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Cholesteric Liquid Crystalline Materials with a Dual Circularly Polarized Light Reflection Band Fixed at Room Temperature

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ABSTRACT: An unpolarized normal-incidence light beam reflected by a cholesteric liquid crystal is left- or right-circularly polarized, in the cholesteric temperature range. In this article, we present a novel approach for fabricating a cholesteric liquid crystalline material that exhibits reflection bands with both senses of polarization at room temperature. A cholesteric liquid crystal that presents a twist inversion at a critical temperature T_c is blended with a small quantity of photopolymerizable monomers. Upon ultraviolet irradiation above T_c, the liquid crystal becomes a polymer-stabilized liquid crystal. Below T_c, the material reflects a dual circularly polarized band in the infrared. By quenching the experimental cell at a temperature below the blend's melting point, the optical properties of the material in an undercooled state are conserved for months at room temperature, which is critical to potential applications such as heat-repelling windows and polarization-independent photonic devices.
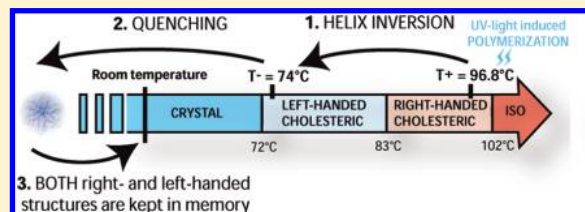
1. INTRODUCTION

1.1. Motivation. The helical structure of cholesteric liquid crystals (CLCs) gives rise to the fundamental property of selective light reflection.[1-3] At normal incidence, the mean reflection wavelength λ_0 is directly related to the helical pitch p (the structural periodicity that gives the distance along the axis that corresponds to a rotation of 360° in the orientation of the rod-like molecule) by the Bragg law $\lambda_0 = np$, where n is the average refractive index [$n = (n_o + n_e)/2$ where n_o and n_e are the ordinary and extraordinary indices, respectively]. The reflected light is circularly polarized with the same handedness as that of the CLC structure, which constitutes the polarization-selectivity rule.

Thus, light reflected from a CLC is circularly polarized with a single handedness, so a CLC cannot reflect more than 50% of a normally incident unpolarized light beam and reflects 0% when the incident beam is circularly polarized with a handedness opposite that of the CLC. The correspondence between the chirality of the structure and the physical properties still remains an open question, so the development of novel cholesteric liquid-crystalline structures that do not obey the polarization-selectivity rule is desirable. Overcoming this challenge at room temperature (RT) can lead to a host of innovative applications such as hyper-reflective (polarizer-free) displays, electro-optical glazing structures to dynamically control electromagnetic radiation, and, more generally, polarization-independent photonic devices.

1.2. State of the Art and Objectives. To fabricate CLC reflectors that exceed the reflectance limit in a single frequency band, different multilayer systems have been provided: cholesteric films with the same pitch but inverse twist handedness by using low-molar-mass CLCs in distinct glass cells[4,5] or stacked CLC films in the glassy solid state;[6] a polymer nematic defect layer sandwiched between polymeric CLC films with the same pitch and inverse twist handedness,[7,8] which was inspired by the chitin-made cuticle of the *Plusiotis resplendens* beetle;[9] an isotropic poly(vinyl alcohol) layer sandwiched between polymeric CLC films, again with the same pitch and inverse twist handedness.[10]

