

Color-Tunable Mirrors Based on Electrically Regulated Bandwidth Broadening in Polymer-Stabilized Cholesteric Liquid Crystals

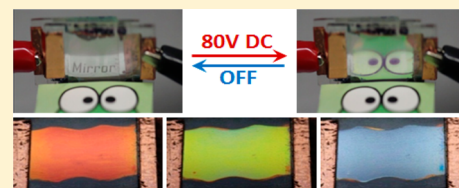
Kyung Min Lee,[†] Vincent P. Tondiglia,[‡] Michael E. McConney, Lalgudi V. Natarajan,[‡] Timothy J. Bunning, and Timothy J. White*

Air Force Research Laboratory, Materials & Manufacturing Directorate, Wright-Patterson Air Force Base, Ohio 45433-7750, United States

Supporting Information

ABSTRACT: We report on the preparation of color-tunable mirrors based on electrically regulated bandwidth broadening of the circularly polarized reflection of polymer-stabilized cholesteric liquid crystals (PSCLCs). A number of improvements relating to the practical implementation of these materials are detailed including color and bandwidth stability, baseline optical properties, and response times. Experimentation reported herein focuses on the contribution of structural chirality, viscoelastic properties of the polymer network architecture, and electro-optic drive schemes. Through the examination of samples prepared in different conditions and compositions, we further elucidate the dominant role of structural chirality as well as the impact of cross-linking of the polymer stabilizing network on the threshold voltage and relative change in bandwidth per voltage ($\Delta(\Delta\lambda)/V$). Furthermore, the appearance of nonideal optical properties (scatter and haze) in some samples is shown to be correlated with the polymer/LC compatibility and effectiveness of structural templating. Due to the employment of an electromechanical displacement mechanism, the switching times of the PSCLCs are slower than mechanisms based on liquid crystal reorientation. However, a potential approach is identified to reduce the on and off switching times to approximately 1 s.

KEYWORDS: liquid crystals, optical materials, polymer stabilization, color, photonic band gap



Cholesteric liquid crystals (CLCs) in the planar orientation self-organize into a helical superstructure described by either a right-handed (RH) or left-handed (LH) circular rotation of the liquid crystal director along a helical axis.^{1,2} The periodicity of the index variation dictates a spectral reflection centered at the wavelength $\lambda_0 = n_{av} \times p_0$, where n_{av} is the average refractive index of the liquid crystal (LC) and p_0 is the pitch length. Due to the handedness of the helical superstructure, CLCs reflect only 50% of unpolarized light within the photonic band gap (bandwidth). The bandwidth ($\Delta\lambda$) of CLCs is typically 50–100 nm in the visible/near-infrared region and a product of the birefringence (Δn) of the LC host and the cholesteric pitch as $\Delta\lambda = \Delta n \times p_0 = (n_e - n_o) \times p_0$ (where n_e is the extraordinary refractive index and n_o is the ordinary refractive index).

A number of previous examinations have shown that the bandwidth of a CLC can be broadened by heterogeneous photoinitiated polymer stabilization,^{3,4} as recently reviewed by Mitov.⁵ Photoinitiator concentration, UV curing intensity, and the introduction of radical inhibitors have all been shown to enable heterogeneous photopolymerization of primarily (meth)acrylate liquid crystal monomers (LCMs) across the sample thickness.^{6–19} The heterogeneous photopolymerization dictates gradients in the concentration and cross-link density of the polymer stabilizing network, which disrupts the local pitch across the cell gap.

Dynamic variation of the position or bandwidth of the spectral reflection of CLCs has been long pursued.^{20,21}

Variation in the position or bandwidth of CLCs can be induced with thermal, photonic, or electrical stimuli.²² This contribution focuses on electrically induced optical responses. A number of recent reports^{22–35} detail electrically induced tuning or broadening of the bandwidth of CLCs. Prior efforts to induce color-selectivity in CLCs have focused on switching the reflection notch of CLCs on or off in samples based on dual-frequency liquid crystal hosts^{30,33,34} or with polymer stabilization.^{35,36}

Recently we reported as much as a 7-fold increase in bandwidth of the spectral reflection of PSCLCs prepared with negative dielectric anisotropy liquid crystal hosts at moderate dc fields (0–4 V/ μm).^{27,28} The bandwidth broadening is symmetric about the center of the reflection notch and completely reversible. The initial report²⁷ excluded a number of mechanisms based on common ionic, polar, and polymeric interactions previously observed in liquid crystalline systems. Recently, electro-optic experiments (primarily in polymer-stabilized nematic samples) strongly indicate that the mechanism is attributable to ionic charge trapping on and within the polymer network.²⁸ Liquid crystal mixtures typically contain a residual concentration of ions (10^9 – 10^{14} ions/ cm^3) attributable to synthetic and/or purification steps (catalysts, salts, moisture, and dust). Ionic contaminants from alignment layers³⁷ or from degradation of LCs^{38–41} have been reported.

Received: July 16, 2014

Published: September 17, 2014

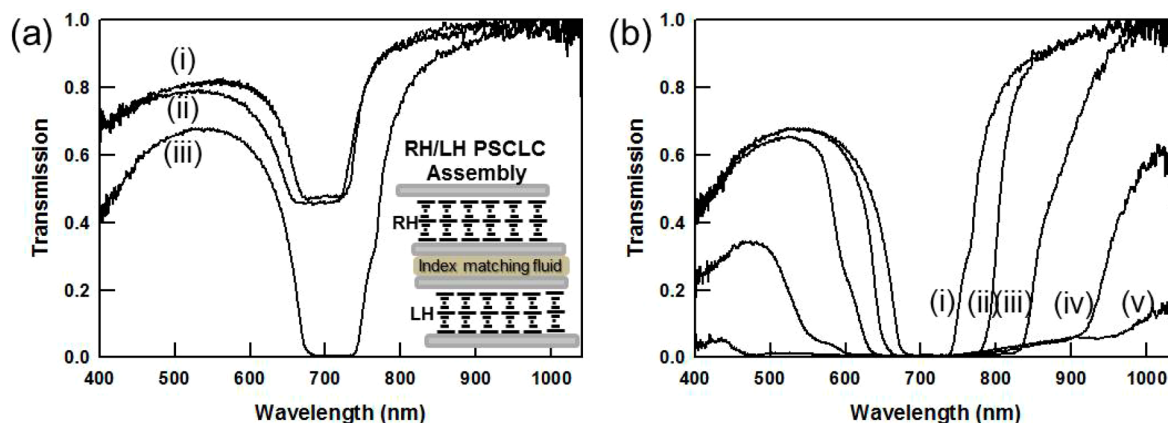


Figure 1. (a) Transmission spectra of a (i) right-handed PSCLC prepared from a mixture of 5 wt % R1011/5 wt % R811/5 wt % RM82/84 wt % ZLI-2079, (ii) left-handed PSCLC prepared from a mixture of 5 wt % S1011/5 wt % S811/5 wt % RM82/84 wt % ZLI-2079, and (iii) assembly of RH PSCLC in (i) and LH PSCLC in (ii). (Inset) Graphical depiction of the assembly of the RH/LH PSCLC examined in (iii). (b) Transmission spectra of the LH/RH PSCLC assembly before and during application of a (i) 0 V, (ii) 40 V, (iii) 70 V, (iv) 80 V, and (v) 100 V dc.

