Responsive surface topographies : liquid crystal networks and polymer hydrogels forming micrometer sized surface structures triggered by light, heat or pH

Liu, D.

DOI: 10.6100/IR747584

Published: 01/01/2013

Citation for published version (APA):
Responsive Surface Topographies

Liquid crystal networks and polymer hydrogel forming micrometer sized surface structures trigged by light, heat or pH

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de rector magnificus, prof.dr.ir. C.J. van Duijn, voor een commissie aangewezen door het College voor Promoties in het openbaar te verdedigen op donderdag 31 januari 2013 om 16.00 uur

door

Danqing Liu

geboren te Chengdu, China
Dit proefschrift is goedgekeurd door de promotoren:

prof.dr. ir. J.M.J. den Toonder
en
prof.dr. D.J. Broer

A catalogue record is available from the Eindhoven University of Technology library

ISBN: 978-90-386-3317-6

Copyright © 2013 by Danqing Liu

The research described in this thesis has been financially supported by the Dutch Polymer Institute (DPI), Project number 699 ‘ArtFlag’
Table of contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Introduction</td>
<td>7</td>
</tr>
<tr>
<td>1.1 Responsive Surface Topologies</td>
<td>7</td>
</tr>
<tr>
<td>1.2 Responsive Liquid Crystal Networks</td>
<td>10</td>
</tr>
<tr>
<td>1.3 Responsive Hydrogel Networks</td>
<td>24</td>
</tr>
<tr>
<td>1.4 Outline of the thesis</td>
<td>34</td>
</tr>
<tr>
<td>1.5 References</td>
<td>35</td>
</tr>
<tr>
<td>2. Dynamic Surface Topographies Formed in Chiral-Nematic Networks</td>
<td>41</td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>41</td>
</tr>
<tr>
<td>2.2 Fabrication of Thin Coating of Cholesteric Polymer Network</td>
<td>43</td>
</tr>
<tr>
<td>2.3 Formation of Dynamic Surface Topographies</td>
<td>46</td>
</tr>
<tr>
<td>2.4 Density Measurement</td>
<td>48</td>
</tr>
<tr>
<td>2.5 Thermal Effect</td>
<td>49</td>
</tr>
<tr>
<td>2.6 Effect of Molecule Order</td>
<td>51</td>
</tr>
<tr>
<td>2.7 Conclusions</td>
<td>52</td>
</tr>
<tr>
<td>2.8 Experimental Section</td>
<td>53</td>
</tr>
<tr>
<td>2.9 References</td>
<td>54</td>
</tr>
<tr>
<td>3. Permanent Surface Topographies Formed in Chiral-Nematic Networks</td>
<td>57</td>
</tr>
<tr>
<td>3.1 Introduction</td>
<td>57</td>
</tr>
<tr>
<td>3.2 State of the Art</td>
<td>58</td>
</tr>
<tr>
<td>3.3 Elasticity of the Cholesteric Networks</td>
<td>59</td>
</tr>
<tr>
<td>3.4 Formation of Permanent Surface Topographies</td>
<td>62</td>
</tr>
<tr>
<td>3.5 Characterization of Permanent Protrusions</td>
<td>64</td>
</tr>
<tr>
<td>3.6 Conclusions</td>
<td>67</td>
</tr>
<tr>
<td>3.7 Experimental Section</td>
<td>68</td>
</tr>
<tr>
<td>3.8 References</td>
<td>68</td>
</tr>
<tr>
<td>4. Switchable Surface Topographies by Using Patterned Cholesteric Coating</td>
<td>72</td>
</tr>
<tr>
<td>4.1 Introduction</td>
<td>72</td>
</tr>
<tr>
<td>4.2 Cholesteric/ Isotropic</td>
<td>73</td>
</tr>
<tr>
<td>4.3 Cholesteric/Homeotropic</td>
<td>79</td>
</tr>
</tbody>
</table>
5. Structured pH Responsive Hydrogel ......................................................... 87
  5.1 Introduction .............................................................................................. 87
  5.2 Reversible Swelling of Crosslinked Poly(acrylic acid) ................................ 89
  5.3 Formation of Surface Topographies ........................................................ 95
  5.4 Free Standing Morphing Structures ........................................................ 100
  5.5 Conclusions ............................................................................................ 103
  5.6 Experimental Section .............................................................................. 103
  5.7 References ............................................................................................... 104

6. (Photo-) Thermal Responsive Hydrogel .................................................. 108
  6.1 Introduction .............................................................................................. 108
  6.2 Swelling Experiments at poly(N-isopropylacrylamide) ............................ 109
  6.3 Switchable Asymmetric Protrusions ....................................................... 114
  6.4 Asymmetric Surface Profiles .................................................................. 119
  6.5 Conclusions ............................................................................................ 121
  6.6 Experimental Section .............................................................................. 122
  6.7 References ............................................................................................... 123

7. Technology Assessment .............................................................................. 125
  7.1 Introduction .............................................................................................. 125
  7.2 Switchable Mixing in Microfluidic Devices ............................................. 126
  7.3 Tuneable Wetting and Self-cleaning Surfaces ........................................... 129
  7.4 Tribology .................................................................................................. 132
  7.5 Switchable Optical Elements ................................................................... 133
  7.6 References ............................................................................................... 135

Samenvatting .................................................................................................. 139
概要 ............................................................................................................... 141
Acknowledgements ......................................................................................... 143
Curriculum Vitae ......................................................................................... 146
Responsive Surface Topographies

Summary

Accurate and dynamic control over surface topographies in the (sub) micrometer range might find applications in many areas. The optical properties of thin films and coatings, for example, are largely affected by transformations in surface structure and shape. Also, lens structures can be formed in a dynamic and autonomous manner by controlling the surface topography, while their focusing depth might adapt to an external stimulus such as light and its directionality. In relation to this, also appearance related properties like scattering, diffraction or reflection can be modulated by switching surface topography. Besides these optical effects, also surface mechanical properties can be altered by the appearance or disappearance of protrusions in the surface. In particular, tribological properties such as friction, stick and adhesion are important in the fields of haptics and human-machine interfaces. In microfluidic devices, mixing can be induced by surface topologies present on the microchannel walls. Dynamic control over these surface topologies enables switching between a mixing and a non-mixing state thus having active control over fluid flows and the occurrence of reactions. It is also possible to control the wettability of surfaces by sub-micron surface reliefs. Up to now, many of these surface properties have been studied and tuned in a static way where the fixed surface topography is obtained by lithography or by embossing. We have developed materials and technologies to obtain dynamic surface topologies where the surface can be switched between a flat (off) and a corrugated (on) state or a state with well-defined protrusions.

In the thesis we explore materials and methods to switch surface topologies in a thin coating on a solid substrate. We study two categories of materials and associated technologies with different underlying switching mechanisms. The first technology is based on helicoidally ordered liquid crystal (cholesteric) polymer networks. The principle is based on photo-induced reduction of the molecular order in these chiral-nematic networks which cause a macroscopic expansion along the helical axis. Three types of chiral-nematic
configurations are studied.

(1) A coating consisting of a single-phase chiral-nematic layer with planar orientation.

(2) A patterned coating with alternating stripes with planar chiral-nematic order and isotropic order.

(3) A patterned coating with alternating areas with planar chiral-nematic order and homeotropic order.

The height of the surface topographies formed depends on the coating thickness. We demonstrate that the strain of the surface topography could reach values close to 20%.

The second approach is based on sol-gel transitions in polymer hydrogels. We studied three types of triggers to actuate the hydrogel to form responsive surfaces.

(1) A pH responsive thin coating, that can be modulated dynamically and reversibly between a smooth surface and a surface with microscopic topologies when exposed to an acidic and alkaline environment, respectively.

(2) A thermally responsive coating, in which surface structures can be formed and erased by cycling the temperature below and above 32°C.

(3) A light responsive coating, that is based on a thermal responsive hydrogel, while elements embedded in the coating or on the substrate that absorb light, convert this into heat locally. The “light to heat” energy conversion is achieved by patterned black chromium dioxide structures previous applied on substrate.

The surface topographies formed in the hydrogel-based coatings are larger than in the liquid crystal coatings and can easily reach tens of μm in a 50 μm thick film. However, compared to the liquid crystal network coatings, the hydrogels may be less suitable for some applications considering their mechanical compliance and need for a liquid environment.

We anticipate that the basic principles that we developed for the fabrication of the switchable surface topologies can be widely used varying from liquid transport in microfluidics to light tracking optical elements in solar energy applications.
1. Introduction*

1.1 Responsive Surface Topologies

1.1.1 Background and Motivation

Throughout the course of evolution, living creatures have developed a wide range of motions and survival strategies based on the unique topologic patterns on their surfaces. See Figure 1.1. Gecko lizards can climb on tilted, vertical, or even inverted surfaces yet, they do not slip and still can easily detach due to the microstructures on their feet. Thanks to the complex and fine architectures on their surface, lotus flower leaves exhibit high repellence of water, moreover, dirt particles can be picked up by the water droplets as they roll over the leaves. So that they can stay clean. And even our human respiratory system makes use of little moving protrusions and cilia to protect the nasal passageways and other parts of the respiratory tract, filtering out dust and other particles that enter nose with breathed air. Another example providing an optical function are the glass sponges that live at the depth from 10 to 6770m in the ocean where no sunlight accessible. With lens-like structures at the end of fiber they can effectively collect the ambient light. These species are resemble commercial optical fibers but are more robust and can form under low-temperature conditions. And many mammals exhibit the pilomotor reflex on their skin, better known as goose bumps, to create insulation and warmth in cold conditions or protect by scaring away the enemy when the body becomes larger.

* This chapter is partially based on: Danqing Liu, Cees W.M. Bastiaansen and Dirk J. Broer, Liquid Crystal Polymer Networks: Towards Soft Actuators and Dynamic Surface Reliefs, Handbook of Liquid Crystals” edited by Goodby, Collings, Kato, Tschierske, Gleeson, and Raynes, Wiley-VCH Verlag GmbH & Co. KGaA (to be published)
Figure 1.1 (a) microstructures on a gecko foot that induces adhesion to the surfaces. (b) microscopic structures on lotus surface that repels water droplets. (c) A photograph of the actual glass sponge.

As human tries to understand Nature’s concepts, they are also inspired by the clever and elegant solutions Nature has developed – solutions that can also be used to our benefit. Self-cleaning surfaces on plant leaves (lotus effect) inspired the development of fog-free finish for transparent surfaces, water proof coatings and even optical displays that use water for writing, erasing, and storing information. Robots that climb are designed with feet like geckos. Gecko feet also inspired the invention of ‘super glue’ which exhibits adhesive force capacities of almost 3 kN. However, all these examples elaborate surface structures that are static that cannot be switched off when not desired and can be easily damaged or worn out. The availability of dynamic surfaces whose topologies can be switched on and off upon applying external triggers would enable new applications, increase effectiveness, better control, and robustness. Modern applications would benefit from switchable surface topologies, for example microfluidic device to regulate fluid flow or induce active mixing, touch-in-put devices for haptics feedback by roughness change upon touching. Here, we focus on responsive surface topologies which can be controlled in a pre-determined manner.

1.1.2 State of the Art

To date, many efforts have been made to produce dynamically tunable surfaces through both new fabrication strategies as well as through introducing new materials. Surface wrinkling or buckling of compressing thin film on a compliant substrate is the most common way to introduce the formation of surface patterns (Figure 1.2 (a), (b)). This process involves coating a thin hard skin on a softer elastomer sheet. Upon dimensional changes the modulus difference between them leads to a compressive stress that triggers buckling and forms various wrinkle patterns. Though the topologies of the wrinkled patterns
can be controlled by the initial geometry and material properties, the mechanisms are still not fully clear to create preset structures of any desired shape or dimension. The typical dimension of the pattern is hundreds of micrometers.

![Figure 1.2 Structures prepared based on surface plate buckling. (a) The microstructure as the applied biaxial strain is increased 18. (b) Optical microscopic image of surface structures formed on the constrained poly(acrylamide-co-sodium acrylate) hydrogel at the swollen state 19 with the initial film thickness of: (1) 3 μm, (2) 40 μm, (3) 160 μm.](image)

Another similar mechanism to form complex patterns via material instability is based on the swelling of constrained hydrogels 20, 21, 22. In this case the formation of surface structures is dedicated to the competition between osmotic pressure within the gel and compressive stress from the substrate. The constrained hydrogels swell anisotropically perpendicular to the surface which generates unidirectional osmotic pressure along the film thickness. When the osmotic pressure is sufficiently high, surface buckles to locally relieve the compressive stress. However, due to the lack of control over osmotic pressure the morphology of the final patterns is unstable and limited in dimension and shape. Figure 1.2 (c) presents a typical surface pattern created by this method.

Generation of surface relief gratings (SRG) in thin films by using azobenzene containing polymers is also reported by several groups 23, 24, see Figure 1.3 25. Gratings are fabricated by irradiating the thin film though a single beam of polarized light. Although the mechanism is still not fully clear, it is expected that the isomerization of the azobenzene unit leads to the mass transport of polymer chains 26, 27. The polymers that are being used consist of linear chains without crosslinks inherent to the mechanism of mass transport. Consequently the structure dimensions that can be made are dependent on polymer
properties like molecular weight, glass transition and the presence of addictives. The linearity of the polymer chains also makes the structures sensitive to elevated temperatures which are used to erase the formed surface topologies.

![Surface relief patterns formed on azo polymer films. (a) Beat structure; (b) Orthogonal gratings.](image)

Other attempts including liquid crystal network, traditional photolithography and etching steps, and imprinting have shown possibilities in creating responsive surfaces with different materials and technologies.

In order to expand on new principles to create surface topographies in thin films and coatings and to make them dynamic, such that they can be switched on and off, we present in this thesis new principles and methodologies. The methods investigated and presented are based on two types of materials: liquid crystal networks and polymer hydrogels. For each of those two materials, we have developed a variety of technologies resulting in different trigger principles, different responses with respect to size and speed, different conditions (dry or wet), and different properties with respect to mechanics and size. We believe that this set of conditions and properties will enable their use in a variety of applications meeting different requirements.

1.2 Responsive Liquid Crystal Networks

1.2.1 Liquid Crystal Networks

Liquid crystals (LC’s) are materials that have the appearance like liquid, but the molecules are ordered like in a crystal. In general terms LC’s are divided into two classes: thermotropic liquid crystals whose liquid crystal phase forms when heated above melting temperature, and lyotropic liquid crystals in which their liquid crystal phase forms in solution at a specific concentration range. In this thesis, we deal with thermotropic liquid crystals.
General speaking thermotropic liquid crystal phases form in materials that are built up from molecules with an anisotropic shape such as molecular rods or molecular discs and only occur in certain temperature range. When temperature is too high, the material will transfer into an isotropic liquid phase whereas at too low temperature, it forms crystalline solid. In the liquid crystal state, several phases may exist, which are characterized by the degree and type order. An LC material may possess either one liquid crystal phase between melting and the transition to isotropic. Or a sequence of different LC phases may occur where the most common behavior is that the phase with the highest degree of order occurs at the lowest temperature. In the so-called nematic phase, the rod-like molecules are aligned in a common direction, called the director but have no positional order. But tilt with an average angle of $\theta$. See Figure 1.4. The average angle $\theta$ that molecules make with the director determines the order parameter. In the smectic phase, the molecules keep their common director, have an increased order and are packed in layers or planes. There are different types of smectic phases. For example, as shown in Figure 1.4, in the smectic-A phase, molecules are aligned normal to the layer while in the smectic-C phase, they are tilted away from normal with certain angle. In general processing of nematic materials is easier and therefore this thesis mainly concerns with the materials that possess a nematic phase. A special case of the nematic phase is the cholesteric phase or the chiral-nematic phase. This phase is obtained when either the liquid crystal contains a chiral center in its molecule or when a chiral molecule is added as dopant. The nematic director starts to rotate such that on average a molecular helix is being formed. The pitch of the helix varied by the amount of chirality in the system and be adjusted somewhere between several tens of nanometer up to infinity. In the latter boundary case of course a normal nematic phase is obtained. When the pitch of the cholesteric helix is brought in the region of the wavelength of visible light interesting optical properties are obtained with polarization determined Braggs reflection of a wavelength $\lambda_r = n_{av} \times p$ where $n_{av}$ is the in plane average refractive index and $p$ is the pitch of the helix. Later we will see that especially this cholesteric phase has also our interest for our surface mechanical properties because of its in plane symmetry and out of plane anisotropy.
Figure 1.4 Types of LCs phases can be established by changing the temperature.

Liquid crystal monomers are LC molecules with polymerizable groups and are the basic elements to build up a polymer network. The polymerizable group can be an acrylate, methacrylate, an epoxide, etc. In this thesis we concentrate ourselves on the acrylate. Normally, a blend of liquid crystal monomers is chosen to tailor properties. For instance, in the monomeric state relevant properties are, LC transition temperature and flow viscosity in order to optimize the processing window. And in the polymeric state, the elastic modulus, glass transition temperature ($T_g$) and the refractive indices can be rendered. Polymerizing LC monomer mixture (See Figure 1.5) which consists of more than one polymerizable group (referred to as polyfunctional) leads to Liquid Crystal Networks (LCNs). This densely cross-linked polymer where liquid crystal units are linked at both sides to a polymer backbone, exhibits a stable molecular organization, even when heated up to a temperature as high as the polymer degradation starts taking place. In that sense one should distinguish them from the linear LC side-chain polymers that are formed e.g. from monoacrylates. There have been reported over thirty years ago that they combine both anisotropy of liquid crystal mesogens and mechanical properties of polymers. However, the real fixation of molecular order in this case often does not occur. During the polymerization process phase transitions might take place and the formed polymer might lose the molecule order and might transfer to isotropic state during heating or to a different phase when cooling down to room temperature. Moreover, if the LC state of the polymer does not mix with that of the initial
monomers then phase separation takes place and leading to defects and optical imperfections.

Using light to initiate the polymerization is highly preferred. Unlike thermal polymerization where the polymerization temperature often conflicts with the temperature range of the LC phases and premature polymerization may occur before the desired molecular order is established. At this temperature the photo-initiated free-radical polymerization of the LC monomer blends (consisting of polyfunctional monomers) produces a stable polymer with a texture and order that is identical to that of the monomer.

Therefore, the general approach sued nowadays to establish liquid crystal networks (LCNs) is via photopolymerization of liquid crystal monomer blend $^{33,36,38}$ as sketched in Figure 1.5. Working with the low-molar-mass reactive mesogens gives the access to the various states of liquid crystal order. Examples are shown in Figure 1.5 where from top to bottom are: the twisted nematic (TN), the splay-bend, a tilted uniaxial, and the cholesteric alignment. They all can be preserved in the photopolymerization process$^{39,40,41}$. There are several techniques to establish monolithic molecular order in LCs. For example rubbed surfaces, surfactant treated surfaces, external electric or magnetic fields or flow can be applied, or combined to create films of even more complex molecular architectures$^{42}$. The use of light to initiate the polymerization process allows selective polymerization via photomasks. Therefore, the dimensions of the structures can be on the order of micrometers or larger. The combination of self-organization and lithography is an example of a combined bottom-up and top-down structuring technology.
Figure 1.5 Schematic representation of the formation of a liquid crystal network (LCs). The example molecule (1) has a nematic phase. Molecular can be aligned in various configurations. From top to bottom: twisted nematic (TN), splay-bend, tilted uniaxial, and cholesteric alignment (2). Ordered molecules are polymerized by UV light thus forming a polymer network with a frozen-in molecular order. Photomask (insert microscopic picture) can involve in the polymerization to deliver structures of micrometer dimensions (3).

1.2.2 Anisotropic Deformation

In the nematic phase, the preferred orientation of the molecule is described by a unit vector $\mathbf{n}$, referred to as the director. The degree of the ordering is quantified by an order parameter $S$ indicating how well the molecules are aligned. $S$ is defined by

$$S = \left( \frac{3 \cos^2 \theta - 1}{2} \right)$$

Eq. 1.1

Where, $\theta$ is the angle between the director and the molecule axis, see Figure 1.6 (a) left. Brackets denote an average value over the sample. When molecules are randomly aligned in the isotropic configuration, $S$ equals zero. Whereas, for an ideal alignment, $S$ evaluates one. Typical order parameter for nematic liquid crystal values between 0.3 and 0.8.
When the order parameter reduces (Figure 1.6 (a) right), the increasing average tile of molecules $\theta$ leads to a decreasing in projection of molecule end-to-end length, presenting as $L_T < L_0$, where $L_0$ is the original projected length of the molecule. And the change in length parallel to the director is then estimated using

$$\left( \frac{\Delta L \parallel}{L_0} \right)_s = \frac{(2S_T - 2S_0)}{2S_0 + 1} ^{1/2} - 1$$

Eq. 1.2

In this formula $S_0$ and $S_T$ refer to the order parameter before and after the change, respectively. $L_0$ and $L_T$ are the corresponding reference lengths along the director, e.g. that of an average molecular unit, where $\Delta L$ equals to $L_0 - L_T$.

![Figure 1.6](image)

Figure 1.6 (a) Representation of the network order with director $\mathbf{n}$. The length changes from $L_0$ to $L_T$ when the average angle between the mesogenic units and the director increases from $\theta_0$ to $\theta_T$. (b) Homeotropically aligned network and the corresponding deformation upon a reduction in order parameter.

One way to decrease the order parameter is via heating. Below $T_g$ the system expands with temperature mainly due to an increasing molar volume. The preferential expansion direction is perpendicular to the long axis of the molecule, as the expansion is dominated by increasing intramolecular distances. Around and above $T_g$ there is a small and reversible loss of the degree of molecular order causing additional deformation. Therefore, the total length change parallel to director is the sum of length change caused by molar volume increase and the loss of ordering

$$\left( \frac{\Delta L \parallel}{L_0} \right) = \left( \frac{\Delta L \parallel}{L_0} \right)_v + \left( \frac{\Delta L \parallel}{L_0} \right)_s$$

Eq. 1.3
Chapter 1

Table 1.1 lists the length change by heating from room temperature to 150°C of several LC networks. The calculated and measured results are compared showing the consistence between them\textsuperscript{43,44}. The LC networks used here are based on the polymer networks that are illustrated in Figure 1.7. It is the best studied glassy liquid crystalline system for MEMS applications\textsuperscript{45}. \(x\) indicates the length of the flexible spacer on both side of the rigid core, \(R\) stands for the side group of the rigid core which can be either a hydrogen (H) or methyl (M) group.

<table>
<thead>
<tr>
<th>LC network</th>
<th>(S)</th>
<th>(T_g) (C)</th>
<th>(\Delta n/(\Delta n)_0) at 150 °C</th>
<th>((\Delta L/L_0)_{\text{calc}}) at 150 °C</th>
<th>((\Delta L/L_0)_{\text{meas}}) at 150 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>H</td>
<td>0.56</td>
<td>118</td>
<td>0.98</td>
<td>-0.005</td>
</tr>
<tr>
<td>5</td>
<td>H</td>
<td>0.66</td>
<td>-</td>
<td>0.96</td>
<td>-0.011</td>
</tr>
<tr>
<td>6</td>
<td>H</td>
<td>0.68</td>
<td>83</td>
<td>0.95</td>
<td>-0.015</td>
</tr>
<tr>
<td>6</td>
<td>CH(_3)</td>
<td>0.58</td>
<td>83</td>
<td>0.92</td>
<td>-0.018</td>
</tr>
<tr>
<td>8</td>
<td>H</td>
<td>0.68</td>
<td>71</td>
<td>0.93</td>
<td>-0.020</td>
</tr>
<tr>
<td>10</td>
<td>H</td>
<td>0.68</td>
<td>55</td>
<td>0.92</td>
<td>-0.023</td>
</tr>
</tbody>
</table>

Table 1.1 Measured change in birefringence by heating from room temperature to 150°C for various LCNs. From the change in birefringence the change of characteristic length parallel to the director was calculated using Eq. 1.2 and Eq. 1.3 and compared with measured values. Table is derived from ref. 43.

The reduction of order is favorable for entropic reasons but is limited by the polymer network. The measured change in order parameter is small, only in the order of a few percent as concluded from birefringence measurements, but geometrical arguments show that this indeed explains the observed dimensional changes.

