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Study of selectively reflecting characteristics of polymer stabilised chiral nematic liquid crystal films with a temperature-dependent pitch length

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Chiral propane-1,2-di-(4-(4-heptylcyclohexyl)benzoate) (PPCB) and 1-phenylethane-1,2-di-(4-(4-heptylcyclohexyl) benzoate) (PEPB) were synthesised and used as chiral dopants to induce chiral nematic liquid crystals (N*-LCs). Since the helical twisting power of the former first decreased and then increased as a result of thermally induced inversion helicity sense, and those of the latter changed little with increasing temperature, the pitch lengths of the N*-LCs prepared from (N-LC)/PPCB/(R)-PEPB and N-LC/PPCB/(S)-PEPB mixtures decreased and increased with increasing temperature respectively. Then, based on these two kinds of N*-LCs, polymer stabilised liquid crystal films were obtained, in which the bandwidth of the selective reflection spectra increased with increasing temperature.

Keywords: selective reflection; polymer stabilised liquid crystal; temperature-dependent; pitch gradient

1. Introduction

Polymer stabilised liquid crystal (PSLC) materials, in which a desired macroscopic orientation of liquid crystal (LC) directors can be stabilised or frozen by a cross-linked network, have been attracting much interest because of their ability to selectively reflect circularly polarised light [1–4]. Recently, some PSLC films, which can reflect circularly polarised incident light with a much wider reflection band than a single-pitch nematic liquid crystal (N*-LC), have been studied from the perspectives of reflective coloured displays [5], brightness enhancement films of LC displays [6, 7], window glass films of buildings to block infrared reducing unwanted rays from the sun [8, 9], or other optical elements [10, 11].

Generally, the N*-LCs can be achieved by adding a certain quantity of chiral dopant to a nematic liquid crystal (N-LC), in which the long axis of the LC molecule rotates about a helix. As a result of the periodic variation of LC molecules rotating about a helix, the N*-LC can be used for optical filters. A single-pitch N*-LC reflects selectively the light of a wavelength between $\lambda_{\min} = pn_o$ and $\lambda_{\max} = pn_e$. Here, n_e and n_o are the extraordinary and ordinary refractive indices of the locally uniaxial structure respectively, and p is the pitch length. Then, the bandwidth of the selective reflection spectrum is characterised by $\Delta\lambda = \lambda_{\max} - \lambda_{\min} = (n_e - n_o)p = \Delta np$. Here $\Delta n = n_e - n_o$ is the birefringence. Within this reflection band, the right polarised light is reflected by a right-handed helix, whereas left polarised light is transmitted. Outside the band is transmitted [12].

Broer *et al.* [6] obtained a wide-band PSLC film from the photopolymerisation of a N*-LC monomer of diacrylate/N-LC monomer of a monoacrylate/dye/photoinitiator mixture, in which the dye absorbs UV light and then a gradient in the intensity of UV light forms in the mixture layer. As the N*-LC monomer of diacrylate has twice as high a probability of polymerisation as the N-LC monomer of monoacrylate, the former has a greater tendency to diffuse towards the side of the mixture layer with stronger UV intensity during polymerisation. The prepared PSLC film had a gradient distribution of pitch length, which could reflect incident light over the range 400–75nm. Bian *et al.* [7] prepared an N*-LC gel film with a non-uniform pitch distribution by mixing molecules with different pitches of the chiral nematic (N*) phase together with the Cr phase and making LC monomer molecules cross-linked by photopolymerisation in the planarly oriented N* phase. The bandwidth of the reflection spectrum and the location of the reflection band of gel film could be controlled by controlling the pitch lengths of the N* phase of the molecules.

The aim of this research was to control the helical pitch of N*-LCs by changing the screw direction of the

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chiral guest 1-phenylethane-1,2-di-(4-(4-heptylcyclohexyl) benzoate) (PEPB) in N*-LCs, through which the selective reflection spectrum of the expected PSLC can be controlled. To our knowledge, no similar work has been reported up to now.

In this study, chiral propane-1,2-di-(4-(4-heptylcyclohexyl)benzoate) (PPCB) in which the helical twisting power (HTP) first decreased and then increased with increasing temperature due to the thermally induced inversion helicity sense and (R)-PEPB ((S)-PEPB), in which the HTP changed little with temperature, were synthesised. By photopolymerisation of the mixtures from the photopolymerisable monomer/N-LC/PPCB/(R)-PEPB/photoinitiator and photopolymerisable monomer/N-LC/PPCB/(S)-PEPB/photoinitiator, two kinds of PSLC films were prepared and their characteristics of selectively reflecting incident light were investigated.

