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Polymer-stabilised cholesteric liquid crystals with a double helical handedness: influence of an ultraviolet light absorber on the characteristics of the circularly polarised reflection band

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An ultraviolet light absorber was introduced in the composition of a polymer-stabilised cholesteric liquid crystal (PSCLC) for which a thermally-induced helicity inversion occurs. The PSCLC exhibits a strong structural discontinuity and two distinct reflection bands with inverse circular polarisations that correspond to polymer-poor and polymer-rich phases. The temperature can be tuned so that the material exhibits a single reflection band with the amount of reflected light close to 90% and both circular polarisations after an electric field has been applied.

1. Introduction

Polymer-stabilised liquid crystals (PSLCs) are composite materials made by in situ photopolymerisation and crosslinking of liquid crystalline monomers dispersed in a low molecular weight LC. The modulation of the optical reflection properties of cholesteric LCs (CLCs) is a practical goal related to applications in the field of direct view (polariser-free) reflective displays with no backlight requirement (*1*), polarisers and colour filters (*2*), mirror-less lasing (*3*) or smart switchable reflective windows for the dynamic control of solar light (*4*). The maximum reflection of ambient (unpolarised) light from a single-layer CLC is never greater than 50% at normal incidence and we have recently shown that this theoretical limit might be exceeded for a single-layer PSCLC by using CLCs exhibiting the property of thermally-induced helicity inversion (*5–7*). However, most of research efforts have focused on the broadening of the reflection bandwidth (*4, 8–46*). The fundamental objective is to fabricate novel CLC materials with a pitch gradient or multidomain helical structure. Among these studies, a few have dealt with the use of an ultraviolet (UV) absorbing dye to create an intensity gradient through the thickness of a solid cholesteric polymer network (*8, 17, 32*) or a field-switchable CLC gel (*14*). Polymerisation at the surface closest to the source is much faster than at the bottom of the layer. When a cholesteric diacrylate is blended with a nematic monoacrylate, the former component has a twice as a high probability as the nematic component to be incorporated into the polymer network and a transverse pitch gradient is obtained (*8*).

In this paper, we consider PSCLCs exhibiting the property of thermally-induced helicity inversion, for which the blend contained a UV absorber. We investigated the behaviour of the reflection band of such a composite material after UV curing, as a function of temperature and when it was subjected to an electric field. It was found that the reflection of both circularly polarised components may be obtained from a PSCLC slab exhibiting a strong in–depth discontinuity between polymer-poor and polymer-rich phases.

2. Experimental

Blend

A CLC oligomer (from Wacker Chemie Ltd) was blended with the chiral low molecular weight LC, (*S*,*S*)-EPHDBPE or 4-[(*S*,*S*)-2,3-epoxyhexyloxy]phenyl 4-(decyloxy)benzoate (from Sigma-Aldrich), which is the helix-inversion compound (HIC). The oligomer was a cyclic polysiloxane molecule with two types of mesogen as lateral chains: a chiral (cholesterol group-bearing) mesogen and an achiral (biphenyl group-bearing) mesogen (*47*). The pitch of the cholesteric phase and the associated reflection wavelength depend on the number of chiral mesogens. Two types of oligomer were chosen: a photocrosslinkable oligomer, designated RMR, and a non-photocrosslinkable oligomer, designated SR. As pure materials, RMR and SR lead to a selective light reflection occurring at nearly the same wavelength, in the red part of the visible spectrum. RMR and SR were mixed together in equal proportions. This two–component mixture was then blended with the HIC at a ratio equal to

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12.5:87.5 wt%. The concentration in the network-forming material was thus equal to 6.25 wt%. Finally, 2 wt% (compared to the RMR content) of photoinitiator (Irgacure 907 from Ciba Specialty Chemicals) and 1 wt% (compared to the total weight) of a UV absorber (Tinuvin 1130 from Ciba Specialty Chemicals) are added. The temperature, T_c, at which the helicity inversion occurs, and a nematic structure is reached, was equal to 83.2°C. The cholesteric structure is left- (right-)handed below (above) T_c.

