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Easily-processable and programmable responsive semi-interpenetrating liquid crystalline polymer network coatings with changing reflectivities and surface topographies

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The fabrication of stimulus-responsive coatings that change both reflectivity and topography is hampered by the lack of easily processable, patternable and programmable elastomers. Here, we report on an easily applied reflective coating based on a semi-interpenetrating polymer network composed of a liquid crystal elastomer and a liquid crystal network (> 15 wt%). The reflective wavelength of these polysiloxane elastomer photonic coatings could be readily programmed by the concentration of chiral reactive mesogen dopant that formed the network. The coatings showed a fast and reversible decrease in reflection band intensity with increasing temperature, which could be tuned

by the polymer network density. In addition, hierarchical surface relief structures were prepared which could be reversibly changed with temperature.

1. Introduction

In nature, stimulus-responsive surfaces play a major role. Organisms are protected from environmental influences by a multi-responsive and multi-functional skin.^[1] Mammalian skin, for instance, is able to adopt its topography, colour and pore size when triggered by light or temperature to regulate internal processes. Other animals, such as chameleons or cephalopods, are able to change their coloration for camouflage, temperature maintenance and communication.^[2] These responsive properties have inspired many researchers to fabricate stimulus-responsive coatings for various applications, such as smart adhesives, self-cleaning surfaces, sensors and displays.^[3-11] Responsive surfaces have been fabricated using polymer brushes, shape memory polymers, self-assembled block copolymers or hydrogels.

A next step in stimulus-responsive surfaces would be combining different responsive and functional properties into one coating, which opens up routes towards new applications *e.g.* self-cleaning reflectors or haptic displays and sensors. However, the fabrication of easily-processable and programmable stimulus-responsive polymer coatings that change multiple properties, such as reflectivity and topography, remains a challenge. Cholesteric liquid crystals (CLCs), which reflect light of a specific wavelength corresponding to the pitch of the self-organizing molecular helices are an interesting class of materials to prepare such coatings. The liquid behaviour of liquid crystals (LCs) increase their processability and the colour, shape and response of CLCs are easily tuned by the chemical composition and processing conditions. These properties led to a range of CLC materials that are responsive to various stimuli (*e.g.* light, electric fields or temperature) and change properties such as

reflectivity or surface topography.^[12-26] For the fabrication of stimulus-responsive LC polymer films, both polymer liquid crystalline elastomers and glassy networks have been used.^[12]

Polymer liquid crystalline elastomers (LCEs), which possess flexible main chains such as polysiloxanes, demonstrate a fast response to external stimuli. When macroscopically aligned, such materials also exhibit large dimensional changes making them interesting as actuating polymers. Both stimulus-responsive free standing films as well as LCEs confined to a solid substrate have been reported with programmable shapes and topographies.^[27-39] For CLC elastomers, dimensional changes along the helical pitch direction even resulted in changes in reflective colour.^[40-43] However, simultaneously changing both the topography and reflectivity by one stimulus remains a challenge. Alignment of LCE polymers is commonly done via mechanically stretching or by polymerization in a cell containing alignment layers. Other materials like polysiloxanes can be knife coated, but this method requires addition of LC monomer to increase the processability.^[44-45]

An alternative route towards forming stimulus-responsive LC coatings is based on the in-situ photo-crosslinking of oriented LC monomers (RMs) that form more stiff liquid crystalline networks (LCNs) with in general higher glass transition temperatures.^[12, 46] These materials are easy to process, since prior to polymerization the monomers have a relatively low viscosity and conventional LC alignment techniques can be used. After polymerization, a non-volatile coating is obtained of which the responsive properties can be tuned by the choice of monomers.^[46-50] In addition, patterned surfaces of RMs can easily be fabricated by photo-induced diffusion to create structured optical features and surface topographies.^[26, 46, 51-59] Usually, the topographical and reflectivity responses are limited due to the high crosslink density of these glassy networks, so solvents or low molecular weight LCs are required to

enhance the response. For example, Stumpel *et al.* reported on a hydrogen bonded LCN in which swelling and deswelling by water resulted in topography and reflectivity changes.^[60-61]

Here, we report on responsive coatings based on polysiloxane and reactive mesogens, combining the best features of both LC families to create films that change their reflectivity and topography by altering the temperature. The semi-interpenetrating network (semi-IPN) coating, in which a non-crosslinked LCE interpenetrates a crosslinked LCN, is fabricated by a simple coating technique and operates in a dry environment. We tuned the reflective wavelength of the coating by the chemical composition of the mixture and locally varied the composition to allow geometric patterning of the surface. The polymer coatings respond quickly to temperature changes by altering reflectivities and surface topographies.

