

# Polymer stabilization of phototunable cholesteric liquid crystals

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Prior examinations of azobenzene-based cholesteric liquid crystals (azo-CLCs) have primarily focused on light-directed tuning of the photonic bandgap, with particular attention paid to the magnitude of the shift of the reflection (tuning range). One potential limitation of these materials is the days-long dark restoration of the CLC from the photodisplaced spectra. This work demonstrates that polymer stabilization of azo-CLCs can dramatically reduce the time necessary for restoration from both the photoinduced isotropic (PHI) state and the photodisplaced CLC phase to the original spectral characteristics including position, bandwidth, and reflectivity. Specifically, an unstabilized azo-CLC takes 70 h to restore from the PHI state while a polymer stabilized azo-CLC regenerates the CLC phase in minutes and restores the original spectrum in a couple of hours. It is established herein that polymerization in the CLC phase is of critical importance to the restoration of highly reflective azo-CLC to the original spectral state (position, reflectivity, bandwidth, and baseline transmission). Polymerization in the CLC phase templates the polymer network with the original pitch which effectively guides the restoration of the azo-CLC helix from the photodisplaced state (isotropic or CLC). This work is another step toward the development of light-directed CLC devices capable of direct on–off binary optical switching or instantaneous tuning/relaxation, with potential applications in lasing, photonics, and imaging.

## Introduction

The helical order of cholesteric liquid crystals (CLCs) selectively reflects circularly polarized light.<sup>1</sup> The relationship between the wavelength of reflected light, the helical pitch of the CLC, and the refractive index is given in eqn (1):

$$\lambda_b = \bar{n}P \text{ where } \bar{n} = \frac{(n_o + n_e)}{2} \quad (1)$$

where  $\lambda_b$  is the center wavelength of the reflection notch,  $\bar{n}$  is the average refractive index of the LC, and  $P$  is the pitch of the CLC. The pitch ( $P$ ) of a CLC helix is defined as the unit length for a complete rotation. In CLCs with visible light reflection, the pitch is of the order of 250–420 nm.

Light-driven reflection tuning (phototuning) has been demonstrated in CLC materials using UV or in some cases, visible radiation to impart photochemical changes to chromophore-based liquid crystal materials.<sup>2–13</sup> Early efforts reported maximum wavelength shifts of 100–150 nm. We have recently observed phototuning ranges of over 400 nm.<sup>14–20</sup> The key element to the improved tuning range is the development and use of azobenzene-based nematic LC (azo-NLC) mixtures which possess large mesogenic temperature ranges well-above room

temperature<sup>18</sup> to compose a large portion of the CLC. The high concentration of azobenzene (25–92%) in these azo-CLC formulations increases the sensitivity of the large color tuning to  $\mu\text{W}$  and even  $\text{nW}$  power levels.<sup>14–17,21</sup>

Phototuning of azobenzene CLCs (azo-CLCs) is driven by the photoisomerization (*trans*–*cis*) of the azobenzene core. Driving the azo-NLC from the *trans* to the *cis*-isomer affects both the molecular order and the ‘effective’ helical twisting power (HTP) of the mixture, causing the reflection notch to tune in accordance with the change in the pitch ( $P$ ) and/or the refractive index (eqn (1)). Once irradiated, the materials are stable for long periods of time and in most cases, the reverse wavelength shift can be induced with higher wavelength (>530 nm) irradiation. With continued exposure, some azo-CLC compositions transition into the photoinduced isotropic (PHI) state. The reverse transition from the PHI state into the CLC phase can take days before the original reflection color is restored. When using the PHI state as a writable imaging substrate<sup>15,16</sup> or as an autocued filter,<sup>14</sup> this metastability is a positive characteristic of these materials. Conversely, there are many potential applications where it is desirable that the photodriven changes are only observed in the presence of the light stimulus. Together, the kinetics of the *cis*–*trans* back relaxation and the thermodynamics of helix reformation are the source of the days-long process. While the *cis*–*trans* dark relaxation can be expedited by exposure to higher wavelength light or thermal treatment, ideally, the restoration of the azo-CLC color/phase change would necessitate no external stimulus.

