Dynamic High Contrast Reflective Coloration
From Responsive Polymer/Cholesteric Liquid
Crystal Architectures

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Dynamic high contrast reflective coloration from responsive polymer/cholesteric liquid crystal architectures†

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We report on high reflectivity CLC structures (R > 50%) whose wavelength can be thermally tuned reversibly by a de-swelling/re-swelling transition unique to ordered solvent-gel systems. The system contains no chiral dopant and the coloration is completely induced by a responsive chiral structured gel. The de-swelling transition, leading to blue tuning, occurs at the nematic-isotropic transition of the liquid crystal, which is a result of a mismatch in the orientational energy of the isotropic liquid crystal and the anisotropic gel. The re-swelling transition subsequently occurs at the nematic-isotropic transition of gel, due to the miscibility of the isotropic liquid crystal and the isotropic gel, which induces a red-shift in the coloration. Examination of varying clearing point liquid crystal solvents, contact angle measurements, and white light optical profilometry localized thickness measurements shed light on this de-swelling/re-swelling transition. A dynamic, high reflectivity cell was demonstrated by combining both a left-handed chiral gel with a right handed chiral gel, both of whose initial periodicities were equal. Heating of this so-called hyper-reflective cell drove reversible and large scale wavelength changes (100’s of nm) while maintaining large reflectivity (R ~ 90%).

I. Introduction

The photonic properties of cholesteric liquid crystals (CLCs) are well known and advantageous in a wide range of applications due in part to their ease of fabrication and their response to electric fields. The helicoidal structure of the CLC phase can be left-handed or right-handed and reflect light when the pitch length is on the order of the wavelength of light.1,2 The Bragg reflection wavelength, \( \lambda_B \), is governed by

\[
\lambda_B = \bar{n}P
\]

where \( \bar{n} \) is the average refractive index and \( P \) is the pitch length of the CLC. The LC reflects circularly polarized light with the same handedness as that of the helical structure of the liquid crystal. The pitch can be directly controlled through the use of chiral dopants which follows the inverse relation,

\[
P = \frac{1}{C_{RH} \times HTP_{RH} - C_{LH} \times HTP_{LH}}
\]

where \( C \) is concentration, \( HTP \) is the helical twisting power of the chiral dopant and the subscripts \( RH \) and \( LH \) refer to right-handed and left-handed, respectively. A negative value of the pitch length from the previous equation refers to a left-handed pitch. It is apparent that left-handed and right-handed dopants have a cancelling effect when mixed together, as the net HTP is the weighted average of the two concentrations. CLCs are thus limited to a single handedness and limited in their reflectivity to 50% when unpolarized light is used.3 It is interesting to note that biology has shown the ability to form static cholesteric-like materials that reflect more than 50% of unpolarized light4,5 due to novel structural architectures. CLCs can be formed without chiral molecules by using structured porous materials to induce the macroscopic helicity.6,7 Unfortunately, this approach typically eliminates the dynamic properties of CLCs, one of the major utilitarian properties of these materials. It is therefore not surprising that template-induced CLCs have remained largely unexplored, despite certain potential advantages over those formed using chiral dopants.

The alignment of liquid crystals at a surface is a well known phenomenon.4 Simple alignment surfaces can be easily generated by rubbing a polymeric surface with a piece of velvet or coating a surface with a surfactant. This phenomenon can be extended into three dimensions through the use of porous structured materials.8 An elegant and early example of a CLC phase induced through this approach was generated by back-filling a porous helicoidal structured material fabricated through glancing angle deposition with a nematic liquid crystal.8 Porous
structured materials offer an impressive degree of control over the self-assembly of liquid crystals, including the possibility of controlling photonic defects.\textsuperscript{10} Up to now, such structurally induced CLCs have been static in nature. Presented here is an approach to fabricate structured chiral templates formed via polymerization imprinting under conditions where the templates can be stimuli-responsive. In addition to the myriad of display applications,\textsuperscript{11} such chiral materials also have utility in a variety of applications including optical diodes,\textsuperscript{12} lasing,\textsuperscript{13} and even in controlling nanoscale frictional forces.\textsuperscript{14} The stereoselective properties of chiral structured materials are especially promising for the pharmaceutical industry as separation media for separating racemic mixtures into enantiomeric constituents.\textsuperscript{15–17}

