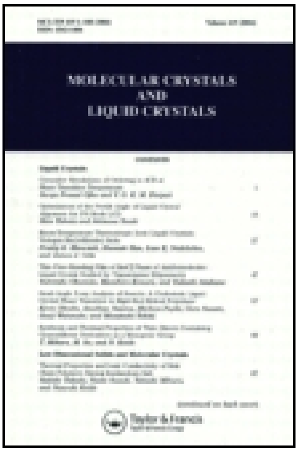

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Tuning of the Reflection Properties of Templated Cholesteric Liquid Crystals using Phase Transitions

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Tuning of the Reflection Properties of Templated Cholesteric Liquid Crystals using Phase Transitions

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The magnitude of the color changes induced by heating chiral templated polymer structures formed in spatially heterogeneous cells is examined. The large blue and subsequent red tuning of the selective reflection wavelength, caused by deswelling/reswelling of the network at the transition temperatures, is affected by the network crosslink density, heating/cooling rates, and architecture of the cell. The system is stable to multiple heat/cool cycles and shows large scale coloration changes at heating rates up to 10°C/min. At higher heating rates, a distortion of the selective reflection notch shape occurs during tuning. The magnitude of the color change is not affected by rate. At both high and low crosslink density, no tuning is observed. A window of network elasticity and responsiveness is needed to enable the anisotropic contraction/expansion processes to be observed macroscopically. Finally, the magnitude of tuning relative to the cell thickness and spatial heterogeneity across the thickness direction is explored. In thin cells, the tuning range was substantially diminished.

Keywords Cholesteric LC; LC gel; phase transition; temperature tuning; templated polymer; wavelength tuning

1. Introduction

Cholesteric liquid crystals are fascinating optical materials exhibiting vivid ROYGBIV selective reflection properties when the pitch lengths are the appropriate dimension [1,2]. They have been examined by the display industry for a number of specific applications, most of them based on color switching. As interesting as these materials are, there are a number of drawbacks for non-display applications being investigated. The first is that the switching behaviour is reversed for many applications where there is a desire for the color to be ‘off’ and then turned ‘on’ upon application of a stimulus [3]. Second, the single film reflection is usually limited to 50% due to the single handedness of the chiral mesoscale structure [4]. Third, the ability to tune the color rather than switch it on and off would enable simplicity in the design of a number of display and nondisplay applications [3].

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Recently, our group has been successful in enabling single cell reflectivities to be much larger than 50% by introducing a spatially heterogeneous polymer architecture through the cell thickness [5,6]. Our work builds off the pioneering work of two groups both of whom used a two-step photopolymerization process to enable the simultaneous existence of both R- and L-handed regions [7–10]. We showed that surface-initiated polymerization of reactive LC monomers in a cholesteric LC phase (and subsequent solvent exchange) templates a polymer structure tethered to only one of the substrates that traversed a fraction of the total cell thickness. The polymer gel anchoring attachment mechanism is still unclear. Ongoing research is attempting to ascertain whether there is chemical attachment to the polyimide buffering layer, entanglements, or strong physical bonding. Despite the uncertainty of the attachment mechanism, our prior work has confirmed that under the photopolymerization conditions, cell thickness, and monomer concentrations employed, the templated chiral polymer only spanned a fraction ($\sim$2/3) of the cell thickness. We have previously shown that this structure is stable allowing the cell to be drained and then re-filled with materials of opposite chirality [5,6]. In doing so, a system where high reflectivity (R $>$ 99%) and good out of band transmission was demonstrated. The contrast of this system could be modulated by introducing a stimuli-responsive liquid crystalline fluid into the backfilled. During these explorations, we also observed that under specific photopolymerization conditions, the reflection notch arising from the templated chiral polymer structure was itself responsive to temperature [11]. Heating of the cell to temperatures near the clearing temperature of the low molar mass nematic liquid crystal resulted in large ($>$500 nm) blue shifts in the central selective reflection wavelength with little change in the reflectivity magnitude. Further heating eventually red-shifted the peak wavelength back towards the original value and subsequently the depth of the notch diminished.