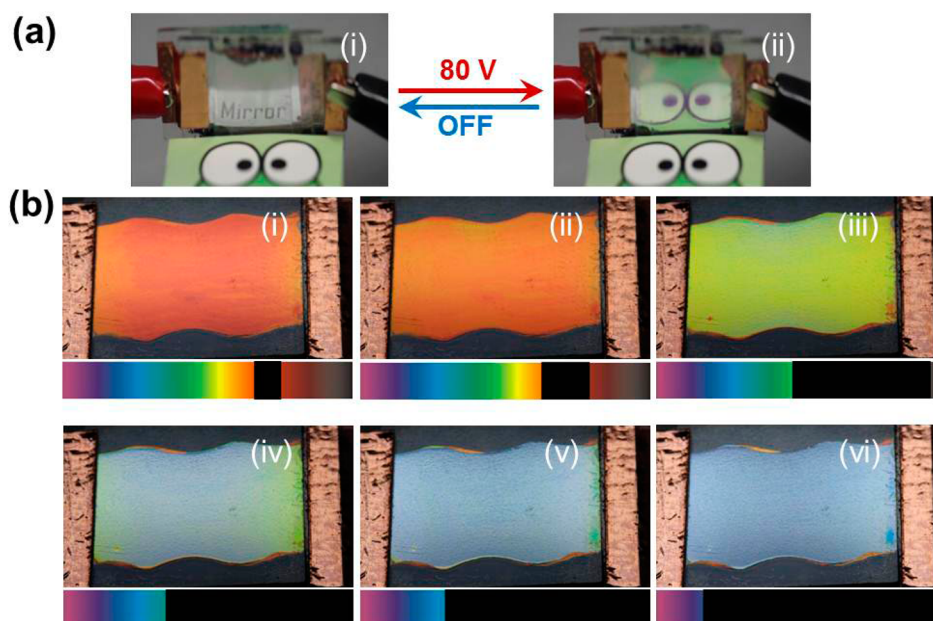


Figure 2. (a) Photographs illustrating the reflection/transmission of the LH/RH PSCLC assembly (i) at 0 V and (ii) at 80 V (see also Video 1, Supporting Information). (b) The color-tunability of the reflection from the LH/RH PSCLC assembly is visualized at (i) 0 V, (ii) 15 V, (iii) 30 V, (iv) 60 V, (v) 90 V, and (vi) 110 V. Schematics depicting the bandwidth broadening are inset beneath each image.

Accordingly, the polarity of the applied dc field results in ionic charge migration and buildup.^{42–45} However, our recent work has postulated that trapped ions (within or on the surface of the polymer stabilizing network) impart a force onto the polymer network in the presence of a dc field. The electromechanical force is large enough to displace the polymer stabilizing network, visually observed in a recent report²⁸ employing patterned electrodes. We hypothesize that the distortion of the polymer stabilizing network enables bandwidth broadening by chirping the local structure (orientation) of the polymer stabilizing network, which then affects the orientation of the low molar mass liquid crystal (structural chirality). Importantly, upon removing the dc field, the PSCLC bandwidth of the PSCLC restores to the original bandwidth.

The goals of this work are to demonstrate the potential functionality of electrically regulated bandwidth broadening of PSCLCs as color-tunable mirrors and to further elucidate the

powerful role of structural chirality. A variety of formulations are examined to isolate the role of polymer network viscoelasticity to enable optimal electro-optic responses. The large, electrically regulated control of the bandwidth of the spectral reflection of PSCLCs is potentially useful in many application areas such as displays, smart windows, and optical systems.

RESULTS AND DISCUSSION

The electrically regulated bandwidth broadening of an optical element prepared by stacking a left-handed and right-handed polymer-stabilized cholesteric liquid crystal (PSCLC) is illustrated in Figure 1. The PSCLC samples were prepared in 30 μm thick alignment cells by photopolymerization of a mixture containing 5 wt % of the liquid crystal diacrylate monomer RM82, chiral dopants (either S1011/S811 or R1011/R811), and the negative dielectric anisotropy ($-\Delta\epsilon$) nematic

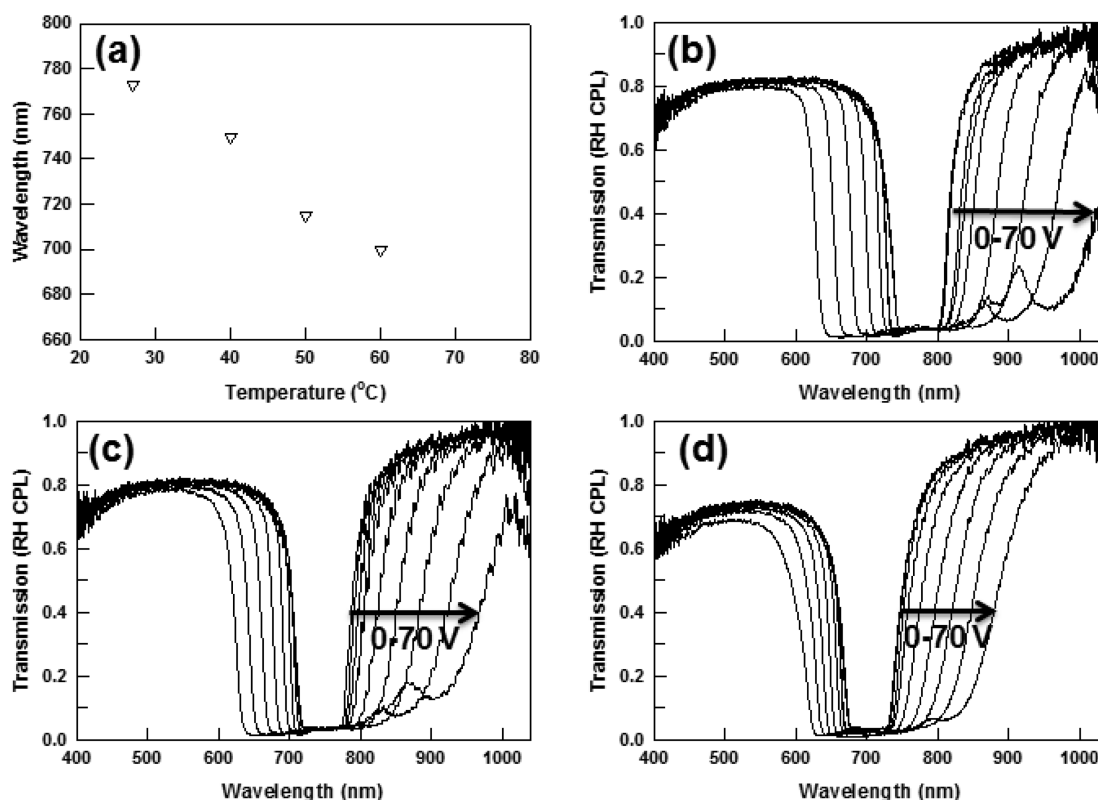


Figure 3. (a) Thermo-chromic color tuning of the spectral reflection of the PSCLC mixture (4 wt % R1011/5 wt % R811/5 wt % RM82/85 wt % ZLI-2079). The templating and retention of “structural chirality” were elucidated by photopolymerizing the mixtures at (b) room temperature, (c) 40 °C, and (d) 60 °C. The optical properties of the PSCLCs were stable for at least 6 days (Figure S1, Supporting Information). The samples were subjected to applied dc voltages to induce bandwidth broadening. The transmission spectra were collected from an optical setup in which the white light probe was right-handed circularly polarized.

