Toluene-Induced Phase Transitions in Blue Phase Liquid Crystals

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Supporting Information

Characterization of the phase behaviour of cholesteric and BPs

To characterize the phase behavior of the LC mixture containing 32.5 wt. % of S-811, we placed the LC between two glass slides separated by 18 um thick spacers. The sample was mounted onto a heated stage and observed under a light microscope using crossed-polarizers. The initial observations of the cholesteric LC were made using transmitted-light and a representative image is shown in Figure S1a. This image, obtained at room temperature (26.0 °C), shows the characteristic Grangjean texture of a cholesteric with planar anchoring conditions at the top and bottom interfaces with glass. The optical texture of the cholesteric changed little until the temperature was increased to 47.5 °C, at which point the sample abruptly lost birefringence and appeared dark when viewed using transmitted light. However, when the sample was imaged using reflected light, brightly colored granular domains with blue and red colors were observed at 47.5 °C (Figure S1b). This optical texture persisted as the temperature was increased to 48.7

°C. At this temperature, a second abrupt change in the optical appearance of the sample occurred and we observed bright-green granular domains (Figure c). Finally, at 50.5 °C, we observed the sample to appear dark when viewed with transmitted or reflected light, consistent with an isotropic phase of the material (Figure). The sudden changes in appearance of the sample at 47.5 °C and again at 48.7 °C are characteristic of first-order phase transitions in the LC [1]. Moreover, the bright granular texture evident under reflected-light illumination (Figure b-c) is consistent with light (Bragg) reflection from a material composed of a periodic lattice. Past studies have identified two distinct phases that possess periodic cubic structures: BP I (body-centered cubic) and BP II (simple cubic), with BP I more stable relative to BP II at lower temperatures [2,3]. When combined, these observations lead us to conclude that the images presented in Figure b and Figure c correspond to the phases BP I and BP II, respectively. Another phase, BP III, which is characterized by a hazy blue appearance and occurs at higher temperatures than the BP II but below the clearing point, was not observed in this sample. Further evidence that supports the assignment of these phases to BP I and BP II will be presented below in the context of measurements of the reflectance spectrum of the LCs.

First, we measured the reflectance spectra of the cholesteric LC containing 32.5 wt. % of the chiral dopant at different temperatures. These measurements allowed us to quantify the temperature-dependent changes in the pitch of the cholesteric and to confirm the presence of BP I and BP II at elevated temperatures. A representative spectrum of the BP-forming cholesteric LC at room temperature (26 °C) is presented in Figure a, which shows a single peak at 492 nm. This peak is associated with the Bragg reflection from the helical distortion in the director of the cholesteric LC [4]. The relationship between the pitch of the cholesteric, p, and the measured wavelength of reflection, λ, is $\lambda = p\bar{n}$, where $\bar{n}$ is the average refractive index of the material

[5]. To calculate the cholesteric pitch from reflectance spectrum, we used the average refractive index of MLC-2142 provided by the manufacturer: $\bar{n} = 1.6356$. Using this value, we calculate that the pitch of the cholesteric mixture containing 32.5 wt. % is 301 nm at room temperature. Henceforth, the values of the cholesteric pitch that we report were calculated using the wavelength of maximum reflection obtained from the reflectance spectra and the value of the average refractive index of MLC-2142 provided by the manufacturer. The temperature-dependent changes in the pitch of the cholesteric mixture containing 32.5 wt. % of S-811 are presented in Figure b. We observed that increasing the temperature of the cholesteric LC led to a decrease in the pitch. At 47.4 °C, just below the phase transition into the BP I, the pitch decreased to 288 nm, a change of 13 nm as compared to the room temperature measurement. This temperature-dependent behavior is consistent with previous observations of LC mixtures containing S-811. A past study by Shim et al., for example, reported a cholesteric mixture of ML-0643 (nematic LC from Merck) and S-811 to exhibit a decrease of 70 nm in the pitch as the mixture was heated from 30 °C to 46 °C [6]. We note, however, that whether the pitch of a cholesteric LC increases or decreases with temperature depends on the chemical nature of the chiral agent and nematic matrix [5,6].

