Broadband reflection characteristic of polymer-stabilised cholesteric liquid crystal with pitch gradient induced by a hydrogen bond

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A polymer-stabilised cholesteric liquid crystal (PSChLC) was fabricated by ultraviolet (UV) induced polymerisation of photopolymerisable acrylate monomers mixed in a cholesteric liquid crystal (ChLC). A polymer network with a concentration gradient, which was induced by UV light absorption of dye along the propagation direction, was formed. A hydrogen bond, arising between the polymer network with a concentration gradient containing carboxyl as proton donors and chiral dopant (CD) as proton acceptors, induced a pitch gradient in PSChLC and then, as a consequence, broadband reflection. The broadband reflection is associated with the concentration and the composition of photopolymerisable acrylate monomers, the concentration of CD and the polymerisation temperature. Examining the morphologies of the polymer network by scanning electron microscopy, the helix structure and pitch gradient were verified, confirming the pitch gradient of the PSChLC and revealing the essence of the formation of broadband reflection.

Keywords: hydrogen bond; polymer stabilised cholesteric liquid crystal; pitch gradient; broadband reflection

1. Introduction

A cholesteric liquid crystal (ChLC) is formed when a nematic liquid crystal (NLC) is doped with chiral dopant. In cholesteric phase, the long axis of the LC molecules rotates about a helix. The pitch length, P, of the helix corresponding to a 2π molecular rotation is determined by the concentration of the chiral dopant, decreasing with its increasing fraction. Because ChLC has a periodic variation in refractive index, it can be used for optical filtering of circularly polarised incident light of the same handedness as its helix. A single-pitch ChLC reflects selectively 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. 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 reflection band, both polarisation states are transmitted [1, 2]. Since the value of Δn for colourless organic materials does not exceed 0.3, the bandwidth of a single-pitch ChLC in visible regions is less than 100 nm. The potential to adjust Δn to obtain a wideband reflection is very limited. Thus, adjusting the pitch, P, (i.e. in the

cholesteric liquid crystal system) to form a pitch gradient distribution or non-uniform pitch distribution can substantially broaden the reflection bandwidth [3, 4].

In recent years, there have been many theoretical studies and experimental methods aimed at forming a pitch gradient distribution or non-uniform distribution in order to achieve broadband reflection [5–20]. Broer *et al.* [3, 4] prepared a ChLC gel film with a pitch gradient from the photopolymerisation of a ChLC monomer of diacrylate/NLC monomer of monoacrylate/dye/photoinitiator composite in which the dye absorbs ultraviolet (UV) light and a gradient in the intensity of UV light forms in the composite layer. Because the ChLC monomer of diacrylate has a higher probability of polymerisation than the NLC monomer of monoacrylate, the former has a greater tendency to diffuse towards the side of the composite layer with stronger UV intensity during polymerisation. Due to the pitch length decreasing with increasing fraction of a chiral component in a ChLC composite, the prepared polymer film has a pitch gradient of about 270–450 nm, reflecting incident light with the wavelength range of 400–750 nm. Hikmet and Kemperman [8, 9] fabricated a gel film which reflects circularly polarised visible light with an electronic switching property by dispersing the photopolymerisable liquid crystal monomer into low molecular weight liquid

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crystal to achieve a stable non-symmetrical pitch polymer distribution. This mode is known as a polymer-stabilised cholesteric liquid crystal (PSChLC).

Cholesteric liquid crystal materials with broadband reflection are widely used in high-power UV polarisers, liquid crystal display, information display and storage materials, infrared radiation shielding devices, military infrared detectors, 'smart windows' and other areas with enormous potential for development [21, 22].

In this paper, utilising PSChLC mode, a broadband reflection is realised due to the hydrogen bond (H-bond) between the polymer network and the chiral dopant which is confirmed using Fourier transform infrared spectroscopy (FTIR). Here, the concentration gradient of the polymer network and that of the chiral dopant are formed by photopolymerisation of the photopolymerisable monomers. Using scanning electron microscopy (SEM), the pitch gradient of the polymer network of PSChLC can be observed, thus confirming the formation mechanism of the broadband reflection. The relationships between the ratio of polymerisable monomer composition, polymerisation temperature and the reflection bandwidth were investigated.