liquid crystal host ZLI-2079 ($\Delta\epsilon = -6.1$). On the basis of the relation $\Delta\lambda = \Delta n \times p_0$, both PSCLC samples exhibit a bandwidth of 70 nm after preparation (measured from the full-width at half-maximum (fwhm)). The 70 nm bandwidth measured for the PSCLC samples in Figure 1 deviates only by a few nanometers from the bandwidth measured before photopolymerization. The spectral reflection of the LH and RH PSCLC is centered at approximately 700 nm in the transmission spectra in Figure 1a. When stacked, the high contrast reflection band nearly completely reflects 690–720 nm light from the unpolarized white light probe and maintains a bandwidth at the fwhm of nearly 100 nm.⁴⁶ Both cells were simultaneously subjected to a dc field of identical strength (Figure 1b). As the dc voltage was increased stepwise from 0 to 100 V, the bandwidth of the LH/RH PSCLC optical element increased from 100 nm to nearly 600 nm. As detailed in our previous report,²⁷ the broadening is symmetric about the center point of the reflection notch (approximately 700 nm) before, during, and after application of the dc field. After the field is removed, the bandwidth of the LH/RH PSCLC optical element restores to the original value of 100 nm. Although not shown here, the bandwidth of the individual cells can be driven separately as desired.

The high-contrast and color-tunable mirror is visually illustrated in Figure 2 in photographs isolating the optical properties of a PSCLC as a function of voltage. The ability to dynamically switch the selective reflection from selectively reflective (colored) into a broadband reflection (mirror) is shown in Figure 2a. The initial notch position was arbitrarily formulated to reflect red light. The word “mirror” is visible

behind the PSCLC before application of the dc field. Upon application of an 80 V dc bias, the image (frog) is reflected by the mirror-like reflection of the PSCLC and the word “mirror” can no longer be observed. The colored appearance of the optical element at intermediate bandwidths is depicted in Figure 2b images i–vi. Here, the PSCLC is set at an angle to reflect light into the camera. Initially, the PSCLC exhibits a red reflection. With application of 15 V (ii), 30 V (iii), 60 V, (iv) 90 V (v), and 110 V (vi) the color of the PSCLC changes from red to green to broadband (blue-silver). After the dc field is removed, the optical properties restore to those evident in Figure 2a-i or b-i. The color evident in the images in Figure 2b is attributable to the content of spectral reflection, as illustrated in the graphical insets below each corresponding image.

Our previous report²⁷ discusses and excludes a number of potential mechanisms. A recent report²⁸ details electro-optic experiments that strongly indicate that the mechanism is ionic in nature and attributable to displacement of the polymer network within the PSCLC. In this recent report,²⁸ the displacement of the polymer network is visually observed in control experiments employing alignment cells with patterned electrodes wherein the polymer network aggregates on the negatively charged electrodes. The distortion of the polymer network does not affect the chemical chirality of the CLC fluid. Rather, we believe that the polymer-stabilized network templates the superstructure of the low molar mass host liquid crystal and becomes a “structurally chiral” hierarchical alignment scaffold.^{47–50} To introduce and elucidate the dominance of structural chirality in this mechanism, Figure 3 summarizes the characterization of electrically induced bandwidth broad-

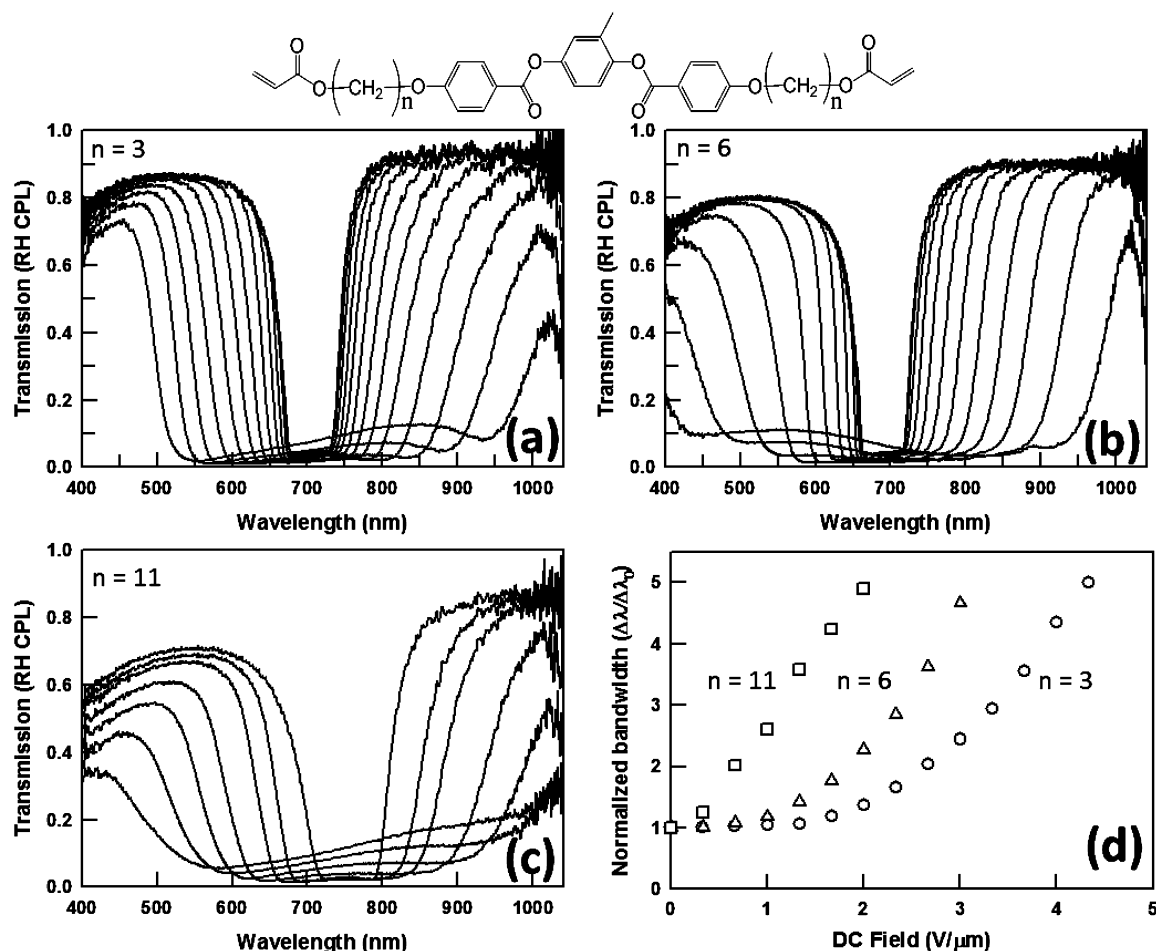


Figure 4. (Top) General chemical structure for the liquid crystal monomers examined here. Samples were prepared from formulations containing 5 wt % R1011/5 wt % R811/84 wt % ZLI-2079 mixed with 5 wt % liquid crystal monomer. (a) Transmission spectra of a PSCLC sample prepared from RM257 ($n = 3$) before and during application of a 0–140 V dc. (b) Transmission spectra of a PSCLC sample prepared from RM82 ($n = 6$) before and during application of a 0–110 V dc. (c) Transmission spectra of a PSCLC sample prepared from M04301 ($n = 11$) before and during application of a 0–70 V dc. (d) The normalized bandwidth of the PSCLCs examined in a–c is summarized as a function of applied dc field ($\text{V}/\mu\text{m}$). The transmission spectra were collected in a setup in which the white light probe was right-handed circularly polarized.