As an alternative to multilayer systems, which would result in devices with reduced complexity and decreased optical losses (reflections from multiple interfaces), a novel research direction was recently opened by the fabrication of single-layer polymer-CLC composites.[11,12] To fabricate this system, photopolymerizable monomers are introduced into a low-molar-mass CLC, and the blend undergoes a thermally induced inversion of twist handedness at its critical temperature T_c. The blend is cured with ultraviolet (UV) light when the helix is right-handed, and the result is a polymer-stabilized CLC (PSCLC or CLC gel).[13] Then, the reflectance of PSCLCs exceeds 50% in the infrared (IR) portion of the spectrum when measured at the requisite temperature for a cholesteric helix with practically the same pitch but a handedness (i.e., left) that is opposite to the handedness of the CLC when the photocuring occurred.[14,15] The polymer concentration and the application of an electric field during the thermal process have a clear impact on the reflectance characteristics, as demonstrated in ref 16. The optical properties of double-handed cholesteric structures were described theoretically by numerical simulations that used a stochastic approach based on concurrent and randomly interlaced right- and left-handed helices.[17]
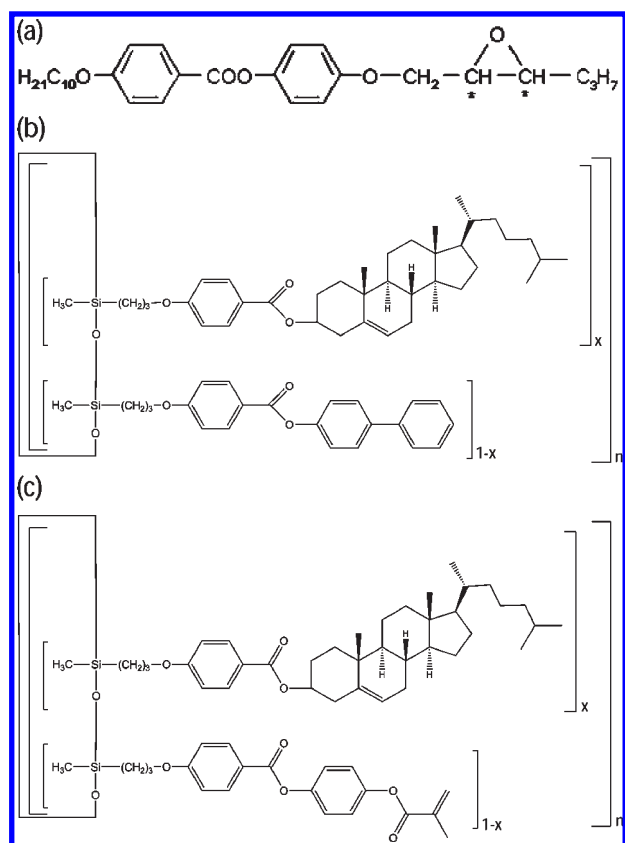
Figure 1. Chemical structures of materials. (a) Helix-inversion compound: (S,S)-EPHDBPE or 4-[(S,S)-2, 3-epoxyhexyloxy]-phenyl-4-(decyloxy)-benzoate. (b) Nonphoto-cross-linkable cholesteric liquid crystal oligomers (image by courtesy of Dr. E. Hanelt). x is the molar fraction of the chiral mesogen, and n represents the ring size of the siloxane backbone. (c) Photo-cross-linkable cholesteric liquid crystal oligomers (image by courtesy of Dr. E. Hanelt). x = 0.31 and n = 4 for both compounds RMR and SR.

The procedure in refs 11 and 12 has given rise to variants. For example, including an UV absorber in the PSCLC may promote a strong structural discontinuity in the PSCLC layer,[18] and the wash-out−refill method[19−23] consists of clearing the PSCLC of its low-molar-mass CLC and filling the porous network with a CLC that has an inverse helicity handedness.

The purpose of the present article is to describe a generic procedure to produce PSCLCs that present a double-handed circular reflection band at RT. Thus, one is not obliged to account for the details of the polymorphism of the LC mixture and, in particular, for the presence of a cholesteric phase at RT. As a result of the quenching step called for in the experimental protocol, the reflection properties of the undercooled CLC material remain remarkably constant over a period of months, which property is critical to all possible applications.

2. EXPERIMENTAL SECTION

2.1. Material. CLC oligomers from Wacker Chemie Ltd. are blended with the chiral low-molar-mass 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) (Figure 1a). The CLC oligomers are cyclic polysiloxane molecules with lateral chains consisting of two types of mesogen: a

chiral (cholesterol-group-bearing) mesogen and an achiral (biphenyl-group-bearing) mesogen.[24−26] The pitch of the cholesteric phase and the associated reflection wavelength depend on the number of chiral mesogens. Two types of CLC oligomers were chosen: a nonphoto-cross-linkable oligomer SR (Figure 1b) and a photo-cross-linkable oligomer RMR (Figure 1c). As pure materials, SR and RMR lead to selective reflection at nearly the same wavelength (in the red portion of the visible spectrum). SR and RMR are mixed at a 44:56 wt ratio to obtain the desired concentration of network-forming material in the final mixture. This two-component mixture is then blended with the HIC at 12.5:87.5 wt % so that the concentration of network-forming material is 7 wt %. Finally, 2 wt % (relative to the RMR content) of the photoinitiator Irgacure 907 (from Ciba Specialty Chemicals) is added to promote photo-cross-linking.

