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Bistable switching of polymer stabilized cholesteric liquid crystals between transparent and scattering modes

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Abstract

We report on the ability to switch an optical material composed of a polymer stabilized cholesteric liquid crystal (polymer stabilized cholesteric texture, PSCT) between stable transparent (reflective) and scattering modes. The degree of scattering is controllable with the strength of the applied electric field. The mechanism for bistable switching of the PSCT is distinguished from prior examinations by employing electromechanical displacement of a stabilizing polymer network. The stable transparent (reflective) or scattering modes are induced with a variety of driving schemes employing both alternating and direct current fields. The relative degree of scattering can be varied to allow for grayscale control potentially useful in smart window and display applications.

Cholesteric liquid crystals (CLCs) are materials that naturally organize into a one-dimensional photonic crystal exhibiting a Bragg reflection which is expressed by $\lambda = nP_0$, where λ, n, and P_0 are notch position, average refractive index, and pitch, respectively. The bandwidth of the reflection is expressed by $\Delta\lambda = \Delta n P_0$, where Δn is the birefringence.[1,2] The position of the reflection notch is controlled by the concentration of chiral dopant mixed with the nematic liquid crystal. The reflection of light from CLCs is naturally circularly polarized. If unpolarized incident light is exposed to the right-handed (RH) CLC, RH circularly polarized light (CPL) is reflected, whereas opposite handedness left-handed CPL is transmitted.

A CLC can be prepared to be reflective or scattering[3–19] when the alignment is planar in the ground state (0 V). When the CLC is prepared from a positive dielectric anisotropy ($+\Delta\varepsilon$) nematic liquid crystal host, the CLC can be switched to optically transparent by an applied electric field that orients the liquid crystal molecules into the homeotropic orientation. After the field is removed, the liquid crystal will exhibit a metastable scattering texture as the material transitions to form focal conic domains. Stabilizing the low molar mass CLC with a polymer network has been shown to allow for bistable switching between reflective and scattering textures typically formulated from $+\Delta\epsilon$ nematic liquid crystal hosts.[4–15] These materials are generally described as polymer stabilized CLCs (PSCLCs) but historically scattering systems have been referred to as polymer stabilized cholesteric textures (PSCTs). PSCTs exhibit two types of switching modes. Switching from scattering to clear (or reflective) states is defined as "normal mode"[3,16,17] and switching from reflective to scattering state as "reverse mode".[3,18,19] The operation mode (normal or reverse) is dictated primarily by the sample preparation conditions. Application of an electric field during photopolymerization aligns the polymer networks normal direction to the cell in the planar geometry. After the field is removed, the composite forms the scattering focal conic texture of mixed homeotropic and planar domains. Upon application of an electric field, the liquid crystal orients to a homeotropic orientation (clear state). When the material system is prepared in the absence of an electric field, a stable reflective texture is achieved. However, often the reflection notch is positioned well outside of the visible range rendering this state as optically transparent. Application and removal of an electric field can result in the formation of an extremely long-lived metastable scattering state. Intermediate control of scatter has been reported in.[4,5,9,10]

Recently, we have reported on the ability to electrically induce bandwidth broadening[20–23] and tuning[24,25] of the reflection notch of PSCLCs formulated with negative dielectric anisotropy ($-\Delta\varepsilon$) nematic liquid crystal hosts. As confirmed in a series of recent reports,[20–22] the mechanism for the dynamic response is related to electromechanical displacement of the polymer stabilizing network. The stabilizing polymer network, although typically only 5 wt% in composition, maintains a "structural" chirality that dominates the natural "chemical" chirality of the low molar mass CLC formulation. As such, upon application of a direct current (DC) field, trapped ionic impurities within the polymer fibrils or on their surface

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subject the network to force which serves to distort or displace the polymer network affecting the local "structural" chirality and the optical properties of the device. Here, we report bistable switching response of PSCTs formulated with −Δε LC. Unlike PSCT's having +Δε the low molar mass liquid crystals within the composite cannot be reoriented by the application of an electric field across the cell gap. Accordingly, as in our recent reports we hypothesize that the polymer network is distorted and displaced by electromechanical force induced by the coupling between trapped ions on the polymer network. We explore the utility of this mechanism to control light transmission through scattering. Further, a variety of electro-optic methods to switch from scattering to clear (reflective) are examined include alternating current (AC), direct current (DC), and AC/DC. Notably, like prior efforts, the modes are bistable and the magnitude of scatter can be dialed in by choice of the field strength.