To provide further characterization that supports the presence of the BPs in the mixtures used in our study, we measured the reflectance spectra of the cholesteric mixture containing 32.5 wt.% of S-811 at elevated temperatures. The spectra were measured at wavelengths between 400-800 nm, which is the relevant range for characterization of the optical textures presented Figure . As discussed above, when this mixture was heated between 47.5- 48.4 °C, we observed granular textures with blue and red domains (Figure b). In this temperature range, the reflectance spectrum of the LC exhibited two peaks characteristic of Bragg diffraction from a

periodic lattice. As will be discussed below, the positions of the peaks in the reflection spectra depend on the temperature of the sample. At 47.8 °C, for example, the peaks appeared at 642 nm and at 454 nm (see Figure a, red trace). The ratio of these two wavelengths is 1.41, or $\sqrt{2}$, which characterizes the selection rules for Bragg reflection from body-centered cubic lattices [3,7]. In particular, for BCC structures, the largest reflection wavelength is associated with the (110) planes while the second largest reflection wavelength is associated with the (200) planes [3]. For the BCC lattice, the relationship between the lattice spacing, a, and the reflection wavelength from the (110) plane, $\lambda_{(110)}$ is $a = \lambda_{(110)} / \left(\bar{n}\sqrt{2}\right)$, where $\bar{n}$ is the average refractive index [8]. Thus, we calculate the lattice spacing for the BCC structure at 47.8 °C to be 278 nm (using $\bar{n}$ = 1.6356). Since BP I possesses a BCC structure, we conclude that the LC phase observed between 47.5- 48.4 °C with 32.5 wt.% of S-811 corresponds to BP I [3,4,7,8].

At higher temperatures, between 48.5 °C and 50.4 °C, we observed the sample to display a granular texture with a uniform green color. Consisted with this color, the reflectance spectrum of the LC exhibited a single peak at 537 nm when heated to 48.7 °C (see Figure a, green trace). Because only a single peak is observed in the reflectance spectrum, the structure of the lattice cannot be assigned based on the data presented here. Based on previous reports that identify the phase occurring at higher temperature than BP I as the BP II phase [3,7,9], we follow a similar assignment for the phase observed between 48.7 °C and 50.4 °C. BP II is reported to have a simple cubic lattice structure, where the largest reflection wavelength is associated with the (100) plane. [3,7] For the simple cubic lattice of BP II, the lattice spacing can be calculated by the formula $a = \lambda_{(100)} / \left(2\bar{n}\right)$. Thus, at 48.7 °C, we conclude that the lattice spacing of BP II is 164 nm.

By collecting the reflection spectra of the BP I and BP II phases at various temperatures, we observed that the position of the reflection peaks depended on the temperature of the sample containing 32.5 wt. % of S-811. This observation indicates that the spacing of the cubic lattices changed with temperature. The results for the calculated lattice spacing of BP I and BP II, as a function of temperature, are presented in Figure b. Interestingly, we note that the temperature dependence of the lattice spacing is opposite for BP I and BP II. For BP I, the lattice constant decreased from 284 nm at 47.5 °C to 259 nm at 48.4 °C; for BP II, the lattice constant increased linearly from 164 nm at 48.7 °C to 171 nm at 50.4 C. However, we do not yet understand the origin of temperature-dependent these effects on the lattice spacing of BP I and BP II.

We also characterized the pitch of the cholesteric LC as a function of the concentration of chiral agent in the mixture. As shown in Figure a, the relationship between the concentration of chiral agent in the mixture and the pitch of the resulting cholesteric is non-linear. At 20 wt. % of S-811 the cholesteric has a pitch of 410 nm at room temperature; however, a mixture containing 45 wt. % of the chiral agent had a pitch of 262 nm. As described below, only mixtures containing 25.0 wt. % or more of the chiral agent exhibited a BP. These mixtures had a pitch of 375 nm (for 25 wt.% S-811) or less at room temperature. Though it is commonly reported that the pitch of the cholesteric is inversely related to the concentration of chiral agent in the mixture, our mixture did not follow this relationship [5]. As shown in Figure b, the data of the inverse pitch against the weight fraction of chiral dopant exhibits a deviation from the expected linear behavior.