2.2. Experimental Conditions. The transmittance properties were investigated for normal-incidence light between 2.0 and 4.5 μm with a Perkin-Elmer IR spectrometer Spectrum 100. The baseline was acquired with the blend in the nematic state at T_c = 83 °C. Home-made circular polarizers were used when investigations required polarized incident light; we have given experimental details about the fabrication of such polarizers in refs 11 (in the Supporting Information) and 14 (in section 2.4). These polarizers were made from a blend of BL094 and BL095 cyanobiphenyl CLCs (from Merck Ltd.). These compounds are enantiomeric mixtures, both with a RT reflection wavelength of 548 nm. The cholesteric structure of BL094 (BL095) is right- (left-) handed. A nematic structure is reached when the compounds are blended at a 1:1 wt ratio, so it is possible to fabricate circular polarizers with a tunable-wavelength reflection band and either a right- or left-handed helix by varying the relative concentration of the two components in the mixture. The polarizers are also reflectors: a left- (right-) handed helix gives rise to a right- (left-) handed circular polarizer because of the polarization-selectivity rule. A 25 ± 5 μm thick indium−tin-oxide- (ITO) coated glass sandwich cell with a planar alignment (provided by rubbed polyimide layers) was filled with the BL094-BL095 blend to create a pass-band filter with the pass band superimposed over the reflectance band under investigation. For Figures 5 to 7, the pass band is tuned to the 2.4−3.3 μm range, which means that the left (right) circular polarizer corresponds to a BL094:BL095 wt % ratio of 59 ± 1:41 ± 1 (41 ± 1:59 ± 1). Because the reflection bandwidth is about 300 nm, four (narrow-band) polarizers, which correspond to four BL094-BL095 blends, are required to cover the full wavelength range under investigation. The baseline takes into account the transfer function of each polarizer.

3. RESULTS AND DISCUSSION

3.1. Polymorphism of the Mixture. Figure 2 shows the variation with temperature of the mean reflection wavelength in the IR.

The helicity inversion occurs at T_c = 83.0 °C, for which a nematic structure is reached. The cholesteric structure is left- (right) handed below (above) T_c. The cell will be cured with UV light at T^+ = 96.8 °C, as a result of which the CLC will become a PSCLC. The material design targets T^- = 74.0 °C as the temperature at which both helicities will coexist, after the photocuring step, the thermal process, and the field application have occurred.

3.2. Preparation of the Sample. The mixture is introduced by capillarity at 83 °C into a 25 ± 5 μm thick ITO-coated glass

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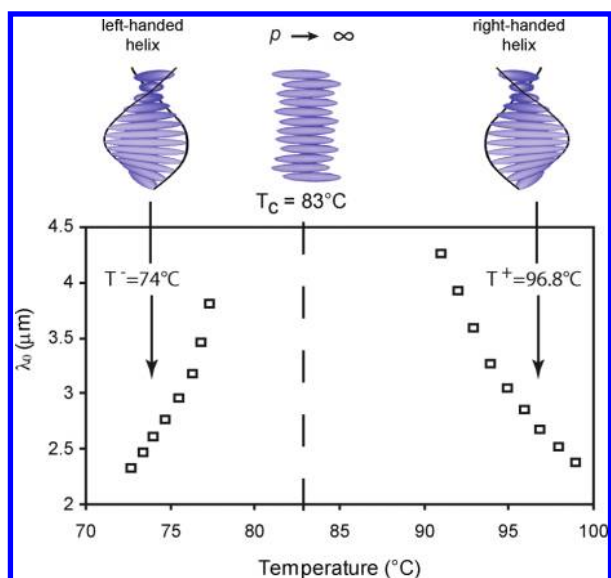dx.doi.org/10.1021/jp2014622 |J. Phys. Chem. B 2011, 115, 6421–6426

