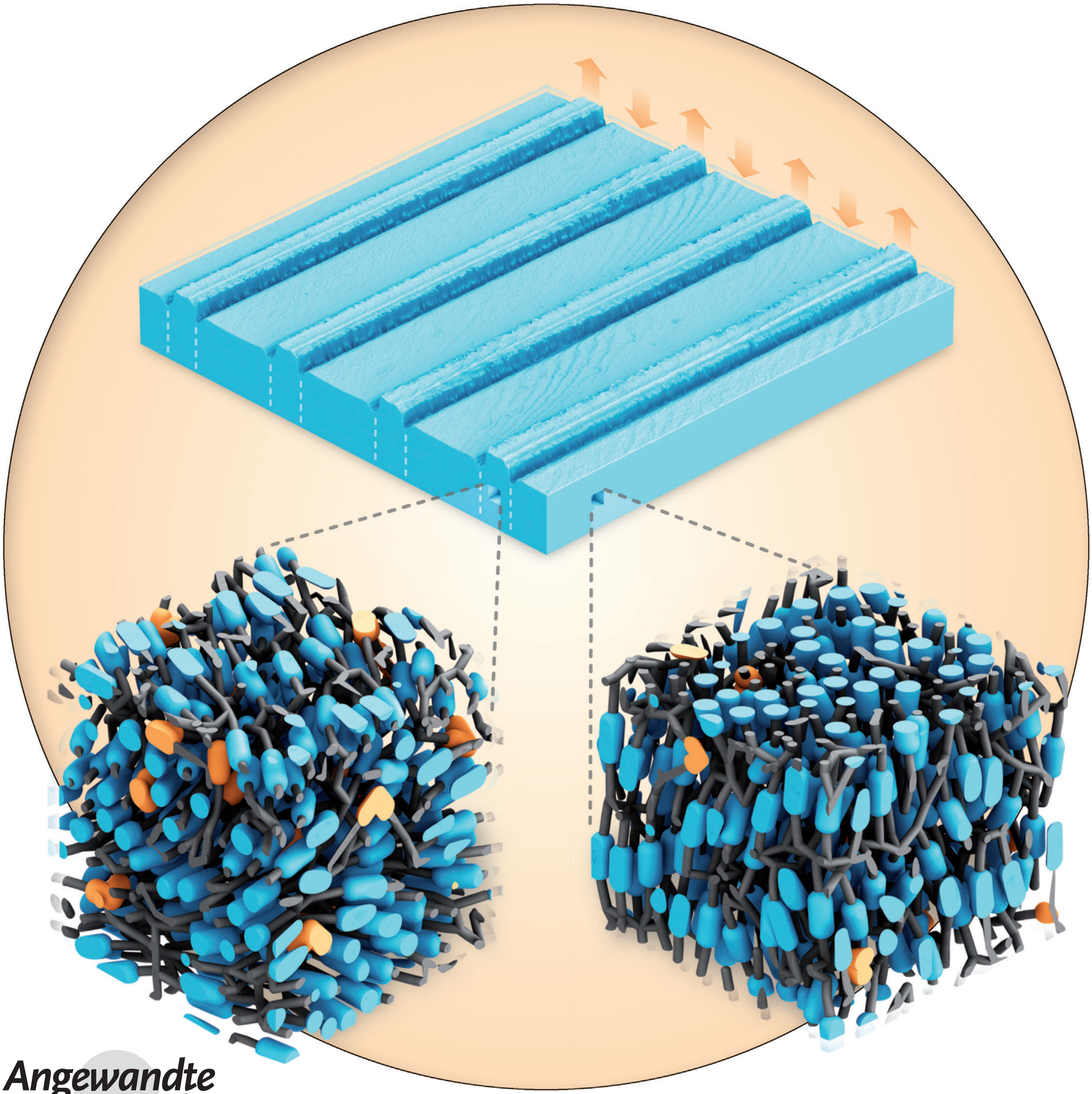

Control of the surface topology in the micrometer range by active switching between two states is of interest for a wide variety of applications. For instance, a topology-modulated change in the friction coefficients finds its application in the field of haptics where robotic manipulation and touch-input devices are of importance.[1] Also the optical properties are strongly affected by changes of the surface topology, for example, the directionality of diffusive reflection[2] or the modulation of diffractive properties. We can also think of even more advanced applications such as switchable wettability or adhesion control as, for example, the adhesion induced by geckos climbing surfaces. Furthermore, in microfluidic applications diffusion and fluid mixing can be substantially enhanced by introducing microscopic topologies on the surface.[3] In many current implementations the switching of the surface topology is triggered by an electric field using electrostatic or piezoelectric effects.[4] This requires the direct vicinity of electrodes and wires for driving the process. Alternatively, thermal effects based on thermal expansion effects[5] or phase transitions can be used.[6] In buffer solutions surface switching is established in hydrogels by either pH or thermal effects and is often proposed to control protein or cell adhesion in biological systems.[7]

Here, we will use light for the dynamic actuation of a surface relief. The use of light has several advantages. The surfaces can be addressed remotely avoiding the fabrication of electrode structures or special means for localized heating. It also avoids the presence of a buffer solution for swelling and deswelling. Moreover, it can be directed locally by focused or patterned exposure. In the literature azobenzene-containing linear polymers are reported that form surface reliefs based on light-driven material transport.[8,9] These materials have been widely studied and are proposed for holographic gratings and optical data storage. The system operates under exposure to laser light and is in principle rewritable although this is complex because a second exposure is needed.