Characterization of lattice spacing or pitch with respect to ternary components in LC

In Figure 5 we present the lattice constant of BP I for the different LC mixtures (containing

ternary compounds) plotted at the temperature at which the cholesteric-BP I transition was observed. For the mixture without additives, the cholesteric to BP I transition occurred at 47.5 °C, and at this temperature the lattice spacing of BP I was measured to be 284 nm. For the mixture containing pyrene, the lattice spacing was 286 nm at the phase transition, while for the BP I containing RM257 the lattice spacing was 283 nm at the transition temperature. We note that the differences in lattice constants for these BPs are relatively modest compared to the effect of the ternary compounds on the transition temperatures of the BPs. These results indicate that ternary compounds do not significantly change the lattice constant of BP I.

To further explore the effects of ternary additives on the phase behavior BP-forming LCs, we studied a cholesteric LC containing high concentrations of RM257 or pyrene. These two compounds were selected because they change the order-disorder temperature (clearing point) of the BP-forming LCs in opposite directions without changing the temperature range over which the BPs are observed. Pyrene decreases this transition temperature while RM257 increases it. We used a cholesteric LC films containing 0.3 wt. % of S-811 in MLC2142 and various amounts of pyrene or RM257 (up to 15 wt.%). The LC films were sandwiched between two glass slides coated with dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride (DMOAP), which induces homeotropic alignment of the LC. The fingerprint texture, visible when the LC film was observed under the microscope, was used to calculate the pitch of the cholesteric at room temperature. Without any ternary component, the cholesteric had a pitch of 28 μm and a clearing point temperature of 94 °C. As summarized in Figure a, adding RM257 or pyrene to the cholesteric did not have a significant effect on the pitch. All the mixtures exhibited a finger print texture with pitch of ~28 μm, regardless of the concentration of RM257 or pyrene used. In contrast, the change in the clearing point temperature of the mixtures changed dramatically with

the addition of the ternary compounds (Figure b). Adding pyrene decreased the clearing point temperature linearly (~2.7 °C / wt. % of pyrene). At ~14 wt. % of pyrene in the cholesteric, for example, the clearing point temperature of the mixture had decreased by 40 %, from 94 °C to 58 °C. RM257 had the opposite effect on the clearing point temperature, which increased by ~0.37 °C / wt. % of RM257. Adding 15 wt. % of RM257 to the cholesteric led to a 5 % increase in the clearing point temperature, from 94 °C to 99 °C.

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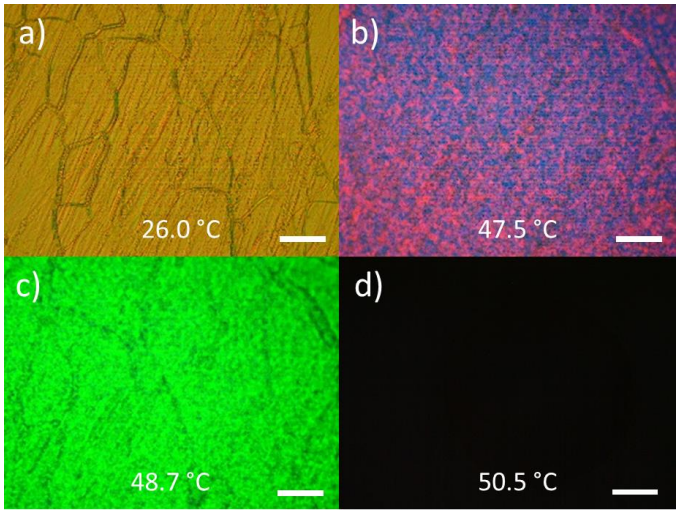

Figure S1. Images of a BP-forming LC containing 32.5 wt. % of S-811 at different temperatures: (a) 26.0 °C (cholesteric phase); (b) 47.5 °C (BP I phase); (c) 48.7 °C (BP II phase); and (c) 50.5 °C (isotropic phase). Image (a) was obtained with a crossed-polarized light microscopy using transmitted-light illumination. Images (b)-(d) were obtained using reflected-light illumination. Scale bar corresponds to 100 μm.

