Re- and Preconfigurable Multistable Visible Light Responsive Surface Topographies

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Light responsive materials that are able to change their shape are becoming increasingly important. However, preconfigurable bistable or even multistable visible light responsive coatings have not been reported yet. Such materials will require less energy to actuate and will have a longer lifetime. Here, it is shown that fluorinated azobenzenes can be used to create re writable and pre-configurable responsive surfaces that show multi-stable topographies. These surface structures can be formed and removed by using low intensity green and blue light, respectively. Multistable preconfigured surface topographies can also be created in the absence of a mask. The method allows for full control over the surface structures as the topographical changes are directly linked to the molecular isomerization processes. Preliminary studies reveal that these light responsive materials are suitable as adaptive biological surfaces.

1. Introduction

Photoresponsive polymer surfaces that are capable of converting light stimuli in topographical changes have been a class of materials of great interest,[1–10] ranging from oscillating surfaces[11,12] to on-demand structure formation[7,13–15] and friction control.[16] Using light to induce dimensional or structural changes is appealing since it can be done locally without contact. Most of these light responsive surfaces are based on photochromic azobenzene dyes incorporated in a linear amorphous polymer[17–25] or a liquid crystalline network.[26–29] In the former case, often masks or interference patterns in combination with a single light source are used to create a surface relief grating while in the latter case a patterned film is frequently applied to produce a surface topography that requires ultraviolet (UV) and blue light to induce \( \text{trans} \rightarrow \text{cis} \) and \( \text{cis} \rightarrow \text{trans} \) isomerizations, respectively.

Light responsive polymer networks only show two states as the photoresponsive molecules employed only have two states that are accessible by switching on/off the light. For accessing the on state, however, often harsh (UV) illumination conditions are required with intensities ranging from 100 to 1000 mW cm\(^{-2}\).[11,30–34] Furthermore, the photothermal component required to actuate these materials is often significant, locally heating the material.[31,32] Therefore many light responsive materials require a lot of energy and show the immediate return of the actuated state to the initial state after switching off the stimulus.[24,25] Alternatively, researchers have also shown reconfigurable systems, where the final state remains after removal of light.[19,20,22,23,35] However, the generation of these topographies requires the use of a mask or interference pattern. For many applications preconfigurable, bistable, or even multistable states would be very appealing where the different states can be formed and erased by multiple wavelengths of light can be generated[18,21,36] without the use of a mask or interference pattern during actuation. These states should be stable in the timeframe of the application and require little energy. Moreover, the harsh intensities and the use of UV light should be avoided in order to prolong the lifetime of the material. Visible light responsive molecular switches have been reported,[37–42] including fluorinated azobenzenes that display remarkable
2. Results and Discussion

The light-responsive, cholesteric liquid crystalline material was fabricated using a mixture of (meth)acrylate functionalized ortho-fluoroazobenzene and liquid crystalline monomers (Figure 1). This mixture was aligned in-plane by shear forces on a glass substrate and then photopolymerized resulting in an 18 µm thick film. Using a cholesteric liquid crystalline coating allows to predominantly induce changes upon actuation in the direction of the helical axis.

Reconfigurable topographical features where endowed by illuminating the coating through a mask containing equidistant (20 µm) hexagonal spaced circular features (20 µm) with 530 nm green light (6 mW cm⁻²) for 35 min to keep the dose of light required to form structures as low as possible. Illumination replicates the pattern of the mask in the coating resulting in a hexagonally arranged pillared structure (Figure 2). The peak-to-valley height was found to be 150 nm (Figure 2a). Mask illumination with green light of the films leads to local trans → cis isomerization of fluorinated azobenzene molecules incorporated in the network, resulting in a local formation of protrusions in the illuminated areas (vide infra). The structures formed in this glassy polymer correspond to a strain of approximately 1% of the total height. To determine the stability of the surface topography, the sample was monitored continuously with a digital holographic microscope (DHM) in the absence of blue and green light. After 12 h, no significant change in the surface pillars was found proving that stable topographies were created. This experiment was performed again, leaving the sample in the dark for 12 d. Measurements of the same pillars revealed a reduction in pillar height of roughly 50% and after 50 d, a loss of the features was observed. Experiments on similar pillars were also performed at 80 °C, resulting in a gradual loss of the surface structures in 4 h. Additionally, the structures can be erased rapidly upon irradiation with blue light (Figure S1, Supporting Information), providing the first evidence of the bistable properties of these films.