2. Results & discussion

2.1 Preparation of the CLC mixture

We obtained a coating mixture by mixing an achiral side chain LC polysiloxane (**SCLCP**) elastomer with a chiral diacrylate dopant **RM-1** (mixture **M1**, 21 wt% **RM-1**). To ensure good mixing, RMs with a similar mesogenic moiety as the **SCLCP** elastomer were chosen. Furthermore, a photo initiator (Irgacure 651, 1 wt%) and a perfluoro surfactant (1 wt%) were added to be able to photo polymerize and align the mixture at the polymer air interface, respectively (**Figure 1A**). Differential scanning calorimetry (DSC) of the LC mixture prior to photopolymerization showed a glass transition at -23 °C and a transition to the isotropic phase at 47 °C, which were close to the transition temperatures of the **SCLCP** (Figure 1A). Polarized optical microscopy (POM) images of the mixture showed a Grandjean texture, which is characteristic for a planar aligned CLC phase, indicating good mixing of the RM and elastomer (**Figure S1**).^[63]

Figure 1 - (A) Components used in the mixtures including their individual phase behaviour.^{[46,}

^{62]} G refers to glassy, SmC to smectic C, SmA to smectic A, Cr to crystalline, N* to cholesteric and I to isotropic. The blue cylinders indicate the mesogenic moiety of the components (B) Schematic drawing of the coating application.

Viscosity measurements revealed that the mixture has a large increase in viscosity at the phase transition when cooling from the isotropic to the cholesteric phase (**Figure S2**). In addition, in the cholesteric phase the mixture showed a shear thinning behaviour, most likely caused by realignment and suppression of the cholesteric order. At the high shear rates used during the coating application (vide infra), the viscosity is low (< 6 Pa.s) and thus the material will flow nicely in the slit of the gap coater, which is required for obtaining a homogeneously planar aligned CLC coating.^[64]

2.2 Coating preparation

To induce planar alignment, we applied the mixture on a glass substrate modified with a thin rubbed polyimide coating. After evaporation of solvent, the CLC mixture (50 wt% in toluene) was coated using an automatic gap applicator (**Figure 1B**). The coating was applied at a substrate temperature of 45 °C, just below the clearing temperature of the mixture. After application, the coating was UV-cured. FT-IR showed full conversion of the acrylate reactive

groups (**Figure S3**). The final coating had a thickness of approximately 16 μm . DSC of the polymerized coating showed a similar cholesteric-to-isotropic transition temperature as the non-polymerized mixture (44 $^{\circ}\text{C}$, **Figure S4**). The orange-red coloured coating reflected left circularly polarized light of 662 nm at room temperature (**Figure 2A**). Transmission electron microscopy (TEM) images of the cross section of a coating of **M1** showed a uniform layered morphology with an average pitch of 385 nm (**Figure 2B**). The pitches were perpendicular to the coating thickness and homogeneously distributed throughout the whole thickness of the coating (**Figure S5**). These results show the formation of a well-mixed and planar aligned cholesteric semi-IPN, in which the LCE homogeneously interpenetrates the LCN.

We tuned the reflective wavelength of the semi-IPN coating by varying the concentration of **RM-1** (25.5 and 14.9 wt% for mixtures **M2** and **M3**, respectively). The coatings of **M2** and **M3** reflected light of 524 and 1004 nm, respectively (**Figure 2C**). A plot of the wavelength against the reciprocal of the concentration showed a linear relation, indicating proper mixing between the LCN and the polymer elastomer (**Figure 2D**).^[14]

Figure 2 – (A) Transmission spectra of a coating of **M1** including a photograph of the prepared film on a black background. (B) TEM of a cross section of a coating of **M1** including a zoom-in showing a pitchlength. (C) Vis-NIR spectra of coatings of **M1**, **M2** and **M3**. (D) Reflection wavelength versus the reciprocal of the **RM-1** concentration showing a linear relationship.

