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Trans-cis isomerization and the blue phases

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A new class of photoactive chiral liquid crystals based on a photoactive nematic host material and a photoinactive chiral dopant was utilized to investigate the behavior of the blue phases when *trans-cis* isomerization is induced. While the general behavior follows what has been observed in the cholesteric phase, the sensitivity of the blue phases to external parameters causes different behavior when these systems are exposed to UV radiation. The results for four different mixtures are reported and include (1) modulation of the blue phase selective reflection wavelength with low levels of UV and visible light, (2) conversion of one blue phase to another upon exposure to UV light, and (3) induction of blue phases due to UV irradiation when no blue phases are stable beforehand. It is also noted that the supercooled blue phase behaves differently from the other blue phases. All of these results can be understood qualitatively from the ratio of non-nematogenic *cis* isomers to nematogenic *trans* isomers and chiral molecules.

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I. INTRODUCTION

During the past five years, the interest in the optoelectronic properties of cholesteric liquid crystals has increased significantly. This is due to the fact that the selective reflection band is sensitive to external fields [1,2]. The maximum wavelength of the selective reflection band λ_{\max} depends on the average index of refraction n and pitch of the cholesteric helix P in the following way:

$$\lambda_{\max} = nP = \frac{(n_e + n_o)}{2}P, \quad (1)$$

where n_e is the extraordinary refractive index and n_o is the ordinary refractive index. The width of the selective reflection band $\Delta\lambda$ is given by

$$\Delta\lambda = (n_e - n_o)P. \quad (2)$$

Recent work has demonstrated that the selective reflection band can also be controlled by changing the wavelength of light incident on the liquid crystal. Such photo-optic effects are usually produced by adding a conformationally photoactive dopant (less than 10 wt. %) to the liquid crystal system. The dopant is either achiral and added to a cholesteric liquid crystal, or the dopant is chiral and is added to a nematic liquid crystal. Several examples of the former scheme were reported recently by several groups [3–6] and an example of the latter scheme was described in Ref. [7]. Three reviews discussing both schemes and also work done with polymeric liquid crystals have also been published recently [8–10]. The extensive research in this area has demonstrated that the selective reflection band of these cholesteric liquid crystals can be reversibly switched between quite different values by illumination with either UV light or short wavelength visible light. Reversible switching has also been accomplished by illumination with right- and left-handed circularly polarized light. Switching times range from seconds to minutes. Be-

cause the amount of photoactive material in these systems is small, little change in the average index of refraction occurs, indicating that the significant change of the selective reflection wavelength with irradiation must be due to a change in the pitch [6,11].

Even more recently, a very different scheme has been investigated, namely, systems with a photoisomerizable nematic component typically comprising 60–80 wt. % of the sample, with the rest of the sample being a photoinactive chiral compound [12]. Various nematic liquid crystals with different conformationally active moieties, such as azo-, azoxy-, and cinnamic acid, were utilized. Experimental investigations showed that UV light can cause a change in the refractive indices with no change in the cholesteric pitch or it can also cause a change in the cholesteric pitch itself. The decrease in pitch after irradiation with UV light was observed in mixtures in which the pitch increases with temperature, decreases with temperature, or is relatively constant with temperature. This change of the pitch can be explained by the lowering of the concentration of linear *trans* isomers of the nematic host material as some of the molecules are transformed to bent *cis* isomers. In fact, a host material that is nematic when the concentration of *trans* isomers is high can lose its liquid crystal phase altogether after irradiation with UV light [13]. Quite simply, the decrease in the number of linear *trans* isomers increases the concentration of optically active dopant molecules relative to *trans* isomers, resulting in a decrease in the pitch. Simultaneously, the refractive indices change due to both the decrease in the order parameter and the change in the polarizability of the host material [14]. Thus the observed changes due to UV irradiation in these systems stem from both the decrease in birefringence of the nematogenic host material and the change in the molecular interactions that result in the helical twisting power of the chiral dopant [15–17].