The samples examined here were prepared by mixing 0.4 wt% of the photoinitiator (Irgacure 369, BASF), two RH chiral dopants (5 wt% R1011 and 5 wt% R811, Merck), 2 wt% of an achiral liquid crystal monomer (RM257, Merck), and 87.6 wt% of an achiral nematic liquid crystal (ZLI-2079, Merck) with a negative dielectric anisotropy. It should be noted that the switching reported here was more readily observed in formulations with reduced polymer concentration. Self-made liquid crystal alignment cells were prepared with either 15 or 30 μm thickness by a method previously described.[20–24] Subsequently, the cells were filled with the LC mixture at room temperature and the polymer stabilizing network was formed by photopolymerization with 30–50 mW/cm^2 of 350–500 nm light (Exfo) for 3 min.

Transmission spectra were collected with a fiber optic spectrometer at normal incidence. Unpolarized or RH CPL was used as a probe beam. Transmission spectra were collected before, during, and after application of DC or AC fields. Response times were obtained by modifying this setup and replacing the Ocean Optics spectrometer with a photodetector connected to an oscilloscope. Optical and polarized optical microscopes (POM) were employed to characterize the scattering and reflective states of the PSCTs.

To enable bistable switching between scattering and clear (reflective) modes the samples were first subjected to a strong electric field after preparation. The optical response of a representative sample is illustrated in Fig. 1. After preparation, the sample exhibits a reflection notch centered at 680 nm. As evident in the transmission spectra, at 0 V the PSCLC sample maintains a reflection notch at 680 nm. The inset POM image [Fig. 1(viii)] of the cell in this state is typical of a CLC with oily streak defects that are synonymous with this mesophase. As the strength of the DC voltage is increased the reflection notch initially broadens and also begins to scatter [60 V DC, Fig. 1(ii)] and the scatter increases further at 100 V DC [Fig. 1(iii)]. As the voltage is increased to 250 V DC [Fig. 1(vi)], the initial reflection is recovered. From the micrographs inset in Fig. 1, the 0 [Fig. 1(viii)] and 250 V DC [Fig. 1(x)] states are distinguished. At this point, the texture as prepared PSCLC texture or the initial electro-optic response illustrated in Fig. 1 is not recoverable. Instead, the system retains (memorizes) the state after the removal of the electric field.

The inset POM images taken in reflection of another representative sample during application of 250 V DC from the positive [Fig. 1(xi)] and negative [Fig. 1(xii)] electrodes indicate that the texture across the cell gap is affected. We propose that as in our prior reports, the polymer network is subjected to distortion. Here, due to the comparatively low polymer content (2%) to our prior work (>5%) and the preapplication of a large electric field allows for translational mobility of the network. At 250 V, the polymer network seems to be highly localized near the negative electrode. Comparatively, there are very few defects evident in the texture near the positive electrode which may indicate a comparatively low concentration of polymer. Nearly identical reflective POM images are observed on polarity reversal confirming that the polarity of the applied DC bias is dictating the directionality and surface localization of the texture. Once the sample is subjected to preapplication of voltages exceeding 200 V DC, only switching responses are observed by the application of the electric field and the induced textures are stable.

Figure 2 details the stability of the clear (reflective) and scattering modes. Switching from scattering to transparent states by the application of two DC voltages to yield a normal mode PSCT is shown in Fig. 2(a). The reflective state in Fig. 2(a-ii) is achieved by application of 210 V DC from the scattering state [Fig. 2(a-i)] and remained as the voltage is turned off. A scattering state is achieved again by the application of −45 V DC and is stable as the voltage is removed. Thus, stable

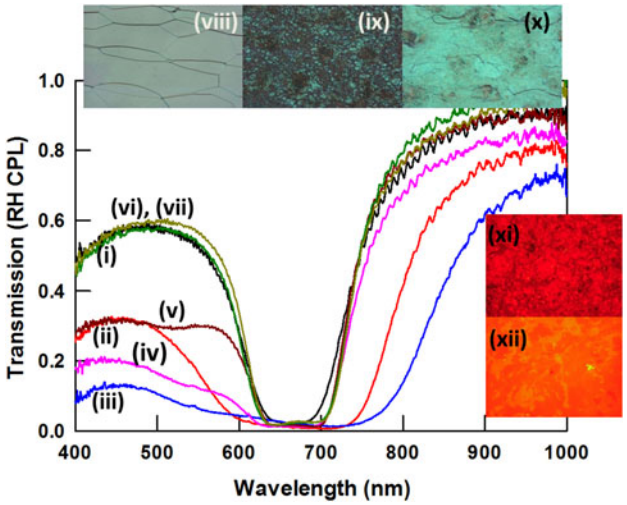


Figure 1. Transmission spectra of a PSCLC as the strength of DC voltage is increased from 0 to 250 V: (i) 0 V, (ii) 60 V, (iii) 100 V, (iv) 150 V, (v) 200 V, (vi) 250 V, and (vii) −250 V DC. (Inset) Polarized optical micrographs (POM) of the sample in transmission at (viii) 0, (ix) 100, and (x) 250 V. Another representative sample was examined under POM in reflection at 250 V and the textures evident on the (xi) negative electrode and (xii) positive electrode are also shown.