This tuning behaviour, recently published, was attributed to the chiral polymer template itself being responsive, in this case stimuli-responsive to temperature [11]. Upon heating, the periodic structure of the swollen gel compresses, which results in a blue shift in the color. In general, stimuli-responsive polymers are promising materials for smart sensors, passive actuators, and a variety of other applications [12]. Furthermore, cross-linked polymers can respond to a variety of stimuli including heat [13,14], chemicals [15–17], electric fields [18,19], and light [20,21]. In the liquid crystal arena, stimuli-responsive LC polymeric gels consist of an ordered gel swollen with a low molar mass LC liquid. All previous work has focused on nematic systems where both the polymer network and the bulk fluid were nematic. In these previously reported nematic gels swollen with nematic liquid crystals, a thermally induced deswelling/reswelling transition has been observed for certain systems [22–24]. The deswelling transition occurs when the system is heated above the solvent nematic-isotropic transition temperature because the nematic gel and the isotropic solvent have a poor interaction energy. Upon further heating to above the gel nematic–isotropic transition temperature, a reswelling transition occurs because the isotropic gel and the isotropic solvent favorably interact. The macroscopic manifestation of this behaviour is a substantial contraction of the film at the deswelling temperature followed by a subsequent re-expansion of the film at the system isotropic transition temperature. In our recent work with templated chiral nematic swollen gels, a large blue shift of the color followed by a subsequent red shift was observed. The temperatures where the tuning occurred and changed direction were correlated with the transition temperatures leading us to speculate that the fundamental driving mechanism for this color change is the same as previously seen in the nematic system. Thus, the volume phase transition which causes macroscopic contraction and expansion in a nematic system appears to be occurring in a chiral system and the expansion and contraction is along the pitch helix direction. In this scenario, large changes in the pitch (and thus reflection wavelength) would be expected.

In the work presented here, we explore several aspects of the system in greater detail with regard to the observed color tuning phenomenon and discuss the structure/property relationships in the context of the above explanation. Specifically, variables examined here briefly include the relative crosslink density, the heating/cooling rate dependencies, and cell architecture. We examine the coloration changes and critical onset phase transition temperatures as a function of temperature for all three variables. All the results are consistent with the previously hypothesized mechanism.

2. Experimental

Cell Preparation

The fabrication of liquid crystal alignment cells has been previously described in detail [5,6]. A polyimide mixture was prepared from PI2555 polyimide (HD Microsystems), 1-methoxy-2-propanol and N-methyl pyrrolidone (8:9.1:32.5 volume ratio). The polyimide solution was spun coat onto a glass substrate at 3000 rpm for 1 minute and then baked on a hot plate at 80°C for 30 minutes. A polyimide solution doped with initiator was prepared by adding 1% by weight of Irgacure 369 to the previously prepared polyimide solution. A new glass substrate was coated and baked with the initiator-doped polyimide solution under identical conditions. The polyimide films were rubbed with velvet to achieve planar oriented alignment layers. The substrates were then glued together with spacers mixed in with the glue to form a cell.

Chiral Gel Preparation

Cells were capillary filled with mixtures composed from the right-handed chiral monomer mixture RMM691 (Merck), the achiral diacrylate monomer RM257 (Merck), and the nematic liquid crystal host E7 (Merck). The chiral dopants, R1011 and S1011 were added to the mixtures to adjust the pitch of the cholesteric. The filled cells were exposed to 2.6 mW/cm^2 of UV light (365 nm) for 30 minutes. After photopolymerization, the cholesteric liquid crystal solvent and unpolymerized monomer were removed through solvent exchange by immersing the cells in cyclohexane for several days. Subsequently, the cells were dried and refilled with various nematic liquid crystals. Upon reswelling the reflection wavelengths were essentially the same as before the solvent exchange process, confirming the gel reswelled to nearly the original thickness despite the substitution of an achiral mixture for a chiral mixture. This also confirms the selective reflection is due to the chiral nature of the fluid induced by the templated polymer structure. The reflection wavelength changes are sometimes referred to as color changes even though in some cases the wavelength regime of the starting notch is outside the visible part of the spectrum.

Cell Characterization

The thermally induced deswelling/reswelling of the photonic gel was monitored with visible/near-infrared (Vis/NIR) transmission spectrometry and polarized optical microscopy (POM). Vis/NIR spectrometry measurements were performed on samples that were attached with thermal grease to a thermoelectric cooler (TEC) and the TEC was attached to a heat sink. The TEC and the heat sink (aluminum block) both had a small hole to shine the light through. The TEC surface temperature was measured with a thermistor that was epoxied to the surface of the TEC. The surface temperature was controlled with a 2510 TEC controller (Keithley). The spectra were obtained by shining white light through the TEC mounted sample to a split fiber piped to two separate Ocean Optics spectrometers (one covers the range of roughly 400–1100 nm and the other covers the wavelength range of roughly 950–2000+ nm). A custom LabView program interfaced with the temperature controller and spectrometers to automate and synchronize the heating/cooling cycles and spectra acquisition. The sample was heated under POM to confirm the presense of phase transitions at the tuning onset temperatures.

