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Chiral polymer networks with a broad reflection band achieved with varying temperature

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ABSTRACT

In this study, we demonstrate a novel method for fabricating a single layer cholesteric liquid crystal (CLC) film with non-uniform pitch distribution by utilizing the chiral polynetworks. A chiral monomer, the helical twist power (HTP) of which decreases with the increase of temperature, was synthesized. The temperature dependence of the pitch of the mixtures before and after polymerization was investigated. To broaden the reflection band, the experimental processes of thermally induced pitch variation were presented. The results suggest that the chirality of the polymer network plays an integral role in the reflection spectra. Additionally, scanning electron microscopy (SEM) was used to examine the role of the polymer network induced by polymerization temperature. These wide-band reflection optical properties make the CLC gels interesting for their potential applications in many fields, such as colour filters, brightness enhancement films, smart switchable reflective windows etc.

1. Introduction

The applications of polymer network to stabilize cholesteric liquid crystal (CLC) phases, such as flat-panel displays and switchable optical elements, have attracted increasing interest recently [1–8]. Polymer-stabilized cholesteric liquid crystals (PSCLCs) are generally produced by photo-polymerization of a relatively small amount of a photo-reactive, bifunctional monomer and chiral dopant dissolved in the low molar mass LCs. The monomers are often mesogenic themselves and contain end-standing acrylate or methacrylate functional groups, which are polymerized through a radical-chain polymerization in the presence of a photo-initiator and illumination with UV light. PSCLC's fabrication implies an understanding of the relationship among monomer constitution [9], polymerization conditions [10,11], network morphology [12–14] and electro-optical performance [15]. Most of the research efforts have focused on novel polymer composites [16–20].

Due to the unique helical supramolecular structure, CLC can selective reflect circularly polarized incident light with the same handedness as its helical axis. At normal incidence, the wavelength of the reflected light, $\lambda = nP$, here, $n = (n_o + n_e)/2$ is the average of the ordinary (n_o) and extraordinary (n_e) refractive indices of the locally uniaxial structure, P is the cholesteric pitch corresponding to length over which the director rotates 360°. The reflected bandwidth ($\Delta\lambda$) is given by $\Delta\lambda = (n_e - n_o)\,P = \Delta nP$, where $\Delta n = n_e - n_o$ is the birefringence of the liquid crystal. Since Δn value for colorless organic material is generally smaller than 0.3, the bandwidth of a single-pitch CLC in visible region is less than 100 nm. However, a CLC with $\Delta\lambda$ less than 100 nm is insufficient for some applications, such as brightness enhancement films, wide-band reflective polarizers and so on.

To broaden the bandwidth, Broer et al. [21] have prepared the CLC gels with a pitch gradient from the photo-polymerization of a composite comprising diacrylate monomer/LC monomer of monoacrylate/UV absorbing dye composite. Mitov et al. [22] have described that the reflection band in PSCLC films can also be broadened without adding a UV absorbing dye due to the natural UV absorbing properties of the LC composite. Yang et al. [23] have achieved the polymer network/LC/chiral dopant composites whose bandwidth can be thermally controllable. Recently, we have shown that spin-coating PSCLC layer on the substrates using an unsticking technique and photo- and thermally-induced method can obtain the wide-band reflection composite as well [24,25].

Different from the above researches, the present work develops a method to prepare PSCLC gels with a non-uniform pitch distribution.

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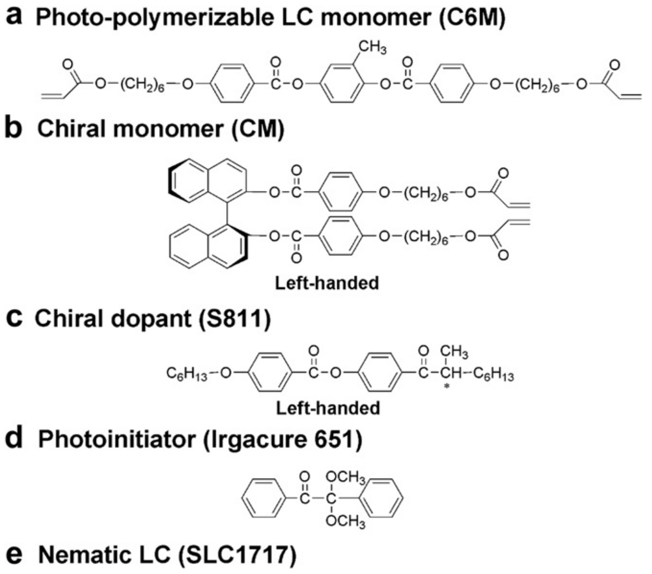

Fig. 1. Chemical structures of the materials used.