It should be noted that during a first heating of the coatings to 120 °C, a blue shift occurs (**Figure S6**). This blue shift is attributed to a degree of phase separation between LCE and LCN, since the elastomer wants to expand upon heating more than the LCN and is therefore expelled by the network (**Figure S7**). This led to some shrinkage of the remaining network and thus a blue shift of the reflective wavelength. In the following section we exclude the first heating and discuss the response of the reflectivity during subsequent temperature cycles.

2.3 Temperature-responsive reflectivity

Upon heating and cooling of coating **M1** between 30 to 120 °C, a reversible change in both reflection band intensity and width ($\Delta\lambda$) is observed (**Figure 3A**, red curve and **Figure S8**). Since the LCE interpenetrates throughout the LCN, the LCN provides a memory effect to assist the **SCLCP** elastomer regain planar alignment after heating above the cholesteric-to-isotropic transition temperature. The reduction of the reflection band upon heating to 120 °C as calculated from the area under curve of the transmission spectra was 65 %, providing a clear optical difference in colour intensity (**Figure 3B**, red curve and **Figure 3C**). The largest decrease in reflection band intensity occurs between 50 and 60 °C, which is just above the cholesteric-to-isotropic transition temperature of the coating. The width of the reflection band decreases, especially at the n_e edge of the reflection band, suggesting that the mesogenic units are more tilted with respect to the initial alignment.^[26]

Figure 3 - (A) Transmission spectra of coatings **M1**, **M2** and **M3** at 30 °C and 120 °C. (B) Area under curve of the transmission spectra as a percentage of the initial area under curve at

30 °C versus temperature. (C) Photographs of coating **M1** at 30 °C and 120 °C on a black background.

We also investigated the temperature responses of coatings **M2** and **M3** to study the influence of the crosslink density. Coatings **M2** and **M3** showed a different behaviour in the decrease of the reflection band intensity at elevated temperatures (Figure 3A and B). Again, the largest decrease takes place between 50 and 60 °C. However, the reduction of the reflection bands at 120 °C were 49 % and 94 % for coating **M2** and **M3**, respectively. A denser network thus provides a stronger anchoring force for the SCLCP elastomer to maintain the cholesteric order at elevated temperatures.

In order to reflect in the visible wavelength regime, while maintaining low crosslink density, we replaced **RM-1** by **RM-2**, an achiral diacrylate, and **RM-3**, a chiral diacrylate with a high helical twisting power (Figure 1A). Only a few wt% (3.3 and 2.7 for **M4** and **M5**, respectively) of **RM-3** was needed to tune the reflective wavelength to the visible light regime. We added **RM-2** to a total RM concentration of 15 wt% for both mixtures. After the first temperature cycle, the coatings reflected at 491 and 652 nm for **M4** and **M5**, respectively, and only showed a strong decrease in reflection band intensity, similar to the previously described coatings. At 120 °C the reflection band reduction was 62 and 79% for the coatings of **M4** and **M5**, respectively (**Figure S9**). These experiments show that the reflective wavelength and reflectivity response to temperature can be tuned separately by the chemical composition.

To test the thermal stability of the coatings we stored **M1**, **M2** and **M3** in an oven at 80 °C for 5.5 months. Transmission spectra were measured at room temperature during this period (**Figure S10**). The coatings did not show a decrease in reflection band intensity nor a shift in

λ_r , which reveals that the temperature response of the coatings is reversible even after long periods of storage at elevated temperatures.

2.4 Temperature responsive surface topographies by photo-induced diffusion

We also prepared temperature responsive surface topographies by polymerization-induced diffusion.^[54-58, 60-61] The red reflecting mixture **M1** was coated and illuminated with UV light through a photomask with hexagonally arranged hexagons. Due to depletion of the RMs by photopolymerization, diffusion of RMs from the non-exposed area to the exposed areas takes place. Subsequently, the photomask was removed and a UV flood exposure was executed, resulting in a fully polymerized film with a spatially modulated crosslink density. Visually, the coating showed green hexagonally arranged pillars embedded in a red reflecting surrounding (**Figure 5A**). The colour shift of the pillars from red to green is due to the higher concentration of chiral dopant **RM-1** in the pillar regions. At room temperature a height difference of 60 nm is found between the pillars and the surroundings. Upon heating to 40 °C, the pillars expanded less than the surrounding areas, due to their higher crosslink density, with an overall effect of surface flattening. When heating further to 50 °C, the surrounding areas even became higher than the pillars, which then appeared as valleys in the coating surface with an average depth of 64 nm. This surface topography transition from hills to flat to valleys induced by temperature was fully reversible (**Figure 5B and C and S11**).

