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Polymer-Stabilized Cholesteric Liquid Crystals with a double helical handedness: influence of an ultraviolet light absorber on the characteristics of the circularly polarized light reflection band

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An ultraviolet light absorber was introduced in the composition of a Polymer-Stabilized 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 polarizations which correspond to polymer-poor and polymer-rich phases. The temperature can be tuned so that the material exhibits a single reflection band with a reflected light amount close to 90% and both circular polarizations after an electric field was applied.

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1. Introduction

Polymer-Stabilized Liquid Crystals (PSLCs) are composite materials made by in situ photopolymerization and crosslinking of liquid crystalline monomers dispersed in a low molecular weight LC. The modulation of the light reflection property of cholesteric LCs (CLCs) is a practical goal related to applications in the field of direct view (polarizer-free) reflective displays with no backlight requirement [1], polarizers and colour filters [2], mirrorless lasing [3] or smart switchable reflective windows for the dynamical control of solar light [4]. The maximum reflection of ambient (unpolarized) 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 from 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 [8-46]. The fundamental objective is to fabricate novel CLC materials with a pitch gradient or multidomain helical structures. Among these works, a few have dealt with the use of an ultraviolet (UV) light 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]. The polymerisation at the surface the 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 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 light absorber. We investigate the behaviour of the reflection band of such a composite material after UV light curing, with the temperature,

and when it is subjected to an electric field. It is shown that the reflection of both circularly polarized 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.) is 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 is 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, as-called RMR, and a non-photocrosslinkable oligomer, as-called 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 are mixed together in equal proportions. This two-component mixture is then blended with the HIC at a ratio equal to 12.5:87.5 wt.%. The concentration in network-forming material is thus equal to 6.25 wt.%. Finally, 2 wt.% (compared to the RMR content) of photo-initiator (Irgacure 907 from Ciba Specialty Chemicals) and 1 wt.% (compared to the total weight) of a UV light absorber (Tinuvin 1130 from Ciba Specialty Chemicals) are added. The temperature T_c for which the helicity inversion occurs, and a nematic structure is reached, is 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 in a 50 (\pm 10) μm thick ITO (Indium Tin Oxide)-coated glass cell. Before curing, the cell was kept at $T^+ = 97^\circ\text{C}$ 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 @ 365 nm) for 4 hours. Finally, the cell was cooled (at 0.5°C/min.) till $T^- = 74.5^\circ\text{C}$.

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 IR spectrometer Spectrum 100. The baseline was made when the blend is in the nematic state at T_c . Home-made circular polarizers were used when investigations with polarized incident light were necessary. For such a purpose, cyanobiphenyl CLC blends BL094 and BL095 (from Merck Ltd.) were made. These compounds are enantiomeric mixtures which 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 is possible to get circular polarizers with a tunable-wavelength reflection band and a helix either right- or left-handed by varying the relative concentration. The polarizers are also reflectors: a left- (right-) handed helix gives rise to a right (left) circular polarizer, due to the polarization selectivity rule. A $25\pm 5 \mu\text{m}$ thick cell was then filled with the BL094–BL095 blend corresponding to a pass-band superimposed with the investigated reflection band of the sample. In Figure 4, the pass-band needs to be in the range 2.6–3.3 μm and consequently the left (right) circular polarizer corresponds to a BL094 : BL095 wt.% ratio equal to $59\pm 1 : 41\pm 1$ ($41\pm 1 : 59\pm 1$). When measurements with circularly-

polarized 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 polymerization, it is spectacularly split into two reflection bands at each side of the pristine band, at 3.0 μm (as-called A-band) and 2.5 μm (as-called B-band). The creation of two distinct peaks upon polymerization 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 polymerization 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.