2. Experimental

2.1 Materials

Figure 1 shows the chemical structure of the materials used. Chiral dopant (CD) was synthesised according to the method suggested by Le and Sadeg [21]. Nematic diacrylate monomer (C6M in Figure 1) and monoacrylate monomer (Acid in Figure 1) were prepared as described by Broer *et al.* [23]. Chiral dopant (CD) was synthesised according to the method suggested by He *et al.* [24]. UV-absorbing dye (Dye in Figure 1) was prepared according to the method suggested by Meijer *et al.* [25]. UV polymerisation initiator (PI), Irgacure 651, was obtained from Ciba-Geigy (Basel, Switzerland) and nematic liquid crystal, SLC-1717, was obtained from Slichem Liquid Crystal Material Co. Ltd (Shijiazhuang, China).

2.2 Testing equipment and experimental methods

The optical textures of liquid crystals were observed using a Zeiss Jena polarising microscope equipped with a hot stage and temperature controller (Mettler Fp82/90). The helical pitch of the ChLC was evaluated using Cano's wedge method [26]. The spectral characteristics were obtained using an unpolarised UV/VIS/NIR spectrophotometer (Shimadzu UV-3100) in transmission mode at normal incidence, while the transmittance of a blank cell was normalised as 100%. As usual, $\Delta\lambda$ was measured from the spectrum by considering the wavelength for the minimum of transmitted light inside the peak and the peak bandwidth at half-height, respectively. The surface morphology of the polymer network was observed by SEM (Hitachi, S-4700) and the fracture surface were observed by JSM 7401F (JEOL).

The cell's two inner surfaces of indium tin oxide (ITO) substrates spin-coated with polyvinyl alcohol layers were rubbed in a perpendicular direction (like a twist nematic cell) to provide a homogeneous orientation of LC molecules; 25 μm thick poly(ethylene)terephthalate (PET) films were used as the cell spacer.
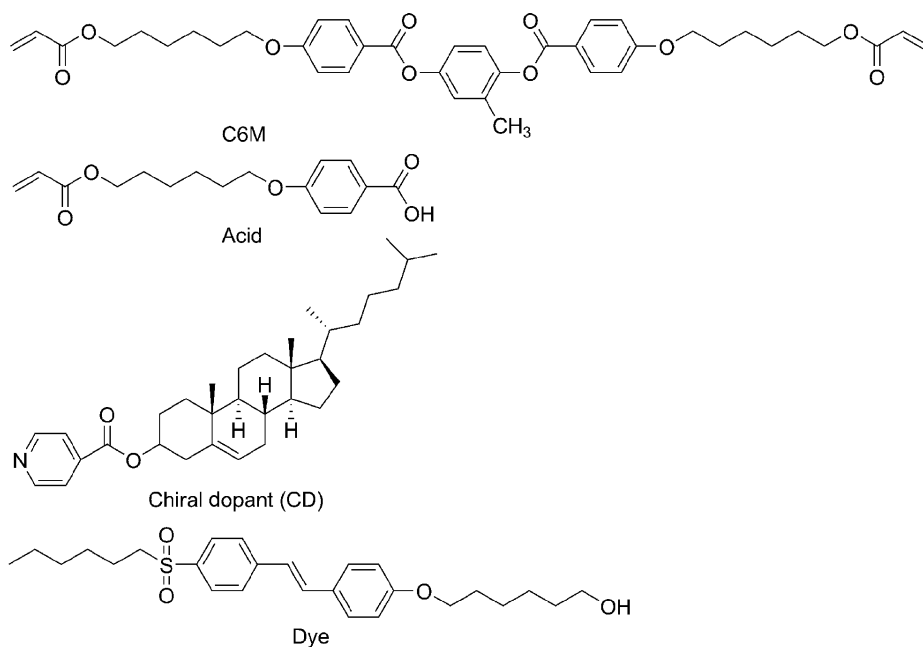

Figure 1.   Chemical structure of the materials used.

The mixture of CD, C6M, Acid, Dye, PI and NLC was heated to the clearing point and cooled to cholesteric (Ch) phase so as to fill the cells by capillarity. The cells were then irradiated with UV light (365 nm) for 40 min to achieve polymerisation and obtain planar-orientated PSChLC materials. The cell was then opened and immersed in cyclohexane for about 48 hours and subsequently in tetrahydrofuran for 20 min to remove the non-reactive LCs from the cell. The cell was kept in a vacuum chamber at 60°C for about 12 hours prior to use for SEM observation.