ening in four samples prepared at a range of temperatures. As discussed in numerous prior examinations,^{21,51–54} CLC mixtures can exhibit thermochromism the range of which largely depends on whether the mixture maintains an underlying smectic phase. The thermally induced variation in the central wavelength of the reflection notch for unstabilized CLC mixtures based on R1011 (4 wt %)/R811 (5 wt %)/RM82 (5 wt %)/ZLI-2079 is shown in Figure 3a. Upon heating from room temperature to 60 °C, the center of the Bragg reflection peak shifts from 775 nm to 700 nm. While small compared to other reports,⁵⁵ we utilize the thermochromism of this mixture to prepare PSCLC samples at room temperature ($\lambda_0 = 775$ nm), 40 °C ($\lambda_0 = 750$ nm), and 60 °C ($\lambda_0 = 700$ nm). As evident in Figure S1 in the Supporting Information, after polymerization and cooling to room temperature, the PSCLC samples retained the identical transmission spectra for 6 days. After 6 days of storage, transmission spectra were taken from the samples before, during, and after applying dc fields (Figure 3b–d). The bandwidths of each of the samples broaden about the center of the starting wavelength. These results confirm the powerful nature of structural chirality. If the “chemical chirality” (that derived from the mixture of R1011/R811/ZLI-2079) was

dominant, the samples would restore to the formulated notch position (775 nm) after preparation upon cooling. Importantly for practical utility, the structural chirality is also retained over time as well as during and after the application of the dc field to induce broadening that is symmetric about the center of the notch position at which the sample was polymer stabilized.

On the basis of the electromechanical displacement mechanism and the demonstrated importance of structural chirality, the viscoelastic properties of the polymer network should be influential to the electro-optic response. The structurally chiral polymer stabilizing network assumes an equilibrium conformation in the absence of the applied dc field. The polymer stabilizing network is then subjected to force and distorted in the presence of the applied dc field. Accordingly, both the on-time and off-time switching speeds and threshold voltages should be affected by the viscoelastic properties of the polymer network. In acrylate-based liquid crystalline polymers prepared by free-radical photopolymerization, the molecular weight between cross-links dictates the network viscoelasticity and can be systematically controlled by varying the flexible spacer length of the monomer precursors. PSCLCs were prepared from liquid crystal monomers (LCMs) with the same mesogenic core with n (the length of the methylene spacer

units) values of 3, 6, or 11 (chemical structure inset in Figure 4).⁵⁶

Transmission spectra collected before and in the presence of a dc field are plotted for 30 μm thick PSCLC samples stabilized with 5 wt % RM257 ($n = 3$), 5 wt % RM82 ($n = 6$), and 5 wt % M04031 ($n = 11$) in Figure 4a–c. The slight differences in the central wavelengths for these three samples are due to minor variations in chiral dopant concentration and cell thickness ($\pm 0.4 \mu\text{m}$). These results are summarized in the plot of bandwidth as a function of applied dc voltage in Figure 4d. Generally speaking, all three samples repeatedly exhibit at least a 5-fold increase in bandwidth that is symmetric about the center of the Bragg reflection. Specifically, the threshold voltage to initiate broadening decreases from 1 V/ μm (RM257, three methylene flexible units) to 0.3 V/ μm (M04031, 11 methylene flexible units). Increasing the length of the flexible spacer increases the relative change in bandwidth per voltage ($\Delta(\Delta\lambda)/V$). Unfortunately these enhancements are accompanied by a noticeable increase in scatter particularly on the blue edge of the reflection notch (Figure 4c). We attribute this increase in scatter for this PSCLC sample to the effectiveness of structural templating of the polymer network. Specifically, liquid crystalline polymer networks (LCNs) prepared from LCMs with longer methylene spacer units are known to form alkyl chain rich areas in the polymer networks, which can destabilize and would potentially impact the templating of the CLC.⁵⁷ We believe that the reduction in threshold voltage is largely attributable to the viscoelastic properties of the polymer network. To confirm this, bulk LCN samples were prepared and the thermomechanical properties of the films were measured with dynamic mechanical analysis. The modulus and glass transition temperature (T_g) of these polymers are summarized in Figure S2 (Supporting Information). As expected, the storage modulus and T_g decrease with increasing number of methylene units in PSCLCs due to the increase in the molecular weight between cross-links as well as the increase in chain mobility.^{57–59} Thus, it is reasonable to assume that in the samples examined in Figure 4 the reduction of the threshold voltage and the increase in the relative change in bandwidth per voltage ($\Delta(\Delta\lambda)/V$) are directly dictated by the viscoelastic properties of the polymer networks.

Lateral modification of the mesogenic core of an LCM also can affect packing and interaction between mesogens in the polymer networks.⁵⁷ Dynamic notch broadening behavior of a PSCLC prepared from the polymerization of M04256 is shown in Figure 5. This monomer is identical to RM82 (Figure 4b) but for the methyl group on the central phenyl ring of the mesogenic unit. Accordingly, PSCLCs prepared from M04256 (Figure 5) and RM82 (Figure 4b) should have the same molecular weight between cross-links but may differ in the ability to retain order and effectively template the CLC.⁵⁷ As evident in Figure 5, the PSCLC prepared from M04256 exhibits nearly identical bandwidth broadening to the PSCLC prepared from RM82 (Figure 4b). One notable difference is the scattering that appears on the blue edge of the reflection notch, similar to that observed in the PSCLC prepared from M04031 (Figure 4c). Accordingly, the results presented in Figure 5 further confirm the crucial role of the interaction of the monomer (polymer) and the liquid crystal in enabling optimal templating of the CLC superstructure to result in a structurally chiral polymer stabilizing network that effectively translates this orientation to the low molar mass liquid crystal fluid.

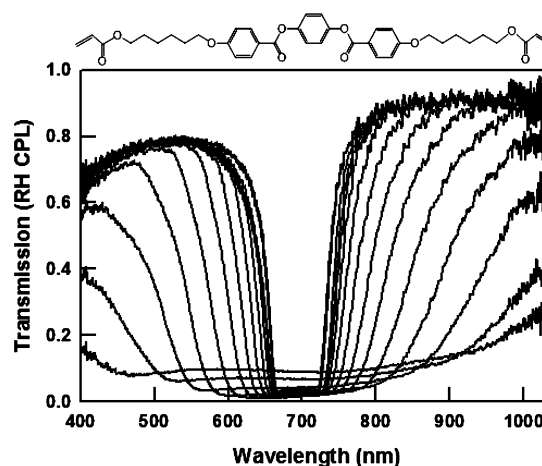


Figure 5. Electrically induced bandwidth broadening in a PSCLC sample prepared from M04256 ($n = 6$, nonmethylated) before and during application of a 0–140 V dc field. The transmission spectra were collected in a setup in which the white light probe was right-handed circularly polarized. The sample was prepared from formulations containing 5 wt % R1011/5 wt % R811/84 wt % ZLI-2079 mixed with 5 wt % M04256.