Previous examinations of the electro-optic properties of CLCs have shown that polymer stabilization of the helix (PSCLC) enables new and potentially beneficial performance attributes.<sup>22–31</sup>

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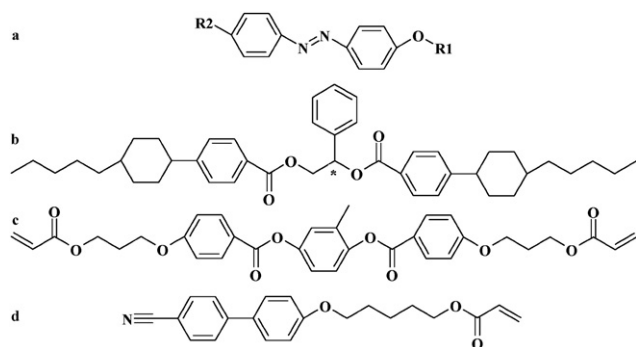
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PSCLCs are formed by mixing a small concentration of LC monomer(s) (~5 to 20 wt%) and initiator into the CLC mixture and curing. PSCLCs are nearly always formed by photopolymerization. A wide range of effects are attributed to polymer stabilization, including direct binary on–off switching.<sup>22–31</sup> Comparatively, the direct electrical switching of most CLCs from the reflective to the homeotropic state is prevented by the appearance of strongly scattering focal conic textures which form after the electric field has been removed. The focal conic scattering state is essentially a metastable intermediate that can be present for many hours. A PSCLC, through the elastic interaction of the CLC with the polymer network, is able to rapidly regenerate the reflective state.

Motivated by the dramatic benefits observed in electro-optic PSCLCs, this work compares the phototuning and dark relaxation of azobenzene CLCs to those that have been polymer stabilized (PSCLCs). It is shown here that polymer stabilization of an azo-CLC based on the chiral dopant S1011 (Merck) and an azo-NLC 1205 (BEAM Co.) restores the CLC phase in minutes and the original notch position in a few hours, in contrast to the days-long dark relaxation of the corresponding unstabilized mixture. The restoration of PSCLC and CLC from the isotropic state is discussed extensively to develop how polymer stabilization expedites the restoration of the original reflection notch.

## Experimental

The azobenzene-based cholesteric liquid crystals (azo-CLCs) examined here are formulated with the commercial chiral dopant S1011 (Merck) and the azobenzene nematic liquid crystal 1205 (BEAM Co.). This mixture has been previously documented to undergo tuning (blue shift) induced by both UV and green light.<sup>21</sup> The properties of the three-component azobenzene mixture 1205 have been reported elsewhere.<sup>18</sup> The chemical structure of S1011 and the azobenzene chromophore for 1205 are shown in Fig. 1. The chiral dopant S1011 (Merck) was used in concentrations ranging from 5–10%. Azo-CLC mixtures were drawn into liquid crystal alignment cells coated with Elvamide (DuPont), rubbed antiparallel, and spaced on the edge with glass bead spacers embedded in a cured adhesive. The liquid crystal monomers RM257 (Merck) and RM23 (Merck) were mixed into



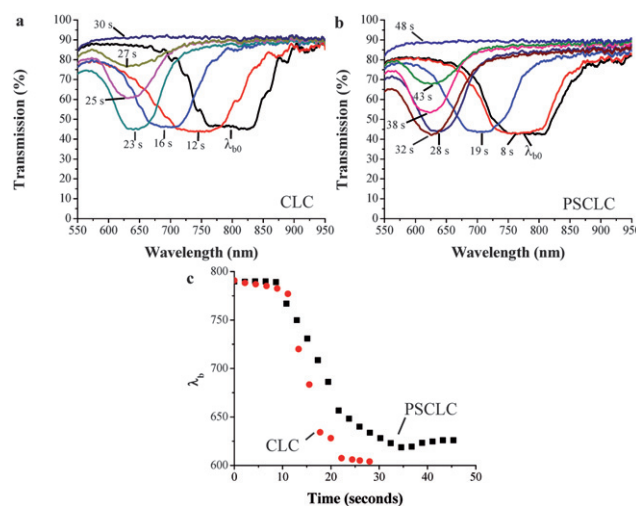
**Fig. 1** Chemical structure for the (a) azobenzene chromophore of nematic liquid crystal mixture 1205, (b) the chiral dopant S1011 (ZLI-4571), (c) the liquid crystal monomer RM257, and (d) the liquid crystal monomer RM23.