Figure 5 – (A) Optical microscopy image in reflection mode. The inset shows an optical microscopy image of the photomask used (at the same magnification). (B) Surface profile at various temperatures, converting from hills ($23\ ^\circ\text{C}$) to flat ($40\ ^\circ\text{C}$) to valleys ($50\ ^\circ\text{C}$). The bar indicates the illuminated ($\square$) and non-illuminated ($\blacksquare$) areas. (C and D) 3D images of the temperature responsive surface topographies of coating **M1** obtained by (C) single mask and (D) dual mask photopolymerization induced diffusion.

It should be noted that the illumination time during the first illumination is critical for the final structure heights and topography. When the illumination time is too low the

concentration gradient of RMs between the illuminated and non-illuminated areas is limited, while too high an illumination time increases viscosity due to polymerization, which limits diffusion of the monomers (**Figure S12**).^[56]

We also prepared temperature-responsive hierarchical surface topographies by dual mask exposure. Again, mixture **M1** was illuminated through the same photomask. Subsequently, the coating was illuminated through a 75 μm spaced line mask. After UV-flood exposure and thermal annealing this resulted in hexagonally arranged patterns of pillars superimposed on top of a line structure. The various areas again displayed optical differences (**Figure S13**). The lines were 620 nm in height, whereas the pillars were 36 and 35 nm on the illuminated and non-illuminated lines, respectively. The smaller structure height of the pillars could be explained by the energetic cost derived from the generation of new surface area, which would be more for smaller feature dimensions keeping the same height.^[56] In addition, the ratio illuminated to non-illuminated area is larger for the line mask compared to the hexagonally arranged hexagon mask, so more acrylates are able to diffuse to the lines. Similar to the single mask exposure coatings, upon heating the pillars flattened at 40 °C and turned into valleys at 50 °C (62 and 64 nm on illuminated and non-illuminated lines, respectively; **Figure 5D** and **S14**). The height of the lines also changed with temperature, but the changes were small compared to the height of the lines and thus they did not appear as valleys at 50 °C. Again, this process was fully reversible. A combination of multiple photo masks can thus be used to fabricate hierarchical temperature responsive surface topography coatings.

3. Conclusion and Outlook

We prepared an easily processable and temperature responsive elastomeric CLC material by combining a polymeric elastomer with an LCN (> 15 wt%) to create a semi-IPN coating. The

reflective wavelength and reflection band response of these coatings were tuned by the chemical composition. Surface topographies were fabricated by photo-induced diffusion using single and dual mask exposures. The surface topographies of the coatings were responsive to temperature as well.

Semi-IPN coatings of this kind are a novel approach towards producing stimulus-responsive coatings. It combines the advantages of both materials: the polymer elastomer provides a non-volatile thermally switchable LC medium, while the LCN provides tunability of the optical and responsive properties of the system and the ability to align and even photo-emboss the material. Apart from temperature-responsive coatings as we showed here, this approach opens up potential routes towards new materials for wavelength shifting coatings, coatings or free standing films that respond to other stimuli, such as light and electric fields, or broadband reflecting coatings.

4. Experimental

4.1 Materials

The SCLCP ((4-methoxyphenyl 4-hexyloxy)benzoate)siloxane) was purchased from Synthon Chemicals GmbH & Co. **RM-1** ((R,R)-1,4-di-(6-acryloyloxy-3-methylhexyloxy)benzoyloxy)benzene) and **RM-3** (1,4:3,6-dianhydro-D-glucitol 2,5-di-(4-(4-(6-acryloyloxyhexyloxy) benzoyloxy)benzoate)) were obtained from Philips Research lab. **RM-2** (RM82, 1,4-phenylene bis(4-((6-(acryloyloxy)hexyl)oxy)benzoate)) was supplied by Merck. Irgacure 651 was purchased from Ciba Specialty Chemicals Inc. The surfactant (2-(N-ethylperfluorooctanesulfonamide)ethyl methacrylate) was purchased from Acros. Polyimide (Optmer AL 1051) was purchased from JSR Micro.

