Wettability in liquid crystal coatings based on switchable surface topographies

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Award date: 2015

Link to publication
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Graduation Project

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Presentation Letter

From nature, it is known that water-repelling properties on a lotus leaf leads to self-cleaning behavior. For this reason the phenomenon of hydrophobicity has gained much attention as a critical property of man-made surfaces. Research has demonstrated that there are two factors important for water repellence, one is surface energy which is determined by chemical composition of the surface and the other is surface roughness which can be enhanced by creating nano- and micro-structures. Based on these, many reports can be found in literature on bio-mimetic attempts inspired by the lotus leaves and other living creatures which were successful in making low-surface-energy substrates and creating surface structures with super-hydrophobicity. These surfaces are static without responses to their environment or stimulus and currently there is a blank in dynamic control of surface structure for reversible wettability.

Azobenzene-modified cholesteric polymer films have reversible surface topographies because of the volumetric change under UV illumination induced by photo isomerization of N=N double bond. The responsive surface deformation leads to switchable wettability when triggered by light and its contact angle increases with the formation of protrusions on the surface under local UV illumination.

This project aims to utilize these responsive films to create (super) hydrophobic surfaces based on their surface topographies. In this project first the surface energy was lowered by chemical modification with perfluoro silane via vapor phase. Surface topographies were then created by UV exposure with different pre-desired patterns. The approach was successful. The results indicated the surface changed from moderately hydrophilic to hydrophobic after modification with perfluoro silane and the contact angle increased from 75° to 120°. After actuating the surface structures, the surface converted from flat state to corrugated state and its contact angle approached to 139° indicating a photo responsive switching to a more hydrophobic state. For the purpose of this study, enabling easy measurement of the contact angles, the surface structures could be made stable by the addition of a polymerization inhibitor, even after long-time storage in the darkness and reheating above T_g.

In this thesis we creatively and unprecedentedly combined hydrophobic surfaces and light responsive polymer films into hydrophobic coatings with switchable wettability under UV actuation. The basic theories of hydrophobicity and light responsive cholesteric polymer networks were introduced, followed by the preparation, fabrication and characterization of films. Surface modification, study of surface topographies and their corresponding wettability explained in detail. There were also constructive suggestions for further research. We anticipate that the liquid crystal polymer film with controllable wettability has great potential in academic research and various technical applications.
### Introduction

#### 1.1 Background: Dynamic Lotus Effect

Wettability is an important property for solid surfaces. In nature many species exhibit water repelling behavior such as lotus leaves\(^1\) (Figure 1). A complex micro- and nano-architecture on the surface (Figure 2) minimizes the droplet's adhesion to the surface and leads to high water-repellence on lotus leaves. The self-cleaning property of superhydrophobic micro-nanostructured surfaces is called "lotus effect". Other plants and animals like water strider’s legs\(^2,3,4\), and cicada orni’s wings\(^5\) show the similar phenomenon.

![Figure 1 Water droplets on a lotus leaf show superhydrophobicity](image1.png)  
*Figure 1 Water droplets on a lotus leaf show superhydrophobicity*

![Figure 2 Microscopic image of the lotus leaf surface depicting the double rough structure\(^6\)](image2.png)  
*Figure 2 Microscopic image of the lotus leaf surface depicting the double rough structure*

The technology controlling the surface wettability has already shown its beneficial aspect and has become crucial in many applications. In printing processes, control of liquid spreading over solid surfaces is important \(^7\). In microfluidic droplets manipulation, wettability is directly related to generation of water droplets \(^8\). For organic solar cell a hydrophobic surface increases power conversion efficiency by its self-cleaning properties \(^9\).

Normally, for preparation of hydrophobic surfaces two approaches are used, top down approaches such as templating \(^10\), lithography \(^11\), or plasma etching \(^12,13\), and bottom-up approaches including chemical deposition \(^14,15\) and layer-by-layer deposition \(^16\), etc. Although these approaches are able to create surfaces with desired wettability, the static protrusions on the surface may introduce mechanical damage due to their fragile properties and accumulation of contaminations because of the gap between of microstructures. This leads to certain available techniques becoming vulnerable to practical use because of their insufficient hardness. These are the major problems for hydrophobic surfaces with static protrusions.

Dynamic-controlled surface topographies can avoid these drawbacks and improve the performance. Surface structures can be “switched off” to prevent abrasion and scratching when they are not in use and the erased structures can protect the surface from accumulation of dirt. In that way, contamination and attenuation of performance can be avoided. The coating will be more useful and valuable in practical application with regard to its advantages; however, there is a lack of technology to make dynamic-controlled hydrophobic surfaces based on switchable surface structures.

From liquid crystal polymer films, it was recently found that they can switch their surface topographies \(^17\). The surface can change from flat state to the surface with pre-designed patterns.
under UV illumination. The idea presented in this report is to combine the effects of low surface energy with the surface dynamics of the liquid crystal polymers so as to control its wettability by switching surface topographies.

1.2 Objective

In previous research, a light responsive cholesteric polymer coating was developed which can transform from flat state to surface with random protrusions\(^\text{18}\). Subsequent studies showed that the flat film had a contact angle of 80°. When addressed with UV light, the protrusions appeared on the surface and contact angle increased to 100°. In this project, the aim was to further increase the hydrophobicity of these films, expecting the contact angle of water increasing up to 130° when the surface topographies were switched on. For reference, by convention the surface can be defined as superhydrophobic when the contact angle exceeds 150°.

Two approaches were used to improve hydrophobicity, one was chemical modification to lower surface tension and the other was to create surface roughness. These two points were directly related to wettability performance. To reduce surface energy, several possible methods are available and currently we utilized silanization with a fluorinated reagent as chemical modification for cholesteric polymer films. To create surface roughness, various patterned masks were selected and tested in the actuation of permanent surface structures on the surface of liquid crystal polymer films. To facilitate the measurement of the contact angle we focused this research of liquid crystal formulations that produce permanent surface structures by a small change in the monomer formulation. It is thereby assumed that the results of the contact angle measurements are indicative for the dynamic films in their ‘switched-on’ state.
1.3 Theory

1.3.1 Hydrophobicity

1.3.1.1 Basic theory of hydrophobicity

Water droplets tend to minimize their surface by forming a spherical shape while on contact with a surface. The hydrophobicity of this surface can consequently be measured by contact angle of the droplets with this surface. For water droplets on a truly flat surface (Figure 3a), wettability is determined by surface free energy as a result of intermolecular interactions between three interfaces, which is expressed by Young’s Equation

$$\cos \theta = (\gamma_{sv} - \gamma_{sl})/\gamma_{lv}$$

Where $\theta$ is the contact angle (intrinsic CA) and $\gamma_{sv}$, $\gamma_{sl}$ and $\gamma_{lv}$ represent surface tension between solid and vapor, solid and liquid, liquid and vapor, respectively. From the equation, surface tension is related directly to contact angle and higher contact angle can be obtained by lowering surface tension of solid substrate.