Figure 2. Mean reflection wavelength λ_0 of the CLC cell as a function of temperature. A nematic liquid crystalline structure (unwound helical structure) is obtained at T_c = 83 °C. The helical structure of the cholesteric phase is right- (left-) handed above (below) T_c. The UV-induced polymerization occurs at T^+ = 96.8 °C. The coexistence of circularly polarized reflection bands with inverse handedness is designed to occur at T^- = 74.0 °C.

sandwich cell with planar alignment. At T^+, the experimental cell exhibits a planar Grandjean texture (the helical axis is perpendicular to the film plane) with an important density of oily streaks (disclination lines). Voltage kicks, generated by turning on and off the power supply (±80 V, 50 Hz, square wave) several times, are applied to annihilate these defects. Because the dielectric anisotropy of the mixture $\Delta\varepsilon = \varepsilon_{||} - \varepsilon_{\perp}$ is negative, application of an electric field makes the planar texture more uniform, thus preserving the optical band gap. The application of an electric field parallel to the helix axis of a CLC with a negative $\Delta\varepsilon$ favors a homogeneous planar texture because it tends to align the small axis of the molecules in the field direction (if $\Delta\varepsilon$ were positive, the helix would be progressively unwound).[27] Therefore, a monodomain texture is favored to the detriment of a polydomain texture. After several kicks, a nice defect-free planar structure is obtained. The voltage is then switched off, and the sample is maintained at T^+ for 1 h to definitely align the texture.

3.3. Temperature Dependence of Optical Properties. The sample was irradiated with UV light (365 nm, 0.13 mW/cm^2) at T^+ for 4 h. As seen in Figure 3, the mean reflection wavelength is slightly blueshifted as a result of polymer network formation in the LC matrix. The helical pitch of the blend is believed to slightly decrease with respect to the volume shrinkage that results from the reaction of polymerization and cross-linking. The same behavior has been observed in other CLC blends.[11,14,15,18,28,29]

An electric field (±80 V, 50 Hz, square wave) was applied to the cell while it cooled at 0.2 °C/min to T^-. Applying an electric field to a PSCLC while its temperature is ramped from T^+ to T^- promotes a monodomain planar texture. When the thermal ramp starts from T^+ toward T^-, the CLC structure of the free-LC fraction undergoes very drastic changes in pitch, which even include an unwinding of the helix at T_c followed by a rewinding below T_c. Moreover, these helical-structure changes occur while the LC is strongly confined in a porous structure with a very large
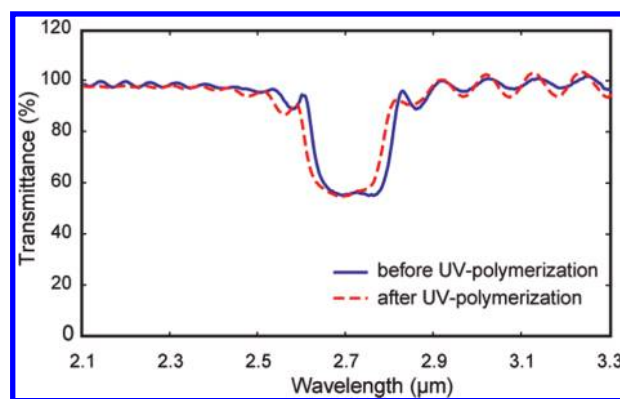

Figure 3. CLC-cell transmittance spectra at T^+ = 96.8 °C before and after photopolymerization. The incident light is unpolarized.
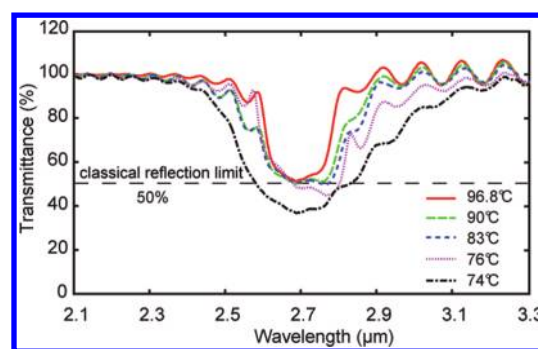

Figure 4. PSCLC-cell transmittance spectra for different temperatures from T^+ = 96.8 °C to T^- = 74.0 °C after photopolymerization at T^+. The incident light is unpolarized.

surface area. It is no longer possible to form a well-aligned monodomain planar structure (which dominated at T^+), and the CLC slab tends to spontaneously produce a polydomain texture upon cooling, which leads to light scattering. In conclusion, the application of an electric field to hinder the nucleation of a polydomain texture (and consequently to limit the transmittance losses) is presently an alternative solution to decreasing the thermal ramp speed from T^+ to T^- as proposed in ref 14.

