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Optical thermal sensor based on cholesteric film refilled with mixture of toluene and ethanol

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Abstract: We demonstrate an optical thermal sensor based on cholesteric film refilled with mixture of toluene and ethanol. The thermal response mechanism is mainly based on the thermal expansion effect induce by toluene, where the ethanol is used for refractive index adjustment to determine the initial refection band position of cholesteric film. The ethanol-toluene mixture was used to adjust the color tunability with the temperature in relation with the habits of people (blue as cold, green as safe and red as hot). A broad temperature range of 86 °C and highly sensitivity of 1.79 nm/ °C are achieved in proposed thermal sensor, where the reflective color red-shifts from blue to red when environmental temperature increases from −6 °C to 80 °C. This battery-free thermal sensor possesses features including simple fabrication, low-cost, and broad temperature sensing range, showing potential application in scientific research and industry.

OCIS codes: (160.3710) Liquid crystals; (160.5470) Polymers; (280.4788) Optical sensing and sensors.

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1. Introduction

Cholesteric liquid crystals (CLCs) are one-dimensional (1D) photonic crystals with self-assembly periodic structure, which have attracted a lot of interests for various applications including displays and photonic devices [1]. CLCs can selectively reflect circularly polarized light with the same handedness. The selective reflection wavelength of CLCs is tunable under various external stimuli that lead to change of helical pitch, which makes it possible to use the CLCs as optical sensor where color change can be observed with the naked eye [2–4]. Cholesteric liquid crystal film [5–9], which is fabricated by liquids crystal and reactive mesogens and appears to be mechanically more stable than pure CLC, has attracted considerable attention for optical sensor application such as pH sensor [10], amino acid sensor [11], alcohol sensor [12], metal ion sensor [13], humidity sensor [14], amine sensor [15], and strain sensor [16].

Temperature sensor based low molar mass CLCs have been widely investigated [17–19]. M. E. McConney *et al.* reported thermally induced, multicolored hyper-reflective cholesteric liquid crystal using surface tethered polymer network, where large-scale tuning of selective reflection notch from the near infrared to blue was achieved [20]. D. J. D. Davies *et al.* demonstrated printable optical time-temperature integrator based on chiral nematic polymer network consisting of hydrogen bonded mesogens, which was useful in food packaging and medical industry [21]. S. S. Lee *et al.* studied the red-shift of color from green to red when temperature increased from 20 °C to 88 °C, based on cholesteric liquid crystal droplets [22].

For CLC polymer, S. T. Kim *et al.* reported cholesteric liquid single-crystal elastomers obtained by an anisotropic deswelling method, where the temperature effect on polymer network dimensions was investigated [23]. H. Hangai *et al.* presented the tunability of the

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reflection notches of the film with cholesteric liquid crystal elastomers by temperature variation and the explained the reflection color-shift phenomena theoretically [24]. A red-shift of color from green to red was obtained when temperature increased from 60 °C to 90 °C. However, they only studied the thermal expansion of the CLC template and didn't discuss the thermal expansion effect refilling materials. Most importantly, the reported tuning temperatures were operated in relatively high temperature range (>60 °C), which were not well accordant with people's daily life experience that treats blue as cold, green as normal, yellow as warning, and red as dangerous.

In this paper, we demonstrate an optical thermal sensor based on cholesteric film refilled with mixture of toluene and ethanol. The thermal response mechanism is mainly based on the thermal expansion effect induce by toluene, where the ethanol is used for refractive index adjustment to determine the initial refection band position of cholesteric film. Optimized ethanol concentration in toluene of 30% is used to fabricate thermal sensor with broad sensing range of 86 °C and highly sensitivity of 1.79 nm/ °C. The reflective color of sensor red-shifts from blue to red when environmental temperature increases from −6 °C to 80 °C, which is accordance with people's daily life experience and habit that treats blue as cold, green as normal, yellow as warning, and red as dangerous. This battery-free thermal sensor possesses features including simple fabrication, low-cost, and broad temperature sensing range, showing potential application in scientific research and industry.