A chiral monomer of which the HTP decreases with the increase of temperature, was used. To broaden the reflection band, the experimental processes of thermally induced pitch variation were presented. The polymer network is mainly derived from the chiral monomer and nematic photopolymerizable monomer. The memory effect of the polymer network in PSCLC cell was further clarified. Additionally, the morphology of the polymer network of different systems was investigated in order to understand the relationship between the morphology of the polymer network and the reflectance properties.

2. Experimental section

2.1. Materials

In this study, nematic mesogens (SLC-1717, $n_o = 1.519$, $n_e = 1.720$, $\Delta n = n_e - n_o = 0.201$, $T_{N\text{-}I} = 92\,^{\circ}C$, Shijiazhuang Yongsheng Huatsing Liquid Crystal Co.Ltd.), chiral monomer, (S)-(−)-1,1′-binaphthyl-2,2′-diyl bis(4-(6-(acryloyloxy)hexyloxy)benzoate), LC monomer, 1, 4-di-[4-(6-acryloyloxy) hexyloxy benzoyloxy]-2-methyl benzene (C6M), chiral dopant, S811 (Merck Co.Ltd.) and photo-initiator, 2, 2-dimethopxy-1, 2-diphenyl-ethanone (IRG651, TCI Co.Ltd.) were used. C6M was synthesized according to the method suggested by Broer [26]. Chiral monomer above was lab-synthesized. Fig. 1 shows the chemical structures of these materials.

2.2. Synthesis of the chiral monomer

A mixture of (S)-(−)-1, 1′-binaphthyl-2, 2′-diol (2.9 g, 0.01 mol), 4-(6-(acryloyloxy)hexyloxy)benzoic acid (6.4 g, 0.022 mol), N, N′-dicyclohexyl carbodiimide (DCC) (4.5 g, 0.022 mol) and 4-pyrrolidinopyridine (DMAP) (0.12 g, 0.001 mol) dissolved in 200 mL dry CH_2Cl_2 at room temperature and heated to 40 °C under magnetic stirred for 48 h. After filtration and removal of solvent, the residue was dissolved in 200 ml CH_2Cl_2 and washed twice with 40 ml 1 N HCL and twice with 40 ml saturated sodium hydrogen carbonate solution. After removal of the solvent, the residue was recrystallised from 100 ml EtOH and purified by column chromatography (silica gel, ethyl acetate/hexane = 1/3). 4-(6-(acryloyloxy) hexyloxy)benzoic acid was synthesized according to the methods reported in [27].

Characterization Data. White crystal, IR (KBr, cm^{-1}): 1737 (C=O stretching), 1645 (C=C), ^{1}H NMR ($CDCl_3$) δ: 7.97–7.95 (2H, d), 7.90–7.88 (2H, d), 7.59–7.54 (6H, t), 7.45–7.26 (6H, m), 6.71–6.69 (4H, d), 6.37–6.36 (2H, d), 6.18–6.05 (2H, q), 5.81–5.80 (2H, d), 4.18–4.14 (2H, q), 3.94–3.90 (2H, q), 3.77–3.70 (4H, m), 1.80–1.67 (4H, m), 1.47–1.41 (6H, m), 1.26–1.23 (4H, m).

Table 1

Mixture (type)	Weight ratio[a]	T_{Ch-I} (°C)[b]	ΔH(J/g)[c]
1	1.0/0.0/0.0/99.0/0.0	90.6	1.53
2	0.0/1.0/0.0/99.0/0.0	90.8	1.60
3	4.0/0.0/5.0/90.99/0.01	81.5	1.45
4	4.0/0.0/15.0/80.97/0.03	84.8	1.32
5	4.0/0.0/25.0/70.95/0.05	87.4	1.15
6	4.0/10.0/5.0/80.99/0.01	73.6	1.17

[a] Weight ratio: CM/S811/C6M/SLC-1717/IRG651.
[b] T_{Ch-I}: clearing temperature from cholesteric to isotropic phase.
[c] ΔH: Delta H from cholesteric to isotropic phase.

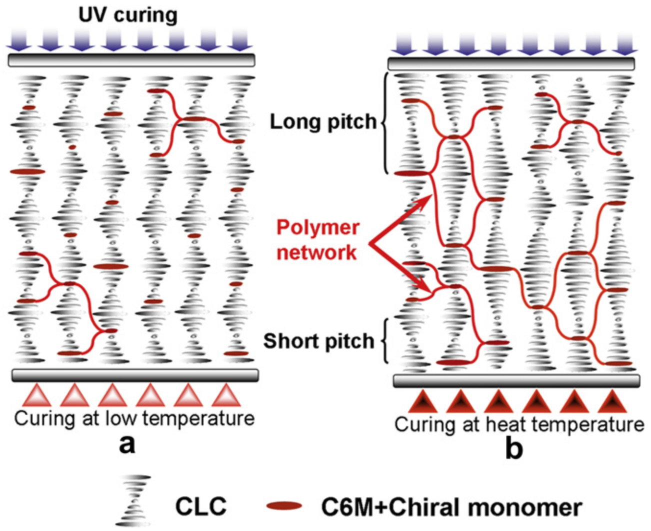

Fig. 2. The schematic of the method to prepare the expected PSCLC cell. (a) UV-curing at low temperature; (b) UV-curing at heat temperature.