2. Experiments

2.1 Materials

Figure 1 shows the chemical structures of the materials used. The photopolymerisable monomer of nematic diacrylate, PPCB, (R)-PEPB and (S)-PEPB were synthesised. The nematic liquid crystal (SN-LC) is a mixture of 4-*n*-pentyl-4′-cyanobiphenyl and 4-*n*-heptyl-4′-cyanobiphenyl (Beijing Tsinghua Yetop Co. Ltd, Beijing, China). 2,2-dimethoxy-2-phenyl-acetophenone (TCI Co. Ltd, University of Science and Technology, Beijing 100083, Ningbo City, People's Republic of China) was used as the photoinitiator.

2.1.1 Synthesis of photopolymerisable nematic diacrylate monomer

All starting materials were commercial products of high purity. The photopolymerisable monomer of nematic diacrylate was synthesised by a consecutive esterification reaction [13]. Purification was carried out by recrystallisation in diethyl ether. The infrared (IR) spectra of these compounds were recorded on a Nicolet-760 (Nicolet Co., Madison, WI, USA). The nuclear magnetic resonance (NMR) spectra were obtained by using a Brucker DRX NMR spectrometer.

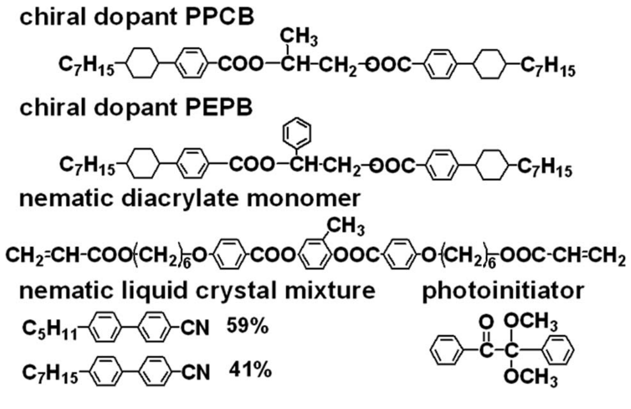

Figure 1. Chemical structure of the materials used.

IR(KBr): 2940 cm^{-1}, 1720 cm^{-1}, 1600 cm^{-1}, 1510 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=8.18 (d, 4H, aromatic). 7.25 (s, 3H, aromatic), 7.0 (d, 4H, aromatic), 6.5–5.8 (m, 6H, vinyl) 4.22 (t, 4H, $COOCH_2$), 4.05 (t, 4H, $PhOCH_2$), 2.24 (s, 3H, CH_3 -aromatic), 1.9–1.3 (m, 16H, aliphatic).

2.1.2 Preparation of chiral dopant PPCB

Chiral PPCB was synthesised as follows: 4-(4-heptylcyclohexyl) benzoic acid 6.04 g (0.02 mol), (S)-propane-1,2-diol 0.76 g (0.01 mol), N,N-dicyclohexylcarbodiimide 4.13 g (0.02 mol) and a catalytic amount of 4-pyrrolidinopyridine were dissolved in 40 ml dichloromethane and stirred for 24 h at room temperature. The precipitate was filtered from the solution. The organic phase was separated and washed three times in deionised water and dried with anhydrous magnesium sulphate. After the solvent was evaporated, the resulting solid was recrystallised twice from ethanol. The product was purified by column chromatography (silica gel, hexane/ethyl acetate=8/2 as eluent). Yield was 91%. Chiral dopant PPEB was synthesised following the same general synthetic procedure.

PPCB: IR (KBr): 2924 cm^{-1}, (C=O) 1717 cm^{-1}, 1609 cm^{-1}, 1420 cm^{-1}. ^{1}H NMR ($CDCl_3$): 7.25–7.94 (8H, Ar-H), 5.48 (1H, C*H), 4.47 (2H, C*-CH_2O-), 2.51 (2H, cyclohexyl-CH-Ar), 1.55–1.88 (18H, cyclohexyl-H), 1.47 (3H, C*-CH_3), 0.88–1.48 (30H, alkyl-H).