Dynamic responses in liquid crystals derived from ionic mechanisms typically exhibit strong temporal variations and irregularities that have precluded the use of these mechanisms in practical applications.^{2,60–63} Although ionic in nature, the fundamental electro-optic mechanism employed here is distinguished from these prior efforts. In order to be useful in functional optical devices, the electrically regulated bandwidth broadening should be stable at a given operating voltage. The stability of the bandwidth broadening was examined by monitoring the transmission spectra for samples subjected to continuously applied dc voltages for 30 min. Unlike in Figures 1–5, the applied dc field was immediately applied to the cells to emulate the conditions expected in applications of the optical phenomena. Figure 6a and c plot transmission spectra collected for a PSCLC sample stabilized with RM82 when subjected to 1.5 V/ μm (Figure 6a) and 2.5 V/ μm (Figure 6c) for 30 min. As has been discussed, the magnitude of the bandwidth broadening can be regulated with the strength of the applied dc field evident in Figure 6a, where 1.5 V/ μm broadens the bandwidth to 200 nm, and Figure 6c, where 2.5 V/ μm broadens the bandwidth to 450 nm. As evident in Figure 6a and c, the transmission spectra are largely unchanged over the course of 30 min of continuous field application in both cases. The creep in bandwidth was also examined in samples prepared with RM257, M04031, and M4256 (Figure S3, Supporting Information). The stability of the bandwidth under applied dc fields does vary slightly with the viscoelastic properties of the polymer network as well as with the field strength. The bandwidth of the reflection notches evident in Figure 6 exhibits only a 3 nm increase (0.7%) (at 2.5 V/ μm) over the course of 30 min. Comparatively, a PSCLC prepared with RM257 subjected to 2.5 V/ μm broadens to a bandwidth of more than 350 nm, but on continuing dc field application the bandwidth decreases by nearly 50 nm over the course of 30 min. PSCLCs prepared with M04031 or M04256 exhibit similar responses to the PSCLC prepared with RM82, as depicted in Figure 6. Thus, importantly for application as functional optical devices, PSCLC samples can be prepared that maintain the bandwidth over sustained field application and do not exhibit the temporal

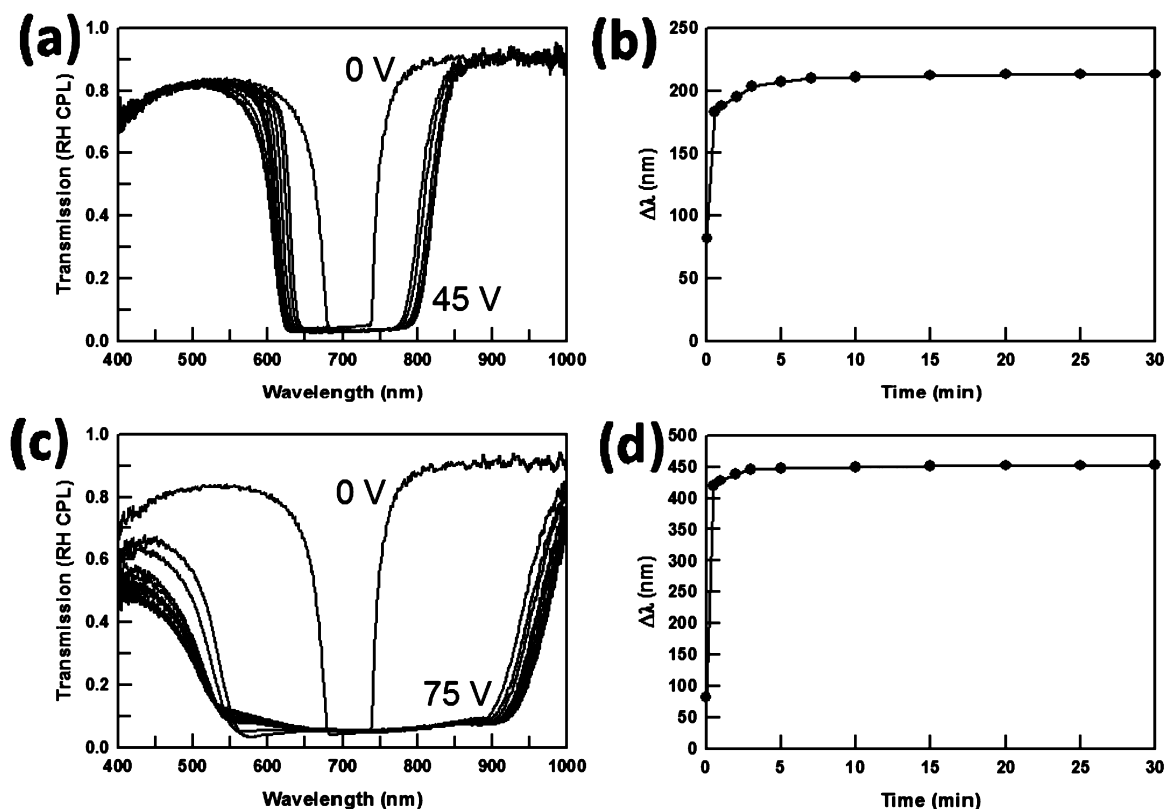


Figure 6. Temporal stability of electrically induced bandwidth broadening in a PSCLC sample prepared from 5 wt % R1011/5 wt % R811/5 wt % RM82/ZLI-2079. (a) Transmission spectra before and during 30 min of continuous application of a 45 V dc field. (b) The bandwidth of the reflection notch is plotted against time. (c) Transmission spectra before and during 30 min of continuous application of a 75 V dc field. (d) The bandwidth of the reflection notch is plotted against time. The transmission spectra were collected in a setup in which the white light probe was right-handed circularly polarized.

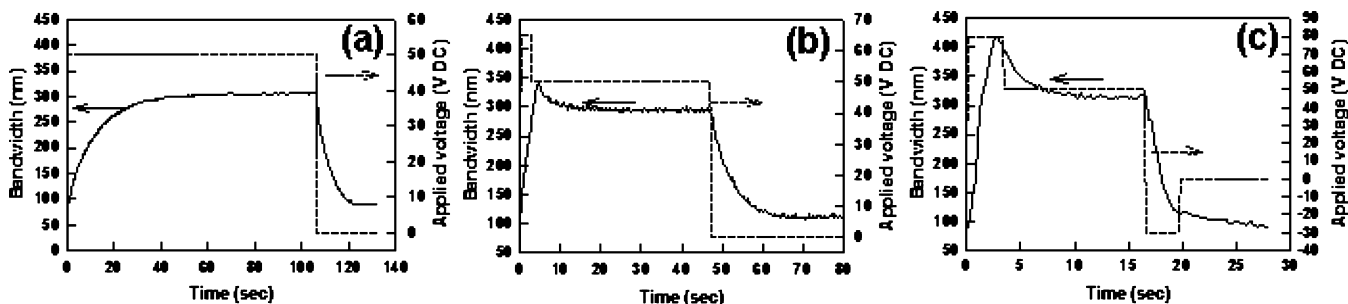


Figure 7. Temporal response of PSCLC samples prepared from 5 wt % R1011/5 wt % R811/ZLI-2079 polymer stabilized with 5 wt % RM82. (a) Bandwidth measured during the application of a 50 V dc for 110 s. The bandwidth restores after the 50 V dc is removed. (b) Response time observed when a 65 V dc was applied for 2 s, followed by reduction to 50 V dc. The dc voltage was turned off at approximately 48 s. (c) Response time observed when an 80 V dc was applied for 3 s, followed by reduction to 50 V dc. The polarity of the dc voltage was reversed (-30 V for ~ 3 s) and switched off.

effects that are synonymous with ionic mechanisms in liquid crystals.