3. Results and Discussion

The large range tuning observed from these liquid crystalline surface tethered polymer networks (STPNs) is illustrated in Fig. 1(a), which plots the transmission spectra of a cell as it is heated from 50°C to 90°C. As with previous reports, the STPN was formed by photopolymerization which was followed by washing of the cholesteric liquid crystal mixture and refilling with an achiral nematic liquid crystal E7. Initial tuning was observed at

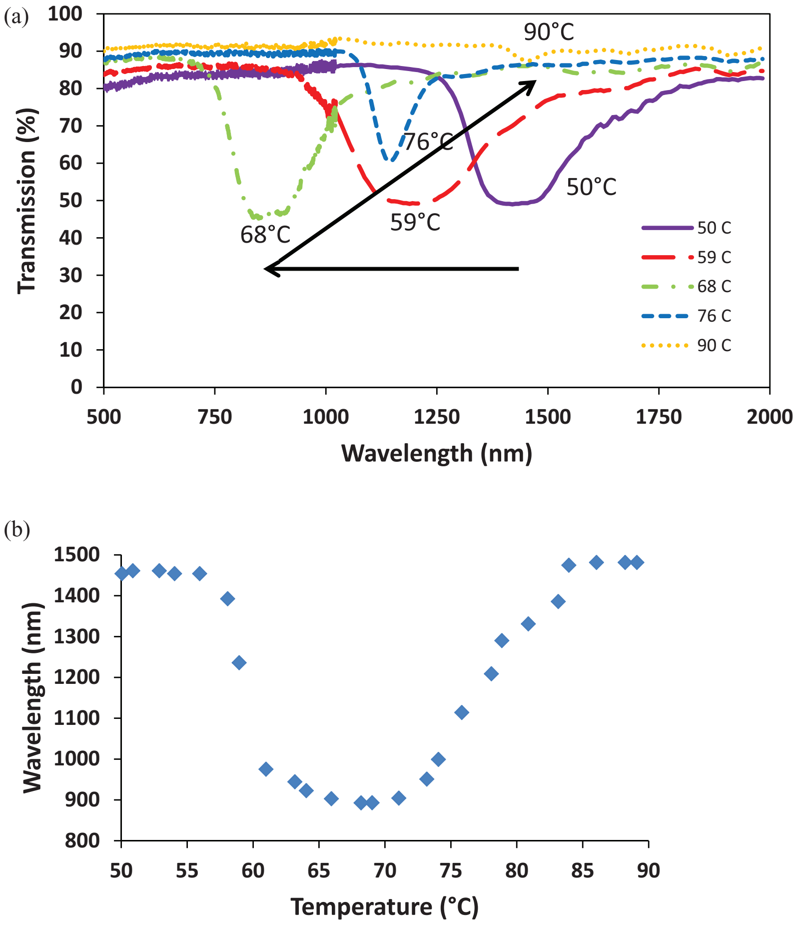


Figure 1. Blue tuning followed by red tuning of selective reflection notch as revealed by transmission versus wavelength as a function of temperature (a) and the characteristic U-shaped curve of wavelength relative to the original wavelength position as a function of temperature (b).

∼60°C, which we have previously ascribed to the nematic-isotropic transition temperature of the liquid crystal solvent. The blue shift in the reflection notch is caused by a contraction of the pitch of the STPN. The pitch contraction observed in these materials is due to a deswelling process driven by a mismatch in the orientational interaction energy between the anisotropic gel and the isotropic solvent. The thermally induced blue shift of the reflection wavelength continued until the sample was heated through the nematic-isotropic transition temperature of the gel at which point the reflection notch red shifted, indicating an expansion in the pitch. The red shift in the wavelength has been ascribed to the reswelling of the gel as it transitions to the isotropic phase. As the gel becomes isotropic, the birefringence of the system goes to zero, which is manifested as a decrease in the reflectivity of the notch (76°C in Fig. 1(a)). The reswelling transition is driven by the favorable interaction energy between the isotropic gel and the isotropic solvent. This behavior, anisotropic contraction and expansion of the pitch length of the polymer itself along the cell thickness, is completely analogous to similar behavior observed in swollen nematic systems [22,23].

