Light Responsive Polymeric Systems

Based on smectic/ homeotropic network stabilized liquid crystal

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In this work, a substrate constrained soft polymeric film has been created by photo-polymerization of a mixture of liquid crystal (LC) monomers and non-reactive liquid crystals. These films form a network-stabilized LC systems aligned homeotropically in the smectic phase. The network is incorporated with a photo-responsive azobenzene mesogen.

By using such alignment, in-depth deformation up to 10 % is obtained. The deformation is reversible and can be repeated many cycles without showing any fatigue.

Furthermore, the system is able to release the non-reactive molecule upon exposure to UV light. While the network contracts, the non-reactive part is displaced toward the surface where droplets are formed which finally convert to a uniform film. We investigated different alignment during this study and it results that polymer-stabilized smectic phase gives the best results in terms of deformation and amount of 8CB released.

Finally, we showed that the non-reactive mesogen can be replaced by other molecules (5CB and EHA have been investigated) by using dichloromethane as exchange solvent. The resulting network can also be actuated with similar properties of in-depth deformation (over 8%) and releasing the new material that is entrapped in the network.
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1. Introduction

1.1. Project theory

a) Smart material

Nature has developed functional, outstanding and smart properties based on their unique and dynamic surface structures which are self-controlled or sensitive to surrounding environment. For example, gecko can walk freely on vertical objects with the ability to stick to the surface in a large force and can also release this force easily. Pine cone can be responsive and adaptive to surrounding environment based on the different expansion speed of inner layer and outer layer with the change of humidity. When wounded by insects or attract predators, tomatoes can self-release some chemicals as an alarm signal so that plants in the neighborhood will prepare for the defense. Chameleons are able to change their skin coloration for functions in social signaling and in response to environment, as well as in camouflage.

These wisdoms of nature are always a source of inspiration for human technical development. Many new materials with superior properties such as super adhesion, structural coloration, hydrophilicity, hydrophobicity have been mimicked from nature by human beings in a static way. These fixed functional properties are often achieved by topographical structures down to a resolution of micro/nanometers by lithography or embossing. But for modern applications, static functional properties are not enough. People realized that stimulus-responsive material which has dynamic rather than static properties would bring more benefits. For this reason, it has become a research interest to make these static functional properties be “smart” to surrounding environment. The functional properties can be adjusted autonomously in a pre-determined manner with an external trigger, which can bring higher effectiveness, better control, and more sustainability. Here we can define “smart materials” as materials that have reversible properties. It can revert back to its original state after the stimuli is removed or changed, and this cycle can be repeated. External stimuli can be temperature, humidity, pH, light, applied electricity, and magnetic field.

One example of humidity-sensitive smart material has been developed by J. Stumpel et al. An IPN optical sensor based on a cholesteric network structure stabilized with 5CB is made. Cholesteric structure has the property to act as Bragg reflector and can reflect the light with the same wavelength as the length of the pitch. The cholesteric structure is frozen by photo polymerization and the 5CB is subsequently removed by heat. In a second step the network is refilled with a water responsive monomer to form an IPN after polymerization. The pitch of the cholesteric network will expand or shrink when the second network will attract or desorb water, resulting in an obvious color shift for this material (illustrated by Fig 1).
Another example of a smart material from our group is a photo-responsive polymeric material with dynamic surface topography made by D. Liu et al. To initiate the light-responsive property, azobenzene units are incorporated in cholesteric liquid crystal network attached to the glass substrate as coating. Upon exposure to UV light, isomerization of azobenzene will reduce the order parameter of the network, resulting in an increase of the cholesteric pitch. In this way, there will be a well-defined protrusion of the surface. This surface topology is dynamic and can be switched on or off in a reversal and fast response way (as shown in Fig 2).

One example of smart materials with liquid release and delivery function are introduced by A. Gutowska et al. Based on the swelling-deswelling characteristics of special hydrogel which are responsive to temperature or/and pH. The hydrogels are obtained by polymerization of sensitive (temperature or pH) monomers such as NiPAAm, BMA, DEAEMA or AAc. The prepared hydrogel was then loaded into a rigid capsule with two releasing holes. After the capsule was immersed in a release medium and the hydrogel was swollen to its equilibrium state, the releasing holes in the capsule would be plugged by the volume enlarged hydrogel. Under an external stimulus, the hydrogel began to shrink, opening the releasing holes and meanwhile mechanically squeezing some of the swollen solution from gel matrix into the capsule, and then freely diffused outside through the releasing holes (a schematic outline of this material is presented in Fig 3).
Inspired by previous work of IPN based optical sensor and photo-responsive dynamic surface topography mentioned above, we also tried to achieve a dynamic and smart material based on liquid crystalline polymer. We choose light as external trigger and induce azobenzene molecule to make our material light-responsive “smart”. With cooperative effect from liquid crystalline polymer structure, we are aiming to transfer this molecular light-sensitive property to a macroscopic light-responsive property.

b) Liquid crystal polymer

Liquid crystal (LC) is an intermediate state in between conventional isotropic liquid and anisotropic crystal. It combines some typical properties of the liquid (e.g., no fixed shape, fluidity) as well as some crystalline properties (molecules organization, anisotropy in optical, electrical, and magnetic properties). Due to steric repulsion by anisotropic shape, LC molecules can have phase stability optimal at some intermediate state of orientation with long range order in 1 or 2 dimensions.

In general terms LC’s can be classified as two families; thermotropic liquid crystals for which the phase state changes with temperature; lyotropic liquid crystals for which the phase state changes with the concentration of LC solution. In this thesis, we deal with thermotropic liquid crystal, for which, by decreasing the temperature from isotropic state to crystalline state, several LC phases may exist, which are characterized by the orientational order. In general, the highest degree of order occurs at the lowest temperature. Three of the most common LC phases are the following; nematic, cholesteric and smectic phases, (Figure 1).