Another important consideration for practical utility is the response time. The native response time for a PSCLC prepared with RM82 is illustrated in a plot of bandwidth as a function of time (Figure 7). Evident in Figure 7a, the bandwidth slowly increases upon application of 50 V with a switching on time of 24 s to reach a normalized bandwidth value of 3.3. After the 50 V dc voltage is removed, the bandwidth returns to the original value in approximately 10 s. However, on the basis of the electromechanical displacement mechanism, both the switching on time and switching off time of these devices can be sped up. As illustrated in Figure 7b, increasing the initial voltage supplied

to the device (“overdriving”) can result in faster bandwidth broadening. Here, a 65 V dc field is applied for approximately 2 s, after which the dc voltage is reduced to 50 V. Employing this method reduces the switching on time from 24 s to 2.3 s. The switching off time can be improved by reversing the bias for a short time. As illustrated in Figure 7c, the normalized bandwidth of the PSCLC was increased to 3.3 by applying an 80 V dc field for approximately 3 s, followed by a reduction to 50 V dc voltage (switching on time of 1 s). At 17 s, the polarity of the dc field was reversed such that the sample was subjected to -30 V dc for 3 s and switched off. The polarity reversal reduced the switching off time from 10 s (Figure 7a and b) to 2.1 s. While the response times are slow compared with liquid

crystal material systems employed in display devices, the response times reported here may be sufficient to actively control the content and intensity of irradiation in some applications, such as smart windows. Future work will continue to pursue strategies to reduce the response times by improving the elastic properties of the polymer stabilizing network.

CONCLUSIONS

We report large and stable electrically regulated control of the bandwidth of the spectral reflection of polymer-stabilized cholesteric liquid crystals. Due to the dominant role of “structural chirality” in the formulations examined here, the displacement of the polymer network results in a variation in pitch across the cell, which is observable as broadening of the bandwidth of the spectral reflection. Through formulation studies, the contribution of the polymer network architecture (the molecular weight between cross-links) and order retention were examined. Broadening was observed in all the samples examined here, but was found to be optimal in PSCLCs prepared from RM82 (six methylene spacing units). Despite the ionic mechanism, stable and reversible color changes of PSCLCs were observed. Due to the polymer displacement mechanism, the native switching on and off times of the effects are slow. However, adjusting electro-optic drive schemes shows a path forward to reducing switching times to at least 1 s.

METHODS

Preparation of $-\Delta\epsilon$ PSCLCs. Alignment cells were self-prepared from ITO-coated glass slides (Colorado Concepts). The glass slides were each coated with a polyimide or Elvamide alignment layer. The alignment layers were rubbed with a cloth, and the cell was constructed to yield planar alignment conditions. The cell gap was controlled by mixing 15, 36, or 50 μm thick glass rod spacers into an optical adhesive. Samples were prepared by formulating 1 wt % of the photoinitiator Irgacure 369, two right-handed chiral dopants (5 wt % R1011 and 5 wt % R811 or 5 wt % S1011 and 5 wt % S811, Merck), 5 wt % of an achiral liquid crystal monomer (as specified), and 84 wt % of a $-\Delta\epsilon$ achiral nematic liquid crystal (ZLI-2079, Merck). The polymer stabilizing network was formed within the samples by photoinitiated polymerization with 50–80 mW/cm² of 365 nm light (Exfo) for 3 min. To ensure homogeneous curing conditions, the cell was rotated at an angular velocity of 200 Hz during polymerization. While samples prepared with more traditional, one-sided curing exhibit similar electro-optic responses to that reported here, the consistency and sample-to-sample repeatability are improved by rotating the sample during curing. The polymer stabilizing network was prepared from the homopolymerization of four different LCMs (RM257 (Merck), RM82 (Merck), M04301 (Alpha Micron), and M04256 (Alpha Micron)). These monomers were intentionally selected for a large variation in flexible spacer length as well as mesogenic methylation. All materials were used as received without any purification.

Experimental Setup and Measurements. Transmission spectra were collected with a fiber optic spectrometer. Unless otherwise mentioned, the white light probe was unpolarized. Transmission spectra were collected before, during, and after application of dc fields. Response times were obtained using this setup. The ion density of the mixtures was measured with a commercial instrument from LC Vision in the homeotropic alignment cells. During the experiment, the samples were

subjected to a 1 Vp bias at a frequency of 3 Hz. The ion density values reported in Table S1 (Supporting Information) are the average of five measurements. There is no switching response of liquid crystals because the applied alternating voltage (1 Vp) is below the threshold voltage. The ion density is calculated from current measurements with the triangle method. Optical and polarized optical microscopy was employed to characterize the PSCLCs. The mechanical properties of polymers prepared from homopolymerization of the four LCMs were examined in samples prepared from 2 wt % Irgacure-369 initiator and 98 wt % LCM. The thermomechanical properties of the resulting liquid crystal polymer networks were determined in specimens with a gauge length of 10 mm \times 2 mm \times 30 μm (length, width, and thickness). Storage modulus (E') and $\tan \delta$, summarized in Figure S2 (Supporting Information), were obtained by dynamic mechanical analysis (RSA III, TA Instruments) at a strain of 0.5% and frequency of 1 Hz with a heating rate of 2.5 $^{\circ}\text{C}/\text{min}$ over the temperature range 20–200 $^{\circ}\text{C}$.

ASSOCIATED CONTENT

Supporting Information

Supplementary Figures: Figure S1, evidence of structural chirality of PSCLCs prepared at various temperatures; Table S1, ion densities of four mixtures with various liquid crystal monomers; Figure S2, thermomechanical data for three liquid crystal polymer networks prepared by three liquid crystal monomers with various alkyl chain lengths; Figure S3, temporal stability of electrically induced bandwidth broadening in four PSCLC samples; Figure S4, electric field induced bandwidth broadening of PSCLCs with various cell thicknesses. Supplementary video: Video 1, high-contrast, color-tunable mirror from an assembled LH/RH PSCLC depicted in Figure 2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: Timothy.White.24@us.af.mil. Tel: 937-255-9551.

Present Addresses

[†]Also with Azimuth Corporation, 4134 Linden Avenue, Dayton, Ohio 45432, United States.

[‡]Also with Leidos, 3745 Pentagon Boulevard, Beavercreek, Ohio 45431, United States.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge funding from the Materials and Manufacturing Directorate of the Air Force Research Laboratory and the Air Force Office of Scientific Research.