The physical contraction and expansion of the STPN yields a U-shaped curve when the central reflection wavelength is plotted against temperature (Fig. 1(b)). This shape is similar to the shape of the equilibrium swelling ratio for the swollen nematic polymer previously reported [23]. As apparent in Fig. 1(b), heating the mixture does not yield color tuning until a threshold temperature is reached—correlating to the nematic-isotropic phase transition temperature of the backfilled liquid crystal mixture. Above this temperature, large range blue color tuning is observed until the temperature reaches the nematic-isotropic phase transition temperature for the gel. Subsequent heating of the cell above this temperature results in red tuning of the reflection wavelength until the reflection notch disappears. The vertical depth of the U-shaped curve as shown in Fig. 1(b), is a measure of the blue tuning magnitude, and it can be plotted in either absolute or relative terms. Data in this manuscript is plotted both ways, depending on what aspect is being highlighted. Tuning ranges exceeding 500 nm have been reported.

The data in Fig. 1 as well as that in our previous report [11] employed a heating rate of 1°C/min which is very slow for most practical applications. To explore the limits of the thermal responsivity of the mixture, we systematically studied the optical response of the STPN system using different heating and cooling rates. Figure 2(a) clearly indicates that the optical response of the system is robust exhibiting large scale, reproducible tuning over the range of heating and cooling rates from 1–10°C/min. These cells were approximately 30 microns in thickness and the initial reflection center wavelength was approximately at 1500 nm. There was little dependence on the heating rate of the total blue shift of the wavelength change as all samples exhibited between 500–600 nm tuning range. Also important, Fig. 2(a) indicates that little hysteresis exists between the heating and cooling cycles indicating reversibility in the underlying physical mechanism occurring. Although all the heating rates examined here exhibit approximately identical tuning ranges, the shape of the reflection notch was distorted when the heating rates were greater than or equal to 3°C/min. The selective reflection notch broadened and developed two distinct peaks during the heating. This phenomenon was particularly pronounced above 7°C/min, as illustrated in Fig. 2(b). Splitting was similarly observed while cooling with elevated rates. The singular notch shape was recovered during reswelling/red tuning. The presence of notch broadening and splitting during blue tuning suggests that heterogeneous domains develop within the polymer network through the thickness of the cell. This may be due to the geometry of the thermal experiments or due nonuniformity in crosslink density across the polymer structure itself (through the thickness). Heating occurred from only one side of the cell and at higher rates, non-equilibrium behavior will be expected through the thickness.

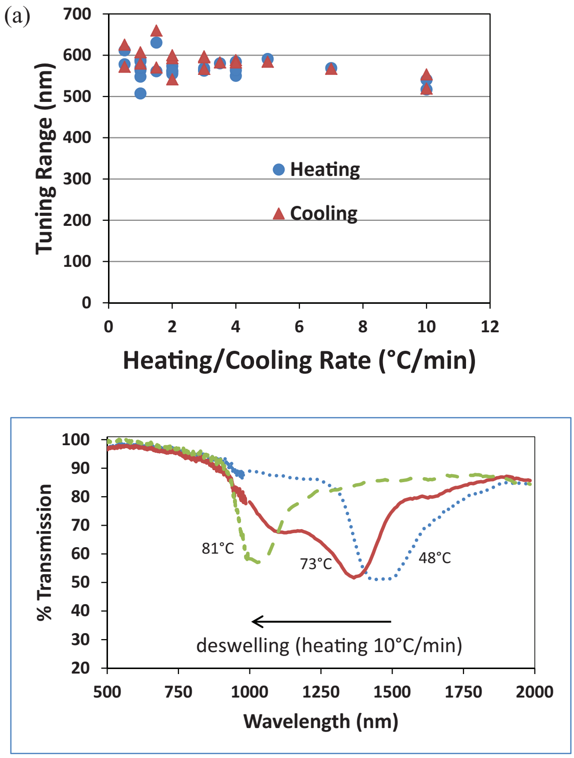
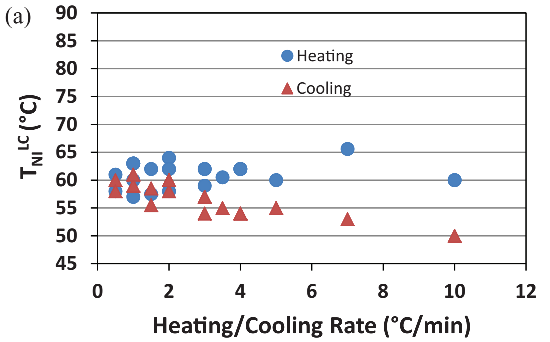


Figure 2. The absolute tuning range as a function of heating and cooling rates (a) and the distortion of the selective reflection notch during heating when using a heating rate above 7°C/min (b).