the azo-CLC at a weight ratio of 1: 9 and the polymer concentration of the PSCLC was 10% by weight. Photopolymerization was initiated by Irgacure 784 by 5 min exposure to 5 mW cm<sup>-2</sup> of the 532 nm line of a Nd:YAG laser at room temperature, unless otherwise noted.

Phototuning was driven with a high pressure mercury lamp (Exfo Acticure) filtered to 365 nm at an intensity of 1 mW cm<sup>-2</sup>, unless otherwise noted. Spectral changes were monitored using an Ocean Optics spectrometer and an unpolarized white light probe. Restoration kinetics were monitored with a Perkin Elmer Lambda 900 UV-VIS-NIR spectrometer collecting spectra at 5 min time intervals.

## Results and discussion

The azobenzene cholesteric liquid crystal (azo-CLC) mixture S1011–1205 has been previously shown to have visible-near infrared (VIS-NIR) reflection at concentrations from 7–11 wt%.<sup>21</sup> Fig. 2 presents the phototuning properties of S1011–1205 mixtures with (PSCLC) and without (CLC) polymer stabilization. The reflection notch of the S1011–1205 mixture is blue shifted by the addition of the RM23–RM257 monomer mixture.<sup>32</sup> To maintain an equivalent starting spectrum ( $\lambda_{b0} \approx 800$  nm), the S1011–1205 CLC sample contains 8.4 wt% S1011–1205 while the PSCLC sample contains 10.3 wt% S1011–1205. The transmission spectra of the S1011–1205 CLC and PSCLC are shown in Fig. 2a and b both before and during phototuning. The initial transmission spectra of the samples are essentially identical. As seen in Fig. 2, exposure to 1 mW cm<sup>-2</sup> of 365 nm light causes a blue shift in the reflection notch, represented in Fig. 2c as  $\lambda_b$  (the center of the reflection notch). In Fig. 2c, an 8–10 s lag in photoresponse to UV exposure is observed in both samples, and is attributed to the timescale of generation and diffusion of the *cis*-isomer. This lag in photoresponse is reduced with higher intensity exposure. Thereafter, the unstabilized S1011–1205 CLC tunes at a slightly faster rate than the polymer stabilized S1011–1205. As shown in Fig. 2a and b, the phototuning of



**Fig. 2** Transmission spectra before ( $\lambda_{b0}$ ) and during tuning for (a) S1011 (8.4 wt%)–1205 and (b) polymer stabilized S1011 (10.3 wt%)–1205. (c) Comparison of the center of the reflection notch ( $\lambda_b$ ) versus UV exposure time for the S1011–1205 CLC (●) and PSCLC (■).

S1011–1205 CLC and PSCLC reaches a maximum wavelength shift at which point the reflection intensity decreases until the samples are completely isotropic. The difference in the maximum reflection displacement between the CLC ( $\sim 600$  nm) and PSCLC ( $\sim 620$  nm) is caused by the ratio of S1011–1205, not the added polymer.

The phototuning rate of azo-CLCs is related to the ability of the generated *cis*-isomers to affect the pitch. The slight decrease in tuning rate with polymer stabilization therefore is likely related to a reduction in diffusivity associated with volume constraints and elastic interactions between the azobenzene liquid crystal and the polymer network. At maximum notch displacement, the S1011–1205 helix of both the CLC and the PSCLC begins to disorganize, starting from the exposed side. The reduction in reflectivity (Fig. 2a and b) is caused by an effective decrease in the number of pitches ( $P$ ) over the cell thickness ( $d$ ). Eventually, the S1011–1205 azo-CLC reaches the photoinduced isotropic (PHI) state where no reflection is evident.

