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Temperature-Responsive, Multicolor-Changing Photonic Polymers

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ABSTRACT: A new principle is developed to fabricate temperature-responsive, multicolor photonic coatings that are capable of switching color. The coating is composed of a non-cross-linked liquid crystal siloxane-based elastomer that is interpenetrated through an acrylate-based liquid crystal network. Discrete temperature changes induce phase separation and mixing between the siloxane and the acrylate polymers and change the reflective colors correspondingly. The temperature-responsive color change of the coatings can be programmed by the processing conditions and coating formulation, which allows for the fabrication of photo-patterned multicolor images. The photonic ink can be coated on flexible poly(ethylene terephthalate) films using roll-to-roll flexographic printing, making these temperature-responsive, multicolor-changing polymers appealing for applications such as responsive color decors, optical sensors, and anticounterfeet labels.

KEYWORDS: stimulus-responsive materials, cholesteric liquid crystals, photonic coatings, structural color change, flexographic printing

INTRODUCTION

Throughout history colors have always played a vital role in human life. We recognize objects based on their colors, like fruits, vehicles, your favorite sports team, and the amazing colors of paintings or art objects.1 Appealing are iridescent structural colors, arising from the presence of a periodic modulation of refractive indices, of which the color changes as the viewing angle changes.2–8 These materials can be temperature-responsive and are potentially interesting for applications in energy saving, health care, and food safety.9–13

Shape memory polymers have been used as temperature-responsive structural color-changing materials. These photonic coatings can be deformed to a temporary state after which they recover their original shape upon heating above the glass transition temperature accompanied with a color change.14–16 Also, photonic hydrogels and block copolymers have been used, which change color depending on the temperature of the swelling solvent.17–26

Cholesteric liquid crystals (CLCs) are a special class of photonic materials having iridescent structural colors. A CLC has a helical periodic structure due to which a variation of refractive indices is obtained along the helical axis, causing reflection of a specific wavelength.25–31 Temperature-induced color change has been achieved in CLC polymers containing low-molecular-weight liquid crystals.32–41 Recently, a temperature-induced color change has also been reported in a polymer coating. Using liquid crystal elastomers (LCEs), a 200 nm red shift of the color across the visible spectrum upon heating from 25 to 200 °C was observed.42 However, the fabrication of temperature-responsive, multicolor-changing photonic polymers remains a challenge. So far, only temperature-responsive, multicolor-changing photonic polymers have been reported that needed solvents or deformation steps.5,11,12

Recently, we reported reversibly responsive cholesteric coatings based on semi-interpenetrating networks (semi-IPNs) of non-cross-linked LCEs and purely diacrylate-based cholesteric LC networks (LCNs). These coatings showed a reversible reflectivity decrease upon heating since the LCE loses order.43 However, these coatings did not change color, as the LCE was too much constrained to diffuse out of the LCN and thus the periodicity of the helical structure remained unchanged. In this report, we fabricate multicolor semi-IPN coatings based on siloxane-based LCEs interpenetrating through monoacrylate-containing cholesteric LCNs that show...
a reversible hundreds of nanometers blue shift of the color upon heating above the cholesteric-to-isotropic transition temperature ($T_{Ch-I} = 47 \degree C$, Figure 1). The color change is based on the in and out diffusion of the LCE causing winding and unwinding of the helical structure of the LCN. The temperature-responsive color change can be tuned by changing the processing conditions and the coating formulation, allowing fabrication of multicolor-changing coatings by photolithography (Figure 1). Furthermore, the cholesteric liquid crystal ink can be coated using flexographic printing, making these temperature-responsive, multicolor-changing polymers appealing for optical applications.

**EXPERIMENTAL SECTION**

**Materials.** LCE-1 was purchased from Synthon Chemicals GmbH & Co. RM-1 (RM-82) and RM-3 (RM-105, Figure S8) were purchased from Merck. RM-2 was supplied by the Philips Research lab. 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.