A decreasing order parameter reflects to the polymer networks as a dimensional change with the sign depending on the molecular director. An example is given in Figure 1.6 (b) where liquid crystal mesogens align perpendicularly. The reduction in order parameter results in a contraction parallel to the director and to an expansion perpendicular to it. There are two expansion directions, one is illustrated in the scheme and the other is directed out of the paper.

During heating the volume of the LC networks increases just like isotropic polymers.
However due to the alignment they display a strong anisotropy in their thermal expansion coefficients, as shown in Figure 1.7. Below the glass transition the thermal expansion in both directions is small. When the temperature is above the glass transition, the thermal expansion parallel to the director becomes negative. This negative expansion explains the large linear contraction that occurred at this temperature. On the other hand, perpendicular to the director, thermal expansion increases rapidly without reaching a constant value as is the case for isotropic materials where the expansion in the rubber plateau is a constant value. As expected, the systems with a longer aliphatic spacer display a larger temperature response. There is also a minor effect of the initial order parameter. The order parameter increases with the decreasing polymerization temperature $T_p/T_c$, being the curing temperature divided by nematic-to-isotropic temperature of the monomer, inserted in Figure 1.7. The reduced temperature, being the curing temperature divided by the nematic-to-isotropic temperature of the monomer, is listed in Figure 1.7.

![Figure 1.7 Linear thermal expansion measured for uniaxially aligned networks. Networks were made at various reduced temperatures ($T_p/T_c$) and some structural variations with respect to spacer length and core substituents.](image)

This anisotropic deformation of liquid crystal networks proves to be very useful in creating soft polymer actuators and sensors. An example in Figure 1.8 presents a heat
induced bending deformation. Molecules are in a splayed configuration where the molecular
director rotates gradually from in-plane alignment to homeotropic (perpendicular to the
substrate) alignment over the thickness of the film (Figure 1.8 (a)). Upon a reduction in the
order parameter $S$ through an increase in temperature, the top of the film expands and the
bottom of the film contracts. Subsequently, a downwards bending behavior without the
inducing of bi-layer system can be obtained. It should be noted that the bending film in
Figure 1.8 (b) is clamped inversely after fabricated in the form of (a).

The simply example demonstrated in Figure 1.8 already shows that the deformation
configuration of the LC network depends on the molecule alignments or on the combination
of the molecular alignment. Different configurations can be established through a range of
technologies including rubbed polyimide layer, electric filed and magnetic field prior to
polymerization at the monomeric state. A variety of molecular alignments are investigated
for the difference purposes. In the surface topologies formations described in the thesis
we focus on the chiral-nematic alignment, in literature also denoted as cholesteric alignment.
Because of the chirality brought into the system by modification of liquid crystal molecules
or by chiral dopants, the nematic director describes a helix. Where the surface conditions
promote planar alignment of the molecules, the helix axis will be perpendicular to the film
surface. Because of this geometry, one could measure a large expansion normal to the plane
of the film and close to zero expansion can occur in the plane.

![Figure 1.8 Temperature triggered deformation in LC network films with molecule in a splayed configuration.](image)

(a) splay alignment and its deformation upon decreasing in the degree of alignment and (b) bending of the
film with alignment (a), film is clamped inversely after fabricated from (a).
1.2.3 Thermal Responsive Surface Topologies

When the LC polymer network is attached to a rigid surface, the constraint dimensions in the plane of the film may lead to the formation of a surface relief when the molecular order changes. Thermally actuated surface topologies formed in a patterned cholesteric LC polymer coating have been reported by Sousa et al.\textsuperscript{51}. The patterned polymer coating consists of isotropic and cholesteric regions, as shown in Figure 1.9 (a). The fabrication of this pre-patterned film involves photopolymerization the monomer in the ordered cholesteric phase through a photomask. In the illuminated areas monomer polymerizes and the chiral-nematic (cholesteric) alignment is fixed. Subsequently, this partly cured coating is subjected to a heating step and the non-reacted monomer is converted to the isotropic phase which is subsequently frozen-in by a second polymerization step using a flood exposure.

The polarizing optical microscope (POM) image reveals 300 µm black circles of isotropic “island”, surrounded by a “sea” of cholesteric materials (green). At room temperature there is a slight height difference less than 200 nm between two regions (Figure 1.9 (b)). Upon heating of this patterned polymer network the order parameter of cholesterically ordered areas decrease. This results in a large local thermal expansion in the direction perpendicular to the plane of the film. However, at the disordered isotropic areas only a relatively small bulk thermal expansion occurs. Consequently, upon heating of the film, a surface relief (Figure 1.9 (c)) appears in accordance with the image of the photomask (Figure 19 (a) inset picture). After cooling to the initial temperature, the surface structures retain to their initial close to flat configurations.
Figure 1.9 Polarizing optical microscope images and interference microscope images of polymer cylinders with isotropic order surrounded by areas with cholesteric order. The inset in (a) shows the photomask used for polymerization of the cholesteric area during the first UV exposure. Images (b) and (c) are white-light interferometer images taken at RT and at 200 °C respectively.

We advanced this system into photo-switchable surface topologies via integrating azobenzene moiety into the LC polymer matrix. Moreover, inspired from this work a series of light responsible surface topologies modulated in different manner are designed. Details of those will be elaborated in Chapter 2-4.

1.2.4 Light Responsive Polymer Networks

For many applications the use of light, rather than using heat, is preferred to trigger the deformations. It enables remote control of a localized actuation in a non-contact manner. In general, liquid crystal networks are made photoresponsive by co-polymerizing azobenzene containing monomers and also the photoresponsive properties of liquid crystal networks described throughout this thesis is achieved by incorporating azobenzene molecule. Azobenzene is well-known for its photo-switching property. It experiences reversible trans-cis isomerization upon illumination with light of an appropriate wavelength. The elongated trans isomer is thermodynamically more stable by approximately 50 kJ/mol\(^52\) than the bent cis isomer. The energy barrier to the isomerization is nearly 200kJ/mol\(^53\). Therefore, in the dark or under the ambient light conditions azobenzenes are found predominantly in its trans form.
Upon irradiation with light that addresses the \textit{trans} absorption band which is positioned between 300 and 400 nm the \textit{cis} isomeric state is formed (Figure 1.10). The conversion proceeds until the photostationary state is formed which is determined with the rate of formation of \textit{cis} molecules and the thermal back reaction to \textit{trans} state. Moreover, this equilibrium may shift further to the \textit{trans} state in the presence of visible light that addresses the absorption band at wavelength $> 400$ nm of the \textit{cis} state. Under unconstrained conditions the photo-isomerization is very fast, typically picoseconds$^{54}$. The back reaction is much slower, often hours.

![Equilibrium reaction between the trans and the cis isomers of azobenzene](image)

\textit{Figure 1.10 Equilibrium reaction between the trans and the cis isomers of azobenzene. Azobenzene converts to the cis state under UV illumination and reverses to the trans state thermally or by visible light.}

The monomer we utilize to copolymerize with our LC monomers is shown in Figure 1.11. During polymerization, the \textit{trans} state is maintained utilizing photoinitiators that respond to wavelength $> 400$ nm. After polymerization the population of \textit{cis} isomer can be generated by irradiation with 365 nm light. And the \textit{trans}-azobenzene can be regenerate by illuminated with 440 nm light. Without illumination, the \textit{cis} isomer will thermally recover back to the more stable \textit{trans} state. As shown in Figure 1.11, the absorption spectra of \textit{trans} and \textit{cis} isomer are distinct but overlapping.
The isomerization of azobenzene leads to changes in its properties. For example, \textit{trans}-azobenzene exhibits a planar configuration and has the dipole moment near zero whereas the bent \textit{cis} isomer with its phenyl rings twist roughly 55° out of the plane has a dipole moment of 3 Debye\textsuperscript{55}. Based on this change switchable surface wettability has been reported to move or control the liquids motion on the surface\textsuperscript{56,57}. The isomerization also results in geometrical changes of the molecular conformation and size. As such this provides a photo-mechanical response, which in general is relatively limited in its magnitude. Finkelmann et al. demonstrated that this conformational change of azobenzene can be amplified when embedded in a liquid crystal elastomer matrix\textsuperscript{58}. The shape change of the azobenzene induces a phase transition in the liquid crystal polymer thus leading to large shrinkage along the director. This principle was further elaborated for more densely crosslinked networks that do not undergo a phase transition as for the elastomer, but make use of changes in the order parameter under the conformational change of azobenzene\textsuperscript{47,59,60}. In that sense, the mechanism is similar as the thermal induced changes discussed in Section 1.2.2. Studies also show that the dichroic nature of azobenzene moiety makes it possible to control the deformation direction by the polarity of the light\textsuperscript{61,62,63}.

An elegant way to create surface effects using these materials has been worked out by
van Oosten et al\textsuperscript{50}. By means of inkjet printing combined with a sacrificial orientation layer cilia were created at the surface that can change their shape from flat to curl when addressed by light. Figure 1.12 shows some results\textsuperscript{64}. Light response is obtained by integrating the azobenzene functionality into the liquid crystal network. Photoresponsive curling is obtained by a gradient in director as described in section 1.2.2. The splayed director pattern provides the curled response showed in Figure 1.12 d, e and f.

![Figure 1.12 Inkjet printed cilia. (a) An array of cilia printed on a glass substrate; (b) same cilia observed by scanning electron microscope; (c) a cross-section of the cilia observed by scanning electron microscope demonstrating a gradient in molecular alignment from homeotropic at the bottom to planar at the top; (d,e,f) side view of the cilia before (d) and during exposure after 2s (e) and 10 s (f). Pictures are copied from thesis Casper van Oosten\textsuperscript{64}.

In this thesis, we study the photo-isomerization of azobenzene to induce surface topologies. Rather than using inkjet printed cilia which are rather vulnerable to external forces we are aiming for the formation of the more mechanically stable protrusions pulling out of an initially flat surface. The changes in molecular order parameter that are previously used to induce geometrical changes in free standing films are now utilized under the in-plane constrained conditions of a coating on a rigid substrate. And as we will see later in Chapter 2 to 4, the thereby built-up stresses manifest themselves by the formation of strained protrusions at the free surface.
1.3 Responsive Hydrogel Networks

1.3.1 Introduction

Hydrogels are polymer networks containing hydrophilic groups that have a high affinity to water. Water can penetrate into the polymer network, but due to the presence of crosslinker it keeps the three dimensional structures without dissolving. Both widely used are natural and synthetic hydrogels which have the capacity to absorb water weighing hundreds of times their own weight. These classes of materials are often referred to as ‘super absorbents’. Living tissues, biofilm, and plants all have hydrogel structures. For instance, hydrogels can be found in corns, wheat, seeds or roots in which they exist in the form of starches. And also proteins such as collagen and gelatin are polymers which can take up large amounts of water. Living tissues, biofilm, and plants all have hydrogel structures. The modern history of synthetic hydrogels dates back to 1960s, when pioneering workers Wichterle and Lim\textsuperscript{65} published a paper in *Nature* describing the formation of a hydrophilic gel of poly 2-hydroxyethyl methacrylate (HEMA) which was intended for the biological applications. This work leads to the invention of soft contact lens and is still under continuously exploration in many areas. Particularly, the high water content and non-toxicity make it a biocompatible material. Their mechanical properties is close to that of living tissues so that they are widely applied in tissue engineering in terms of artificial skins, heart and cell culturing\textsuperscript{66,67}.

There are considerable varieties in both natural and synthetic hydrogels. Each of them has different structures and exhibits different properties which are important for the selection of materials to meet specific requirements. Hydrogels can be depending on their chemical nature, their crosslinking chemistry or their properties. For instance, hydrogels can be either chemically or physically crosslinked. Chemically crosslinked hydrogels are in general more mechanically and thermally stable compared to the physically crosslinked gels. Hydrogels that are physically crosslinked are held together by entanglements between polymer chains and other physical forces, such as electromagnetic attractive interaction of hydrogen bonds, ionic bonds or hydrophobic forces. The hydrogel system utilized throughout the experiments discussed in this thesis are chemically crosslinked by free radical polymerization in the presence of a cross linking agent.
In Accordance with their polar, often as side chain pedant groups, hydrogels can be classified as either neutral or ionic. Figure 1.13 presents some examples of neutral, acidic and basic side groups. The pendant groups can be precisely controlled by the type of monomer during synthesis. The swelling of the neutral hydrogels is based on the water-polymer thermodynamic mixing and the opposing elastic restoring the force of polymer chains. Ionic hydrogels contain either acidic or basic groups, such as carboxylic or amines. In aqueous media with proper pH, ionization occurs and fixed charges are formed in the gel. The influx of new ions creates osmotic pressure that drives swelling.

<table>
<thead>
<tr>
<th>Neutral groups</th>
<th>Acid groups</th>
<th>Basic groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly(ethylene oxide) / poly(propylene oxide)</td>
<td>poly(acrylic acid) / poly(methacrylic acid)</td>
<td>poly(aminooethyl methacrylate)</td>
</tr>
</tbody>
</table>
| \[
\begin{array}{c}
\text{CH}_2\text{-CH}_2\text{-O} \quad \text{CH}_3 \\
\text{CH}_2\text{-CH}_2\text{-O} \quad \text{CH}_3 \\
\text{CH}_2\text{-CH}_2\text{-O} \quad \text{CH}_3 \\
\end{array}
\] | \[
\begin{array}{c}
\text{OH} \\
\text{C} \quad \text{O} \\
\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-C} \quad \text{CH}_3 \\
\end{array}
\] | \[
\begin{array}{c}
\text{C}_2\text{H}_4\text{NH}_2 \\
\text{O} \\
\text{C} \quad \text{O} \\
\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-C} \quad \text{CH}_3 \\
\end{array}
\] |
| poly(vinyl alcohol)            | poly(p-styrene sulfonic acid)         | poly(vinyl pyridine)                   |
| \[
\begin{array}{c}
\text{CH}_2\text{-CH}_2\text{-O} \\
\text{CH}_2\text{-CH}_2\text{-O} \\
\text{CH}_2\text{-CH}_2\text{-O} \\
\end{array}
\] | \[
\begin{array}{c}
\text{OH} \\
\text{C} \quad \text{C} \quad \text{O} \\
\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-C} \quad \text{CH}_3 \\
\end{array}
\] | \[
\begin{array}{c}
\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-C} \quad \text{CH}_3 \\
\text{N} \quad \text{O} \\
\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-C} \quad \text{CH}_3 \\
\end{array}
\] |
| poly(vinyl acetate)            | poly(crotonic acid)                   |                                         |
| \[
\begin{array}{c}
\text{CH}_3 \\
\text{C} \quad \text{O} \\
\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-C} \quad \text{CH}_3 \\
\end{array}
\] | \[
\begin{array}{c}
\text{OH} \\
\text{C} \quad \text{O} \\
\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-C} \quad \text{CH}_3 \\
\end{array}
\] |                                         |

Figure 1.13 Examples of polymers with different side groups that can be used as basis for hydrogels

Additionally, depending on the method of preparation, they can be homopolymer or co-polymer when one, two or more hydrophilic monomers are present in the polymer networks. Moreover, based on the physical structure, they can be amorphous, semi-crystalline, hydrogen bonded supermolecule structures, or hydrocolloidal aggregates\(^68\).
1.3.2 Equilibrium Swelling Theory

Considerable studies have been carried out on hydrogels since they have been developed artificially in 1960s. Together with exploring the applications, a number of theoretical models have been developed to describe the equilibrium swelling behavior of hydrogels. Although till now no theory can predict the exact complex physical process or the mechanical behavior in hydrogels due to the non-ideal thermodynamic polymer solution, Flory-Rehner thermodynamic model is most widely used with success for an isotropic, non-ionic gel. It states when a slightly crosslinked polymer network is subjected to aqueous solution, it starts to swell until the equilibrium is reached due to the compatibility of polymer chains and water. Two opposing forces exert, the thermodynamic force of mixing and the elastic retractive force due to the crosslinks of the network. At the equilibrium state, those two forces should be equal, see equation 1.4 describes this in terms of Gibbs free energy.

\[ \Delta G_{total} = \Delta G_{elastic} + \Delta G_{mixing} \]

Eq. 1.4

Where, \( \Delta G_{elastic} \) is the elastic retractive force, \( \Delta G_{mixing} \) is the mixing process of polymer chains and water indicating the compatibility of polymer and the surrounding solvent and is expressed by polymer-solvent interaction parameter \( \chi \). The chemical potential change of solvent can be derived from differentiation of Equation 1.4 in terms of the number of solvent molecules and at the constant temperature and pressure.

\[ \mu_1 - \mu_{1,0} = \Delta \mu_{elastic} + \Delta \mu_{mixing} \]

Eq. 1.5

Here, \( \mu_1 \) is the chemical potential of solvent in the polymer gel, \( \mu_{1,0} \) is the chemical potential of pure swelling solvent. \( \Delta \mu_{elastic} \) and \( \Delta \mu_{mixing} \) are the elastic and mixing force that contribute to the chemical potential change. At equilibrium, the chemical potential of solvent in the polymer gel and outside of the gel must be equal, as shown in equation 1.6. Therefore, the elastic and mixing force must balance each other.

\[ \Delta \mu_{elastic} + \Delta \mu_{mixing} = 0 \]

Eq. 1.6
\( \Delta \mu_{\text{mixng}} \) can be expressed by the Flory-Huggins thermodynamic polymer solution theory as,

\[
\Delta \mu_{\text{mixng}} = -RT[\ln(1 - v_2) + v_2 + \chi v_2^2]
\]

Eq. 1.7

And elastics retractive force induced chemical potential change can be obtained by rubber elasticity theory\textsuperscript{71,72}. See Equation 1.8, which describes hydrogel polymer networks prepared with the absent of solvent.

\[
\Delta \mu_{\text{elastic}} = \frac{RTV_1}{\bar{V}M_c} \left( 1 - 2 \frac{M_c}{M_0} \right) \left( v_2^{1/3} - \frac{v_2}{2} \right)
\]

Eq. 1.8

Where, \( V_1 \) is the molar volume of solvent and \( \chi \) is the polymer-solvent interaction parameter, \( v_2 \) is the volume fraction of polymer in the swollen mass and is the reverse of swelling ratio \( q_2 \), \( \bar{V} \) is the specific volume of hydrogel, \( M_c \) is the average molecular mass between the crosslinks, \( M_0 \) is primary molecular mass which means the molecular weight of linear polymer chains prepared under the same conditions without crosslinking agent. Combining Equation 1.6-1.8 derives,

\[
-\ln[(1 - v_2) + v_2 + \chi v_2^2] = \frac{V_1}{\bar{V}M_c} \left( 1 - 2 \frac{M_c}{M_0} \right) \left( v_2^{1/3} - \frac{v_2}{2} \right)
\]

Eq. 1.9

The average molecular weight can be linked to the degree of crosslinking \( X \), defined as the distance (molecular weight) between two crosslinks on the same polymer chain.

\[
M_c = \frac{M_0}{2X}
\]

Eq. 1.10

Equation 1.9 is then expressed as

\[
-\ln[(1 - v_2) + v_2 + \chi v_2^2] = V_1 \left( \frac{2(X - 1)}{\bar{V}M_0} \right) \left( v_2^{1/3} - \frac{v_2}{2} \right)
\]

Eq. 1.11
When polymer is loosely crosslinked, it can be assumed that the swelling ratio defined as the volume ratio of swollen gel to that of the dried hydrogel, \( q_2 > 1 \) \((q_2 = 1/v_2)\), \( v_2^{1/3} \) is much bigger than \( v_2/2 \), so that the equation 1.11 can be approximated to

\[
q_2^{5/3} = \frac{\nu M_0}{2(1-X)} \left( \frac{1}{2} - x \right)
\]

Eq. 1.12

When the chemical components of hydrogels are certain and solvent is constant. From equation 1.12 it is clear that the fraction of crosslinker dominates the maximum degree of swelling of the network. Larger amounts of crosslinker lead to a more densely crosslinked polymer network and immobilizes the polymer chains. The swelling capacity is thus hindered by the tightly structured network.

The crosslink concentration also determines the mechanical properties of the hydrogels. A higher degree of crosslinking results in a stronger gel, however with lower elasticity. On the other hand, a loosely crosslinked hydrogel is more elastic but fragile. Hence, for optimum prosperities with respect to handling and swelling capacity the right balance must be found depending on the application.

The swelling ratio can also be determined by many factors other than crosslinking density. For example, the chemical structure of the polymer where hydrophilic pendant groups containing polymer swells more than the one with the more hydrophobic groups, polymer-solvent interaction \( (\chi) \), and ionic strength resulting in osmotic pressure that causes swelling.

In our work, we mainly focus on controlling the swelling capacity of hydrogel by crosslinks concentration. We developed a technology that can introduce inhomogeneous by controlling the crosslinker distributions along hydrogel film. This gives rise to the non-uniform swelling of a hydrogel sheet. Chapter 5-6 will present both the formation of surface topologies and the creation of 3D morphing structures based on this principle.

### 1.3.3 Kinetics of Swelling

The equilibrium swelling of hydrogel has been extensively studied both experimentally and theoretically. In the last section (1.3.2 Equilibrium Swelling Theory), we
introduced Flory-Rehner theory which is now widely accepted in describing equilibrium swelling of a neutral gel. This theory combines the theory of thermodynamic mixing and rubber elasticity suggesting that the maximum swelling capacity of the hydrogel network is determined by the degree of crosslinking and the type of solvent as shown in equation 1.11 and 1.12.

Of equal importance for the applications are the kinetics of the hydrogel network when it approaches the equilibrium state. This swelling process has been analyzed by Tanaka and Fillmore\textsuperscript{73}. In their theory, a displacement vector \( \mathbf{u}(r,t) \) is introduced to describe the kinetic displacement of a point \( r \) in the network from its final equilibrium swelling location. The swelling state of a gel can be uniquely determined if one knows the vector for every point \( r \) in the gel\textsuperscript{73}. By definition, at infinite time \( t = \infty \) when gel reaches the equilibrium state the displacement vector \( \mathbf{u} \) equals zero. Through solving the equation of motion\textsuperscript{74} where the displacement vector \( \mathbf{u}(r,t) \) as the function of space and time describes an isotropic, spherical swelling gel network, an expression is given. One should notice that the theory of the kinetics swelling is under the assumption that the degree of swelling is within the range that Hooke’s law is valid to describe the elasticity of the gel network.

\[
\mathbf{u}(r,t) = -6\Delta a_0 \sum_{n=1}^{\infty} \frac{(-1)^n}{n\pi} \left[ \frac{X_n \cos X_n - \sin X_n}{X_n^2} \right] \times \exp \left( -n^2 t / \tau \right)
\]

Eq. 1.13

Where in this equation,

\[
X_n \equiv n\pi (r/a)
\]

Eq. 1.14

and

\[
\tau \equiv a^2 / D
\]

Eq. 1.15

Here, \( a \) is the radius of the spherical gel in the equilibrium state, \( \Delta a_0 \) denotes the increased radius of gel during the swelling process, \( D \) is the diffusion coefficient of the gel network which has been introduced early by Tanaka et al\textsuperscript{4}. \( D \) is defined as \( D = (K + \)}
where  is the characteristic time of swelling. Basically, the kinetics of swelling of the gel is a diffusion-related process which consumes time. Equations 1.13 to 1.15 relate the kinetics of swelling of the gel to the diffusion coefficient of the polymer network other than that of the fluid molecules from the previous theory. This theory predicts that the characteristic time of swelling is directly proportional to the square of the linear size of the gel and inversely proportional to the diffusion coefficient of the gel network. Therefore, hydrogel should be as small as possible in order to reach the equilibrium state in a short time scale. Gel diffusion coefficient is on the order of $10^{-6}$ to $10^{-8}$ cm$^2$/s for common hydrogels. Calculations from those equations suggest fast response less than 1 second is possible if at least one dimension of the gel is less than 10 μm. Based on this theory, our hydrogels are designed with tens of the micrometer dimensions.

### 1.3.4 Responsive Hydrogel

Some hydrogels can exhibit a dramatic volume change in response to an environmental change such as pH, temperature, humidity, light and electric fields. The ability to cycle between the swollen and the unswollen state reacting to an external trigger marks them as ‘smart materials’ or ‘intelligent materials’. In this thesis we will focus on the pH-responsibility and temperature-sensitivity of hydrogels.

