## Liquid Crystals

Publication details, including instructions for authors and subscription information:
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**To cite this Article** Huang, Wei , Zhang, Xiaoguang , Guo, Jinbao , Zhang, Lipei , Bian, Zhenyu , Zhao, Dongyu , He, Wanli , Cao, Hui and Yang, Huai(2009) 'Super wide-band reflective polarisers from polymer stabilised liquid crystal films', Liquid Crystals, 36: 5, 497 — 501, First published on: 05 November 2010 (iFirst)

**To link to this Article: DOI:** 10.1080/02678290903029753

**URL:** http://dx.doi.org/10.1080/02678290903029753

*Liquid Crystals,*
Vol. 36, No. 5, May 2009, 497–501

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# Super wide-band reflective polarisers from polymer stabilised liquid crystal films

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*(Received 23 March 2009; final form 8 May 2009)*

A polymer stabilised liquid crystal film with the order and the molecular alignment of a smectic-A phase at a microscopic level, but with the planar molecular alignment of a chiral nematic phase at a macroscopic level, was prepared. This kind of order and alignment of the molecules of the liquid crystal resulted in the film reflecting circularly polarised incident light with the bandwidth of the spectrum over the wavelength range of 300–2500 nm.

**Keywords:** chiral nematic; smectic A; polymer network; pitch; wide-band reflection

Polymer stabilised liquid crystal (PSLC) films have provided a new field of liquid crystal (LC) science and technology (*1–7*), in which a desired macroscopic orientation of LC directors can be stabilised (*4–6*) or frozen (*7*) by the crosslinked network dispersed within the LC. For example, the three-dimensional cubic structure with lattice periods of several hundred nanometres in a blue phase, of which the temperature range is usually less than a few kelvins, can be stabilised over a temperature range of more than 60 K (*5*). The planar molecular alignment of a chiral nematic (N*) phase can also be stabilised in a smectic-A (SmA) phase at a macroscopic level, and then the SmA phase has both the optical characteristics similar to those of a N* phase and the mechanical properties of a SmA phase (*6*). Recently, the PSLC films, which can reflect circularly polarised incident light with a much wider reflection band than a single-pitch N*-LC, are very attractive from the perspective of reflective coloured displays (*1*, *8*), brightness enhancement films of LC displays (*7*), window glass films for buildings to block infrared light, thereby reducing unwanted rays from the sun (*9*, *10*), or other optical elements (*11*, *12*).

In a N* phase, the long axis of the LC molecules rotates about a helix. The pitch length, $P$, of the helixcorresponds to a $2\pi$ molecular rotation. Because a N*-LC has a period variation in the refractive index, it can be used for optical filtering of circularly polarised incident light of the same handedness as its helix. A single-pitch N*-LC selectively reflects light of a wavelength between $\lambda_{\min} = Pn_o$ and $\lambda_{\max} = Pn_e$. Here, $n_o$ and $n_e$ are the ordinary and extraordinary refractive indices of the locally uniaxial structure, respectively. Then, the bandwidth of the reflection spectrum, $\Delta\lambda$, is given 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 the bandwidth, right-circularly polarised light is reflected by a right-handed helix, whereas left-circularly polarised light is transmitted. Since the $\Delta n$ value for colourless organic materials is typically smaller than 0.3, the bandwidth in visible regions is less than 150 nm (*7*, *13*).