In addition to cholesteric liquid crystals, the optoelectronic properties of the blue phases have drawn increased

interest due to possible applications [15–21]. The blue phases occur between the cholesteric and isotropic phases in some chiral liquid crystals. Theoretical and experimental studies show that cholesteric liquid crystals of short pitch can form up to three distinct blue phases. In order of increasing temperature, they are BP_I, BP_{II}, and BP_{III}. BP_I and BP_{II} have body-centered cubic and simple cubic symmetry, respectively. BP_{III} is characterized by a disordered (amorphous) structure. A fourth blue phase has been observed transforming from the supercooled BP_I and has been named BP_{IA} in [22] and BPS in [23]. Recently, blue phases have been induced by doping a cholesteric liquid crystal (possessing no blue phases) with achiral molecules [24].

In this paper, we report on measurements taken on the blue phases of systems with a nematic host that undergoes *trans-cis* isomerization. In some cases the selective reflection wavelength is not affected by UV irradiation. In other systems, λ_{\max} in BP_I, BP_{II}, and BPS increases or decreases with exposure to UV light. In yet another mixture, a system with no blue phases before UV irradiation possesses one or more blue phases (in both heating and cooling) after UV irradiation. The selective reflection wavelength of the cholesteric phase, BP_I, and BP_{II} always decreases upon exposure to UV radiation. This is true regardless of whether the temperature dependence of the pitch in the cholesteric phase is positive or negative.

II. MATERIALS AND METHODS

Three different nematic host materials were used in this investigation. ZhK-440 (NIOPIK) is a mixture of two-thirds *p-n*-butyl-*p*-methoxyazoxybenzene and one-third *p-n*-butyl-*p*-heptanoylazoxybenzene. ZhK-537 (NIOPIK) is the ester of 4-cyanophenyl and 4-heptylcinnamic acid. Both of these host materials undergo *trans-cis* isomerization. ZLI-1695 (Merck) was also used, but this nematic host material does not undergo *trans-cis* isomerization. Two different chiral dopants were added to these nematic hosts: CB-15 (4-cyano-4-(2-methylbutyl)biphenyl, Merck) and MLC-6248 (2011R, Merck). CB-15 possesses liquid crystal phases while MLC-6248 does not.

The materials were contained in 10 μm cells and selective reflection wavelength measurements were made using a Specord M 40 spectrophotometer. UV irradiation was accomplished with a 100 W mercury lamp (CBD-120) with either a 240–390 nm UFS bandpass filter or 365 nm or 436 nm interference filters. The distance from the lamp to the cell was about 15 cm. The intensity of the UV light at the sample was about 0.1 mW/cm². Thermal relaxation times after UV irradiation varied from several hours to several days, depending mostly on the temperature but also on the compound under study and the type of sample cell. Measurements performed after UV irradiation in this investigation were completed in less than 20 min in order to make sure the data were not affected by thermal relaxation.

III. EXPERIMENTAL RESULTS

The photoactive nematic mixture ZhK-440 has a maximum in its absorption at 342 nm when the mixture consists

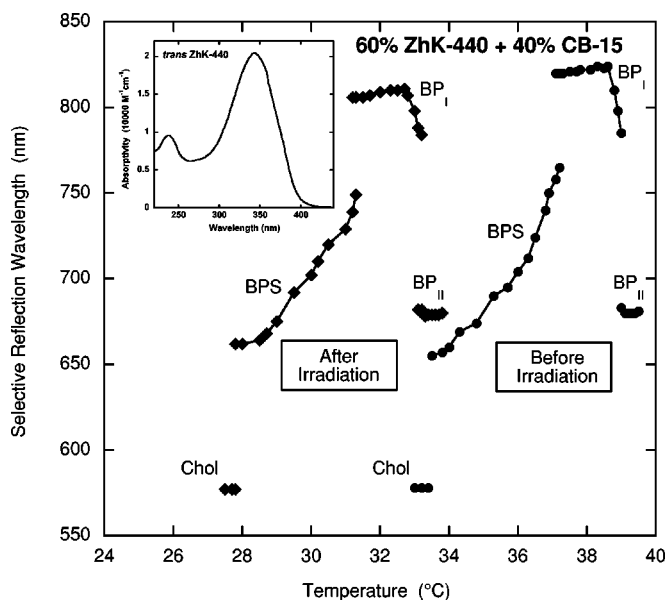


FIG. 1. Selective reflection wavelength of mixture I. Circles: before irradiation; diamonds: after irradiation for 5 min with the mercury lamp and UFS filter. The inset shows the absorptivity of a dilute solution of *trans* ZhK-440 in methanol.

of *trans* isomers. The absorption spectrum of a dilute solution of *trans* ZhK-440 in methanol is shown as an inset in Fig. 1. The absorptivity of the 342 nm peak decreases slightly and the absorptivity of the weaker peak around 240 nm increases slightly as *trans-cis* isomerization occurs.