To gain more insight into the origin of the stable surface topographies, UV–vis measurements were performed to study the photoisomerization of the fluorinated azobenzenes in the liquid crystalline network (Figures S2 and S3, Supporting Information). Before illumination an absorption maximum at 470 nm corresponding to the n → π* transition of the trans isomer was measured. When illuminated with 530 nm green light, inducing the trans → cis isomerization of the fluorinated azobenzene, a decrease of the absorption at 470 nm occurred, while an increase in the n → π* band of the cis isomer was measured (425 nm), indicating that the trans isomer was partially converted to the cis isomer. This process was found to be slower than the back-isomerization in the dark, requiring roughly 30 min to fully achieve the photostationary state (pss). Exposing the sample using 405 nm blue light, resulted in back-isomerization from cis → trans in less than 10 s. Interestingly, when the polymer coating was exposed to green light for 30 min to reach the pss, relaxation in the dark was found to be associated with a thermal half-life (t1/2) of 281 h at room temperature, as estimated by extrapolating the UV–vis data assuming first order kinetics. This value corresponds well with the 12 d that were found in Figure 2 for the surface topographies created by green light. Increasing the temperature accelerated the back-isomerization as expected, resulting in $t_{1/2} = 56$ h at 40 °C, 15 h at 60 °C, and 3 h at 80 °C. This data reveals that there is a correlation between the isomerization of the molecule and the stability.
After exposure to blue light (405 nm), the order parameter, leading to expansion along the helical axis resulted in a small decrease of the local molecular order, i.e., conformational changes in the cholesteric liquid crystalline coating generate local decrease in order caused by the change in cis and trans isomer population.

To determine whether these structures could be reconfigured, the same flat cholesteric liquid crystalline coating was reused. Illumination of the sample through a zig-zag-patterned mask for 30 min using green light (530 nm, 6 mW cm$^{-2}$) resulted in inscription of the zig-zag based structure being present on the mask (Figure 3), which were erased in 10–15 min using <1 mW cm$^{-2}$ 455 nm light instead of 405 nm light. Illumination with 455 nm light allows to work with light that is even less harmful than 405 nm light.[47] When exposed through a hexagonal-circular-patterned mask for 30 min using green light (530 nm, 6 mW cm$^{-2}$), pillars were formed, showing that the topographical features can be fully erased and rewritten. The pillars were erased again using 455 nm light. Due to the visible, low energy illumination no fatigue of the film was observed.

In order to obtain multistable intermediate states, pre-configured surface topographies were fabricated. For this, the cholesteric liquid crystalline mixture was deposited on glass and shear aligned with a mask. Followed by UV light illumination through this mask containing a line pattern. Due to depletion of the reactive mesogens by photopolymerization, diffusion of liquid crystals from the nonexposed area to the exposed areas took place.[13] Subsequently, the sample was turned around and UV flood exposed at the isotropic temperature, resulting in a fully polymerized film with a spatially modulated crosslink density and molecular orientation. Visually, the patterned coating showed alternating red cholesteric and black isotropic line domains in the film (Figure 4B) between crossed polarizers. The height between these alternating lines is ~100 nm.

First, the light induced topographical changes were monitored with DHM by illuminating with 530 nm light, 20 mW cm$^{-2}$ at 20 and 40 °C (Figure 4B). After 2100 s (35 min), the illumination was ceased and the material was kept in the dark for 1500 s (25 min). Subsequently, the material was illuminated with <1 mW cm$^{-2}$ of 455 nm light for 1400 s. During the first illumination with 530 nm light, an increase in height difference between the cholesteric and isotropic material was measured. As the isomerization kinetics are temperature dependent, the rate of forming the topographies is also temperature dependent. The polymer film at 40 °C showed a maximal difference of 135 nm after roughly 1000 s, while the sample at 20 °C showed a steady increase during this time, but did not reach the maximum height. After switching off the illumination, both materials showed no height changes, having a height difference of 40 nm for the sample at 20 °C and 135 nm for the sample at 40 °C. Upon illumination with 455 nm light, the polymer film at 20 °C only recovered partially in the timeframe of 1500 s, while the sample measured at 40 °C fully recovered. Please note that the illumination intensities were lower in this case compared to the kinetic experiments to ensure biocompatible conditions. To show that multistable surface topographies can be made, a stepwise illumination of the surface topographies. Please note that the decrease of the pillar size at 80 °C is faster than isomerization (Figure S2, Supporting Information), which might be caused by the enhanced mobility of the system above the glass transition temperature ($T_g = 53$ °C, as measured by dynamic thermal mechanical analysis, Figure S8, Supporting Information). Most likely after exposure to 530 nm green light, the generation of cis isomers resulted in a small decrease of the local molecular order, i.e., the order parameter, leading to expansion along the helical axis of the cholesteric liquid crystalline film and shrinkage along the planar side.[46] After exposure to blue light (405 nm), the flat state was attained again, showing that the process is fully reversible. In the dark, the disappearance of the topography followed the thermal isomerization of the cis isomers suggesting that other mechanisms such as rapid trans $\rightarrow$ cis $\rightarrow$ trans isomerization and photothermal effects play a minor role. Our results indicate that the changes in molecular shape of the photoresponsive molecule in the cholesteric liquid crystalline coating generate local decrease in order caused by the change in cis and trans isomer population.
was performed. Hereby illumination with 6 mW cm\(^{-2}\) was performed for 10 min, followed by ceasing the illumination for 10 min, which was repeated four times. As can be seen in Figure 4C, a 10 min illumination resulted in the formation of a height change of 12.5 nm, which remained after the light was switched off. The second, third, and fourth illumination cycles showed height changes of 20, 28, and 35 nm, respectively, all showing a stable plateau when not illuminated. In order to form the topographies fast and monitor a longer time, intensities were increased to 50 and 5 mW cm\(^{-2}\) for 530 and 455 nm, respectively (Figure 4D and Figures S4 and S5, Supporting Information). During monitoring for 16 h, the height of the topographies showed near zero decay. Upon illumination with 5 mW cm\(^{-2}\) of 455 nm light, the topographies fully decayed.