Stimuli-responsive polymers are promising for a variety of applications including sensors, smart actuators, tunable catalysis, and drug delivery.\textsuperscript{18,19} A variety of stimuli can be used to trigger the response of these materials including temperature,\textsuperscript{20–23} chemistry,\textsuperscript{24} and light.\textsuperscript{25,26} While there are a variety of stimuli-responsive materials, swellable gels are a major class that has received much attention. Typical stimuli-responsive gels consist of isotropic liquids and disordered polymers and utilize swelling/de-swelling phase transitions to introduce changes in macromolecular conformation and size. A small number of stimuli-responsive swollen, ordered gels, driven by order-disorder volume phase transitions, have been recently reported and represent a relatively new sub-class of responsive materials.\textsuperscript{27,28} Specifically, Urayama and co-workers have explored a unique de-swelling/re-swelling phase transition in nematic gels swollen with nematic liquid crystals.\textsuperscript{29–31} The de-swelling transition occurs in the temperature range between the nematic-isotropic transition temperature of the LC solvent and the nematic-isotropic transition of the gel. The phase transition is driven by an unfavorable interaction energy resulting from the mismatch in orientational order between the ordered gel and the isotropic LC solvent. Simplistically, dynamic chiral analogues possessing coloration are explored here.

II. Materials and methods

The fabrication and use of chiral structured gels with temperature-responsive photonic properties driven by order-disorder transitions in the liquid crystal environment is described here. The chiral structured gels were fabricated by photo-polymerizing the LC monomer in the presence of a CLC, thereby using the CLC as a “smart solvent” to imprint a gel with a helicoidal structure giving rise to structural coloration. Most material systems combining both liquid crystals and polymer stabilization utilize a one-pot synthesis approach.\textsuperscript{32–34} Polymer stabilization is a ubiquitous tool that is typically used to alter the thermodynamically stable states and/or kinetic pathways of LCs, such as broadening the temperature range of blue phases\textsuperscript{35} or accelerating the dark-relaxation of photo-responsive mesogenic molecules.\textsuperscript{36} Recently developed two-pot synthesis techniques have enabled imprinted CLCs by de-coupling the gel from the imprinting mixture.\textsuperscript{37–41} The imprinted reflection wavelengths of these systems are fixed once fabricated. These static helicoidal structured gels have been combined with dynamically tunable LC solvents to enable dynamic ‘on-demand’ hyper-reflectivity. In the work here, we have tailored the templated polymerized structure to generate high reflectivity in the baseline condition without the need for chiral dopants and whose reflection wavelength can be modulated with temperature. An ‘always-on’, high contrast condition whose color can be reversibly controlled in a single sample is enabled.

The fabrication process is schematically shown in Fig. 1a. The polymer structures formed were tethered to only one surface of the cell by immobilizing an initiator on one substrate only. Upon polymerization of a monomer templated by a nonreactive chiral LC fluid, a slight change in the notch position of the initial cholesteric template was observed as shown Fig. 1b. This shift depends on the content of the templating mixture and the role that the monomer plays in the net helical twisting power of the mixture. Upon removal of the chiral templating mixture and refilling with a nematic LC E7 (two-pot approach), the reflective properties are completely restored indicating the polymerized structure re-swells to the original state and is unaffected by the refilling process (Fig. 1b). The details of each step in the fabrication process are described below.