The nematic to isotropic phase transition temperatures of the solvent and swollen gel also do not seem to depend on heating or cooling rate, as summarized in Fig. 3. The temperature at which blue shifted tuning is observed correlates well with the clearing temperature of the liquid crystal employed here. The onset temperature for blue tuning is effectively constant, even at elevated heating or cooling rates. Similarly, the temperature at which red tuning is observed also shows little dependence on heating rate at the lower values. However, some deviation is observed above 4°C/min. Both these studies indicate that the templated structure is physically robust and will undergo reversible and repetitive swelling/deswelling processes. At the lower heating rates, samples have been cycled numerous times with no degradation of the notch shape or change in the tuning characteristics.

Considerable information can be extracted from the examination of the optical response of the STPN cell during heating. However, practical employment of these STPN cells for color tuning/switching will necessitate rapid responses to temperature changes. To explore limitations in this system, a 30 μm cell was subjected to a rapid temperature change spanning the LC and gel nematic-isotropic transition temperatures (from the tip to the base of the U in Fig. 1(b)). The dynamics of the system to this step change in temperature are shown in Fig. 4. The temperature increased from 50 to 65°C over the course of 15 seconds. The actual temperature of the apparatus overshot to nearly 70°C and equilibrated at 65°C after 40 seconds. The notch wavelength decreased over the course of several minutes. This



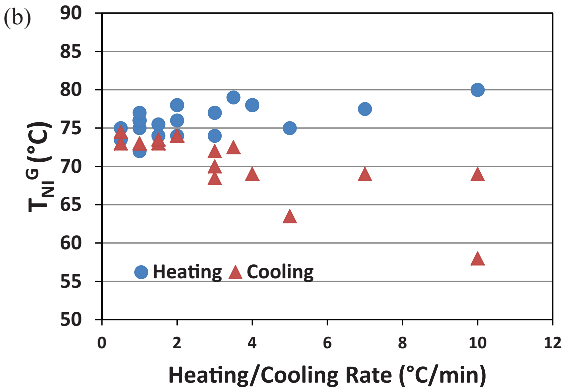


Figure 3. The nematic-isotropic liquid crystal transition temperature (a) and the nematic-isotropic gel transition temperature (b) as a function of temperature.

experiment has also been repeated to examine the response of the mixture to rapid cooling. In all cases, the response time of the system exceeds two minutes. Again, even under extreme temperature ramping conditions, the reflection notch tuning was repeatable and no physical degradation of the system was observed during numerous cycles.

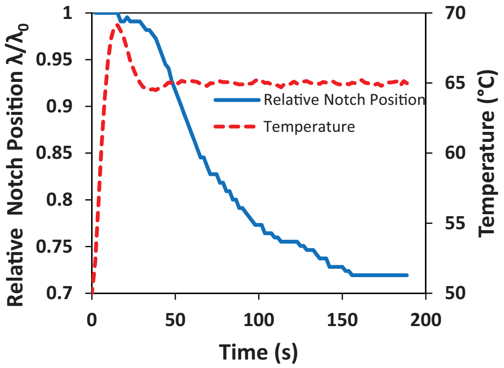


Figure 4. The relative notch position as a function of time as the system temperature is jumped into the transition temperature regime.

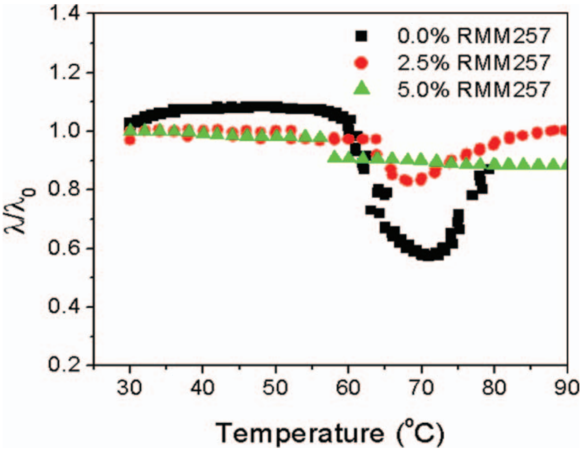


Figure 5. The relative notch position as a function of temperature for three differing relative crosslink densities.