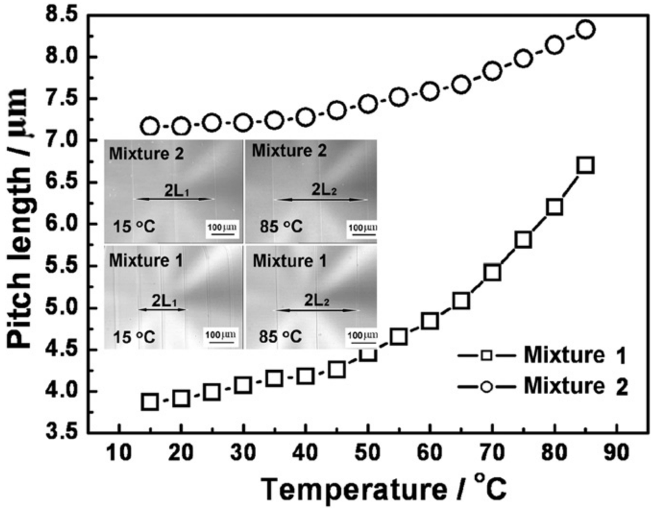

Fig. 3. Temperature dependence of the pitch length of mixtures 1 (CM/S811/C6M/SLC-1717/IRG651 = 1.0/0.0/0.0/99.0/0.0) and 2 (CM/S811/C6M/SLC-1717/IRG651 = 0.0/1.0/0.0/99.0/0.0); the insets are the corresponding POM micrographs taken in the Cano wedges at 15 and 85 °C.

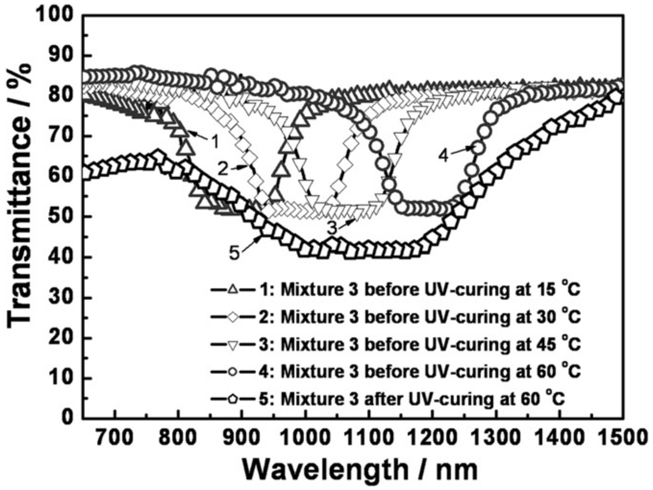

Fig. 4. The transmission spectra of mixture 3 (CM/S811/C6M/SLC-1717/IRG651 = 4.0/0.0/5.0/90.99/0.01) shifts to longer wavelength as temperature increases before UV-curing and after UV-curing.

2.3. Characterization and measurements of mixtures

The synthesized compounds were characterized by FT–IR (Perkin Elmer Spectrum One) with wavenumber ranging from 400 to 4000 cm^{-1}, ^{1}H NMR (Bruker DMX-400 spectrometer) with $CDCl_3$ as the solvent. The optical textures of mixtures were observed by a polarizing optical microscope (POM, Olympus BX51) with a hot stage calibrated to an accuracy of ±0.1 K (LinkamTHMS-600). The differential scanning calorimetric (DSC, Perkin Elmer Pyris 6) analysis was used with a heating and a cooling rate of 10 °C/min under a dry nitrogen purge. The transmission and reflection spectras were obtained with a UV/VIS/NIR spectrophotometer (JASCO V-570). The morphology of the polymer network was observed by scanning electron microscopy (SEM, Leicas 440I).

2.4. Preparation of the cells

The cell's two inner surfaces with polyvinyl alcohol (PVA) layers were rubbed in perpendicular directions to provide a homogeneous orientation. 50-μm-thick PET (polyethylene terephthalate) films were used as spacer of the cells. All the mixtures exhibited a cholesteric phase at room temperature and were filled into the cell by capillary action. The composite exhibited a planar texture when it was filled into cell under homogeneous boundary conditions.

The PSCLC cells (mixtures 3–6) were prepared by carrying out the following procedure. The cells of mixtures were irradiated with UV light (5 $\mathrm{mW/cm^2}$, 365 nm) for 10 min while the temperature increased from 15 °C to 60 °C gradually, during which polymer network was formed from the photo-polymerization of C6M and chiral monomer.