The broadening of the reflection band has been studied by obtaining a single layer 'that achieves its wide selective reflection band because of its engineered pitch distribution'. Broer and Lub (*7*) have obtained a reflective film with a pitch gradient from the photopolymerisation of a N*-LC monomer of a diacrylate/nematic (N)-LC monomer of a monoacrylate/ultraviolet (UV) absorbing dye/photoinitiator composite. The photoinduced diffusion during the crosslinking reaction occurring in N*-LC and N-LC monomers with different UV reactivities well explained the origin of forming a pitch gradient (*7*). Li and Faris (*14*) and Kralik *et al.* (*15*) have achieved a reflective PSLC film that has a very broadband approaching 2000 nm. The mechanism of UV polymerisation-induced molecular re-distribution, which is responsible for creating a non-uniform pitch distribution, has been investigated. Relaix *et al.* (*16*) described that the reflection band in PSLC films can also be broadened without adding an UV absorbing dye, due to the natural UV absorbing properties of the LC constituent. Hong *et al.* (*17*) and Huang *et al.* (*18*) have demonstrated the gradient pitch approach theoretically and experimentally for achieving the broadband reflective films. In addition, PSLC films with electrically switchable bandwidth have also been studied (*19*, *20*). The author and colleagues have systematically studied PSLC films with non-uniform pitch distribution and with a thermally switchable bandwidth (*5*, *6*, *10*, *21–24*). However, to our knowledge, a polariser that can reflect incident light with the

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ISSN 0267-8292 print/ISSN 1366-5855 online

DOI: 10.1080/02678290903029753
http://www.informaworld.com

bandwidth over the wavelength range of 300–2500 nm has not been reported up until now.

In the present study, we achieve the super wideband polariser by a PSLC film with the order and the molecular alignment of a SmA phase at a microscopic level, but with the planar molecular alignment of a N* phase at the macroscopic level. Figure 1 shows the chemical structures of the materials used. The SmA-LC, the side chain type liquid crystalline polymer (SCTLCP), the photo-polymerisable monomer (PPM) and the chiral dopant (CD) were lab-synthesised (*10*, *25–27*). A mixture (called mixture 1 here), in which the weight ratio of SmA-LC/E48/SCTLCP/CD = 66.3%/10.0%/5.0%/18.7%, was prepared. Its crystal (Cr)–SmA, SmA–N* and N*–isotropic (I) phase transition temperatures were 266.9 K, 312.0 K and 450.7 K, respectively.

Figure 2 shows the temperature dependence of the pitch length of the N* phase and the patterns of wide angle X-ray diffraction (WAXD) for mixture 1 at 320.2 K and 370.2 K, respectively. It is shown in Figure 2 that the pitch length increases with temperature decreasing in the temperature range from 345.0 K to 405.0 K, indicating that the helical twisting power of the CD decreases with temperature decreasing. Moreover, in the temperature range from 315.0 K to 345.0 K, the pitch length increases more drastically. It has been known that it is difficult for the layer structure of a SmA phase to buckle or to twist. As the temperature decreases towards the SmA–N* phase transition, the LC molecules start to momentarily and only locally arrange themselves in layers, that is, smectic-like short-range ordering (*28*, *29*) begins to form. However, the temperature is too high for these layers to establish themselves permanently. As the temperature gets closer to the phase transition, the size of the group of these molecules with smectic-like short-range ordering gets much larger, which makes it increasingly difficult for LC molecules to twist, causing the pitch length to be more drastically longer (*29*). It is shown in Figure 2 that the WAXD pattern at 320.2 K has a sharper ring at the small angle region than that at 370.2 K, which indicates that smectic-like short-range ordering at 320.2 K was greater than that at 370.2 K in mixture 1 (*28*, *29*).

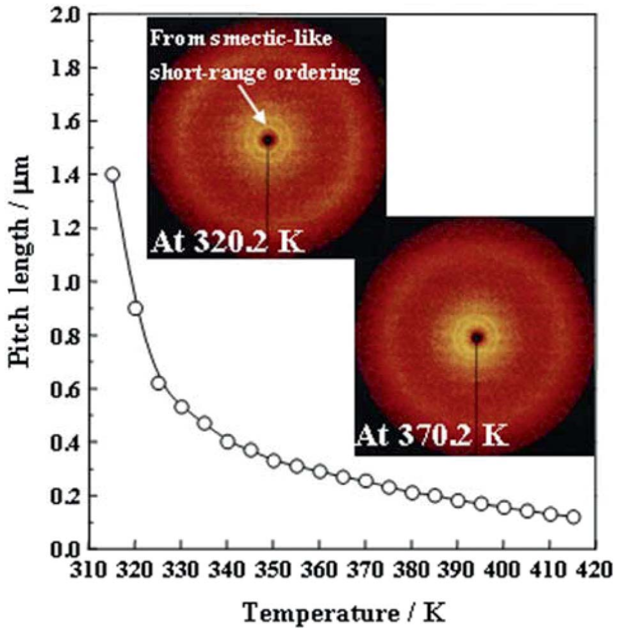

Figure 2. Plot of temperature versus pitch length and the WAXD patterns for mixture 1 at different temperatures.