Preparation of samples

The mixture was introduced at 89°C by capillarity into a 50(±10) μm thick ITO (indium tin oxide)-coated glass cell. Before curing, the cell was kept at $T^+=97°C$ for a few minutes to favour the planar alignment of the right-handed CLC structure. The sample was then irradiated with UV light (0.1 mW cm^{-2} at 365 nm) for 4 h. Finally, the cell was cooled (at 0.5°C min^{-1}) to $T^-=74.5°C$.

Investigation of transmittance properties

The transmittance properties were investigated at normal incidence by infrared (IR) spectroscopy between 2.0 and 4.5 μm with a Perkin–Elmer Spectrum 100 IR spectrometer. The baseline was obtained when the blend is in the nematic state at T_c. Home-made circular polarisers were used when investigations with polarised incident light were necessary. For such a purpose, cyanobiphenyl CLC blends BL094 and BL095 (from Merck Ltd) were made. These compounds are enantiomeric mixtures that selectively reflect light at 548 nm at room temperature. BL094 (BL095) is right- (left-)handed. A nematic structure is obtained when the compounds are blended at 1:1. Thus, it was possible to obtain circular polarisers with a wavelength-tuneable reflection band and a helix either right- or left-handed by varying the relative concentration. The polarisers also acted as reflectors: a left- (right–)handed helix gives rise to a right (left) circular polariser, due to the polarisation selectivity rule. A 25±5 μm thick cell was then filled with the BL094–BL095 blend corresponding to a pass–band superimposed with the investigated reflection band of the sample. As shown on Figure 4, the pass-band needs to be in the range 2.6–3.3 μm and consequently the left (right) circular polariser corresponds to a BL094:BL095 wt% ratio equal to 59±1:41±1 (41±1:59±1). When measurements with circularly-polarised incident light were performed, a 25±5 μm thick cell of pure BL094 (non-reflecting in the IR spectrum), in addition to a cell filled with the blend in the nematic state at T_c, was positioned between the source and the experimental cell during the baseline step. When required, an electric field of amplitude 91.5 V and frequency 50 kHz was applied.

3. Results and discussion

Figure 1 shows the transmission spectra before and after UV light curing when measured at T^+. The mean reflection wavelength of the band is initially about 2.6 μm. After polymerisation, it is spectacularly split into two reflection bands at each side of the pristine band, at 3.0 μm (designated the A-band) and 2.5 μm (designated the B-band). The creation of two distinct peaks upon polymerisation instead of a broadened peak is indicative of a discontinuous phase separation within the system. Due to the presence of the dye, which absorbs UV light in the same region as the photoinitiator, a photo-induced diffusion with simultaneous polymerisation occurs and two layers are fabricated with a discontinuous frontier, from which the splitting of the peak arises. It is expected that the upper layer, the closest to the UV light beam, corresponds to a polymer-rich phase, whereas the lower layer corresponds to a polymer-poor phase.

As can be seen in Figure 1, the two bands exhibited different behaviours as a function of network concentration when the material was subjected to an ac electric field. The HIC compound has a negative dielectric anisotropy $\Delta\varepsilon$ and an electric field tended to favour formation of a planar texture. The position of the B-band was shifted from 2.5 to 2.4 μm and corresponds to the reflection properties of a zone with a poor amount of network. This *blue shift* of the mean reflection wavelength is an electrohydrodynamic distortion effect of the planar texture, which may arise in CLCs with a negative $\Delta\varepsilon$. It comes from the field-induced pitch contraction as a consequence of the increase of the number of helices across the planar layer (*48–50*). The formation and the stability of this texture are known as depending largely on the magnitude of the negative $\Delta\varepsilon$. The position of the A-band at 3.0 μm was weakly altered: the CLC structure is frozen into the material because the polymer concentration is high; the network stabilises the initial texture and preserves it from instabilities.