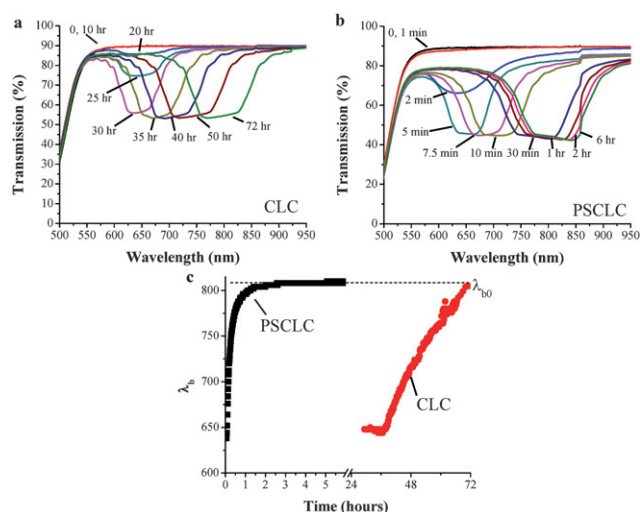
It has previously been shown<sup>14–17</sup> that azo-CLCs can be restored from the PHI state with exposure to higher wavelength light or heat, both of which serve to expedite the backward *cis*–*trans* isomerization. In certain applications, the restoration of an azo-CLC from the PHI state would ideally occur autonomously and not require secondary sources. Fig. 3 compares the dark relaxation of the S1011–1205 CLC and PSCLC samples examined in Fig. 2. Fig. 3a and b shows the transmission spectrum during the dark relaxation while Fig. 3c plots  $\lambda_b$  as a function of time. The CLC phase in the unstabilized sample is not observed until 26 h after exposure. The restoration of the unstabilized S1011–1205 CLC spectra to  $\lambda_{b0}$  takes nearly three days. Comparatively, the CLC phase is observed in minutes in PSCLC S1011–1205. The PSCLC S1011–1205 approaches  $\lambda_{b0}$  in just over an hour, and realizes the original  $\lambda_{b0}$ , reflectivity, baseline transmission, and bandwidth ( $\Delta\lambda$ ) in 2 h. Polymer stabilization reduces the time necessary for restoration from the

PHI state by more than two orders of magnitude. Notably, the processes by which the S1011–1205 CLC and PSCLC samples restore are very similar but occur over very different time scales. In both cases, the regeneration of the CLC helix begins at the maximum tuning range, growing from the PHI state baseline to maximum reflection (50%). Only after the notch is completely restored to maximum reflection do the S1011–1205 samples exhibit red shifted spectral changes.

The dark relaxation process is visually summarized in Fig. 4, which compares images of S1011–1205 CLC (in this case 10.4 wt% S1011–1205) and S1011–1205 PSCLC (in this case 11.4 wt% S1011–1205) throughout the process. The initial reflective state of the samples is shown in Fig. 4a and e. The samples were partially masked and exposed to UV light of  $5 \text{ mW cm}^{-2}$  for 5 min. The exposed portion of the CLC and PSCLC samples is driven to the PHI state (bottom half of Fig. 4b and f) while the masked portion of the cells retains the original color (top half of Fig. 4b and f). Within 2 h, the color of the PSCLC sample was regenerated (Fig. 4g) while the CLC sample remained in the isotropic state (Fig. 4c). After three days in the dark, the CLC sample restored to its original notch position (Fig. 4d).