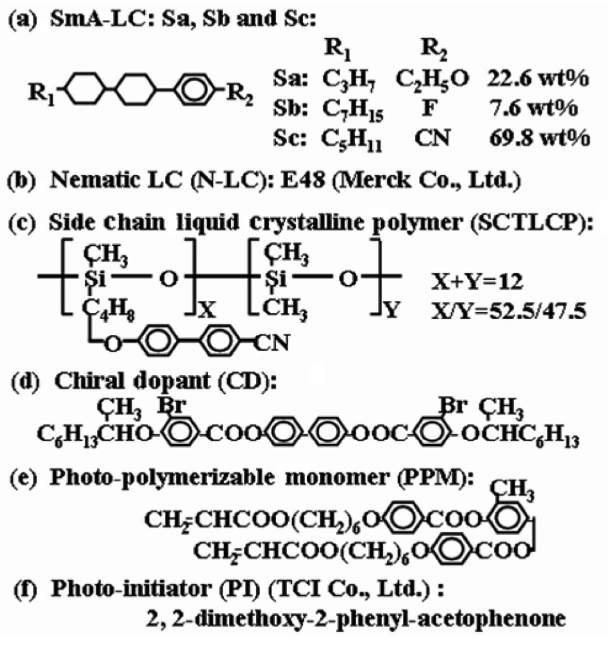

Figure 1. Chemical structures of the materials used.

The other mixture (called mixture 2 here) was prepared by adding 11.0 wt% PPM and 1.0 wt% PI to mixture 1, that is, the weight ratio of PPM/PI/mixture 1 in mixture 2 = 11.0%/1.0%/88.0%. In order to avoid thermally-induced crosslinking between the molecules of PPM, 50 ppm of *p*-methoxyphenol (TCI Co., Ltd.) was added to mixture 2. After mixture 2 was filled into a 203.0 $\mu$m thick cell, the inner surfaces of which had been treated for homogeneous orientation of LC molecules by capillary action at 405.2 K followed by the cell being annealed at 405.2 K for about 10.0 minutes, the N* phase of mixture 2 adopted a planar molecular alignment. On the one hand, when a N*-LC is filled into a cell in its N* phase, affected by capillary action, it is easy for the N*-LC to adopt a planar molecular alignment induced by a shear force at the interface between the LC film and the inner surface of the cell, even if the inner surfaces of the cell have not been treated for planar orientation. In other words, fluid orientation of the N*-LC molecules occurs during the filling of the N*-LC into the cell in its N* phase. On the other hand, a planar alignment of a N* phase is more stable than a focal conic alignment at a high temperature (*30*, *31*). The results in the N* phase of mixture 2 adopted a planar molecular alignment. A similar experimental phenomenon had also been demonstrated in previous work (*21*). Then, the cell was irradiated by UV light (9.0 mW cm$^{-2}$, 365 nm) at 405.2 K for about 20.0 minutes, and a polymer network was formed in the mixture from the crosslinking between the molecules of the PPM. Thus, a PSLC film was prepared. It has become clear that the polymer network also had a helical structure and its pitch length was approximately equal to that of the N* phase of mixture 2 at 405.2 K (*1*, *2*, *10*–*12*, *20*).