As a classical interpretation Young’s mode is the simplest prediction of wettability. However in many cases surfaces are far from this ideal smooth situation and surface roughness also influence wettability, therefore it is necessary to consider this effect and introduce roughness factor into the equation, as described by Wenzel’s Equation

$$\cos \theta_w = r(\gamma_{sv} - \gamma_{sl})/\gamma_{lv}$$

$\theta_w$ is the apparent contact angle and $r$ is the roughness factor. In Wenzel’s mode, liquid droplet completely penetrates into the corrugations present at the surface (Figure 3b). Besides this basic assumption, by combination of these two equations there is a linear relationship between $\theta$ and $\theta_w$.

$$\cos \theta_w = r \cos \theta$$

Which indicates roughness enhances both hydrophobicity and hydrophilicity depending on the nature of surface wettability.

Nevertheless, with the roughness increasing, contrary to Wenzel’s mode the liquid droplet is observed suspending on top of the corrugations with air trapped in grooves (Figure 3c), this defines Cassie -Baxter’s mode\(^\text{20}\). In Cassie -Baxter’s theory $\theta_a$ is correlated with the fraction of wet-contact area $f$ and the resulting contact angle is simply written as

$$\cos \theta_{CB} = f(1 + \cos \theta) - 1$$

Unlike Wenzel’s theory, the contact angle will increase in pace with roughness regardless of the intrinsic CA over 90° or not. The present of trapped air pockets plays a significant role in enhancing hydrophobicity especially in cases of superhydrophobic surfaces.
Except difference in prediction of static CA, dynamic behavior is also different in these two states. It can be observed when the surface is in Wenzel’s mode liquid droplets remain pinned even if the surface is tilted to a large angle, while it slides off easily at a slightly tilted angle in Cassie-Baxter’s mode. This sliding behavior is also a criterion for hydrophobicity and evaluation of water repellency and it is caused by contact angle hysteresis. When liquid droplet moves in contact with a surface, only the molecules on the contact line have velocity because of boundary condition. For most materials, droplet remaining on a surface will rest at a minimum energy with a fixed three-phase contact line. The energy barrier between advancing and receding is the cause for CA hysteresis. In the transition from Wenzel’s state to Cassie-Baxter’s state, the trapped air pockets lower energy barrier and make it apt to be overcome by external forces such as gravity. Therefore increasing surface roughness state to keep in Cassie’s state is of great use to lower CA hysteresis and a key of superhydrophobicity.

However, even with the same roughness a surface can still differ in hydrophobicity. Another factor contributing to the contact angle and CA hysteresis is the nature and the geometry of the surface topography. Tuning surface topography by minimizing wet-contact area leads to a lower energy barrier between advancing and receding which is the cause for hysteresis, and relatively close distance between pillars on the surface prevents intrusion of liquid and transition from Cassie’s state to Wenzel’s state. Therefore, such surface geometrical structure exhibiting a short three-phase contact line is favorable for high contact angle and low CA hysteresis. Also the pinning effect of topographies can obstruct the spreading of three-phase contact line and increase the advancing contact angle and hydrophobicity. It should be noted that there is no declaration of the optimal structures for a superhydrophobic coating.

Conclusively, to prepare a surface with superhydrophobicity, a comprehensive approach integrates both surface roughness and geometrical structures with low-surface-energy materials. The basic theories of wettability and mechanism of hydrophobicity described in this section guide the researches and preparations of surfaces, which is to use low-surface-energy rough substrate with suitable surface topography.

1.3.1.2 Superhydrophobic surfaces

Nature gives us many distinguished water-repelling phenomena. For example, a lotus leaf with hierarchical double architecture (Figure 2) on the waxed surface exhibits self-cleaning property, while rose petal (Figure 4 a) shows superhydrophobicity with adhesion due to its water-permeable micro papillae with impermeable nano folds. Not only plants, animals also possess anti-wetting surfaces like water stride’s legs (Figure 4 b) which have nanosized grooves on the microseta surfaces and cicada ornii’s wings with regularly sculptured nanostructure.
Their specific surface energy and elaborate surface structure have inspired plenty of artificial superhydrophobic surfaces by cooperation of material modification and surface topography design. Low surface energy is prerequisite for a hydrophobic coating and the outermost chemical groups determine wettability of a surface. Many authors reported higher hydrophobicity by introducing components with low surface energy such as fluorinated groups. For example, modifying with fluorinated additives in the bulk reduced the surface energy of a polymer film and fluorinated polymer coatings on the surface brought enough hydrophobicity. Superhydrophobic fibers were obtained via electrospinning of block copolymer containing poly siloxane. Amorphous Teflon can be used to be spin-coated on the surface. Treatment of the surface with fluoro-containing plasma is also feasible. One of the efficient strategies to introduce low surface energy compounds on surface is via self-assembly of fluoroalkylsilane and multiple methods are available for coating. Reactions in solution and by chemical vapor deposition are promising for practical applications as rapid and simple one-step methods.

Not only low-surface-energy materials, but also roughness is indispensable for hydrophobic surface. Up to now, many technologies have been developed to produce rough surfaces. Radio frequency plasma was used to create roughness on semicrystalline polypropylene surface with Poly(tetrafluoroethylene). Phase separation induced by polymer additive can control the dimension of crater-like microstructure of the films. Superhydrophobic surfaces were prepared by poly(methyl methacrylate) or polystyrene modification on an optimized anodic aluminum oxide honeycomb-like structure surface. Other methods like sol–gel method, electroless deposition process and template-based method are also widely studied and applied.

Learned from nature many attempts successfully mimicked the water-repelling surface of plants and animals or draw inspiration from them. Raspberry-like duel-structures on the surface have been reported, imitating the hierarchical properties of lotus leaves. Similar to wing surface of Cicada orni, the surfaces with aligned PS nanofibers were made to prevent strong attachment of water droplets onto the surfaces. Jin et al. reported a superhydrophobic aligned polystyrene nanotube film mimicking Gecko’s feet. Except for biomimic, other topographies with different shapes and dimensions are also frequently reported and pillars were prepared by various methods and achieved superhydrophobicity in a wide range of dimensions. Figure 5 shows images of surfaces with different posts and spacing. The micro-pillars were ordered or randomly placed on the surface in micro or nano scale with regular or unique patterns. Some water-repellent surfaces are fabricated with a hierarchical integration of nano- and micro-scale textures.
Hydrophobic surfaces with various geometric patterns were created. However those approaches were all in a static condition without dynamic control and switchable properties. Smart materials with controllable wettability have attracted plenty of attention in both of academic fields and industrial areas because of their great potentials in a wide range of allocations. Currently switchable wettability has been achieved by modifying the surfaces with stimuli-responsive organic compounds. Lahann et al, Wang et al used electrical potential to trigger a conformational change of molecules\textsuperscript{62,63}. Other publications describe the use of temperature to induce controllable wettability based on sol-gel transitions in by poly(N-isopropylacrylamide)\textsuperscript{64}. Switchable wettability via illumination is another common method and isomerization of photo-sensitive azobenzene was greatly adopted to create reversible hydrophilic-hydrophobic transition on the surface\textsuperscript{65,66,67}.