When the temperature is decreased after polymerisation, each reflection band exhibits its own behaviour, as it can be seen in Figure 2.

The B-band position is temperature-dependent and similar to that of the blend before polymerisation, with a discontinuity because the pitch diverges at T_c. In contrast, the position of the A-band is very

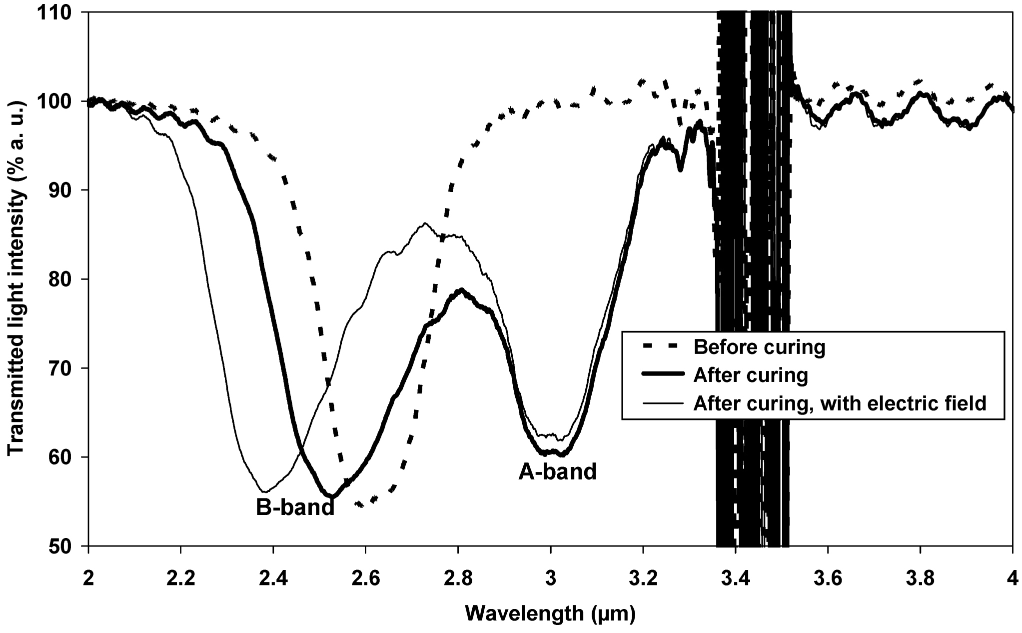

Figure 1. Transmission spectra of the blend (before curing) and the PSCLC (after curing) without and with an electric field (91.5 V, 50 kHz). The incident light is unpolarised. A chemical absorption band occurs around 3.4 μm. The temperature is T^{+}=97°C.