2. Experiment

The pre-polymer mixture used in our experiment consisted of cholesteric liquid crystals (74 wt%), reactive mesogens (25 wt%), and photo-initiator Darocur1173 (1 wt%, Sigma-Aldrich). The cholesteric liquid crystal was prepared by nematic liquid crystal E7 (97.2 wt%, n_e = 1.74 and n_o = 1.52, HCCH) and chiral dopant R5011 (2.8 wt%, HTP = 94 μm^{-1} in E7, HCCH). The reactive mesogens (RM) consisted of RM257, RM82, RM006, RM021, and RM010 (all from Shijiazhuang Sdyano Fine Chemical), with weight ratio of 30: 20: 20: 20: 10 [25, 26]. The RM257 and RM82 were macromolecules materials, which could form a polymer network structure. The RM 006, RM021 and RM010 were small molecules materials, which could blend into the CLC molecules and hold the helix structure. The effect of using five RMs was better than using one alone. Figure 1 demonstrates the fabrication process of cholesteric template film. Firstly, the LC/RM sample was mixed by a magnetic stirrer at 70 °C for 20 minutes (step I, Fig. 1(a)), and then injected into a LC cell (thickness was 45 μm) that was assembled by two indium tin oxide (ITO) coated glasses with anti-parallel rubbing using polyimide (step II, Fig. 1(b)). Then, the sample was exposed in an ultraviolet (UV) light (UVEC-4II, LOTS) at intensity of 15 mW/cm^2 for 15 minutes to photo-polymerize the LC/RM mixture and form a cholesteric liquid crystal film (CLCP) (step III, Fig. 1(c)). Finally, the sample was immersed in toluene for 2 minutes to soak out CLC and unreactive monomers and a CLC template was fabricated (step IV, Fig. 1(d)).

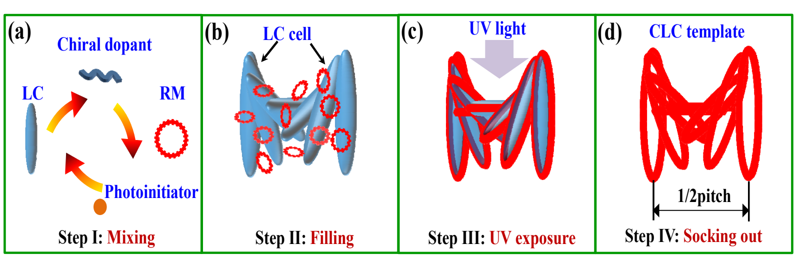

Fig. 1. Schematic of fabrication process of cholesteric liquid crystal template. (a) Mixing of LC, chiral dopant, RM, and photoinitiator; (b) Filling the mixture into a LC cell with anti-parallel rubbing; (c) The sample was exposed under UV light; (c) Soaking CLC and unpolymerized monomers out by immersing the sample in toluene.

3. Results and discussion

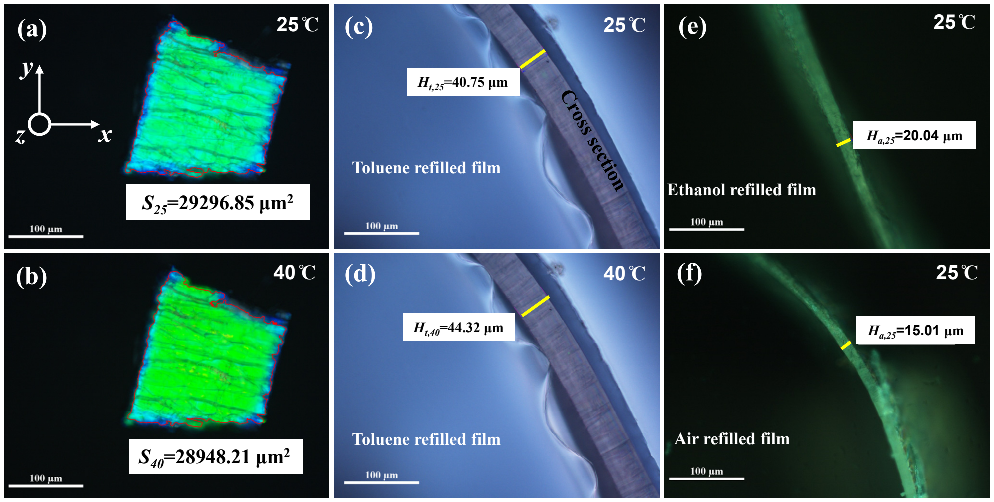

Fig. 2. Surface images of cholesteric template refilled with toluene observed under POM at (a) 25 °C and (b) 40 °C, where the surface area in *x-y* plane was measured to be S_{25} = 29296.85 μm^2 and S_{40} = 28948.21 μm^2, respectively. Cross section images of cholesteric template refilled with toluene observed under optical microscopy at (c) 25 °C and (d) 40 °C, where the thickness along *z*-axis was measured to be H_{25} = 40.75 μm and H_{40} = 44.32 μm, respectively. The photo images of film refilled with (e) ethanol and (f) air at room temperature of 25 °C, respectively.