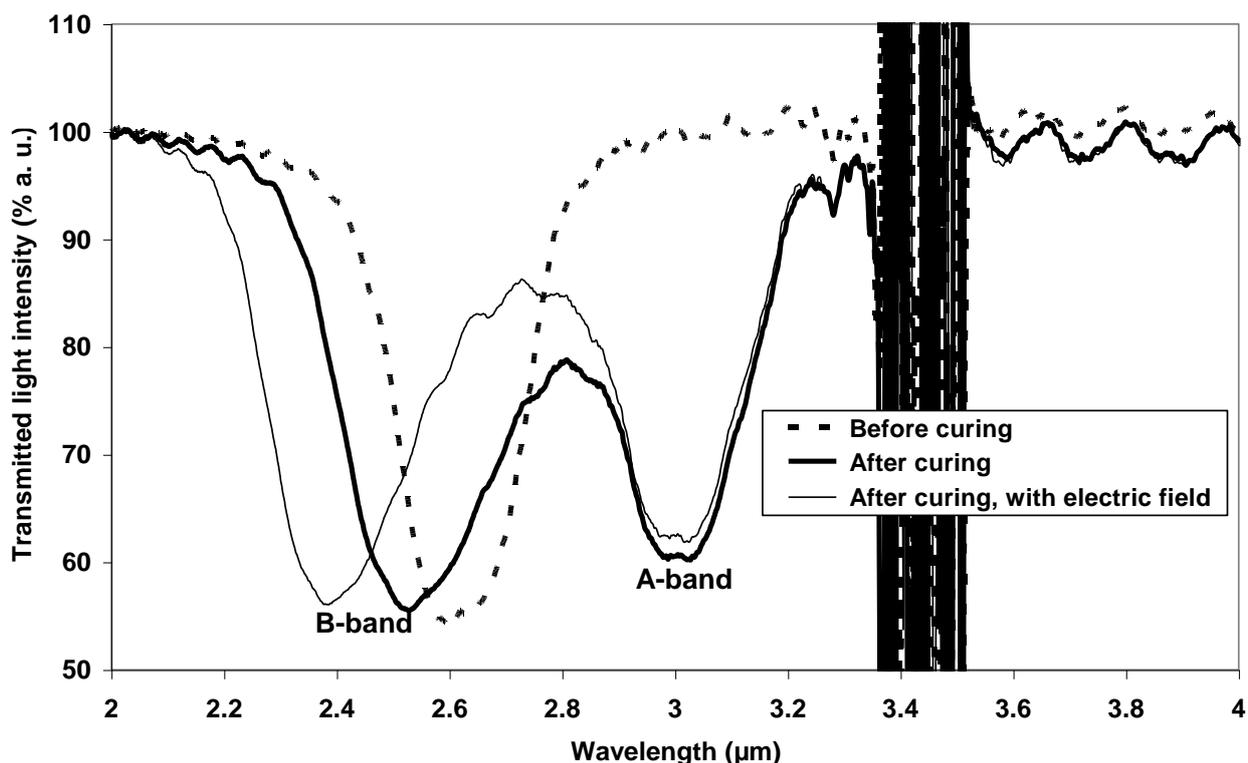


Figure 1. Transmission spectra of the blend (*before curing*) and the PSCLC (*after curing*) without and with an electric field (91.5 V @ 50 kHz). The incident light is unpolarized. A chemical absorption band occurs around 3.4 μm . The temperature is $T^+ = 97^\circ\text{C}$.

The two bands have different behaviours in relation with the network concentration when the material is subjected to an alternative electric field. The HIC compound has a negative dielectric anisotropy $\Delta\epsilon$ and the role of the electric field will consist in favouring a planar texture. The position of the B-band is shifted from 2.5 to 2.4 μm and describes 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 $\Delta\epsilon$. 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 $\Delta\epsilon$. The position of the A-band at $3.0\ \mu\text{m}$ is weakly altered: the CLC structure is frozen into the material because the polymer concentration is high; the network stabilizes the initial texture and preserves it from instabilities.

