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Temperature-Responsive Polymer Wave Plates as Tunable Polarization Converters

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A temperature-responsive polarization converter, which reversibly changes from a full-wave to a half-wave plate upon heating, is developed. The polymer wave plate has a controlled thickness and is based on a uniaxial aligned nematic semi-interpenetrating network coating containing a specific concentration of a non-crosslinked liquid crystal elastomer. Upon heating, the effective birefringence of the wave plate halves without changing the thickness. The function of the wave plate is demonstrated by sandwiching the tunable polarization converter between two identical right-handed circular polarized light reflective films with a wavelength around 770 nm. At low temperatures, this optical device reflects 50% of light at 770 nm, whereas at elevated temperature 81% is reflected. Such temperature-responsive optical devices have potential applications for both aesthetic purposes as well as energy saving windows.

1. Introduction

Polarization conversion is a common practice in many optical elements present in, for example, displays, antennas and beam splitters.[1-7] A polarization converter that is often used is a wave plate; a birefringent element that converts a polarization state by inducing a phase shift between orthogonal electric-field components of electro-magnetic waves. The simplest wave plates have a homogeneous uniaxial birefringence ($\Delta n$) with a thickness ($d$) and induce a phase shift between the two orthogonal waves according to

$$k = \frac{d\Delta n}{\lambda} \quad (1)$$

in which $\lambda$ is the wavelength and $k$ the induced phase shift divided by $2\pi$.[1,8-9]

Liquid crystals (LCs) are frequently used as wave plate materials. By programming the $\Delta n$ and $d$ of a uniaxial aligned LC quarter- and half-wave plates can be easily fabricated. Also achromatic polarization converters can be obtained by stacking multiple wave plates using the principle of retardation compensation or using configurations involving twisted nematic LCs.[1,8-18] Wave plates based on non-polymerized LCs in cells can also be switched using electric fields, which among others resulted in the billion dollar LC display industry.[1,19,20] To widen its application range it would be appealing to make wave plate films that are responsive to other stimuli such as temperature. However, stimuli-responsive polymer wave plates have never been reported so far.

We recently reported on a reflective LC coating based on a semi-interpenetrating polymer network (semi-IPN) composed of a LC elastomer (LCE) and a helical LC network (LCN). The coating showed a fast and reversible decrease in reflection band intensity with increasing temperature, which could be tuned by the polymer network density.[21] In this work, we developed temperature-responsive polymer wave plates, which reversibly change from a full-wave to a half-wave plate upon heating. The wave plate consists of a uniaxial aligned nematic semi-IPN in which a non-crosslinked LCE penetrates through an LCN. Upon heating above the nematic-to-isotropic transition temperature ($T_{N-I}$) of the semi-IPN, the LCE loses order and the effective $\Delta n$ of the material halves, while $d$ remains constant, thereby changing the polymer film from a full-wave to a half-wave plate. We demonstrate its function by sandwiching the temperature-responsive wave plate between two identical cholesteric LC (CLC) polarizers reflecting right-handed circular polarized (CP) light around the $\lambda$ for which the wave plate is operative (Figure 1). Below the $T_{N-I}$, the left-handed CP light transmitted by the first polarizer is effectively not affected by the full-wave plate and thus also transmitted by the second polarizer, resulting in an overall reflectivity of 50%. Upon heating above $T_{N-I}$, the wave plate turns into a half-wave plate, which converts the
left-handed CP light transmitted by the first polarizer to right-handed CP light, which is then reflected by the second polarizer, increasing the overall reflectivity of the optical device to 100%.

2. Results and Discussion

2.1. Designing the Temperature-Responsive Polymer Wave Plate Material

To obtain a semi-IPN coating with the desired optical properties we need a wave plate in which $d\Delta n$ halves upon heating (Figure 1). For this reason, we filled LC cells, thereby fixing $d$, with mixtures containing various ratios of LCE and reactive mesogen (RM). Furthermore, we added photoinitiator (Irgacure 651, 1 wt%) to be able to photopolymerize the RM, which then forms the LCN (Figure 2A). After photopolymerization, the effective $\Delta n$ decreases to 27%, 53%, and 57% of its initial value upon crossing the $T_{NI}$ from 20 to 61°C for mixtures containing 25.0, 31.5 and 35.0 wt% RM, respectively (Figure 2B). The $\Delta n$ of the semi-IPNs decreases upon heating as the non-crosslinked LCE loses order, which is programmed by the concentration LCN. With more LCN, the LCE is more constrained and the effective $\Delta n$ decrease upon heating is less. The effective $\Delta n$ does not decrease to zero as some of the order is preserved by the LCN. It should be noted that the initial effective $\Delta n$ for all semi-IPNs is relatively low (0.11) compared to pure LCN systems. Mixing of the LCE thus reduces the effective $\Delta n$.