Here, we propose a new method to modulate dynamically the surface topology of a coating that operates under conditions of relatively low light intensity. The principle is based on anisotropic geometric changes of a liquid-crystal network upon a change of the molecular order parameters. Liquid-crystal networks are obtained by in situ photo-polymerization of a polyfunctional liquid-crystal monomer in its monolithically oriented state.[10,11] Upon polymerization the monomer order is maintained and complex director patterns are frozen-in which are controlled by interfacial conditions and masked exposures.[12] By decreasing the degree of orientation, as quantified by the order parameter, the dimension tends to increase in the direction perpendicular to the direction of the average molecular orientation and to decrease in the direction parallel to it.[13] Based on this principle, morphing surfaces were reported for a thermally responsive system based on patterned chiral nematic networks,[5] where isotropic areas are integrated in media of helicoidally ordered polymer films (cholesteric films). We now advance this system into photo-switchable surface topologies through integration of azobenzene-containing cross-linkers into a structured chiral nematic network. Including the azobenzene compound in the liquid-crystal network, we can reversibly modulate the order of the liquid-crystal network by light using the *trans–cis* isomerization reaction of the azobenzene group.[14–16] The azobenzene compound in its *trans* state complies with the orientation of the network molecules. When addressed with UV light the azobenzene unit converts to its *cis* state, which reduces the molecular order in the liquid-crystal network because of its bent conformation. The use of azobenzene to induce a photo-mechanical response in polymer films and polymer beams has been investigated by several groups.[16–22] Our innovation here is that we apply this photo-responsive principle on a thin film coated on glass substrates, thus inducing the desired modulation of the surface topology in response to light. Furthermore, we enhance the depth of the surface modulation by bringing areas with homeotropic (perpendicular) molecular alignment into a cholesteric film (Figure 1). Those two types of molecular order have opposite photo-mechanical responses, the combination of which results in a larger effect than that of the previous patterned systems.[5] In the chiral nematic area, where the molecules are oriented on average planar to the surface, reduction of the order parameter results in a positive expansion normal to the plane whereas the expansion in the plane is close to zero or even negative. In the homeotropic area the opposite occurs. When the molecular order is reduced we will observe expansion within the plane of the film and contraction perpendicular to the film surface.