PPEB: IR (KBr): 2924 cm^{-1}, (C=O) 1721 cm^{-1}, 1609 cm^{-1}, 1420 cm^{-1}. ^{1}H NMR ($CDCl_3$): 7.49–7.99 (8H, Ar-H), 7.25 (5H, C*-Ar-H), 6.38 (1H, C*H), 4.68 (2H, C*-CH_2O-), 2.50 (2H, cyclohexyl-CH-Ar), 1.55–1.87 (18H, cyclohexyl-H) 0.96–1.45 (30 H, alkyl-H).

2.2 Measurements of helical pitch and HTP of N*-LC

The helical pitch of the N*-LC was evaluated by Cano's wedge method [14], using a polarised optical microscope under temperature control (heating and cooling rate of 1°C min^{-1}). The microscope observation was carried out under crossed nicols using a Nikon Eclipse E400 Pol polarising optical microscope equipped with a Nikon Coolpix 950 digital camera

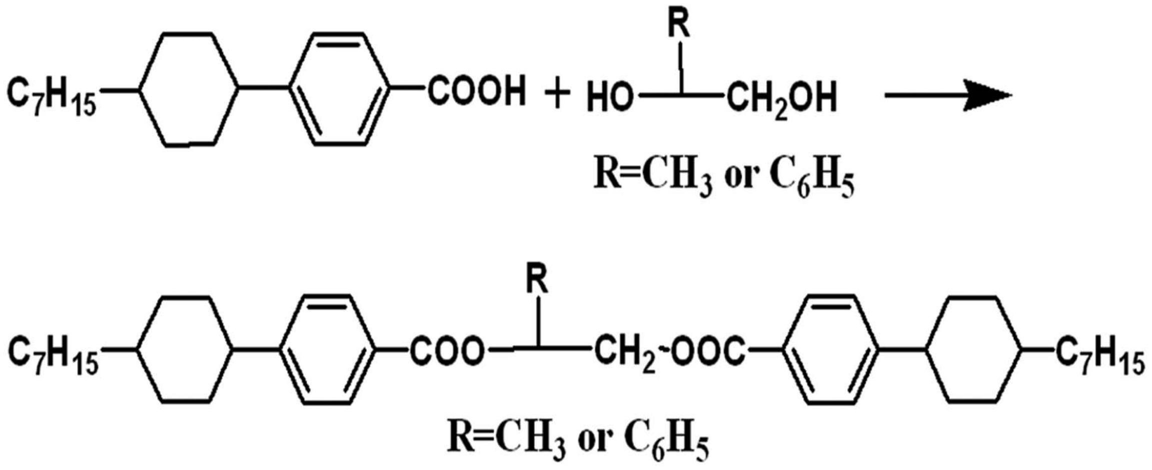

Figure 2. Synthetic route of chiral dopant propane-1,2-di-(4-(4-heptylcyclohexyl)benzoate) and 1-phenylethane-1,2-di-(4-(4-heptylcyclohexyl) benzoate).

and a Linkam TH-600PM and L-600 heating and cooling stage with temperature control.

The Cano's wedge method is schematically described in Figure 3. When the N*-LC sample was inserted into a wedge-type cell with gradient thickness, the discontinuity lines named Cano lines appeared on the surface of the cell under crossed nicols. The helical pitch (*p*) was evaluated by measuring the distance (a) between Cano lines as follows:

$$p = 2a \tan\theta \tag{1}$$

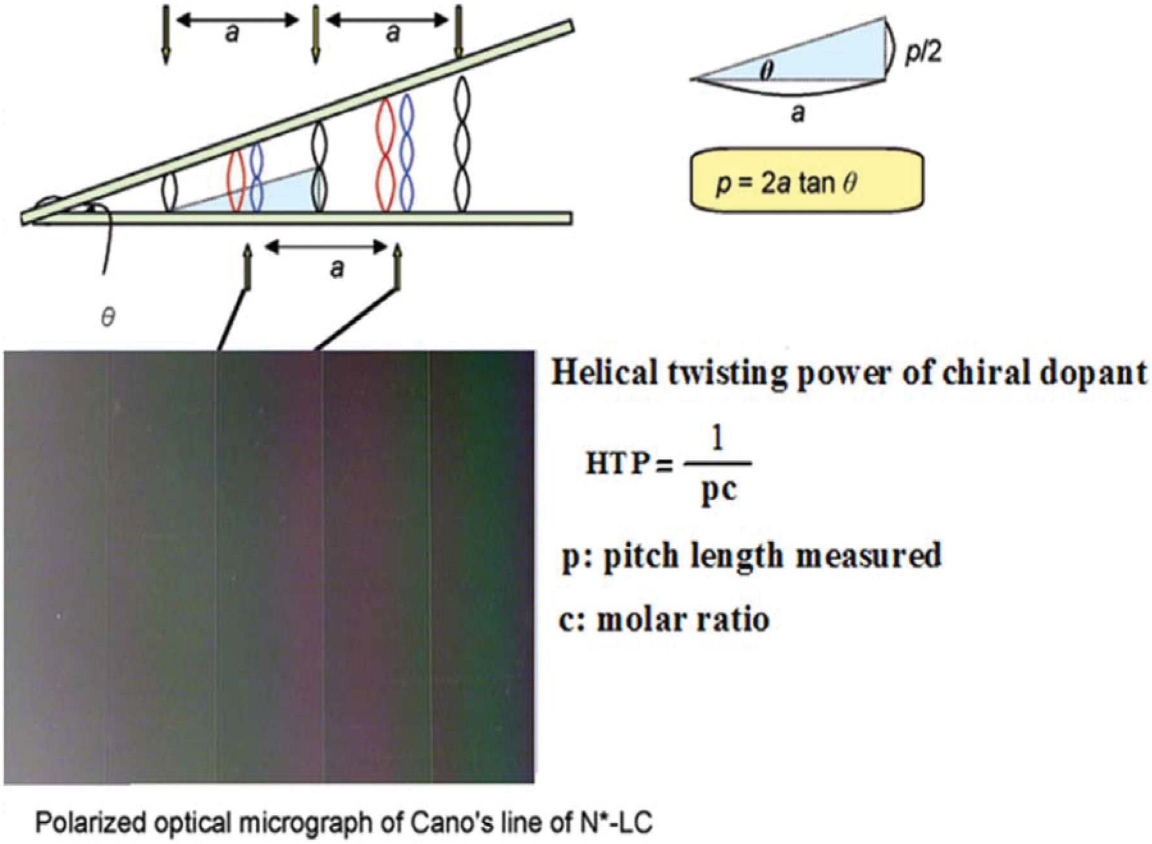

Figure 3. Cano's wedge method for the helical pitch (p) and helical twisting power (HTP) of the chiral dopant in a nematic liquid crystal (N*-LC) (colour version online).

where θ is the angle of the wedge of the cell. The HTP of the chiral dopant was evaluated with the following equation:

$$\mathrm{HTP} = 1/pc \tag{2}$$

where c is the chiral dopant concentration in mole fractions. Here, the N*-LCs were prepared as follows: PPCB/SN-LC, 18.0/82.0 wt%; (R)-PEPB/SN-LC, 3.0/97.0 wt%; PPCB/(R)-PEPB/SN-LC, 18.6/2.9/78.5 wt% and PPCB/(S)-PEPB/SN-LC, 18.6/2.9/78.5 wt%.

2.3 *UV irradiation-induced photopolymerisation*

The expected composite (polymer network/N-LC/chiral dopant) was prepared from photopolymerisation of a mixture of photopolymerisable monomers of nematic diacrylate/N-LC/host-guest chiral dopants/photoinitiator. First, the (photopolymerisable monomer/SN-LC/PPCB/(R)-PEPB (or(S)-PEPB)/photoinitiator) mixture was placed in a cell that was homogenously oriented and 100 μm thick poly(ethylene terephthalate) films were used as spacers of the cells. Then, the cell was irradiated with UV light (0.1 mW cm^{-2}, 365 nm) at 273.2 K for about 10 min and a polymer network was formed. PSLC1 was prepared from photopolymerisable monomer/SN-LC/PPCB/(R)-PEPB/photoinitiator (3.7/74/18.6/2.9/0.8 wt%) and PSLC2 was prepared from photopolymerisable monomer/SN-LC/PPCB/(S)-PEPB/photoinitiator (3.7/74/18.6/2.9/0.8 wt%).