- Most current LC phase in rod-like LCs is the nematic phase with long range order in one dimension. Molecules have only directional order but no positional order.
- The cholesteric phase is induced by chiral molecules. Cholesteric phase is a special case of nematic LC. The molecules are rotating to form a helicoidally structure.
- The smectic phase is long range ordered in 2 dimensions. Besides the directional order, the molecules also have positional order with center of gravities aligned in layers, but no configurational order within the layer. For smectic A phase (S_a or SmA), the direction of organized molecules is perpendicular to layers, while for smectic C phase (S_c or SmC), molecules are tilted in compared with SmA phase.
Without precautions liquid crystals form multiple domains and have different directors within each domain. Different methods have been found to promote mono-domain alignment, such as boundary surface treatment, linear polarized light photo-polymerization (LPP), SiO₂ evaporation and Langmuir-Blodgett film. With these methods, the LC molecules can be aligned in planar (molecules are parallel to the surface), homeotropic (molecules are perpendicular to the surface) and tilted (orientation in between homeotropic and planar). Homeotropic alignment is aimed for this study. To do so, we combine boundary surface silane treatment with an electric field.

Liquid crystal monomers are LC molecules with polymerizable end groups such as (meth)acrylates, vinyl ethers, epoxides, thiol-enes or oxetanes. These molecules have the ability to build up a polymer with liquid crystal aligned structure. Liquid crystal polymers are mainly divided into 3 families; LC main chain polymers, LC side chain polymers and LC networks (Figure 2).

For the reason that the polymerization temperature often conflicts with the temperature control for liquid crystal phase formation and maintenance, people generally use the photo polymerization approach instead of thermal polymerization to make liquid crystal polymer. Induced by UV light, free radicals are released by the photo-initiator and react with the double bonds of the monomers. By this method, the three-dimensional liquid crystal ordered structure can be maintained during the polymerization. In this study, we aim to make highly crosslinked polymer network which is
thermally stable, and can preserve the liquid crystal organization within a large temperature range. The polymerization process is sketched in Figure 3.

To make our material stimuli sensitive, we incorporate an azobenzene with two reactive end groups into the polymer network to bring the photo-response property, shown in Figure 4. Here we induced the system of network-stabilized liquid crystal (introduced below). In this way, polymer network can follow the orientation of the surrounding LC molecules such as 8CB. The cross link density can be tuned by adjusting the amount of bi-functional molecules (azo-based cross linker and C6H). Lower cross link density allow more motion but mechanical properties are diminished while high cross link density lead to more stiff and rigid polymer but the mobility is strongly reduced.

Light responsive materials can show different properties in response to different wavelength, polarization, direction, or intensity. There have been many reports of light responsive polymeric material with properties such as reversible bending of polymer film, shape memory polymer, release of biomolecules, and formation of surface topology. Since the activating process of such materials can be rapid, clean, localized and remote, light responsive materials have attracted much attention for their potential applications, such as drug delivery, diagnostics, actuators and sensors.
To be photo-responsive, polymeric polymers have to be incorporated with photo-sensitive functional structures or fillers. Figure 5 gives an overview of the most studied light sensitive molecules, which can be classified into three groups\(^{18}\):

a) Photo-isomerizable molecules such as stilbenes and azobenzenes
b) Leuco and spiropyran derivatives that can undergo photo-induced ionic dissociation
c) Photo-dimerizable molecules, such as cinnamates, coumarins, and anthracenes.

As mentioned above, we use azobenzene based molecules to induce the light responsive property in our work for the rapid, reversible and high quantum yield photo isomerization\(^{19}\). Azobenzene is an aromatic molecules with an azo linkage (-N=N-) between two phenyl rings. By substituting the aromatic rings with various substituents, we can get a large group of Photo-isomerizable compounds (usually simply referred to as ‘azobenzenes’ or ‘azos’). Azobenzene have isomers in trans and cis state, which can be switched in a reversible fashion by use of specific wavelength of light (365nm for isomerization from trans to cis, and >400nm for back-isomerization from cis to trans), as illustrated in Figure 6. During this process, there is a large change in the molecular length: the distance between 4- and 4’- carbons decreases from 9.0 Å (trans) to 5.5 Å (cis)\(^{20}\).
With such photo-isomerizable azobenzene molecule, we can find a functionalization process that can transfer effects from the molecular level into macroscopically visible level. From the historical perspective, Agolini and Gay firstly prepared a series of semi-crystalline polyimides containing main-chain azobenzene structure. The thick film they got can reversibly deformed by 0.23% when exposed to UV light at $200^\circ C$. In 1975, de Gennes et al. firstly proposed a theoretical concept of the possibility of uniaxial contraction in the direction of the director axis by the isomerization process of azobenzene molecules embedded into a liquid crystal elastomer matrix, which was later confirmed experimentally by Finkelmann with a liquid crystal elastomer bounded with azobenzene. By adding photo-responsive molecules to a LCN matrix, the network deformation can be a larger scale than the dimensional change of a single molecule. By adding only few percent of a photo responsive molecule, more than 10% network deformation can be obtained. This magnification can be explained by the cooperative motion of the molecules in the vicinity of the molecules that undergoes dimensional changes.

Although there have been many reports of macroscopic deformation of liquid crystalline elastomers incorporated with azobenzene moieties, there still remain some problems to be solved for practical applications. Usually the crosslink density has a great influence on the macroscopic properties and the phase structures of liquid crystal elastomers (LCEs). On one hand, the mobility of mesogenic segment is reduced with an increase in density of cross-linking points, and consequently the mobility of mesogens in the vicinity of a cross-link is suppressed. The magnitude of photomechanical response is reduced with the increasing crosslinking density. On the other hand, the cooperative motion induced by confinement of network may bring larger change than a linear LCP in response to external stimuli. Besides, for more densely crosslinked polymers networks, they do not undergo a phase transition as for the elastomers at ambient temperature. To the contrary, highly crosslinked polymers are stiff and brittle, and it will become difficult for processing. Various methods have been proposed to improve photo-responsive and mechanical properties of LCPs. For instance, Tomiki Ikeda developed bilayer films of crosslinked azobenzene LCPs and flexible polyethylene, and also interpenetrating polymer network (IPN) structures. The IPN films, which are composed of azobenzene liquid crystalline polymer (LCP) and polymethacrylates, show reversible bending behavior upon exposure to UV and visible light with faster bending speed.
Actually, the system we use during our project is neither liquid crystal nor liquid crystalline polymer. Our smart film is made of polymer/liquid crystal composite and has different characteristics from the individual components of liquid crystal and liquid crystalline polymer.