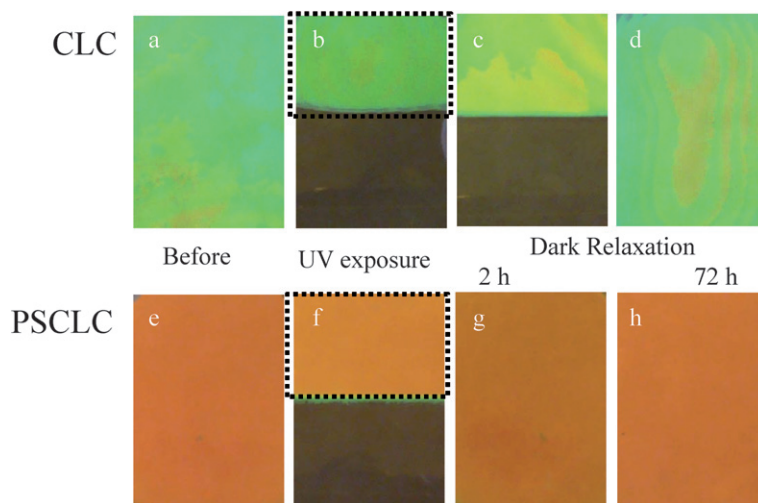
The underlying source of the expedited dark relaxation in S1011–1205 PSCLC cannot be discerned from Fig. 2–4. To further uncover the mechanism of this process, Fig. 5 presents the data from the simultaneous examination of the CLC reflection and the *cis*–*trans* kinetics. Fig. 5a and b presents both the notch position ( $\lambda_b$ ) and the normalized absorbance at 432 nm for S1011–1205 CLC and PSCLC, respectively. The maximum absorbance peak of the *cis*-isomer is at 432 nm in these mixtures. Both samples were exposed to equivalent doses of UV light ( $5 \text{ mW cm}^{-2}$  for 2 min) and driven to the PHI state. The notch position and the kinetics of the *cis*–*trans* isomerization from the PHI state were monitored *via* absorption spectroscopy. The original notch position of the S1011–1205 mixtures was shifted into the NIR so as to not influence the absorption measurements. The absorbance at 432 nm for the S1011–1205 PSCLC decreases rapidly from 1.0 to 0.86 in 2 h in the dark. In the same time period, the normalized absorbance of S1011–1205 CLC does not change to an appreciable extent. In total, the time necessary for the *cis*-azobenzene absorbance at 432 nm of the unstabilized azo-CLC to decrease to 0.86 is nearly 65 h. Under the concentration and exposure conditions examined here, 0.86 is the equilibrium absorbance value for the original *trans*-based spectra. Close examination of the *cis*-azobenzene absorbance for S1011–1205 PSCLC (Fig. 5b) shows that the absorbance value increases to a maximum at 10 min, which coincides with initial restoration of the CLC reflection. A similar local maximum can be observed in the S1011–1205 CLC (Fig. 5b) that also coincides with the initial restoration of the CLC reflection. These increases in the local *cis*-azobenzene absorbance indicate that the helical restoration causes local changes in the *cis*-azobenzene concentration.

Most obvious in the comparison of the data presented in Fig. 5a and b is the impact of polymer stabilization on the *cis*–*trans* kinetics of azobenzene in these mixtures. Weiss and Wang have extensively examined photochemical events in polymers, reporting faster *cis*–*trans* kinetics in low-density polyethylene (LDPE) that is a product of the order of the system imparting both confinement and interactive effects (van der Waals forces).<sup>33</sup>

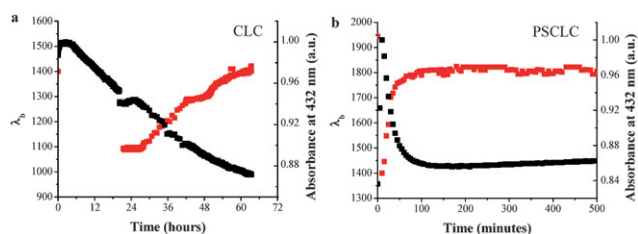


**Fig. 3** Transmission spectra of the dark relaxation from the photoinduced isotropic state of (a) S1011 (8.4 wt%)–1205 and (b) polymer stabilized S1011 (10.3 wt%)–1205. (c) Comparison of the center of the reflection notch ( $\lambda_b$ ) versus time for dark relaxation of the S1011–1205 (●) CLC and (■) PSCLC.





**Fig. 4** Images of S1011 (10.4 wt%)-1205 (top) and polymer stabilized S1011 (11.4 wt%)-1205 (bottom). Pictures taken (a, e) before UV exposure, (b, f) after UV exposure to photoinduced isotropic state (boxed region masked), (c, g) after 2 h dark relaxation, and (d, h) after three days dark relaxation.