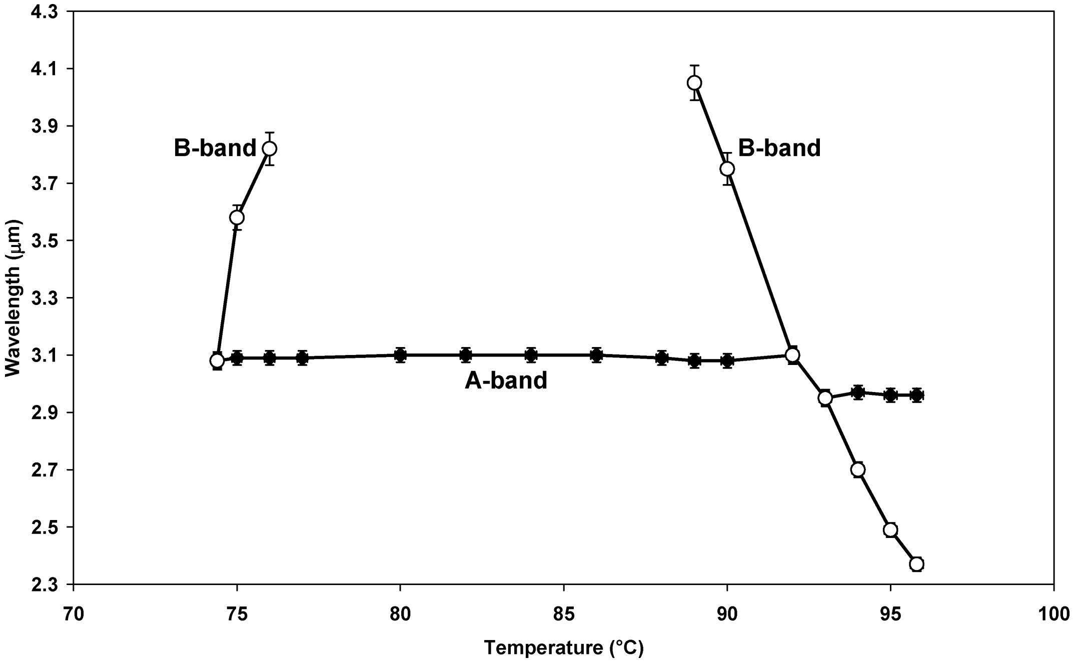

Figure 2. Mean reflection wavelength of the PSCLC as a function of temperature for both bands. The incident light is unpolarised. The B-band exhibits a discontinuity because the pitch diverges at T_c.

weakly temperature-dependent. Both investigations, i.e. field and temperature effects, support our suggestion that the A-band corresponds to the CLC structure dominated by the network, whereas the B-band is related to the polymer-poor area of the composite layer. At T^{-}, the two bands have the same mean wavelength. The amount of light reflected that corresponds to the A-band is expected to be right-handed circularly polarised since the CLC organisation, pitch as well as helicity sense, has been frozen when the polymerisation occurred at T^{+}. In contrast, the B–band corresponds to the behaviour of free LC molecules: the related CLC structure adopts the left-handed sense after cooling. For this reason, the reflected light which corresponds to the B-band is expected as left-handed circularly polarised. Interestingly, the material is thus liable to reflect both circularly polarised light bands at T^-.

The interfacial surface between the LC and the network is very high and the pitch value of the CLC structure of the free fraction undergoes very drastic changes from T^+ to T^-. As a consequence, the material exhibits a polydomain texture from which a light scattering phenomenon arises. As can be seen in Figure 3, the reflected light intensity of both bands reaches less than 35% of the unpolarised incident light intensity at T^- after cooling. It was then decided to apply an electric field to the cell after polymerisation at T^+ and to keep it during the cooling process. As a consequence of the planar alignment induced by the electric field (because the HIC compound has a negative $\Delta\varepsilon$), the reflected light for both bands was drastically enhanced. The reflected intensity is progressively increased when the temperature decreases and is even higher than 50% for temperatures close to T^-. A monodomain texture is promoted, giving rise at T^- to a hyper-reflector system, the reflection performance of which at 3 µm is nearly 90%.

The transmittance at T^- after cooling is shown in Figure 4(a) for different polarisations of the incident light. When the incident light was left or right circularly polarised, approximately the same amount of light was reflected (close to 40%) at zero field, which suggests that the pitch and the number of helical turns of both structures are comparable. Figure 4(b) shows the transmittance after the cell (kept at T^-) has been subjected to a field. The measurement was performed after the field had been switched off. The transmission losses out of the Bragg band are suppressed, whereas the reflected flux inside the Bragg band is increased. As in the previous case (without field), the amounts of polarised reflected light flux are comparable, which may be seen as the achievement of a dual band distribution of the helical organisation with the same pitch but inverse twist senses. These conditions offer the opportunity to switch the reflected intensity from approximately 30% of an unpolarised incident light beam up to nearly 90% by subjecting the PSCLC layer to an electric field.