**d) Polymer/liquid crystal composite**

Polymer/liquid crystal composite is made from a blend of polymer with liquid crystal. Compared to liquid crystals, this composite system may have important features such as: the film formation ability, reversible orientation and shape memory ability. Compared with liquid crystalline polymer, this composite system may have more fluidity and flexibility, easier for processing. For these reasons, polymer/liquid crystal composites can offer more flexibility and much richer functionality than LC or LCP alone.

Polymer/LC composites include polymer dispersed liquid crystals, polymer stabilized liquid crystals, LC polymer/LC composites, polymer/ ferroelectric LC composites. They have attracted great interest over last decades, for their potential application as light shutters, privacy windows, or paper like reflective displays.\(^{28}\)

With different monomer concentration, polymer/LC composites can be divided into different categories for their different properties. Polymer –dispersed LCs (PDLCs) are systems dispersed as micro-sized droplets in a continuous and isotropic polymer matrix. For polymer stabilized liquid crystals (PSLCs), LC material represents the continuous matrix, while a small amount of polymer is dispersed in an anisotropic LC phase. These polymers structure are stabilized following the orientation of surrounding LC directors. The presence of polymer network in LC matrix can not only enhances the LC phase stability with larger temperature range, but can also help the LC molecules to return to a desired stable configuration with a shorter response time. PSLC materials are transparent for the initial surface configuration induced orientation of LC and polymer network. But with an external voltage applied to realign LC to uniform directions, the materials can be scattering (illustrated by Fig 10).

![Figure 10: Transmitting (left) and scattering (right) state of polymer stabilized LC](image)
The most common polymer/liquid crystal composite is polymer network-stabilized liquid crystals (PSLC). For the previous work of this material, light-responsive PSLC is reported for promising application of spatial light modulators (SLMs). They do not require a photoconductive or photoelectric layer and electrode. The optical properties of azobenzene liquid crystals can be modified by photo-chemical isomerization and back-isomerization process, resulting in the change of molecular anisotropy. Our project is also to investigate the properties and potential applications of this light-responsive PSLC system.

1.2. Project aim
The main aim of this project is to prepare a thick film made of smectic/homeotropic polymer network-liquid crystal composite. With azobenzene contained smectic/homeotropic network, we try to obtain a light-responsive “smart” material. With polymer/liquid crystal composite system, properties of in-depth deformation and release may also be realized at the same time.

Later, we aim at replacing the released LC within the composite with other materials without destroying the smectic/homeotropic aligned network. In this way, light controlled functions are maintained but further applications are extended. For example, we can make use of this light controlled release property if we replace the non-reactive LC with other functional molecules. This new composite system can be used for light controlled actuator, in healthcare and drug delivery. This refilling material can also be a mixture of monomers and initiator, and thus we can obtain an IPN material after we polymerize the second material within the first network, which may have better mechanical properties over the initial film. This may have potential application in microfluidic device, light triggered robotic.

1.3. Project approach
The approach for our project is briefly illustrated by Figure 11. Firstly, with photo-polymerization method, we try to obtain a thick composite film from a mixture of azobenzene reactive molecule and a non-reactive LC molecule in smectic/homeotropic phase.

After this smectic/homeotropic polymer network stabilized liquid crystal is obtained (initial film), we try to replace the non-reactive LC with other molecules. During this process, the network structure
and orientation is expected to not be destroyed, thus the light controlled properties of new composite can be maintained. For the preliminary try of new material filled film, we choose a molecule similar to 8CB (5CB) and a reactive monomer (EHA) as the refilling materials.

Figure 11: Approach of the project
2. Experimental

Our experimental part can be divided into four sections, 1) the preparation of initial film and its characterization, 2) photo-actuation of the film, 3) new materials refilling and 4) actuation of the refilled film.

2.1. Materials

Below is an overview of the chemicals used in this study.

A6MA is the photo responsive molecule that allows the system to undergo deformations under UV exposure. Indeed, A6MA contains an azobenzene core that can isomerize from the trans to the cis isomer while exposing to 365 nm light. Furthermore, A6MA, as well as RM23 and C6H possess acrylate end groups able to polymerize to form a network. Finally, the 8CB is the non-reactive mesogen. It has a smectic phase at room temperature which is expected to prevent the disruption of
aligned network while storing the initial film at room temperature. Since 8CB is a non-reactive mesogen, it can be exchanged with other molecules to obtain new systems in a later step.

EHA (ethyl hexyl acrylate) will be used in a second time. The aim is to replace 8CB by another molecule, for instance to introduce another property such as mechanical response to a second trigger. We chose for the time being EHA as a model compound, which is nonresponsive. It is chosen as model compound which is chemically sufficient different from 8Cb and is photo-polymerizable. After photo-polymerization it is of interest for its mechanical properties. It is hoped that the low Tg of the polymer will allow the network to deform and speed up the relaxation of the deformation.

Besides these main compounds, for the first step polymerization, Ciba Irgacure 819 is also used as the photo initiator.

2.2. Mixtures preparation
The first step was to prepare a mixture containing appropriate ratio of chemical compounds to obtain a homogeneous smectic/homeotropic aligned system. In our experiment, we prepared the mixture containing A6MA, C6H, RM 23, and 8CB with a ratio of 12/8/10/70 (wt %) respectively and 1% wt of a photo-initiator (Irgacure 819) is added later on.

The whole mixture is dissolved in a large amount of dichloromethane to obtain a homogeneous solution and finally dried under argon for one hour.

2.3. Initial film preparation
The film preparation is a multi-step process as shown in the following picture. It consists of cell preparation, mixture filling, and photo polymerization.

![Figure 13: Procedure for film preparation](image)

a) Cell preparation
In our experiment, we try to obtain a thick film preferentially attached to one of the glass substrate. ITO coated glass plates are used in our study since voltage may be applied to obtain a well aligned sample. This point will be further explained in the next section. After immersion of these ITO plates in ethanol and placed in an ultrasonic bath for 20 minutes, these plates are activated in the UV-ozone (UV-Ozone Photoreactor™ PR-100) for 20 min. The cleaning procedure is required for film preparation because we found that the dust inside the glass cell can easily perturb the final smectic/homeotropic alignment.