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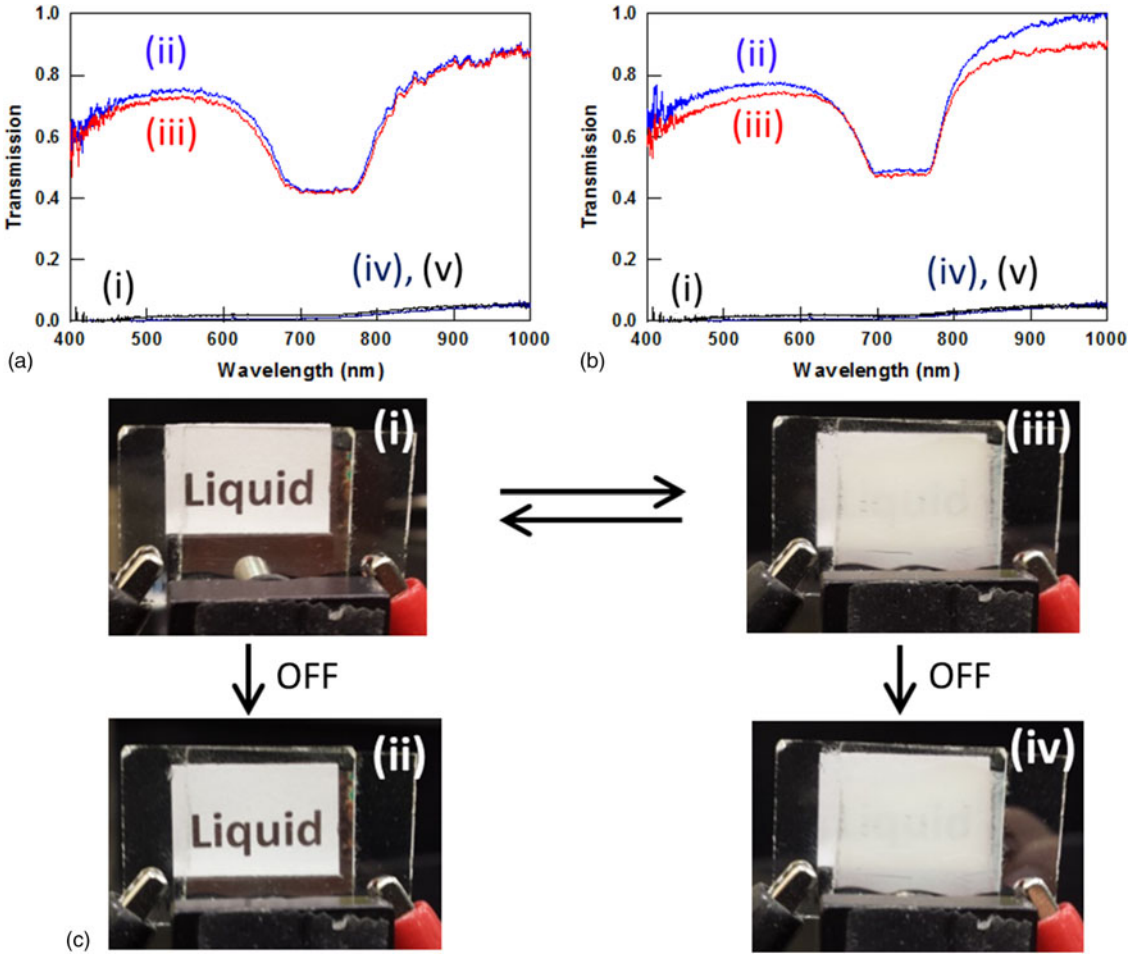


Figure 2. Bistable switching behavior of PSCLCs with (a) 30 μm gap thickness: normal mode with (i) 0 V, (ii) 210 V DC, (iii) OFF (0 V), (iv) −45 V DC, and (v) OFF (0 V), (b) (i) 0 V, (ii) 100 V AC, (iii) OFF (0 V), (iv) 45 V DC, and (v) 0 V, and (c) photographs of samples with 15 μm thickness at (i) 50 V AC, (ii) 0 V, (iii) 100 V DC, and (iv) 0 V.