The first mixture investigated, mixture I, was 60% ZhK-440 and 40% CB-15 (by weight). In cooling, this mixture before UV irradiation has the following phase sequence: isotropic, BP_{II}, BP_I, BPS, cholesteric. Figure 1 shows the selective reflection wavelengths before UV radiation over the temperature ranges for which these phases are stable. Figure 1 also shows the selective reflection wavelengths after 5 min of UV irradiation using the mercury lamp and the UFS filter with the sample held at the BP_{II}–isotropic transition temperature of 39.5 °C. Although the transition to the isotropic phase is lowered by 5.7 °C, the selective reflection wavelengths are virtually unaffected. This is very similar to the behavior of cholesteric phases using CB-15 as the chiral dopant, in that UV irradiation affects the refractive indices more than the selective reflection wavelength [17]. Note that coexistence is observed at some of the phase transitions. These transitions can be fairly slow as one phase nucleates in the other, causing coexistence to occur with the rate of temperature change used in these experiments.

The next mixture studied, mixture II, was 52% ZhK-440 and 48% CB-15 (by weight). The pitch of this mixture was less and the mixture possessed BP_{III} in addition to the phases of the previous mixture. The selective reflection wavelengths of these phases upon cooling and before UV irradiation are shown in Fig. 2. During irradiation using the mercury lamp and a 365 nm interference filter, the sample was kept at 29 °C where the selective reflection wavelength in BP_I is not strongly affected by temperature. As can be seen from the inset in Fig. 2, the selective reflection wavelength of BP_I

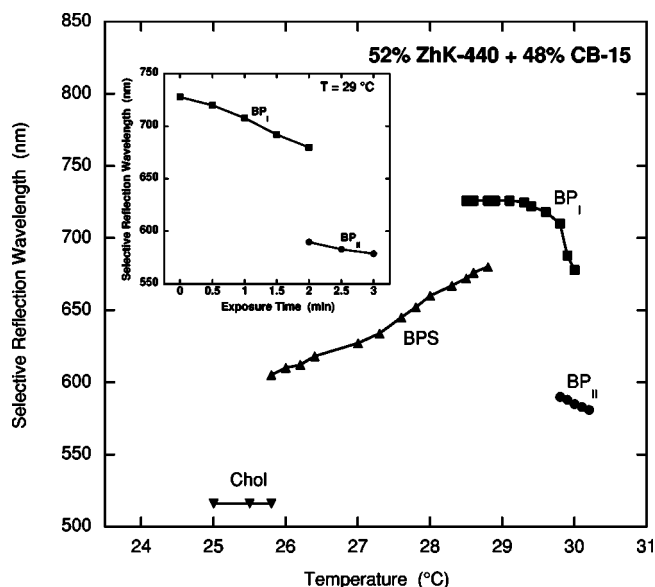


FIG. 2. Selective reflection wavelength for mixture II before irradiation. The inset shows the time dependence of the selective reflection wavelength at 29 °C when exposed to UV light from the mercury lamp and 365 nm filter. The sample transformed to BP_{III} after 3 min of irradiation and then to the isotropic phase about a minute later.

decreases with exposure to UV light, with the sample converting to BP_{II}, BP_{III}, and the isotropic phase after about 2, 3, and 4 min, respectively. A transition from BP_I to BP_{II} has been previously observed in electric fields with cholesterics having positive dielectric anisotropy [19]. Interestingly enough, if the mixture is held at 27.3 °C during UV irradiation (in the BPS phase), the selective reflection wavelength increases with exposure time. This is shown in Fig. 3. BPS has been observed to be affected oppositely from the other