Building from this understanding, we now shift to further elucidate the role that the composition and mechanical properties of the polymer network has on the thermal response of the STPN system. Towards this end, the crosslink density of the STPN was varied by adding the diacrylate liquid crystal monomer RM257. The optical response of these samples was examined as a function of temperature (Fig. 5). Previous literature examining volume changes of swollen nematic liquid crystal elastomers clearly indicates a strong dependence on the magnitude of the effect with crosslink density [25]. Thus, to optimize the polymer response to temperature, the key is to have the proper crosslinker concentration. If the crosslink density is too low the system is physically not a gel and will not exhibit reversible behavior due to a lack of integrity. On the other hand, if the crosslink density is too high then the network response will be minimal due to the high elastic modulus. Figure 5 confirms that in the STPN system, the tuning behavior can be strongly disrupted by adding crosslinker.

Unfortunately, the mixture RMM691 is a proprietary mixture composed of an unknown concentration of crosslinked chiral and achiral monomers. To further understand the impact of crosslink density in STPNs, we have systematically varied crosslink density in a formulation composed from achiral monoacrylate RM23 and diacrylate RM257. The RMM691 is replaced with non-reactive chiral dopant. Figure 6(a) clearly shows a decreasing magnitude of the red shift tuning range with increasing crosslinker concentration supporting the data shown in Fig. 5. Relative tuning is used as a measure with the smallest tuning magnitude observed at the highest crosslink density being assigned a value of 1. Increased range of tuning to close to 3 times this value is enabled by very small reductions in the crosslink density showing the large sensitivity. Attempts to further decrease the amount of crosslinkers were not successful due to poor compatibility of the monoacrylate monomer.

Figure 6(b) shows that the onset temperature of the red tuning increases with crosslink density. This is also consistent with previous literature on the swollen nematic liquid crystal elastomers where a slight increase in the nematic gel transition temperature was observed with increasing crosslink concentration [25]. Our previous work and the literature indicates that the gel transition temperature, T_{NI}^{G}, is well predicted by the following simple

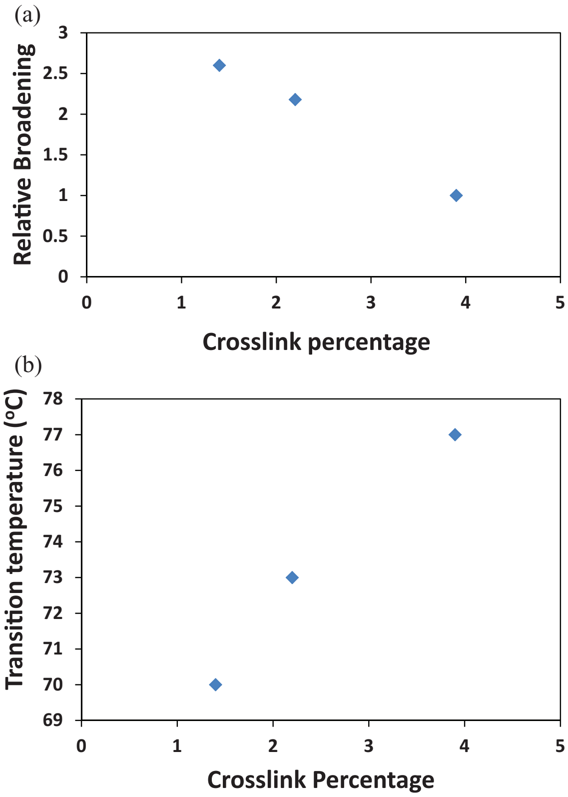


Figure 6. The magnitude of the color change in terms of relative values (a) and the evolution of the gel nematic-isotropic transition temperature (b) as a function of crosslink density.

empirical equation, $T_{NI}^{G} = V_{LC} * T_{NI}^{S} + (1 - V_{LC}) * T_{NI}^{dryG}$, where T_{NI}^{dryG} is the nematic-isotropic transition temperature of the dry gel, V_{LC} is the volume fraction of the liquid crystal solvent, and T_{NI}^{S} is the nematic-isotropic transition temperature of the liquid crystal solvent [11,23]. Thus, the increase in red tuning onset temperature with an increase in the crosslinker concentration is likely the result of an increased dry gel nematic-isotropic transition temperature. Our previous work indicated that a significant fraction of monomer was left unreacted before solvent exchange [11] and therefore, the increased transition temperature may also be a result of a higher gel volume fraction caused by the improved double bond conversion. Although the temperature range increases, there is a decrease in the magnitude of the contraction observed upon heating, which manifests itself as a lower overall tuning range (depth of the U in Fig. 1(b)). The reduced responsivity that accompanies the increase in crosslinker concentration is due to an increase in the elastic modulus due to an increased volume fraction of the gel.