At T^+, the helical structure becomes partially frozen into the composite material because, upon photopolymerization, the polymer network acts as a template for the CLC structure.[30−32] The fraction of the CLC close to the polymer network surfaces interacts strongly with it and is called the *bound-LC fraction*. As the temperature is lowered, the network is sufficiently dense, and the elastic interactions of the network with the LC are sufficiently strong to hinder the reorganization of this fraction of LC molecules. However, the cholesteric structure of the *free-LC fraction* (i.e., the fraction of the CLC far from the polymer surfaces) retains its ability to change with temperature. The question of size domains has been addressed in refs 11 and 14. Detailed numerical simulations in ref 17 have shown that the optical and structural properties are derived by the concurrent and randomly interlaced presence of both helicities, for polymer strands thicknesses in the 150−250 nm range and thicknesses of the bound right-handed CLC material ranging from 0.5−0.7 μm to 4.0−4.2 μm.

Figure 4 shows transmittance spectra that correspond to unpolarized normal-incidence light and for temperatures ranging
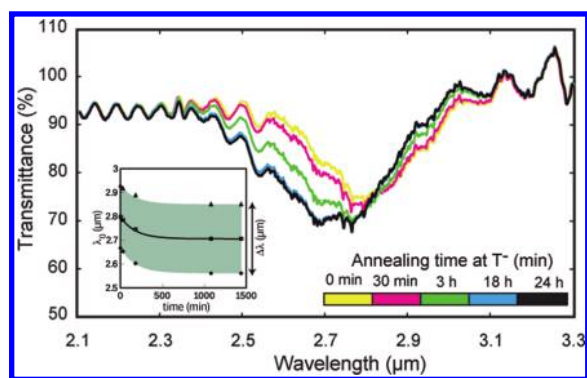
Figure 5. PSCLC-cell transmittance spectra at T^- = 74 °C for different annealing times at T^- when the incident light is left-circularly polarized. The inset shows the mean reflection wavelength λ_0 and the optical-band gap width $\Delta\lambda$ as a function of annealing time; the solid line corresponds to the exponential fit of λ_0 (the e-folding time is 3 h).
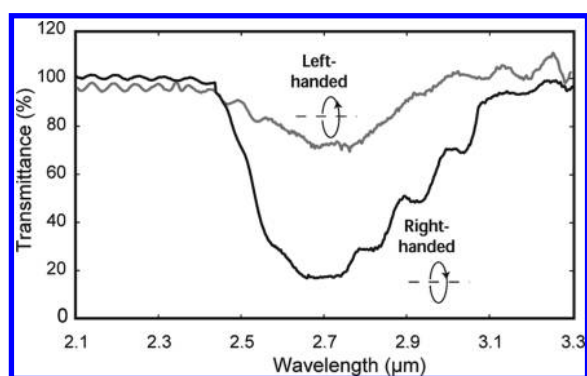

Figure 6. PSCLC-cell transmittance spectrum at T^- = 74 °C when the incident light is right-circularly polarized. The transmittance spectrum when the incident light is left-circularly polarized (annealing time = 24 h) is shown for comparison (data from Figure 5).

from T^+ to T^-. From T^+ to T_c (83 °C), the reflection band gap is slightly widened. Below T_c, the band gap becomes deeper and wider, while the scattering remains weak. Outside of the band gap (i.e., in the 2.1−2.3 μm range), the mean transmittance is about 95%, which indicates that less than 5% of the normal-incidence light intensity is scattered.