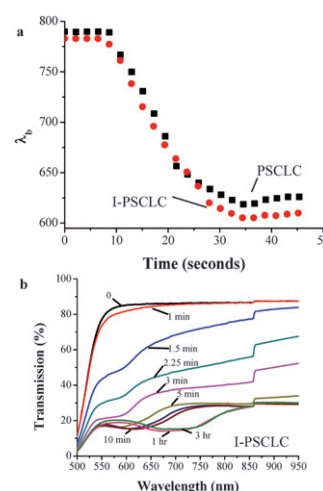


**Fig. 5** Spectroscopic analysis of dark relaxation of (a) S1011–1205 CLC (5 wt% S1011) and (b) PSCLC (4.5 wt% S1011 to 1205) from the PHI state. The notch position (red) and the absorbance of *cis*-azobenzene (black) at 432 nm are plotted as a function of time.

Our system is distinguished from the referenced work, in that the system used here is predominately liquid crystalline with only a small concentration of polymer. We propose that the rapid helical restoration observed in S1011–1205 PSCLC is caused by the local interaction of the azo-NLC and the polymer network. The polymer network, through confinement effects or interactive effects, drives *cis*–*trans* isomerization, which now places a high concentration of *trans*-azobenzene near the helical microstructure. The helical microstructure is able to generate the CLC order locally, and a small reflection is evident. Thereafter, the diffusion of the *cis*-isomers throughout the environment caused by the onset of helical restoration, subsequent molecular ordering, and resulting pitch enlargement increase the likelihood of encounter with the polymer network. It is important to note that while the improvement in the temporal relaxation of this phototunable system is similar to that observed in electrically switchable PSCLCs, the mechanism at the root of the effect is entirely distinct.

The interaction of the polymer microstructure and the azo-CLC helix is further probed in the comparison of two polymer stabilized S1011–1205 samples, one polymerized at room temperature (in the CLC phase, PSCLC) and the other polymerized at 70 °C (in the isotropic phase, I-PSCLC). Fig. 6 compares the spectral and phototuning properties of PSCLC and I-PSCLC. In Fig. 6a, the PSCLC and I-PSCLC samples tune at

the identical rate under exposure to 1 mW cm<sup>−2</sup> of 365 nm light. The restoration of these two samples from the PHI state can be compared by examining Fig. 3b and 6b. As discussed previously, the helix of PSCLC (Fig. 3b) rapidly regenerates in a two-step manner—first deepening to the maximum reflection and secondly, red shifting back to the original notch position. In Fig. 5b, however, the restoration of the CLC helix in I-PSCLC is accompanied by the onset of a strongly scattering texture. The baseline transmission of the I-PSCLC sample decreases from 90% in the PHI state to 20–30% in the restored CLC state within 5 min. A small reflection is observed in the sample after 1.5 min in the dark. The reflection of the I-PSCLC remains minimal even after 3 h in the dark, only 10–15%, and continues this way unless heat treated and rubbed. The dark relaxation of I-PSCLC is

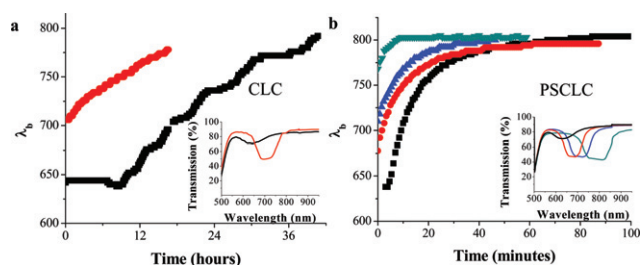


**Fig. 6** (a) Comparison of the center of the reflection notch ( $\lambda_b$ ) versus time for UV-driven (1 mW cm<sup>−2</sup>) phototuning of polymer stabilized S1011 (10.3 wt%)-1205 at (black) room temperature (PSCLC) and at (red) 70 °C (I-PSCLC). (b) Transmission spectra of the dark relaxation from the photoinduced isotropic state of polymer stabilized S1011 (10.3 wt%)-1205 at 70 °C, in the isotropic phase (I-PSCLC).

similar to the focal conic state observed after an applied field is removed from a CLC.