After cleaning the glass plates, the two ITO surfaces are spin-coated (3000rpm, acceleration 1000rpm/sec, time 45 sec) with a solution of trimethoxy(octadecyl)silane (promote surface
configuration for homeotropic alignment) and 3-(trimethoxysilyl)propylmethacrylate (promote the adhesion of film with glass substrate). The solution of silane or methacrylate is 100ul of silane or methacrylate in 10ml Ethanol. After placing the coated glass plates on a hot plate at 110°C for 10 min, the remaining solvent is evaporated and a thin coating of silane and methacrylate on ITO substrates is obtained.

During our study, we made initial films with different thickness (6um, 10um, 20um, 50um). For the first three thicknesses, two glass plates are glued together by deposing 2 stripes of glue containing beads with well-defined diameter. For the 50um thick film, two glass plates are stuck together by 2 stripes of double faced tapes. The distance between the glass plates is determined by the thickness of the tapes, which is roughly 50um.

b) Mixture filling and alignment
The mixture is brought to isotropic phase and then injected into the prepared glass cell at 70°C by capillary force. The temperature is chosen to be in the isotropic phase (low viscosity) in order to fill the cell in a relatively short time.

After the cell is filled, it is cooled to 15°C very fast to suppress kinetically crystal formation and macrophase separation inside our system. After this cooling down process, our mixture is in the smectic/homeotropic phase and is observed by microscopy to be homogeneous.

However in our study, we found that for relative thick films (20um, 50um), silane treatment of glass surface configuration is not sufficient to completely induce homeotropic alignment for the whole film. We need to apply external electrical field for better alignment, and this is the reason why ITO coated glass is used for the glass cell preparation. Electrical field is conducted by electrode connected to alternative current (AC) with voltages of 50 Volts (Clairtronic Adaptor). The best timing to apply electrical field is during the cooling down process at about 35°C, where the mixture is in nematic phase.

c) Photo-polymerization
After the temperature reaches 15°C, we can start the photo-polymerization to obtain a polymerized film. UV irradiation for the polymerization was carried out with a high-pressure mercury lamp (365nm). UV intensity was controlled by keeping the distance between the lamp and LC cells the same for each sample (30 cm above the sample). A 400nm cut-off filter is placed at about 15 cm above the sample between the UV lamp and sample to avoid photo-induced isomerization process of azobenzene structure during the polymerization.

The time needed to complete the polymerization at 15°C is dependent on the film thickness. Due to the light extinction effect when penetrating through the film longer time is needed for thick samples. For 6um film, 20 min photo-polymerization is enough. For 50 um film, we need about 1 hour for polymerization. Considering that photo diffusion occurs during the polymerization we expect the cross link density to be higher at the exposed side. Furthermore, as described earlier, we have chosen to use acrylate coating to ensure the adhesion of the film at the surface. Thus, to have the biggest chances to obtain good adherence the acrylate coated plate is placed such that it is toward the light.
2.4. New molecules refilling
To replace 8CB inside our network-LC composite film with other molecules, we tried different solvents to remove 8CB. For the initial film, we place the film in dichloromethane (DCM) for 10 min. Following by evaporation at room temperature for 5 min to remove DCM inside the film, we get a collapsed network film in brittle state. IR and TGA were used to monitor whether all the 8CB has been removed completely.

Once 8CB is removed and DCM is evaporated, the network collapse and it appeared to be very difficult to refill the network. To circumvent this problem, the film is placed in DCM for 10 min. Then the swollen film is transferred into a medium of new molecules (5CB or EHA) at 70°C. In this way, DCM in the film will be evaporated and 5CB or EHA can enter the network gradually. After immersed in 5CB or EHA for 10 min, we get out the new film and use clean tissue to remove remaining liquid material on the surface of new film. The process of refilling is shown as Figure 14.

![Figure 14: Schematic representation for new materials refilling](image)

2.5. System actuation
Both the initial film and new film refilled with 5CB or EHA can be actuated by mean of UV light exposure. The UV light used is an LED light with narrow bandwidth of the wavelength. The films are actuated by exposing with $\lambda = 365$ nm and recovered back with $\lambda = 455$ nm for a certain time.

2.6. Characterization

a) Infrared spectroscopy (IR)
In this work, FT-IR techniques (mainly reflection FT-IR) have been used to identify the compounds present in the sample and to follow the progress in the initial polymerization and refilling process.
The measurement is carried out with a Varian 670IR FT-IR golden gate – Excalibur series spectrometer, using a reflection mode.

The progress in the polymerization is followed with the peak at 1630 cm\(^{-1}\), which is related to the C=C bond of the acrylate groups. When the peak at 1630 cm\(^{-1}\) is completely disappeared, we can consider that the polymerization is complete. The refilling process is followed by the peak at 2220 cm\(^{-1}\), which is related to the C≡N bond of the cyano group (8CB and 5CB) and the peak at 1630 cm\(^{-1}\), which is related to the C=C bond of the acrylate groups (EHA).

**b) Polarized optical microscopy (POM)**
POM is usually used to determine the mesogenic phases and transition temperature for liquid crystals. While changing the temperature of thermotropic liquid crystal, due to the orientation and degree of order, different structures can be observed between crossed polarizers. In order to characterize the temperature range of the smectic phase for our mixture, a temperature control (Instec SRC 200) was placed in the Leica microscope.

In our study, we combined POM with differential scanning calorimetry (DSC) to characterize temperature range for smectic phase of our mixture.

**c) UV-visible spectrophotometer (UV-vis)**
UV-visible spectrophotometry measures the absorption or reflectance of the sample with light in the UV spectral region. UV-vis spectrophotometer can be used to study the kinetic of absorbance and isomerization azobenzene molecule contained in the film. During the measurement, films were placed under UV light for a certain period, and UV-vis spectra were recorde between 700 nm and 320 nm. It is assumed that the time and intensity of the lamp of the machine is very low compare to the UV lamp used for the activation and this light exposure during the measurement will not influence the actuation.

The evolution of the isomerization is characterized by a decrease of the peak at 365 nm and the appearance of the peak at 450 nm. The opposite is also monitored for the back-isomerization study. The equipment used is a Shimadzu UV-3102PC, UV-vis NIR Scanning Spectrophotometer.

**d) Michelson Interferometer**
The interferometer we used is a Fogale Nanotech, Zoonsurf 3D. In this characterization, we use the interferometer to measure the deformation of the film thickness before and after exposure to LED light with wavelength of 365nm and 455nm as well as the initial thickness.