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

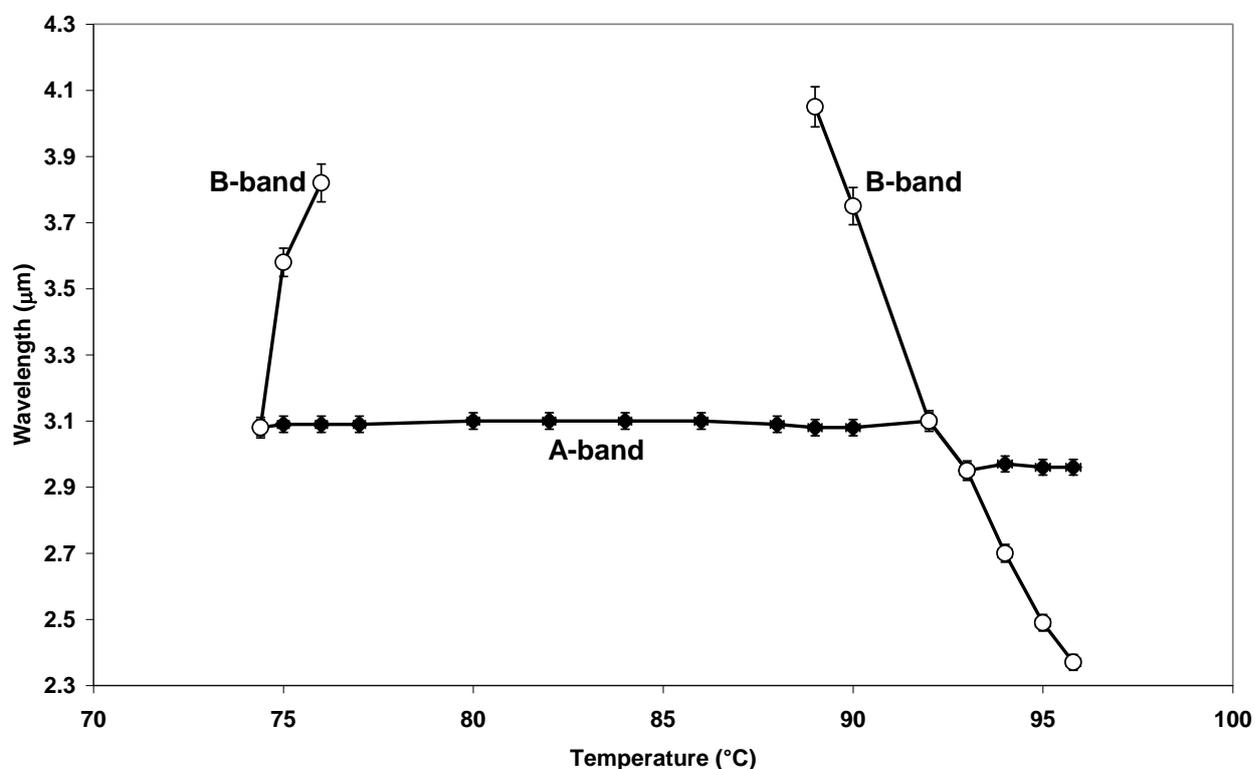


Figure 2. Mean reflection wavelength of the PSCLC as a function of temperature for both bands. The incident light is unpolarized. The B-band exhibits a discontinuity because the pitch diverges at T_c .

The B-band position is temperature-dependent and similar to that of the blend before polymerization, with a discontinuity because the pitch diverges at T_c , whereas the position of the A-band is very weakly temperature-dependent. Both investigations – 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 which corresponds to the A-band is expected to be right-handed circularly polarized since the CLC organization – pitch as well as helicity sense – has been frozen when the polymerization occurred at T^+ . On the contrary, 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 polarized. Interestingly, the material is thus liable to reflect both circularly polarized 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 seen in Figure 3, the reflected light intensity of both bands reaches less than 35% of unpolarized incident light intensity at T^- after cooling. It was then decided to apply an electric field to the cell after polymerization at T^+ and to keep it in the course of cooling. As a consequence of the planar alignment induced by the electric field (because the HIC compound has a negative $\Delta\epsilon$), the reflected light for both bands is now 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 whose the reflection performance at $3\mu\text{m}$ is nearly 90%.