Figure 3 shows the wavelength dependence of the reflectance of the PSLC film measured at 405.2 K (curve 1), 370.2 K (curve 2), 325.2 K (curve 3), and 298.2 K (curve 4), respectively. It should be mentioned that, in the present study, the reflection peaks located in the wavelength range smaller than 300 nm could not be measured by the used instrument. Since the LC domains in the PSLC film have a very short pitch at 405.2 K, as shown in Figure 2, the reflection peak must exhibit in the wavelength range smaller than 300 nm and then cannot be observed from curve 1. It is shown in Figure 3 that the bandwidths of curves 2–4 increase in sequence and the bandwidth of curve 4 is over the wavelength range of 300–2500 nm. The CD used in this study was left-handed, so, left-circularly polarised light was reflected by the PSLC film, whereas right-circularly polarised light was transmitted within the bandwidth. Therefore, the reflectance of curves 2–4 within the bandwidth are near 50%. The origin of the oscillations of curve 4 in the 1.0–2.5 $\mu$m region could be attributed to the overtone absorption of LC materials (*32*). In the 1.0–2.0 $\mu$m region, some higher harmonics of the fundamental molecular vibration bands exist. For example, the 1.7 $\mu$m band is likely to originate from the second harmonic frequency of the hydrocarbon vibration centred at ~3.4 $\mu$m. Consequently, several prominent absorption bands centred at 1.2, 1.4 and 1.7 $\mu$m could well explain the oscillations of the reflectance curve at the corresponding locations. From 2.0–2.5 $\mu$m, the tightly-overlapped absorption bands lead to a relatively large baseline absorption and make the reflectance curve oscillate drastically.

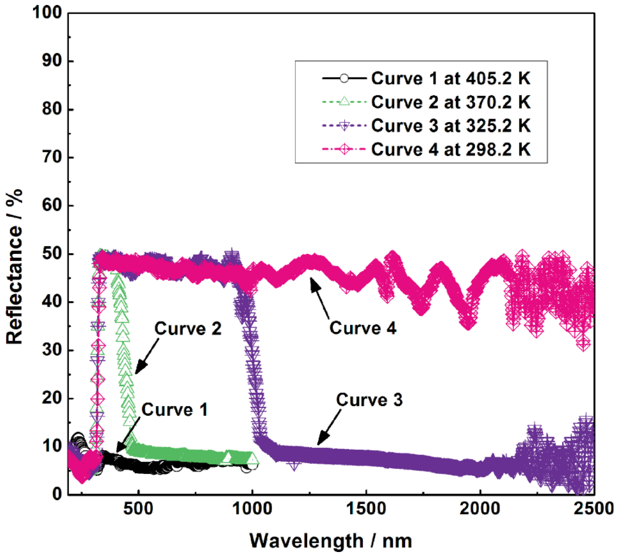

Figure 3. Plot of wavelength versus reflectance for the PSLC film at different temperatures.

In the PSLC film, the pitch length of the polymer network was unchangeable, but the pitch length of the N* phase of the LC domains had a tendency to increase with temperature decreasing. In some small local regions, where the density of the polymer network was higher, or the LC molecules were nearer to the polymer network, the anchoring effect of the polymer network on the LC molecules should be stronger. The alignment of the LC molecules should be better stabilised by the polymer network and the rearrangement of LC molecules should be more difficult. Then, the pitch lengths in these regions should change less with temperature. However, in some small local regions, where the density of the polymer network was lower or the LC molecules was farther from the polymer network, the pitch length should lengthen more with temperature decreasing. Thus, with temperature decreasing, a non-uniform pitch distribution, that is, the pitch lengths being different in different regions, must form in the PSLC film. Meanwhile, it is easy to understand that a greater decrease in temperature should result in a greater non-uniform pitch distribution, which should be the reason why the bandwidth of curve 3 is broader than that of curve 2.