**e) Differential scanning calorimetry (DSC)**
Differential scanning calorimetry was used to measure the exact phase transition temperature range for each phase of the mesogen. In our experiment, we combined DSC data with POM picture of the mixture to know the temperature range we need to keep during polymerization to get the initial film in the phase we want (smectic, nematic and isotropic). The initial film and refilled new film is also analyzed by DSC.

The equipment used is a DSC Q1000. The measurement was realized with a temperature ramp of 1°C/min from -60°C until 150°C. Two cycles were performed.
f) Thermogravimetric analysis (TGA)
For our network-LC composite and network-EHA composite, TGA is a useful measurement to know the ratio of network phase and liquid crystal phase (or EHA phase) inside our films.

This equipment we used is a TGA Q500. In our measurement, we choose to gradually increase the temperature of the oven from 20°C to 600°C in an air atmosphere.

g) Digital holographic microscopy
DHM is a unique technique based on the strength of holography, which enables concomitant recording of both phases and amplitudes of light waves. The most fascinating feature of holography is that it can record and display a complete 2D/3D image of a surface morphology with no scanning and contact of the sample.

The equipment we use is the reflection digital holographic microscopy (DHM-R1000). In our experiment, we use DHM to monitor the liquid release “sponge” phenomenon for initial film and also 5CB refilled new film. During the measurement, we record the process of the surface morphology changing with sample being exposed to light with wavelength of 365nm and 455 nm.
3. Results and discussion

3.1. Mixture phase characterization

To find the best ratio of mixture in order to have an ideal temperature range for smectic phase state for initial film polymerization, different mixtures were analyzed with DSC, light box and POM.

Firstly, we need to investigate mixtures with different amount of components to find the suitable ratio for each molecule. Since A6MA is responsible for the photo-mechanical effect and RM23 is responsible for homogeneous mixing and avoiding phase separation, we aim to use high amount of A6MA and RM23. Meanwhile, a suitable amount of 8CB needs to be chosen to form a polymer-stabilized LC system. After investigation, we found that mixture containing A6MA, C6H, RM23, and 8CB with a ratio of 12/8/10/70 (wt %) can give a homogenous and smectic phase at room temperature which is suitable for our experiment (this ratio may not necessary be the optimal mixture, and this can be further investigated).

The Figure 15 shows the observed phase (POM) and temperature transitions (DSC graph) for the mixture before polymerization. Observed from the polarized optical microscopy, the mixture is first complete black at high temperature, which means that the molecules are in isotropic phase. When the temperature of the mixture is lowered to about 35°C, we can see the schlieren-patterns around the so called dislocations in the structure, which means that our system is in nematic phase. When the temperature of the mixture is lowered to about 25°C, we can see the characteristic line textures for smectic phase. When the temperature reaches about -10°C, rod like structures are formed, which means that our mixture is already crystalline solids.

With DSC measurement, we can know the phase transition temperature more precisely. From DSC figure, we found upon cooling from the isotropic phase that the temperature range for smectic polymerization is between 27°C and -11°C. In our experiment, we took the polymerization temperature at 15°C, 35°C and 65°C for the initial film in smectic, nematic and isotropic phase respectively. These results match with the data we got form POM roughly.
After the mixture is cooled down from isotropic to smectic or nematic phase, the homeotropic alignment can be checked between cross polarizers. If the mixture is perfectly aligned perpendicular to the glass/ITO substrate, the film will be black between crossed polarizers. In our experiment, we found that for thick films we need to apply external electrical field to establish a better orientation of the LC molecules in addition to glass surface silane coating. As shown in Figure 16, before applying an alternative current (AC) to the glass cell, mixture is yellow under polarized light. As soon as an AC voltage of 50 V is applied, the mixture turns black immediately. But when the AC is switched off, the system will return back to yellow slightly. So we need to keep the AC field on before and during the polymerization process, until the network is formed and the homeotropic alignment can be maintained by the network.

Figure 15: DSC couple with POM picture for the mixture

Figure 16: Alignment of mixture before and after AC applied
3.2. Initial film polymerization

To obtain a 100% conversion of the acrylate group, the polymerization process is monitored with IR. The characteristic peak at 1630 cm\(^{-1}\), which stands for the acrylate group, will disappear if the polymerization is complete (shown in Fig 17).

![Figure 17: Comparison of IR spectrum before and after polymerization](image)

During polymerization, there are two ways to place the glass cell. One is silane coating glass side up during polymerization; the UV light penetrates the mixture from silane interface to acrylate interface. Another one is acrylate coating glass side up, and UV light penetrates the mixture from acrylate interface to silane interface. When we place these two kinds of films in DCM, different phenomena can happen. The film polymerized with acrylate coating side up will stay attached to the acrylate coated substrate. But for the film polymerized with silane coating side up, the film will fall from the substrate and become free standing film. This difference may different crosslinking density distributions. For the film polymerized with acrylate coating side up, the crosslinking density at the interface between film and acrylate is strong and the film is attached to substrate strongly. For our experiment, we need the film to stay at the surface during DCM swelling for easy operation of new molecule refilling process. So we choose to polymerize the initial film with acrylate coating side up.

3.3. Isomerization and back-isomerization study

The ratio of A6MA in trans state and cis state can be monitored by the peak at 365nm (trans) and the peak at 460nm (cis) from the UV-vis spectrum. In our characterization, we used the thin (6 um) polymeric film (our original 50 um thickness film is out of measurement range of the UV-visible spectrophotometer). The isomerization and relaxation process can be observed by the change of the peak at 365nm (trans) and the 460nm (cis). As illustrated by Figure 18, with more UV exposure,
there is a decrease of the peak at 365nm (trans) and the appearance of the peak at 460 nm, which means that our system goes from trans state to cis state.