To show a potential application of the multistable visible light responsive surface topographies, preliminary cell studies were performed. Living cells were cultured on the patterned surfaces, showing cell biocompatibility, as well as a response towards the surface post actuation. The NIH 3T3 fibroblast cells were allowed to spread on the surface, characterized and sequentially exposed to the blue light built-in laser source of the microscope (405 nm), to remove any prematurely induced surface structures while preparing the sample. Monitoring the cells after this illumination for 1 h, revealed that the cells generally retained their shape. Subsequent illumination with green light (built-in laser source, 561 nm), which induces trans \(\rightarrow\) cis isomerization, resulted in a response of the cells, where it was seen that retraction occurs after illumination for 35 min (Figure 5 and Figure S6, Supporting Information). In this case, most changes were observed within a timeframe of 2 h after illumination with green light and thus well within the limits of how long the formed structure heights were stable. It should be noted that small changes in surface roughness might also play a role.\[13,17,48\] Imaging of living cells after 2 days of cell seeding and spreading, and after illumination (depicting the experiment given in Figure 5) showed the biocompatibility of both surface and illumination conditions (Figure S7, Supporting Information).

3. Conclusion

In conclusion, we created reconfigurable visible light responsive surfaces that show multistable topographies. Photoisomerization of the incorporated ortho-fluorinated azobenzene moieties induces the formation of surface topographies with heights that are dictated by the ratio of trans and cis isomers. This results in the formation of multistable visible light responsive films by re- and preconfigured actuation under mild illumination conditions. Moving away from UV light and using
kinetically stable photochromic molecules gives more sustainable photoresponsive polymers that require less energy with an enhanced stability. Such light responsive polymers are not only interesting for biological applications but are also appealing to fabricate, for example, configurable multistable visible light actuators or applications in microfluidic devices, where no continuous exposure to light is desired.

4. Experimental Section

**Chemicals:** The monomers used are depicted in Figure 1C. The azobenzene (1) was synthesized according to procedure reported in ref. [42]. All other chemicals were obtained from commercial sources and used without further purification, unless stated otherwise. The chiral dopant (2) was obtained from BASF. Molecules (3), (4), and (5) were obtained by Merck. Irgacure 819 (6) was obtained from Sigma-Aldrich.

**Preparation of the Cholesteric Liquid Crystal Film:** To create the cholesteric liquid crystal, the monomers were dissolved in THF (1:4 ratio), resulting in a total concentration of 0.25 g monomer mL\(^{-1}\). Thin films were created by evaporating the solvent on an acrylate functionalized glass slide. This glass slide was achieved by spincoating a 1 vol% solution of 3-(trimethoxysilyl)propyl methacrylate on an oxygen plasma treated glass slide. On the four corners of this glass slide, glue with 18 µm glass bead spacers was applied and topped off with a fluorinated glass slide for easy removal. This glass slide was achieved by spincasting a 1 vol% 1H,1H,2H,2H-perfluorodecyl-triethoxysilane in ethanol. The sample was photopolymerized (Exfo...
Omnitron S2000) for 10 min using a cut-off filter (Edmund Industrial Optics Stock No. 54 516) to prevent the azobenzene from isomerization. Subsequently, the cell was heated to 120 °C to postcure the material. In case of the preconfigured surface, the fluorinated glass was replaced with the desired mask. The sample was illuminated for 180 s with an intensity of 15 mW cm⁻² at room temperature, flipped over and heated to 90 °C and polymerized for 5 min.

Light Actuation of the Cholesteric Liquid Crystalline Film: The light-emitting diode (LED) lamps used were obtained from Thorlabs (M405L3, M455L3, and M530L3). UV–vis measurements were performed on a Shimadzu UV-3102 PC spectrophotometer with a temperature control stage (Linkam). To measure the topographies during illumination, Digital Holographic Microscopy (Reflection DHM Lynceè Tec) was used and illumination was performed with the LED lamps from below (10–20 mW cm⁻², 530 nm and <1 mW cm⁻², 455 nm collimated LEDs). Creation and measurement of the reconfigurable pillars was performed by illuminating the sample through a mask with a collimated 530 nm LED (6 mW cm⁻² for 30 min), followed by DHM observation in dark and under 455 nm illumination (<1 mW cm⁻² for 10–15 min, until fully erased). Optical micrographs were achieved by a Leica DM2700M equipped with polarizers and a Leica DFC320C camera. Dynamic Mechanical Thermal Analysis was used to measure the glass transition temperature, performed on a Shimadzu UV-3102 PC spectrophotometer with a temperature control stage (Linkam). To measure the topographies performed on a Shimadzu UV-3102 PC spectrophotometer with a temperature control stage (Linkam). To measure the topographies.