Finally, the role of cell architecture (thickness) on the optical response of thermally-responsive STPN cells is examined. A schematic illustration of the baseline cell architecture through its thickness is presented in Fig. 7. The data reported here as well as our previous reports [5,6,11] have examined cells with a thickness of approximately 30 μm. We have confirmed that after refilling these 30 μm thick cells there are two distinct regions labeled A and B in Fig. 7(a) [5,6]. Region A contains the STPN attached to the substrate within

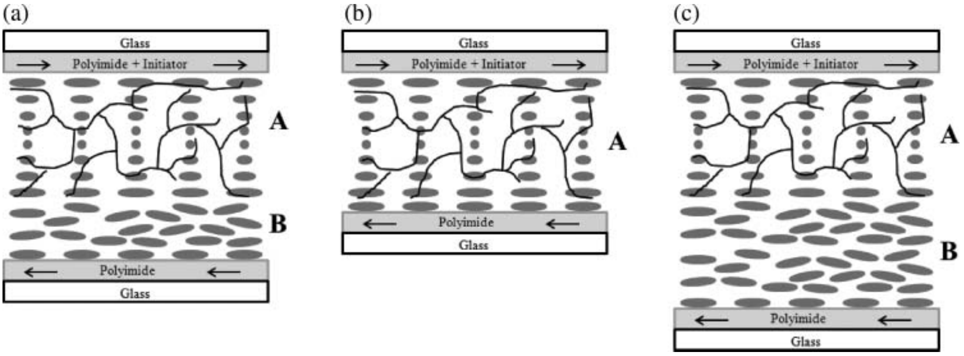


Figure 7. The proposed cell architecture as a function of total cell thickness. (a) shows the baseline architecture while (b) and (c) show relatively thinner and thicker cell designs.

which the photoinitator was embedded. Region B contains polymer-free LC fluid. This cell architecture was intentionally designed to enable backfilling of an opposite handed cholesteric liquid crystal mixture to achieve large reflectivity. To examine whether the two region architecture is required to realize the thermally-tunable optical responses presented here, we prepared cells with overall thicknesses substantially smaller (7b) and larger (7c). In the cell geometry illustrated in Fig. 7(b), the STPN traverses the entirety of the cell thickness (region A) while in the case of the cell illustrated in Fig. 7(c) the thickness of Region B is considerably increased. The proposed resulting architectures in Fig. 7(a) and (c) are based on observations of the architecture in Fig 7(b) and the premise that the gel thickness is limited by termination and by limited availability of initiator molecules in the mixture. The effect of the cell thickness on the gel growth is the subject of another study [26].

The optical responses of the STPN cells with various architectures are shown in Fig. 8. From Fig. 8, it is clear that there is little dependence on the magnitude of the tuning range observed for cell thicknesses above 20 μm. However, below 20 μm, the tuning range noticeably drops. One potential explanation is that the gel in the thinner cells did not completely reswell. One indication of this is that the reflection wavelength for the reswollen STPN thin cells (<20 μm) was greater than 400 nm less than the reflection wavelength

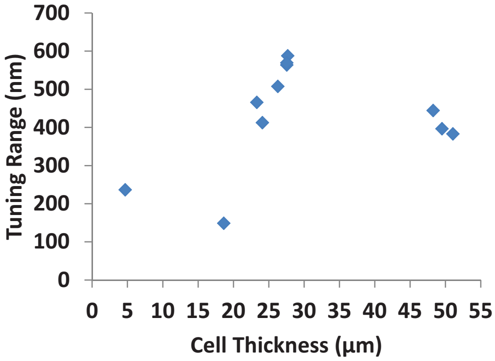


Figure 8. The absolute tuning range as a function of cell thickness.

observed in STPN cells with thickness greater than 20 μm. Also, the reflection band exhibited by the 5 μm cell was highly scattering and had a very small reflection notch depth. These results are consistent with previous data that shows a swollen polymer thickness of around 20 μm in a 30 μm cell. One would expect that the polymer would extend the entire cell thickness for cells thinner than 20 μm, leaving less space for the LC solvent and leading to difficulty in reswelling. Although the tuning ranges of the cells less than 20 microns were substantially less than the tuning ranges of the thicker cells, the presence of significant tuning in these thin cells is surprising. Some mobility is expected as long as one end of the templated polymer is untethered.

Conclusions

The effects of heating/cooling rates, crosslink density, and cell architecture were explored as they relate to the magnitude of the large color changes driven by volume phase transition behavior in a chiral templated LC system. Wavelength changes greater than 500 nm were observed using heating rates up to 10°C/min. Some anomalous reflection notch shape changes are reported at the higher rates, but the overall magnitude of the change is robust. Little hysteresis between heating/cooling cycles are observed and the system behavior is repeatable over numerous heating/cooling cycles. The magnitude and onset of thermal tuning is strongly correlated with the crosslink density of the system, consistent with previous work on swollen nematic liquid crystal elastomers. Cell architecture can impact the tuning range in cells less than 20 microns. The directionality of the chiral pitch and its attachment to a single substrate enables the macroscopic expansion/contraction in these swollen gels to manifest themselves in large color changes.