3. Results and discussion

To investigate the influence of the chiral polymer networks on the performance of PSCLC cells, the mixtures 1–6 were prepared as listed in Table 1. Here, the chiral monomer was left-handed helix. The mixture 6 contains chiral dopant S811, thus, the position of the reflection band can be adjusted by choosing an appropriate concentration of S811. The schematic of the method to prepare the expected PSCLC cell is as shown in Fig. 2. At low temperature, short pitch CLCs were fixed by polymer networks formed firstly, at high temperature, long pitch CLCs were fixed by polymer networks formed subsequently. We show in this paper that the cell structure

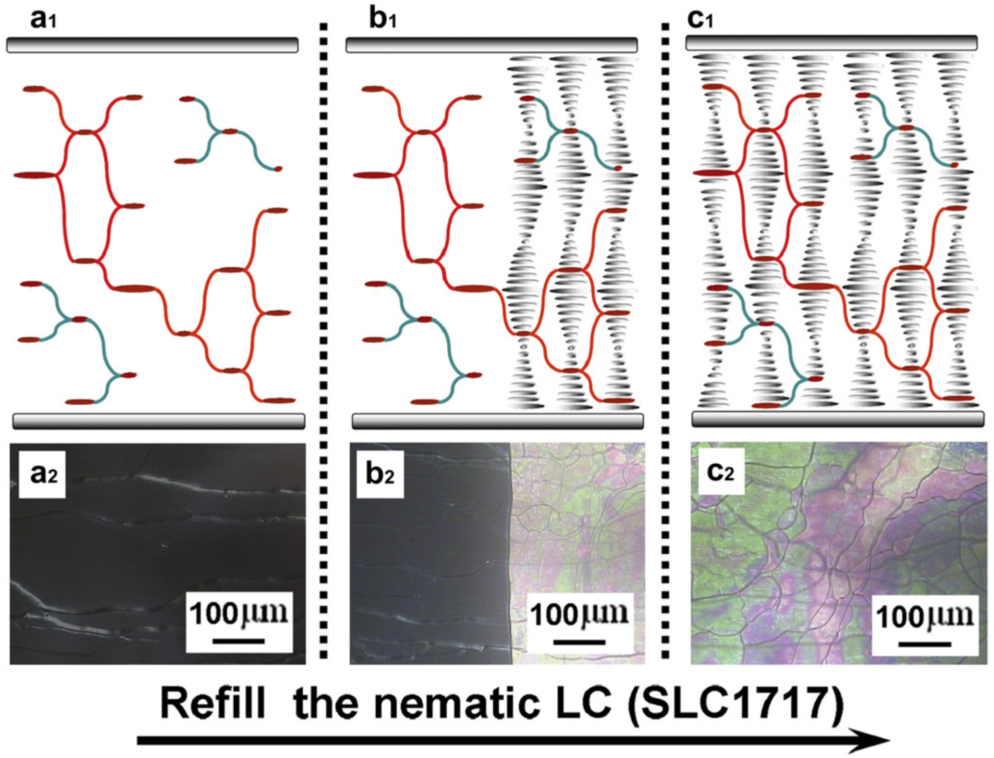

Fig. 5. The schematic representation and POM photographs of the cell containing mixture 3 before and after wash-out/refilling method. a_1: after wash-out, b_1: half refilled, c_1: fully refilled.

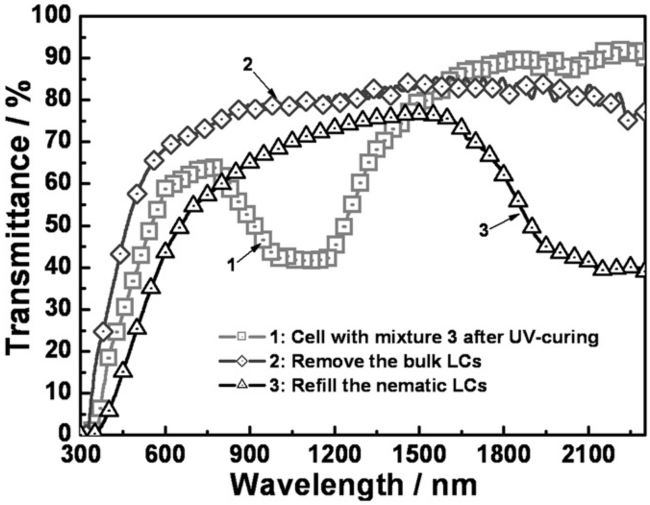

Fig. 6. The transmission spectra of the composite 3 before and after wash-out/refilling method. Curves 1, 2 and 3 corresponding to the cell with mixture 3 after UV-curing, remove the bulk LCs and refill the nematic LCs respectively.

is constructed by the permanent solid helical structure of the polymer networks.