**Preparation of Rubbed Polyimide Glass Substrates.** Rubbed polyimide substrates were prepared by cleaning $3 \times 3 \text{cm}^2$ glass plates using ultrasonication in ethanol for 30 min and a subsequent UV-ozone treatment (PR-100, Ultra Violet Products) for 20 min. A polyimide layer was spin-coated on these glass plates using a Karl Suss CT 62 spin coater by rotating at 800 rpm for 5 s, followed by 5000 rpm for 45 s. The polyimide-coated glass slides were first placed at 100 °C for 15 min and subsequently at 180 °C for 1.5 h to ensure thermal annealing. The substrates were then rubbed on a velvet cloth.

**Coating Fabrication.** The coating formulation components were weighed in the desired ratio and subsequently dissolved in toluene (ca. 50 wt %) using a moving plate for at least 1 h. Coatings were prepared using an RK Print Coat Instruments K control coater. Mixtures (50 μL) were applied on a rubbed polyimide substrate and placed at 105 °C for about 35 min to evaporate the solvent. When the mixtures turned completely white at room temperature, it was assumed that all solvent had evaporated. For the application of the mixtures, the 10 μm gap of a four-sided applicator (10–25 μm gaps, ZFR 2040, Zellmex) was used, which was automatically pushed forward over the mixture. Mixtures were coated at 53 °C. The thickness of the coatings was controlled by adjusting the speed between approximately 1.0 and 1.25 cm/s. Photopolymerization of the coatings was done at 40 °C in a nitrogen environment using an EXFO Omnicure S2000 mercury lamp for 10 min with an intensity of 32 mW/cm², unless specified otherwise. The UV intensity was measured using an Opsytec Dr. Gröbel Radiometer RM12 with a UV-A detector.

**Cell Fabrication.** A filled alignment cell was prepared by shearing the coating formulation between two rubbed polyimide glass plates having UV-curable glue (UVS91, Norland Products Inc.) containing 10 μm polystyrene beads (SP-210, Sekisui Chemical Co.) on the edges. After curing the coating formulation, the cell was sealed with glue to limit the possibility for the material to expand as much as possible.

**Flexographic Printing.** The coating formulation components were weighed in the desired ratio and subsequently dissolved in cyclopentanone (ca. 50 wt %) using a moving plate for at least 1 h. The coatings were prepared on an IGT F1 printability tester in a flexography mode. Biaxially oriented black poly(ethylene terephthalate) (PET) (Tenolan OCN0003, 36 μm thickness) was used as the substrate. The coated substrates were heated to 40 °C for at least 3 min to evaporate the solvent.
Coatings were prepared by illuminating through a photomask at 40 °C in a nitrogen environment using an EXFO Omnicure S2000 mercury lamp. A photomask with a clover leaf image or negative clover leaf image was fabricated by printing three layers of the image on a transparent overhead sheet. Through the transparent part of the lithographic mask having 20 μm-spaced lines, we blade-coated a coating formulation with a di-/monoacrylate ratio of 1:8 and illuminated the coating through a projector. After waiting for 1 min, we removed the mask and postcured the entire coating (I = 32 mW/cm² for 10 min). To generate a 20 μm-spaced line pattern, we blade-coated a coating formulation with a di-/monoacrylate ratio of 1:8 and illuminated the coating through a projector. After waiting for 1 min, we removed the mask and postcured the entire coating (I = 32 mW/cm² for 10 min).

**Thickess Measurements.** The thicknesses of the coatings were measured using a three-dimensional interferometer (Filip Nanotech Zoomsurf). For the coatings fabricated using flexographic printing, the thickness was measured using a digital caliper (Helios Preisser Digimet 1865 510, accuracy 0.001 mm).

**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.

**UV–Vis–Near-Infrared (NIR) Spectrophotometry.** Transmission spectra were measured on a Shimadzu UV-3102 PC. Temperature-dependent measurements were performed using a Linkam temperature control stage. The transmission at half-height was calculated by averaging the baseline of the spectra with the lowest transmission point of the reflection band. The difference between the corresponding wavelengths closest to the transmission at half-height was taken as the full width at half-height (FWHH). The central wavelength was calculated by averaging the wavelengths closest to the transmission at half-height. The transmission and reflection spectra of the patterned coatings were measured on a PerkinElmer Lambda 750 UV–vis–NIR spectrophotometer. For fitting the color changes, an exponential function (eq 1) and the first blue and red shift cycles were used.