3. Results and discussion

3.1 *HTP and screw directions of the N*-LC*

The N*-LCs were prepared as follows: PPCB/SN-LC, 18.0/82.0 wt%; (R)-PEPB/SN-LC, 3.0/97.0 wt%; PPCB/(R)-PEPB/SN-LC, 18.6/2.9/78.5 wt% and PPCB/(S)-PEPB/SN-LC, 18.6/2.9/78.5 wt%. Figure 4(a) shows temperature dependence of pitch length of these mixtures. Curve 1 shows how the pitch length of PPCB/SN-LC increases before 295.6 K and subsequently decreases after 295.6 K. It indicates that the HTP of the N*-LC decreases before 295.6 K and then increases with further increases in temperature. The property is different from the helical pitch change of the general N*-LC previously reported in the literature [15, 16]. The possible reasons are a thermally induced helicity sense reversal. The chiral dopant PPCB possibly showed a different sign of helicity sense at different temperatures. Left-hand (or right-hand) helicity sense of PPCB is the favoured group at low temperature. With increasing temperature, the concentration ratio

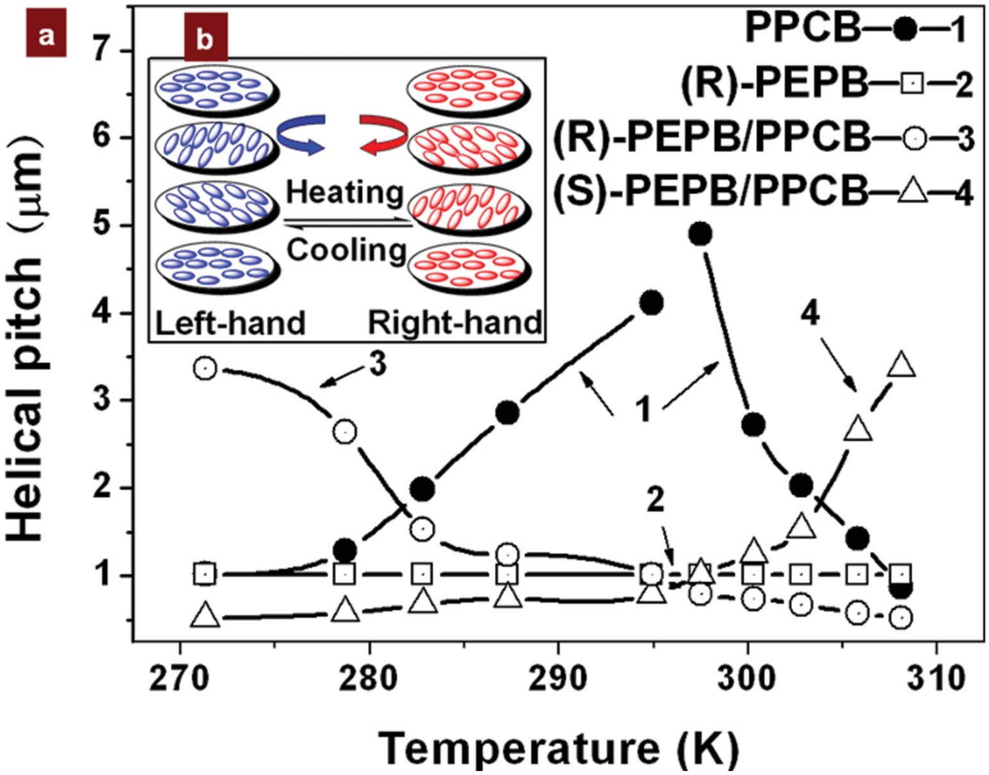

Figure 4. (a) Effect of temperature on the pitch length of a nematic liquid crystal. (b) Reversible inversion of the liquid crystal molecule arrangement in a nematic liquid crystal with changing temperature.

of right-hand (left-hand) helicity sense of PPCB increases gradually and the HTP of PPCB begins decreasing in induced N*-LCs. When the temperature is around 295.6 K, the concentration of left-hand (right-hand) helicity sense conformation is equal to that of the right-hand (left-hand) in induced N*-LC. Therefore, the helical pitch is tending to infinity. With further increasing the temperature, enhancement of HTP of PPCB was obtained again and indicates that the concentration ratio of right-hand (left-hand) helicity sense of PPCB is increasing.

Curve 2 shows that the pitch length of (R)-PEPB/SN-LC changes little with increasing temperature. This indicates that the HTP of the mixture does not change with temperature. To validate the thermally induced inversion helicity sense of PPCB, the dual chiral dopant was developed. If the screw direction of the N*-LC by PEPB is the same as that of PPCB, the pitch length of the mixture will increase; otherwise, it will decrease.