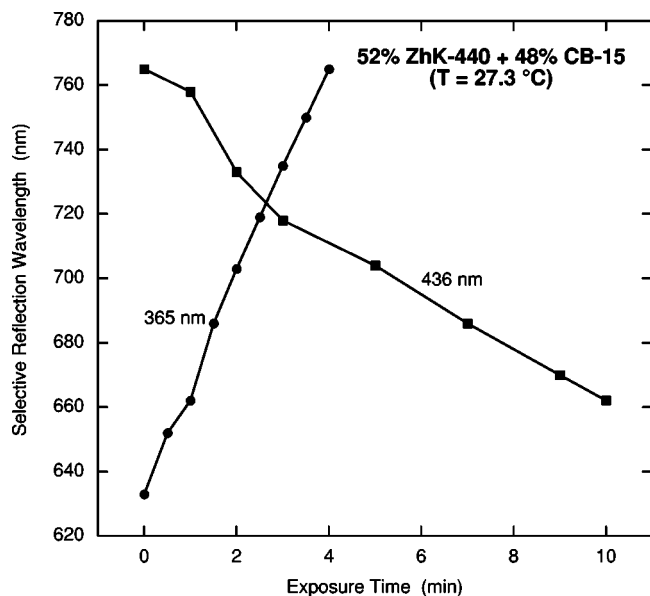


FIG. 3. Selective reflection wavelength of mixture II in BPS (27.3 °C) as a function of time when exposed to the UV lamp first with a 365 nm filter and then with a 436 nm filter.

blue phases when electric fields are applied [19]. However, if the filter is then changed from 365 to 436 nm, the selective reflection wavelength of BPS decreases, demonstrating the reversibility of the effect (also shown in Fig. 3). Changes in the selective reflection band are also reversible for the cholesteric, BP_I and BP_{II} phases, but the effect is shown for BPS because the selective reflection band shifts the most in this phase. If irradiation is stopped at any point, the wavelength of the selective reflection band ceases to change except for the very slow thermal relaxation (hours to days) as the molecules convert to the *trans* conformation. If UV exposure is continued for a longer time than shown, the sample eventually transforms to the isotropic phase.

Mixture III was a mixture of 75% ZhK-440 and 25% MLC-6248 (by weight), which possesses no blue phases before irradiation with UV light. After irradiation with the mercury lamp and 365 nm filter for 22 min at room temperature, BP_{II} was observed in heating and BP_I and BP_{II} were observed on cooling. This is the first time blue phases have been induced by *trans-cis* isomerization. The selective reflection wavelengths for the induced blue phases and the cholesteric phase are shown in Figs. 4 and 5. Notice that the temperature for the transition to the isotropic phase decreases by 17 °C after UV irradiation and that the temperature dependence of λ_{max} is weak or negative in all phases. When the cholesteric phase is irradiated with UV light at room temperature, λ_{max} and the full width at half maximum of the reflection band both decrease with increasing exposure time. Figure 6 displays these data. As with previous studies on cholesteric liquid crystals with photoactive nematic hosts, the change in molecular shape when *trans-cis* isomerization occurs causes n_e to decrease and n_o to increase. This decrease in birefringence results in a decrease in the half-width of the selective reflection band according to Eq. (2). The decrease in *trans* isomers also increases the helical twisting power of the photoinactive chiral molecules, leading to a

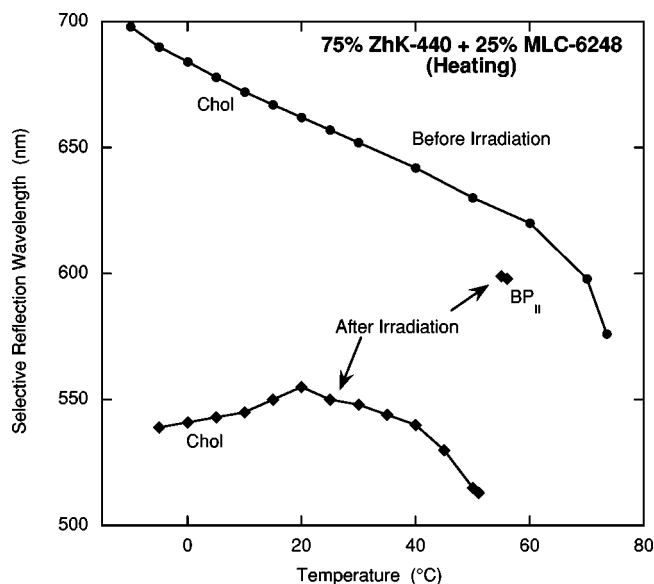


FIG. 4. Selective reflection wavelength of mixture III upon heating. Circles: before irradiation; diamonds: after irradiation for 22 min with the mercury lamp and 365 nm filter.