Surface initiation cell preparation

A mixture of polyimide solution was prepared by thoroughly mixing 8 mL of PI2555 polyimide (HD Microsystems), 32.5 mL of N-methyl pyrrolidone (Aldrich) and 9.1 mL of 1-methoxy-2-propanol (Aldrich). The polyimide solution was filtered through a 0.45µm filter (Pall, Acrodisc PSF syringe filter) onto a glass substrate mounted on a spin coater (APH, spin 150). Spin-coating commenced by ramping up to 1500 rpm for 15 s followed by

Fig. 1  A) A schematic diagram of the sample fabrication process. B) The transmission spectra of a sample before polymerization, after polymerization and then after solvent exchange and refilling with an achiral nematic liquid crystal.
spinning at 3000 rpm for 1 min. The coated glass was baked on a hot plate at 80 °C for 30 min. Separately, a polyimide solution doped with initiator was prepared by mixing the previously prepared polyimide solution with 1% by weight Irgacure 369 (Ciba). A new glass substrate was coated and baked with this initiator-doped polyimide solution under identical conditions. Films were rubbed with velvet using a rubbing machine to achieve planar oriented alignment layers. Glass substrates were glued together with a slight offset by putting droplets of glue on two of the edges of the glass with 30 μm spacers mixed in with the glue.

### Polymeric scaffold preparation

Cells were capillary filled with a mixture containing 20% right-handed chiral monomer RMM691 (Merck) and 80% achiral nematic E7 (Merck). To template the system to a particular wavelength and handedness, appropriate amounts of the right-handed chiral dopant, R1011, or left-handed chiral dopant, S1011, were added. The capillary filling of the cells commenced under isotropic conditions (~70 °C). The cells were then allowed to cool to room temperature and were lightly rubbed on the outside of the cells until the out of band baseline transmission was almost 90%. The polymer gel scaffold was prepared by exposing the cells to 1.7 mW cm⁻² of UV light (Exfo Omnicure S1000, 300–500 nm with the peak at 365nm) for 30 min. The side with photo-initiator was facing the UV light.

### Removing the LC and refilling

Through solvent exchange the liquid crystal could be removed from the gel. The solvent exchange was accomplished by immersing the cells in cyclohexane for 1 week. After the solvent exchange was complete the cells were nearly transparent with a faint blue color that did not change with time. The cells were allowed to dry under atmospheric conditions, which typically took 10 to 60 min. The samples with de-swollen structured polymer were then free to be capillary filled with an LC mixture. All thermally tunable samples were refilled with 100% achiral nematic liquid crystals. If not specifically stated, samples were refilled with E7. The photo-tunable sample was refilled with an azo-nematic liquid crystal called 1205 from BEAM Engineering.

### Sample characterization

Transmission spectra of the samples as a function of temperature were obtained by attaching samples to a thermoelectric cooler (TEC) with thermal grease. The TEC had a hole in it that facilitated the transmission measurements. The TEC temperature was measured with a surface mounted thermistor and controlled with a 2510 TEC controller (Keithley). Transmission spectra were taken with an USB2000+ vis-NIR spectrometer (Ocean Optics). The heating cycles and transmission spectra acquisition were automated and synchronized with a custom LabView program. Differential Scanning Calorimetry (DSC) samples were prepared by carefully scraping the chiral polymer material from the glass surface into a DSC pan and measurements were done in a standard fashion to 100 °C. Optical profilometry (Wyko, Veeco Instruments) was used to directly measure the thickness to confirm that the change in the reflection wavelength was in fact due to de-swelling and re-swelling of the gel. The optical profilometry was performed on open-faced samples to measure the thickness of the gel as a function of temperature.

### III. Results and discussion

The dynamic properties of the samples were investigated by monitoring the reflection wavelength as the samples were heated. As mentioned, the reflective color is due to the templated chiral structure, not due to a chiral dopant in a nematic phase. The focus of this work is the large and complex changes in reflection color of samples upon heating as shown in Fig. 2. These samples undergo a de-swelling transition upon heating to the nematic-isotropic temperature of the nematic LC solvent, T_{NI}, which

![Fig. 2](image-url)
results in a pitch contraction of the polymer helicoidal structure. The pitch contraction causes the reflective wavelength to blue-shift as shown in Fig. 2a and 2b. The sample goes through a re-swelling volume transition after the sample is heated past the nematic-isotropic temperature of the gel, \( T_{\text{NI}} \). During the re-swelling transition the reflection wavelength red-shifts back to the original position as the pitch lengthens due to isotropic solvent diffusing back into the gel. The contrast of the reflection color also decreases in this regime as the overall order (and thus birefringence) decreases (Fig. 2c). Visually, one can observe the behavior by polymerizing through a mask and then monitoring the color as a function of temperature as shown in Fig. 2d. The black areas in the image contain no templated polymer and thus are transparent when backfilled with only a nematic LC. Where the chiral template exists, color associated with selective reflection are transparent when backfilled with only a nematic LC. Where the chiral template exists, color associated with selective reflection is observed and is controllable and reversible with temperature.