Curve 3 gives the temperature dependence of pitch length of the mixtures of N*-LCs by PPCB and (R)-PEPB (right-handed). As the HTP of (R)-PEPB is minified owing to PPCB with left-handed sense before 295.6 K and is magnified in succession owing to PPCB with right-handed sense after 295.6 K, the HTP of the mixture continuously increases with increasing temperature. Curve 3 indicates a continuous decrease in helical pitch. From curve 4, the N*-LC from PPCB/(S)-PEPB/SN-LC shows an opposite trend to that of PPCB/(S)-PEPB/SN-LC in the change in helical pitch with temperature. For the same reason, the HTP of (S)-PEPB is magnified and minified in succession. The HTP of the mixture continuously decreases with increasing temperature. So, PPCB/SN-LC shows different signs in helical sense with temperature. As shown in Figure 4(b), the sign is left-handed and right-handed when temperature is lower and higher than 295.6 K, respectively.

3.2 Selectively reflecting characteristics of the PSLC

Figure 5(a) shows the selective reflection spectra of PSLC1 at different temperatures; the composite has no reflection in the wavelength range 800–2500 nm at 273.2 K. With increasing temperature from 273.2 K, the reflective bandwidth of the spectrum of PSLC1 gradually becomes broader and reflects most of the light in the wavelength range 860–2500 nm at 307.2 K. In other words, the selective reflection light of PSLC1 shifts from long wavelengths to short wavelengths until a wide reflective band is obtained with increasing temperature. A possible consideration of the result is the thermally induced inversion helical sense of the N* phases and the anchoring effect of the polymer network when the temperature changes [17, 18]. Figure 5(b) shows a schematic of SN-LC molecule rearrangement in PSLC1 at 273.2 K. Single helical pitch length is achieved when the mixture is polymerised at 273.2 K. With increasing temperature from 273.2 K, a gradation of pitch length is obtained due to the different distances of LC molecules to the polymer network and the continuous decreasing helical pitch of PPCB/(R)-PEPB/SN-LC. In some small local regions near the polymer network, where the anchoring effect on the LC molecules is strong, the alignment of the LC molecules in the regions is well frozen by the polymer network and the rearrangement of LC molecules with temperature is difficult. In some local regions where the density of the polymer network is lower or the LC molecules are further from the polymer network, the anchoring effect on LC molecules is not enough to prevent LC molecule rearrangement. In the furthest regions from the polymer network, helical pitch lengths decrease as easily as those of N*-LC with changing temperature. Figure 5(c) shows a schematic of molecule rearrangement of the composite at 307.2 K. Thus, PSLC1 can reflect most of the light in the wavelength range 860–2500 nm at 307.2 K.

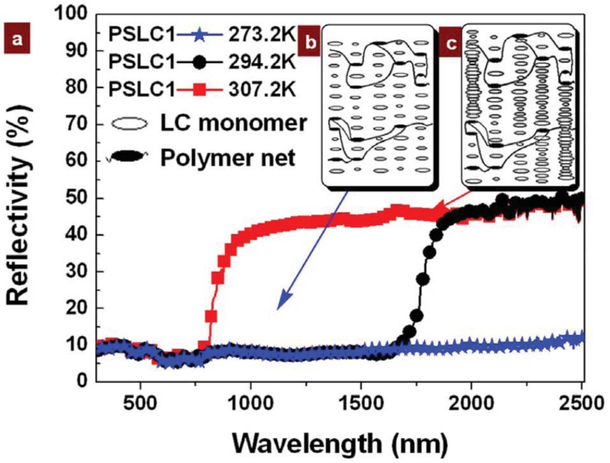

Figure 5. (a) Selective transmission spectra of a polymer stabilised liquid crystal (PSLC1) measured at different temperatures. (b) Schematic of liquid crystal molecule rearrangement of PSLC1 at 273.2 K. (c) Schematic of liquid crystal molecule rearrangement of PSLC1 at 307.2 K.

Figure 6(a) shows the selective reflection spectra of PSLC2 at different temperatures; the composite reflects the wavelength range 860–1180 nm at 273.2 K. With increasing temperature from 273.2 K, the reflective bandwidth of the spectrum of PSLC2 becomes gradually broader and reflects most of the light in the wavelength range 860–2500 nm at 307.2 K. That is, the selective reflection light of PSLC2 shifts from short wavelengths to long wavelengths with