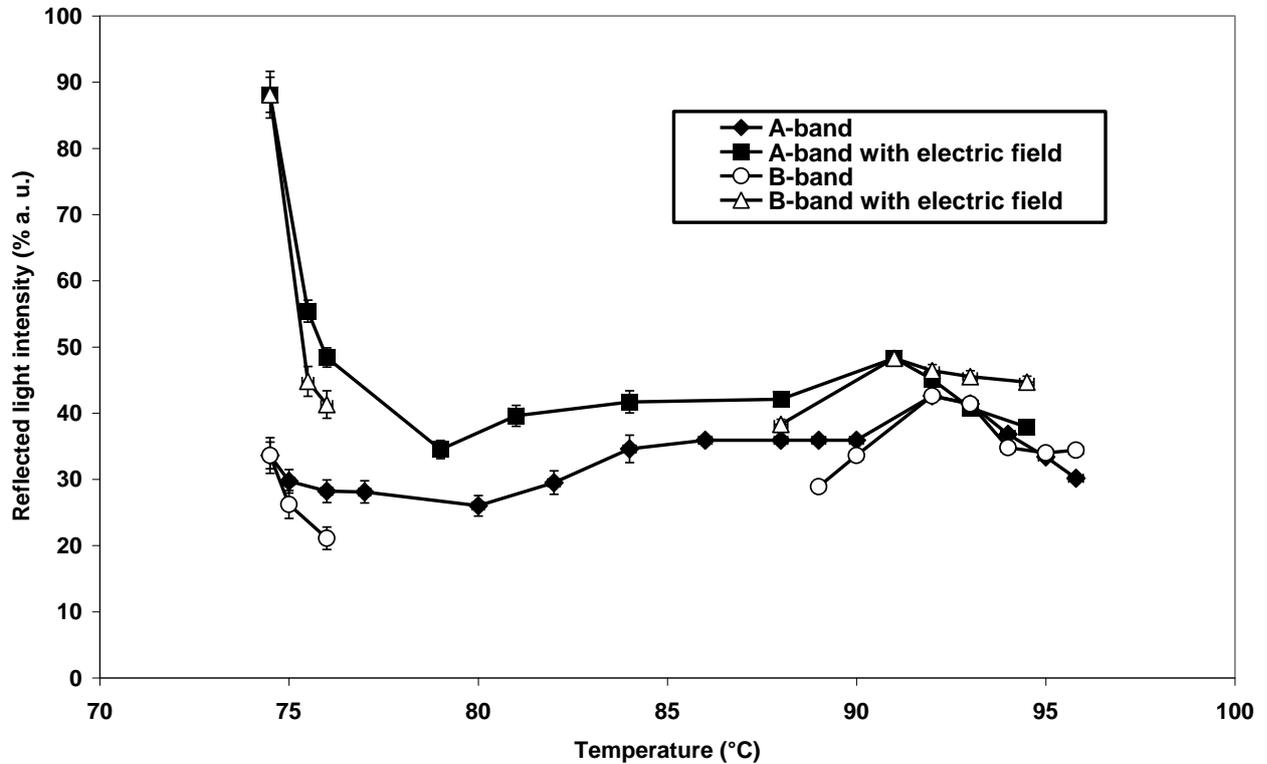
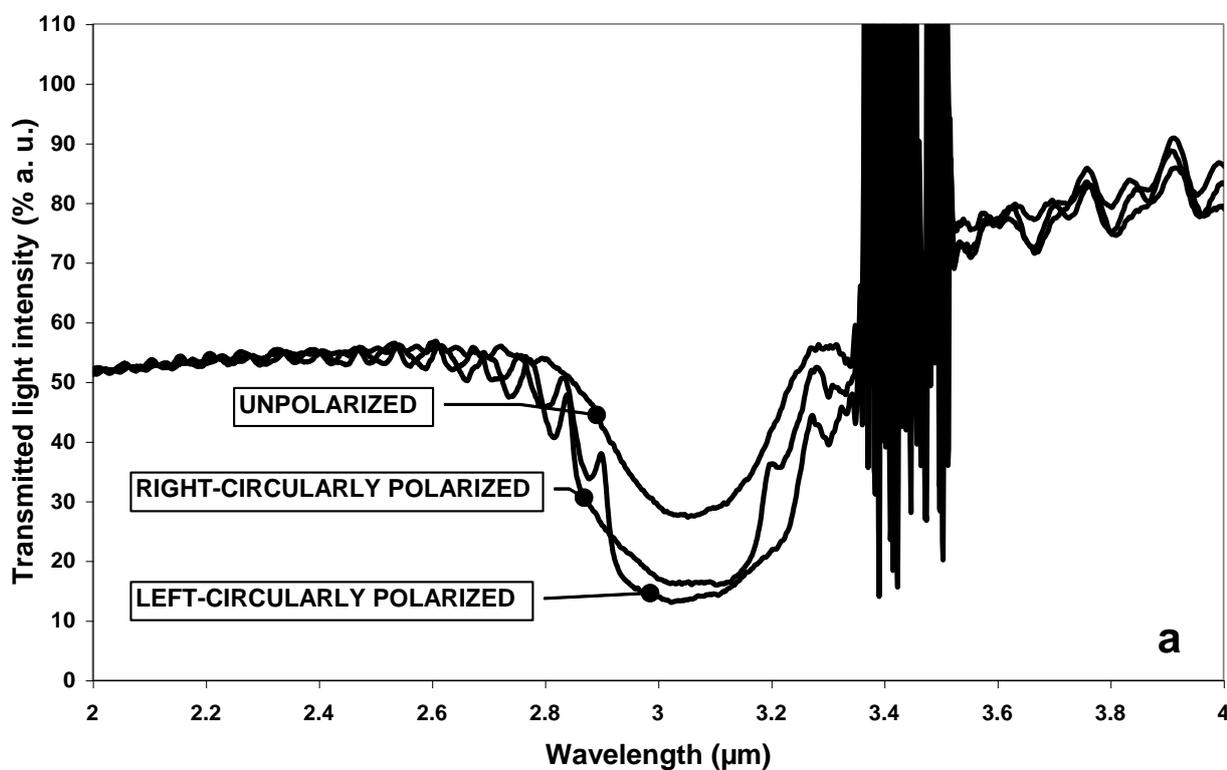


Figure 3. Reflected light intensity of the PSCLC as a function of temperature for both bands, when an electric field (91.5 V @ 50 kHz) is applied or not. The incident light is unpolarized.