All these methods mentioned above were based on the switching of intrinsic hydrophobicity and the surface topographies were remained unchanged. With microstructures on the surface, accumulation of contamination and mechanical damage are inevitable and make materials vulnerable for practical use. Considering the drawbacks, we propose to use switchable surface topographies of responsive materials for controllable wettability. Hydrophobicity can be improved with the surface converting from flat state to corrugated state. The microstructures on the surface are desired to be responsive under external stimuli in order to avoid dirt and damage during sustainable use.
1.3.2 Responsive Liquid Crystal Networks

1.3.2.1 Liquid Crystal Polymer Networks

Liquid crystals are materials that have the appearance like liquid, but the molecules are ordered like in a crystal. Between melting state and isotropic state, three classifications of phases may exist. In nematic phase, the rod-like molecules exhibit a directional order without positional order. Molecules in smectic phase have both directional and positional order with higher order parameter. The average angle of tilting determines the order parameter. A special case of nematic liquid crystal is cholesteric phase (or called chiral nematic phase). Molecules self-organize in helixes when the liquid crystal system contains a chiral center or chiral dopant which produces intermolecular forces that favor alignment between molecules at a slight angle to one another. The pitch of the helix depends on the helical twisting power of the chiral dopant and its concentration. A higher amount of chiral dopant leads to a smaller pitch.

Mesogens with polymerizable groups such as acrylate, methacrylate or epoxide are the basic components for liquid crystal polymer networks. With liquid crystal units linked to a polymer backbone at both sides, the densely crosslinked polymer network establishes a stable molecular organization and molecular order can be locked into a polymer network by polymerization procedure (Figure 6). Via polymerization, the liquid crystal networks combine the advantages of both liquid crystal mesogens and polymers, possessing both anisotropic and strong mechanical properties, which have been reported repeatedly.

There are various means to initiate chain-growth polymerization. Using light can avoid losing molecular order and facilitate to a stable polymer network with the same texture and order as that of the monomers. Moreover it only needs several minutes to prepare and has the advantage that phase separation and phase transition are kinetically suppressed because of fast polymerization.

![Figure 6](image_url)

*Figure 6  Scheme of ordered liquid crystal molecules polymerize with cross-linkers under UV illumination and form a polymer network in a frozen-in molecular order.*

1.3.2.3 Light Responsive Polymer Network

To achieve light responsive properties, azobenzene moieties are used as cross linker in liquid crystal polymer network. Azobenzene is well-known for its photo-switching property. As showed in Figure 7, azobenzene moiety has two configuration state, an elongated trans state and a bent cis state. The two isomers can be switched under particular wavelengths of light. The barrier to photo-isomerization is approximately 200 kJ/mol energy. The trans state is more stable by approximately 50 kJ/mol than the cis state, so under the ambient light or in a dark condition, most azobenzene moieties will keep their trans state. When illuminated with UV light between 300-400 nm wavelength, the energy gap of π-π* transition is conquered and trans-to-cis conversion occurs. In
the presence of visible light with an absorption band at wavelength $>400\text{nm}$, cis state converses back to the trans state. This photo-isomerization of an individual molecule occurs very fast, typically in picoseconds. The thermal back reaction makes that the trans and cis states under illumination are in equilibrium which defines as the photo-stationary state. The time to reach the photo-stationary state takes typically seconds to minutes.

Figure 7 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.

By integrating the azobenzene compound into liquid crystal network, the molecular order is changed under UV exposure. Before UV exposure, the azobenzene units in trans state complies with the orientation of the network molecules. When addressed with UV light, the azobenzene units convert to bent cis state. This leads to a reduction in order parameter. Many applications have been made based on this principle. The azobenzene units were integrated into a LC elastomer to get mechanical responses and into splayed nematic networks to get dynamically mechanical behavior.

In this project, we used azobenzene moieties as cross linkers in cholesteric polymer films. The isomerization of azobenzene driven by UV light reduces molecular order as the cooperative disordering of the aligned molecules, and thus induces a decrease in density and increase in volume. Cholesteric order allows symmetric deformation in the plane of the film and the pitches of LC helixes expand in the direction perpendicular to the surface. Consequently under local UV illumination the expansion of pitches in the exposure area leads to the desired protrusions, and surface structures with different patterns can be created, shown in Figure 8.

Figure 8 Scheme of the density-induced formation of protrusions by patterned UV exposure. The exposure area gets protrusions on the surface while the covering area has no deformation.
2.1 Fabrication of Cholesteric Polymer Films

For light responsive surface deformation, we used cholesteric order rather than nematic or smectic order because of its in-plane symmetry largely reduces the possibility of lateral in-plane stresses building up and the consequent asymmetric anisotropic deformation. The cholesteric polymer films were made on polyimide-coated glass substrates by photo polymerization of reactive mesogens and additives. The mixture of materials we used is shown in Figure 9.

Figure 9 Materials used for responsive liquid crystal films. 1-3 are liquid crystal acrylate monomers. 4 is chiral dopant. 5 is azobenzene. 6 is photo-initiator. 7 is inhibitor.

Monomers 1-5 were elongated rod-shaped molecules. Their anisotropic geometry can lead to uniaxial alignment. Monomers 1-3 exhibit in nematic phases. The somewhat complex blend of LC monomers was used to adjust temperature range of the liquid crystal phase, optimize viscosity and crosslink density. The latter property affects the elastic modulus and the glass-transition temperature. Monomer 4 was introduced as a chiral dopant to form the cholesteric phase in the monomer mixture to make the helices with the helix axis perpendicular to the average orientation of the long axes of the molecules. The pitch length of the molecule helix is related to the helical twisting power (HTP) and concentration of chiral dopant. This chiral dopant has a comparatively large HTP, so a small amount is enough to make overall chirality efficiently. Monomer 5 was the azobenzene for photo-sensitive deformation. 6 was bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide, a free-radical-generating photo initiator for polymerization.

7 was p-methoxyphenol, an inhibitor to reduce the kinetic chain length of the acrylate main chains and enable sufficient mobility for the realignment of the molecules induced by azobenzene. The realignment keeps a permanent change in polymer network proven by the stability test mentioned below. It is essential to make the permanent surface topography to enable the contact angle measurements. Without 7, the cholesteric polymer film could have dynamic surface topographies.
and as soon as the UV light is switched off the film recovers to its initial state and the structures disappear.

The mixture was filled between two polyimide-coated glass plates by capillary force. A rubbed polyimide layer was used to establish the planar LC monomer orientation. Prior to the rubbing this coating was applied by spin coating on cleaned glass plates. By using thin cholesteric films the alignment of mesogens is facilitated and the light absorption of the azobenzene is minimized to avoid the inevitable gradient effect of photo-responsive property over the thickness of the film. The photo polymerization was conducted in chiral-nematic phase with wavelengths >400nm to prevent trans-to-cis conversion of azobenzene already during photo-polymerization. After that, post-cure was needed since during the polymerization step, vitrification may take place and further reaction of unreacted molecules is hindered because of a limited mobility of the unreacted acrylate groups. The temperature of post-cure was above \( T_g \) to ensure higher conversion. FT-IR spectrum of polymer is showed in Appendix Part 1.