An interesting issue of this system would be to use a dual LC, sign of $\Delta\varepsilon$ of which changes with frequency, making possible the realisation of a switch between a non-reflective cell (by application of a field at a frequency for which $\Delta\varepsilon>0$) to a highly reflective cell (frequency for which $\Delta\varepsilon<0$), giving access to a system with different reflectance levels.

4. Conclusion

Incorporation of a UV absorber into a helicity-inversion CLC blend may lead to specific spectral

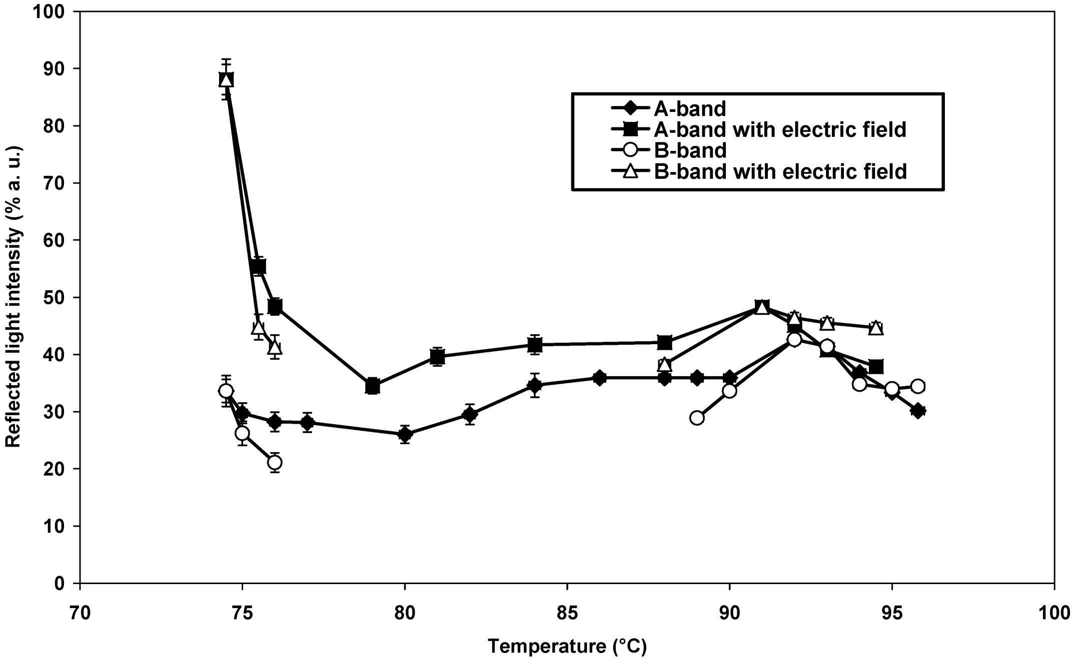

Figure 3. Reflected light intensity of the PSCLC as a function of temperature for both bands, when an electric field (91.5 V, 50 kHz) is applied or not. The incident light is unpolarised. The B-band exhibits a discontinuity because the pitch diverges at T_c.