To better understand the kinetic of the isomerization and relaxation process, we also measured the time needed for the film to reach the maximum cis state (isomerization process) and trans state (back-isomerization process) under the exposure of light with 365nm and 455nm respectively. In the isomerization process, the film needs about 10 seconds to reach the maximum ratio of cis state. For the back-isomerization process, the 6 um polymeric film needs about 5 seconds to reach the maximum ratio of azobenzene in trans state when exposed to 455 nm and few hours (>6hr) to relax in the dark at room temperature. The back isomerization with 455 nm light is much faster than the actuation process by 365 nm light, and needs about half time of the actuation process.
3.4. Extinction of UV light

In the above polymerization part, we have already discussed difference of the crosslinking density distribution resulted by the attenuation of UV light intensity during polymerization. Actually, this extinction effect also exists when we use 365 nm LED light to actuate initial film. From the film isomerization study part, we already knew that there is a large decrease for the absorbance peak at 365 nm between initial film (dominant azobenzene in trans state) and fully actuated film (dominant azobenzene in cis state), which means that extinction effect will decrease during the isomerization process of film.

To investigate the extinction effect of 365nm UV light, we prepared films with different thickness (but still relatively thin films in comparison to the films used for actuation to maintain within the measurement range of the UV-vis). With Beer–Lambert law \(A = \log \left( \frac{I_0}{I} \right) = ecL\), we can calculate the extinction coefficient is 1.292M\(^{-1}\)um\(^{-1}\) for initial film (trans dominant) and 0.519M\(^{-1}\)um\(^{-1}\) for actuated film (cis dominant).

![Figure 20: Extinction effect of 365 nm light for initial/actuated film](image)

Also from Beer-Lambert law, we can calculate the relative intensity of 365 nm light compared with initial intensity before penetrating the film and get the UV extinction curve of relative intensity for the initial film and the actuated film with different depth. The extinction curve will gradually change from the red curve to blue one during the illumination time. This is also the reason why the thin film (6um) needs just 10 seconds but the thick film (50 um) needs several minutes to reach maximum actuated state. From this extinction curve, we estimate that after 12um thickness for initial film and 33um for actuated film, the intensity of the light is close to zero at 365 nm.
3.5. Surface deformation

For our initial film of smectic/homeotropic network-LC composite, when partly exposed to 365 nm light for some time, there will be a visible color shift for the exposed area, from yellow to orange, which indicates that the isomerization of azobenzene occurs. When we expose the film locally through a mask we measure by interferometry a contraction (valley) for the exposed area (shown in Figure 22). For the film of 50 um thick, the maximum deformation is 5.4 um, which is over 10% of the initial thickness (shown in Figure 23). This thick film needs more than 4 minutes of exposure to reach the maximum deformation. After the 365 nm light actuation, this deformation can slowly recover back and needs more than ten hours to become flat surface again at room temperature. However, if the deformed area is exposed with 455 nm light, the deformation will recover back very fast, within 2 minutes, which is half of the time for deformation process. This result matches with the isomerization and back-isomerization study described in the section above.
With the thin film of 6 um thick, we repeatedly actuated and relaxed the film with 365 nm light and 455 nm light respectively. As Figure 24 shown, except for the extreme large deformation of 1.0 um for the first time, the deformation and relaxation can be reversible and repeated several times. The possible explanation for the extreme large deformation of first time actuation may be that, the film is aligned with silane surface treatment and AC field in a nice smectic/homeotropic way. But after actuation and relaxation process, although the film surface returns to flat surface again, order degree of the network cannot return back to original state. Compared with never-actuated initial film, order parameter of this film decreases slightly and thus, deformation is slightly smaller.

The explanation for anisotropic deformation of liquid crystal system is discussed in some literatures\textsuperscript{30-31}. This deformation is related with the degree of order of a system $S$, which is the order parameter indicating how well the molecules are aligned. When molecules are randomly aligned in the isotropic configuration, $S$ equals zero. If the system is in an ideal alignment, $S$ equals one. For nematic liquid crystal, typical $S$ values between 0.3 and 0.8. It has been proved that when the system order parameter reduces, the increase average tilt of molecules leads to a decreasing in projection of molecule end-to-end length. The change in length parallel to the director can be estimated using
\[
\left( \frac{\Delta L}{L_0} \right)_S = \left( \frac{2S_T - 2S_0}{2S_0 + 1} + 1 \right)^{\frac{1}{2}} - 1
\]

Eq. 1

In this equation, \( S_0 \) and \( S_T \) stand for the order parameter before and after the change, respectively. \( L_0 \) and \( L_T \) are the corresponding lengths along the director, and \( \Delta L \) equals to \( L_0 - L_T \).

Figure 25: Order parameter reduction induced deformation

For our homeotropically aligned film, due to the reduction of order parameter \( S \) induced by isomerization process of azobenzene structure, there will be a contraction parallel to the molecular director. Here we can have a rough estimation of this contraction induced by order decrease for nematic/homeotropic aligned polymer network. From literature, we can assume the order parameter of nice nematic liquid crystal equals 0.8. For nematic polymer network, the phase transition temperature \( T_c \) has no temperature dependence. After fully actuated by UV light (cis state in dominant), \( S_T/S_0 \) will be approximate 0.75\(^{12} \). Thus from Eq. 1, we can estimate that \((\Delta L/L_0)\) will be -8.01%.

For film in smectic/homeotropic phase, we know that polymer network is in multi-layer structure. Assuming that, the thickness of layer structure of the initial film is the same as the length of A6MA molecule in trans state, 3.4nm. After UV actuation, this layer structure remains but the layer thickness contracts to the length A6MA in cis state (illustrated by Figure 26). We can also have a rough estimation of the film thickness decrease; for thick film of 50 um, there will be about 14706 layers. After the isomerization process, the length decrease of A6MA is 0.4nm, which is also the contraction of each layer structure. For these 14706 layers, the total decrease will be 5.8 um, nearly 11.8% of the initial thickness. This result matches with the deformation results we measured well.

Figure 26: Multi-layer structure contraction induced deformation
3.6. Light triggered sponge

During the measurement of the surface deformation, we found that, after actuated by 365 nm UV light, some liquid droplets at the surface of our film are formed. After placing the film under 455 nm light for several minutes, or dark room for more than 24 hours, these liquid droplets will disappear. We anticipated these liquid to be liquid crystal 8CB squeezed out from the composite film, which can be proved by Fig 27. In this IR spectrum, the peak in 2220 cm$^{-1}$ represents the cyano group in our sample (made of 8CB and RM23). Here we partly exposed the initial film to 365 nm UV light for 5 minutes, and then use a clean tissue to carefully remove all liquid on the surface of exposed area. As shown in Fig 27, green curve is the IR of initial film. Black curve is the IR of actuated and liquid removed film. Compared all the peaks of these two TR spectrums, we can conclude the changes of IR spectrums come from the reduction of 8CB amount, which can indirectly prove that the liquid that is released by the film and removed by tissue is 8CB.