The static contact angle on surface of cholesteric polymer film was measured. The results revealed the surface was moderately hydrophilic with a contact angle of around 75° ±3°. Since there were no hydrophobic elements on the surface, this contact angle was within the expectation.

2.2 Actuation of Surface Topographies

A rough surface is essential for superhydrophobicity and switchable wettability is based on the light responsive surface topography. After a flat surface was fabricated, the next issue was the creation of roughness. The cholesteric polymer film we made contained azobenzene monomer which has photo isomerization property. Under UV illumination, azobenzene unit converted from an elongated trans state to a bent cis state. The mobility of this polymer network was sufficient and allows molecular reorganization followed by the bending of azobenzene units. The molecular order of the liquid crystal network was thus reduced as an amplification of the conformational change of azobenzene molecules. The change of order led to a decrease in density and a related increase in. Since cholesteric polymer network was attached to a stiff surface rather than being-standing, UV-induced changes in the order parameter and density resulted in the formation of the surface relief and the film expanded in the direction of the helix axis.

Various surface topographies can be built with the patterned protrusions by local UV illumination. We controlled the pattern shape and size by using different photo masks in UV illumination. The exposure area gave volume increase and formed corresponding protrusions on the surface while the covering area stayed unexposed and certainly no deformation happened. The chosen composition of the polymer network, including the high concentration of inhibitor, allows enough mobility in the network for the azo moieties to reorient towards the direction of the propagating light and a permanent change in order of the mesogenic network. The lack of elasticity in the network and the glassy properties of the network avoided full relaxation to the initial flat state and the structures remained, even after the light was switched off. After UV actuation temperature of the film decreased, the patterned protrusions corresponding to the different masks can be observed and the surface was characterized by interference microscopy.

The stability of light-induced surface topography was checked by reheating the film above \( T_g \) and there were no changes in the protrusion height as well as pattern deformation under the
observation of interferometer. After stored in the dark for months, the surface topography also remained same as that of newly actuated film.

2.2.1 Absorption band of azobenzene

The cholesteric polymer network contained azobenzene monomers which have two isomeric states. When illuminated with UV light in its absorption band at 365 nm, azobenzene transits from the elongated trans state to the bent cis state. The reserve reaction occurs thermally or by illumination with white light.

The absorption spectrum of the films with azobenzene (Figure 10) was measured. The result showed absorption band at 365nm before and after UV illumination. With similar film thickness, absorption intensity of the film decreased after UV illumination since part of azobenzene molecules may rotated out of plane of the film when converted back from cis to trans state.

![Figure 10 Absorption spectrum of cholesteric polymer film with azobenzene before and after UV illumination.](image)

2.2.2 Mobility of p-methoxyphenol-modified polymer network

P-methoxyphenol as an inhibitor was added to the monomer mixture to reducing the kinetic chain length of the acrylate main chains, which increased the polymer network mobility. The sufficient mobility allowed the reorientation of mesogenic units and the reduction of molecular order. This could be observed from the difference of the UV/Vis spectra of the cholesteric polymer films before and after UV exposure.

The transmission spectra of the p-methoxyphenol modified cholesteric polymer films (Figure 13) were measured. The absorption at 700 nm belonged to the cholesteric reflection band. Before UV illumination, the reflection band width was 90 nm while after UV illumination, the band width reduced to 65nm. The selective reflection was originated from the pitch of the cholesteric polymer network with the equation\[\Delta \lambda = (n_e - n_o) p\], in which \(n_e\) represents extraordinary index and \(n_o\) is ordinary index. The fact that \(\Delta \lambda\) decreased and \(p\) increased (or may unchanged) after UV illumination
led to the conclusion that \((n_e-n_o)\) decreased. Since \(n_o\) was unchanged, \(n_e\) was decreased after UV illumination which indicated that molecules reoriented themselves towards the direction perpendicular to the plane of the film. This proved a permanent change in the molecular order of the p-methoxyphenol modified cholesteric polymer network after UV illumination with sufficient mobility for the realignment of molecules.

![Figure 11](image)

*Figure 11* UV/Vis spectra (with un-polarized light) of the cholesteric polymer film before (red line) and after (blue line) UV exposure.

2.2.3 Pattern Choice

As mentioned above, the pattern of the surface topography of cholesteric polymer film was determined by the mask used for local UV illumination. Among all the masks we tested the masks with either a grid pattern or a dot pattern performed best in height difference under UV illumination.

The grid pattern had open areas of orthogonal lines with width of 25 \(\mu\)m and the distance between each unit is 200 \(\mu\)m. *Figure 12* showed the 3D image and cross-section surface profile of surface topography made by the use of this grid pattern. The protrusion height can reach to 0.8 \(\mu\)m corresponding to a deformation strain of 6% defined as protrusion height divided by the initial film thickness. The protrusions were highly consistent with regular height.

![Figure 12](image)

*Figure 12* 3D image and surface profile in cross-section of surface topographies of cholesteric polymer film with grid pattern after UV activation.
The surface topography that we obtained with a dot patterned photomask was the closest pattern to the lotus surface and other artificial hydrophobic surfaces. The protrusion height was 1.2μm with 16.5μm film thickness. The deformation strain had up to 7.3%.

![Figure 13 3D image and surface profile in cross-section of surface topographies of cholesteric polymer film with dot pattern after UV activation.](image)

The two selected patterns had both a positive performance in relation to the surface deformation, however their wettability were different. Using the mask with the grid pattern, we got the largest static contact angle increase of 23°±2° while the dot pattern had smaller contact angle increase of 9°±2° (Figure 14).

![Figure 14 Contact angle of water droplets on different surface of cholesteric polymer films. Flat surface of cholesteric polymer film (left), corrugated surface with dot pattern (middle) and corrugated surface with grid pattern (right).](image)

We speculate that one reason was because of the different protrusion height, however the dot pattern had higher protrusions on the surface than that of grid pattern indicating higher surface roughness and this should contribute to larger contact angle. For this concern, we studied the hydrophobic performance of these two patterns with the same protrusion height, which was in the section 2.2.4.3. The other reason for different wettability was the pattern difference. Comparing these two patterns, the pinning strength to water droplets brought by the grid pattern was much greater than that of dot pattern. The grid structure acted as a barrier for the moving of the three-phase contact line of the water droplets which prevents the further spreading of the water droplet in all planar directions on the surface. Referring to dot pattern, less pinning strength was brought by the dispersed protrusion structure which has less ability to prevent the moving of contact line.