In our experiment, the cholesteric template was refilled with different materials (so called fillers) including toluene, ethanol, and air, for thermal expansion property measurement. Our results indicated that the toluene refilled cholesteric film demonstrated a significant thermal expansion while the other two of ethanol and air had no apparently thermal expansion effect. Figures 2(a) and 2(b) show the photo images of cholesteric template refilled with toluene in polarizing optical microscope (POM) at 25 °C and 40 °C, respectively. At 25 °C, the measured surface area in *x-y* plane and thickness along *z* direction of the film was S_{25} = 29296.85 μm^2 (Fig. 2(a)) and H_{25} = 40.75 μm (Fig. 2(c)), respectively. Therefore, the volume of cholesteric film at 25 °C was $V_{25} = S_{25} \times H_{25} = 1.19 \times 10^6$ μm^3. When the temperature increased to 40 °C, the surface area decreased to S_{40} = 28948.21 μm^2 (Fig. 2(b)) while the thickness increased to H_{40} = 44.32 μm (Fig. 2(d)), leading to an increase of the volume to $V_{40} = 1.28 \times 10^6$ μm^3. In Figs. 2(a) and 2(b), we can clearly see that the color of film red-shifted from blue-green (490 nm) to green (558 nm). This phenomenon can be explained by thermal expansion effect of film [24]: the pitch (*p*) of the CLC template increases during thermal expansion, resulting in redshift of central wavelength in reflection band according to $\lambda_0 = n_{av} *p$, where λ_0 is the central wavelength in the reflection band, n_{av} is the average refractive index of cholesteric film, and *p* is the pitch length. According to the expansion coefficient formula: $\gamma = (V_{40}/V_{25} - 1)/\Delta T$ [27], where the γ is expansion coefficient, V_{25} and V_{40} is the volume of cholesteric film refilled with refiller at 25 °C and 40 °C, respectively, and ΔT is the temperature difference. The calculated expansion coefficient of the cholesteric film refilled with toluene is $\gamma = 4.9*10^{-3}$. However, the expansion coefficient of the toluene and reactive mesogen is ~$1.2*10^{-3}$ and ~$0.085*10^{-3}$, respectively (data from manufacturer), which are significantly less than the value of $4.9*10^{-3}$. The experimental data show that for the film refilled with toluene, the thermal expansion is related to not only the cholesteric template itself but also the material refilled. Figures 2(e)-2(f) show the cross section images of cholesteric film refilled with ethanol and air observed in optical microscope, respectively. The thickness of the film refilled with ethanol and air was measured to be 20.04 μm, and 15.01

μm, respectively, at temperature of 25 °C. It is worth mentioning that, when the fluid component was present or not in the polymer-stabilized CLCs, the polymer network would swell or collapse due to the swelling of the open macromolecular network, which had been demonstrated by transmission electron microscopy by Agez *et al.* [28].

According to the above experimental results, property selected refiller of cholesteric template would affect the thermal expansion ability of cholesteric film. Therefore, we chose the toluene as the major refiller in our following experiment. In addition, for application of thermal sensor/indicator used in daily lift such as milk for baby, hot water indicator and so on, the human-friendly thermal sensor/indicator with blue, green, yellow, and red color in low, room, high, and dangerous temperature, respectively, is highly required. Because it is accordant with people's experience and habit, where the green color usually means safety and the red color means danger. Therefore, we added ethanol into toluene and use the mixture as the refiller, due to excellent compatible of these two materials. The ethanol-toluene mixture was used to adjust the color tunability with the temperature in relation with the habits of people (blue as cold, green as safe and red as hot). It is noticed that, in our experiments, we used epoxy resin to seal the LC cell with thickness of 150 μm, where the CLC film refilled with mixture of toluene and ethanol. The epoxy resin could prevent the mixture of toluene and ethanol from evaporating.