Combined with the IR spectrum of 8CB fully removed sample (red curve), we can have a rough calculation of the 8CB that is squeezed out and removed by the tissue. After all these three IR spectrums are normalized, we know that the cyano peak intensity of red curve 0.076 represents the amount of RM23 within our film. The cyano peak intensity of green curve 0.61 represents the amount of 8CB and RM 23. Thus, the intensity equivalent to 8CB is 0.534. Then the ratio of RM 23 and 8CB is 10/70.26, which matches with the ration of RM23 and 8CB we added to our mixture before polymerization (10/70). The cyano peak intensity of black curve 0.38 represents the amount of remaining 8CB and RM 23. Subtracted by the intensity of RM 23, we can know the intensity of remaining 8CB is 0.304. The percentage of 8CB that is released by the initial film and removed by the tissue is about 43.1%.

![Figure 27: IR spectrum of initial film, tissue removing film and 8CB removed film](image-url)
This interesting “light triggered sponge” phenomenon is further investigated with digital holographic microscopy. 

As shown in the snapshots of the video taken by digital holographic microscopy (Figure 28), during the surface deformation of the film by 365 nm UV light, 8CB liquid was gradually released from the film as a result of squeezing mechanism. With just 2 seconds of UV exposure, we can observe from DHM that the film surface was already full of small and separate droplets. When the deformation reached the maximum, the squeezed-out 8CB droplets are spread over the film surface and transferred from separate droplets to uniform liquid layer. After that, we used 455 nm light to recover the deformation. These liquid will diffuse back into the film gradually. The uniform liquid layer returns back to droplets, and finally all disappear from the film surface. This light controlled release and reabsorb of 8CB can have potential application in microfluidic device or drug delivery biomedical.

**3.7. Comparison of film in different alignments**

To better understand the effects of phase and orientation of network on light triggered in-depth deformation and liquid release properties, we prepared initial films under different condition, such as different temperature for polymerization or different glass cell configuration. As denoted by the DSC graph of the mixture, we did the polymerization at 15°C, 32°C and 65°C to obtain the initial film in smectic, nematic, and isotropic phase respectively. Besides, we also prepared film in smectic/planar alignment for more comparison. During our project, we tried to quantify the amount of 8CB that is released with a tissue to remove the liquid on the surface and measure the weight change of the tissue. But we found this measurement is not reliable since the amount of 8CB released is very
small and the weight change of tissue changes a lot with the pressure we use when removing the 8CB depth. So we choose to qualitatively analysis the release property. As shown in Table 1, the smectic phase has the maximum deformation with 11.56% and nematic phase has the second deformation with 8.42%. These two data match with the rough calculation based on the deformation explanation we mentioned above. These two phases also have nice liquid release property (network with smectic phase better). For film in isotropic or smectic/ planar alignment, we can hardly recognize any deformation or liquid release after UV actuation. From this comparison, we know that there are two requirements for initial film to have the deformation and liquid release properties: 1) network in liquid crystal phase, 2) network-stabilized liquid crystal is homeotropically aligned.

<table>
<thead>
<tr>
<th>Alignment</th>
<th>Smectic/homeotropic</th>
<th>Nematic</th>
<th>Isotropic</th>
<th>Smectic/planar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial thickness (um)</td>
<td>47.6</td>
<td>48.7</td>
<td>50.0</td>
<td>5.5</td>
</tr>
<tr>
<td>Deformation (um)</td>
<td>-5.5</td>
<td>-4.1</td>
<td>-0.3</td>
<td>+0.1</td>
</tr>
<tr>
<td>Deformation percentage</td>
<td>-11.56%</td>
<td>-8.42%</td>
<td>-0.6%</td>
<td>+1.92%</td>
</tr>
<tr>
<td>Liquid release</td>
<td>•••</td>
<td>••</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 1: Comparison of initial films with different alignments

3.8. New material refilling
For further application based on the properties of our initial film, we try to replace 8CB component in the composite film with other materials. To realize this, firstly we need to find a suitable solvent which can remove 8CB from the film. After be placed in dichloromethane solvent for 10 minutes, all 8CB component can be dissolved in DCM solvent and material within the network structure is exchanged by DCM. After room temperature evaporation for 5 minutes, DCM within the network will disappear and only collapsed network remains. This 8CB removing process can also be monitored by the IR spectrum. In the IR spectrum (Fig 29), the peak at 2220 cm\(^{-1}\) represents the cyano bonds. Compared with the initial film, the peak at 2220 cm\(^{-1}\) of the DCM washed film decrease a lot (only a small peak left, which corresponds to the cyano group of RM 23). Quantitatively, this new cyano peak is 13% of the initial intensity. This result matches the amount of CN group in the film, which is divided between RM 23 and 8CB in a ratio 12.5% / 87.5% respectively. So we can conclude that, after placed in DCM for 10 minutes, all cyano group of our film comes from RM23, which means that 8CB in the system has almost been removed.
The samples of initial film and film washed by DCM are analyzed by TGA (Fig 30). For the initial film, the TGA curve shows a 64.37% loss of weight from 150°C until 250°C. After that, the weight of sample becomes stable until 340°C when it starts to decrease again. For sample washed by DCM, the weight loss before 250°C is 3.2%. The weight of the sample starts to decrease also at about 340°C. Comparing the TGA curves of initial film and film washed by DCM, we can conclude that 8CB in the initial film can be evaporated between 150 and 250°C. The weight loss between this temperature range agrees with the percentage of 8CB we added to the mixture before polymerization. At about 340°C the polymer network starts to degrade. For the film washed by DCM, the degradation process starts at the same temperature, which means that the 8CB removing process has not destroyed the network structure. Besides, the small weight loss (3.2%) between 150°C and 250°C shows that DCM washing cannot remove 8CB completely. There are still very few and negligible amount of 8CB dissolved in DCM within the network structure.
We tried to evaporate DCM swelled in our initial film and then refill the polymer network with a second material. But finally we found that once DCM is evaporated from the network structure, the network will collapse and it becomes impossible for the second molecules to enter the network. Finally, we come up with a method to immerse DCM filled film in the new material liquid medium for 10 minutes at high temperature. During this process, DCM will evaporate from the network gradually and meanwhile, new material will also enter the network gradually. In this way, 8CB is firstly exchanged by DCM, and then DCM is exchanged by new material. We can finally obtain the film refilled with a new molecule.