Hydrogels containing acidic or basic ionisable groups, Figure 1.13 are showing pH-dependent swelling behavior. Osmotic pressure between the interior of the gel network and outside the solution, as caused by ionisable (charged) pendant groups and their tendency to attract ions inside the network, is the main driving force for the swelling. For anionic hydrogels, such as acrylic acid or sulfonic acid, ionization occurs when environmental pH is above the pKa of the polymeric network. The fixed negatively charged acidic groups on the polymer attract cations from exterior solution generating large osmotic pressure which leads to the swelling of hydrogel. Reducing the pH of aqueous media below pKa will protonate the ionized pendant groups again. This process results in the dehydration of the hydrogel. Conversely, cationic materials such as amines ionize at pH below pKa. Thus at lower pH
environment gel swells whereas increasing pH leads to de-swell of the gel.

pH sensitive hydrogels are used for detecting and measuring pH level of surrounding environment\textsuperscript{82}. Also they are extensively studied for drug delivery applications. Various pH in human body may open or close the gel carrier thus initiating a release mechanism of a medicine load at the desire location in the body.

Another type of smart material is the temperature responsive hydrogels. They can experience a volume phase-transition or a sol-gel phase-transition at a critical temperature. At this point of view, they are classified in two types. One class has the upper critical solution temperature (UCST). They experiences dehydration and exhibits hydrophilic-hydrophobic transition upon decreasing the environmental temperature below their UCST. It is referred to as positive-sensitive systems. Most of the thermo-sensitive hydrogel however have a lower critical solution temperature (LCST). They undergo opposite transition as UCST hydrogels, i.e. deswell upon heating, and are known as negative-sensitive systems. A polymer network based on N-isopropylacrylamide is a typical LCST hydrogel with LCST at around 32˚C. It contracts when aqueous media heating above LCST and expands when temperature below that.

Thermo-responsive hydrogels have the advantages that they do not require organic solvent or a change of the chemical conditions to stimulate swelling/deswelling and only need changing of the surrounding aqueous temperatures.

Another significant superiority of the thermo-responsive hydrogel is that it can be relatively easy rendered into light-responsive hydrogel by integrating light absorption particles. It is realized by a so called light-to-heat energy conversion method. The light absorbing elements, such as gold particles\textsuperscript{83} or carbon nano-tubes\textsuperscript{84} dispersed in the hydrogel can convert light into temperature. The subsequent temperature rise causes the volume changes of hydrogels. It is therefore, referred to as ‘heat mode’. In case of positive-sensitive systems, this means the volume increase and for negative systems volume decrease will appear. Based on this technology, West at al\textsuperscript{83}. demonstrated light controllable microfluidic valves. In our work, we also demonstrate light responsiveness in hydrogel through the indirect way of converting light to heat which will be elaborated in Chapter 6.

Somewhat beyond the scope of this thesis there are many other types of stimuli-responsive hydrogels, like those responding to magnetic field\textsuperscript{85}, humidity or electric filed.
As with the pH and temperature responding hydrogels have been investigated extensively for a long time in a large number of applications ranging from pumps or valves to regulate and control flows in microfluidic devices\textsuperscript{86} to drug delivery\textsuperscript{87,88,89}, actuators and sensors\textsuperscript{90,91}. Our research is along these lines with the specific aim to explore the known mechanisms to address the actuation of surface topographies, the topic of this thesis, by making use of interfacial constrained hydrogel films.

### 1.3.5 Constrained Films

For many applications hydrogels, such as robotics, biomedical, optics\textsuperscript{92}, and drug delivery\textsuperscript{89}, hydrogels are applied in a free-suspended manner. This means that when the chemical components are homogenously distributed around the hydrogel polymer network it exhibits isotropic swelling behavior. However, the requirements of swelling change when hydrogel pillars need to be anchored to substrate to block and open channel in microfluidic system\textsuperscript{86}, when being used as tissue culture substrates\textsuperscript{93} or as gel membrane to regulate flow. The constraints due to the presence of a non-compliant surface, changes the swelling behavior into anisotropic. And also for the formation of responsive surface topologies in our concern, hydrogel polymer films are required to be constrained to rigid substrates, as shown in Figure 1.14 (b).

![Figure 1.14 Schematic view of a free suspended film (a) and substrate confined film (b). Darker region represents the initial dry gel, the lighter region stands for the volume after swelling. Arrows in both images represent swelling directions.](image)

Due to the confinement of the rigid substrate, swelling properties hydrogel coating is
different from the free standing film. For the free suspended film, see Figure 1.14 (a), swelling is isotropic. This means the swelling degrees are identical in all directions (x, y, and z) and are allowed to reach the equilibrium swelling freely. Whereas for the constrained film as illustrated in Figure 1.14 (b) it exhibits highly anisotropic swelling property in the direction perpendicular to the substrate in z direction. Swelling is largely restricted in the plane of the film (in x and y direction) and can be neglected to only minor deformation effects at the edges of the coating. The confinement of the hydrogel film on one hand permits a large swelling capability in one direction that is normal to the surface, on the other hand it limits the total swelling degrees even up to a factor of 6\(^{94}\). Toomey et al. deduct from Flory – Rehner theory of the equilibrium swelling that the overall swelling degrees of constrained hydrogel network is approximately the square root of that non-constrained network\(^{95}\). This theory finds a good experimental agreement in dimethylacrylamide (DMAAm) gel. With regards of the hydrogels we are using (poly (N-isopropylacrylamide) and poly (acrylic acid)) the swelling degrees of both free standing and constrained films are measured. Results show similar trends as suggested by the theory.

Besides the changes in swelling behavior the restriction from the substrates also impacts the hydrogel other properties, such as shape, mechanical properties, and swelling kinetic\(^{95}\). Remarkably, it was found that the constraints may even raise the transition temperature of poly (N-isopropylacrylamide). Moreover, when a hydrogel film is subjected to a larger compressive stress than the adhesion forces from the substrate it can experience delamination from the substrate. Another significant phenomenon of the swollen gel is its upper surface can be buckled, creased or wrinkled due to the inhomogeneous stress that is exerted on the gel. During swelling, the constrained gel is subjected to two forces, the large osmotic pressure in the direction of film thickness that drives anisotropic swelling and the mechanical strains that restrict in plane swelling. Those two forces are competing with each other. When the osmotic force is large enough, the outer surface of the gel is buckled leading to the surface patterns. Based on this observation, many efforts have been made in this area to create surface patterns by using the nature of constrained swelling\(^{20,21,22}\), see Figure 1.2 (b). Various studies are carried out to explore further the formation of the surface patterns in a more controllable and predictable way. However, due to the lack of control of osmotic pressure and the limitation embedded in the theory and mechanism the formed surface
patterns are limited in the dimensions and configurations. In the thesis, we are introducing a
different principle to structure surface patterns. Our methods allow full control over the
formation of surface topologies without relying on the nature process. These make the
formed patterns more predictable and more varieties can be obtained.

## 1.4 Outline of the thesis

The objective of this thesis is to explore potential technologies to create responsive
surface topologies. We define responsive surface topologies as the ability of a surface to be switched between a flat state and a state with protrusions, where the protrusions preferable can be controlled in size and shape. For this purpose, we investigated two categories of materials: liquid crystal networks and hydrogel networks, and we developed a variety of fabrication principles to realize surface topologies.

Chapters 2, 3 and 4 focus on liquid crystal networks that are functionalized with light responsiveness. Chapter 2 and 3 present surface relief structures formed on a single-phase cholesteric liquid crystal network via localized light exposure. Both a dynamic response, where the structures disappear after exposure (Chapter 2), and a static response where the deformations remain permanently when the light is switched off (Chapter 3) are developed. In Chapter 4 we show patterned cholesteric coating that can be actuated via a uniform light illumination. Design of isotropic area embedded in cholesteric liquid crystal network is introduced first. To further enhance the deformation degrees, a homeotropic alignment is chosen to replace the isotropic regions.

In Chapter 5 and 6 we studied the responsive hydrogels which operate in an aqueous environment. pH responsive poly(acrylic acid) is the focus in Chapter 5. In this chapter we have described an approach to create pre-determined complex deformation shapes in a swelling hydrogel by employing polymerization-induced crosslinker diffusion during photopolymerization. The in-plane modulation of the crosslink density was utilized to make surface relief structures that can be switched on and off by changing the pH of the buffer solution. Furthermore, we designed the out-of plane modulation of crosslink density to make free-standing films that upon pH switching form complex three-dimensional shapes from an initially flat state.

Structuring the thermal responsive hydrogel poly(N-isopropylacrylamide) is the topic
of Chapter 6. Through utilizing this material we developed technologies that enable actuation of surface structures in either a symmetric or an asymmetric configuration, the latter leading to ratchets that are of potential interest for liquid transport principles in microfluidics. Besides using temperature for the actuation we also demonstrate the possibility of light triggering.

In the last chapter, we will address some new findings and preliminary research to the applications of the surface responsive liquid crystal networks and hydrogels. It is of interest to compare the two principles in terms of properties and employability. Based on that, we sketch new application areas to be explored in future research.

1.5 References


6 http://gtresearchnews.gatech.edu/newsrelease/gecko-feet.htm.

7 Photograph by William Thielicke from Wikipedia.com.


22 Jungwook Kim, Jinhwan Yoon and Ryan C. Hayward, Nat Mater., 2010, 9, 159–164.


56 Kunihiro Ichimura, Sang-Keun Oh, Masaru Nakagawa, Science, 2000, 288, 1624-1626.


2. Dynamic Surface Topographies Formed in Chiral-Nematic Networks*

2.1 Introduction

The formation of dynamic protrusions, that can switch on and off by external means, are of interest for many practical applications. By controlling the surface topography tunable lens structures may form in an autonomous manner and their focusing depth might adapt to an external stimulus such as the light and its directionality. But also appearance related properties like scattering, diffraction or reflection may be modulated\(^1,2,3\). Besides the optical effects also surface mechanical properties can be altered by the presence or absence of protrusions in the surface. Properties such as tunable friction, stick and adhesion are important in the fields of haptics and human-machine interfaces\(^4\). In microfluidic applications mixing and liquid transport can be controlled by surface topographies in microchannels\(^5,6\). Dynamic control over these surface topographies enables switching between a mixing and a non-mixing state thus having active control over fluid flows. Also it will become possible to control the wettability of surfaces by sub-micron surface reliefs\(^7,8\).

In Chapter 1 we provide two distinctive methods to generate surface topographies. The first general method is based on the change of molecule organization in highly ordered networks. This procedure proceeds in the dry state at hard surfaces. The second method is based on volume changes by uptaking or expelling of liquid (swelling/ deswelling). This

---

process proceeds only in the presence of a liquid, mostly water and is therefore considered to be a wet process. The swollen volumes are often relatively soft and sometime vulnerable for mechanic deterioration.

Here, the general method we describe here to create surface topographies falls in the category of dry film. The uniform, molecularly ordered film is based on a liquid crystal network. A local change in the degree of molecular order, which results in a local expansion of the film leading to the desired protrusions, is induced by localized exposure, e.g. by patterned UV exposure. For this purpose, we select helicoidally ordered liquid crystal (cholesteric) polymer network obtained by polymerization of chiral-nematic monomers. We selected the cholesteric order rather than e.g. planar nematic for its property to be symmetric in the plane of the film excluding undesired in-plane directional effects.

Cholesteric polymer film has been used before to provide surface topographies by heat. To create locally different volumetric responses patterned cholesteric films containing isotropic area are fabricated. Here, we generate localized response in a homogenous cholesteric film by selective actuation of desired regions via light. For many applications, using light for activation has several advantages over for instance thermal or electrical triggering. The surfaces can be addressed remotely and it avoids 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 a focused or patterned exposure.

To initiate the response to light we make use of azobenzene units that are chemically attached as crosslinks to the polymer network of the coating. Upon exposure with patterned UV light the molecular order parameter in the network is decreased by the trans to cis isomerization of the azobenzene resulting in an increase of the cholesteric pitch, a reduced order parameter, a reduced density, and an increase of the corresponding local volume. Laterally constrained by the adhesion to the glass substrate, the density decrease manifests itself as the formation of protrusions in the surface as illustrated in Figure 2.1. The coating is modulated in a dynamic manner which includes that the structures disappear upon removing of the light source.
The organization of this chapter is as follows: First the selection of materials will be discussed in detail. Then we will explain the underlying mechanism of the formation of protrusions based on the density decrease. A novel way is presented to track and measure the density changes during the exposure. Furthermore, we are able to distinguish and quantify the contributions of light-induced effect and thermal-induced effect by well-designed experiments.

2.2 Fabrication of Thin Coating of Cholesteric Polymer Network

We made an elastic thin coating of cholesteric polymer network on a glass substrate by photopolymerization of a mixture of liquid crystal monomers in their chiral-nematic phase. We have chosen a cholesteric order for its in-plane symmetry rather than planar uniaxial order which is expected to build up lateral stresses upon deformation related to the in-plane anisotropy.

The mixture of liquid-crystal acrylate monomers is shown in Scheme 2.1. The exact monomer composition is provided in the Experimental Section. The liquid crystal phases origin from the molecules with an anisotropic shape, i.e. monomers 1-5. As such monomers 1-3 exhibit a nematic phase in which the molecules tend to align uniaxially along a common director. This mixture of mono-and di-acrylates has been chosen such that it has good

---

**Figure 2.1** Schematic view of a cholesteric polymer film (a) and the density-induced formation of protrusions under the influence of loss of order (b)
processing properties in the monomeric state (transition temperature and viscosity) and good mechanical properties in the polymeric state with glass transition temperature well above room temperature. The presence of the chiral molecule 4 induces a chiral-nematic phase in which the average molecular orientation describes a helix. The chiral-nematic order is schematically shown in Figure 2.1(a). We should point out that the molecular order is not as perfect as this figure suggests and that the direction of the long axes of the drawn individual molecules resembles more the local common director than the direction of each molecule separately. The order parameter of the molecules in our system is between 0.6 and 0.7, meaning that the molecular distribution around the rotating common director is between +/- 45 degrees. To this chiral-nematic monomer mixture we added a small percentage of reactive azobenzene monomer 5 and photoinitiator 6. This mixture is applied between two glass substrates, both provided with rubbed polyimide, to enforce planar alignment with the helix axes perpendicular to the substrate, and photopolymerized in the chiral-nematic state. We selected wavelengths > 400 nm to initiate the photopolymerization to exclude premature conversion of the trans azobenzene compound to its cis state. To ensure full conversion of the monomer we gave the sample a post-bake at 120 °C for 30 minutes. We checked the preservation of order by polarization microscopy which showed the oily streak figures that are characteristic for planar aligned chiral-nematic films.
Scheme 2.1. Materials used for photosensitive chiral-nematic compositions. Materials 1-3 are liquid crystal monomers. 4 is chiral dopant. 5 is azobenzene. 6 is photoinitiator. 7 is a UV absorber.

After polymerization an adhering hard and glassy film is formed. The coating shows its typical cholesteric, polarization-dependent reflection at around 630 nm as caused by constructive interference at the periodicity of the molecular helix. The coating has reddish appearance because of its reflection at around 630 nm caused by Bragg related constructive interference at the periodicity of the molecular helix (Figure 2.2 (a)). From the position of the reflection band we calculated the pitch of the molecular helix to be 394 nm. Allowing for a small deviation related to a different monomer composition this value is in agreement with the prediction based on the helical twisting power of the chiral component that has been published before20.
2.3 Formation of Dynamic Surface Topographies

The cholesteric polymer network we made contains azobenzene monomer 5 which is homogeneously distributed as crosslink over the network. Azobenzene is known for its photochromic and photomechanical properties\textsuperscript{21,22,23,24}. The azobenzene unit has two isomeric states, as shown in Figure 2.2(b). An elongated trans state and a bent cis state. In its trans state this molecule is rod-like and adapts the order and orientation of the other liquid crystal moieties. By illumination with UV light, preferably in its absorption band at 360 nm (Figure 2.2(a)), it undergoes a transition from its ground trans state to the thermally more unstable cis state. The cis state of azobenzene molecule can reduce the molecular order in the liquid crystal network because of its bent conformation. The reverse reaction to the trans state may occur thermally or by illumination with white light where the absorption band of the cis state at around 450 nm is addressed.

![Diagram](image)

*Figure 2.2 Transmission spectrum for circularly polarized light (a) of a chiral nematic film modified with azobenzene (b).*

The isomerization of azobenzene leads to a shape change on molecular level which on itself might result in relatively small macroscopic changes of the geometry as observed in isotropic polymers containing azobenzene crosslinks\textsuperscript{25}. Earlier work have demonstrated the possibility to amplify the conformational change of azobenzene molecules to the
Dynamic Surface Topographies Formed in Chiral-Nematic Networks

macroscopic domain by integrating the azobenzene unit into a liquid crystal elastomer. When this azobenzene moiety is embedded in a liquid crystal polymer matrix that the trans to cis isomerization leads to a reduction of the molecular order and a corresponding change in dimensions and/or geometry.

Based on this effect, morphing was demonstrated by various groups also in liquid crystal materials with higher modulus. And also our group created similar responses in films consisting of splayed nematic networks.

Most often, the photomechanical effects of azobenzene modified liquid crystal networks were demonstrated on free standing beams of films showing bending or curing deformations. We are now using this response to induce protrusions in the cholesteric liquid crystal coating. Thereby we expose the film through a mask by which the film surface deforms to form protrusions at the irradiated area. However, the formation of the surface relief during UV exposure is only visible to the eye during the duration of exposure and very shortly thereafter. Upon removing of UV light, the initial flat surface is retained within the time frame that a quantitative measurement can be performed. Thus we developed an indirect approach to record the deformation of surface topographies by capturing the deformation in PDMS. Liquid PDMS precursor is casted to cover the initial flat cholesteric coating. Using a photomask we exposed the cholesteric film locally to create surface topographies in the coating. The still liquid PDMS complies with the surface deformation of the cholesteric. PDMS is cured during the continuous exposure and captures the surface topographies of the underlying layer in a reversed image which is negative of the protrude cholesteric coating. Once UV light is removed, the cholesteric coating retains its initial flat surface immediately releasing itself already partly from the cured PDMS. The process is depicted in Figure 2.3 (a-c). The surface topography captured in the PDMS was analyzed by interference microscopy. Figure 2.3 (d-e) shows the result for the case where a line mask with a pitch of 2mm and aperture of 1mm is used. Related to the thickness of the cholesteric coating the surface expansion of 1 µm corresponds to a linear strain of 10%. As the lateral dimensions of the cholesteric film remain the same, being adhered to the glass substrate, this thickness increase of the cholesteric scales inversely with the density decrease between the exposed and the non-exposed areas, making this value remarkably high. One might argue that the results are somewhat influenced by the coverage of the film with PDMS which
reduces the interfacial surface tension. We anticipate that this effect is small and can be mainly found, if any, at the edges of the structures where the surface area is enlarged by the surface deformation. The intensity of light used is 50 mW/cm². Higher intensities, up to 150 mW/cm² do not lead to a further increase of the height of protrusions.

Figure 2.3 Schematic representation of the PDMS procedure proceeds to replicate surface topographies (a-b). (a) liquid PDMS is casting on the flat cholesteric coating. (b) curing of liquid PDMS is performed during the exposure, and (c) solidified PDMS captures the formed topographies after the exposure. 3D Interferometer image (d) showing PDMS replications of dynamic surface topographies formed in chiral-nematic films containing azobenzene 5 and its surface profile (e).

2.4 Density Measurement

To verify this remarkably high density decrease of the azo-modified cholesteric film under exposure with UV light we performed density measurements of a free standing film of the same composition in the exposed and in the non-exposed state. In the non-exposed state the density of the film was measured by a density column at RT to be 1.217 g/cm³. By immersing this film in salt brine of different densities, but lower than that of the cholesteric film, prior to exposure we could study the density decrease of the film when the film undergoes the transition from sinking to floating. The experiment is demonstrated in Figure 2.4. In this particular experiment the cholesteric film was immersed in salt brine of the
density of 1.202 g/cm³ which makes the film to sink. Upon exposure with UV light the film starts floating as soon as the light is switched on. Switching off the light source makes it to sink again. From a series of these experiments with different salt concentrations we could estimate that the density of the exposed cholesteric film is 1.106 g/cm³. This corresponds to a density reduction of 9.8%, close to the linear strain values measured by interference microscopy at the cholesteric coating.

Figure 2.4  Density change in a chiral nematic film containing azobenzene 5 and Tinuvin 7, resp. (a) before UV exposure, both the Tinuvin and azobenzene film are at the bottom of flask, (b) snapshot of films during exposure showing the azobenzene film to float and the Tinuvin film to remain at the bottom, and (c - e) after removing of UV light, the azobenzene film starts sinking to its reaches initial position at the bottom. The Tinuvin modified film remained at the bottom.

2.5 Thermal Effect

To reveal the origin of the large density decrease we performed a number of control experiments. Firstly we estimated the influence of heating of the coating and the free standing film by light absorption. The constraints of the glass substrates in the case of the cholesteric coating impose that we should calculate the height increase using volume thermal expansion coefficients rather than the linear expansion. The volume thermal expansion coefficient of the chiral-nematic film is estimated from linear expansion measurements in the direction parallel to the helical axis and perpendicular to that to be 285 ppm below the glass transition temperature and 552 ppm above that. The glass transition of the polymer is found to be around 60 °C. In order to describe a volume expansion of 10% to temperature changes
alone, the temperature should increase from RT to an estimated temperature of 220 °C. This value might be unlikely, especially in the water immersed case, but not completely impossible for the coating embedded between glass and the silicone rubber. To verify this further we performed reference experiments with a dye with the same absorption characteristics as the azobenzene. For this experiment we created a formulation similar as the one studied before but we exchange the azobenzene with compound 7 (Tinuvin, see Materials Section) which has an absorption spectrum than coincides with that of the azobenzene compound, as shown in Figure 2.5.

![Figure 2.5 Comparison of the absorbances of azobenzene 5 and Tinuvin 7.](image)

Experiments were carried out identically as described for azobenzene containing film. The linear strain measured is 0.33µm which corresponds to a surface expansion of 3.3%. These results show that thermal effect indeed plays a role and the azobenzene isomerization is only partly responsible for the deformation. Due to the light-absorption, the film is heated up leading to thermal induced deformation. From the measured strain and the thermal expansion coefficients we could make an estimation of the temperature rise. In this particular experiment we started at a temperature of 40 °C. A volume increase of 3.3 % can then be explained by a temperature rise to 110°C (ΔT = 70°C). By subtracting the temperature effect from the measurements, we estimated the light effect on the deformation is approximately 6%.
Figure 2.6 Interferometer microscopic measurements show 3D image (a) of PDMS replications of surface topographies formed in chiral-nematic films containing Tinuvin 7 and the its surface profile (b).

The same Tinuvin modified film was subjected to the density measurement by the immersion method. As can be seen in Figure 2.6 this sample cannot be brought to floating as the azobenzene containing film. From this experiment it becomes clear that the volume increase for the Tinuvin sample is smaller than 0.15%. This means that the temperature increase in this in water immersed case is estimated to be less than 6 °C.

2.6 Effect of Molecule Order

After having discriminated between the effects of the conformation change of the azobenzene and temperature increase caused by absorption we were curious to what extent the molecular order of the liquid crystal network plays a role. It is argued in earlier publications that the azobenzene not only may induce geometrical changes because of its isomerization reaction but also that the change in molecular conformation affects the order of the surrounding molecular units. In order to get information on the contribution of the decrease of order parameter we performed an experiment where the composition of the azobenzene containing blend was polymerized at elevated temperatures in the isotropic state. By polarizing microscopy we checked that indeed the isotropic phase was frozen in the network.

This coating we subjected to the same experiment as the network with chiral-nematic order exposing it through a mask with UV light while the deformation was captured in a curing PDMS film. The results are shown in Figure 2.7.

Clearly the deformations in the isotropic polymer network are much smaller than those of the cholesteric network. The density decrease estimated from this measurement is 1.2%. This value corresponds to the values reported in the literature for isotropic polymers.
modified by azobenzene moieties.

Figure 2.7 Interferometric microscopic measurements show 3D image (a) of PDMS replications of surface topographies formed in isotropic films containing azobenzene and its surface profile (b).