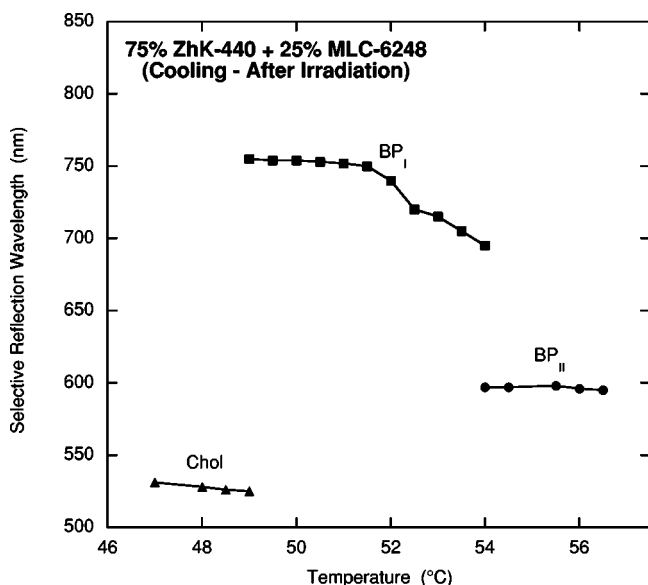


FIG. 5. Selective reflection wavelength of mixture III upon cooling after irradiation for 22 min with the mercury lamp and 365 nm filter.

decrease in the pitch, and as can be seen from Eq. (1), a decrease is the wavelength of selective reflection. In the specific case of mixture III, a little more than half an hour of exposure to the UV light source reduces the pitch to roughly three-quarters of its value before irradiation and decreases the birefringence to less than half of its value before irradiation. The latter decrease is not surprising, since a 20 °C or more decrease in the isotropic transition temperature can easily cause such a decrease in the order parameter.

Mixture IV was 76.5% of a 1:1 mixture of ZhK-537 and ZLI-1695 and 23.5% of MLC-6248 (by weight). In this mixture, ZhK-537 is the only component undergoing *trans-cis* isomerization. The selective reflection wavelength increases

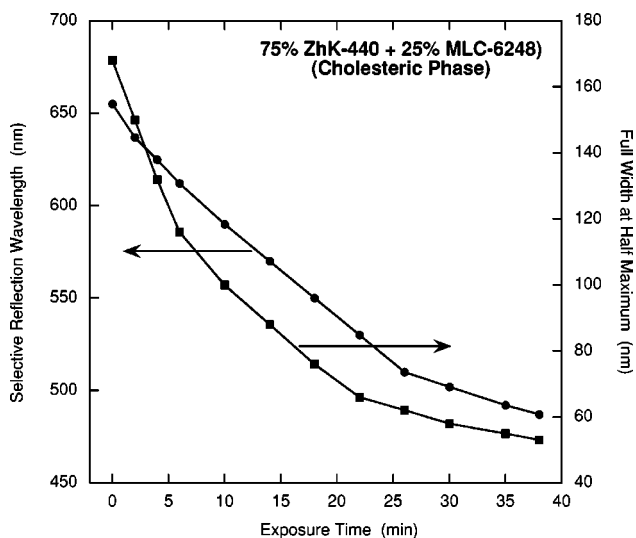


FIG. 6. Selective reflection wavelength and width of the selective reflection band for the cholesteric phase of mixture III at 25 °C upon exposure to UV light from the mercury lamp and 365 nm filter.

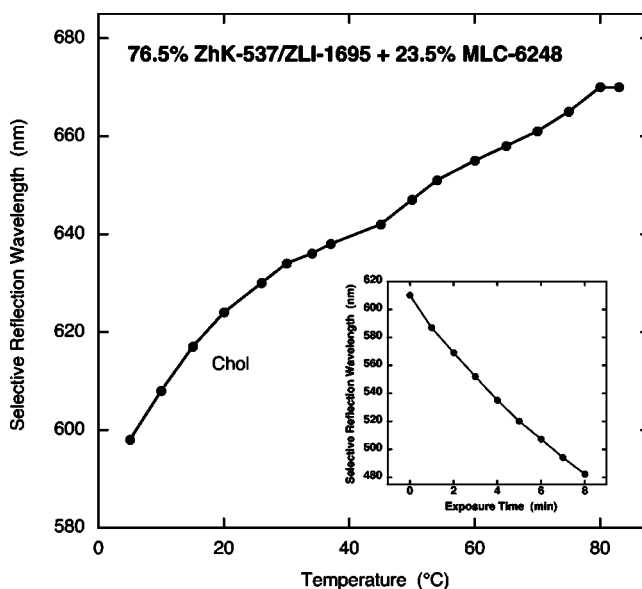


FIG. 7. Temperature dependence of the selective reflection wavelength before irradiation for mixture IV. The inset displays the time dependence of the selective reflection wavelength at 25 °C during exposure to UV light from the mercury lamp and UFS filter.