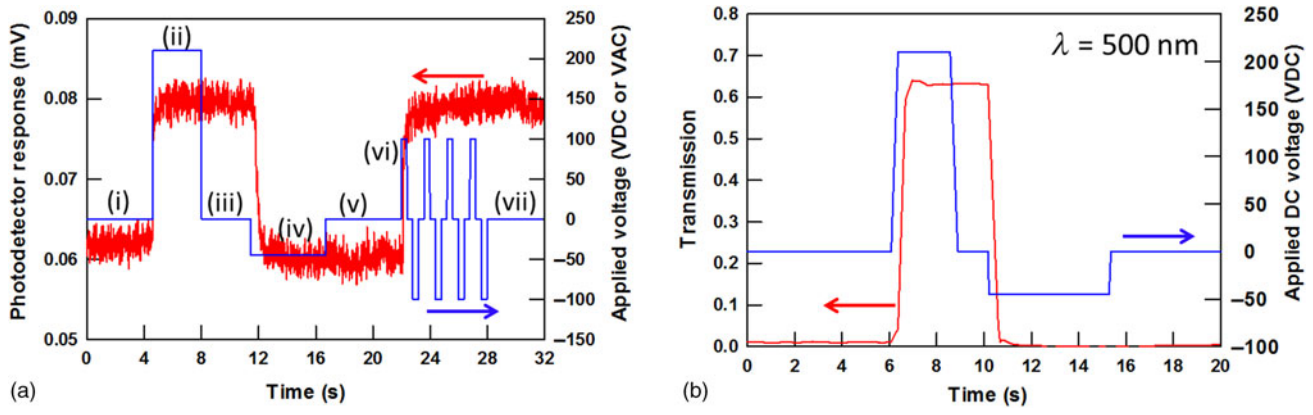


Figure 3. Response time of PSCTs with 30 μm thickness. An optical setup employing a photodetector connected to an oscilloscope measured the relative intensity (a.u.) of light transmission as the PSCT was subjected to (a) at (i) 0 V, (ii) 210 V DC, (iii) 0 V, (iv) −45 V DC, (v) 0 V, (vi) 100 V AC with 1 kHz, and (vii) 0 V over various time intervals. (b) The transmission of unpolarized light at 500 nm to measure response time is illustrated.

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scattering and transparent states are observed. Previously, we have reported on the polarity sensitivity of the electromechanical mechanism.[23,25] Here, reflective and scattering states could be achieved by either 210 and −45 V DC application or by −210 and 45 V DC application. Figure 2(b) details the bistable switching of the PSCT from scattering to reflective states (also "normal mode") by the application of DC and AC voltages. Application of 100 V AC with 1 kHz frequency to the cell induces a reflective state and once again, the scattering state is observed with either applied ±45 V DC. Note that high-frequency AC field should not displace the polymer network as it will affect the local alignment of the negative dielectric low molar mass liquid crystals. The selection of the ground state mode is arbitrary and thus the samples can also be operated in "reverse mode" (not shown). Figure 2(c) shows photographs of a PSCT sample with 15 μm thickness by application of 50 V AC and 100 V DC. Both transparent (reflective) and scattering states are stable for multiple months.

Figure 3 shows the response times of PSCT prepared with 30 μm thickness. Figure 3(a) illustrates the optical response of the PSCT to applied DC and AC fields by plotting both the transmission as well as the strength of the applied field. In Fig. 3(a), the sample was initially scattering at 0 V [Fig. 3(a-i)] and was made reflective by the application of 210 V DC [Fig. 3(a-ii)]. From this reflective mode, the scattering mode is induced by application of −45 V DC [Fig. 3(a-iv)]. Interestingly, the reflective state is also achieved by the application of 100 V AC [Fig. 3(a-vi)]. As evident in Fig. 3(a), the scattering and reflective modes show no changes in the 0 V condition [Fig. 3(a-iii, v, vii)]. In Fig. 3(b), unpolarized light at 500 nm wavelength was used for response time measurements. The sample in the scattering mode passes <1% due to the cell thickness employed. Applying 210 V DC induces 60%–70% transmission at 500 nm. This transmission is retained as the voltage is turned off. Subsequently, −45 V DC reintroduces the scattering state. Response times were measured from the data in Figs. 3(a) and 3(b), using the so-called 90%–10% method. On average, 200 ms from scattering to reflective (normal mode) and 350 ms from reflective to scattering (reverse mode) times were measured.