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**Figure 1.** Schematic drawing of the temperature-responsive wave plate sandwiched between two identical CLC polarizers. Below the $T_{NI}$ of the wave plate, the reflectivity of the optical device is 50%. Above the $T_{NI}$, the reflectivity increases to 100%.

**Figure 2.** A) Chemical structures of the compounds used to fabricate the temperature-responsive wave plate material, including the transition temperatures of the LCE. G refers to glassy and I to isotropic. B) Effective $\Delta n$ against temperature for LC cells containing polymerized mixtures with varying concentration RM.
Δn of the material. The effective Δn of the semi-IPN containing 31.5 wt% RM approximately halves and thus we selected this mixture to fabricate our temperature-responsive wave plate.

2.2. Fabrication of the Temperature-Responsive Polymer Wave Plate Coating

We blade-coated the temperature-responsive wave plate mixture on a rubbed polyimide glass substrate. After photopolymerization, we obtained a semi-IPN coating with a T_N-I of the LCE-rich domains of 48 °C, which is same as the transition temperature of the pure LCE (Figure S1, Supporting Information). The coating has a d of 8.4 ± 0.4 µm, which remains constant upon heating (Figure 3A). The effective Δn of the wave plate decreases from 0.092 to 0.042 at a λ of 644 nm, while crossing the T_N-I upon heating from 22 to 70 °C (Figure 3B). The initial effective Δn of the coating is somewhat lower compared to the cell, as only one alignment layer is used. We measured the effective Δn dispersion at room temperature as a function of λ, which we fitted with a two-coefficient Cauchy model (Δn = 0.089 + 4930.1/λ^2, adj. R-square = 0.99, Figure 3C). Using the effective Δn dispersion and Equation (1), k can be calculated as a function of λ, which reveals that we obtained a full-wave plate for a λ of 715 nm (Figure 3D). We assume that the relative Δn decrease upon heating is similar for all wavelengths. As the wave plate reduces its effective Δn approximately to half the initial value, while d remains constant, the wave plate turns into a half-wave plate upon heating for wavelengths around 715 nm.

2.3. Fabrication of a Temperature-Responsive Optical Device

To demonstrate the function of the temperature-responsive wave plate, we sandwiched the wave plate between two identical CLC polarizers reflecting right-handed CP light (Figure 1). The polarizers reflect 47% of incoming unpolarized light at 770 nm (Figure S2, Supporting Information). The reflectivity of the resulting optical device increases from 50% to 81% at a λ of 770 nm upon crossing the T_N-I of the wave plate from 26 to 56 °C (Figure 4A,B). The temperature-responsive optical device does not increase its reflectivity from 50% to 100% as depicted in Figure 1, because the CLC polarizers reflect somewhat less than 50%, the wave plate does not exactly go from a full-wave to a half-wave plate at 770 nm and because of losses due to scattering. The optical device is visibly transparent regardless of the temperature and the temperature-response is completely reversible (Figure 4C). Upon increasing the angle of incidence of the incoming light, the optical device shows a blue shift and reflectivity increase (Figure 4D). This can be explained by the increase of the effective d and decrease of the effective Δn of the wave plate and the CLC polarizers reflecting at lower λ and transmitting more elliptically polarized light rather than CP light upon increasing the angle of incidence. Therefore,
the wave plate at room temperature will deviate from a full-wave plate, thereby increasing the reflectivity. The decrease in transmission outside the reflection band region can be attributed to the additional interfaces of the CLC-wave plate-CLC stack with respect to the baseline measurement. Furthermore, the $\lambda$ of the optical device can be programmed by modulation of the CLC polarizers by the chiral dopant concentration and changing the thickness of the wave plate accordingly (Figure S3, Supporting Information). In addition, the wave plate can be sandwiched between broadband CLC polarizers.[27] The resulting stack increases its reflectivity around the $\lambda$ for which the wave plate is programmed, similar to narrowband reflecting stacks, but shows an altered temperature-response for other wavelengths, due to the effective $\Delta n$ dispersion of the wave plate (Figure S4, Supporting Information).