3.9. 5CB refilled film
We firstly choose 5CB as the second molecule for its similar structure with 8CB. The IR spectrum of initial film is shown as the green curve in Fig 31. After immersed the initial film in DCM for 10 minutes, we divided the film into two parts. One part is room temperature evaporated to remove DCM. Another part is immediately swelled with 5CB solvent at 70°C. The IR spectrums for these two parts are shown as blue and red curves respectively. For the 8CB removed sample, the cyano peak at 220cm\(^{-1}\) decrease to 15% of initial intensity. For the 5CB swelled sample, this peak returns back to almost the same intensity of initial film, which means that we have successfully replaced 8CB with 5CB to obtain the new film.
With interferometer, we also measured the thickness change during the whole process and deformation properties after actuation (Tab 2). After 8CB is removed from the initial film, the collapsed network decreases 40% of initial thickness. This thickness is a little larger than the weight ratio of polymer structure (30%), which means that although the network collapsed, there are still some voids within the film. After refilled with 5CB, the thickness of new film slightly larger than the thickness of initial film, which may be the swelling effect of new material. With 365 nm UV actuation, we found the new film also has in-depth deformation, the film thickness decrease about 8% of initial thickness.

<table>
<thead>
<tr>
<th>Film</th>
<th>Initial</th>
<th>Collapsed</th>
<th>5CB replace</th>
<th>UV actuation</th>
<th>Deformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (um)</td>
<td>46.9</td>
<td>18.6</td>
<td>51.2</td>
<td>47.0</td>
<td>8.20%</td>
</tr>
</tbody>
</table>

Table 2: In-depth deformation of 5CB refilled film during refilling and actuation process

After thickness measurement, we also check the light triggered release behavior. After fully actuating part of the new film with 365 nm UV light, we can obviously see the liquid layer for UV exposed area. The light triggered release property is perfectly maintained after we replace 8CB with a new material. After placing the actuated film at dark room for more than 24 hours, the liquid layer diffused back to the film slowly (as shown in Fig 32).
Figure 32: Pictures of 5CB refilled film after partly UV actuation and dark room relaxation

Same as the initial film, this "light triggered sponge" phenomenon of 5CB refilled new film is also investigated with digital holographic microscopy. For this new film, we only record the process of 365 nm UV actuation (Fig 33), which is almost the same as that as initial film under holographic microscopy.

Figure 33: Light triggered sponge phenomenon of 5CB refilled film
3.10. EHA refilled new film

Besides 5CB, we also tried EHA as the second molecule, EHA is very commonly used as a monomer for elastic polymer. From the IR spectrums (Fig 34) at peak 1630 cm⁻¹ of initial film (red curve), 8CB removed film (green curve), and EHA refilled film (black curve), we can also conclude that 8CB has already been removed and EHA molecule can filled in the network to form new film.

![Figure 34: IR spectrum of initial film, 8CB removed film, and EHA refilled film](image)

With EHA refilled film, we also test the in-depth deformation. After full actuation, the thickness of the new film decreases about 8% of the initial thickness. This deformation is also reversible with 455 nm light. Since EHA can be used as the second step refilling material, it would be interesting to further investigate this system. If we can fill in the network with EHA, initiator, and crosslinker, and perform a second polymerization, we can hopefully obtain an IPN with better mechanical properties, which we expect will enhance the photomechanical deformation property.

<table>
<thead>
<tr>
<th>Film</th>
<th>Initial</th>
<th>Collapsed</th>
<th>EHA replace</th>
<th>UV actuation</th>
<th>Deformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (um)</td>
<td>46.8</td>
<td>15.2</td>
<td>48.4</td>
<td>46.5</td>
<td>8.06%</td>
</tr>
</tbody>
</table>

Table 3: In-depth deformation of EHA refilled film during refilling and actuation process
4. Conclusions and recommendations

In conclusion, we have successfully obtained a light responsive film with a smectic/homoeotropic network, stabilized with 8CB. For thin film (less than 20 μm), only silane surface treatment is enough for alignment. For thicker film, we need to apply an external alternative electrical field for perfect homoeotropic alignment. The film can go isomerization and back-isomerization process with 365 nm light and 455 nm light respectively. For 6 μm film, it needs about 150 seconds to reach the maximum deformation and about 60 seconds for the relaxation. For 50 μm film, it needs more than 5 minutes for deformation and relation. We explain this difference by the extinction effect of light during actuation and relaxation. We estimated that, for 365 nm actuation light, after 12μm thickness for initial film and 33μm for actuated film, the intensity of the light is close to zero.

This film can have large and reversible in-depth deformation (>10%) and can release the 8CB contained in the film under exposure to 365 nm UV light. When exposed to 365 nm light, 8CB is gradually squeezed out from the film and forms droplets at the surface. During continuation of the exposure the droplets merge to form a uniform layer finally. With 455 nm light exposure, this uniform layer of 8CB diffuses back into the film in a reversible and fast way.

Based on this initial film, we found a method to replace 8CB component with a second molecule. During our project, 5CB and EHA have been investigated to refill the network. For these new films, in-depth deformation and liquid release under UV light are maintained. This light controlled release of chemicals can be further investigated for its potential application in microfluidic device or drug delivery in biomedical application.

For the outlook of our project, characterization of structure changes by X-ray diffraction can be investigated to understand the structure orientation change between the initial film, the film without 8CB, the UV actuated film, and the films refilled with 5CB/EHA. It would also be interesting to investigate the release new molecules or to form an IPN which can be of interest for double response.
5. Acknowledgements

In the last part of my report, I would like to thank my supervisors, colleagues and friends. First of all, I would like to thank Prof. Dick Broer for his supervision and the availability to drop by in his office for questions and discussions during my project. I would also like to thank Anne Helene Gelebart for her kindly tutoring and guidance from lab work to paper work. I would also like to thank Prof. Albert Schenning, Dr. Cees Bastiaansen, Dr. Catarina Esteves for being part of my graduation committee.

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References