3. Results and discussion

Figure 2 shows a typical transmittance spectrum of PSChLC with the corresponding composition. Before polymerisation, a narrow reflection with a bandwidth of about $\Delta\lambda = 200$ nm with the centre located at about 1400 nm can be seen; after polymerisation, the reflection bandwidth, $\Delta\lambda$, was greatly broadened at about 1200 nm.

By adding a small amount of UV-absorbing dye, with an absorption maximum at 337 nm (as shown in Figure 3), upon exposure to weak UV (0.065 mW cm^{-2}), close to that of the photoinitiator and an extinction coefficient two orders larger than that of the photoinitiator, a gradient in UV intensity can be achieved over the thickness of the cell. The polymerisation rate will then be faster at the top of the cell (lamp-side) resulting in a faster consumption of the most reactive monomer at the same location. The difference in reactivity between diacrylate monomer, C6M, having two reactive sites per molecule, and monoacrylate monomer, Acid, having only one reactive site, provides a means to achieve this.
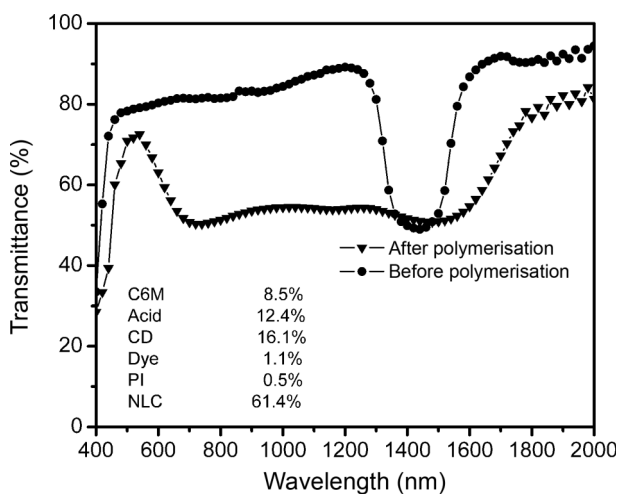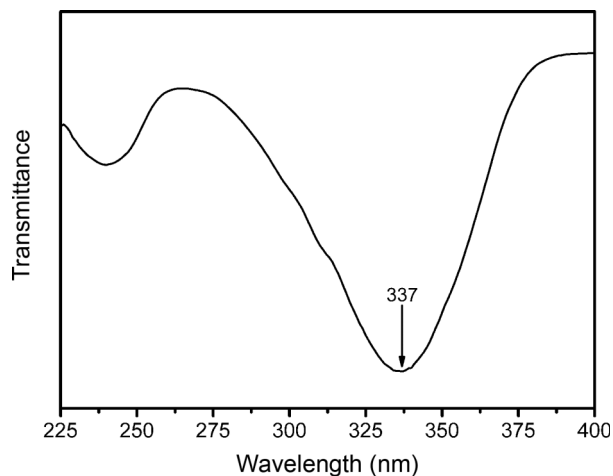

Figure 3. UV transmission spectrum of UV-absorbing dye.

The depletion of this monomer starts a diffusion process in which the upper part of the layer is enriched with diacrylate monomer, C6M, and the lower part with monoacrylate, Acid.

Whether a H-bond has been formed in the mixture can be confirmed directly by FTIR. Figure 4 shows the FTIR spectrum of CD, Acid and the mixture, respectively. The associated broad peak located between 2500 cm^{-1} and 3500 cm^{-1} of Acid indicates that Acid exists in the form of dimer, which disappears in the complex. Meanwhile, two H-bonded characteristic peaks centred at about 2500 cm^{-1} and 1900 cm^{-1} were observed in the H-bonded complex and the mixture, indicating the existence of a stably strong H-bond. Furthermore, the two H-bonded characteristic peaks appearing in the mixture spectrum were stronger, indicating that NLC has a similar role to solvent which, in turn, is conducive to the formation of a H-bond. As a result because of the presence of the monomer concentration gradient (formed by the photopolymerisation polymer network) and the H-bond formed between CD and Acid, the concentration of CD has the same tendency as that of Acid, which leads to a pitch gradient of PSChLC. To be more exact, the pitch is longer at the lamp-side while shorter at the down-side of the cell.