Since the monomers used here are liquid crystalline, the formation of the polymer network in the CLC phase templates a microstructure matching the original CLC pitch. Evidence of this morphology has been previously reported.<sup>34,35</sup> Heating the mixture to 70 °C ( $T_{cl}$  of S1011–1205 is 50–55 °C) removes the template for the polymerization. One commonality of the dark relaxation of PSCLC and I-PSCLC is the nearly immediate spectral changes caused by the polymer–azo-NLC interaction. This is in stark contrast to the unstabilized S1011–1205 mixture (Fig. 3a, c), which demonstrates no observable spectral changes in the PHI state over the course of 26 h. The rapid spectral changes evident in Fig. 6b for I-PSCLC corroborate the kinetic effect of the polymer network on the azobenzene *cis*–*trans* kinetics. Notably, these results indicate that the faster *cis*–*trans* kinetics may be more associated with polymer–*cis*-azobenzene interaction than related to the templated microstructure. However, the regeneration of the original spectrum of the PSCLC including notch position, bandwidth, reflectivity, and baseline transmission is mitigated in the case of I-PSCLC. While the interactive effects and the resulting hastening of the *cis*–*trans* isomerization kinetics are likely similar in S1011–1205 PSCLC and I-PSCLC, the isotropic polymer network in the I-PSCLC generates a scattering texture that is indicative of locally ordered microdomains. This result indicates that the helical microstructure of the S1011–1205 PSCLC (cured in the CLC phase) is of critical importance in regenerating the original reflection notch position ( $\lambda_{b0}$ ), bandwidth ( $\Delta\lambda$ ), reflectivity, and baseline transmission.

The benefit of polymer stabilization to the restoration of azo-CLCs is not limited to the restoration from the PHI state. Fig. 7 compares the dark relaxation of the S1011–1205 CLC and PSCLC samples when tuned to fractions of the maximum tuning range, all maintaining the CLC phase. Insets in Fig. 7 are the photodisplaced spectra at which dark relaxation began. In Fig. 7a, the dark relaxation of the S1011–1205 CLC is slow, taking more than a day to return to the original  $\lambda_{b0}$ . As expected, the restoration of the PSCLC  $\lambda_{b0}$  from intermediate phototuning is much faster regardless of how far the notch is displaced from the original spectrum (Fig. 7b).



**Fig. 7** Comparison of the center of the reflection notch ( $\lambda_b$ ) versus time for dark relaxation of (a) S1011 (8.4 wt%)–1205 CLC from the CLC phase with 645 nm reflection (■) and the CLC phase with 700 nm reflection (●) (inset is the associated spectra at time = 0 for dark relaxation) and (b) polymer stabilized S1011 (10.3 wt%)–1205 from the CLC phase at 640 nm (■), 680 nm (●), 700 nm (▲), and 770 nm (▼) (inset is the associated spectra at time = 0 for dark relaxation).

## Conclusions

Polymer stabilization of azobenzene cholesteric liquid crystals (azo-CLCs) dramatically reduces the time necessary for dark relaxation of a photodriven notch (photoinduced isotropic (PHI) or photodisplaced CLC) to the original spectral position. While an unstabilized azo-CLC takes 70 h to restore from the PHI state, polymer stabilized azo-CLC regenerates the CLC phase in minutes and returns to the original spectrum in a few hours. Polymerization in the CLC phase is critically important for the restoration of highly reflective azo-CLC to the original spectral state (including reflectivity, baseline transmission). Polymerization in the CLC phase templates the polymer network with the original pitch which effectively guides the restoration of the azo-CLC helix from the photoinduced isotropic state. Comparatively, restoration of an isotropic PSCLC network forms a highly scattering multidomain structure. The contribution of polymer stabilization to dark restoration is a promising means to attain a photosensitive device capable of binary switching either between a clear and reflective state, or between reflection colors. Future work will further study the impact of polymer chemistry by examining variables such as crosslinker concentration, polymer concentration, and photopolymerization light intensity on the structure retention shown here to be critical in these materials.

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