3.1. *The temperature dependence of pitch length of the composites*

The pitch lengths of mixtures 1 and 2 were measured by the Cano wedge technique [28]. In this measurement, a wedge-shaped cell with a wedge angle (KCRK-07, Japan, θ: 0.01937 rad), was used and the inner surfaces of its two glass substrates were treated to provide a homogeneous orientation of LC molecules. After the mixtures were filled into the cell, a Grandjean–Cano texture formed with disclination lines separated by a distance $L_1$and L_2 at different temperature as can be seen from Fig. 3. The pitch length P is determined from $P = 2L\tan\theta \approx 2L\theta$. The temperature dependences of the helical pitch for mixtures 1 and 2 are shown in Fig. 3. Such as, the pitch length of mixture 1 increased from 3.6 to 6.7 µm with increasing temperature from 15 to 85 °C. This is due to that the helical twist power (HTP) of the chiral monomer decrease with increasing temperature.

Fig. 4 shows that the reflection spectra of mixture 3 shifts to longer wavelength with the increase of temperature measured by an UV/visible/near infrared spectrophotometer. It can be found that the reflection bands are located in the wavelength of 891 nm, 993 nm, 1065 nm and 1192 nm at 15 °C, 30 °C, 45 °C and 60 °C (Curves 1–4), respectively. Curve 5 shows that the bandwidth of the spectra of mixture 3 becomes broadened after UV-curing at 60 °C. It should be noted that the mixture reflect light flux range of 860–1300 nm after polymeration and the prepared PSCLC cell has a wide-band reflection effect.

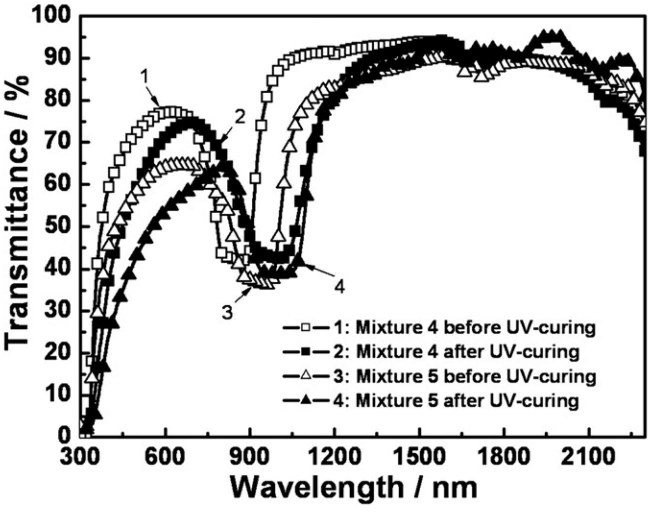

Fig. 7. The transmission spectra of mixtures 4(CM/S811/C6M/SLC-1717/IRG651 = 4.0/0.0/15.0/80.97/0.03), 5(CM/S811/C6M/SLC-1717/IRG651 = 4.0/0.0/25.0/70.95/0.05) before and after UV-curing.