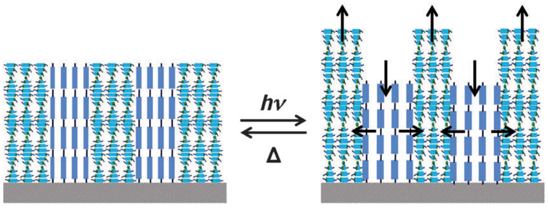

Figure 1. Liquid-crystal network containing striped patterns of alternating areas with chiral nematic order and homeotropic orientation. Upon exposure the chiral nematic areas expand perpendicular to the plane of the film and the homeotropic areas contract in the perpendicular direction. In the plane of the film the chiral nematic areas contract and the homeotropic areas expand.

We prepared our responsive coatings by photo-polymerization of a mixture of liquid-crystal acrylate monomers. The mixture consists of a balanced composition of mono- and

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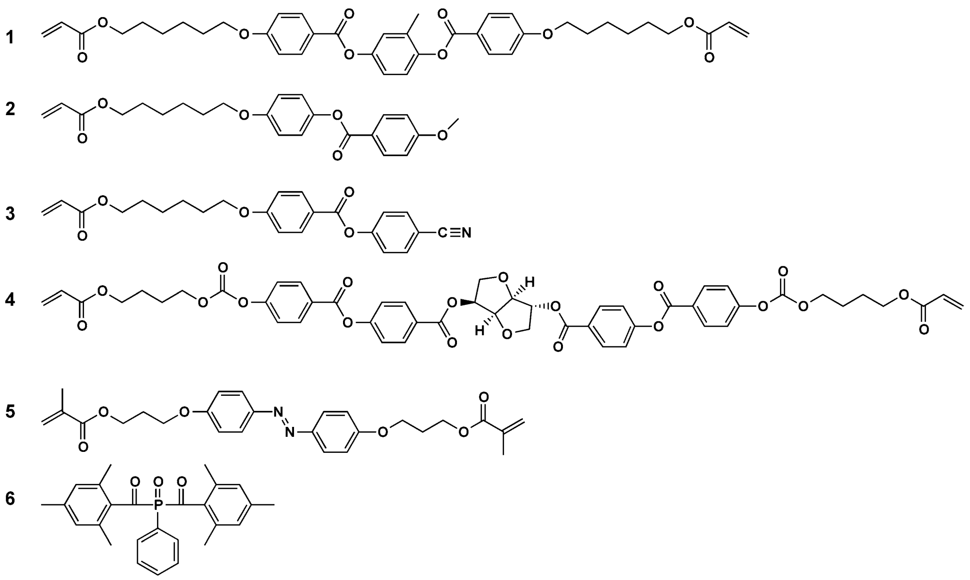

Scheme 1. Materials used for photo-sensitive chiral nematic compositions.

diacrylates **1**–**3** (Scheme 1) to tune the density of crosslinkers and thereby the position of the glass-transition temperature (around 80 °C) and the molecular mobility towards changes of the order parameter. Monomer **3** also has the function to induce a positive dielectric anisotropy in the mixture which makes the alignment of the film in an electric field possible. The mixture contains further the chiral diacrylate **4** to induce the chiral nematic phase and the azobenzene containing dimethacrylate **5** to provide the photo-responsivity. The photo-initiator **6** was chosen for photo-initiation of the polymerization by exposure to light of wavelengths $\geq$ 400 nm to avoid premature conversion of the azobenzene compound.

Prior to polymerization we prepared patterned films with alternating planar chiral nematic areas and homeotropic polymer networks. Therefore, we started with a monomer film in its planar chiral nematic state. We used an electric field to obtain the homeotropic phase aligning the molecules along localized field lines. The co-existence of chiral nematic and homeotropic phases can simply be realized by the use of patterned indium tin oxide (ITO) electrodes. This dual alignment is frozen by a single photo-polymerization step. After preparation of the sample, the top-patterned electrodes are removed. A polarization microscope picture of a film is shown in Figure 2.