References

[1] de Gennes, P.-G., & Prost, J. (1995). *The Physics of Liquid Crystals*, Oxford University Press: Oxford, U.K.

[2] Wu, S. T., & Yang, D. K. (2001). *Reflective Liquid Crystal Displays*, John Wiley & Sons: West Sussex, U.K.

[3] White, T. J., McConney, M. E., & Bunning, T. J. (2010). *Journal of Materials Chemistry*, *20*, 9832.

[4] Makow, D. M. (1980). *Applied Optics*, *19*, 1274.

[5] McConney, M. E., Tondiglia, V. P., Hurtubise, J. M., White, T. J., & Bunning, T. J. (2011). *Chemical Communications*, *47*, 505.

[6] McConney, M. E., Tondiglia, V. P., Hurtubise, J. M., Natarajan, L. V., White, T. J., & Bunning, T. J. (2011). *Advanced Materials*, *23*, 1453.

[7] Mitov, M., & Dessaud, N. (2006). *Nature Materials*, *5*, 361.

[8] Mitov, M., & Dessaud, N. (2007). *Liquid Crystals*, *34*, 183.

[9] Guo, J., Cao, H., Wei, J., Zhang, D., Liu, F., Pan, G., Zhao, D., He, W., & Yang, H. (2008). *Applied Physics Letters*, *93*, 201901.

[10] Guo, J., Wu, H., Chen, F., Zhang, L., He, W., Yang, H., & Wei, J. (2010). *Journal of Materials Chemistry*, *20*, 4094.

[11] McConney, M. E., White, T. J., Tondiglia, V. P., Natarajan, L. V., Yang, D.-K., & Bunning, T. J. (2011). *Soft Matter.*, DOI: 10.1039/C1SM05980G

[12] Stuart, M. A. C., Huck, W. T. S., Genzer, J., Muller, M., Ober, C., Stamm, M., Sukhorukov, G. B., Szleifer, I., Tsukruk, V. V., Urban, M., Winnik, F., Zauscher, S., Luzinov, I., & Minko, S. (2010). *Nature Materials*, *9*, 101.

[13] Kim, J., Yoon, J., & Hayward, R. C. (2010). *Nature Materials*, *9*, 159.

[14] Karg, M., Pastoriza-Santos, I., Pérez-Juste, J., Hellweg, T., & Liz-Marzán, L. M. (2007). *Small*, *3*, 1222.

[15] Kang, Y., Walish, J. J., Gorishnyy, T., & Thomas, E. L. (2007). *Nature Materials*, *6*, 957.

[16] Singamaneni, S., McConney, M. E., & Tsukruk, V. V. (2010). *Advanced Materials*, *22*, 1263.

[17] Singamaneni, S., McConney, M. E., & Tsukruk, V. V. (2010). *ACS Nano*, *4*, 2327.

[18] Urayama, K., Honda, S., & Takigawa, T. (2006). *Macromolecules*, *39*, 1943.

[19] Urayama, K., Kondo, H., Arai, Y. O., & Takigawa, T. (2005). *Physical Review E*, *71*, 051713.

[20] White, T. J., Serak, S. V., Tabiryan, N. V., Vaia, R. A., & Bunning, T. J. (2009). *Journal of Materials Chemistry*, *19*, 1080.

[21] White, T. J., Tabiryan, N. V., Serak, S. V., Hrozhyk, U. A., Tondiglia, V. P., Koerner, H., Vaia, R. A., & Bunning, T. J. (2008). *Soft Matter*, *4*, 1796.

[22] Urayama, K., Okuno, Y., Kawamura, T., & Kohjiya, S. (2002). *Macromolecules*, *35*, 4567.

[23] Urayama, K., Okuno, Y., Nakao, T., & Kohjiya, S. (2003). *The Journal of Chemical Physics*, *118*, 2903.

[24] Arai, Y. O., Urayama, K., & Kohjiya, S. (2004). *Polymer*, *45*, 5127.

[25] Okuno, Y., Urayama, K., & Kohjiya, S. (2003). *Journal of Chemical Physics*, *118*, 9854.

[26] Duning, M. M. (2012). Master's Thesis, University of Dayton.