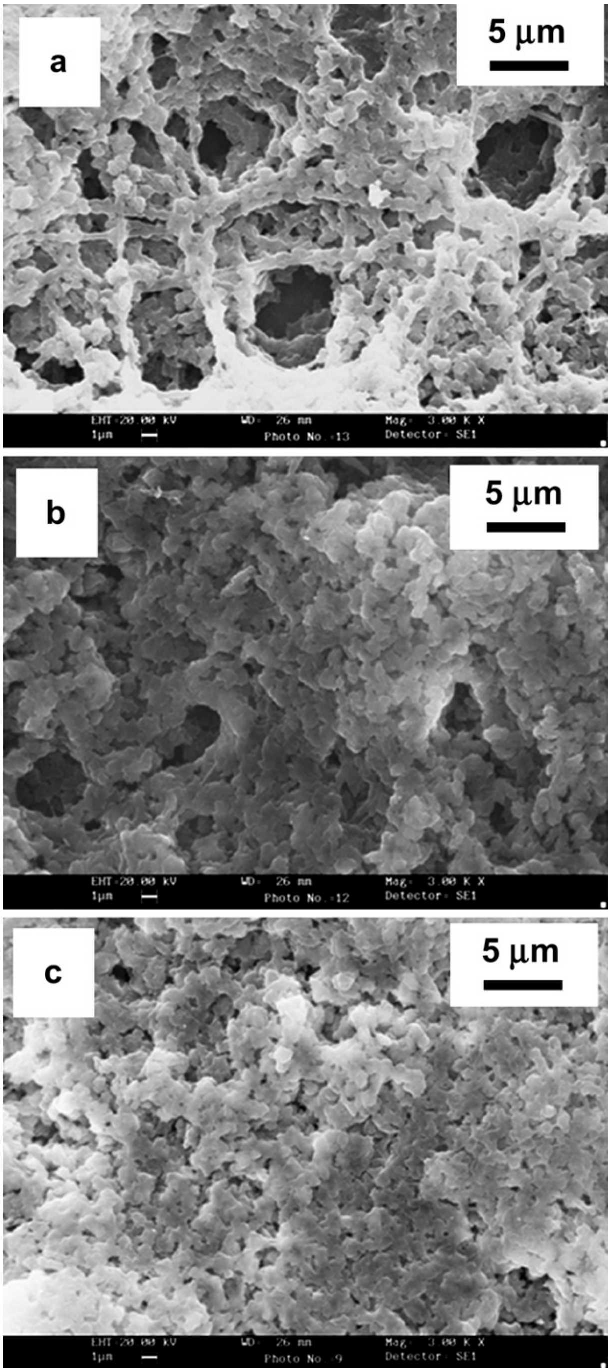

Fig. 8. SEM photographs of the surface morphology of the cells containing (a) mixture 3, (b) mixture 4, (c) mixture 5 after UV-curing.

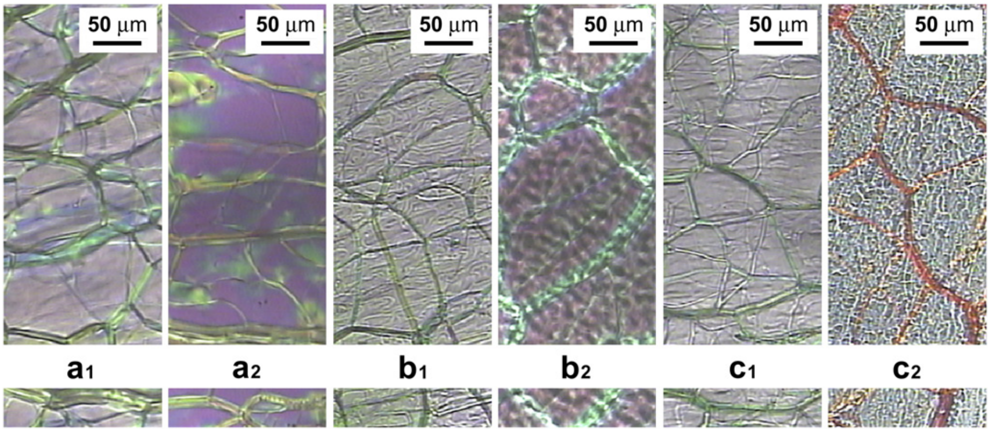

Fig. 9. POM photographs of mixtures 3–5 before (a1, b1 and c1) and after (a2, b2 and c2) UV-curing.

To examine the effect of polymer network on the performance of PSCLC cell, a wash-out/refilling method and UV/VIS/NIR spectrophotometer text were used. The cell of mixture 3 ,after polymerization, was dipped into n-hexane for 24 h at room temperature, and then the cell with polymer network was dried for 12 h under vacuum. According to the fabrication process as shown in Fig. 5, the left-handed polymer network was prefabricated (a_1, a_2) and then the nematic LCs (SLC-1717) are infiltrated into the network (b_1, b_2). Usually, the nematic LCs has thread texture or schlieren texture. But the resulting cell has a good planar Grandjean texture again (c_1, c_2). Fig. 6 shows the transmission spectra of mixture 3 before and after wash-out/refilling method. Curves 1, 2, 3 show the spectra of the cell after UV-curing, remove the bulk LCs and refill the nematic LCs, respectively. It can be seen that the middle position of the reflection band moves from 1080 to 2200 nm when LCs refill the mixture 3. Due to the anchoring effect of the polymer network on the nematic LC molecules, the nematic LCs should template the cholesteric order of the network. When refill the nematic LCs, the environment near the polymer network changes and the anchoring effect of the polymer network decreases, so the pitch of LC cholesteric order increases which caused that the reflection band moved to 2200 nm. The results strongly suggested that the memory effect brought by the polymer network controls the cell properties.

3.2. The effect of LC monomer C6M

Fig. 7 shows the transmission spectra of mixtures 4 and 5 before and after polymerization, respectively. As the increase of concentration of LC monomer C6M, the wide-band reflection spectra change little after UV-curing. In order to demonstrate the influence of the concentration of C6M, the network surface morphology was observed with a scanning electron microscopy (SEM). The network voids become smaller with the increase of the concentration of C6M as shown in Fig. 8a–c. There is an evidence that smaller voids network are good for fixing CLCs [29]. Additionally, the polymer morphology ensures memory effects of the orientational order present when its formation occurs (anisotropic growth of polymer units, for example, oriented fibres) [30–33]. Thus, the wide-band reflection spectra of mixtures 4 and 5 change little after UV-curing, the reflection bandwidth can be controlled by adjusting the concentration of C6M.