The thermal responsive mechanism is depicted in Fig. 3a. Initially, at \( T < T_{\text{NI}} \) the gel is swollen with the nematic LC solvent because the interaction energy between the nematic liquid crystal and the mesogenic helicoidal structured network is favorable. In the temperature range of \( T_{\text{NI}} > T > T_{\text{SN}} \), there is an unstable coexistent phase consisting of isotropic LC, polymer stabilized nematic LC, and the chiral nematic gel. The de-swelling volume transition is driven by the unfavorable interaction energy between the isotropic LC molecules and the anisotropic gel and the remaining nematic LC, thereby driving the isotropic LC molecules out of the gel. The mismatch in orientational order between the solvent and the gel energetically drives the volume transition. It is well known that the positional entropy associated with polymer-solvent mixing is quite low because of the limited permutations that network segments can populate due to the presence of cross-links. Therefore, the de-swelling transition is partially driven by liquid crystal orientational entropy gain of nearly \( 1/2 \kappa T \) upon escaping the stabilizing effects of the gel. Upon heating to \( T > T_{\text{SN}} \) the gel becomes isotropic and thereby no longer has an order stabilizing effect on the surrounding LC. At this point, there is no longer an unfavorable interaction energy associated with an orientational order mismatch between the gel and the LC solvent. These factors combined with the entropy of mixing drives the solvent back into the gel leading to a red-shift of the color and a loss of the reflectivity as the system completely transitions into an isotropic phase. The de-swelling and re-swelling transition temperatures correspond to the blue and red tuning onset temperatures, respectively. The \( T_{\text{NI}} \) of the gel, \( T_{\text{NI}}^G \), is reached at 71 °C, whereby the system undergoes a re-swelling transition, which is evident in the transmission spectra and thickness data shown in Fig. 2a and 2b, respectively. The DSC data presented in Fig. 3c confirms the presence of two transitions, the LC solvent nematic-isotropic transition and the gel nematic-isotropic. The onset temperature of the blue tuning directly corresponds to the LC solvent nematic-isotropic transition temperature and the onset temperature of the red tuning corresponds to the gel nematic-isotropic temperature. Polarized optical microscopy studies confirmed this behavior. Contact angle measurements were used to qualitatively probe the mechanistic role of the interaction energy between the LC and the network as shown in Fig. 3d. The contact angle jumps by \( \sim 25° \) upon heating the sample above the \( T_{\text{NI}}^G \), indicating the unfavorable energy is the dominant driver in de-swelling transition. These measurements are done when the gel is in the unswollen state and thus the entropic considerations of mixing can be ignored.

Previous work on nematic gels has demonstrated that the \( T_{\text{NI}}^G \) is significantly affected by the liquid crystal via a plasticizing effect. Specifically, the following empirical equation has proven useful in predicting this plasticizing effect,

\[
T_{\text{NI}}^G = V_{\text{LC}} X T_{\text{NI}} + (1 - V_{\text{LC}}) X T_{\text{SN}}^{G}\tag{3}
\]

where \( T_{\text{SN}}^{G} \) is the nematic-isotropic temperature of the dry unswollen gel and \( V_{\text{LC}} \) is the volume fraction of the liquid crystal. To probe whether cholesterics gels follow the same empirical

![Fig. 3](image-url)