**Photographs.** Photographs of the samples after various exposure times during the blue and red shifts are captured at room temperature. The samples were cooled to room temperature after which the blue or red shift at 65 or 38 °C, respectively, is continued. The red shift of the coatings at room temperature is slow (hours, vide infra), compared to the time it takes to cool down to room temperature and capture a photograph (minutes), due to which no observable color change is visible at room temperature in the timeframe of minutes.

**RESULTS AND DISCUSSION**

**Preparation and Temperature-Response of the Color-Changing Photonic Coatings.** We prepared semi-IPN cholesteric polymer coatings by blade coating and photopolymerization of a mixture containing LCE (77 wt %), achiral diacylate RM-1 (5 wt %), and chiral monoacrylate RM-2 (16 wt %). The addition of monoacrylates reduces the cross-linking density of the resulting LCN compared to that of previously reported semi-IPNs containing purely diacrylate-based LCNs. Furthermore, we added a photoinitiator (Irgacure 651, 1 wt %) and a surfactant (1 wt %) to photopolymerize the RMs and align the mixture to the coating–air interface, respectively (Figure 1A).

The nonpatterned photonic coatings were cured by a 10 min exposure with a mercury lamp at a light intensity of 32 mW/cm². The photopolymerized coating had a thickness of 14 μm and the Tch was 47 °C upon heating and 42 °C upon cooling as determined by DSC (Figure S1). The coating reflected in the near-IR region (799 nm, Figure 2A, black solid line). Upon heating to 65 °C (T > Tch), the reflectivity partly vanishes since nonconstraint LCE-rich domains lose the cholesteric...
order, while some cholesteric order is preserved by the LCN, similar to earlier findings (Figure 2A, black dashed line). When maintaining this temperature, the coating immediately shows a color change and gradually blue-shifts from 799 to 515 nm in 3.75 h (Figure 2A, dashed lines, and Figure 2B,C). Upon cooling to 38 °C (just below T_{Ch,l}) the LCE gains order and the reflectivity increases again (Figure 2A, solid blue line). The coating now scatters more than in the initial state, indicating that the LCE is less ordered than the initial state. When maintaining the temperature at 38 °C, the coating red-shifts back to 706 nm, while reducing scattering, in approximately a week (Figure 2A, solid yellow and red lines, and Figure 2C,D). The reflection band does not completely red-shift to the initial reflective wavelength. However, after the first heating and cooling cycle, the coating can be blue- and red-shifted reversibly (Figure S2). During both blue and red shifts, the reflection band first broadens and then narrows (Figure S3). The blue and red shifts can be fitted with an exponential function

\[ \lambda = \lambda_{\text{init}} + \Delta \lambda \times e^{-k \Delta \lambda t} \]

in which \( \lambda \) is the central reflection wavelength, \( \lambda_{\text{init}} \) is the asymptote or final wavelength, \( \Delta \lambda \) is the difference between start and end points, \( k \) is the rate constant, and \( t \) is the time in hours (Figure 2B,D, solid lines). The rate constants for the blue and red shifts are 0.46 and 0.03 h^{-1}, respectively. To determine the activation energy, we measured the rate constants of the blue and red shifts at various temperatures above and below T_{Ch,l} respectively (Figure S4). The temperature directly influences the rate constants according to the linear form of the Arrhenius equation

\[ \ln(k) = \ln A - \frac{E_{\text{act}}}{R \times T} \]

in which \( A \) is a pre-exponential factor, \( E_{\text{act}} \) is the activation energy, and \( R \) is the gas constant. This finding suggests diffusion of the LCE out of and back into the LCN during the blue and red shifts, respectively. The \( E_{\text{act}} \) for the blue and red shifts are 81 and 148 kJ/mol, respectively, which means that the red shift is more sensitive to temperature changes compared to the blue shift. This might be explained by a larger change in viscosity when changing the temperature below T_{Ch,l}.