A well-oriented planar texture plays a crucial role in the optical performances of prepared CLC composite cells. In a planar texture, all the helical axes are arrange in the direction perpendicular to the substrate surfaces. The CLC reflects circularly polarized light with the same helical sense as its helical structure. If the incident light is unpolarized, the maximum reflectance is nearly 50%. While in

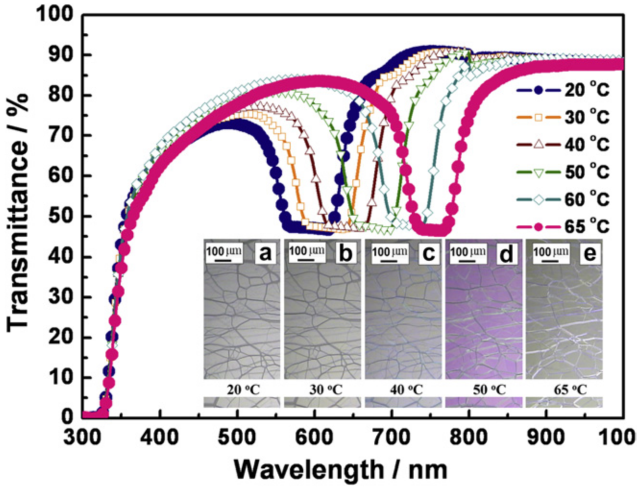

Fig. 10. The transmission spectra of mixture 6 (CM/S811/C6M/SLC-1717/IRG651 = 4.0/10.0/5.0/80.99/0.01) at different temperature and the POM photographs corresponding to temperature.

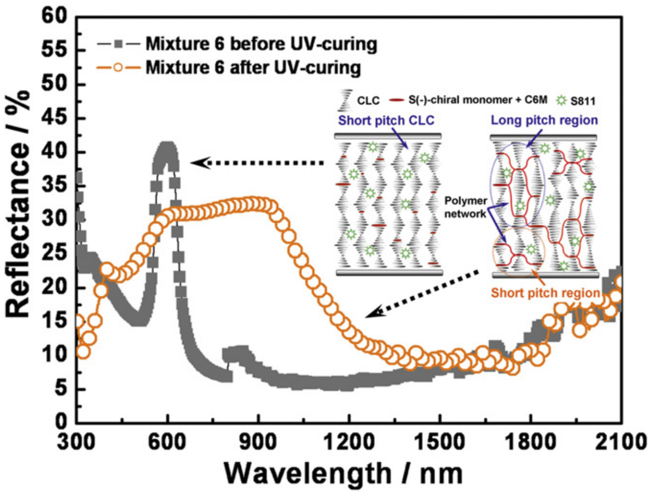

Fig. 11. Reflection spectra of a cell containing mixture 6 before and after UV-curing; the insets are the schematic representation of CLC molecules and the UV-curing polymer network before and after photo-polymerization.