Based on the hydrophobic performance of surface structures formed through masks of different patterns, we chose these two masks with grid pattern and dot pattern in the following experiments and developments of switchable wettability because of their better performance in protrusion formation and improvement in hydrophobicity.
However there is limit on the pattern choice currently for further hydrophobic performance. Referring to many natural and artificial hydrophobic surfaces with micropillars on the surfaces, we can see the distances between the micro pillars were all close to or even smaller than the height of micro pillars to prevent the intrusion of water droplets, while for our responsive film, the pattern on our surface depends on the mask used in the local UV illumination. The distance of each unit on the mask was in tens or hundreds micrometers while the largest height of protrusions we got on the surface was lower than 1 μm. The height difference we had was much smaller than the spacing of the structures on the surface and this facilitates the intrusion of water droplets into the protrusions. However currently we had not such photomasks available for use. If the distance of protrusions on the surface could reach to 1 μm or even smaller value, the hydrophobicity might be much higher than the current stage.

2.2.4 Study of protrusion height on corrugated surfaces

2.2.4.1 Deformation time of the surface topographies

An important feature for surface topography is the height of protrusions or deformation strain on the corrugated surface. We performed several control experiments to further investigate the factors that affected the height difference and deformation strain.

The exposure time for the formation of surface structures was studied. We used the grid mask to conduct this series of experiments. Figure 15 showed the different deformation strain on the surface under UV illumination with maximal UV intensity for different duration from 10 minutes to 2 hour. Deformation strain increased with increasing time and then leveled off. The surface structure formed under 10 minutes had height deference within 100nm, while the 1hour increased to nearly 0.8μm with the deformation strain of 6.15% and above 1h the strain did not show its time-dependence. With longer duration as 2 hours, the protrusion strain did not increase further. This indicated that either longer time was needed for molecules to reorganize themselves because of the viscoelasticity of the polymer network or the sufficient UV dose was required for the fully isomerization of azobenzene because of its photo-chemistry.

![Figure 15 Strain of protrusions formed on the surface of cholesteric polymer film under UV exposure with maximal intensity through a grid mask for different duration.](image-url)
2.2.4.2 Effect of UV intensity in the illumination process

There are other factors related to protrusion height and deformation strain of our light responsive film surface for example the density of light-responsive azobenzene or the concentration of chain transfer agent, as well as UV intensity. In this project we kept composition of monomer mixture unchanged since the previous study had proven its optimum. The UV intensity was adjusted to investigate its effect on surface deformation. Figure 16 showed the relationship between deformation strain and UV intensity under the same exposure time 1 hour and experiment setup. We used both grid and dot pattern to conduct the experiments. UV intensity was measured by UV power puck (EIT standard Power Puck) in the range of UVA (wavelength 315-400nm) in accordance with the absorption wavelength of azobenzene (365nm).

The deformation strain of the surface with both patterns increased with the increasing UV intensity and then leveled up over 650mW/cm². There was no larger deformation strain observed even up to 1000mW/cm² for both patterns. Dot pattern had larger deformation strain than grid pattern under the whole range of UV intensity. With grid pattern, under the UV intensity of 668mw/cm² the deformation strain reached up to 6% while the deformation could not be observed at the intensity of around 100mw/cm². Between the intensity ranges from about 550mw/cm² to 650mw/cm² the deformation strain increased much faster than that under lower UV intensity. However with dot pattern, the deformation strain increased gradually with the intensity and the highest deformation strain was 7.3%. This demonstrated UV intensity plays a significant role in the formation of protrusions on our light responsive films. To get larger deformation and higher protrusions on the surface, UV intensity around 650mW/cm², which was close to the maximal UV intensity of a single UV lamp, is proposed to use for illumination.

Figure 16 Deformation strain on the surface of cholesteric polymer film by local UV illumination in grid pattern and dot pattern with different UV intensity. Red line was the result of films with surface topography of dot pattern and blue line was of grid pattern.
2.2.4.3 Contact angle increase of the corrugated surfaces

The protrusion height determines the surface roughness and greatly contributes to hydrophobicity. To investigate the relationship between protrusion height and hydrophobicity, we conducted contact angle measurement on surfaces with different protrusion height. Both of the two patterns were used for a comparison. Figure 17 showed that the contact angle increases with the increasing height of protrusions with both patterns on the surface. The maximal height of 0.8 μm with grid pattern we got resulted in an increase of 23° in contact angle while with dot pattern the maximal 1.25 μm brought about 9° increase in contact angle, much smaller than the grid pattern. When the protrusion height lowered the contact angle increase reduced correspondingly and under the same protrusion height the surface with grid pattern always had more contact angle increase than the one with dot pattern and the reason explained before. It can be concluded that with the same pattern higher protrusion led to larger contact angle and the grid pattern induced more hydrophobicity on the surface.

Figure 17 The effect of protrusion height of a corrugated surface on the contact angle increase.
2.3 Surface Modification

The surface of cholesteric polymer film was moderately hydrophilic with a contact angle of 75°±3°. After actuation of surface topography, the contact angle reached up to maximal 98° which was still not qualified as a hydrophobic coating. Under this consideration chemical modification on the surface of our cholesteric polymer film is necessary to further increase its hydrophobicity.

Currently we modified the surface via silanization with fluorinated groups. Many reports have studied and confirmed the improved hydrophobicity of surfaces functionalized by fluorinated alkyl silane. Due to weaker interfacial dispersion forces associated with fluorocarbons, the terminal fluorinated alkyl chains results in lower surface tension and larger contact angle of water. Several authors also have been studied wettability trends of fluorinated layers and results showed factors which contribute to the ability of an organosilane to generate a hydrophobic surface are organic substitution, the extent of surface coverage, residual unreacted groups (both from the silane and the surface) and the distribution of the self-assembled silane on the surface.

The 1H,1H,2H,2H-perfluoro-dodecyl-trichloro-silane we used has trichloro groups to ensure its reactivity. Many researches have succeeded in making hydrophobic and superhydrophobic materials with this silane on different surfaces. The longer fluorinated alkyl chains led to a better water-resistant performance. The distribution of the chemical adsorption sites on the substrate is the driving force for silanization, so the surface is pre-treated with short-time oxygen plasma to get more oxygen-containing sites on the surface in order to facilitate silanization.

The silanization process is illustrated in Figure 18. The sample was firstly pre-treated with oxygen plasma to create reactive sites and then silanization reaction was conducted.

![Figure 18 Scheme of the silanization process. First, use oxygen plasma to create more hydroxyl groups on the surface and then modify with silane via vapor phase in 90°C for 20 minutes.](image-url)
After silanization via vapor phase, contact angle measurement was conducted, showing surface energy was lowered and the contact angle increased from $75^\circ \pm 3^\circ$ to $116^\circ \pm 2^\circ$ (Figure 19), indicating a conversion from hydrophilicity to hydrophobicity. This support that fluorinated groups had successfully introduced to the surface and a hydrophobic surface was made by silanization via vapor phase.

![Figure 19 Contact angle increase after silanization. Left: contact angle of flat film without silanization is around 76°. Right: after 20 min silanization, the contact angle increased to about 116°.](image)

2.4 Actuation of surface topography based on silane-modified films

The UV exposure activated the surface structure and the contact angle increased by $23^\circ \pm 2^\circ$ in the case of grid pattern, meaning the approach of creating surface roughness led to an improved hydrophobicity. In the meantime, chemical modification by silanization on flat surface without patterned structure also increased contact angle to $116^\circ \pm 2^\circ$. Both of the two approaches proved effective for higher hydrophobicity. The next issue was the combination of two approaches.