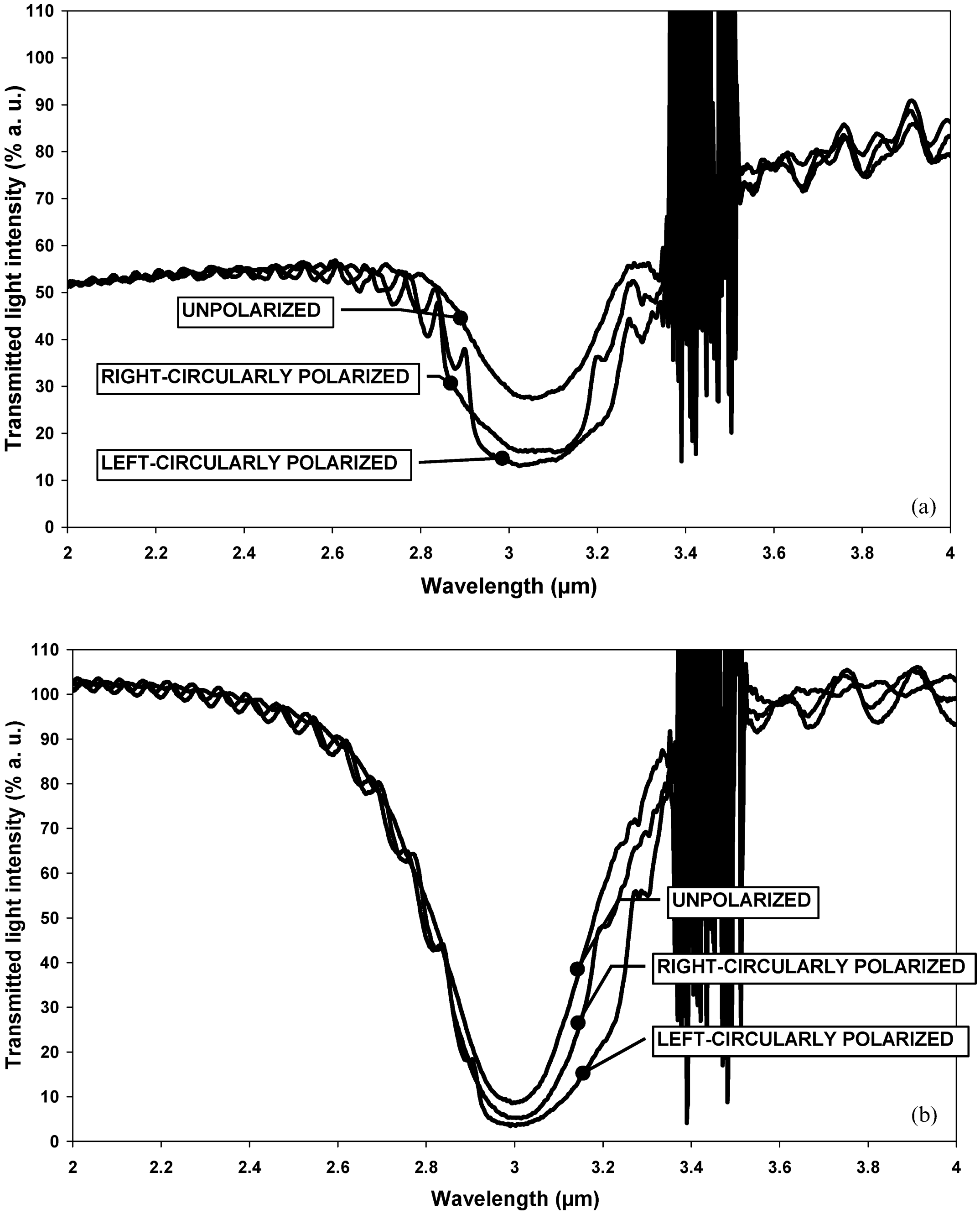

Figure 4. Transmittance spectra of the PSCLC for different polarisations of the incident light beam, without (a) and with (b) an electric field (91.5 V, 50 kHz). A chemical absorption band occurs around 3.4 μm. The temperature is T^{-}=74.5°C.

characteristics after polymerisation: two distinct bands are obtained, which correspond to the reflection of discontinuous areas with different network concentrations. One band appears to be temperature independent and corresponds to a CLC slab for which a right-handed helical structure has been frozen in, due to the template effect induced by the polymer network. The position of the other band varies with temperature, as a consequence of a polymer-poor phase, with the related CLC structure of left-handed helicity below T_c. The two reflection bands merge at T^{-} and contribute to a CLC slab with a single pitch and two different helical senses. Although the texture is light scattering, field-induced planar alignment makes it possible to obtain a reflected light intensity close to 90% for an unpolarised incident light beam. In addition, the alignment effect of the electric field is also efficient a posteriori, which offers the opportunity to switch the cell from a scattering state to a hyper-reflective one.

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