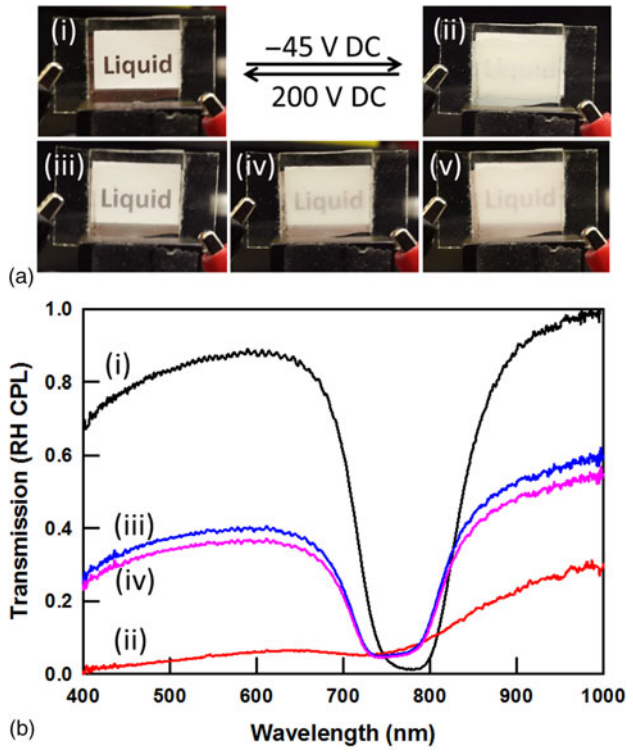


Figure 4. Grayscale control of transmission in the PSCLC: (a) photographs of the sample in the (i) reflective mode (clear state), (ii) scattering mode, and then three intermediate states (iii) −100 V DC, (iv) −55 V DC, and (v) −50 V DC and (b) transmission spectra with (i) reflective state at 200 V DC, (ii) scattering state at −45 V DC, (iii) grayscale state at −55 V DC, and stability of grayscale state at (iv) 0 V.

The degree of scattering can be controlled. As evident in Fig. 4, application of higher DC voltages can yield a hybridized mode that is scattering in the visible spectra (with a reflection notch evident in the IR). This type of grayscale control of the degree of transmission could be useful in optics and smart window applications. Shown in Fig. 4 are the transmission spectra of the scattering and reflective mode as well as an example of the grayscale mode reached by applying −55 V DC to the sample. All the three modes illustrated in Fig. 4 are stable in the absence of applied field.

In general, switching behavior of +Δϵ PSCLCs and PSCTs is achieved by reorientation of the LC molecules along the electric field. Here, we intentionally prepare the PSCTs from achiral nematic liquid crystal hosts with a −Δϵ. Accordingly, upon application of an electric field the planar alignment is maintained since the induced dipoles are already aligned normal direction to the cell. Building from our recent efforts in inducing bandwidth broadening[20–23] and reflection notch tuning,[24,25] we propose that the mechanism of the dynamic scattering reported in this work is also attributable to electromechanical displacement of the polymer stabilizing network. The distortion and displacement of the polymer stabilizing network is potentially related to trapped ions (within or on the surface of the polymer stabilizing network) which when subjected to a DC field, are drawn and concentrated at the surface of the alignment cell. The electromechanical force is large enough to displace the polymer stabilizing network, visually observed in recent reports.[21,23] Applying a higher strength DC field may result in the reformation of a planar alignment and reflective state by either reducing the ionic species on or within the polymer network by attracting the free charges to the surfaces (charge screening) or by compressing the polymer network to the surfaces to form such a thin layer that the bulk of the CLC is planarly aligned by the applied field. Comparatively, the induction of the transparent (reflective) state with an applied AC field is more straightforward. Since the polarity of the bias inverts, the polymer network will not concentrate to the surfaces and be restored to the original near-homogenous distribution across

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the sample thickness. We propose that the grayscale control presented in Fig. 4 is a mixture of these two phenomena in which the sample exhibits a scattering layer near the surfaces but also maintains a planar alignment in the center of the cell due to the alignment of the $-\Delta\epsilon$ molecules by the presence of the DC field.

In summary, we report on bistable switching of polymer stabilized CLCs between reflective and scattering states. Two switching modes are demonstrated. Similar to recent demonstrations of reflection notch tuning and bandwidth broadening, the bistable switching is attributed to an electromechanical polymer displacement mechanism. Optically, the switching speeds are 200–350 ms. The bistable switching and the ability to access stable grayscale scattering levels could be used in smart windows and display applications. Further research is necessary to reduce the field requirements as well as to explore the environmental robustness.

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