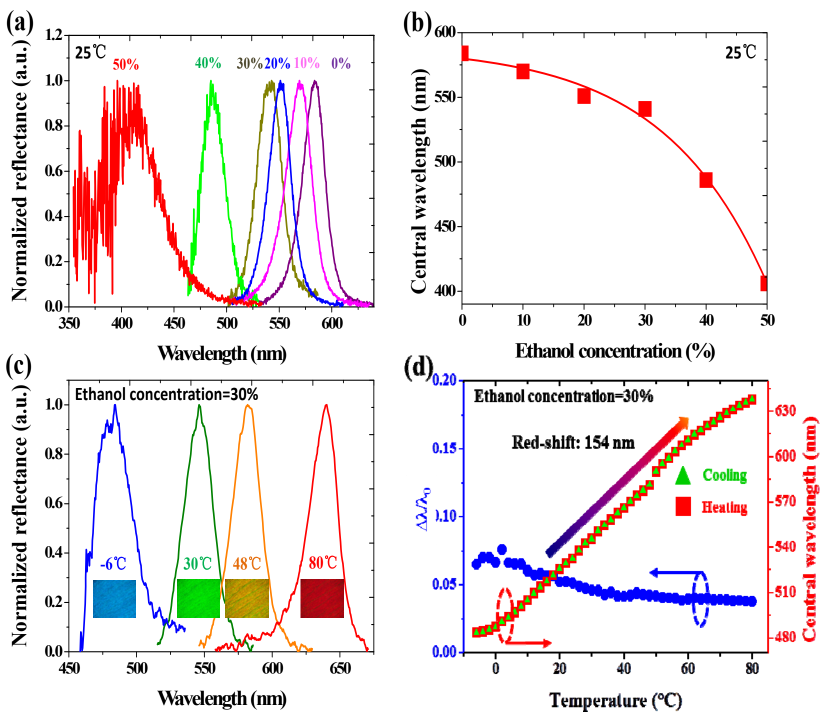

Fig. 3. (a) The normalized reflectance of cholesteric films refilled with different mixture with 50%, 40%, 30%, 20%, 10%, and 0% concentration of ethanol. (b) The central wavelength of film as a function of the concentration of ethanol within toluene. (c) The reflectance spectrum of the cholesteric template film as a function of temperature from −6 °C to 80 °C. Insets show the images of the sample taken on polarizing optical microscope. (d) The center wavelength of the bandgap and the $\Delta\lambda/\lambda_0$ as a function of temperature. The hysteresis effect is demonstrated by red square and green triangle corresponding to heating and cooling process, respectively.

Six groups of sample were prepared by refilling mixture of ethanol and toluene into cholesteric template film, where the concentration of ethanol varied from 0% to 50%, beyond which the reflective color of film will appear in ultra violet (UV) range in room temperature and will not suitable for daily life thermal sensor/indicator mentioned above. The effective

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refractive index of mixture was determined by the volume ratio of ethanol and toluene, which finally determined the average refractive index of cholesteric film. The reflection central wavelength of cholesteric film can be calculated by equation of $\lambda_0 = n_{av} * p$, where λ_0 is the central wavelength in the reflection band, n_{av} is the average refractive index of cholesteric film, and p is the pitch length. The average refractive index $n_{av} = n_p*\varphi_1 + (n_t*(1-\varphi_2) + n_a*\varphi_2)*(1-\varphi_1)$ [29], where n_p, n_t and n_a are refractive index of polymer (1.56), toluene and ethanol refractive index, respectively. φ_1 and φ_2 are the volume fractions, φ_1 is the polymer volume fraction of the component in the film, and φ_2 is the ethanol volume fraction of the component in the filler. In our experiment, the refractive index of toluene and ethanol was n_t = 1.49 and n_a = 1.36 (at 25 °C), respectively. According to the formula of $\lambda_0 = n_{av} *p$, the λ_0 should change linearly with φ_2. However, in our experiment, the λ_0 changed nonlinearly with φ_2 (as shown in the Fig. 3(b)). The reason might be the different swelling capacity due to the mixture of toluene and ethanol, which leads a complicated relationship of average index and central wavelength. Figure 3 (a) plots the normalized reflectance spectra of six samples corresponding to 50%, 40%, 30%, 20%, 10% and 0% concentration of ethanol in refiller mixture at 25 °C. It can be seen that, at fixed temperature, the central wavelength of cholesteric film shifts from 584 nm to 406 nm with the increase of ethanol concentration from 0% to 50%, as shown in Fig. 3(b).

Herein, cholesteric film refilled with toluene/ethanol mixture containing 30% concentration of ethanol was characterized as thermal indicator due to its reflective green color in room temperature. The sample was placed on a hot-stage (INSTEC, MK2000) and a fiber optic spectrometer (Ocean optics, USB2000) was used to measure the reflection spectrum of film at different temperatures, for all spectral data acquisition, the fiber probe direction is designed to be perpendicular to the film surface As shown in Fig. 3(c), the central wavelength of the reflection bandgap redshifts from 481.5 nm (blue) to 638.8 nm (red) while the temperature increases from −6 °C to 80 °C. The photo images of cholesteric film observed under polarization optical microscopy, corresponding to temperature at −6 °C (blue), 30 °C (green), 48 °C (yellow), and 80 °C (red) were shown in insets of Fig. 3(c). Our experiment demonstrates a significant color-shift of the cholesteric film from blue to red corresponding to change of environmental temperature, working as a highly-sensitive thermal sensor. The response time of the thermal sensor was about 8 seconds when the temperature suddenly increased from −6 °C (blue) to 80 °C (red). The summarized relationship of central wavelength versus temperature is plotted in Fig. 3(d). The central wavelength linearly red-shifts about 154 nm within temperature change of 86 °C (from −6 °C to 80 °C) and sensitivity is calculated to be 1.79 nm/ °C. The hysteresis effect is demonstrated by red square and green triangle corresponding to heating and cooling process, respectively, as shown in Fig. 3(d). It can be seen that there is no significant hysteresis effect in our thermal sensor.