Figure 4 shows the pattern of WAXD at 298.2 K (Figure 4(a)), the photographs of polarised optical microscopy (POM) at 370.2 K (Figure 4(b)) and at 298.2 K (Figure 4(c)), and the schematic representation of the molecular alignment of the SmA phase in the PSLC film (Figure 4(d)), respectively. The same as demonstrated in previous work (*6*), it had been verified by WAXD studies, differential scanning calorimetric (DSC) measurements and POM observation that the mesophase of the PSLC film in the temperature range from 266.9 K to 312.0 K had the order and the molecular

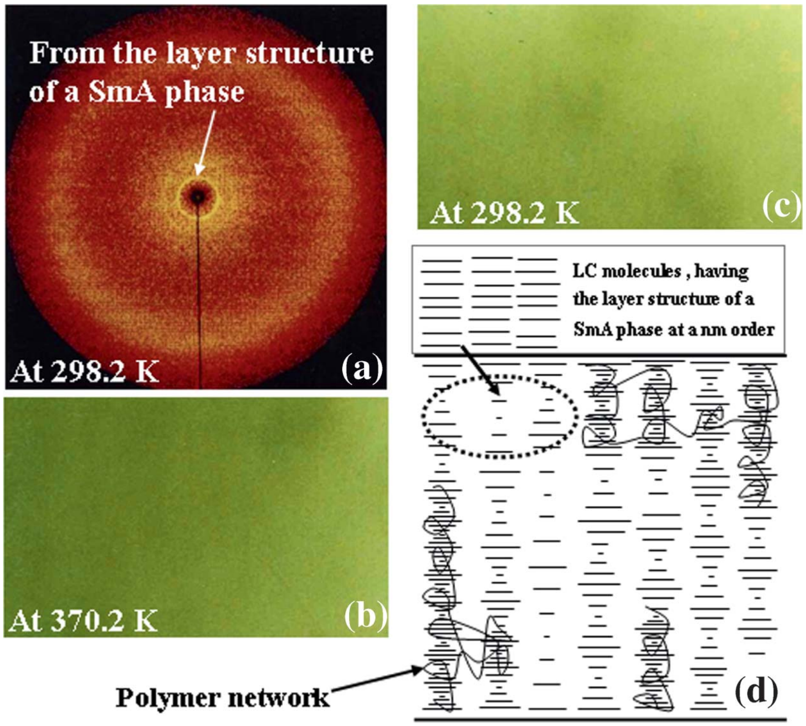

Figure 4. WAXD pattern at 298.2 K (a), POM photographs at 370.2 K (b) and 298.2 K (c), and schematic representation of the molecular alignment of the SmA phase of the PSLC film (d), respectively.

alignment of a SmA phase at a microscopic level, as shown in Figure 4(a), in which the very sharp ring occurs at a small angle region resulting from the layer structure of a SmA phase at a nm order. This is the reason why the mesophase is still called a SmA phase here. Upon cooling the PSLC material from the N* to the SmA phase, the planar molecular alignment of the N* phase was stabilised in the SmA phase at a macroscopic level by the polymer network, as shown in Figures 4(b) and 4(c), which exhibit the optical textures of planar molecular alignments at a $\mu$m order. Therefore, the SmA phase could selectively reflect incident light just like the N* phase. However, because it is difficult for the molecules of a SmA phase to twist, the pitch length of the LC domains should have a tendency to become infinite at 298.2 K. Meanwhile, because the stabilising effect of the polymer network with a permanent solid structure of helix on the rearrangement of the LC molecules in different local regions was different as mentioned above, a very large non-uniform pitch distribution, as schematically shown in Figure 4(d), should form in the PSLC film at 298.2 K rather than at 325.2 K. Based on this, the SmA phase of the PSLC film could reflect the light covering the wavelength range of 300– 2500 nm.

As discussed above, a super wide-band reflective polariser from the PSLC film has been prepared. The bandwidth of the reflection spectrum is changeable with temperature and the maximum value can be over the wavelength range of 300–2500 nm.

## Acknowledgements

This research was financially supported by the National Natural Science foundation (Grant No. 20674005), the National High Technology '863' Program of China (Grant No. 2006AA03Z108) and the Doctoral Fund of the Ministry of Education of the People's Republic of China (Grant No. 20050425850).

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