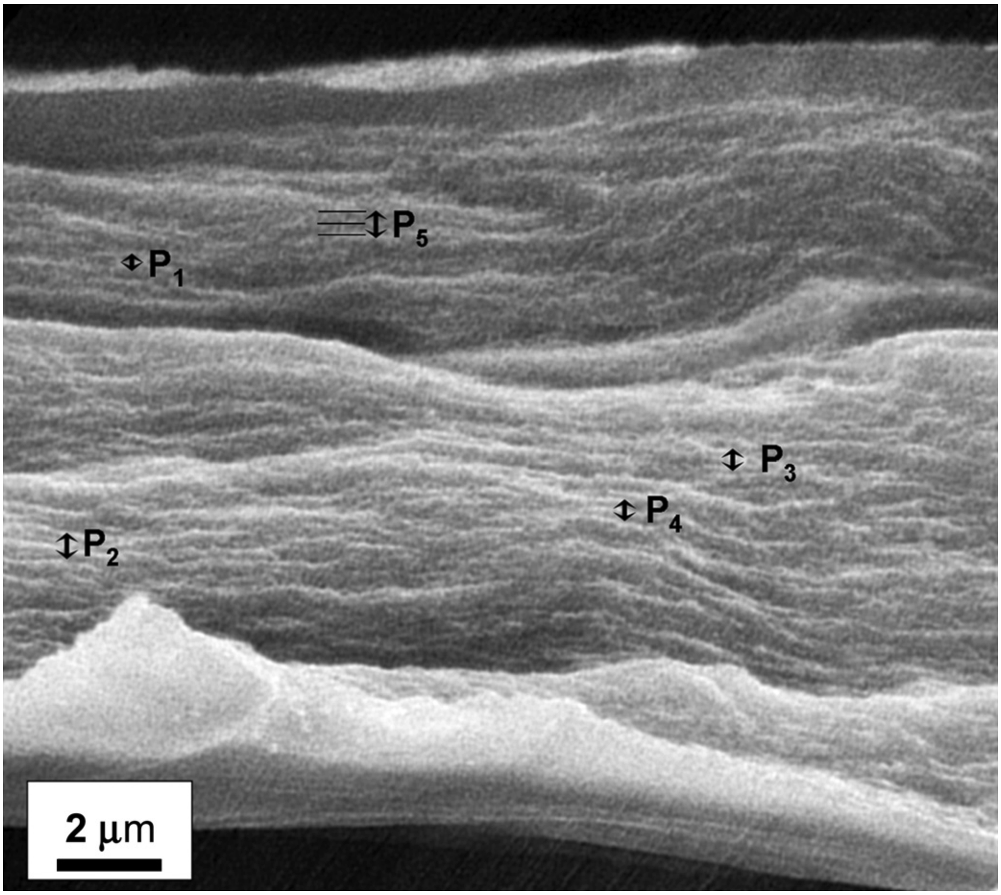

Fig. 12. SEM image of the fractured surface of cross-linked mixture 6. The dimension of the bands in the fine structure on the fractured planes corresponds to a π molecular rotation, it is $P/2$.

a focal conic texture, the helical axes are randomly arranged. This texture shows strong light scattering because of the discontinuous spatial change of the refractive indices at the domain boundaries, and it will decrease the reflective intensity of PSCLCs. Fig. 9 shows the POM photographs of mixtures 3–5 before and after UV-curing, respectively. Because the inner surfaces of the cells had been treated for homogeneous orientation, the cell exhibited a well aligned planar texture with a moderate presence of oil streaks before polymerization as shown in Fig. 9 (a_1, b_1, c_1). After polymerization induced by UV-curing, the cell still remained in planar texture as shown in Fig. 9 (a_2, b_2, c_2). This demonstrated that UV exposure process did not disrupt the orientation of the LCs, which ensured the high reflective intensity of PSCLCs.

3.3. *The effect of chiral dopant S811*

It is well known that the reflection band can be located in the range from near IR to visible by adjusting the composition of the chiral dopant. So mixture 6 which added S811 based on mixture 3 was prepared and its reflection band moves to visible range as shown in Fig. 10. The reflection spectra of mixture 6 shifts to longer wavelength and it remained good planer texture with the increase of temperature from 20 to 65 °C as shown in Fig. 10. It should also be noted that mixture 6 reflect the visible light flux range of 400–820 nm after polymerization as can be seen from Fig. 11. A conceivable explanation to this phenomenon is given considering anchoring effect of the polymer network and the change of pitch length in cholesteric blend when temperature changes. The HTP of the chiral monomer and chiral dopant (S811) decrease with the increase of temperature, the pitch length of the blend has tendency to increase as the temperature rising. As the schematic representation of CLC molecules shown in Fig. 11, at beginning of UV-curing, some monomer polymerized, the short pitch of CLCs in this specified regions surrounded by the polymer network is frozen. When temperature increases, the anchoring effect of the polymer network is not enough to prevent the CLC molecules from rearranging in some other regions, and the pitch length of CLCs become long. Then some other monomer polymerizes, and long pitch CLCs were fixed by polymer networks formed subsequently. Thus, a non-uniform pitch distribution forms inside of the composite cell.

In order to demonstrate the mechanism described above, the non-uniform pitch distribution of mixture 6 was observed with a scanning electron microscopy (SEM). Fig. 12 shows the microstructures of the freeze-fractured surface of the CLC composite cell. Observing SEM is a method to detect the pitch of cholesteric LCs [34]. The dimension of the two bands in the fine structure on the fractured planes corresponds to a π molecular rotation, it is $P/2$. The dimension of the three bands is P. It is clear that there are different pitch lengths in different regions, such as P_1, P_2, P_3, P_4 and P_5, while pitch length changes nearly from about 0.25 µm (P_1) to about 0.5 µm (P_5). According to the equation, $\lambda = n\mathrm{P}$, $n = (n_o + n_e)/2 = (1.519 + 1.720)/2 = 1.6195$, λ_1 should be 405 nm while λ_5 should be 810 nm on theory. This demonstrates that polymer networks formed at different temperatures can induce a non-uniform pitch distribution in the studied mixture and the explanation of the mechanism above is reasonable.

4. Conclusion

We described the synthesis of a chiral monomer whose HTP decreased with the increase of temperature. A series of PSCLC cells were prepared in order to investigate the influence of the polymer network on the reflectance properties. The results indicated that the chirality of the polymer networks plays an integral role in the wide-band reflection spectra and the PSCLC cells with non-uniform pitch distribution were then created. Furthermore, as the increase of concentration of LC monomer C6M, the wide-band reflection spectra change little after UV-curing. Finally, the SEM studies suggested that a non-uniform pitch distribution in the cell has been formed. In view of practical applications, broadband reflective cholesteric films may be interesting for colour filters, the brightness enhancement films and smart switchable reflective windows.

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