Despite the similarity of chemical compound, the density of isotropic polymer network is much lower than that of the ordered polymer network. This leads to the conclusion that the reduction of the initial order is responsible for the density decrease by a reduction of reduced molecular packing of rod-like unites in the system and the increase in free volume of the system by the combined thermal and photomechanical effects. It is important hereby to note that the system does not undergo the full phase transition to the isotropic phase but keeps its chiral-nematic order, but with reduced order parameter.

2.7 Conclusions

In conclusion, by re-arrangement of the molecular orientation in a crosslinked polymer network with chiral-nematic order we can induce changes in the topography of a film or coating surface by means of light. The photo-induced isomerization of an integrated azobenzene compound initiates a change of the order of the liquid crystal molecular units in the network. This leads to a decrease of density and a related increase in volume. By exposing the film locally the volume increase forms a protrusion at the exposed area. When the chiral-nematic network has been made by photopolymerization of the reactive mesogens under standard conditions, the polymer network exhibits a fully elastic response. This means that the deformation can only be observed under the condition of continuous irradiation with UV light. As soon as the UV light is switched off the polymer network recovers its initial state and the structures disappear.

The formation of surface topographies on a homogenous cholesteric film not only provides a simple and straightforward method to fabricate the dynamically protruding films,
but also provides insight into the mechanism of actuation and gives us the possibility to quantify the contributions of light-induced and thermally-induced effects. Although the use of photomasks, or other means to expose the area in a patterned way, adds somewhat complexity to the system, next to the ease of fabrication there are also other advantages. As the surface topographies disappear as soon as the UV light source is switched off, the surface can be subjected to a variety of successive patterns. This can for instance be used to generate a peristaltic wave on the surface that can be used for transport of solids, liquids or gases. Especially the combination with accurate projection system as dynamic mirror devices provides a wealth of possibilities connecting the surface topography to dynamic images created by digital media.

2.8 Experimental Section:

Materials: An overview of the materials is provided in Scheme 2.1. Monomers 1 to 3 were obtained from Merck UK. Monomer 4 was obtained from BASF. Monomer 5 was custom-synthesized by Syncom (Groningen, Netherlands). Typically thin films were fabricated from a mixture containing 20 w% monomer 1, 42 w% monomer 2 and 28.5 w% monomer 3, 5.5 w% monomer 4, 2 w% monomer 5, and 2 w% photoinitiator 6-2-(2H-benzotriazol-2-yl)-4,6-di t-pentylphenol 7 (Tinuvin 328, Ciba Specialty Chemicals, Basel, Switzerland) has an absorption spectrum that coincides with that of the azobenzene compound and was occasionally added to exchange the azobenzene to study thermal effects. In that case the mutual ratio of other monomers and the concentration of photoinitiator was kept the same. The constituents were mixed by dissolving in dichloromethane which was evaporated subsequently. DSC results show that the mixture has the chiral-nematic phase in the temperature range between 40°C and 60°C. At higher temperatures it becomes isotropic.

Sample preparation: Rubbed polyimide AL 1051 (JSR Corporation, Japan) was used to obtain planar alignment of the liquid crystal monomer mixture. It was spin coated on cleaned glass, followed by baking and rubbing with a polyester cloth. The monomer mixture was capillary filled in between two such treated glass plates and subsequently cured by UV exposure at 45 °C for 30 minutes using a mercury lamp (EXPR Omnicure S2000) equipped with a cut-off filter transmitting light > 400 nm (Newport FSQ-GG400 filter). The samples
were post-baked at 120°C to ensure full cure of the acrylate monomers.

**Creation of surface profiles:** Samples were exposed to UV at RT through a line or checker board mask with the mercury lamp (EXPR Omnicure S2000) at light intensities between 10 and 700 mW/cm².

**Sample Characterization:** The cholesteric film was checked by polarized microscopy. The surface topography was measured using a 3D interferometer (Fogal Nanotech Zoomsurf). The absorbance and transmission spectrum were measured by UV-VIS (Shimadzu, UV-3102 PC). For polarized reflection the light path in the spectrometer was provided with a polarizer and a quarterwave filter to generate circularly polarized light. Density measurements were performed in a density column (ETH Zurich, Switzerland) and by standard salt solutions in water. Volume thermal expansion coefficients are calculated from TMA (PerkinElmer) linear expansion measurements in to all three directions.

**PDMS replication of the dynamic surface topographies:** Prior to mask exposure uncured liquid PDMS (Sylgard 184-Dow Corning, USA) was poured on the surface of the polymer coating. Curing of the PDMS takes place while the polymer coating is mask exposed to replicate the forming surface structure. The replication process takes 2 hours under UV illumination.

### 2.9 References


3. Permanent Surface Topographies Formed in Chiral-Nematic Networks*

3.1 Introduction

In the previous chapter, we studied the use of azobenzene modified liquid crystal networks to create dynamic surface reliefs. Thereto the polymer network was exposed through a mask. In the exposed area, besides some expansion through thermal heating, prominent protrusions were found as a result of a decrease of the molecular order leading to decrease in density of the polymer. Especially the use of a chiral nematic network proved to be very useful for this purpose as it provides in plane symmetry despite the required molecular order. The fact that our polymer network behaved fully elastic resulted in a fully reversible process. The structures that were formed during exposure with UV or blue light directly disappear as soon as the exposure stops.

While studying this process we found that under special conditions also a permanent structure could be made that remains after the exposure has stopped. In this chapter, we will report on this formation of permanent surface topographies in a crosslinked chiral-nematic network. The protrusions are created by mask exposure under moderate-intensity UV light. The process proceeds in the ‘dry state’ and the structures are permanent. The network properties make the structure resistant against high temperatures and mechanical damage. In addition to the mechanical features the structured films have specific optical properties as

caused by the 1D bandgap properties of the chiral-nematic material. We believe that the method we developed can find its application in soft lithography, thin film optics, thin film mechanics and mold fabrication.

3.2 State of the Art

Optical lithography is a well established technology for the formation of geometrical structures\(^1,2,3\). It has formed the basis for the developments in microelectronics\(^4\). It has been instrumental in the generation of molds with sub-micron topological dimensions that are for instance used for the production of optical discs. And within optics, lithography is also applied to create surface relief gratings\(^5\), micro lenses\(^6\), lens arrays\(^7\), Fresnel lenses\(^8\) and optical filters. In general lithography is a subtractive process in the sense that a continuous flat optical sensitive film is applied on a substrate and that the structure is formed by partially removal of material by dissolving or etching. These processes require additional production steps, excess of material and are often environmentally unfriendly. Occasionally, photonic processes have been proposed that are additive, such that the structure is formed in the film without removal of material. Elegant examples are photoembossing using mask exposure\(^9\) or holography in monomer-polymer mixtures\(^10,11\) and the formation of surface topographies in azobenzene modified polymers by laser exposure\(^12,13\). The latter techniques proved to be useful for the formation of well-defined topological structures that can for instance be used for gravure printing, offset printing or microcontact printing\(^14\). A specific advantage of these methods is that the structures are obtained by dry processes. Once the polymer film or coating has been formed there is no solvent processing needed or treatment with hazardous etch baths.

A number of groups\(^15,16,17\) have demonstrated the generation of surface relief gratings (SRG) in thin films by using azobenzene containing polymers. Gratings are fabricated by irradiating the thin film though a single beam of polarized light. Although the mechanism is still not fully clear, it is expected that the isomerization of the azobenzene unit leads to the mass transport of polymer chains\(^18,19,20\). The polymers that are being used are linear inherent to the mechanism of mass transport. Consequently the structure dimensions that can be made are dependent on molecular weight. The linearity of the polymer chains also makes the structure are sensitive to elevated temperatures which makes them less useful for use as mold
for thermal embossing because of softening and flow.

### 3.3 Elasticity of the Cholesteric Networks

In the experiments in Chapter 2, upon UV exposure of the chiral-nematic film through a mask, the density reduction results in the formation of protrusions. However this protrusion is only visible under continuous mask exposure. As soon as the light is switched off the protrusion disappears. The polymer network behaves fully elastic resulting in a full recovery of the initial flat state. The azobenzene falls back to its planar-aligned $\text{trans}$ state and the molecular packing is recaptured. The chemical composition of the monomer used earlier is given in Scheme 3.1 (compound 1-6).

However from previous publications\textsuperscript{16,19} we know that an azobenzene moiety can be realigned when exposed to UV light. This phenomenon is related to the dichroic nature of the $\text{trans}$ azobenzene molecule. With its transition moment parallel to the electrical field vector of light it becomes excited and converts to the $\text{cis}$ state. From the $\text{cis}$ it falls back to the $\text{trans}$ state in its original position. After which the process is repeating itself. But if the re-orientational mobility of the azobenzene is sufficient the group can also rotate out of the plane during conversion from the $\text{cis}$ to the $\text{trans}$ state. Now with the transition moment out of the plane of the electrical field of light the azobenzene is less subjected to become excited and occupies in principle a more stable topological position. The reason why this does not occur in the system described in Chapter 2 is that the formed network is relatively elastic. The network allows isomerization and the related formation of disorder on local scale by deforming itself. But the network does not allow for molecular reorganization as a consequence of realignment of the azobenzene molecules and as soon as the driving force for realignment is removed the network takes its original arrangement.
The network properties can be changed by reducing the kinetic chain length of the acrylate main chains and by introducing more dangling chain ends in the polymer network. Based on the chemical composition used in Chapter 2 which forms a rigid network, we add \( p \)-methoxyphenol 8 to the monomer formulation prior to polymerization. See Scheme 3.1, the highlighted compound. \( p \)-Methoxyphenol is known as chain stopper and free radical scavenger.\(^{21,22,23}\) Normally it is added to formulations in concentrations of tens of ppm’s to stabilize reactive acrylate mixtures improving their storage life. Here we added it in concentrations between 1 and 4 w\(^{\circ}\). A first indication that this attempt is successful we get from the reflection spectrum of the chiral-nematic film shown in Figure 3.1. The position of the reflection band \( \lambda_r \) relates to the in-plane average refractive index of the network.
Permanent Surface Topographies Formed in Chiral-Nematic Networks

\( \bar{n} \) through \( \lambda_r = \bar{n} \cdot P \) with \( P \) being the pitch of the chiral-nematic network (see also Figure 2.1 (c)).

![Figure 3.1](image)

Figure 3.1 Transmission spectra of the chiral nematic film modified without (a) and with \( p \)-methoxyphenol chain transfer agent (b) before (solid line) and after (dashed line) UV exposure. The peak at 630 nm corresponds to the reflection band of the chiral-nematic network.

Before exposure the reflection band has a width of 75 nm. In case of the network that was formed in the absence of \( p \)-methoxyphenol the band width remained unchanged when measured after the exposure has taken place, Figure 3.1 (a). This is very different for the samples that are polymerized in presence of 2 w\% \( p \)-methoxyphenol. In that case after exposure the band has narrowed to a width of 50 nm. At position \( a \) in the spectrum the reflection wavelength relates to the ordinary indices \( n_{o,i} \) and \( n_{o,e} \), respectively before and after the exposure. The wavelength at position \( b \) relates to extraordinary index after exposure \( n_{e,e} \). And the wavelength at position \( c \) to the extraordinary index before exposure \( n_{e,i} \). This
Chapter 3

gives the following set of equations:

\[ \lambda_{i}^{a} = n_{o,i} \cdot P_{i} \]

\[ \lambda_{e}^{a} = n_{o,e} \cdot P_{e} \]

\[ \lambda_{e}^{b} = n_{e,e} \cdot P_{e} \]

\[ \lambda_{e}^{e} = n_{e,i} \cdot P_{i} \]

Eq. 3.1

\( P_{i} \) and \( P_{e} \) are the pitches of cholesteric helix before and after exposure, respectively.
The fact that \( \lambda_{i}^{a} = \lambda_{e}^{a} \) and \( \lambda_{e}^{b} < \lambda_{e}^{e} \) and assuming \( P_{e} \geq P_{i} \) point to a decrease of especially the extraordinary index of the network molecules and thus to a reorientation of the mesogenic units into the direction perpendicular to the plane of the film. Consequently we can conclude that the \( p \)-methoxyphenol modified network enables sufficient mobility for realignment of the azobenzene compound and a permanent change in order of the mesogenic network.

3.4 Formation of Permanent Surface Topographies

Now we are studying the surface deformation of the \( p \)-methoxyphenol modified film upon patterned exposure through a line mask with 100 µm openings with the pitch of 500 µm. The surface was analyzed before and after exposure by interference microscopy. Before the exposure the surface is flat. The surface topography after exposure is shown in Figure 3.2. Unlike the results discussed in Chapter 2 and shown in Figure 2.2 we now can measure a permanent deformation of the surface. When exposed with a light intensity of 700 mW/cm² we measure the formed ridges to be 0.7 µm high, corresponding to a linear strain of around 7%, defined as the modulation depth divided by the film thickness. Under the assumption that the total number of rotations of the molecular helix does not change, being fixed by the boundaries of the network, the linear strain scales with the pitch of the chiral-nematic helix. We therefore can assume that the pitch increases from \( P_{i} = 390 \) nm to \( P_{e} = 413 \) nm. Using the equations 3.1 we can now estimate that the ordinary index is around 1.51 before and 1.43
after exposure and that the extraordinary index decreases from 1.71 to 1.55. Although there is inaccuracy in these numbers because of some focal conic organization in the helicoidal structure it ambiguously points to an out of plane rotation of the mesogenic molecules next to an overall decrease in density. It must be emphasized at this point that these results were obtained by the presence of only 2 w% of the azobenzene compound 5. This percentage has been chosen to minimize gradient effects over the thickness of the film because of the light absorption of the azobenzene, although this cannot be completely prevented.

To investigate the stability of the protrusions we performed experiments where the coatings, after formation of the protrusions, were subjected to a thermal relaxation process at 120 °C. When the networks still exert elastic forces on the reoriented mesogenic units we expect them to relax and disappear when heated above the glass transition temperature of the network. The glass transition of the network is measured to be around 60 °C. The sample was cooled down slowly to room temperature to avoid free volume build-up by fast cooling. No trace of relaxation was found in the deformed areas. Even after few months of storage in the dark, the surface topographies have not change from their original deformed structures. We further tried to estimate the influence of the possible presence of unreacted
material. We exposed the films before and after exposure to a solvent (THF) extraction. These treatments did not change the results. This result also rules out that transport of unpolymerized low molecular weight material during UV exposure is responsible for the formation of the protrusion.

### 3.5 Characterization of Permanent Protrusions

To find further proof for the assumed mechanism we performed control experiments similar to those of the dynamic protrusions. In a first experiment we estimated the influence of sample heating during UV exposure by exchanging azobenzene 5 for Tinuvin 7. Experiments were carried out identically as described for the azobenzene containing film. The surface expansion measured for Tinuvin containing film is 0.28 µm which corresponds to a linear strain of 2.8%. This suggests that the photomechanical effect due to the isomerization of azobenzene is only partly responsible for the deformation. Due to the light-absorption, the film is heated up leading to thermal induced deformation. By subtracting the temperature-induced effect from the previous measurements, we estimate that of the 7% of total deformation obtained for the azobenzene containing film (see Figure 3.3), 4.2% is due to the light-induced effect.

![Figure 3.3](image)

**Figure 3.3** (a) Comparison of the absorbances of azobenzene 5 and Tinuvin 7 in terms of absorbance. Surface profiles in cross-section (b) and in 3D view (c) of permanent protrusions made by exposing Tinuvin containing chiral-nematic film through a line mask as in Figure 3.2 (a). The surface profile (b) and 3D picture (c) were made by interference microscopy.
In order to confirm the positive influence of the presence of chiral-nematic molecular order on the surface deformation we performed an experiment with an isotropic film, see Figure 3.4. Thereto the same composition with the azobenzene monomer 7 and 2 w% \( p \)-methoxyphenol chain transfer agent 8 was polymerized in the isotropic state. The height of the protrusion in this case is only a fraction of the ordered network, indeed demonstrating that the reduction of molecular order is responsible for the observed effects.

The investigations on thermal effect and the influence of molecular ordering are also conducted for the creation of dynamic surface topographies in Chapter 2. Results show accordance between elastic and visco-elastic cholesteric networks.

Two parameters proved to be critical in the process, the concentration of the chain transfer agent and the UV intensity. We performed experiments with 0, 1, 2 and 4 w% \( p \)-methoxyphenol. The reminiscent deformation as expressed in strain is 0, 0.5, 8 and 3.5 % respectively. We should remark that the latter value is far from accurate because of the poor resolution of the structures formed. For this reason we have chosen 2 w% as the optimum concentration. The linear strain of the formed gratings by mask exposure depends on dose and intensity. Figure 3.5 shows the deformation for the azobenzene sample and the Tinuvin sample. The deformation increases with increasing intensity. We kept the exposure time constant meaning that the \( x \)-axis can also be read as dose. Nevertheless we believe that intensity is more relevant than the dose. This can be seen from the Tinuvin reference curve which follows the same profile indicating that the intensity dependent temperature plays an important role. Above 700 mW/cm² the intensity dependence has leveled off, indicating that

![Figure 3.4](image-url)
the temperature has now been raised well above the glass transition of the polymer network.

![Figure 3.5 Strain of the protrusions formed by UV exposure through a line mask (Figure 3.2 (a)) for a p-methoxy phenol modified chiral nematic film containing azobenzene 5 (o) and for a composition where the azobenzene has been replaced by Tinuvin compound 7 (□).](image)

The standard concentration of the crosslinking diacrylate 1 in the formulations is 20 w%. We varied this concentration between 0 and 30 w% under the assumption that the crosslink density must have an influence on the strain in the protrusions formed. Within the concentration range given, the strain results were however independent of the crosslinker concentration. We should remark here that the crosslink density never reached zero because of the presence of the crosslinking monomers 4 and 5.

In a last experiment we varied the size and form of the masks that we used. Figure 3.6 shows two examples which were obtained by exposure of the chiral-nematic coating through a mask containing squares with square opening of 80μm and a pitch of 100μm (a) and square lines with a line opening of 40 μm and a pitch of 200 μm (b). In general we conclude that deformations of any size in x and y directions can be formed at small dimensions limited by the resolution limits of our optical set up. The dimension of the protrusion in z-direction is determined by the thickness of the initial film and the absorption of the azobenzene compound.
3.6 Conclusions

We demonstrate that it is possible to create light responsive surface topographies in a helicoidally ordered (cholesteric) liquid crystal network via patterned exposure. The photomechanical property of the coating is induced by incorporating small amount of azobenzene monomer which has trans and cis isomeric states. Addressing UV light, the photo-induced isomerization of the azobenzene compound initiates the re-arrangement of the liquid crystal molecular units in the network. Reduction of order in the network leads to a decrease of density and the related increase in volume. By exposing the film locally the volume increase forms a protrusion at the exposed area.

We are able to modulate the stability of the surface topographies by adjusting polymer network elasticity. When the chiral-nematic network has been made by photopolymerization of the reactive mesogens under normal conditions, i.e. with relatively low concentrations of photoinitiator and in the absence of chain transfer agent, the polymer network exhibits a fully elastic response. This means that the deformation can only be observed under the condition of continuous irradiation with UV light. The structures disappear as soon as the UV light is switched off. When the polymer networks has been formed in the presence of a
chain transfer agent, the topological response of the polymer network becomes more viscoelastic and permanent reorientation of the mesogenic units can take place. The protrusions that are now being formed remain after removal of the light source and are durable, also upon heating or solvent treatment. Reference experiments revealed that the surface deformation is predominantly photoinduced but that there is also a thermal contribution due to local heating of the sample. In the absence of molecular order, but with the same molecular composition, the dimensions of the formed protrusions at the exposed area were only a fraction of the ones formed in the presence liquid crystalline order.

The process of permanent surface topographies proceeds in the ‘dry state’ and therefore it is an environmental friendly procedure without the use of solvent based wet etching or developing steps. The network properties make the structure resistant against high temperatures and mechanical damage. In addition to the mechanical features the structured films have specific optical properties as caused by the 1D bandgap properties of the chiral-nematic material. We anticipate that the permanent surface topographies can be used in the applications for example in optical gratings or lenses, especially under the extreme conditions that requires device of high stability.

3.7 Experimental Section

In general, the experimental procedures are similar to those in Chapter 2, Section 2.8 (Experimental Section) and the readers can refer to that chapter.

The differences is the addition of p-methoxyphenyl 8 (Sigma-Aldrich) to the formulation, see Scheme 3.1. Typical concentration is 2 w% but other concentrations are used where mentioned.

Where in the experiments the concentration of compound 1 and 8 were varied, the mutual ratio of other monomers was kept the same as well as the absolute concentration of the photoinitiator.

3.8 References

Permanent Surface Topographies Formed in Chiral-Nematic Networks


16 Yuri Gritsai, Leonid M. Goldenberg, and Joachim Stumpe, Optics Express., 2011, 19, 18687-18695.


APPENDIX:

Surface Topographies Formed in Homeotropic Networks

Having found arguments in the foregoing that for the formation of protrusions the order parameter related density arguments are more relevant than the arguments on order parameter related linear geometrical change of dimensions, we verified the theory further by a local exposure of a uniform homeotropic coating where mesogenic units are aligned perpendicularly to the substrate surface. Following the classical linear geometrical arguments the coating should contract at the exposed places thus forming indents as illustrated in Figure 3.7. In contrast, if density decrease is the dominant factor, expansion should take place and the protrusions should stick out.

![Figure 3.7 Representation of homeotropically aligned network and the corresponding deformation upon a reduction in order parameter (S).](image)


For this experiment we prepared homeotropically aligned liquid crystal monomer mixture comparable to the mixture shown in Scheme 3.1 but in the absence of the chiral component. This mixture aligns homeotropically at oxygen plasma treated glass plate. After photopolymerization and thermal postcure we subjected the coating to a patterned exposure through a line mask with a pitch of 400 µm and opening of 200 µm. The exposure conditions are kept identical as the cholesteric film. The surface topography after exposure is analyzed by interferometer and result is shown in Figure 3.8. A recording of the exposed areas was obtained by administration of the open lines from the mask edges and the resulted topographic structures.

Figure 3.8 Surface profiles in cross-section and in 3D view of protrusions made by exposing the azobenzene modified homeotropic film through a line mask with a periodic pitch of 400 µm and an opening of 200 µm. The 3D picture(a) was made by interference microscopy and show the profiles of the homeotropic film(b).

Unlike predicted by the linear expansion theory, the exposed area does not form valleys; instead, protrusions formed in a similar manner as in the planar cholesteric film. This result strongly suggests the effect of density decrease is dominant in the surface constrained film and the linear expansion does not, or to a far lesser extent, plays a role. Protrusions are formed as the result of decrease in order en the related formation of free volume inducing the density decrease, which is independent from the molecular alignment configurations. Because of the homeotropic alignment of the azobenzene, absorption is less and the mechanical response is somewhat smaller than with the films containing planar alignment.
4. Switchable Surface Topographies by Using Patterned Cholesteric Coating*†

4.1 Introduction

In the previous two chapters, we presented approaches to create surface topographies in a uniform cholesteric liquid crystal coating via localized exposure. Depending on the polymer network is ideal or not and its related elastic behavior, the surface structures can be created either dynamically meaning the initial flat surfaces will immediately retain when the illumination stops (Chapter 2) or permanently without losing the configurations after removing of light source (Chapter 3). This technology proves to be very general applicable in terms of the fabrication process where only a coating and mask wise exposure steps are involved. However, forming surface topographies through focused light or patterned exposure are not always favorable for some practical reasons, because they require a more complex light source than flood exposure. For example, a photomask needs to be located just above or preferably in contact with the coating for a better resolution. Moreover, the light source must be collimated requiring additional optics. This is not a convenient choice in most cases especially when the coating is embedded in another system such as, microfluidic

This Chapter is partially based on:


Switchable Surface Topographies by Using Patterned Cholesteric Coating

channel, in the waveguide, or even in the touch input devices. Therefore, the coating that can respond to an unpatterned light source by changing its surface topographies is required for these new applications and this will be the focus of this chapter.