3. Conclusion

In conclusion, we have fabricated a temperature-responsive polymer wave plate, which reversibly changes from a full-wave to a half-wave plate upon heating. The wave plate consists of a uniaxial aligned nematic semi-IPN with a controlled $d$. We programmed the effective $\Delta n$ decrease upon heating by the concentration of non-crosslinked LCE, so that it halves upon crossing the $T_{N-I}$ of the coating. We have demonstrated its function by sandwiching the wave plate between two identical CLC polarizers. Below the $T_{N-I}$, the optical device reflects 50% at the $\lambda$ for which the polarizers and wave plate are programmed as the CP light transmitted by the first polarizer is unaffected by the full-wave plate and also transmitted by the second polarizer. Above the $T_{N-I}$, the optical device reflects 81% at the programmed $\lambda$ as the CP light transmitted by the first polarizer is now converted by the half-wave plate and reflected at the second polarizer. The operating $\lambda$ and band width of the optical device can be readily programmed in a modular way. Furthermore, we anticipate modulation of the transition temperature of the optical device by using other LCEs. Such programmed optical devices have potential for use in energy saving smart window applications for example.[32–42]

4. Experimental Section

Materials: LCE (4-methoxyphenyl 4-(hexyloxy)benzoate)siloxane dimethylosiloxane copolymer) was purchased from Synthon Chemical GmbH & Co. RM (RM-82, 2-methyl-1,4-phenylene bis(4-(6-(acryloyloxy)hexyl)oxy)benzoate)) was purchased from Merck, as well as RM-96 ((S)-4’-(2-methylbutyl)]-[1,1’-biphenyl]-4-yl 4-(6-(acryloyloxy)hexyl)oxy)benzoate) and RM-257 ((2-methyl-1,4-phenylene bis(4-(3-(acryloyloxy)propoxy)benzoate)), which we used for the fabrication of the CLC polarizers.[27] The photoinitiator Irgacure 651 (2,2-dimethoxy-1,2-diphenylethan-1-one) and UV-absorber T }</t>
were placed at elevated temperatures to evaporate the solvent. Various test mixtures were filled into LC cells for planar alignment (5.0 or 7.7 µm thick, Instec) by capillary action overnight at elevated temperatures (between 50 and 60 °C) and subsequently cured at 45 °C using an EXFO Omnicure S2000 mercury lamp with an intensity of 16 mW cm⁻² for 10 min.

Rubbed Polyimide-Coated Glass Substrates: Glass slides (3 × 3 cm) were cleaned by ultrasonication in ethanol for 30 min and subsequently UV–ozone (UVP PR-100) treatment for 20 min. A polyimide (JSR Optmtr AL1051) layer was spin-coated on these glass substrates by rotating at 1000 rpm for 5 s, followed by 5000 rpm for 40 s using a Karl Suss CT 62 spin coater. After spin coating, the substrates were placed on a hotplate at 100 °C for 15 min and subsequently placed in an oven at 180 °C for 90 min. The cured polyimide glass substrates were rubbed over a velvet cloth before use.

Fabrication of the Temperature-Responsive Wave Plate Coating: The selected mixture (containing 31.5 wt% LCE, 90 µL) was placed on the edge of a rubbed polyimide glass substrate and the solvent was evaporated by heating the mixture stepwise to 80 °C preventing the formation of air bubbles. Subsequently, the mixture was coated antiparallel with respect to the rubbing direction of the substrate using an RK printcoat instrument K control blade coater and the 10 µm gap of a four-sided applicator (10–25 µm gaps, ZFR 2040, Zehntner) with a speed of about 1 cm s⁻¹ at a substrate temperature of 53 °C, which is just below the Tᵤotropic of the LC mixture (58 °C). Subsequently, the coated substrate was transferred to a hotplate at 50 °C in a nitrogen atmosphere using a preheated metal plate to prevent the coating to cool down. Here, the coating was cured by UV-light having an intensity of 23 mW cm⁻² for 10 min using an EXFO Omnicure S2000 mercury lamp. We used a spot with a d of 9.1 µm for the birefringence and birefringence dispersion measurements as well as for the fabrication of the CWC-wave plate-CWC stack.