For ChLC, according to $p = [(HTP)X_c]^{-1}$ where X_c is the concentration of chiral dopant and HTP is the helical twist power of chiral dopant, without changing the polymerisable monomer, dye and initiator concentration as well as polymerisation conditions, the central reflection wavelength will shift to the short wavelength region [1]. In addition, according to $\Delta\lambda = n\Delta P$, in the short wavelength region, a shorter
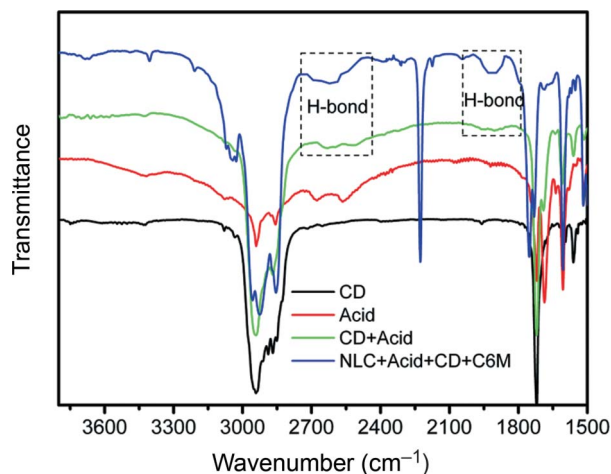

Figure 2. Typical transmission spectrum of ChLC before polymerisation (●) and PSChLC, with broadband reflection, after polymerisation (▼).

Figure 4. FTIR spectrum for CD, Acid, H-bond complex and ChLC mixture.

Figure 6. *R*, ratio of Acid/C6M dependence of $\Delta\lambda$ for the composition as shown.

pitch, *P*, results in a shorter reflection bandwidth. Figure 5 shows the relationship between the concentration of CD, the pitch and the reflection wavelength, respectively; the bars on the reflection curve illustrate the reflection bandwidth of the corresponding PSChLC and the pitch of the corresponding ChLC is measured before polymerisation. It can be seen that, with increasing concentration of CD, the pitch of ChLC becomes shorter. After polymerisation, the corresponding reflection bandwidth of PSChLC becomes narrower; this is consistent with the theoretical analysis presented above.

Figure 6 shows the relationship between reflection bandwidth and the composition of polymerisable monomers with the other components unchangeable at the same polymerisation conditions (365 nm, 0.065 mW cm^{-2}, 25°C, 40 min). Here, *R* is defined as the ratio of the content of Acid and C6M; in other

words, *R* = content of Acid/content of C6M. With *R* increasing, the reflection bandwidth, $\Delta\lambda$, increases to reach the maximum at about *R* = 1.5, then subsequently decreases. When *R* is relatively small, the difference in the polymer network formed by photopolymerisation is inconspicuous. Therefore, the pitch gradient of PSChLC induced by the concentration of CD, which is determined by the concentration of Acid in the polymer network, is difficult to distinguish. With *R* increasing further, as mentioned above, an appropriate polymer network will be formed due to the 'diffusion process' of the photopolymerisable monomers, which induces an appropriate concentration gradient of CD by H-bond and ultimately induces a maximum reflection bandwidth. Here, the *R* value is about 1.5. However, when *R* ≥ 1.5, the formed polymer network is flooded with Acid and so, at any region in the polymer network, it is almost homogenous. The difference in the polymer network formed by photopolymerisation is inconspicuous again, resulting in a narrow pitch gradient of the formed PSChLC. Thus, the reflection bandwidth becomes narrower again.

Figure 7 shows the transmission spectrum of PSChLC at different temperatures under fixed polymerisation conditions (365 nm, 40 min). The reflection bandwidth becomes wider as the temperature increases. Meanwhile, the lower limit of the reflection wavelength, $\lambda_{\min}$, shifts significantly to the short wavelength direction. It can be observed that the viscosity decreases with the increase of polymerisation temperature. Furthermore, the diffusion rates of the monomers and CD also increase.