The image shows black lines between crossed polarizers that remain black upon rotation of the polarizers, showing a perfect homeotropic alignment in these areas. The chiral nematic area shows blue lines between the crossed polarizers caused by the selective reflection of the film and the wavelength-dependent rotation of polarized light near the bandgap of the chiral nematic network. At the edges the film lightens up because of a transition from planar to homeotropic alignment which occurs over a finite distance as determined by the director rotation set by the elastic constants of the liquid-crystal monomer mixture prior to polymerization. The limits of resolution depend on the materials and processes used herein and are found in the micrometer range.

The interference microscope images show a small initial surface relief (height of about 70 nm) prior to the actuation step (Figure 3). This is caused by replication of the ITO pattern that was used to provide the local electric field for the alignment of monomers.

Upon actuation of the films by irradiation with UV light at a wavelength of 365 nm a large deformation is visible as shown in Figure 3. When the UV light is switched off the initial flat surface is retained within seconds. Therefore the photo-induced surface reliefs could only be measured upon

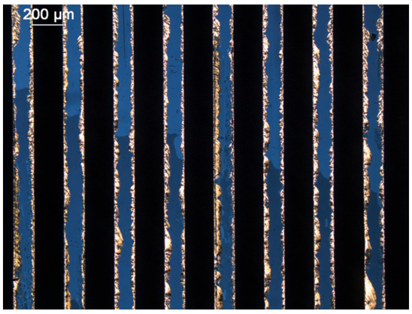

Figure 2. Optical microscopy images of a film with alternating chiral nematic and homeotropic stripes, between crossed polarizers.

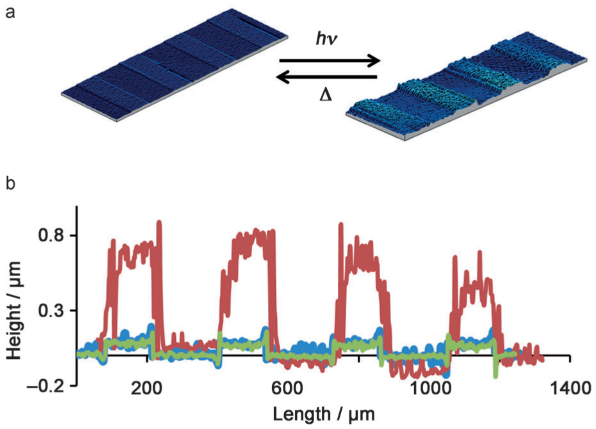

Figure 3. Interferometer measurements at a patterned chiral nematic–homeotropic film containing 4 wt% azobenzene: a) 3D images of surface topologies at the original state (left) and during illumination with UV light (right). b) Surface profiles of the initial profile (blue), during UV illumination (red), and after removal of the illumination (green).

continuous UV exposure. The surface expansion of 0.8 μm corresponds to a linear strain perpendicular to the surface of around 20 % defined as the modulation depth divided by the initial film thickness. We anticipate that this remarkably high value is achieved by the double action of the liquid-crystalline network. First the chiral nematic network tends to expand perpendicular to the surface, upon a decreasing molecular order induced by the *trans*-to-*cis* isomerization of azobenzene. Simultaneously the homeotropic areas tend to expand in the plane of the film and to contract perpendicular to it. Not only the contraction of the homeotropic field enhances the topological effect, but also the homeotropic fields exert an additional shear force at the chiral nematic fields supporting the expansion along the normal. For example, a coating with a transition form chiral nematic to isotropic areas where a single action occurs from the cholesteric region gives an expansion of around 5 %.[5]

Expansion in the cholesteric region is accompanied with a change in the optical properties. The increase in pitch would give rise to the expectation that the reflection wavelength shifts to higher values based on the relation $\lambda_r = \bar{n}p$ with λ_r is the reflection wavelength, $\bar{n}$ is the average in-plane refractive index, and p is the pitch at the cholesteric helix. However, with the change in pitch also the in-plane projection of the extraordinary refractive index is reduced because of the reorientation of the molecules. This reduces $\bar{n}$ and compensates for the pitch-induced wavelength shift. The change in effective birefringence Δn results in a narrowing of the reflection band at the same position.[23]