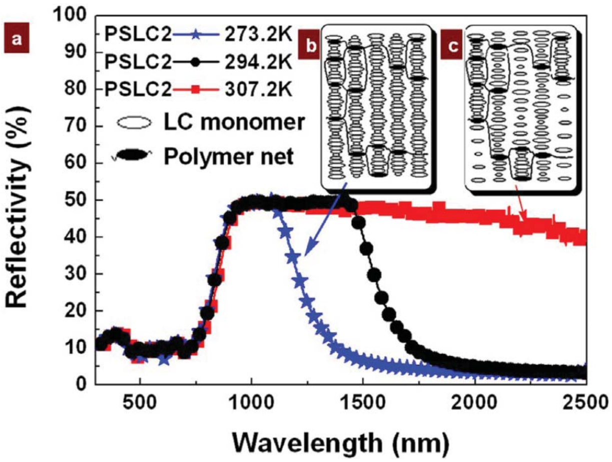

Figure 6. (a) Selective transmission spectra of a polymer stabilised liquid crystal (PSLC2) measured at different temperatures. (b) Schematic of liquid crystal molecule rearrangement of PSLC2 measured at 273.2 K. (c) Schematic of liquid crystal molecule rearrangement of PSLC2 at 307.2 K.

increasing temperature and a wide reflective band is also achieved. The helical pitch distributions in PSLC2 at 273.2 K and 307.2 K are shown in Figure 6(b) and (c), respectively. In the high density regions of the polymer network, PSLC2 retains the shortest helical lengths due to the same screw direction of the composite induced by PPCB and (S)-PEPB at 273.2 K (Figure 6(b)). In the lower density regions of the polymer network, when the temperature is increased, the helical pitch gradually increases owing to the thermally induced inversion helical sense of PPCB (Figure 6(c)). Thus, the helical pitch length of PSLC2 becomes longest in the furthest regions from the polymer network. As a result, a wide reflective bandwidth is also achieved in PSLC2 with increasing temperature and most of the light over the wavelength range 860–2500 nm is reflected at 307.2 K.

Furthermore, the different bandwidths of the reflection spectrum of PSLC can be controlled by adjusting the ratio of PPCB to PEPB with changing temperature. Figure 7 shows digital photographs of the visible light spectrum of the thermal sensing film. The film was prepared at 273.2 K from the photopolymerisation of nematic monomer diacrylate /SN-LC/PPCB/(R)-PEPB/photoinitiator, 3.7/74/18/3.5/0.8 wt%.

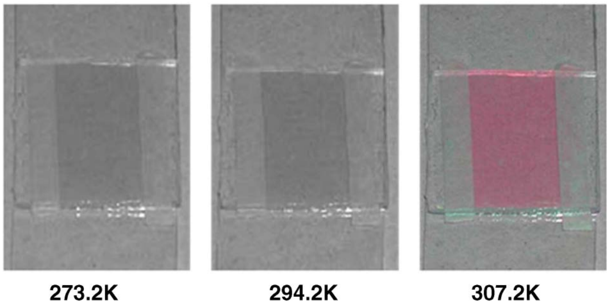

Figure 7. Selective reflection cell of a polymer stabilised liquid crystal (PSLC1) (nematic monomer diacrylate /SN-LC/PPCB/(R)-PEPB/photoinitiator, 3.7/74/18/3.5/0.8 wt%) measured at different temperatures.

4. Conclusions

The HTP of PPCB molecules first decreases and then increases with increasing temperature due to thermally induced inversion helicity sense. The combination of the chiral PPCB and PEPB provides fundamental aspects for temperature control of the helical structure, such as temperature control of the helical pitch in any direction to longer or shorter. A PSLC film doped with the chiral host-guest dopant was synthesised from the photopolymerisation of nematic LC diacrylate monomer/N-LC/chiral host-guest dopants/photoinitiator. Based on the thermally induced inversion helical sense of the N*-LC induced by PPCB and the anchoring effect of the polymer network, the selective reflection spectrum of the composite can be controlled by changing the screw directions of chiral guest dopants. The reflection band of PSLC1 with (R)-PEPB shifts to short wavelengths and gradually broadens with increasing temperature. Shifting the other way, the reflection band of PSLC2 with (S)-PEPB gradually broadens with increasing temperature.

The IR light in the wavelength range 800–2000 nm constitutes over 90% of all solar IR energy [19], therefore the composite has potential for a constant temperature device by IR heating. In addition, the transflective band can also be located in the UV or visible light range by increasing the content of the chiral dopant in the composite. The composite also has possibilities for a special UV-resistant (or visible light-resistant) device at some temperatures.

Acknowledgements

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