It should be noted that, given the concentration gradient of chiral dopant is induced by the diffusion of polymerisable monomers and thus forms a pitch
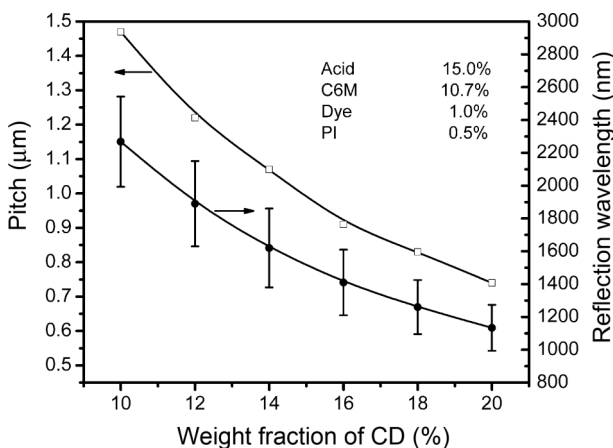

Figure 5. Concentration of CD dependence of pitch, *P*, and reflection bandwidth, $\Delta\lambda$, respectively for the sample as shown.
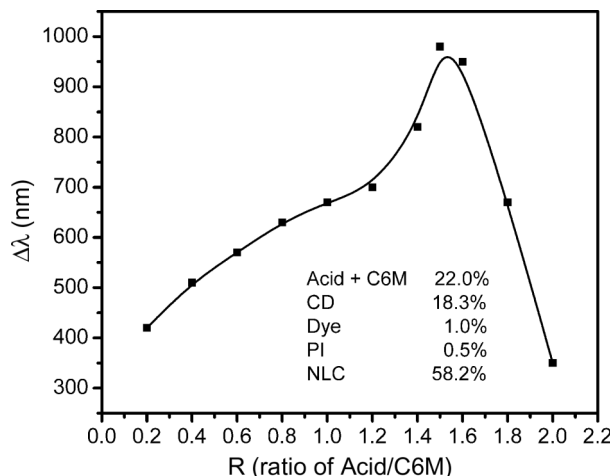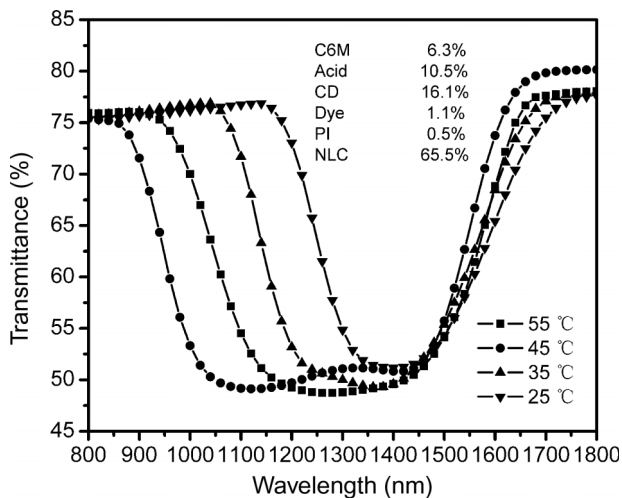
Figure 7.   Temperature dependence of reflection wave and reflection bandwidth for the composition as shown.

The polymer network morphology, as investigated by scanning electron microscopy (SEM), exhibits smooth polymer strands (Figure 8(a)) where $R = 1.4$ and the total content of the polymerisable monomer in the mixture before polymerisation accounts for 14.7% (like the signature of good solubility of the monomers within the LC). The behaviour may be understood in the context of the Flory–Huggins model of polymer solubility [27], which is the primary factor determining the network morphology. The helical superstructure of the polymer network formed in the Ch phase can be clearly imaged as shown in Figure 8(a). The SEM investigations suggest the transfer of the organisation of the mesophase order to the structure of the network.

When the photopolymerisable monomer content is low, it is insufficient to form a continuous polymer network and it is difficult to observe the fracture surface morphology of the polymer network. Experimental results show that, when the monomer content is higher than 30%, it is possible to observe the fracture surface morphology of the polymer network. But it should be noted that, when the monomer content is too high, the clear point and birefringence of ChLC will decrease and cannot even fabricate PSChLC with broadband reflection. Figure 8(b) shows the fracture surface SEM image of the polymer network with the photopolymerisable monomer content of 32.4%, where $R = 1.6$. A layer structure can be seen from the image; the dimension of the bands between the adjacent layers in the fine structure, displayed on the fracture surface, corresponds to a π molecular rotation (i.e. $P/2$). The bands decrease linearly in thickness from the top to the bottom of the cross-section of the film. That is, there is a pitch gradient. Close to the lamp-side (top) it is long pitch while, at the bottom, it is short pitch; this offers a strong evidence for the above arguments.

gradient, the polymerisation and diffusion rates should be well-balanced to obtain the best reflection. In the studied systems, the polymerisation temperature is not 'the higher the better'. If the polymerisation temperature is too high, then too fast a diffusion rate of the polymerisable monomer will actually weaken the formation of the gradient. Therefore, selecting the optimal polymerisation temperature for the composite system is particularly important to obtain broadband reflection.