2.4.1 Surface topography with grid pattern

2.4.1.1 Importance of washing step after silanization

We did the silanization first, followed by local UV illumination using the grid pattern. In the practice, we found that the washing step after silanization was important for the formation of surface topography and hydrophobicity performance. Without the washing step, the contact angle increased from $75^\circ \pm 3^\circ$ to $116^\circ \pm 2^\circ$ after chemical modification and it decreased to $111^\circ \pm 1^\circ$ after UV illumination.

![Figure 20 Contact angle changes in the process of silanization and UV activation: contact angle of flat surface (Left), flat surface modified by silane (Middle) and corrugated silane-modified surface (Right).](image)
Surface topography (Figure 21) showed an unclear pattern and the protrusion height was under 0.4μm. The 3D image indicated protrusions were not fully formed on the film and the pattern was incompletely under UV actuation.

Surface profile of silane-modified film without washing step was checked by interference microscopy and the result (Figure 22) showed a flat surface with silane aggregates on the surface. After washing step, surface profile showed the height difference reduced without aggregates on the surface.

The thickness of unmodified film was 6 μm and after silanization, the thickness increased to 6.4± 0.1 μm. The film was then cleaned and washed with solvent and distilled water and its thickness reduced to 6.04±0.1 μm. Figure 23 clearly showed the surface profiles. The washing step was necessary for a flat modified surface to eliminate excess silane and especially aggregates on the surface.
At the same time, it was also observed that the contact angle slightly increased to $121^\circ \pm 3^\circ$ (Figure 24) after washing out the aggregates. It was probably because the aggregates may induce the penetration of water into the aggregates, so washing step played an important role to maximize the hydrophobic effect of silanization.

UV actuation was conducted on the silane-modified film with washing step. Protrusions were fully formed on the surface and the pattern was clear (Figure 25). Protrusion height was close up to 0.7μm corresponding to a deformation strain of 6% the same as the corrugated unmodified film.

Contact angle was measured before surface modification, after surface modification and after the formation of protrusions on the surface. The results (Figure 26) showed that the contact angle was still reduced by 6° after UV illumination.
2.4.1.2 UV illumination in N₂ box

It is known that hydrophobicity is not only related to surface structure but also related to chemical composition on the surface. To avoid any change in surface chemistry, we used N₂ box in the UV illumination procedure for silane-modified films. Contact angle measurement was conducted after actuation of surface topographies. Figure 27 showed the results. With the formation of protrusions on the surface, the contact angle increased from 121° ±3° to 136° ±3° which means the usage of N₂ box was effective for further hydrophobicity.

![Contact angle changes after the process of silanization with washing step and UV activation of silane-modified cholesteric polymer film with grid pattern: contact angle of flat surface (Left), flat surface modified by silane (Middle) and corrugated silane-modified surface (Right).](image)

There was also negative effect of N₂ box. With the glass cover of N₂ box between UV lamp and sample, the UV intensity illuminated on the sample surface was 502mW/cm² and reduced by 26% compared to maximal UV intensity of UV lamp. As a consequence the height difference as well as the deformation strain of the surface was much lower than the films actuated under maximal UV intensity. According to Figure 16, we could expect a deformation strain of 1.8% under this lowered UV intensity. The result of the film UV-actuated in N₂ box was the same as expectation. The surface measurement of silane-modified film (Figure 28) showed it had protrusion height of 0.2 ±0.05 μm and the deformation strain was around 2% with reduced UV intensity inside N₂ box.

![3D image and surface profile in cross-section of surface topography of silane-modified cholesteric polymer film with grid pattern after UV illumination in N₂ box.](image)

Figure 29 as a derivative chart of Figure 16 clarified this comparison. From these facts, it can be concluded a lower UV intensity caused by the usage of N₂ box contributed to a smaller deformation strain. However, using N₂ box was necessary as mentioned above to prevent further oxidation on the surface which affects more in aspect to hydrophobicity.
Even with a lower deformation strain, the silane-modified film can still have a highest contact angle of 139° under UV actuation while the contact angle was lower when the film was flat before UV illumination. The stability of surface protrusions and hydrophobic performance was tested by heating the film above T_g and its surface topography and contact angle kept same after reheating. After storing in the dark for months, its performance remained the same.

In order to clarify the roles of washing step and illumination in N_2 box, Table 1 was made to compare the contact angle and deformation strain of each different sample. Washing step was necessary for the formation of clear surface topography and better hydrophobicity. UV illumination in N_2 box was critical to get larger contact angle with corrugated surfaces though it brought reduced UV intensity.

<table>
<thead>
<tr>
<th>Fluorinated surface</th>
<th>Without washing step</th>
<th>With washing step</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>flat</td>
<td>corrugated</td>
</tr>
<tr>
<td>Contact Angle(°)</td>
<td>116±2</td>
<td>111±1</td>
</tr>
<tr>
<td>Deformation Strain(%)</td>
<td>0</td>
<td>unclear</td>
</tr>
</tbody>
</table>

*Table 1 Contact angle and deformation strain on the surfaces of different samples.*
2.4.2 Surface topography with dot pattern

The silane-modified cholesteric polymer film had an increase of the contact angle of 15° after local UV illumination with grid pattern which proved this switchable hydrophobic coating was successfully fabricated. Since dot pattern is the most obvious approach to the surface topographies of lotus leaf and other artificially hydrophobic coating, we also used dot pattern in the UV illumination of silane-modified film to check its performance and compare with grid pattern. The dot mask was the same as the one we used in the actuation of surface topography on unmodified films with dot size of 25μm and a distance of 75μm. The comparison of hydrophobic performance between two topographies was conducted under the same protrusion height of 0.2 μm. According to Figure 16, UV intensity inside the N\(_2\) box for UV illumination should be controlled around 200mW/cm\(^2\). The other experiment conditions and setup were the same as the UV illumination with grid pattern. Figure 30 showed its surface topography of dot pattern with the designed protrusion height.

![Figure 30 3D image and surface profile in cross-section of surface topography of silane-modified cholesteric polymer film with dot pattern after UV illumination in N\(_2\) box.](image)

Contact angle was measured after each step and Figure 31 showed the final contact angle was around 124°±1°, which was lower than the final contact angle of films with surface topography of grid pattern through the protrusion height of both corrugated surface was almost the same. This result was expected and the reason was explained in the section of actuation of surface topography based on unmodified films. Grid pattern was more efficient in preventing the movement of three-phase contact line of water droplets and the further spreading of water droplets on the surface.