Fabrication of the CLC Polarizers and CLC-Wave Plate-CLC Stacks: The CLC mixture components were weighed in the desired ratio together with Irgacure 651 (1 wt%) and stirred at 105 °C. LC cells for planar alignment were fabricated by gluing two rubbed polyimide glass substrates in an antiparallel fashion using UV-curable glue (Norland Products Inc UVS 91) containing 10 µm polystyrene beads (Sekisui). Small drops of glue were placed on the four corners of one substrate and the substrates were pressed together using clamps. The glue was cured using a low intensity UV-lamp (4 Philips CLEO 15W lamps) for 30 min. The cells were filled with the CLC mixture at 105 °C by capillary action and left for 30 min to improve alignment. Subsequently, the CLC cells were photopolymerized at 105 °C by UV light having an intensity of 7.5 mW cm⁻² for 10 min using an EXFO Omnicure S2000 mercury lamp. Broadband CLC polarizers were fabricated from a mixture containing UV absorber (Tinuvin-328, 1 wt%). Filled cells were illuminated with a divergent UV light source of intensity =0.02 mW cm⁻² for 60 min and thermally postcured at 120 °C for 10 min. CLC-wave plate-CLC stacks were assembled by sandwiching a temperature-responsive wave plate between two CLC cells using double sided tape.

Differential Scanning Calorimetry (DSC): Transition temperatures of the LC mixtures and temperature-responsive wave plate coatings were measured using a TA Instrument DSC Q2000. Measurements consisted of 3 cycles at a rate of 5 °C min⁻¹.

Birefringence and Birefringence Dispersion Measurements: Temperature-dependent effective Δn values for a λ of 644 nm were measured using a polarized optical microscope (Leica DM 2700M) equipped with a Linkam PE95/795 temperature control stage and a compensator crystal. The effective Δn dispersions of the temperature-responsive wave plate coatings were measured on a Shimadzu UV-3102 PC UV/vis/NIR spectrophotometer equipped with three sets of crossed polarizers, which operated at various λ ranges (400–700 nm (Edmund Optics, linear glass polarizing filter), 600–1100 nm (Thorlabs, LPN1RE050-B), and 1050–1700 nm (Thorlabs, LPIREA050-C)). A glass slide in combination with one polarizer was used for the baseline of each measurement. The optical axis of the wave plate coating was placed at an angle of 45° with respect to the crossed polarizers. Transmission spectra obtained from these measurements show maxima and minima from which effective Δn values can be obtained according to

$$\Delta n(\lambda) = \frac{(2b-1)}{2} \frac{\lambda}{d}$$  \hspace{1cm} (2)

in which Δn(λ) is the effective Δn at the λ where an extreme occurs and b is the peak order.[43,44] The obtained effective Δn values were fitted with a two-coefficient Cauchy model:

$$\Delta n(\lambda) = A + \frac{B}{(\lambda - \lambda_p)^2}$$  \hspace{1cm} (3)

where A and B are fitting parameters.[23–26]

Thickness Measurements: The thicknesses of the temperature-responsive wave plate coatings were measured with an interferometer (Forgale Zoomsurf 3D).

UV/Vis/NIR Spectrophotometry: Transmission spectra were measured on a Shimadzu UV-3102 PC UV/vis/NIR spectrophotometer equipped with a MFC-3100 sample compartment and a Linkam TMS93/LMP93 temperature control stage. Glass slides, equal in number to the glass slides of the sample to be measured, were used as baseline. The actual temperature at the wave plate coating was measured using a thermometer probe (Comark KM340). Angular-dependent measurements were performed on a Perkin Elmer Lambda 750 UV/Vis/NIR-spectrophotometer equipped with an automated reflectance/transmittance analyzer accessory that utilizes a 60 mm integrating sphere mounted on a goniometer with PMT and InGaAs detectors.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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