We varied the concentration of the azobenzene compound. Figure 4 shows that already with 2 wt % of azobenzene the system exhibit a large photo-responsive effect. This relatively large effect at such a low azobenzene concentration can only be explained by cooperative disordering of the aligned molecules when the azobenzene molecules are bent to their *cis* state rather than by the deformation of the azobenzene group alone. In a control experiment we exposed a similar film in the absence of azobenzene. This film clearly proves to be not photo-responsive and by exposure to UV light the surface topology remained in its original state.

In another control experiment we investigated the influence of thermal effects. We heated the sample in the dark to 140 °C, and although some minor structure formation was visible, the strain was about 2 %, the formed surface structures were much smaller than those obtained by the photo-responsive effect.

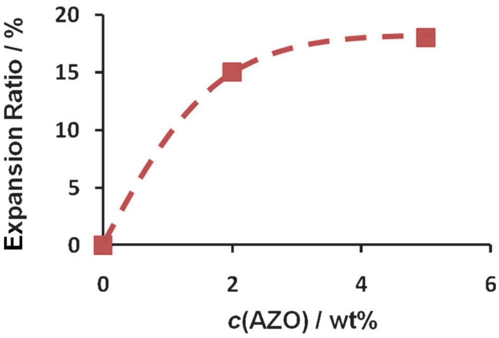

Figure 4. The effect of azobenzene concentration on the expansion ratio of the cholesteric–homeotropic films.

In conclusion, we have described a new approach for the design of smart surface coatings that undergo changes in their surface topology upon irradition by UV light. A change in the surface topology is observed by irradiation of a patterned film which contains planar chiral nematic areas next to homeotropic areas. The mechanism of this remarkable photomechanical property is based on the reversible change of order parameters by a photo-induced conformational change of azobenzene units in a liquid-crystal network. The degree of strain along the normal in response to the UV light varied for the different types of molecular order and reached values close to 20 %. We anticipate that the smart surfaces can be used in a variety of applications ranging from liquid transport in microfluidics to light-tracking optical elements in solar energy applications.

Experimental Section

Monomers **1** to **3** were obtained from Merck UK. Monomer **4** was obtained from BASF. A concentration of 5.5 wt % of monomer **4** was used in the mixture to give a pitch of the chiral nematic helix of 0.312 μm. Monomer **5** was custom-synthesized by Syncom. The constituents were mixed by dissolving in THF which was evaporated subsequently. Differential scanning calorimetry (DSC) results suggest that the mixture is nematic in the temperature range between 40 and 60 °C above which it is isotropic.

Thin monomer films were made by capillary filling of two glass plates spaced at around 4 μm by the monomer mixture in its molten state at 80 °C. The chiral nematic state is planarly aligned by coating the glass plates with polyimide (AL1051) that is unidirectionally rubbed by a polyester fabric.

A stripe-patterned coating of alternating areas with planar chiral nematic and homeotropic order was obtained by using a striped ITO electrode pattern at the cover glass plate and a continuous ITO layer at the bottom substrate. The ITO was patterned through spin-coating of the photo-resist, exposure through a mask, and etching. To convert the mixture from its planar chiral nematic to the homeotropic orientation, a voltage of 70 V was applied between patterned ITO and continuous ITO glasses. The alternating order was frozen in the polymer network by a single photo-polymerization step using a mercury lamp (EXFO Omnicure S2000 lamp) at wavelengths of ≥ 400 nm and a cut-off filter to prevent isomerization of the azobenzene group during the polymerization.

The homeotropic and cholesteric regions were checked by the crossed polarizer integrated in an optical microscope (Leica). The surface topography was measured using a 3D interferometer (Fogal Nanotech Zoomsurf). Following the initial measurement, the sample was illuminated by UV light; the measurement was done under continuous UV illumination with an intensity of 30 mW cm^{-2}. When the UV light was switched off, measurement was performed in the same location on the sample to verify that the change in the surface topography is reversible and the height change is repeatable.