**Fig. 3** a) A schematic of the thermal tuning mechanism. b) The thickness of the E7 swollen gel as a function of temperature. c) Differential scanning calorimetry data for the gel swollen with E7. d) Photographs of a droplet of E7 on the dry polymer surface below and above the nematic isotropic transition of E7. Notice the significant difference in the contact angle.
relationship we acquired UV-vis spectrum as a function of temperature for identically prepared samples swollen with E7, 5CB, and 1444, which are all achiral nematic liquid crystals with cyanobiphenyl functionality. The red and blue tuning on-set temperatures plotted as a function of the liquid crystal nematic-isotropic temperature are shown in Fig. 4. The $T_{NI}^{dry G}$ was measured under POM by qualitatively measuring the birefringence. The transition was very broad, but was measured to be about 200 °C. Eqn (3) predicted a $V_{LC}$ of 0.92 ± 0.01 for all three nematic liquid crystals, when the blue tuning onset temperature is the $T_{NI}$. The $V_{LC}$ should be the same for these samples because the polymer was prepared identically and upon re-swelling all the notches returned to nearly the same position. Thus, it appears that our data fits this empirical rule of mixtures equation. That said, it is somewhat surprising that the polymer volume percent is only 8%. This is likely a result of our polymer initiation method, whereby we embed the initiator in the polyimide anchoring film.

To further probe the color tuning mechanism and demonstrate the ubiquitous nature of these LC-based responsive materials, we have backfilled the imprinted polymer with an azo-nematic liquid crystal, 1205, that undergoes photo-isomerization and becomes non-mesogenic after exposure to UV light. It is well known that such azo-rich chemicals undergo a variety of photoisomerization processes upon exposure to radiation, which can lead to a variety of photo-induced effects in liquid crystals. An isothermal nematic-isotropic transition can occur when the azobenzene group in a mesogenic azo-LC compound is driven from an elongated trans configuration to a kinked cis configuration after absorbing a critical amount of UV light. The interaction energy between the imprinted swollen gel and the light induced isotropic solvent becomes unfavorable and the LC is driven out of the gel yielding a blue shift in the wavelength, completely analogous to the thermally driven de-swelling mechanism presented earlier, as shown in Fig. 5. This photo-induced isotropic mixture induced blue-tuning is expected if the mechanism discussed earlier is valid. The lack of red-tuning is also consistent as the photodriven isothermal transition never enables the gel itself to clear (as it is not heated past its $T_{NI}$). It should be mentioned that much more complicated phase transitions have been predicted in similar systems, implying that the ability to tailor the responsive properties of these ordered systems has considerable potential.

We further show that by controlling the fabrication architecture, dynamic, high contrast (>90% reflectivity) behavior, can be obtained from a single liquid crystal cell. We have combined two surface tethered helicoidally structured polymers with equal and opposite handed pitch each on their own substrate to fabricate a single liquid crystal cell, which was then subsequently filled with nematic liquid crystal as shown in Fig. 6a. The reflection spectra of the cell at different temperatures are presented in Fig. 6b. Reflectivity much greater than 50% is obtained from a single liquid crystal cell.
indicating that components of both left and right handed polarization are being reflected. More importantly, upon heating, the two surface tethered gels respond in unison, blue shifting the high contrast reflection over 100’s of nanometres. Upon reaching the second transition temperature, the notch peak wavelength red shifts and the magnitude of the reflectivity decreases. A movie of the thermal tuning of the high contrast CLC is available in the electronic supporting information. It should be evident that a dynamic high contrast CLC cell, such as presented here, could not be generated solely with chiral dopant-based CLCs. Dynamic structured materials, like those presented here, allow the liquid crystal structure to be spatially controlled while maintaining the responsive properties.

IV. Conclusions

Dynamic CLCs were fabricated from helicoidal structured materials, which offer several advantages over chiral dopant-induced cholesters, such as the ability to form polarization independent CLCs. This work overcame two major limitations of using structured materials to control the self-assembly of liquid crystals, namely the difficulty in fabrication and the static nature of the structured materials. A tunable (100’s of nanometres), high contrast (R > 90%) cholesteric system that reflects unpolarized light in a single cell was demonstrated. Tuning was enabled by heat and light and was a direct result of volume phase transition equilibrium between low molar mass liquid crystals and templated liquid crystal polymer materials.

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