For the system as shown in Figure 7, the reflection bandwidth reaches its maximum value when the polymerisation temperature is 45°C, while at 55°C it is narrower. At a certain temperature, with the widest pitch gradient, the lower limit of reflection wave, λ_{min}, corresponds to the minimum; the concentration of CD near the lamp-side is lower while the down-side is higher, leading to the upper limit of reflection wave, λ_{max}, also decreasing slightly.
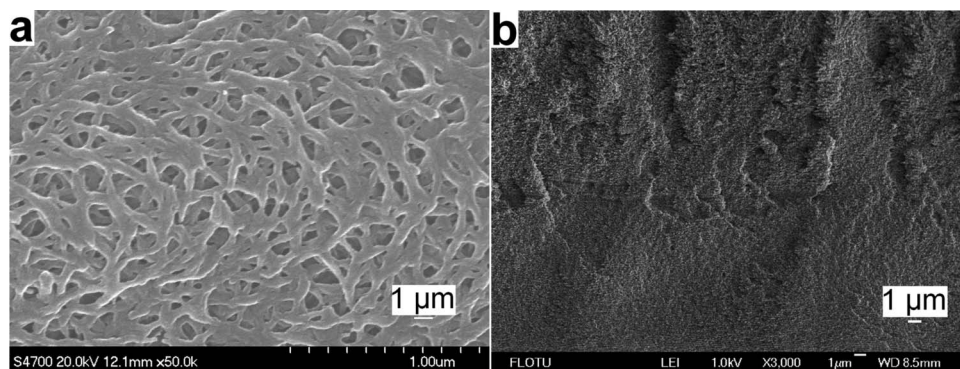

Figure 8.   SEM images of the polymer network: (a) surface morphology and (b) fracture surface morphology.

4.   Conclusions

PSChLC was formed by UV-induced photopolymerisation of photopolymerisable monomers contained in a ChLC mixture. By adding a small amount of UV-absorbing dye, upon exposure to UV light, a gradient in UV light intensity can be achieved over the thickness of the cell. The polymerisation rate will then be faster at the top of the cell (lamp-side), resulting in a faster consumption of the most reactive monomer at the same location. The difference in reactivity between diacrylate monomer, having two reactive sites per molecule, and monoacrylate monomer, having only one reactive site, provides a means to achieve this. The depletion of this monomer starts a diffusion process in which the upper part of the layer is enriched with diacrylate monomer and the lower part with monoacrylate. The H-bond, which is formed between the monoacrylate monomer (Acid) and chiral dopant (CD), determined that the concentration of CD in PSChLC has the same tendency as that of Acid. Therefore, a pitch gradient is formed in PSChLC, which enables the broadband reflection.

Under the constant polymerisation condition, the central reflection wavelength of PSChLC shifts to a shorter wavelength with increasing concentration of chiral dopant, while the reflection bandwidth becomes narrower. The reflection bandwidth also changes when the ratio of mono- and di-polymerisable monomers changes. Experiment proves that the reflection bandwidth is the widest when the ratio reaches an appropriate value. This is because the polymer network formed at this time had the largest concentration gradient.

Polymerisation temperature is another important factor associated with the reflection bandwidth. When polymerised at a higher temperature the reflection bandwidth is widest; it becomes narrow with increasing temperature. This is because the higher temperature is favourable to the diffusion of polymerisable monomers. But at too high temperature, the diffusion of the two kinds of polymerisable monomer is similar while polymerising. Therefore, the concentration gradient in the formed polymer network becomes narrow, resulting in the reflection bandwidth becoming narrow again.

SEM has proved that the polymer network formed by polymerisation is a discontinuous network containing mesh and the fracture surface SEM image confirms a pitch gradient in the polymer network. This result suggests the existence of a pitch gradient in PSChLC.