Flood exposure over a homogenous cholesteric coating might lead to a volume change but does not lead to the surface topological changes. In order to create surface structures via uniform illumination, cholesteric coating needs to be patterned. This means regions should be included that have a different height change than the cholesteric area in response to UV light. Using liquid crystal, we consider locally altering molecular alignments in the cholesteric matrix to induce surface topographies. One option is through incorporation of a local isotropic alignment where molecules are randomly arranged. Under the flood exposure, cholesteric regions form protrusion while isotropic area barely deform. We will describe this method in the first part of the chapter. In order to enhance the deformed topographies, isotropic region can be replaced by homeotropic alignment where molecules are perpendicularly aligned. Under the illumination, cholesteric regions undergo expansion normal to the surface while the homeotropic areas experience an opposite action such that they contract perpendicular to the film surface. This mechanism seems contradicting with the findings in Chapter 2 and Chapter 3 where volumetric changes rather than linear changes were dominating the structure formation. However, we anticipate that having orthogonal orientations next to each other, a shear expansion/contraction in the plane of the film might occur which enables the orchestrated in-plane deformations where the cholesteric areas shrink and the linear areas expand. Cholesteric coatings that embed regions with a homeotropic alignment will be the topic in the second part of this chapter.

4.2 Cholesteric/Isotropic

Early work of morphing surfaces for a thermally responsive system was reported by Sousa et al. It is based on patterned cholesteric where isotropic areas are integrated in cholesteric media, as described in Chapter 1 (Section 1.2.3 Thermal Responsable Surface Topographies). Prior to heating, the coating has a relatively flat surface. Upon heat to 175°C, the cholesteric (chiral nematic) region exhibits a strong anisotropic expansion normal to the film surface while non-ordered isotropic areas have bulk thermal expansion. The height differences in two region result in the surface topological changes as protrusions formed in
Chapter 4

the coating.

We are now advancing this thermal-sensitive coating into photo-switchable surface topographies via integrating azobenzene containing crosslinks into the structured chiral-nematic network. As shown in Figure 1.4, when addressed with UV light azobenzene converts to the bent cis state which reduces the molecular order in the liquid crystal networks. In the chiral nematic areas, 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, depending on the temperature. In the isotropic area where molecules are randomly arranged, there is no reduced order parameter further possible and hence no anisotropic deformation other than imposed by the constrains of the surface adhesion.

![Figure 4.1 schematic presentation of liquid-crystal network containing striped patterned of alternating area with chiral nematic order and isotropic orientation. Upon exposure with UV light the chiral nematic areas expand perpendicular to the plane of the film and the isotropic areas have bulk thermal expansion.](image)

### 4.2.1 Sample Preparation

We prepared our responsive coatings by photopolymerization of a mixture of liquid crystal acrylate monomers in their chiral-nematic phase. A typical composition is provided in the Experimental Section and Scheme 4.1. The mixture consists of a balanced composition of mono- and di-acrylates 1 – 3 (Scheme 1) to tune the crosslink density and therewith the position of the glass transition temperature (between 60 and 100 °C) and the molecular mobility towards changes of the order parameter. Monomer 3 also has the function to make the dielectric anisotropy to be positive in order to enable easy alignment in an electric field where necessary. The mixture contains the chiral diacrylate 4 which is known to have a helical twisting power HTP, as defined by \( HTP = 1/pc \) with \( p \) the pitch of the chiral
nematic helix and $c$ the concentration of chiral dopant, of 58 $\mu$m$^{-1}$. By using a concentration of 5.5 w% the pitch of the chiral-nematic helix is 0.312 $\mu$m. The azobenzene containing di-methacrylate 5 was added to provide the photoresponsive properties based on its UV induced trans to cis isomerization by exciting the molecule in its absorption band at 360 nm. Its concentration is varied, but typically around 5 w%. The photoinitiator 6 was chosen to enable photo-initiation of the polymerization by exposure with blue light. Unless reported otherwise, the wavelength for polymerization was chosen to be $\geq$ 400 nm to prevent isomerization of the azobenzene group during polymerization. Films were prepared between two glass plates provided with rubbed polyimide and cured by exposure with light $> 400$ nm by means of cut-off filter.

Scheme 4.1 Materials used for the polymerization of photosensitive chiral-nematic compositions with alternating isotropic/homeotropic order. Materials 1-3 are liquid crystal monomers. 4 is chiral dopant. 5 is azobenzene. 6 is photoinitiator.

The stripe patterned coating with alternating stripes with planar chiral-nematic order and stripes with isotropic order was made by mask exposure of the monomer mixture in its chiral-nematic state followed by a flood exposure after heating the unpolymerized area to the isotropic state, as shown in Figure 4.2. The chiral nematic regions polymerized during the
first exposure are not affected by the heating for the second polymerization step of isotropic regions. After those two steps of exposure a polymer coating consists of alternating chiral-nematic and isotropic areas are formed.

![Figure 4.2 Schematic view of the fabrication process of the a coating consisting of alternating chiral-nematic and isotropic stripes. (a) Mixture consists of compound in Scheme 1 was filled in two rubbed glass plates (b) Selective exposure through a photomask is carried out in the chiral-nematic state of the monomer mixture. At the illuminated areas, the monomers polymerize. (c) the still unpolymerized monomers are heated to their isotropic state and polymerized during the second flood exposure (d) the resulting film containing isotropic and chiral nematic regions.](image)

The polymer coating containing the alternating lines of planar chiral-nematic network and isotropic network, schematically depicted in Figure 4.1, was studied prior to the UV exposure by polarizing optical microscopy and interference microscopy, see Figure 4.3. The polarization microscopy picture shows clear black lines corresponding to the 200 µm wide isotropic lines and the 100 µm colored lines originating from the chiral-nematic area. The color originates from the anomalous and strongly wavelength-dependent optical rotation of polarized light near the chiral-nematic 1D bandgap. The interference microscopy image demonstrates some elevation at the chiral-nematic lines accompanied by some deeper ridges at the edges. This surface profile, shown quantitatively in Figure 4.3 (c), is inherent to the fabrication of the samples by mask exposure and the formed structure is typical for
polymerization-induced diffusion taking place during the first exposure step. Similar structures were observed during the manufacturing of patterned optical retarders by using subsequently a mask and a flood exposure. Especially the most reactive components of the mixture tend to diffuse to the exposed area leaving a deficit at distances corresponding to the diffusion distance.

Figure 4.3 (a) polarization microscope image taken with crossed polarizers showing black isotropic lines and bright colored chiral-nematic areas, inset is the photomask used, (b) 3D image taken by interference microscope just after fabrication of the film before UV exposure for actuation, and (c) surface profile derived from interference measurement.

### 4.2.2 Actuation of Cholesteric/ Isotropic Coating

Upon exposure with a continuous light beam of 365 nm a relatively large surface deformation takes place as shown in Figure 4.4.

Figure 4.4 3D images taken by interference microscopy showing the surface profile before (a) and after UV exposure (b), and the surface profile (c) before (blue), during (red) and after UV exposure (green) showing that the deformation is permanent.
However in contrast to the exposure of the dynamic cholesteric films without chain transfer agent presented in Chapter 2, no recovery of the initial state is observed after the UV exposure step, not by temperature and not by exposure with white light. Instead the coating remains highly deformed, even after longer storage times at room temperature (days) or after heating (100 °C). Figure 4.5 shows the deformation as a function of the azobenzene concentration. Most remarkable aspect of this figure is that already without the presence of azobenzene moieties a considerable deformation is taking place.

The model to explain this remarkable non-reversible behavior is based on volume relaxation. During the fabrication of the layers materials transport to the irradiated area took place during the first exposure step. This process is called polymerization-induced diffusion and can be explained in terms of chemical potentials of the reactants and the polymers formed. Important parameters are concentration gradients in a reacting system, Flory-Huggins interaction parameters between the monomers and the forming network, the elasticity of the forming network and diffusion rates. Normally this would already directly result in a deformed surface but because of the presence of the surface cover the surface remains flat. Consequently this leads to a density difference between the exposed and non-exposed areas. This is even further enhanced during the second exposure at higher temperatures. Upon cooling to room temperature, well below the glass transition temperature of the polymer network, and removal of the cover plate only a small deformation takes place as much as the glassy state of the polymer permits (Figure 4.3). However upon agitation by the trans/cis isomerization reaction combined with heating by the lamp, density driven relaxation can take place leading to the large irreversible deformation. This also explains the observation that a heating step without exposure leads to a similar result and, moreover, that also the absence of azobenzene gives a surface deformation.

The effect of the azobenzene concentration on the formation of this permanent structure is shown in Figure 4.5. It shows the effect at zero azobenzene concentration and a gradual increase with increasing azobenzene. This increase can be explained in terms of polymerization rate which has been slowed down by the presence of absorbing azobenzene thus allowing polymerization-induced diffusion to be more prominent.
In order to overcome the stress/volume relaxation phenomena as a result of a mask-wise exposure, the patterned cholesteric coating needs to be frozen by a single polymerization step where the two regions of different orders are polymerized at the same time. Therefore, we developed cholesteric coating patterned with homeotropic region.

4.3 Cholesteric/Homeotropic

As argued in the previous section, it has an advantage to polymerize the two areas of different photo-response in a single polymerization step. Thereto, we developed the patterned coatings with alternating planar chiral-nematic area and homeotropic (perpendicularly oriented) area which already established in the monomeric state and the structure is frozen in by a single photopolymerization step, thus preventing monomer diffusion during polymerization.

An additional advantage of this procedure is that the chiral-nematic and homeotropic molecular alignments have opposite photomechanical response, the combination of which might result in a larger effect than the previous patterned system. Upon UV irradiation, azobenzene coverts in to cis state, which reduces the molecular order in the liquid crystal network because of its bent conformation. In the chiral-nematic area, this results in a positive expansion along the film thickness, perpendicular to the plane while the in - plane
expansion is close to zero or even negative. In the homeotropic area, the opposite occurs when the molecular order is reduced. It will undergo expansion within the plane of the film and contraction perpendicular to the film surface. See Figure 4.6. This effect will be in competition with the density effects as discussed in the previous chapters, and will depend whether the in-plane shear can take place on a sufficient level.

![Schematic presentation of a liquid crystal network containing striped pattern 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 direction perpendicular. In the plane of the film the chiral-nematic areas contract and the homeotropic areas expand.](image)

We prepare this responsive coating by photopolymerization of a mixture of liquid crystal acrylate monomers as illustrated in Scheme 1.

The patterned films with alternating planar chiral-nematic area and homeotropic areas were established while still in the monomeric state. Thereto we started with a monomer film that is in its planar chiral nematic state. And we used a local electrical field to align the molecules along localized field lines, thus overruling the chiral-nematic order. For that monomer $3$ is included in the formulation to induce a (more) positive dielectric anisotropy in the mixture in order to enable easy alignment in an electric field during film fabrication. Using this principle, the co-existence of chiral nematic and homeotropic phases can simply be realized by the use of patterned indium tin oxide (ITO) electrodes at one side of the cell and a continuous ITO coating at the opposite side over which we applied an electric filed of 60 to 80 Volts. This dual-alignment is frozen in by a single photopolymerization step.

After preparation of the sample, the top patterned electrodes are removed. A polarization microscope picture of a film is shown in Figure 4.7. The image show black stripes when observed between crossed polarizers that remain black upon rotation of the
polarizers, showing a perfect homeotropic alignment in these areas. The chiral-nematic area shows here as blue lines between crossed polarizers as caused by the selective reflection of the film and the strong wavelength dependent rotation of polarized light near the bandgap of the chiral-nematic network. At the edges, the film lightens up at the transition from planar to homeotropic alignment, which occurs over a finite distance as determined by director rotation set by the elastic constants of the liquid crystal monomer mixture prior to polymerization.

Interference microscope images show a small initial surface relief (height about 70 nm) prior to the actuation step (Figure 4.8 (a)). This is caused by replication of the ITO pattern that was used to provide the local electrical field for monomer alignment.

4.3.1 Actuation of Cholesteric/Homeotropic Coating

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 4.8. 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 continuous UV exposure. Unlike in Chapter 2, we could measure this directly in the interference microscope because no photomask was needed to generate the patterns, thus avoiding the need for PDMS method to replicate surface structures. The 0.8 μm surface expansion 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 number 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 does the contraction of the homeotropic field enhance the topological effect, also the homeotropic fields exert an additional shear force at the chiral-nematic fields supporting the expansion along the normal even more. A coating with chiral-nematic next to isotropic area where a single action happens at cholesteric region whereas the non-ordered isotropic area has barely deformation gives an expansion in the order of 5% (Section 4.2).
Chapter 4

Figure 4.7 Optical microscopy images of a film with alternating chiral nematic stripes and homeotropic stripes, between crossed polarizers.

Figure 4.8 Interferometer measurements at a patterned chiral-nematic–homeotropic film containing 4 wt% azobenzene: (a) 3D images of surface topographies 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).

Expansion in the cholesteric region is accompanied with a change in the optical properties. The increase in pitch $P$ would give rise to the expectation that the reflection wavelength shifts to higher values following the relation with the wavelength, reflection being $\lambda r = \bar{n} \cdot P$. However, similar to the continuous cholesteric films in Chapter 2 and 3, with the change in pitch also the in plane extraordinary reflective index is reduced because of
re-orientation of the molecules. This compensates for the pitch-induced wavelength shift. But the change in effective birefringence $\Delta n$ results in a narrowing of the reflective band at the same position.8

We varied the concentration of azobenzene compound. Figure 4.9 shows that already with 2wt% 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 a 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 exposing with UV light the surface topography remains its original state.

![Figure 4.9 The effect of azobenzene concentration on the expansion ratio of the cholesteric-homeotropic films](image)

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

### 4.4 Conclusions

We have described a new approach in the design of a smart surface coating that can undergo changes in its surface topography upon illumination with UV light. This can be
done by irradiation of a patterned film which containing planar chiral-nematic areas next to homeotropic areas. The mechanism of this remarkable photomechanical property is based on reversibly changing the order parameter induced 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 but could reach values close to 20%. We anticipate the smart surfaces to be applicable in a variety of applications varying from liquid transport in microfluidics to light tracking optical elements in solar energy.

4.5 Experimental Section

**Materials** An overview of the materials used is provided in Scheme 1. Monomers 1 to 3 were obtained from Merck UK. Monomer 4 was obtained from BASF. Monomer 5 was custom-based synthesized by Syncom. Typically thin films were fabricated from a mixture containing 30w% monomer 1, 36w% monomer 2 and 20w% monomer 3, 5 w% monomer 4, 7 w% monomer 5 and 2 w% photoinitiator 6. In the experiments the concentration of 5 was varied. In that case the mutual ratio of the other monomers was kept the same as well as the concentration of the photoinitiator. The monomer mixture was stabilized with 200 ppm p-methoxy phenol. The constituents were mixed by dissolving in THF which was evaporated subsequently. DSC results suggest that the mixture has the chiral-nematic phase in the temperature range between 40°C and 60°C. At higher temperatures it becomes isotropic.

**Sample preparation** 30cmx30cm glass slides were cleaned in acetone in an ultrasonic bath and then soaked in deionized water to remove the acetone residue, followed by drying under a stream of nitrogen. Rubbed polyimide AL 1051 was used to obtain planar alignment. It was first spin coated on a cleaned glass slide, followed by baking on a hot plate for 10min @ 100°C and later in a convection oven for 90min @ 180°C. Through manually rubbing it with a velvet cloth, oriented grooves are formed which align the monomer mixture in its liquid crystal phase. Layers are formed between two treated glass plates and subsequently cured by UV exposure by a mercury lamp (EXPR Omnicure S2000) through a cut-off filter at 400 nm (Newport FSQ-GG400 filter).

For the samples containing chiral-nematic stripes next to homeotropic stripes
commercially available ITO glass with the thickness of 70nm has been used. The ITO was patterned through spin coating of photoresist, exposure through a mask and etching. The ITO stripes were 200 μm wide with a pitch of 100 μm. To obtain molecule in homeotropic order, a voltage of 70V was applied between patterned ITO and continuous ITO glass. The resulting alternating pattern is frozen in by photopolymerization similar to the procedure described above.

**Sample actuation** For actuation of the surface topography all samples are exposed at a temperature above the glass transition temperature which is 125°C and cool down below Tg (room temperature) under continuous exposure, assuming here that deformation is hindered by the glassy state of the polymer. By cooling to RT under exposure the deformation is frozen in by the glassy state.

**Sample Characterization** The isotropic / 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, during the measurement the UV light was removed which interferes the measurement results. Furthermore, the sample was exposed to the white light and the measurement was performed in the same location to verify that the surface topography change is reversible and the height change is repeatable.

### 4.6 References


3 Jefferson Y. Han, **2005**, *Proceedings of the 18th annual ACM symposium on User interface software and technology*, 115-118.


5. Structured pH Responsive Hydrogel*

5.1 Introduction

In the last three chapters (Chapter 2, 3, 4), responsive surface topographies have been created based on cholesteric liquid crystal networks. This class of materials has the advantage that the coatings can be operated in the dry state, i.e. localized volume changes can be generated in the absence of a second compound, e.g. a solvent or liquid to locally swell/deswell the coating. The disadvantage of these materials is that there is a limitation to the height of the protrusions that can be obtained. In our best samples we obtain a maximum strain of 20%, which is considerable but for some application maybe not enough. Therefore, in this chapter we turn our focus to the hydrogels. There are two types of hydrogels: pH responsive and thermal responsive. The latter will be presented in Chapter 6. Here, we will focus on pH responsive hydrogels based on poly(acrylic acid). The principle is based on swelling and deswelling depending on the pH of the media in which the sample immersed. This requires the films must be always used in the presence of liquid medium, preferable water or water based buffer solution. This is a disadvantage in comparison with liquid crystal networks. The advantage is that larger local deformations can be realized. For some applications the presence of the second media is inherent to the device structures. For instance, in microfluidic sensors as used for biosensors or lab-on-a-chip application water based media obviously are presented during their operation.

* This Chapter is partially based on: Danqing Liu, Cees W.M.Bastiaansen, Jaap M.J.den Toonder, and Dirk J.Broer, Single-Composition Three-Dimensionally Morphing Hydrogels, Soft Matter, DOI:10.1039/C2SM26543E.
Shape changing hydrogel structures in response to environmental signals receive considerable interest as they find broad applications ranging from mimicking natural motion\textsuperscript{1,2,3} and optical manipulation\textsuperscript{4,5} to environmental sensing\textsuperscript{6,7} and energy control\textsuperscript{8,9}. A wide range of materials and technologies has been developed to meet this purpose\textsuperscript{10,11,12,13,14,15,16,17}. Stimuli-responsive hydrogels that cycle between swollen and unswollen states in response to the environmental triggers (humidity\textsuperscript{18}, pH\textsuperscript{19}, temperature\textsuperscript{20}, light\textsuperscript{21}, etc.) are one class of such materials. The fact that the hydrogels operate in an aqueous environment has inspired research into their application in microfluidic devices, for example to regulate flow, and in biological systems as for instance tissue engineering and controlled cell culturing. As the applications of responsive hydrogels expand into more and more areas, many efforts have been made to develop sophisticated fabrication strategies that either permit scaling down to nano- and micro-features\textsuperscript{22,23,24} with arbitrary topographies,\textsuperscript{10,25,26,27,28} or enable to realize complex, but controlled swelling behavior\textsuperscript{29,30,31,32}.

We propose here a method to induce non-uniform swelling of pH responsive hydrogel sheets or coatings. It is based on polymerization induced diffusion that takes place during the formation of the hydrogel by photopolymerization. The photoactive monomer mixture containing acrylic acid and a diacrylate crosslinker is UV exposed with a spatially varying light intensity. The favored depletion of the more reactive diacrylate in areas where the polymerization rate is highest results in its diffusion towards the areas with maximum UV intensity. The resulting spatially modulated crosslink density enables a spatial variation of hydrogel swelling degrees. In the plane of the film the light intensity variation is obtained by means of lithography\textsuperscript{33,34} or to be more specific through the use of a photomask during exposure to create regions with distinct intensities. As for the direction perpendicular to the plane of the film, the light intensity gradient is established by a dye of which the absorption spectrum overlaps with the photoinitiator excitation wavelength. This phenomenon has been explored earlier in chiral-nematic liquid crystal network to create more complex molecular arrangements\textsuperscript{35,36}. Combination of both effects provides three-dimensional control over the distribution of the crosslink density and thus over the localized swelling.

Using this approach we demonstrate (1) a substrate confined device: switchable surface topographies that can be modulated dynamically and reversibly from a smooth surface to a surface with microscopic topographies, and (2) a free standing device in the form
of a film that exhibits preset and tunable configuration changes in a 3D manner.

5.2 Reversible Swelling of Crosslinked Poly(acrylic acid)

Hydrogels containing acidic or basic ionisable groups, see Figure 1.11 (b) and (c) are showing pH-dependent swelling behavior. In our study, we focus on poly(acrylic acid) containing carboxylic acid group. In this hydrogel, ionization of carboxylic acid groups occurs when the aqueous media has an appropriate pH above the pKa of the poly(acrylic acid), releasing H+, see shown in Figure 5.1 (1). At high ionic group density, fixed carboxylate anions repel one another. This process drives swelling but it is not the main driving force for swelling under typical conditions. In the next step (Figure 5.1 (2)), H+ recombines with OH- of the liquid media to give water decreasing the charges in the interior gel. Charge is then compensated by diffusion of cations (e.g. Na+) and OH-into the gel (Figure 5.1 (3)). Influx of new ions creates an osmotic pressure with respect to the surrounding media. And this is the main driving force of the swelling (Figure 5.1 (4)).

We prepared our pH responsive poly(acrylic acid) hydrogels by photopolymerization of the monomer mixture consisting of acrylic acid 1, diacrylate TPGDA 2 and a small amount of photoinitiator 3 (Scheme5.1). The use of photo-initiation allows spatial modulation of the polymerization reaction. Crucial for the formation of structured hydrogels that exhibit locally controlled swelling is the transport of cross linker during UV illumination.
to the exposed area by polymerization induced diffusion. This results in a non-uniform, but controlled, distribution of the crosslinks over the hydrogel film. We performed experiments with different polyether diacrylate crosslinkers of various molecular sizes. Best results we obtained with TPGDA (monomer 2) which has the lowest molecular weight of the materials we tested and therefore most likely the highest diffusional mobility. Material details can be found in Experimental Section.

Scheme 5.1 Materials used for pH switchable hydrogel compositions. Materials 1-3 are used to make poly (acrylic acid) and 4 is a UV absorber.

Before studying the structured hydrogels we studied the swelling characteristics of hydrogels with a homogeneous distribution of the crosslinks throughout the whole film. We made the films by polymerizing the monomer mixture by means of UV light with a homogeneous intensity distribution. The equilibrium swelling of these hydrogels was measured at both low and high pH for various crosslinker concentrations. The linear swelling ratio $a_i$ is calculated by $a_i = L_e/L_o$, where $L_e$ is the length in an arbitrary direction $(x, y, z)$ of the film at the swollen equilibrium state whereas $L_o$ is the length in the same direction in the dry state. The volumetric swelling ratio $S$ of the hydrogel is defined as the volume of a fully swollen film in the aqueous buffer solution $\varphi_e$ divided by the volume in the dry initial

90
We tested the swelling for two types of hydrogel films: freely suspended films that were released from their substrates and films that were firmly adhered to a glass substrate by a silane coupling agent as adhesion promoter. In case of the freely suspended films, where the swelling is isotropic and identical in all directions ($a_x = a_y = a_z$), the relationship $S = a_i^3$ is presumed. In the case of the substrate-attached film the in-plane swelling is constrained by the rigid substrate and swelling effectively only occurs anisotropically in the direction normal to the surface ($z$-direction) neglecting the minor deformation effects at the edges of the coating. Therefore, under these constrained conditions the linear swelling ratio perpendicular to the film $a_z$ and the volumetric swelling ratio $S$ are taken to be equal $37, S = a_z$.

The degrees of linear swelling under high pH conditions were measured for various crosslinker concentrations for both the free standing films and surface confined films; see Figure 5.2(a). We choose a pH=9 which is well above the kPa value of poly(acrylic acid) which is known to be 4.6. In both cases there is a clear trend of decrease swelling with increasing crosslinker concentration. It is noticed that the linear swelling ratio normal to the plane of the surface attached film is larger than that of the freely suspended film, especially at low crosslink density. This phenomenon was observed earlier by Toomey et al.$^{37}$ and explained by free energy considerations using a Flory-Huggins type of approach$^{38,39}$. It was derived that the surface confined polymer network experiences a higher mixing osmotic pressure, which is partially relieved by further extension in its swelling direction, thus leading to a higher linear swelling ratio than is possible in the unconstrained network$^{37}$.