**Temperature-Responsive Color Change Mechanism.**

To shed more light on the temperature-response mechanism, we analyzed the color change of the coatings further by changing the coating thickness, curing light intensity, and cross-link density (Table 1). For thicker coatings, the color change is less and slower (Figure S5). This suggests that the LCE diffuses towards the coating–air interface, which might also limit mixing of the LCE back into the LCN during the red shift. Furthermore, it is striking that the relationship between the rate constant and the thickness is not linear (Figure SSB,D). This suggests a Fickian type of diffusion, revealing a gradient in the solvent penetration front. In our case, this is most likely an LCE diffusion front, which is in line with the initial band broadening observed during the color change (Figure S3).

When increasing the curing light intensity, the color change is larger and slower (Figure S6). Similar to polymer-stabilized liquid crystal systems, increasing the light intensity results in a denser packing of individual LCN polymer strands and more bulklike LCE domains. The larger color change suggests that the degree of phase separation is driven by the ability of the LCE to expand. We verified this by filling and polymerizing the coating formulation in a cell, in which the possibility to expand is limited. We indeed observed no reflection band shift upon maintaining a temperature of 65 °C for 4 h (Figure S7). The decreased rate constant with more bulklike LCE domains suggests that this is not dominated by the ability of the LCE to expand but mostly by the domain size of the LCE as for larger domains there are more enthalpic interactions to overcome to diffuse out and back into the LCN.

When we increase the cross-link density by increasing the diacrylate content (RM-1, Figure 1A), the color change becomes less and faster (Figure S8). With increasing cross-link density, the LCE will be more constrained and less able to expand, resulting in a smaller degree of phase separation and thus color change. Following the same reasoning as with varying the curing light intensity, a smaller nonconstraint LCE domain size in this case results in an increased rate constant, \( k \). The observed trend is also in line with earlier reported semi-IPNs containing purely diacrylate-based LCNs, in which the cross-link density is even higher and the LCE is too much constrained to diffuse out due to which no color change is observed.

Furthermore, it is striking that for lower cross-link densities the color change is larger than what is theoretically possible based on the chiral dopant concentration in the pure LCN (approximately 325 nm). This suggests that, besides diffusion of LCE out of the LCN, the network is also compressed, which might result in an additional energy barrier to overcome for the LCE to diffuse back into the LCN during the red shift. This effect plays a less significant role with higher cross-link densities, which aids the increased rate constant for the red shift. Altogether, we are able to program the temperature-responsive color change by changing the thickness, curing light intensity, and cross-link density (Table 1). We hypothesize a Fickian type of diffusion mechanism in which the diffusion of LCE out of the LCN is driven by the ability of the LCE to expand upon heating above T_{Ch,l}. This driving force is in the direction of the coating–air interface. The diffusion causes a shrinkage of the remaining LCN, which causes winding of the cholesteric pitch and a blue shift. Upon cooling below T_{Ch,l} the LCE orders back into a liquid crystalline state with omnidirectional domains. From here, the LCE slowly diffuses back into the LCN, thereby gaining planar orientation, unwinding the cholesteric pitch, and causing a red shift. The rate with which the LCE diffuses out and back into the LCN is mostly dominated by the nonconstraint LCE domain size (Figure 3).

**Temperature-Responsive, Multicolor Images and Flexographic Printing.** We used the ability to program the

| Coating Thickness Increase |  
| Curing Light Intensity Increase |  
| Cross-Link Density Increase |  

Table 1. Trends Found in the Temperature-Responsive Color Change When Varying Coating Parameters (Thickness, Curing Light Intensity, and Cross-Link Density)

| Coating Parameter | k | Δλ |
|-------------------|---|----|
| Coating thickness increase | ↓ | ↓ | Figure S5 |
| Curing light intensity increase | ↓ | ↑ | Figure S6 |
| Cross-link density increase | ↑ | ↓ | Figure S8 |