UV light for actuation was obtained from an EXFO Omnicure S2000 lamp. Filters were used to select the desired wavelength. Wavelengths of 400 nm and longer were selected using Newport FSQ-GG400 filters.

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[1] C. Mavroidis, C. Pfeiffer, J. Celestino, Y. Bar-Cohen, 26th Biennial Mechanisms and Robotics Conference **2000**, Sept. 10–13.
[2] M. Ibn-Elhaj, M. Schadt, *Nature* **2001**, *410*, 796–799.
[3] H. E. H. Meijer, M. K. Singh, T. G. Kang, J. M. J. den Toonder, P. D. Anderson, *Macromol. Symp.* **2009**, *279*, 201–209.
[4] X. Qiu, *J. Appl. Phys.* **2010**, *108*, 011101.
[5] M. E. Sousa, D. J. Broer, C. W. M. Bastiaansen, L. B. Freund, G. P. Crawford, *Adv. Mater.* **2006**, *18*, 1842–1845.
[6] A. L. Elias, K. D. Harris, C. W. M. Bastiaansen, D. J. Broer, M. J. Brett, *J. Mater. Chem.* **2006**, *16*, 2903–2912.
[7] B. Voit, S. Gramm, Z. Özyürek, C. Werner, *Polym. Mater. Sci. Eng.* **2008**, *98*, 720–721.
[8] T. Fukuda, H. Matsuda, N. K. Viswanathan, S. K. Tripathy, J. Kumar, T. Shiraga, M. Kato, H. Nakanishi, *Synth. Met.* **1999**, *102*, 1435–1436.
[9] L. M. Goldenberg, Y. Gritsai, O. Kulikovska, J. Stumpe, *J. Mater. Chem.* **2009**, *19*, 6103–6105.
[10] D. J. Broer, J. Boven, G. N. Mol, G. Challa, *Makromol. Chem.* **1989**, *190*, 2255–2268.
[11] D. J. Broer, R. G. Gossink, R. A. M. Hikmet, *Angew. Makromol. Chem.* **1990**, *183*, 45–66.
[12] D. J. Broer, I. Heynderickx, *Macromolecules* **1990**, *23*, 2474–2477.
[13] D. J. Broer, G. N. Mol, *Polym. Eng. Sci.* **1991**, *31*, 625–631.
[14] D. Statman, I. Janossy, *J. Chem. Phys.* **2003**, *118*, 3222.
[15] M. Warner, E. M. Terentjev, Liquid crystal elastomers, Oxford University Press, **2003**, ISBN 0198527675.
[16] H. Finkelmann, G. Nishikawa, G. Pereira, M. Warner, *Phys. Rev. Lett.* **2001**, *87*, 015501.
[17] C. L. van Oosten, D. Corbett, D. Davies, M. Warner, C. W. M. Bastiaansen, D. J. Broer, *Macromolecules* **2008**, *41*, 8592–8596.
[18] C. L. van Oosten, C. W. M. Bastiaansen, D. J. Broer, *Nat. Mater.* **2009**, *8*, 677–682.
[19] T. J. Ikeda, Y. L. Mamiya, Y. Yu, *Angew. Chem.* **2007**, *119*, 512–535; *Angew. Chem. Int. Ed.* **2007**, *46*, 506–528.
[20] N. Tabiryan, S. Serak, X. M. Dai, T. Bunning, *Opt. Express* **2005**, *13*, 19.
[21] P. Palffy-Muhoray, M. Camacho-Lopez, H. Finkelmann, M. Shelley, *Nat. Mater.* **2004**, *3*, 307–310.
[22] K. Lee, M. L. Smith, H. Koerner, N. Tabiryan, R. A. Vaia, T. J. Bunning, T. J. White, *Adv. Funct. Mater.* **2011**, *21*, 2913–2918.
[23] Unpublished results.