We derived the volumetric swelling of both the unconstrained and the constrained films from the data presented in Figure 5.2(a). The degrees of volumetric swelling are plotted for various crosslinker concentrations as shown in Figure 5.2(b). It is clear that the swelling degree of unconstrained films exceeds that of the surface attached films. This is due to the fact that the unconstrained film has maximum swelling freedom to reach its thermodynamic equilibrium while the volume change of surface attached film is effectively confined into one dimension and swelling is limited by the built-up in-plane stresses and the constraints of its polymer network. However, the difference is most prominent at low crosslink concentration. The difference in swelling ratio becomes smaller when the polymer chain becomes more and
more tightly linked and is expected to reduce to zero at high crosslink concentration.

The fact that one dimensional deformation of the hydrogel is enhanced by confinement of the hydrogel network can be beneficially utilized for the creation of surface relief structures where swelling is limited in the direction that is perpendicular to the surface. Due to interesting practical applications, constrained swelling of hydrogel has been widely investigated both theoretically and experimentally in various confinement conditions\textsuperscript{37,40}.

![Comparison of swelling ratios between a uniform free standing film (solid line and dots) and a uniform substrate confined film (dashed line and hollow dots) for different crosslink concentrations in an alkaline solution, pH=9. (a) Linear swelling ratio and (b) volumetric swelling ratio.](image)

Figure 5.2 Comparison of swelling ratios between a uniform free standing film (solid line and dots) and a uniform substrate confined film (dashed line and hollow dots) for different crosslink concentrations in an alkaline solution, pH=9. (a) Linear swelling ratio and (b) volumetric swelling ratio.

It is well understood that the swelling equilibrium of a pH responsive hydrogel is determined by the balance between osmotic pressure and the elastic force of the crosslinked polymer chains. In case of poly(acrylic acid), under the high pH conditions the fixed
negatively charged carboxylic acid groups on the polymer chains attract cations from the exterior solution which causes expansion of the gel, initially by Coulomb repulsion but later by the osmotic pressure as caused by the ions in the gel. As also can be concluded from Figure 5.2 the swelling is limited by the crosslinks in the polymer networks which provide an elastic restoring force that counters the expansion. Reducing the pH of the aqueous media below the pKa protonates the carboxylic anions again. This results in a dehydration of the gel to a new equilibrium which is limited by the internal volume of the polymer chains\textsuperscript{41,42}. Consequently, the actuation and relaxation of pH responsive hydrogel based devices can be controlled via altering the surrounding pH conditions. Therefore switching of the degree of swelling of our hydrogel networks between alkaline (pH=9) and acidic (pH=3) conditions is studied and the results are shown in Figure 5.3. In case of the surface-attached film, the linear swelling ratio in the thickness direction is presented. For the free standing gel the volumetric swelling ratio is more interesting. The deformation difference between the alkaline and acidic conditions is larger when the hydrogel network is loosely crosslinked. It becomes smaller, even close to zero, with increased crosslink density. This trend is observed in both the constrained and the unconstrained film (Figure 5.3 (a), (b)). From these plots we can estimate the preferred crosslink concentration for the fabrication of switchable devices that are actuated by changing from acidic to alkaline conditions. As for the substrate confined films, the difference between the linear swelling ratio at low pH and at high pH is very small at high crosslinker concentration. Thus, for the formation of surface topographies in the case when the film is firmly attached to the substrate as discussed in the next section, a compound with low crosslink density, corresponding to TPGDA concentrations < 5 w\%, was necessary in order to realize the switching between small surface relief structures at low pH and relatively large relief structures in a high pH environment. For the formation of switchable 3D structures, discussed in section 5.4, a low swelling ratio difference is already sufficient to achieve substantial deformation differences between the two states, and somewhat higher crosslinker concentrations were preferred to provide mechanical stability with the TPGDA concentration between 10 and 20 w\%.

To estimate the reproducibility we cycled a number of times between the low and high pH conditions (Figure 5.3 (c)). The results show that the swelling and shrinking of pH responsive hydrogel can be operated in a reversible and repeatable way.
Figure 5.3 pH responsive switching between acidic (pH=3) and alkaline (pH=9) solution (a) linear swelling ratio perpendicular to the film surface for the constrained film with varying crosslink concentration. (b) The volumetric swelling of a free standing gel as a function of crosslink density. (c) Cycles of swelling and shrinking in step changes of pH for both the constrained film (green solid line) and the free standing film (blue dashed line) for a crosslink concentration of 1w%.
5.3 Formation of Surface Topographies

The hydrogel coatings we made for the formation of surface topographies are chemically bonded to the glass substrates and are structured via the in-plane diffusion process imposed by a two-step patterned photopolymerization as illustrated in Figure 5.4.

The combination of surface constrained anisotropic swelling and variations in crosslink density creates a predesigned and switchable surface topography. For the creation of patterns with different crosslink density we used polymerization induced diffusion to transport the crosslinking monomer in the polymerizing medium. Polymerization induced diffusion is driven by the chemical potential of the reacting components in the medium which is affected by factors such as monomer reactivity, monomer concentration, size and diffusion constants, interaction parameters between monomer and the forming polymer, network elasticity of the forming polymer network, and the surface free energy. This topic has been extensively studied for acrylate polymer networks\(^43\). Here we simplified the driving force for diffusion to two parameters: 1) UV light intensity 2) difference in monomer reactivity between acrylic acid \(1\) and the crosslinker \(2\) assuming the diffusional mobility of acrylic acid and TPGDA is of the same order of magnitude based on size and intermolecular interaction considerations. Reactivity difference based on functionality, in this case a diacrylate versus a monoacrylate, has been observed in other photopolymerizing acrylate systems and is simply based on the larger capture probability of the diacrylate because of its double functionality.\(^43,44,45\) In the exposed area the diacrylate is consumed faster by the photopolymerization process than the monoacrylate by attachment of at least one of its acrylate groups to the growing network. The resulting concentration gradient of the monomer induces the diffusion to the locally exposed areas or to areas with higher local UV intensity. The higher diacrylate concentration enriches the exposed areas therefore with more crosslinks than the areas which are exposed later or with lower intensity. It is the experience of the authors that in some cases other factors like network elasticity or specific intermolecular interactions might dominate over this process. This is not the case here and has been checked by carefully observing whether the firstly exposed areas show a lesser degree of swelling than the area which were exposed in a later stage, thus pointing to a higher degree of crosslinking.
Figure 5.4 Fabrication steps of coatings with switchable surface topographies. (a) Mask wise exposure to create crosslink-rich regions under the illuminated area. Green arrows indicate crosslinker diffusion to the exposed area. Black regions represent higher crosslink concentration than gray regions. (b) All remaining acrylates are polymerized during 2nd flood exposure.

During polymerization of the monomer mixture, a photomask is employed to control the local UV light intensity (Figure 5.4 (a)). In this case, a line mask with an open line width of 100µm and a pitch of 200µm is used. A flood exposure is performed subsequently without a mask to fully polymerize the whole film (Figure 5.4 (b)). By this process we created a hydrogel coating with controlled regions of different crosslink densities with the lower crosslink densities in the areas that were blocked for UV light during the first exposure step.

Results of the swelling experiments carried out with these formed polymer coatings are shown in Figure 5.5. The coatings were relatively flat under dry conditions with minor reliefs < 0.2 µm at the locations that were illuminated during the first exposure step, see Figure 5.5 (c). This is the result of the accumulation of monomer 2 not fully equalized by counter diffusion of monomer 1 to the dark areas. When this sample is now immersed in an acidic solution (pH=3), relatively small surface relief structures with a height of about 3µm show up (Figure 5.5 (a) and (d) dashed line). It is noteworthy that before immersing, the areas with high crosslink density were protruding, whereas after immersing the weaker crosslinked areas form the highest regions. When we now change the pH of the solution into pH=9 by immersion in an alkaline solution, the protrusions rise to a height of about 14µm (Figure 5.5 (b) and solid line in (d)). The crosslink rich areas swell less and are located in the
valleys of the wavy profile whereas the peaks correspond to the loosely crosslinked regions. By cycling the sample in basic and acidic solution, the topographies can be formed and reduced, respectively.

For this experiment we have chosen to start with an overall concentration of TPGDA crosslinker of 3 w%. At this concentration, under swelling conditions that are only restricted by the adherence to glass substrate the swelling ratio would switch between 2.5 and 3.5, as can be seen in Figure 5.3(a). However, by our process we are modulating crosslink density

Figure 5.5 Interference-microscopy 3D images show surface topographies (pitch = 200 µm) of a poly(acrylic acid) coating with crosslinker TPGDA concentration of 3 w%, cycled between (a) acidic (pH=3) and (b) alkaline (pH=9) solution. Surface profiles of (c) initial dry film and (d) film in low pH (dashed line), high pH (solid line) environments. Please note that the scales in (c) and (d) are different and the profiles are presented as height difference between low and high structures and that the protrusions are out of phase with respect to each other.
around this concentration. By determining the absolution equilibrium swelling at a scratch in the sample where we can relate the heights of the protrusion to the initial thickness of the sample, we found a swelling ratio of 2.7 in the densely crosslinked regions and 4.5 in the loosely crosslinked regions. Assuming that in the center part of the protrusions the swelling is not affected by their adjacent areas. With the help of Figure 5.3 (a), we can now estimate the TPGDA concentration varied between 5 w% and 1 w% as a figure of merit at the high and low crosslinked regions, respectively.

In Figure 5.6 we show the deformation of line patterns in an alkaline environment (pH=9) with a varying line width and pitch. The 200 μm pitch samples shown in this figure have protrusions with a squared shape and a flat top. From this we draw the conclusions that swelling reached its equilibrium value as set only by the glass substrate condition and determined in Figure 5.3. As soon as we make the line width and corresponding pitch smaller, the restrictions imposed by the adjacent areas with less swelling become more dominant. These regions fix the two sides of the higher swelling area and prohibit it from reaching the unconstrained equilibrium. This explains the sinusoidal shape of the swelling patterns in Figure 5.6 for the smaller pitch sizes where at the center the crosslink-poor region may swell as much as the crosslink rich boundaries and the elastic modulus of the hydrogel permit. By modifying the pitch of the crosslink patterns, different levels of the swelling can be obtained. However, this edge-restricted swelling is not the only factor that affects the shape. Also the diffusion length of the crosslinking monomer during the polymerization process plays a role. From modeling studies\textsuperscript{43} it appeared that for the larger pitch sizes maximum crosslink density can be found near the edges of the crosslink rich areas. Simultaneously low crosslink areas can be found at the edges of the crosslink poor regions. The expected formation of higher swelling regions is counteracted by the elastic modulus limited swelling near the crosslink-rich regions.
Figure 5.6 Heights of the actuated surface topographies of the film with overall crosslinker TPGDA concentration of 3 w%, in alkaline solution (pH=9) with varying line width and pitch (where the line width equals half the pitch in all cases). Also, surface profiles are shown for a pitch of 28µm (b), 50 µm (c), 100µm (d) and 200µm (e); note that the vertical scales of (b) to (e) are different. Readers should be reminded here that the profiles measured in (a) are carried out in the water at the equilibrium state, while the profiles shown in (b) to (e) are measured by interference microscope in which some water evaporation cannot be avoided.
5.4 Free Standing Morphing Structures

5.4.1 Bending Film

Controlled monomer diffusion in the direction perpendicular to the plane of the film during polymerization, can create interesting 3D morphologies. In order to demonstrate this, we designed films that can undergo bending and deform into harmonica configurations. Diffusion in the direction of the film thickness is achieved by a gradient in UV intensity during the photopolymerization process of the monomer mixture. The UV gradient is established by including dye 4 in the monomeric mixture. Dye 4 has an absorption spectrum that substantially overlaps with the excitation wavelength of photoinitiator 3. Based on the same mechanisms described above, crosslinker 2 tends to diffuse to the surface where we have the highest UV intensity during the photopolymerization process and consequently, the monoacrylate 1 counter-diffuses to the opposite side. This process creates a gradient in crosslink density with the highest crosslink density at the UV-illuminated side of the film.

Based on this out-of-plane diffusion technology, a polymer strip that can perform a bending deformation in a basic environment and back to rather straight state in an acidic solution was fabricated. The difference in swelling ratios between top and bottom of the polymer strip in alkaline solution results in a bending deformation. It bends towards the side of the strip that was during polymerization directed to the light source, where it has the highest crosslink density, as shown in Figure 5.7. When the polymer is subjected to an acidic environment, the difference in degree of swelling between crosslink rich and poor sides is relatively small and minor bending is observed.

![Figure 5.7 Actuation of bending deformation. (Left) in pH=3 the strip is almost straight and (right) in pH=9 environment it starts bending caused by a swelling gradient over the film thickness.](image)

100
Subsequent immersion of the film into an alkaline solution results in strong bending because of the enhanced difference of swelling ratios and the film tends to curl up. The process proved to be reversible, i.e. immersing again in a low pH solution straightens the film back to its original shape. Traditionally, bending is realized in a bi-layer system\textsuperscript{46,47} where two layers with different expansion coefficient are stacked. This requires two compatible materials and reliable adhesion between the two materials. Our approach only involves one material and a single photo polymerization step.

### 5.4.2 Harmonica Deformation

Having now the possibility to create crosslink patterns into the third dimension we can make more complex 3D structures. Here, we demonstrate a film that morphs from a relatively straight film into a harmonica configuration. To obtain a harmonica or wavy deformation upon actuation, alternating regions that bend towards opposite sides are needed. This means that the direction of the crosslink density gradient from high to low should be reversed in adjacent regions as shown in Figure 5.8 (a). The areas marked as 1 have a high crosslink density near the top surface of the film, which decreases towards the bottom. In regions 2, the crosslinks gradient is reversed. This configuration can be acquired through a two-step polymerization-induced diffusion process as illustrated in Figure 5.8 (b-c). We start again with a monomer formulation containing dye 4 to induce diffusion perpendicular to the film surface. A photomask is employed during polymerization to select regions in which the crosslinker has the same diffusion direction, i.e. towards the UV light source. Subsequently, the illuminated regions are fully polymerized. This film is flipped upside down and a second UV exposure is carried out. In the non-polymerized regions polymerization induced diffusion causes accumulation of the crosslinker again towards the light source, now opposite to the direction induced by the previous step. The schematic view of the final crosslink density distribution in the film is presented in Figure 5.8 (c). According to the crosslink distribution illustrated, region 1 will bend towards the top of the film and region 2 will bend towards the bottom of film.
Figure 5.8 Schematic view of the processing steps to produce a film that forms a harmonic shape under the influence of a pH change. (a) UV exposure through a patterned photomask from the top of the film; in the exposed areas the crosslink density decreases from top to bottom. (b) Exposure through the substrate without the use of a mask; the crosslink gradient is inversed in the newly exposed areas. (c) The final film has alternating regions with opposite crosslink gradient.

The use of the photomask will also induce in-plane diffusion that happens simultaneously to the out of plane diffusion. We anticipated that within the time frame of the photopolymerization process the much smaller dimension in film thickness compared to the mask pitch causes the out of plane diffusion to dominate the deformation process. In Figure 5.9, we demonstrate the shape changing from straight to harmonica deformation. Here, a photomask with opening of 1mm and pitch of 2mm was employed. Immersing it in a high pH aqueous solution a harmonica shape appears as expected. On top of the harmonica deformation an overall bending can be observed towards the top of the film where the overall crosslink density is larger than at the bottom, on average. This is due to a slight unbalance in the two step exposure which can be corrected by optimizing the exposure time during the exposure steps.
5.5 Conclusions

We have described an approach to create pre-determined complex deformation shapes in a swelling hydrogel by employing polymerization-induced crosslinker diffusion during photopolymerization. The diffusion process is induced by a difference in reactivity of polymerizing monomers. In this particular case the crosslinker monomer of our composition diffuses to the regions with the highest UV intensity during photopolymerization. By this process we can control the crosslink density in a hydrogel as a function of location both in the plane of the film as well as in the third dimension perpendicular to the film. The in-plane modulation of the crosslink density was utilized to make surface relief structures that can be switched on and off by changing the pH of the buffer solution. This is presently studied to become utilized in microfluidic systems to control liquid transport and mixing. We designed the out-of-plane modulation to make free-standing films that upon pH switching form complex three-dimensional shapes. This technology can be applied, among others, to fabricate actuators for soft micro-robots.

5.6 Experimental Section

Materials An overview of the materials for our novel system is provided in Scheme 1. Acrylic acid 1 was purchased from Sigma Aldrich. Crosslinker tripropylene glycol diacrylate 2 (TPGDA, Sigma Aldrich, USA) was chosen for its low viscosity and high diffusional mobility. UV photoinitiator 1-[4-(2-Hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propane-1-one 3, (Irgacure 2959, Ciba Specialty Chemicals, Switzerland) is chosen because its polar hydroxyl groups enabling photopolymerization in the presence of water. Dye 2-(2H-benzotriazol-2-yl)-4, 6-di t-pentylphenol 4 (Tinuvin 328, Ciba Specialty Chemicals) has an
absorption spectrum that coincides with the photoinitiator excitation wavelength. Typical surface relief structures were fabricated in a coating made by photopolymerization of a mixture containing 96w% monomer 1, 3w% monomer 2 and 1w% photoinitiator 3. The free standing deformable films were made by photopolymerization of a mixture of 87.5w% monomer 1, 10w% monomer 2, 1w% photoinitiator 3 and 1.5w% UV absorber 4. In some experiments the concentration of 2 was varied. In that case the mutual ratio of other monomers and the concentration of photoinitiator were kept the same.

**Sample preparation** Films were made by polymerizing the monomers in a cell construct. The cells were made from two treated glass plates connected through the spacer of 50 µm. To promote either release or adhesion of the polymer from glass, the surface was treated using a vapor phase reaction by 1H, 1H, 2H, 2H-perfluorodecytriethoxysilane or by Y-methacryloxypropyl-trimethoxysilane (Silane A174), respectively. For both treatments, the glass was first cleaned and put in UV-ozone for 20 minutes. The cells were filled with the monomer mixtures by capillary suction. The UV polymerization was carried out using a mercury lamp (EXFO Omnicure S2000) under a light intensity of 20mW/cm² for 200 seconds.

**Sample characterization** The actuation of either surface relief structures or 3D deformation was performed by immersing the hydrogel films in buffer solution of pH 9 and 3 to initiate swelling or de-swelling. Values are chosen based on published results between 4 to 4.548. The height changes of constrained film were measured when immersed in buffer solution by Stylus Surface Profiling (Dektak 150). The 3D images of surface relief structures were obtain from a 3D interferometer (Fogal Nanotech Zoomsurf). Equilibrium swelling data are obtained by measuring the volume changes until constant in time.

### 5.7 References

14 Jungwook Kim, Jinhwan Yoon and Ryan C. Hayward, Nat. Mater. 2010, 9, 159-164.
Chapter 5


42 Ferenc Horkay, Man-Hee Han, In-Seok Han and Jules J. Magda, *Polymer*, 2006, 47, 7335-7338.


6. (Photo-)Thermal Responsive Hydrogel*

6.1 Introduction

In the last chapter, we described an approach to create pH-responsive films that can transform from a flat state to a pre-described deformation. Our approach to fabricate these films is based on the use of a monomeric mixture of acrylic acid and a diacrylate crosslinker. Upon UV initiated free-radical polymerization the applied monomers have a different reactivity which enables polymerization induced diffusion during spatially modulated UV intensity gradients. By means of this process the crosslink density within the film can be tuned spatially both in-plane and over the film thickness. The crosslink density determines the degree of swelling upon actuation by a changing pH. We demonstrated this effect for pH-switchable systems which are either substrate-attached coatings exhibiting surface topographies upon actuation or free standing films that can undergo geometrical changes in the form of bending, curling or morph into even more complex shapes.

However, to actuate pH responsive hydrogels involves a change of the buffer solution in contact with the gel. This makes application only possible in very special cases where pH changes are either involved or allowed. In order to make the developed principles more universal, we will apply the same structuring mechanism on thermal hydrogels based on poly (N-isopropylacrylamide) (pNIPAAm). Somewhat depending on the conditions and the exact chemical composition this material undergoes its transition from the swollen hydrated state to the shrunk dehydrated state when heated above 32°C. By employing this well-studied

* This Chapter is partially based on: Danqing Liu, Cees W.M.Bastiaansen, Jaap M.J.den Toonder, and Dirk J.Broer, Dynamic Surface Topologies Formed in NIPAM Polymer Network, in preparation
material, next to spatially modulated cross-link principle we designed two other principles to create switchable surface topographies where we use either temperature or light as a trigger. In this chapter we will compare the following methods.

(1) The formation of surface topologies with a symmetric structure as actuated by temperature. Via control of the spatial distribution of the crosslink density, a patterned swelling of the hydrogel film with pre-designed patterns is obtained.

(2) Light triggered surface topographies with symmetric configurations. Light induced response is imparted through integrating local light absorbers converting light energy into heat.

(3) Surface topologies with asymmetric relief structures responsive to heat are designed by geometrical patterning of the substrate to which the hydrogel film is applied, thereby spatially modulating the hydrogel material content.

We present these three basic principles, but as such they can also be used in a mixed way. E.g. the light absorbers can be used in combination with the asymmetric substrate structures to provide either even more complex topographic geometries or provide multiple trigger principles.

6.2 Swelling Experiments at poly(N-isopropylacrylamide)

Poly (N-isopropylacrylamide) (pNIPAAm) is a temperature responsive hydrogel that undergoes a phase transition from a preferential polymer-solution interaction to the preferential polymer-polymer interaction upon a temperature change. See phase diagram of non crosslinked system in Figure 6.1. At low temperatures it dissolves in water. The solution phase separates when temperature is above a critical point, referred to as Lower Critical Solution Temperature (LCST). The LCST of pNIPAAm is about 32°C. In the case of the pNIPAAm is crosslinked the polymer cannot dissolve but expresses it affinity to water by a high degree of swelling. Above the LCST water is expelled from the network and the polymer film collapses.
Figure 6.1 Phase diagrams of the non-crosslinked pNIPAAm/water system. Squares are experimental data, solid line is calculated from the model. Below the phase transition line the polymer ‘P’ and water ‘S’ are mixed (‘PS’). Above they are phase separated into a ‘P’ phase and a ‘S’ phase.

For our experiments we have chosen for a mixture of N-isopropylacrylamide (monomer 1 in scheme 1) and poly (ethylene glycol) diacrylate crosslinker (PEGDA, monomer 2) photopolymerized by means of the added photoinitiator 3.

Scheme 1 Materials: 1-3 used for (photo-) thermal responsive surface topographies. Monomer 4 is used to fabricate ratchet substrate for the formation of asymmetric surface profiles (Section 6.4).
Before structuring the polymerized hydrogel, we first measured the isotropic swelling ratio defined as the ratio of the length of the film at the swelling state to that at the dry state. The equilibrium swelling of these hydrogels was measured at both low and high temperatures for various crosslinks concentrations. Both freely suspended films and surface constrained films were tested. The calculation of the linear and the volumetric swelling of hydrogel can refer to Chapter 5, Section 5.3.3. The free standing film swells isotropically. The linear swelling is identical in all three directions. The volumetric swelling is then calculated as the cubic of the linear swelling ratio, see Figure 6.2. For the surface confined film, where the in-plane swelling is restricted by the substrates, the linear swelling ratio measured perpendicular to the film equals to the volumetric swelling ratio.