with increasing temperature as shown in Fig. 7. Yet when this mixture is irradiated with the mercury lamp and UFS filter at room temperature, the selective reflection wavelength decreases, just as is the case when λ_{max} decreases with increasing temperature (see inset in Fig. 7). This is a clear demonstration that the general tendency for the selective reflection wavelength to decrease with UV exposure is more strongly affected by the change in interactions responsible for the helical pitch than the reduction in the transition temperature to the isotropic phase.

IV. DISCUSSION

These systems with a photoactive nematic host and photoinsensitive chiral component display room temperature and slightly above room temperature blues phases with properties that can be modified by exposure to UV and visible light. The most interesting and potentially most useful behavior is the change in the wavelength of selective reflection and the fact these photoinitiated changes are reversible by just changing the wavelength of the illumination light.

Exactly what is happening in the liquid crystal is not clear, although the general characteristics can be understood. Irradiation with UV light causes a transformation of some of the nematic host molecules from the linear *trans* configuration to the bent *cis* conformation. This changes the polarizability of the molecules and lowers the amount of orientational order. If the behavior of *p*-azoxyanisole can be used as a guide, lowering the amount of orientational order causes the ordinary refractive index to increase slightly while the extraordinary refractive index decreases more significantly [25]. The change in the polarizability of the molecules should behave in somewhat the same way. The net result is a small change in the average index of refraction *n* but a more

significant decrease in the birefringence $\Delta n = n_e - n_o$. Thus one would expect the selective reflection wavelength λ_{\max} to remain fairly constant while the width of the selective reflection band $\Delta\lambda$ decreases. This is what one observes for some materials, specifically mixture I.

However, the increase in the ratio of chiral molecules to *trans* nematogenic molecules due to the conversion of *trans* conformers to *cis* conformers can cause the helical pitch to decrease. This affects the selective reflection wavelength, which depends directly on the pitch. Therefore, in many materials, the selective reflection wavelength λ_{\max} decreases upon exposure to UV light, as is the case for mixtures II, III, and IV.

While this is true for both the cholesteric and blue phases, this decrease in pitch has a much more profound effect on the blue phases. One blue phase can be converted into another blue phase by exposure to UV radiation as is the case with mixture II. Even more significant, blue phases can be stable after UV irradiation when no blue phases were stable beforehand. This is exactly what was observed for mixture III.

This decrease in the pitch due to *trans-cis* isomerization can overpower the other effects. For example, mixture IV possesses a selective reflection wavelength that increases with increasing temperature (and therefore decreasing orientational order parameter). One might expect that *trans-cis* isomerization, which significantly reduces the isotropic transition temperature and therefore lowers the order parameter, would cause the selective reflection wavelength to increase. Just the opposite occurs, demonstrating that in this system the reduction in helical pitch predominates.

Finally, it must be pointed out that BPS can behave quite differently. A partial explanation for this may be due to the fact that the selective reflection wavelength of the BPS normally increases with increasing temperature (and decreasing order parameter). Thus, in a system for which the helical pitch does not decrease significantly upon exposure to UV light, the lowering of the isotropic transition temperature and decrease in the order parameter may dominate and cause the selective reflection to increase. This is what was observed for mixture II.

V. CONCLUSIONS

Just as the blue phases are extremely sensitive to changes in temperature, these studies demonstrate just how sensitive the blue phases are to *trans-cis* isomerization of the nematic host molecules. Low level exposure to UV light can change the selective reflection wavelength significantly, with a return to the original value possible through exposure to visible light. Even more significant, such levels of exposure can also cause one blue phase to change to another or for blue phases to become stable when before exposure none were. All of these effects can be qualitatively understood through the competing effects due to the lowering of the transition temperature to the isotropic phase and the decrease in the helical pitch.

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