![Figure 31 Contact angle changes after the process of silanization with washing step and UV activation of silane-modified cholesteric polymer film with dot pattern: contact angle of flat surface(Left), flat surface modified by silane (Middle) and corrugated silane-modified surface (Right).](image)
2.4.3 Wettability on different surfaces

In order to bring the results together Table 2 compares the contact angles on different surfaces based on cholesteric polymer films. The two patterns we used were listed and each of them was divided into four conditions, surface fluorinated or non-fluorinated, flat surface or corrugated surface. As we discussed before, the unmodified surfaces were hydrophilic with contact angle around 75° while the contact angle was still below 90° with the 0.2 μm protrusions on the surfaces. Silane-modified surfaces performed hydrophobicity with contact angle of around 120° in the flat state. When the surface deformed, the contact angle increased to maximally 139° for topography of grid pattern and 125° for topography of dot pattern. From all the results we got, the UV-actuated silane-modified cholesteric polymer film with topography of grid pattern had the highest contact angle.

<table>
<thead>
<tr>
<th>Pattern of surface topography</th>
<th>Flat surface</th>
<th>Surface with protrusion height 0.2um</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface chemistry</td>
<td>Fluorinated</td>
<td>Non-fluorinated</td>
</tr>
<tr>
<td>Contact angle</td>
<td>121±3</td>
<td>75±3</td>
</tr>
<tr>
<td></td>
<td>136±3</td>
<td>80±3 *</td>
</tr>
<tr>
<td>Fluorinated</td>
<td>118±1</td>
<td>77±3 *</td>
</tr>
<tr>
<td>Non-fluorinated</td>
<td>75±3</td>
<td>75±3</td>
</tr>
</tbody>
</table>

Table 2 Contact angle of different surfaces of cholesteric polymer film. (* These values were calculated from Figure 17.)
Conclusion

In previous studies, we found out an increase in hydrophobicity of a responsive cholesteric polymer film when the surface was converted from flat state to corrugated state under UV illumination. The objective of this project was to further improve its hydrophobicity. According to the factors related to wettability, we approached this in two aspects. One was to lower surface energy; the other was to increase surface roughness and create surface structures.

In order to create the surface roughness, we created light responsive surface topographies in cholesteric liquid crystal polymer network via patterned UV exposure. It was achieved by adding small amount of azobenzene as crosslinkers in the polymer system. The photo-isomerization of azobenzene reduced the order parameter of the liquid crystal network with the reorganization of molecular units, leading to a decrease in density and an increase in volume. By local exposure under different photo-masks, the surface structure was created in a pre-designed pattern. Topography of grid pattern and dot pattern were studied in this project because the better performance in deformation and hydrophobicity. After actuation of surface topography with grid pattern of cholesteric polymer film, the height of protrusions reached up to 0.8μm corresponding to 6% deformation strain. The conversion from flat surface to corrugated surface led to an increase in hydrophobicity and its contact angle increased 23° with the formation of corrugated surface. For dot pattern protrusion height was 1.2 μm corresponding to 7% deformation strain however its contact angle increased less than that with grid pattern, because its topography provided less obstruction of the moving of three-phase contact line on the surface.

Factors that affect the protrusion height or deformation strain were studied included the time for formation of surface structure. UV intensity was related to the deformation strain and under UV intensity of around 650mW/cm² we got the highest deformation strain. The studies of protrusion height related to hydrophobic performance were elaborated in the text as well as a detailed discussion about the topographies formed on the surface.

Considering that the surface of cholesteric polymer film was not hydrophobic enough, we used chemical modification with fluorinated groups to lower surface tension of our films. Treated with 1H, 1H, 2H, 2H-perfluoro dodecyl trichloro silane via vapor phase, the surface modification led to an increase in contact angle of water from 75±3° to 121±3° and changed the LC polymer film from hydrophilic to hydrophobic. In addition, the washing step after silanization was important as discovered in the experiment.

In order to create the surface structures the UV exposure was performed in a N₂ box was in order to prevent the chemical change of the silane-modified surface. After UV illumination, silane-modified surfaces with a grid pattern had a protrusion height of 0.2μm and 2% deformation strain. The lowered deformation strain was caused by a reduced UV intensity within N₂ box in the illumination process. The contact angle went up to maximal 139°, close to a superhydrophobic surface. Thermal stability of surface topographies was checked and there was no relaxation of surface structures. The dot pattern was also used in the actuation of surface topography for a comparison of performance between the two patterns, and with the same protrusion height the contact angle only increased by
7°. Based on silane-modified cholesteric polymer film, the surface topography with grid pattern performed better.

In conclusion, low surface energy was made by surface silanization of cholesteric polymer film and surface roughness was created by actuation of its light responsive surface topography. The switchable hydrophobicity was successfully achieved by cholesteric polymer film with fluorinated surface. The best result came from the film with surface topography of grid pattern whose contact angle changed from 121±3° to maximal 139° after UV illumination.
Outlook

We have achieved switchable wettability for hydrophobic coatings based on switchable surface topographies of light responsive liquid crystal polymer network.

In this project, the method we used to lower surface tension was silanization via vapor phase. Other methods are also feasible for example polymerization of a fluorinated layer on the surface or add fluorinated compounds into monomer mixture for polymer films. For instance spin-coating an ultrathin layer of amorphous Teflon (Teflon AF, DuPont) might be possible.

There are great potential to further improve the surface up to superhydrophobicity by a better setup of UV illumination process. Improving the sensitivity of the films might lead to lower UV doses thus reducing the sensitivity for oxidation. There could be a better choice of photo masks used in the UV illumination to have a more intensive pattern and thus more hydrophobic topography. Furthermore, the cholesteric polymer film can be made to have dynamic surface topographies so that with the UV light on and off, the surface structure can be switchable and the wettability can be controlled between the high and low contact angle.

Different from the cholesteric phase with pitch axis perpendicular to the surface used in this project, the self-assembled chiral nematic polymer network with planar pitch axis can also made hydrophobic by adding fluorinated acrylate in it. The corrugated surface has random fingerprint-like topography which is favorable for a hydrophobic coating. Furthermore, the multi-domain liquid crystal polymer film with fluorinated compounds is recently developed and it converts from a slightly hydrophobic to hydrophobic state with 15° contact angle increase and the height difference of random protrusion is over 1 μm which is positive for superhydrophobicity. We have tried these two methods and they have not been studied deeply but the initial results indicated they might be achievable as switchable hydrophobic coating. Following researches can focus on these two approaches.
Experimental Section

5.1 Materials

The mixture of materials we used is shown in Figure 9. Monomers 1-3 were obtained from Merck UK. Monomer 4 was from BASF. Monomer 5 was custom-synthesized by Syncom (Groningen, Netherlands). 6 is bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide, the photo initiator for polymerization. 7 is p-methoxyphenol, the inhibitor. The mixture contained 19.6 wt% 1, 41.82 wt% 2, 30.77 wt% 3, 3.33 wt% 4, 1.96 wt% 5, 0.98 wt% 6, 2.0 wt% 7.

5.2 Sample Preparation

5.2.1 Formation of Polyimide Alignment Layer

Polyimide AL 1051 (JSR Corporation Japan) was spin-coated on clean glass substrates. After evaporation of the solvent at 100°C for 10 minutes, it was baked at 180°C for 90 minutes and rubbed with a polyester fabric in one direction.