![Figure 6.2 Schematic view of a free suspended film (a) and a substrate-confined film (b). Darker region represents the initial dry gel, the lighter region stands for the volume after swelling. And the corresponding linear and volumetric swelling ratio, respectively. Arrows in both images represent the swelling directions.](image)

The results are presented in Figure 6.3. In both cases there is a clear trend that the swelling decrease with increasing crosslinker concentration, as expected. The linear swelling ratio normal to the plane of the surface attached film is larger than that of the freely suspended film, especially at low crosslink density. This can be beneficially utilized for the creation of surface relief structures where swelling is limited in the direction that is perpendicular to the surface. The volumetric swelling of both the unconstrained and the
constrained films are derived from the data presented in Figure 6.2(a), using the equations listed in Figure 6.2. It is clear that the volumetric swelling degree of unconstrained films exceeds that of the surface attached films. This is due to the fact that the unconstrained film has maximum swelling freedom to reach its thermodynamic equilibrium while the volume change of surface attached film is effectively confined into one dimension and swelling is limited by the built-up in-plane stresses. However, the difference is most prominent at low crosslink concentration. The difference in swelling ratio becomes smaller when the polymer chain becomes more and more tightly linked and is expected approach one at high crosslink concentration.

![Graph](image)

Figure 6.3 Comparison of swelling ratios between a uniform free standing film (solid line and dots) and a uniform substrate confined film (dashed line and open dots) for different crosslink concentrations in an aqueous environment at 45°C. (a) Linear swelling ratio measured perpendicular to the film surface and (b) the derived volumetric swelling ratio.
The switching of pNIPAAm is also studied. For the surface confined film, the linear swelling perpendicular to the substrate is more relevant. As regards of the free suspended film, we investigated the volumetric swelling. Both films are prepared with a low crosslink concentration of 1 w% PEGDA during polymerization. They were subjected to the environmental condition changes, temperature below the LCST (25°C) and above the LCST (45°C), as shown in Figure 6.4.

![Figure 6.4](image_url)

*Figure 6.4 Thermal responsive switching between high (T=45 °C) and low (T=25 °C) solution temperature. (a) linear swelling ratio perpendicular to the film surface for the constrained film with varying crosslink concentration. (b) The volumetric swelling of a free standing gel as a function of crosslink density. (c) Cycles of swelling and shrinking in step changes of temperature for both the constrained film (green solid line) and the free standing film (red dashed line) for a crosslink concentration of 1w%.*
When the temperature is above the LCST, pNIPAAm gel experiences a close to zero swelling (swelling ratio one). This means it recovers to its original dimension. We repeated experiments in four cycles of swelling, showing high reproducibility.

The mechanical properties of the pNIPAAm gel were analyzed by dynamic measurements under shear imposing a shear force of 1N. Figure 6.5 presents the storage modulus standing for the elastic response, of both a free suspended film and a substrate confined film were measured when immersed in water below and above the LCST. The in-phase force required to maintain that rate of shear compression is recorded as the storage modulus. When cooled below the LCST, both films acquire a lower modulus as the water content increases upon water uptake. The presence of water has a plasticizing effect on the polymer network. The substrate confined gel has a higher apparent storage modulus than the free standing film both in the swollen and non-swollen state. This is at least partly due to the reduced water uptake measured in absolute values as caused by the substrate constraints.

![Figure 6.5 Storage modulus for both free standing film (filled marker) and constrained film (hollow marker) at their swollen (23°C) and shrunk state (45°C). The crosslink concentration is 1 w%.

6.3 Switchable Asymmetric Protrusions

6.3.1 Thermal Actuation: Polymerization Induced Diffusion

To create surface topographies in the thermal responsive pNIPAAm hydrogel, we are using polymerization induced diffusion process. We also employed the similar principle for
the formation of surface topographies and complex 3D morphing structures in the pH-responsive hydrogel, results of which are presented in Chapter 5. In short, polymerization induced diffusion occurs during local UV exposure of a photoactive monomer mixture containing monomers with mutually different polymerization or diffusion rates. This creates the spatially modulate crosslink density difference that controls the maximum degree of swelling. The formation of surface topologies occurs when the films are adhered to a solid substrate where the swelling can only take place into the out-of-plane dimension.

In our experiments, we exposed the NIPAAm/PEGDA (95%/3 w/w) blend with 2 w% photoinitiator through a crossed-line mask. In this step, polymerization induced diffusion takes place. This step is followed by a flood exposure to polymerize the previous dark areas. Results of the surface topographies structured in a 16 µm pNIPAAm coating are shown in Figure 6.6. In the experiment, pNIPAAm coating of 16 µm was formed. The crossed-line mask had a line opening of 80 µm and a pitch of 200 µm. Just after polymerization of the initial dry, not water containing coating is relatively flat with a minor surface relief of <100 nm at the illuminated regions when the first mask wise exposure was carried out. In Figure 6.6, both the 3D image and the scanned profiles are shown. A comparison between the patterns of the mask and the configurations in the polymer network unambiguously correlate the somewhat thicker areas to the exposed areas. When this film is immersed in cold (25°C) water the same areas tend to swell significantly (Figure 6.6 (b) and (d)). The protrusions of the surface structures correspond to the small reliefs in the initial dry coating. This lead to the conclusion that, opposite to the observation of the acrylic acid/TPGDA system discussed in the previous chapter, here it is not the crosslinker molecules but the linearly polymerizing molecule that diffuses to the exposed area. We explain this observation by noticing that the much larger crosslinker molecule in the NIPAAm/PEGDA case must have a much lower diffusional mobility than the NIPAAm molecule, thus enhancing both faster consumption of NIPAAm in the exposed area and a faster supply from the surrounding area when it is depleted. The NIPAAm rich, hence crosslink poor regions, swell more and appear as the peaks, whereas, the densely crosslinked areas swell less and are present at the valleys in the profile. The initial flat surfaces are retained when increasing the surrounding temperature. By cycling the sample in cold (25°C) water and warm (45°C) water, the topographies can be formed and removed, respectively.
Figure 6.6 Interference-microscopy 3D images showing surface topographies of a poly (N-isopropylacrylamide) coating with crosslinker PEGDA concentration of 3 w%, cycled between (a) warm (45 °C) and (b) cold (25 °C) water. Surface profiles of (c) the initial dry film and (d) the actuated film in cold (25 °C) water. Please note that the scales in (c) and (d) are different.

6.3.2 Light Actuation

In some applications actuation by light is preferred over thermal actuation, e.g. in devices where contactless or remote control is required. A common method to achieve light actuation is functionalizing the polymer with a photoresponsive chromophore, referred to as “photon mode” 6,7. In this approach leukochromophore 8, spiropyran 9,10 or azobenzene 11,12 moieties are incorporated in the hydrogel polymer network to create photoresponsive properties. The dehydration of the gel caused by the closed-ring
chromophore of spiropyran and the sol-to-gel phase transition of hydrogel due to the photo-isomerization of azobenzene are examples. Also an indirect approach can be used, in which the light is converted to heat, referred to as “heat mode” actuation by light. Here, a light absorbing material is integrated in a thermal responsive matrix. The temperature of the materials increases as it absorbs the light, which then triggers the thermally responsive polymer. Previously, volumetric changes of pNIPAAm containing gold colloids controlled by light illumination have been reported.

However, both technologies described above to provide photo-responsive hydrogel involve quite tedious material synthesis and processing. Our approach to realize a light triggered surface topology simplifies the fabrication to applying a single step of polymerization of the NIPAAm coating, without any need for further complex material syntheses. We coated the NIPAAm/PEGDA layer on a substrate with patterned light absorbers made of CrO2; the latter material can be replaced by any other material that substantially absorbs light, e.g. carbon or black inks. In this sense it has similarities with locally deforming memory materials at printed light absorbing patterns. When illuminated with uniform light, the patterned elements heat up and lead to a local temperature increase of the hydrogel above its LCST and form concave structures in the coating surface.

In our experiments, using this method, we employed substrates with a pattern of light absorbing CrO2 stripes or squares, schematically represented in Figure 6.7 (a) and (b). Dry pNIPAAm/PEGDA (93/5 w/w) films of 1 μm (Figure 6.7 (c)) and 4 μm (Figure 6.7 (d)) were coated on the striped and squared substrates, respectively. Here, we used a relatively high concentration of crosslinker to prevent the film from extending beyond the temperature zone of minimally 32°C by swelling too much in water, which lowers the resolution of the structures formed. However, when crosslink concentration is too high the swelling capability of the hydrogel film will be largely restricted. A balance is found in 5% of PEGDA. When immersing both coatings in water, they swell uniformly to a thickness of around 4 μm (at an initial thickness of 1μm) and 14 μm (at an initial thickness of 4 μm). When the coating has reached its equilibrium thickness at room temperature, the substrate is illuminated by unfocused white light. Surface topologies are formed in the form of dimples at the location of the light-absorbing structures with depths of 0.7 μm and 0.3 μm, as shown in Figure 6.7 (c) to (f). During actuation, the environmental water temperature was kept at 30°C close to
the pNIPAAm transition temperature of 32°C to enhance the effectiveness of the approach. By switching off the light, the surface topologies are erased and the uniform swelling of pNIPAAm coating is retained.

We have varied the dry film thickness between 10μm, 15μm, 20μm, and 50μm, each with a crosslinker density of 5 w% crosslinker which results in a thickness of 35μm, 47μm, 70μm, and 175μm in the swollen state. However, in these cases no surface topologies were observed during actuation. These films may probably have a thickness that extends the temperature zone of 32°C (the transition temperature) generated by the heat absorbers, while the heat spreads out too much in horizontal directions. In Figure 6.8, we plot the height of

![Figure 6.7](image-url)
the surface topologies as a function of the film thickness which leads to the conclusion that the ratio between structure width and film thickness is very critical. With the increasing thickness the surface structures fade. And when the swollen film reaches a thickness of 35 μm and beyond, the coating cannot be actuated with the current approach. For the conditions we used, hydrogel film thicknesses less than 15 μm are preferred.

Figure 6.8 The height of the surface structures decrease with increasing film thickness

6.4 Asymmetric Surface Profiles

The profiles of the surface topographies created by most recent methods are symmetric.  However, for some applications it may be beneficial to have asymmetric ratchet-like profiles, for instance for material transportation and fluidic control. Therefore, we propose a simple approach to meet this purpose. The general approach we develop is to form a coating with locally varying thicknesses by geometrically structuring the substrates. Thereby, when the surface of the hydrogel coating is kept flat, the thickness of the hydrogel becomes modulated. In other words, the change in volume of the film due to the actuation is built in the local dimensions of the hydrogel film in the z-direction perpendicular to the film surface. When actuated by swelling, regions with a larger initial film thickness have also a larger absolute volume change. This effect manifests itself as the formation of protrusions on the coating.

Figure 6.9 (a) shows the substrate we used. It has periodic wedge structures made of poly tripropylene glycol diacrylate (pTPGDA) made by photo-replication using the TPGDA
monomer on a mold with the negative surface profile. The width of each wedge is 6 µm while the maximum height is 1.6 µm. Then a monomer mixture consisting of NIPAAm/TPGDA (95/3 w/w) and 2 w% photoinitiator is coated on the substrate. During polymerization against a tapered glass plat a flat top surface is formed see Figure 6.9 (b). It appeared that the adhesion between the hydrogel and the pTPGDA coating is firm, most likely because of some interlayer crosslinking between remaining acrylate in the pTPGDA and the NIPAAm. The swelling of this coating is performed in an aqueous environment at room temperature. The whole pNIPAAm film swells, however the variations in the initial film thickness lead to an absolute height difference along the coating, as shown in Figure 6.9 (c). The swollen surface topologies have the opposing profiles to the structured substrate. The initial flat surfaces can be retained by increasing the surrounding temperature above the LCST of 32°C.

Figure 6.9  Schematic overview of the processing steps to produce thermal responsive surface topographies via pre-structured substrates. (a) Substrate with periodic wedge structures. (b) A flat pNIPAAm coating is formed on the substrate. The patterned variation in the coating thickness is thus introduced. (c) Upon actuation, the variations in coating thickness transfer into surface topographies.

Some of the results of the responsive coating we realized in this way are shown in Figure 6.10. The coating is relatively flat in its initial dry state with small relief structures <70 nm. We assume that this minor surface relief is due to the polymerization shrinkage during UV polymerization; the thicker areas shrink more than the thinner areas in absolute measures. When this sample is immersed in water at room temperature, clear ratchet
structures of around 0.9 µm unveil, as shown in Figure 6.10 (b). The ratchets orientation is opposite to that in the substrate, as expected. By cycling the sample in water of 25°C and 45°C, the topographies can be formed and removed, respectively.

Figure 6.10  Confocal 3D images show surface topographies delivered from pre-structured substrate method. (a) The initial dry film and (b) actuated film in water environment at room temperature.

This method provides a simple way to form surface relief structures. Both the underlying principle and the fabrication process are rather straightforward. More importantly, it opens a door for the creation of more complex structures, especially for the producing of asymmetric patterns which are otherwise difficult to obtain by other methods.

6.5 Conclusions

We have described methods for the formation of switchable surface topologies based on the thermally responsive pNIPAAm hydrogel network. Three routes have been shown: (1) The introduction of a patterned crosslink density in the hydrogel film leads to a reversibly switchable surface topology that is actuated by a change in temperature. (2) A homogeneous,
uniform hydrogel film can be actuated by light by the integration of light absorbing patterns at the substrate, that locally convert light into heat – leading to patterned swelling and shrinking of the hydrogel film. And (3), a geometrically pre-structured substrate on top of which the hydrogel film is applied leads to a patterned film thickness which results in a patterned surface topology when actuated by a temperature change. We believe the smart surfaces to be applicable in a variety of applications varying from liquid transport in microfluidics to light tracking optical elements in solar energy. The general principles that we developed can be used on themselves, but can also be combined to form even more complex structures with structures and superstructures to for a hierarchical network of switchable surface topologies to be addressed either by temperature changes or by light.

6.6 Experimental Section

Materials An overview of the materials of our system is provided in Scheme 1. N-isopropylacrylamide (monomer 1) was purchased from Sigma Aldrich. Crosslinker polyethylene glycol diacrylate 2 (PEGDA, Sigma Aldrich) was chosen for its solubility in water. UV photoinitiator 2-hydroxy-1-[4-(2-hydroxyethoxy) phenyl]-2-methyl-1-propanone-1-one 3, (Irgacure 2959) (Ciba Specialty Chemicals, Switzerland) is chosen because its polar hydroxyl groups enabling photopolymerization in the presence of water. Typical surface relief structures were fabricated in a coating made by photopolymerization of a mixture containing 95w% monomer 1, 3w% monomer 2 and 2w% photoinitiator 3 dissolved in a 1:1 w/w/ mixture in water. In some experiments, the concentration of 2 was varied. In that case the mutual ratio of other monomers and the concentration of photoinitiator were kept the same. In the case of the replication method to form ratchet structure we used tripropylene glycol diacrylate (TPGDA, monomer 4 in scheme 1, purchased from Aldrich) and we omitted the water to obtain a molten monomer mixture at 90°C to process the material further in the liquefied state.

Sample preparation Coatings were form between two treated glass plates connected through various spacers depending on the applications. Spacers of 50μm were used for hydrogel characterization. Spacers of 20μm were used for polymerization induced diffusion. Spacers of 5μm, 10μm, 15μm, 20μm and 50μm were used for the patterned light absorber
experiments. Between the ratchet structured substrate and top glass plate there are no spacers, instead clips are used to connect the substrate with the top glass plate to minimize the film thickness.

To promote either release or adhesion of the polymer from glass, the surface was treated using a vapor phase reaction by 1H, 1H, 2H, and 2H-perfluorodecytriethoxysilane or by A 174 (Methacryloxypropyltrimethoxysilane), respectively. For both treatments, glasses were first cleaned and put in UV-ozone for 20 minutes. The cells were filled with the monomer mixtures by capillary suction. The UV polymerization was carried out using a mercury lamp (EXFO Omnicure S2000) under the light intensity of 20mW/cm² for 200 seconds. After polymerization an average shrinkage of 20% is observed.

The structured substrates are made by replicating the surface topography of Plane Ruled Reflection Grating (Newport 10RG150-6000-2) using a molten monomer mixture of tripropylene glycol diacrylate 4 (TPGDA, Sigma Aldrich, USA) 98 w% with 2 w% photo initiator 2 (Irgacure 2959) and solidified by UV polymerization.

**Sample characterization** The actuation of surface relief structures was by immersing hydrogel films in DI water. The light source used to actuate pNIPAAm film is halogen cold light (SCHOTT KL2500 LCD). Surface deformations were measured by Stylus Surface Profiling (Dektak 150) and by interference microscopy (Fogal Nanotech Zoomsurf). The 3D images of surface relief structures were obtain from a 3D interferometer (Fogal Nanotech Zoomsurf).

### 6.7 References


2 Herman Feil , You Han Bae , Jan Feijen , Sung Wan Kim, *Macromolecules*, 1993, 26, 2496-2500.


7. Technology Assessment

7.1 Introduction

In this thesis we developed a number of technologies to realize responsive surface topographies based on various materials. In the Chapter 2, 3, 4 we focused on liquid crystal networks (LCNs) where we used manipulation of localized molecular order to induce dimension and/or density changes. We were using either a patterned light source to actuate surface topographies in a uniform, non-structured cholesteric liquid crystal coating (Chapter 2 and 3) or we applied exposure with a uniform light source to trigger patterned cholesteric coatings (Chapter 4). In Chapter 5 and 6, we concentrated on hydrogel networks where pH responsive and thermal responsive hydrogels were explored. Several technologies to fabricate surface topographies and complex 3D morphing structures on hydrogels were investigated.

At this point it might be adequate to point to an important difference between the two basic techniques we explored. The hydrogels are already better known in literature, although not so much in relation to the well-controlled surface topographies. An important drawback of this technique for some applications is the fact that it is based on swelling mechanisms for which always the presence of another component, in our case water, is needed. The advantage of hydrogels is that large deformation can be achieved as the swelling can be as high as a few hundreds of percent (in literature even values exceeding 1000 % percent have been published). In contrast the LCN based technologies are based on ‘dry’ processes which work in the absence of a third material. They do not rely on the in- and out diffusion of e.g. water and are therefore in general responding much faster. A drawback is that, because based on density changes, their strains are smaller than those in hydrogels. Where triggered surface structures of several tens of micrometers are easily possible in hydrogels, the surface topographies in LCNs remain limited to a few micrometers depending on the coating thickness.

Responsive surface topographies can find a variety of applications in modern
technologies, such as controlled wettability, autonomous lenses and haptics surfaces. In this chapter, we will describe a number of potential applications of responsive surfaces in some more detail. The developments of some of the applications have recently been started or are part of subsequent project proposals. In our first application, we introduce a surface in microfluidic devices that induces mixing of laminarly flowing liquids when surface topography is activated. The implementation of a hydrogel for this purpose is under study at the moment. In the second application, a switchable self-cleaning surface by changing the surface topographies will be discussed. This topic has been scheduled for further research. We also anticipate the dynamic surface topographies be employed for tribological applications where the friction can be switched between high and low friction states, and in optical applications where we may switch the scattering, or diffractive state of a surface.

7.2 Switchable Mixing in Microfluidic Devices

Lab-on-a-chip (LOC) devices and micro total analysis systems (µTAS) where complete laboratory functions are miniaturized and integrated, provide the ability to perform complex (bio-) chemical analyses in a well-controlled manner. Precise control over fluids in sub-millimeter channels is often needed which, due to the small scales and dimensions, lead to several challenges in fluid manipulation. Mixing which is important in homogenization of chemical solutions or the dispersion of materials is one of the difficulties. In microfluidic devices the Reynolds number is low which prohibits the mixing generated by turbulence. Mixing by diffusion on the other hand is very slow and requires relatively long channel in devices which are supposed to be small and compact. One way to achieve good mixing under laminar flow conditions is by producing chaotic advection which is done by repeatedly stretching and folding the fluid interfaces increases the mixing efficiency. This can be achieved by passive means through including geometrical structures in the channels that induce special flow patterns.

Several designs of passive mixers have been reported, including a staggered herringbone mixer (SHM), 3D serpentine, a slanted ridge mixer (SRM) or even more complex structures of additional side grooves to the bottom grooves and non-periodic patterning of channels. Figure 7.1 presents two examples of those patterns. The SHM (Figure 7.1 (a)) has herringbone-shaped grooves in the channel floor, organized in adjacent
units with a mirrored asymmetry of the pattern; two consecutive units make up one mixing cycle. The SRM (Figure 7.1 (b)) has the floor covered with ridges that are placed at an oblique angle of $\pm 45^\circ$ with respect to the channel length direction, that are, just like in the SHM, organized in units of which two consecutive form one mixing cycle.

![Diagram](image)

Figure 7.1 Schematic diagram of (a) Staggered herringbone mixer (SHM) showing the floor of channel that is covered with patterns of grooves. And (b) a slanted ridge mixer (SRM) with a Y-shaped channel. Ridges are located on both sides of the channel, their slanted angle changes from $+45^\circ$ at one side to $-45^\circ$ at the other side of the channel.

Figure 7.2 shows the performances of both the SHM and the SRM by depicting cross sections of the channel at different streamwise locations in the channel. Two differently colored fluids, entering through two inlets into the mixing channel, are increasingly mixed by secondary flow patterns induced by the grooves and ridges, and complete mixing is found after around 15 cycles of mixing. The results suggest that the passive mixing through geometric structures in the channel is efficient. It was found that the mixing efficiency is optimal when the ratio of ridge height (or groove depth) to channel height is kept around 0.2. A typical microfluidic channel has a length of several centimeters and a width and height of around hundred micrometers. This means that the height of the ridges (or depth of the grooves) is ideally about 20 µm. The streamwise width of the mixing ridges used in the SRM (Figure 7.1 (b)) is 70 µm and the pitch is 70 µm, while the length of across the channel width is about two-thirds of the channel width.
Currently, most of the passive microfluidic mixers are fabricated from SU-8, PDMS, or injection molded polymers such as PMMA, and therefore they perform in a static manner. This means that mixing always occurs in the channel, and it will automatically continue till mixing is complete. No technology has been developed yet that allows dynamical control over passive mixing processes. In other words, there is no possibility to switch the mixing on and off when desired. This can be realized by switching the mixing patterning on and off.

The hydrogels we have introduced in this thesis can be one of the candidates to fulfill this purpose. The liquid crystal networks we have discussed in this thesis are less suitable for this particular application, since the required dimensional changes, in the order of 20 µm, are more difficult to achieve than with hydrogels. Also, the water that is needed for the hydrogel performance is naturally available in microfluidic channels.

The results in Chapter 5 on pH responsive hydrogel suggest the possibilities of employing poly (acrylic acid) as the switchable mixer. In this case a mixer is created which
reacts autonomously when certain pH conditions are fulfilled. In Figure 5.5 and Figure 5.6 (e) a striped pattern is presented with a pitch of 200\(\mu\text{m}\) and a stripe width of 100 \(\mu\text{m}\) that forms protrusions of around 15 \(\mu\text{m}\) on a 50 \(\mu\text{m}\) thick film. This surface profile together with the degrees of swelling matches the requirements of the slanted ridged mixer. Thus, through the polymerization induced diffusion fabrication technique described in Chapter 5, a surface with ridge pattern as shown in Figure 7.2 (b) is obtained during swelling when surface comes in contact with alkaline solution so that ridges form and mixing takes place, whereas the surface remains rather flat in an acidic environment so that the fluids remains unmixed. Thus, switching mixing on and off is controlled by the pH conditions of the liquids. However, challenges exist including the possible leaking between PDMS based microfluidic channel and hydrogel coating, the balance between achieving stiff hydrogel ridges and sufficient ridges height and the response speed should be fast enough.

Besides the use of poly(acrylic acid) to create a pH switchable mixer, it is also possible to use thermally controlled switching between mixing and non-mixing states by using thermal-responsive poly(N-isopropylacrylamide) or even light-induced switchable mixing through poly(N-isopropylacrylamide) modified with carbon nano-tubes, by integrating light-heat absorber in the substrates as presented in Chapter 6.3.2.

7.3 Tuneable Wetting and Self-cleaning Surfaces

Wettability of a surface, i.e. the ability of a liquid to maintain contact with a solid surface, is very relevant in many aspects of our daily life. The fabric of ski jackets, rain coats, and tents should repel water droplets so as not to become wet; glues on the other hand should wet and adhere to different materials; cosmetic creams are required to spread easily over the skin; and water should roll off a waxed car. Moreover, in more industrial applications, wettability is important for example for droplet manipulation in microfluidics, self-cleaning surfaces (e.g. for low-maintenance luminaires or medical instruments), and for coating and printing processes. In architectural applications one may think of self-cleaning windows in skyscrapers, and graffiti repelling walls.