REFERENCES

- (1) Kitzerow, H.-S.; Bahr, C. *Chirality in Liquid Crystals*; Springer-Verlag: New York, 2001.
- (2) Wu, S.-T.; Yang, D.-K. *Reflective Liquid Crystal Displays*; Wiley: West Sussex, UK, 2001.
- (3) Broer, D. J.; Lub, J.; Mol, G. N. Wide-band reflective polarizers from cholesteric polymer networks with a pitch gradient. *Nature* **1995**, *378*, 467–469.
- (4) Hikmet, R. A. M.; Kemperman, H. Electrically switchable mirrors and optical components made from liquid-crystal gels. *Nature* **1998**, *392*, 476–479.

- (5) Mitov, M. Cholesteric liquid crystals with a broad light reflection band. *Adv. Mater.* **2012**, *24*, 6260–6276.
- (6) Broer, D. J. Deformed chiral-nematic networks obtained by polarized excitation of a dichroic photoinitiator. *Curr. Opin. Solid State Mater. Sci.* **2002**, *6*, 553–561.
- (7) Broer, D. J.; Lub, J.; Mol, G. N. Photo-controlled diffusion in reacting liquid crystals: a new tool for the creation of complex molecular architectures. *Macromol. Symp.* **1997**, *117*, 33–42.
- (8) Broer, D. J.; Mol, G. N.; Haaren, J. A. M. M. v.; Lub, J. Photo-induced diffusion in polymerizing chiral-nematic media. *Adv. Mater.* **1999**, *11*, 573–578.
- (9) Lub, J.; Broer, D. J.; van de Witte, P. Colourful photo-curable coatings for application in the electro-optical industry. *Prog. Org. Coat.* **2002**, *45*, 211–217.
- (10) Lub, J.; Broer, D. J.; Wegh, R. T.; Peeters, E.; I van der Zande, B. M. Formation of optical films by photo-polymerisation of liquid crystalline acrylates and application of these films in liquid crystal display technology. *Mol. Cryst. Liq. Cryst.* **2005**, *429*, 77–99.
- (11) Guillard, H.; Sixou, P. Active broadband polymer stabilized liquid crystals. *Liq. Cryst.* **2001**, *28*, 933–944.
- (12) Guillard, H.; Sixou, P.; Reboul, L.; Perichaud, A. Electrooptical characterizations of polymer stabilized cholesteric liquid crystals. *Polymer* **2001**, *42*, 9753–9762.
- (13) Kralik, J. C.; Fan, B.; Vithana, H.; Li, L.; Faris, S. M. Backlight output enhancement using cholesteric liquid crystal films. *Mol. Cryst. Liq. Cryst.* **1997**, *301*, 249–254.
- (14) Li, J.-F.; Fan, B.; Li, L. Single layer reflective polarizers with electrically controlled spectrum. *SID Symp. Dig. Tech. Pap.* **1999**, *30*, 1066–1069.
- (15) Sixou, P.; Gautier, C. A hybrid-aligned polymer network liquid crystal: optical and electro-optical properties. *Liq. Cryst.* **2002**, *29*, 467–473.
- (16) Sixou, P.; Gautier, C. Passive broadband reflector using photocrosslinkable liquid crystal molecules. *Polym. Adv. Technol.* **2002**, *13*, 329–338.
- (17) Katsis, D.; Kim, D. U.; Chen, H. P.; Rothberg, L. J.; Chen, S. H.; Tsutsui, T. Circularly polarized photoluminescence from gradient-pitch chiral-nematic films. *Chem. Mater.* **2001**, *13*, 643–647.
- (18) Relaix, S.; Bourgerette, C.; Mitov, M. Broadband reflective liquid crystalline gels due to the ultraviolet light screening made by the liquid crystal. *Appl. Phys. Lett.* **2006**, *89*, 251907/1–251907/3.
- (19) Relaix, S.; Bourgerette, C.; Mitov, M. Broadband reflective cholesteric liquid crystalline gels: volume distribution of reflection properties and polymer network in relation with the geometry of the cell photopolymerization. *Liq. Cryst.* **2007**, *34*, 1009–1018.
- (20) Haas, W.; Adams, J.; Wysocki, J. Interaction between UV radiation and cholesteric liquid crystals. *Mol. Cryst. Liq. Cryst.* **1969**, *7*, 371–379.
- (21) Soref, R. A. Thermo-optic effects in nematic-cholesteric mixtures. *J. Appl. Phys.* **1970**, *41*, 3022–3026.
- (22) White, T. J.; McConney, M. E.; Bunning, T. J. Dynamic color in stimuli-responsive cholesteric liquid crystals. *J. Mater. Chem.* **2010**, *20*, 9832–9847.
- (23) Lu, S.-Y.; Chien, L.-C. A polymer-stabilized single-layer color cholesteric liquid crystal display with anisotropic reflection. *Appl. Phys. Lett.* **2007**, *91*, 131119/1–131119/3.
- (24) Bailey, C. A.; Tondiglia, V. P.; Natarajan, L. V.; Duning, M. M.; Bricker, R. L.; Sutherland, R. L.; White, T. J.; Durstock, M. F.; Bunning, T. J. Electromechanical tuning of cholesteric liquid crystals. *J. Appl. Phys.* **2010**, *107*, 013105/1–013105/8.
- (25) White, T. J.; Bricker, R. L.; Natarajan, L. V.; Tondiglia, V. P.; Bailey, C.; Green, L.; Li, Q.; Bunning, T. J. Electromechanical and light tunable cholesteric liquid crystals. *Opt. Commun.* **2010**, *283*, 3434–3436.
- (26) Heikenfeld, J.; Drzaic, P.; Yeo, J. S.; Koch, T. Review Paper: A critical review of the present and future prospects for electronic paper. *J. Soc. Inf. Display* **2011**, *19*, 129–156.
- (27) Tondiglia, V. P.; Natarajan, L. V.; Bailey, C. A.; Duning, M. M.; Sutherland, R. L.; Yang, D.-K.; Voevodin, A.; White, T. J.; Bunning, T. J. Electrically induced bandwidth broadening in polymer stabilized cholesteric liquid crystals. *J. Appl. Phys.* **2011**, *110*, 053109/1–053109/8.
- (28) Tondiglia, V. P.; Natarajan, L. V.; Bailey, C. A.; McConney, M. E.; Lee, K. M.; Bunning, T. J.; Zola, R.; Nemati, H.; Yang, D.-K.; White, T. J. Bandwidth broadening induced by ionic interactions in polymer stabilized cholesteric liquid crystals. *Opt. Mater. Exp.* **2014**, *4*, 1465–1472.
- (29) Ren, H.; Wu, S.-T. Reflective reversed-mode polymer stabilized cholesteric texture light switches. *J. Appl. Phys.* **2002**, *92*, 797–800.
- (30) Liang, X.; Lu, Y.-Q.; Wu, Y.-H.; Du, F.; Wang, H.-Y.; Wu, S.-T. Dual-frequency addressed variable optical attenuator with submilli-second response time. *Jpn. J. Appl. Phys., Part 1* **2005**, *44*, 1292–1295.
- (31) Yang, D. K.; Chien, L. C.; Doane, J. W. Cholesteric liquid crystal/polymer dispersion for haze-free light shutters. *Appl. Phys. Lett.* **1992**, *60*, 3102–3104.
- (32) Yang, D. K.; West, J. L.; Chien, L. C.; Doane, J. W. Control of reflectivity and bistability in displays using cholesteric liquid crystals. *J. Appl. Phys.* **1994**, *76*, 1331–1333.
- (33) Xu, M.; Yang, D.-K. Dual frequency cholesteric light shutters. *Appl. Phys. Lett.* **1997**, *70*, 720–722.
- (34) Gerber, P. R. Two-frequency addressing of a cholesteric texture change electrooptical effect. *Appl. Phys. Lett.* **1984**, *44*, 932–934.
- (35) Chien, L.-C.; Doi, T. Method of making optical compensation film using polymer stabilization technique. U.S. Patent 7,090,901, August 18, 2004.
- (36) Choi, S. S.; Morris, S. M.; Huck, W. T. S.; Coles, H. J. The switching properties of chiral nematic liquid crystals using electrically commanded surfaces. *Soft Matter* **2009**, *5*, 354–362.
- (37) Lu, L.; Sergan, V.; Bos, P. J. Mechanism of electric-field-induced segregation of additives in a liquid-crystal host. *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **2012**, *86*, 051706/1–051706/5.
- (38) Lee, W.; Wang, C.-T.; Lin, C.-H. Recovery of the electrically resistive properties of a degraded liquid crystal. *Display* **2010**, *31*, 160–163.
- (39) Gosse, B.; Gosse, J. P. Degradation of liquid crystal devices under d.c. excitation and their electrochemistry. *J. Appl. Electrochem.* **1976**, *6*, 515–519.
- (40) Wen, C.-H.; Gauza, S.; Wu, S. T.; Wen, C.-H.; Gauza, S.; Wu, S. T. *Liq. Cryst.* **2004**, *31*, 1479–1485.
- (41) Lin, P.-T.; Wu, S. T.; Chang, C.-Y.; Hsu, C.-S. UV stability of high birefringence liquid crystals. *Mol. Cryst. Liq. Cryst.* **2004**, *411*, 243–253.
- (42) Naemura, S.; Nakazono, Y.; Nishikawa, K.; Sawada, A.; Kirsch, P.; Bremer, M.; Tarumi, K. Structure of ions in liquid-crystalline materials. *Mater. Res. Soc. Symp. Proc.* **1998**, *508*, 235–240.
- (43) Neyts, K.; Vermael, S.; Desimpel, C.; Stojmenovik, G.; Verschuere, A. R. M.; de Boer, D. K. G.; de Boer, D. K. G.; Snijkers, R.; Machiels, P.; van Brandenburg, A. Lateral ion transport in nematic liquid-crystal devices. *J. Appl. Phys.* **2003**, *94*, 3891–3896.
- (44) Sawada, A. Internal electric fields of electrolytic solutions induced by space-charge polarization. *J. Appl. Phys.* **2006**, *100*, 074103/1–074103/10.
- (45) Son, J.-H.; Park, S. B.; Zin, W.-C.; Song, J.-K. Ionic impurity control by a photopolymerisation process of reactive mesogen. *Liq. Cryst.* **2013**, *40*, 458–467.
- (46) The increase in bandwidth from 80 nm to 100 nm is due to slight mismatch in the center position of the reflection notches of the RH and LH PSLC samples.
- (47) McConney, M. E.; White, T. J.; Tondiglia, V. P.; Natarajan, L. V.; Yang, D.-K.; Bunning, T. J. Dynamic high contrast reflective coloration from responsive polymer/cholesteric liquid crystal architectures. *Soft Matter* **2011**, *8*, 318–323.
- (48) McConney, M. E.; Tondiglia, V. P.; Hurtubise, J. M.; White, T. J.; Bunning, T. J. Photoinduced hyper-reflective cholesteric liquid crystals enabled via surface initiated photopolymerization. *Chem. Commun.* **2011**, *47*, 505–507.
- (49) McConney, M. E.; Tondiglia, V. P.; Hurtubise, J. M.; Natarajan, L. V.; White, T. J.; Bunning, T. J. Thermally induced, multicolored