5.2.2 Fabrication of Thin Coating of Cholesteric Polymer Network

Two glass plates were closely placed with the PI-treated substrates in the parallel direction of rubbed polyimide. The monomer mixture containing material 1-7 were capillary filled between two glass plates at 90°C. After completely self-filled, it was removed from hot plate and its appearance changed from transparency to translucency, because the decreasing temperature led to phase transition from isotropic liquid phase to nematic phase. It was pulled a bit back and forth in the direction of rubbing to help the formation of cholesteric phase and then cured by UV light using a mercury lamp (EXPR Omnicure S2000) for 5 minutes. The whole glass plates were covered with a cut-off filter (New FSQ-GG400 filter) to eliminate the UV wavelength below 400 nm. The samples were post-cured at 120°C for at least 10 minutes to ensure higher curing of acrylate monomers and slowly lowered temperature to avoid free volume build-up by fast-cooling. The thin films were attached to one of the glass substrates after they were separated by cutters.

5.2.3 Surface Modification

The film was pre-treated with oxygen plasma (Etitech K1050X) under 20 ml/min O₂ flows for and microwave power at 75 W for 30 seconds. The silanization reaction was conducted in a glass vial with a small amount of perfluorododecytrichlorosilane in it and a film glass plate covered on it. The vial was placed on a hot plate at 90°C and the reaction lasted for 20 minutes. The silane was vaporized and diffusion inside the vial was sufficient for an even distribution of silane on the sample surface. For washing step, acetone and distilled water was used after the temperature of films lowered.

5.2.4 Formation of Permanent Surface Topographies

The UV exposure was lasted for 1 hour at 80°C through a photo mask with the UV intensity between 0-700mW/cm² by EXPR Omnicure S2000 (in a N₂ box for silane-modified film). After UV exposure, the
film temperature must be reduced fast. The patterned protrusions corresponding to the different masks can be observed and kept stable after formation.

5.3 Characterization

5.3.1 3D Interferometer

The surface topographies were measured using a 3D interferometer (Fogal Nanotech Zoomsurf). The protrusion height and film thickness was measured by its surface profile in cross-section.

5.3.2 Contact Angle Measurement

The contact angle was determined by OCA 30 contact angle measuring system (DataPhysics Instruments GmbH, Filderstadt) with software SCA 20. Static contact angle images were obtained by camera using sessile drop method.

5.3.3 UV-Vis spectrometer

The UV-Vis spectroscopy of the films was taken by LAMBDA UV/Vis/NIR spectrophotometer from PerkinElmer and UV-Vis spectrometer UV-3102 from Shimadzu.
References

44. Akira Nakajima, Kouki Abe, Kazuhito Hashimoto and Toshiya Watanabe, Thin Solid Films, 2000, 376, 140-143.
Appendix

Part 1 Characterization of LC monomer mixture and cholesteric polymer film

A Varian-3100 FT-IR spectrometer was used to measure IR spectra. Referring to monomer sample, new signals at 1636, 1035 and 985 cm\(^{-1}\) appeared. The absorption at 1636 cm\(^{-1}\) (Enlarged view B) was contributed to the C=C stretching from the acrylate and the absorptions at 1035 and 985 cm\(^{-1}\) (Enlarged view C) were the C-H bending from vinyl group. These absorption peaks could not be clearly observed from the polymer sample and this indicated the high conversion of acrylate. Another prove for this was that the peak at 1730 cm\(^{-1}\) (Enlarged view A) slightly changed which was the absorption from C=O stretching bond.

Figure 32 FT-IR spectra of the monomer mixture and cholesteric polymer film.

\[\text{Figure 32 FT-IR spectra of the monomer mixture and cholesteric polymer film.}\]
Part 2 Characterization of silane-modified cholesteric polymer film

After the fluorination of the cholesteric polymer film, elemental percentage on the film surface changed. From the results of the XPS (Table 3), there was no chlorine groups observed on the surface of the film after silanization which indicated the silane was hydrolyzed. Atom percentage of fluorine groups had a significant increase and that of carbon and oxygen reduced. These facts showed the hydrophobic elements were introduced on the surface after silanization.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atom%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C 1s %</td>
</tr>
<tr>
<td>Before silanization</td>
<td>78.1</td>
</tr>
<tr>
<td>After silanization</td>
<td>34.2</td>
</tr>
</tbody>
</table>

Table 3 Results of XPS elemental analysis of the cholesteric polymer film surface before and after silanization.

From the XPS results, we could not know any information of the bonding between the polymer network and the silane. Based on this concern, FT-IR was used to check the bonding formation. The FT-IR spectrum of the sample after surface modification (Figure 33) had no signals for Si-OH bonding, which were expected between 3600 and 3700 cm\(^{-1}\) and around 900 cm\(^{-1}\). With the XPS result of no chlorine groups on the surface, this was the initial evidence that the hydrolyzed functional groups of the silane were likely to react with the polymer network. In addition, there were small peaks at around 3400-3500 cm\(^{-1}\) and two signals appeared at 1700 and 1370 cm\(^{-1}\). The absorption of 3400-3500 cm\(^{-1}\) and 1700 cm\(^{-1}\) may come from oxidation and signal at 1370 cm\(^{-1}\) belongs to the Si-C bonding of silane itself. The Si-O-Si absorption at 1030 cm\(^{-1}\) was not visible in this spectrum, so there was no evidence for the self-condensation of silane.

Figure 33 FT-IR spectra of the unmodified cholesteric polymer film and silane-modified film.
Acknowledgments

First and foremost, I have to thank my research supervisors, Prof. Dr. Dick Broer and Dr. Danqing Liu. Without their assistance and dedicated involvement in every step throughout the process, this study would have never been accomplished. I appreciate them very much for their support and understanding over these past ten months. I would also like to show gratitude to my committee member, including Dr. Ing. Cees Bastiaansen as the chairman of graduation committee, Prof. Dr. Rint Sijbesma as the member from other research group and Prof. Dr. Albert Schenning as the expert professor in the group.

In April 2014, I entered SFD group (Functional Materials and Devices) to start this master graduation project. My time at SFD has been highly productive and working with was an extraordinary experience. Dr. Danqing as an experienced researcher helped me to involve in an academic environment and find my own solutions to problems. Prof. Dr. Dick Broer kindly assisted me with the analysis in this dissertation and was very patient with the answers of my questions and comments of the report. In the past ten months I got a lot academic support from every member in SFD group and I have many, many people to thank for listening to and discussing with me about the experiments, results and analysis. I express my gratitude and appreciation for their help and friendship. Tom bus as the technician provided the instruction and training for the lab equipment and chemicals. Jeroen ter Schiphorst, Sander Kommeren, Koen Nickmans, Anne Hélène Gelebart, Kamlesh Kumar, Monali Moirangthem and other PHD students as well as Dr. Michael Debije were willing to help me in the laboratory and also discuss with me about my research in the cluster meeting. Also thanks Marjolijn Pessers, secretary in SFD group for the help of arrangement and schedule.

Most importantly, none of this could have happened without my family. My life is filled with their unconditional love and encouragement. Without their support, I have no chance to study abroad and do a project in TU/e.