The wettability of a solid surface is governed by two factors\(^{11,12}\). One is surface energy and surface polarity which are intrinsic prosperities of the material and can be adjusted chemically. The other factor is surface roughness or surface topology\(^{13}\). The control over
wettability normally involves the modulation of both. A typical example from nature that combines both factors is the Lotus leaf, as shown in Figure 7.3. The Lotus leaf is highly water-repellent –superhydrophobic– and can remain clean from dirt particles by water droplets rolling off the surface that collect and remove the particles. The Lotus leaf surface has an extremely small sliding angle – the minimum angle of the surface under which a droplet starts to slide off. The superhydrophobicity of the Lotus leaf is due to the combination of a hydrophobic wax and hierarchical micro/nano. This property is not uniquely possessed by Lotus but is quite common in nature. Many other plants (paddle cactus, cane) and animals like water striders, mosquito eyes\textsuperscript{14,15} demonstrate the similar phenomenon.

![Figure 7.3](image)

Figure 7.3 (a) Water droplets on a lotus leaf. (b) Microscopic image of the surface of lotus leaf showing the double roughness microstructures\textsuperscript{16}

Clearly, the common feature among all those surfaces is their micro/nano-structured surface topography. Many studies have been carried out on the influence of geometrical surface structures on wetting behavior. Models proposed by Wenzel\textsuperscript{17} and Cassie\textsuperscript{18} establish the basis of describing wetting on rough surface. Onda\textsuperscript{19}, Bico\textsuperscript{20}, and He\textsuperscript{12} demonstrate water-repellent surfaces by utilizing artificial rough surfaces. Neelesh\textsuperscript{16} and Nosonovsky\textsuperscript{21} investigate the importance of hierarchical structures on surfaces for water repulsion; it is found that hierarchical surface topology consisting of submicron modulations superposed on micro-sized protrusions is needed to achieve superhydrophobicity. Several techniques have been also developed to mimic and prepare those surfaces through molded polymers\textsuperscript{22} and waxes, by creating well-designed microstructures via micromachining and etching\textsuperscript{23}, and by electrospinning to produce porous microsphere composite film\textsuperscript{24}. Those approaches
successfully create surfaces with desired wettability via various geometric patterns or fabrications process in a static way. However, further adjustability or dynamic control on wetting is prohibited.

Dynamic wetting has attracted considerable attention in the scientific community due to the wide range of potential applications, such as in droplet manipulation, controllable drug delivery, control over coating and printing processes, and self-cleaning surfaces\textsuperscript{25}. Recently, the controlled wetting of surfaces has been achieved by modifying the surfaces with stimuli-responsive organic compounds. Lahann et al\textsuperscript{26}, Wang et al\textsuperscript{27} use an electrical potential to trigger a conformational change of the molecules, resulting in a shift from a hydrophilic to a hydrophobic surface. Moreover, electrowetting has been used to manipulate the contact angle of droplets sitting on surfaces; this principle has been used to create a new display principle\textsuperscript{28} or for droplet manipulation in microfluidics devices\textsuperscript{29}. Temperature induced wettability control has been reported in a poly (N-isopropylacrylamide) modified surface\textsuperscript{30}. Wettability modulation via light illumination is another popular method. Zinc oxide films show the ability to undergo reversible super-hydrophobic-super-hydrophilic transition via cycling between UV irradiation and dark storage\textsuperscript{31,32}. A more commonly adopted way to create light-induced switchable wettability is through the isomerization of photo-sensitive molecules, e.g. azobenzene\textsuperscript{33,34} or, spiropyran\textsuperscript{35}. Other approaches include the adsorption of biopolymers\textsuperscript{36}, and solvent treatments\textsuperscript{37}.

In all these methods, reversibility is established by switching the intrinsic hydrophobicity of the solid material, while leaving the surface topography unaffected. It is the presence of these fragile micro- and nanostructures that make these surfaces vulnerable to accumulation of contamination and mechanical damage. In addition, many of the approaches require multiple production steps or require electrodes, which hamper the application of these self-cleaning surfaces on a large scale. To resolve these drawbacks, we aim to use switchable surface topographies which under the external trigger can undergo from flat surfaces to the surfaces with pre-designed topological patterns. Especially, the liquid crystal networks are considered in these applications as they are not restricted to aqueous conditions as is the hydrogel. We anticipate that our approach has the following advantages:

- adjustability of wettability in a flexible manner- allowing for configurable
hydrophilic-(super-)hydrophobic patterns, that may also have anisotropic wettability properties or spatial gradients of wettability,

- a better performance of self-cleaning due to the additional dynamic effect e.g. the sliding angle can be improved by dynamic effects and solid transport may be enhanced,
- directed flow of droplets to keep flow of contaminated droplets limited and achieve contaminant deposition at pre-set locations.
- the surface is less prone to (mechanical) damage since the surface topography can be "switched off" at times in which it is not needed or when mechanical damage may occur,
- potential to scale up to large areas.

A number of challenges must be tackled before we can achieve switchable self-cleaning / tunable surfaces: First of all, we created structures with typical lateral dimensions of tens of micrometers or more; for wettability control, these need to be downscaled to micrometer or sub-micrometer level. Second, hierarchical structures may need to be made to achieve or improve the hydrophobicity. Creating secondary or superposed surface patterns not only involves enhancing the material resolution but also a fabrication strategy should be developed.

### 7.4 Tribology

Tribology is the science and technology of surfaces in contact with each other, in which friction and wear are important phenomena. It is an important aspect of our daily life. Friction is essential for walking on the street, typing on the keyboard, writing with a pen, the effectiveness of a shaver; wear should be avoided as much as possible for rolling bicycle tires, and mechanical components (e.g. gears) in machines such as cars, and computer hard disks.

The basis of analyzing contact between surfaces is to understand the geometrical surface features at the interfaces, which are vital for friction, wear and lubrication. Many efforts have been devoted to study the importance of surface topology on friction and wear. For example, to prevent wear, textured surfaces have been designed to reduce friction or increase lubrication; but surface topological structures have also been used to increase
friction e.g. for anti-slip bathtubs, footwear and so on.

If the surface topographies can be modulated dynamically either from a flat surface to a structured surfaces (Chapter 2, 4) or from a moderate patterned surface to that with enhanced topographies (Section 5.4 Formation of Surface Topographies, Figure 5.5), the friction will change accordingly. This has a considerable potential in a variety of applications. A special example can be found in haptic applications where tactile feedback to the human user is given during human-machine interaction. The most common examples are mobile phones and tablets where the whole device vibrates when one touches the screen – in this case, the haptic feedback is global, rather than local. This may be achieved locally when considering that, upon touching a surface, the local force, light or humidity conditions change. In a responsive coating that deforms by sensing those stimuli, a localized feedback of the friction change other can a global vibration can be realized. Other applications including remote surgery, robotic manipulations, video games that involve haptics can take the advantage of responsive surface topographies. Apart from haptics, responsive surface topographies can be used in motion control via the change of friction. For example, a breaking mechanism can be switched on or off in machinery. Floors can be switched to a less slippery mode under the wet or icy conditions. And recently many publications came out on the gecko effect enabling adhesion of substrates modified with geometrical structures\textsuperscript{41,42}. Our system in principle should be capable to turn this effect on and off.

The materials introduced in this thesis may form a good basis to achieve surfaces with adaptive tribological properties. In this application, mechanical robustness is an important requirement, and for this reason the liquid crystal network films are more suitable than the hydrogels. Next to achieving the required robustness, a challenge will be to achieve the high aspect ratios that are needed for haptic applications.

### 7.5 Switchable Optical Elements

Surface topology not only affects the wettability and mechanical properties such as friction and adhesion, but it also determines the optical properties of surfaces, in particular reflectivity, scattering, and diffraction properties. The ability to modify surface topology in a controlled manner therefore makes it possible to create surfaces with adaptive optical properties. As an example, by controlling surface topography, structures acting like micro
lenses can form in an autonomous manner, and their focusing depth might adapt to an external stimulus such as the light and its directionality\textsuperscript{43}.

Moreover, the appearance related properties like scattering, diffraction or reflection\textsuperscript{44,45,46} can be altered by the appearance or disappearance of protrusions in the surface. For example, the reflection losses at the air/glass interface can be reduced by switching on the topographies on the surfaces\textsuperscript{47}. However, also light-induced light in-and-out-coupling in waveguides can be controlled, and even color can be adjusted.

In principle, the materials proposed in this thesis can form the basis for surfaces with adaptive optical properties. A challenge however is to tune the intrinsic optical properties of the materials in a suitable range (e.g. their refractive index or transparency), while maintaining the responsiveness.

### 7.5.1 Structural Color

Nature produces color mostly in a chemical way by means of pigmentation. Pigments create color by selectively absorbing parts of the visible light. However, there exists a second way to achieve colors – by means of so-called structural color. Coloration in this method originates pure physically as the results of interaction of light with micro/nano patterns. *Morpho* butterflies (see Figure 7.4) bearing a beautiful blue color in their wings is one of nature’s species that exhibit structural color. Peacock feathers, beetles\textsuperscript{48}, and plants\textsuperscript{49} also create color based on various structures on the surface.

![Figure 7.4](image)

*Figure 7.4* (a) *Morpho* butterfly. (b) an enlarged view of the wing covered with structures of multiple scales\textsuperscript{50}. (c) Transmission electron micrograph (TEM) images of the cross-sections of the wing\textsuperscript{51}.
Structural color is claimed as “The color that never fades”, "It is 10 times more intense and bright than any color achieved with a pigment,”\textsuperscript{52} and it has attracted great interest as it can be used as substitutes for dyes, pigments in paint, cosmetics, and food. Recent research has ready shown applying structural color in textiles via photo-embossing\textsuperscript{53}.

Next to the above given two dimensional grating providing the angular dependent color effect, also in-depth periodicity is of interest providing band-gap effects. In fact our chiral-nematic liquid crystal films combine the switchability of a surface relief structure with the in-depth periodicity of the refractive index as determined by the pitch of the cholesteric helix. This combination is unique and might lead to completely new effects and applications in the worlds of fashion design, architecture, and indoor decoration or can be even used for camouflage.

7.6 References

2 Yong Kweon Suh and Sangmo Kang, Micromachines, 2010, 1, 82-111.
6 Dong Sung Kim, Se Hwan Lee, Tai Hun Kwon and Chong H. Ahn, Lab Chip, 2005, 5, 739–747


22 Yunhong Liu, Guangji Li, *J.Colloid Interface Sci.*, 2012.


50 Dong Zhu and Shuichi Kinoshita, *Phys. Rev. E*, 2009, 80, 051924 (1-12)


Samenvatting

De nauwkeurige en dynamische controle van oppervlakte topologie in het (sub)micrometer bereik is van belang voor veel toepassingen in diverse gebieden. Zo worden de optische eigenschappen van dunne films en coatings sterk beïnvloed door veranderingen in vorm en structuur van oppervlakken. Ook kunnen door het instellen van de oppervlakte topologie lensstructuren worden gevormd, die in respons op externe stimuli zoals licht op dynamische en autonome wijze van focus diepte kunnen variëren. Maar ook eigenschappen van oppervlak zoals verstrooiing, diffractie of reflectie kunnen worden gecodeerd door het veranderen van de oppervlakketopologie. Naast deze optische effecten kunnen ook demechanische eigenschappen van een oppervlakteworden gewijzigd door het laten opkomen of verzinken van structuren op het oppervlak. In het bijzonder kan hierbij worden gedacht aan tribologische eigenschappen zoals wrijving en adhesie, die worden gedacht belangrijk zijn voor haptiek en mens-machine interfaces. In microfluïdische toepassingen is het mogelijk mengstromingen te genereren door het oppervlak van de microkanalen van geometrische topologieën te voorzien. De dynamische controle van deze oppervlakte topologieën maakt het mogelijk het mengen aan en uit te schakelen, en dus actieve controle over de vloeistofstroming te realiseren; op deze manier kunnen (chemische) reacties aan en uit worden gezet. Ook is het mogelijk om de bevochtiging van oppervlakken te variëren door het aanbrengen van (sub-)micron oppervlaktereliefs. Tot nu toe zijn veel van deze oppervlakte-eigenschappen bestudeerd in een statisch setting, waarbij de onveranderlijke oppervlakte topologie wordt verkregen door lithografie of door embossing. Wij hebben materialen en technologieën ontwikkeld waarmee oppervlakte topologieën op een dynamische zijn kan worden gevarieerd, zodat het oppervlak kan worden geschakeld tussen een vlakke (uit) en een reliëf (on) staat met een goed gedefinieerde topologie.

In dit proefschrift onderzoeken we materialen en methoden om oppervlakte topologieën te creëren in een dunne coating. We hebben twee categorieën van materialen en bijbehorende technologieën bestudeerd, met verschillende onderliggende mechanismen. De eerste technologie is gebaseerd op spiraalvormig gerangschikte vloeibaar kristal (cholesterische) polymernetwerken. Het actuatie principe berust op een foto-geïnduceerde
vermindering van de moleculaire orde in deze chirale-nematische netwerken, die een macroscopisch expansie tot gevolg heeft langs de spiraal-as van het vloeibare kristal netwerk. We bestuderen drie soorten chirale-nematische configuraties.

1. Een coating die bestaat uit een eenfasige chiraal-nematische laag met planaire orientatie.
2. Een gepatronerde coating met afwisselende lijnen met planeire chiraal-nematische orde en isotrope moleculaire orde.
3. Een gepatronerde coating met afwisselende gebieden met planaire chiraal-nematische orde en homeotrope orde.

We tonen aan dat we met deze coatings oppervlakte topologie veranderingen kunnen creëren met een typische hoogte van 1 µm.

De tweede benadering is gebaseerd op sol-gel overgangen in polymeer hydrogelen. De oppervlakte topologie veranderingen van de hydrogelen kunnen door drie verschillende stimuli worden getriggered

1. Een dunne coating die reageert op pH veranderingen, zodat deze film op een dynamische en reversibele wijze kan worden geschakeld tussen een glad oppervlak, en een gestructureerd oppervlak door de omgeving te schakelen tussen zuur en alkalisch.
2. Een thermisch responsieve coating, waarin oppervlaktestructuren kunnen worden gevormd en gewist door het varieren van de temperatuur onder en boven 32 °C.
3. Een lichtgevoelig systeem, dat is gebaseerd op een thermisch responsieve coating, en waarbij licht wordt omgezet in een lokale temperatuurverandering door elementen te integreren die het licht absorberen en omzetten in warmte ingebed; dit wordt gerealiseerd door een gestructureerde chroomoxide laag op het substraat te deponeren.

De hoogteveranderingen van de oppervlaktetopologie van de hydrogel coatings kunnen tientallen µm bedragen. In vergelijking met de vloeibaar kristal netwerken zouden de hydrogel coatings minder geschikt kunnen zijn voor bepaalde toepassingen, omdat de hydrogelen veel minder robuust zijn en een vloeibare omgeving vereisen.

We zijn er van overtuigd dat de door ons ontwikkelde basisprincipes voor de fabricage van schakelbare oppervlaktetopologieen op grote schaal kunnen worden gebruikt voor een scala van toepassingen, variërend van vloeistofmanipulatie in de microfluidica tot aan lichtvolgende adaptieve optische elementen in zonnecellen.
概要

（亚）微米范围内表面结构的精确及动态的控制，在许多领域具有应用。例如薄膜和涂层的光学性能会受到表面结构和形状的影响。另外，通过控制，透镜的表面结构能够以动态和自主的方式来形成，其聚焦深度能因外部刺激如光与其方向性而相应的改变。不仅如此，散射，衍射或反射等其它相关性质都可以通过改变表面结构来进行调制。除了光学效应，表面机械性能可以通过其表面凸起的形成或消失来改变。特别是涉及到表面接触的科学，如摩擦，粘性和附着力在触觉和人机界面等领域是非常重要的。在微流体应用中，液体的混合可由在微通道壁上的特定表面形态来实现。通过对表面结构的动态控制，混合可以被开启或关闭，从而控制流体的流动以及一些化学反应的进行。控制亚微米级的表面结构也可以对其润湿性产生影响。目前，许多对表面结构的研究都集中在静态的层面，其形成是由通过光刻或压印的方式来实现的。我们开发了材料及相关技术来获得动态的表面结构，实现了表面结构在平整（关）和有波纹（开）或自定义的凸起这些状态之间切换。

在本论文中，我们探索了实现薄涂层表面结构切换的材料以及方法，研究了两类不同的技术及其机制。第一类技术基于螺旋排列的液晶（胆甾醇）聚合物网络，其原理是基于光致诱导分子有序度的降低，使得手性向列型网络(chiral-nematic)在其螺旋轴方向产生宏观膨胀。我们对三种类型的手性向列型网络进行了研究。

（1）涂层由单一的手性向列型网络构成，分子排列采取平面取向。
（2）涂层由交替的手性向列型以及无序的分子排列构成。
（3）涂层由交替的手性向列型以及垂直的分子排列构成。

用此方法实现的表面构型高度与涂层厚度有关,由此实现了近20% 的表面形变。

另一种方法基于水凝胶中的溶胶 - 凝胶转变。我们研究了三种触发机制来启动水凝胶表面结构。

（1）pH值敏感的薄涂层。该薄膜可动态和可逆地调制，其光滑的表面与具有微观结构的表面能在酸性和碱性环境之间转变。

（2）热反应涂层。表面结构的形成和擦除可以在32℃以下或以上的水环境中循环实现。

（3）光反应涂层。基于热敏感水凝胶，在薄膜或其衬底中嵌入升温元件，此元件可吸收光线，转为热能。通过在基底上涂布黑色氧化碳或在水凝胶中结合入碳纳米管来实现光-热能量的转换。

与基于液晶的薄膜相比，基于水凝胶的薄膜所形成的表面结构更大，并且在一个50微米的膜上可以很容易地形成十或几十微米的表面结构。但是，考虑到机械性能和应用环境(水环境),水凝胶在某些应用中不如液晶。

我们预期我们所研究开发的可转换表面结构的智能涂层，在微流控芯片中的液体传输到光学追踪太阳能的光学元件等领域都有着广泛的应用。

感谢陈于蓝对本章翻译的帮助
Acknowledgements

At the end of these four years, I would like to thank everyone who has been around during this time period for your time, kind help and even just a smile when passing by. All these have made the whole PhD study time very enjoyable.

Especially, I would like to express my gratitude to a number of persons. First of all, I would like to thank the ARTFLAG team for working together during these years. Special thanks go to my promoters Jaap den Toonder and Dick Broer for your guidance throughout the project. Jaap, I remember that I contacted you in the end of 2008, and after few discussions you gave me the opportunity to work on this project. Then I really had a one of the best Christmas and New Year. During these four years, I have benefited from the weekly discussions with you. Your advices on my results helped me to reach a deeper understanding and work further. Also, I would like to thank you for the freedom you gave during the research. You allowed me to try different materials and explore other possibilities which made the project going smoothly. Moreover, I am very grateful for your guidance and timely feedback through my thesis writing. Dick, I owe my deepest gratitude to you. Thank you for being flexible and suggesting me to focus on the topic of “responsive surface topographies” after more than one year struggling. Your supports during difficult meetings let me continue. I am also grateful for your guidance throughout the project. I couldn't have completed this thesis without you. Cees, thank you for all the help especially during my first year when I arrived without any chemistry background as an Electric Engineer, which according to you is even worse than Mechanical Engineer. You tried to teach me working properly in the lab, and with that you even found a chemist to help me. Then I would like to thank the people from Groningen. Patrick, it is a unique experience to collaborate with you. The joint meetings let me aware of how theoretic people look at the questions, and how it is to corporate with theoreticians. Sandeep, it is a pleasure to work with a bright PhD student like you. I like your smart questions during the meetings and our chatting as friends. At this moment, you are also about to finish your project, and here I wish you all the best for your future. Also I would like to thank people from DPI, Monique and John, for occasionally participating in the ARTFLAG meetings with constructive questions and positive feedback.
on our results.

Being officially contracted with the Polymer Technology group at Mechanical Engineering, I would like to thank Han Meijer for your time and advice over the years. Han, it was a pleasure to be located in your group. Although you haven’t been involved directly in the project, yet you stand at a certain level and gave me valuable advice at a critical moment which I didn’t realize myself that time. Probably you have forgotten that when I worked on magnetic swimmer, you warned me about the risk of the project to become either black or white: either I would get the results, or I would fail. I didn’t really understand your point at that time. Later when I started the topic of responsive surface topographies, you told me that you were happy because I had achieved a grey-zone in the project. Looking back, I start really to understand and appreciate your wise words. Now I feel lucky to have you in my defense committee and I would like thank you for reading my thesis.

My gratitude also goes to Prof. Yu Yanlei. Thank you for caring about me and my career. Talking with you is always a nice experience. I really appreciate your advice on how to direct my research and the help you offered. And it was the discussions with you that encouraged me to continue working on the topic of “responsive surface topographies” which was an important decision in my study. I am looking forward meet you in the near future.

Starting a new project is quite a challenge. Without the help from colleges, it would be tougher at the beginning. Working in a chemistry lab, with which I did not have experiences before, is rather difficult. Therefore, my special gratitude goes to Katherine who has been a great help at the beginning. Katherine, thank you for all your help during my project and for continuing to be helpful when I was looking for the job. Also, I would like to thank Francis Fahrm for your patience in explaining me the magnetic actuators and help me with many experiments.

During these four years, I spent most of my time in the SFD group at the Chemistry department. Here, I would like to thank the entire group for the wonderful time of working together. Albert, thank you for being positive about the topic and the results, your attitude is very encouraging. It is nice to work with you and Jelle on photo-sensitive hydrogels. There were many inspiring discussions. Hope we can continue with that topic. Robert, for studying coffee-drop effect together. Claudia, Huub, Iren, Ivelina, Marjolijn, Micheal, My, Nicole,
Paul, and Ties, thank you for your help. I would like to thank my office mates: Mian, Laurens, Anotino, Tom, Yang, Xiaoran, and Julien for the nice working environment and much fun we had.

Being involved in a corporative project, I had the opportunity to work in Polymer Technology group at Mechanical Engineering. I would like to thank all the group members for the support during the past four years. Special thanks go to a number of people. Marc for the great help in the multi-scale lab; Yang for the modeling of the magnetic setup; and Hossein for continuing to work on the magnetic swimmers; Hans and Zahar for the help in rheology measurements; Markus for the nice discussions on modeling and your effort, I am looking forward to further collaboration; Agnese, Sheen, Rene, Ye for the help in the lab session of the course “micro fluidic put to work”; Zhe for being helpful, especially at the last phase of the defense, providing many useful information. Former office mates in room 4.21 and current office mates in 4.09. Marleen, thanks for organizing many things.

I would also like to thank my friends Bing, James, Ping, Ting, Yuping, Hongliang, Jinjing, Jia, Lili, Juan, Junlin, Xixi who have enriched my weekends in Eindhoven, for many laughs, dinners, trips together. Fang, Jie it is so nice to know you and thank you for the nice companies when we were in Delft. It was wonderful to have dinner with you in San Francisco. Cuiqin, thank you for all the nice time of being around and I hope to visit you in the US in the near future.

Last but not least, I would like to thank my parents. Thank you for supporting my study in Delft in the first place, without that step I could never reach so far. Thank you for your love. Also, I’d like to express my gratitude to my aunties, uncles, cousins for taking care of me.
Danqing Liu was born 17th January 1985 in Chengdu, China. After finishing high school in 2002 (Haikou, China), she started to study Physical Electronic Technology at the University of Electronic Science and Technology of China (UESTC, Chengdu, China). After 4 years of study, she received the Bachelor’s degree. In 2006, she came to the Netherlands and started a Master program in Electronic Engineering at Delft University of Technology. During this study, she specialized herself in the field of microelectronics and its manufacturing through photolithography. In 2008, she received her Master’s degree.

In February 2009, she started her PhD at Eindhoven University of Technology (the Netherlands). This PhD research was carried out in two departments. In the group of Polymer Technology with Prof. Dr. Jaap den Toonder at the department of Mechanical Engineering and in the group of functional organic materials and devices (SFD) with Prof. Dr. Dick Broer at the department of Chemical Engineering and Chemistry, leading to the publication of thesis. The four years of doctoral studies were financially supported by the Dutch Polymer Institute (DPI, the Netherlands).