"\( \downarrow \)" Means that \( k \) slows down or that \( \Delta \lambda \) is less. "\( \uparrow \)" means the opposite trend.
temperature-responsive color change by curing light intensity and cross-link density to fabricate multicolor images using photolithography (Figure 1B,C). We fabricated a patterned coating (8 μm thick) by illuminating through a photomask with a semidark clover leaf (0.01 mW/cm²) and a transparent surrounding (2.7 mW/cm², inverted photomask compared to drawing in Figure 1B). Initially both areas are invisible as they reflect in the near-IR region (λ > 750 nm, Figure 4A). As the surrounding is cured at a higher light intensity, the color change is larger (Table 1). Initially, both areas are invisible as they reflect in the near-IR region (λ > 750 nm, Figure 4A). As the surrounding is cured at a higher light intensity, the color change is larger (Table 1). The surrounding area colors orange (λ = 622 nm) upon heating to 65 °C for 0.4 h, whereas the clover leaf image stays near-IR reflective (λ = 693 nm), resulting in a negative of the clover leaf image. Upon cooling to 38 °C, both areas red-shift to a near-IR reflective state (λ > 740 nm) in about 22 h and become invisible again (Figure S9).

Since we used a thin coating and a low curing light intensity to fabricate the multicolor image, the color change is relatively small and fast (Table 1). In a similar way, we fabricated multicolor image coatings using a higher curing light intensity, which followed the expected trend and blue-shifted further at 65 °C (Figure S10).

In addition to macroscopic multicolor images, we can also fabricate micropatterned coatings by polymerization-induced diffusion, which creates areas of different cross-link densities. During illumination through a 20 μm-spaced line lithographic mask, polymerization is initiated in the exposed areas. Since diacrylates have a higher reactivity compared to that of monoacrylates, mostly RM-1 diffuses toward the exposed areas, which then contain a higher cross-link density and less chiral monoacrylate RM-2 compared to the nonexposed areas. This results in a coating (8 μm thick) with IR-reflecting lines for exposed areas and red reflecting lines for nonexposed areas (Figure 4C). Upon heating to 65 °C, both lines change to a wavelength below the visible light regime within 0.25 h (the red reflecting lines already within 0.05 h), coming across red, green, and blue in a different pace, and become optically indistinguishable. As the cross-link density in the initially IR-reflecting lines is higher, the color change is expected to be less (Table 1). Upon cooling to 38 °C, the line pattern becomes

Figure 3. Schematic drawing of the temperature-responsive color-changing mechanism. Upon heating above \( T_{Ch-I} \), the LCE gradually diffuses out of the LCN toward the coating−air interface, causing winding of the cholesteric pitch and thus a blue shift of the reflection band. Upon cooling below \( T_{Ch-I} \), almost all LCE gradually diffuses back into the LCN, causing unwinding of the cholesteric pitch and thus a red shift of the reflection band. This process is reversible. For the sake of clarity, the polymer backbones of the LCN and LCE are not drawn.

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visible again within 46 h, as the initially IR-reflecting lines change color to a higher wavelength.

CONCLUSIONS AND OUTLOOK

We fabricated temperature-responsive photonic coatings based on semi-IPN networks of LCE and monoacrylate-containing cholesteric LCN. The coatings blue- and red-shift above and below the \( T_{\text{Ch-I}} (T = 47^\circ \text{C}) \), respectively, between the near-IR and the visible light regimes. We are able to program the color change by varying the coating thickness, curing light intensity, and cross-link density. We hypothesize that during the blue shift, the LCE diffuses out of the LCN toward the coating–air interface driven by an expansion difference between LCE and LCN. During the red shift, the LCE diffuses back into the LCN. We used this novel mechanism to make multicolor images and micropatterns in which various areas show different temperature-responsive color changes. Furthermore, we fabricated temperature-responsive, color-changing coatings using roll-to-roll flexographic printing.

By choosing the right processing conditions, it is possible to program the appearance (e.g., positive or negative, color change, and time to change color) of the multicolor images and micropatterns at a given temperature, which opens up a versatile approach toward many interesting applications of photonic materials where fast (minutes, e.g., smart windows, textiles, and anticounterfeit labels) or slow (hours or days, e.g., time-temperature integrators) color changes are required. It is foreseen that the temperature-response and color changes of the photonic coatings can be further programmed by changing the chemical composition of the mixture and fabrication methods.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b08827.

- DSC of the coating; reversibility of the temperature-responsive color shift; FWHH during blue and red shifts; Arrhenius plots of the blue and red shifts; influence of coating thickness, curing conditions, and cross-link density on the color-changing behavior; temperature-responsive behavior in a cell; and reflection spectra of the macroscopic patterned coatings on glass and PET (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes
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