References

[1] Chilaya, G. In *Chirality in Liquid Crystals*; Kitzerow, H., Bahr, C., Eds.; Springer Series Partially Ordered Systems; Springer: New York, 2001; Chapter 6.
[2] de Gennes, P.G.; Prost, J. *The Physics of Liquid Crystals*; Clarendon Press: Oxford, 1993.
[3] Broer, D.J.; Lub, J.; Mol, G.N. *Nature* **1995**, *378*, 467–469.
[4] Broer, D.J.; Mol, G.N. *Adv. Mater. (Weinheim, Ger.)* **1999**, *11*, 573–578.
[5] Hajdo, L.; Eringen, A. *J. Opt. Soc. Am.* **1979**, *69*, 1017–1023.
[6] Zografopoulos, D.C.; Kriezis, E.E.; Mitov, M. *Phys. Rev. E* **2006**, *73*, 061701-1–9.
[7] Mitov, M.; Nouvet, E.; Dessaud, N. *Eur. Phys. J. E* **2004**, *15*, 413–419.
[8] Hikmet, R.A.M.; Kemperman, H. *Liq. Cryst.* **1999**, *26*, 1645–1653.
[9] Hikmet, R.A.M.; Kemperman, H. *Nature* **1998**, *392*, 476–479.
[10] Relaix, S.; Bourgerette, C.; Mitov, M. *Appl. Phys. Lett.* **2006**, *89*, 251907-1–3.
[11] Relaix, S.; Mitov, M. *Liq. Cryst.* **2008**, *35*, 1037–1042.
[12] Mitov, M.; Dessaud, N. *Nat. Mater.* **2006**, *5*, 361–364.
[13] Relaix, S.; Bourgerette, C.; Mitov, M. *Liq. Cryst.* **2007**, *34*, 1009–1018.
[14] Yang, H.; Mishima, K.; Matsuyama, K. *Appl. Phys. Lett.* **2003**, *82*, 2407–2409.
[15] Kwon, Y.J.; Lee, W.J.; Paek, S.H. *Mol. Cryst. Liq. Cryst.* **2002**, *377*, 325–328.
[16] Lavernhe, A.; Mitov, M.; Binet, C. *Liq. Cryst.* **2001**, *28*, 803–807.
[17] Fan, B.; Vartak, S.; Eakin, J.N.; Faris, S.M. *Appl. Phys. Lett.* **2008**, *92*, 061101.
[18] Bian, Z.Y.; Li, K.X.; Huang, W.; Cao, H.; Yang, H. *Appl. Phys. Lett.* **2007**, *91*, 201908.
[19] Xiao, J.M.; Zhao, D.Y.; Cao, H.; Yang, H. *Liq. Cryst.* **2007**, *34*, 473–477.
[20] Xiao, J.M.; Cao, H.; Yang, H. *J. Appl. Poly. Sci.* **2007**, *105*, 2973–2977.
[21] Li, L.; Faris, S.M. Single–Layer Reflective Super Broadband Circular Polarizer and Method of Fabrication. US Patent 5, 691.789, November 25, 1997.
[22] Binet, C.; Mitov, M.; Mauzac, M. *J. Appl. Phys.* **2001**, *90*, 1730–1734.
[23] Broer, D.J.; Boven, J.; Mol. G.N. *Makromol. Chem.* **1989**, *190*, 2255–2268.
[24] He, W.L.; Pan, G.H.; Yang, Z.; Zhao, D.Y.; Niu, G.G.; Huang, W.; Yuan, X.T.; Guo, J.B.; Cao, H.; Yang, H. *Adv. Mater.* **2009**, *21*, 2050–2053.
[25] Meijer, E.W.; Hoeve, W.T.; Nijhuis, S.; Rikken, G.L.J.A.; Havinga, E.E. Device for Doubling the Frequency of a Light Wave Comprising a Non-Linear Optical Compound. US Patent 5, 006.729, April 9, 1991.
[26] Cano, R. *Bull. Soc. Fr. Mineral. Cristallogr.* **1968**, *91*, 20–27.
[27] Dierking, I.; Kosbar, L.L.; Ardakani, A.A. *Appl. Phys. Lett.* **1997**, *71*, 2454–2456.