The best performance is obtained at T^- (= 74 °C), at which point the reflectance exceeds 50% because circularly polarized reflection bands with opposite handedness are present. Two CLC structures with opposite helicities coexist: a right-handed helix structure that corresponds to the bound-LC fraction and whose the structure is frozen at T^+ and maintained in this state down to T^-, and a left-handed helix structure, which is the stable structure formed by the free-LC fraction at T^-.

To increase the reflected intensity, a set of parameters would have to be considered and simultaneously optimized, such as the concentration of network-forming material, the flexibility of mesogens (both parameters play an important role in determining the network morphology and the mobility of the free-LC fraction), the temperature (which influences the nature of phase separation between network-forming material and LC), and the profile of the pitch-versus-temperature curve (e.g., the T^+-T^- amplitude plays a role in the final reflectance properties at T^- because it is a part of the thermal history). This question is out of
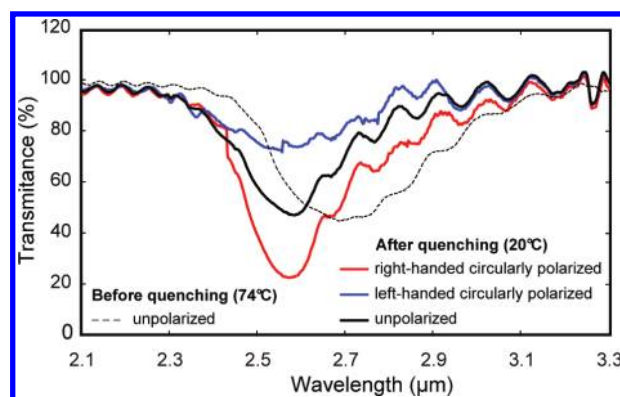

Figure 7. PSCLC-cell transmittance spectra at T^- = 74 °C when the incident light is unpolarized and at 20 °C after quenching from T^- for different incident-light polarizations.

the scope of the present study, which does not aim at records in terms of reflected light flux.

If the temperature is decreased below T^-, the free-LC fraction crystallizes although it is confined in the pores of the fine lattice that is the PSLC. (Note that this desire to return to the crystal phase is not hindered by the presence of the electric field.) In that case, the reflection properties are lost, and the sample becomes strongly scattering.

3.4. Temporal Evolution of Optical Properties. Could an annealing process at T^- promote the growth of the left-handed CLC structure inherent to the free-LC fraction? To address this question, we investigate the temporal evolution of the transmittance spectra with the cell maintained at T^- and left-circularly polarized incident light (Figure 5). In addition, the electrical field is still maintained.

Our metric is the variation in transmitted light, which is related not only to the variation in scattered light but also to the variation in left-circularly polarized light that can be reflected. The transmission properties are investigated over a 24 h period. We find that the transmittance is not significantly altered outside the band gap, which means that the scattered light is not appreciably modified as a consequence of the annealing process. The band gap $\Delta\lambda$ is widened from 250 to 300 nm toward the blue. The associated transmittance progressively increases to about 5% at the end of the 24 h annealing period, which we tentatively attribute to a progressive improvement of the planar alignment of the left-handed helical structure formed by the free LC fraction. The enlargement of the band that results from annealing at T^- is thus objective, although quite modest. The evolution of the position of the optical band gap can be fit with an exponential decay (see insert in Figure 5). The e-folding time[33] is about 3 h. We can thus consider that the optical properties reach a stable state after 24 h.

At T^- we checked the transmittance spectrum for right-circularly polarized incident light (Figure 6). At this point, the electrical field is still maintained. As expected, the reflection band associated with the helical structure of the (robust) bound-LC fraction is stable. The PSCLC still reflects 80% of the right-circularly polarized incident light around a central wavelength of 2.7 μm.