Two mechanisms work together to achieve the color shift in increasing temperature. One is the change of average index refractive of cholesteric film, where the refractive index of film materials (including ethanol and toluene) usually decreases as the temperature increases [30], leading to blue-shift of reflection band. However, for our cholesteric film, the results indicate that the thermal expansion play an important role in red shift of reflection band that is a more significant process comparting to blue-shift from index reduction, finally resulting in the red-shift in increasing temperature. The parameter of $\Delta\lambda/\lambda_0$ is usually used to measure the thermal deformation of material, where $\Delta\lambda$ is the full width at half minimum (FWHM), and λ_0 is the central wavelength of reflection bandgap [24]. The value of $\Delta\lambda/\lambda_0$ does not become zero as the temperature increasing, but gradually tends to around 0.04 as the temperature varies from −6 °C to 80 °C, indicating not significant distortion of cholesteric film and orientation of helical axis [31], as shown in Fig. 3(d).

Figures 4(a)-4(d) shows the photograph of the cholesteric film at different temperatures. The color of the film is blue, green, yellow, and red at −6 °C, 30 °C, 48 °C and 80 °C, respectively. We can see that, the proposed film is an excellent optical thermal senor/indicator with broad temperature sensing and color range that can be observed by naked-eye, where color demonstrated is accordance with people's daily life experience and habit that treats blue as cold, green as normal, yellow as warning, and red as dangerous. In our experiments, glass substrates were used for demonstration. However, flexible substrate such as PET could also be used to provide the freedom of deformation in flexible device applications.

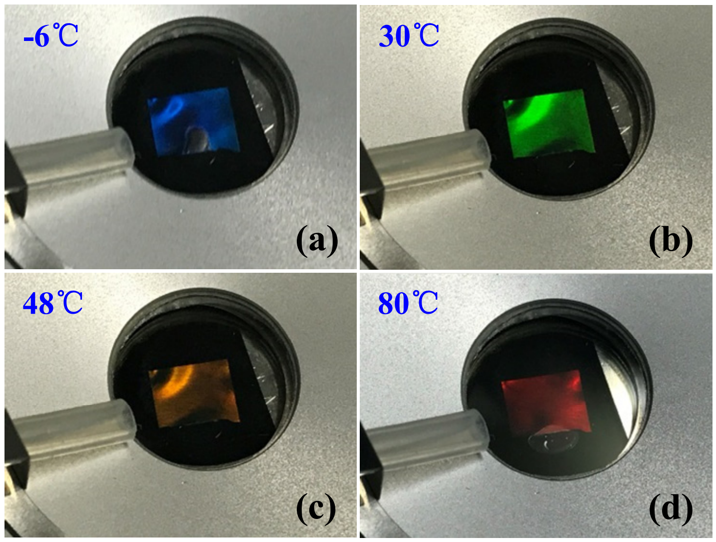

Fig. 4. Photographs of the sample at temperature of (a)-6 °C, (b) 30 °C, (c) 48 °C and (d) 80 °C.

4. Summary

In summary, an optical thermal sensor based on cholesteric film refilled with mixture of toluene and ethanol has been demonstrated experimentally. The thermal response mechanism is mainly based on the thermal expansion effect induce by toluene, where the ethanol is used for refractive index adjustment to determine the initial refection band position of cholesteric film. Optimized ethanol concentration in toluene of 30% is used to fabricate thermal sensor with broad sensing range of 86 °C from −6 °C to 80 °C and highly sensitivity of 1.79 nm/ °C. The reflective color of sensor red-shifts significantly from blue, green, yellow to red (central wavelength varies from 481.5 nm to 638.8 nm) when environmental temperature increases from −6 °C, 30 °C, 48 °C, to 80 °C, which is accordance with people's daily life experience and habit that treats blue as cold, green as normal, yellow as warning, and red as dangerous. This battery-free thermal sensor possesses features including simple fabrication, low-cost, and broad temperature sensing range, showing potential application in scientific research and industry.

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