4.2 Methods

Mixtures. The components were weighed in the desired ratio and subsequently dissolved in toluene (50 wt %) using a moving plate for at least 1 hour.

Polarized optical microscopy (POM). POM images were taken using a Leica CTR6000 polarized optical microscope, equipped with a Leica DFC 420C camera. Temperature was controlled using a Linkam temperature control stage.

Differential scanning calorimetry (DSC). DSC curves were measured with a DSC Q1000 from TA instruments. A rate of 5 °C/min was used for both heating and cooling ramps.

Viscosity measurements. Viscosity measurements were performed on an Anton Paar Physica MCR 501 rheometer using a parallel plate configuration. The measurements were carried out starting from the highest measurement temperature to the lowest. At temperatures below 50 °C a waiting time of 3 minutes was conducted before starting the measurement to allow the material to build up its viscosity. The measurements were carried out at different shear rates ranging from 10 to 60 s⁻¹. Each shear rate was measured for 2 minutes.

Rubbed polyimide substrates. To prepare rubbed polyimide substrates 3 x 3 cm² glass plates were cleaned by ultra-sonication in ethanol for 30 minutes and subsequently UV-Ozone treatment (PR-100, Ultra Violet Products) for 20 minutes. A polyimide layer was spin coated on these glass plates using a Karl Suss CT 62 spin coater by rotating at 1000 rpm for 5 seconds, followed by 5000 rpm for 45 seconds. The polyimide coated glass slides were first placed at 100°C for 15 minutes and subsequently at 180°C for 1.5 hours to ensure thermal annealing. The substrates were then rubbed on a velvet cloth.

Coating preparation. Coatings were prepared using an RK printcoat instruments K control coater. Mixtures were applied on a rubbed polyimide substrate and placed at 100 °C for approximately 35 minutes to evaporate the solvent. When the mixtures turned completely white at room temperature, we assumed that all solvent had evaporated. For the application of

the mixtures, the 10 μm gap of a 4-sided applicator (10 to 25 μm gaps, ZFR 2040, Zehntner) was used, which was automatically pushed forward over the mixture with a speed of approximately 1 cm/s. It is assumed that drag forces during the coating procedure caused the coatings to be thicker than the gap used.^[64] Photopolymerization of the coatings was done at 40 °C in a nitrogen box using an EXFO Omnicure S2000 mercury lamp for 10 minutes.

FT-IR. FT-IR was measured on a Varian 670-IR FT-IR spectrometer used in transmission mode.

Transmission electron microscopy (TEM). The coating for the TEM cross section was applied at 40 °C with a gap of 20 μm and a slightly increased speed. After UV-curing, pieces of coating were scratched from the substrate using a razor blade. Subsequently these were embedded in Epofix Cold-Setting Embedding Resin and microtome cut at -140 °C using a Leica Ultracut EM UC7/FC7 equipped with a Diatome 35° diamond knife. TEM images were taken on a FEI Tecnai G2. The images were analysed using ImageJ software.

Vis-IR spectra. All Vis-IR spectra were measured on a Shimadzu UV-3102 PC. Temperature dependent measurements were performed using a Linkam temperature control stage. The area under curve of the transmission spectra was calculated by baselining the spectra and integration, to exclude differences in scattering between various spectra.

Polymerization induced diffusion. Coatings with surface topographies were prepared by illuminating through a mask at 21 °C. For the single mask exposed coating a UV energy dose of 34.8 mJ/cm^2 (8.7 mW/cm^2 for 4 seconds) was used. For the dual mask exposed coating energy doses of 29.9 (4.4 mW/cm^2 for 6.8 seconds) and 10.2 mJ/cm^2 (16.9 mW/cm^2 for 0.6 seconds) were used for the hexagonal- and line mask, respectively. UV-flood exposure was done at 40 °C for 10 minutes. The coatings were thermally annealed at 50 °C to stabilize the surface structures.

Thickness and surface topography measurements. The thickness and surface topographies of the coatings were measured using a 3D interferometer (Fogal Nanotech Zoomsurf). For temperature dependent measurements a Linkam temperature control stage was used.

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