The cell is stored for 24 h at T^- and then is quenched by placing it in contact for 3 min with a metal plate cooled with liquid nitrogen. This quenching is performed as quickly as possible (<1 s), and the electrical field is maintained during the
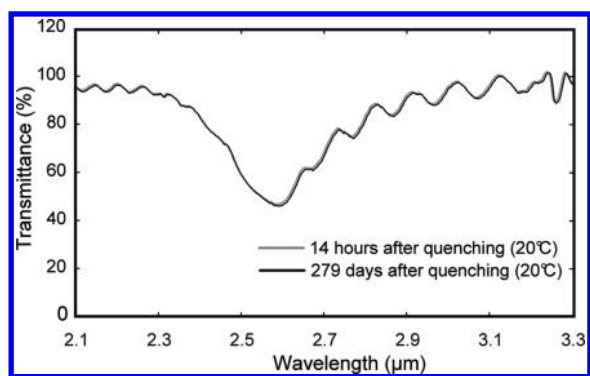
Figure 8. Transmittance spectra of undercooled PSCLC cell at 20 °C for two different times after the sample has been quenched from T^-. The incident light is unpolarized.
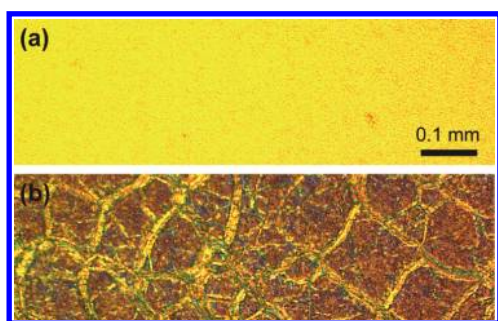

Figure 9. Optical textures (crossed polarizers) of the undercooled PSCLC cell at 20 °C when: (a) an electric field is applied to the cell as the temperature decreases from T^+ to T^-, and (b) no electric field is applied as the temperature decreases from T^+ to T^-.

quenching. The cell temperature then warms slowly to RT, at which point the voltage is shut off. The transmission spectra were recorded immediately after this process (Figure 7).

After quenching, the film shrinks, which causes the band gap to blueshift by about 0.15 μm. However, more interesting is the persistence of the optical properties for different polarizations of incident light. At RT and without requiring temperature regulation or the application of an electric field, the peculiar PSCLC structure remains. The material presents a double memory effect: (i) a right-circularly polarized reflection band that is due to the (temperature-independent) organization of the bound-LC fraction; (ii) a left-circularly polarized reflection band that is due to the (temperature-dependent) free-LC fraction, which is now in a undercooled state. In materials science, quenching is used to prevent low-temperature processes such as phase transformations by restricting to a narrow window the time for which the reaction is both thermodynamically favorable and kinetically accessible. For example, in the present research, quenching can reduce or prevent the formation of crystalline structure. The present undercooled state is possible because the free-LC fraction is confined in a gel structure (i.e., a polymer network surrounded by the bound-LC fraction). If the free-LC fraction were separated from the composite material, this fraction would undergo a phase transition to a crystalline phase.

The undercooled state of the PSCLC and its related physical properties are remarkably stable. When the cell is stored at RT without any special precautions, its transmittance properties remain strictly constant even after 279 days (Figure 8).

As it can be seen in Figure 9a, the PSCLC texture is homogeneously planar over a large surface (this defect-free texture exhibits a uniform yellow color), which is confirmed by the low scattering (less than 10%) evidenced in the transmittance spectra (Figure 8). Without the electric field, oily streaks persist in the texture as seen in Figure 9b. These defects are regions where the polymerization process has begun, and the polymer network is inevitably a template for nonuniform texture. Thus, to avoid light scattering in the final product, it is crucial to hinder disclination formation throughout the fabrication process.

4. CONCLUSION

We have demonstrated a single layer of CLC material at RT that exhibits simultaneously left- and right-circularly polarized reflection bands in the infrared portion of the spectrum. We show that, to reduce optical losses, it is of paramount importance to apply an electric field to the CLC material (which has a negative dielectric anisotropy) as the temperature is changed from the photocuring temperature to the desired application temperature. Under these conditions, the role of thermal annealing in stabilizing the CLC structure of the free-LC fraction before quenching is quite modest. By quenching the PSCLC below the melting point, the reflection properties can be maintained for months at RT, which is critical to applications. The present modus operandi offers freedom from concerns about the LC polymorphism. The quenching process prevents the formation of crystallites, and the applied voltage prevents defect nucleation by acting as an (electrical) constraint. Potential applications include heat-repelling windows, temperature-regulation devices, telecommunications, low-observable technologies, or photonic devices with no polarization dependence.

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■ ACKNOWLEDGMENT

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