The B-band exhibits a discontinuity because the pitch diverges at T_c .

The transmittance at T^- after cooling is shown in Figure 4.a by using different polarizations of the incident light. When the incident light is left or right circularly polarized, approximately the same amount of light is reflected (close to 40%) at zero field, which suggests that the pitch and the number of helix 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 is done after the field has been switched off. The transmission losses out of the Bragg band are

suppressed while the reflected flux inside the Bragg band is increased. As in the previous case (without field), the amounts of polarized reflected light flux are comparable, which may be seen as the achievement of a dual band distribution of the helical organization with the same pitch but inverse twist senses. These conditions offer the opportunity to switch the reflected intensity from approximately 30% of an unpolarized incident light beam up to nearly 90% by subjecting the PSCLC layer to an electric field.



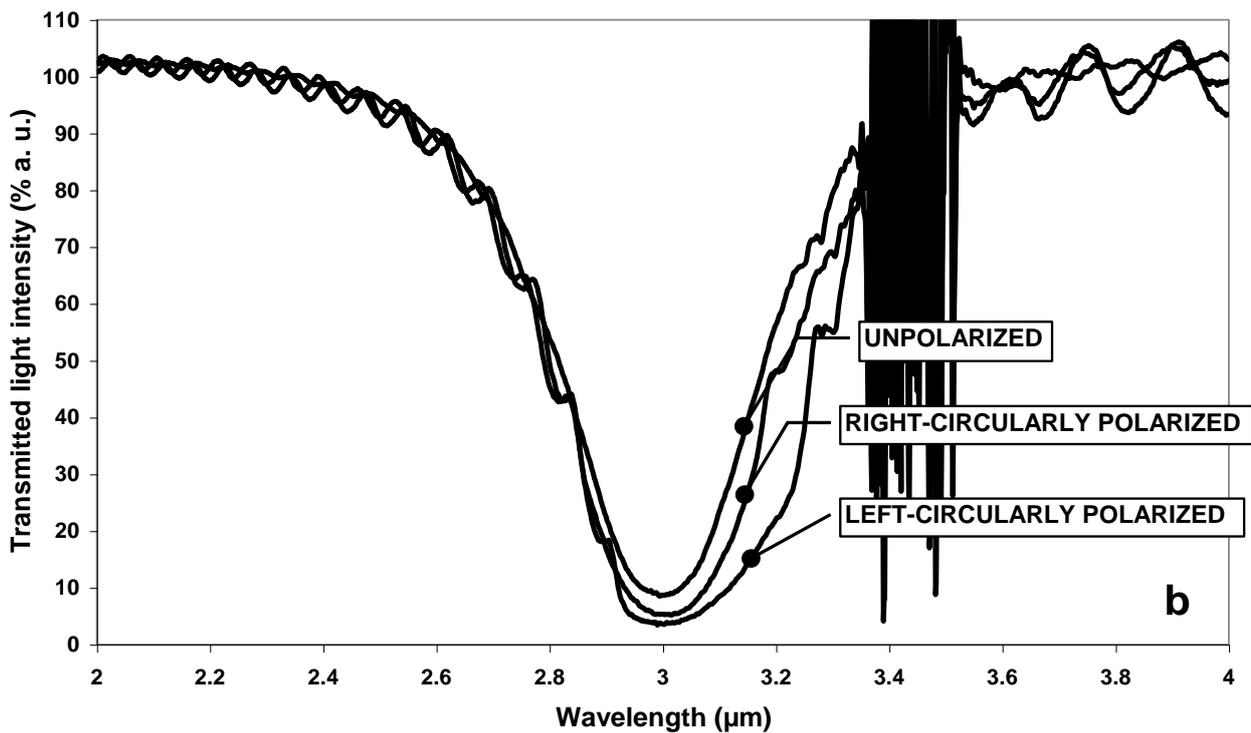


Figure 4. Transmittance spectra of the PSCLC for different polarizations of the incident light beam, without (a) and with (b) an electric field (91.5 V @ 50 kHz). A chemical absorption band occurs around 3.4 μm . The temperature is $T = 74.5^\circ\text{C}$.

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

4. Conclusion

Incorporation of a UV light absorber into a helicity-inversion CLC blend may lead to specific spectral characteristics after polymerization: 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. The texture is light scattering, nevertheless the field-induced planar alignment makes possible to reach a reflected light intensity close to 90% of an unpolarized 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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