hyper-reflective cholesteric liquid crystals. *Adv. Mater.* **2011**, *23*, 1453–1457.

(50) Castles, F.; Day, F. V.; Morris, S. M.; Ko, D. H.; Gardiner, D. J.; Qasim, M. M.; Nosheen, S.; Hands, P. J. W.; Choi, S. S.; Friend, R. H.; Coles, H. J. Blue-phase templated fabrication of three-dimensional nanostructures for photonic applications. *Nat. Mater.* **2012**, *11*, 599–603.

(51) Pindak, R. S.; Huang, C.-C.; Ho, J. T. Divergence of cholesteric pitch near a smectic A transition. *Phys. Rev. Lett.* **1974**, *32*, 43–46.

(52) Lim, K.-C.; Ho, J. T. Cholesteric pitch near the smectic-C phase. *Mol. Cryst. Liq. Cryst.* **1981**, *67*, 199–204.

(53) Ania, F.; Stegemeyer, H. Cholesteric pitch behavior at the phase transition cholesteric to smectic B. *Mol. Cryst. Liq. Cryst., Lett. Sect.* **1985**, *2*, 67–76.

(54) Zhang, F.; Yang, D. K. Temperature dependence of pitch and twist elastic constant in a cholesteric to smectic A phase transition. *Liq. Cryst.* **2002**, *29*, 1497–1501.

(55) Natarajan, L. V.; Wofford, J. M.; Tondiglia, V. P.; Sutherland, R. L.; Koerner, H.; Vaia, R. A.; Bunning, T. J. Electro-thermal tuning in a negative dielectric cholesteric liquid crystal material. *J. Appl. Phys.* **2008**, *103*, 093107/1–093107/6.

(56) The ion density of the mixtures examined in Figure 4 ranges from 3.1 to 5.5×10^{13} ions/cm³ (a molar ratio of 10^{-8} – 10^{-10} , Table S1 in the Supporting Information), confirming that the observed differences in the electro-optic response are due to the viscoelastic properties of the network.

(57) Broer, D. J.; Crawford, G. P.; Zumer, S. *Cross-Linked Liquid Crystalline Systems: From Rigid Polymer Networks To Elastomers*; CRC Press: Boca Raton, FL, 2011.

(58) Broer, D. J.; Heynderickx, I. Three-dimensionally ordered polymer networks with a helicoidal structure. *Macromolecules* **1990**, *23*, 2474–2477.

(59) Hikmet, R. A. M.; Broer, D. J. Dynamic mechanical properties of anisotropic networks formed by liquid crystalline acrylates. *Polymer* **1991**, *32*, 1627–1632.

(60) Chang, C.-C.; Chien, L.-C.; Meyer, R. B. Piezoelectric effects in cholesteric elastomer gels. *Phys. Rev. E* **1997**, *55*, 534–537.

(61) Hu, W.; Zhao, H.; Song, L.; Yang, Z.; Cao, H.; Cheng, Z.; Liu, Q.; Yang, H. Electrically controllable selective reflection of chiral nematic liquid crystal/chiral ionic liquid composites. *Adv. Mater.* **2010**, *22*, 468–472.

(62) Meier, W.; Finkelmann, H. Piezoelectricity of cholesteric elastomers. 1. Influence of the helicoidal pitch on the piezoelectric coefficient. *Macromolecules* **1993**, *26*, 1811–1817.

(63) Patel, J. S.; Meyer, R. B. Flexoelectric electro-optics of a cholesteric liquid crystal. *Phys. Rev. Lett.* **1987**, *58*, 1538–1540.