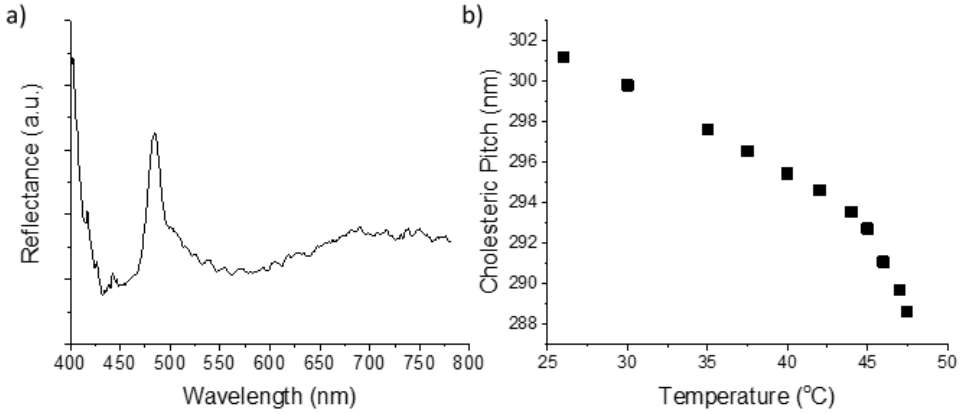

Figure S2. (a) Reflection spectrum obtained from a BP-forming cholesteric LC (containing 32.5 wt.% of S-811) at room temperature. Peak at 492 nm corresponds to Bragg reflection due to helical distortion of the LC director. (b) Pitch of helical director in the cholesteric LC as function of temperature.

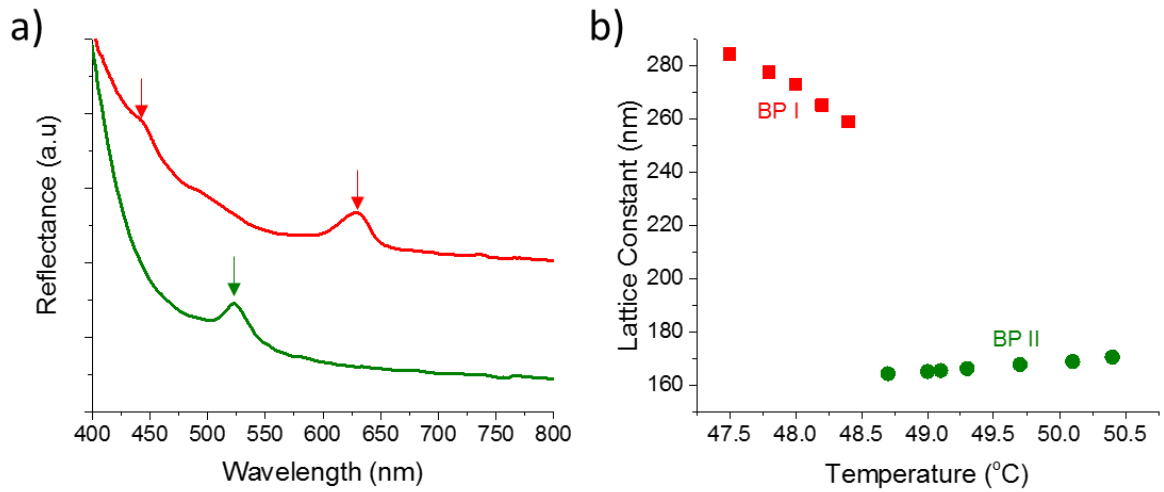

Figure S3. (a) Reflection spectra of BP-forming LC containing 32.5 wt. % of S-811 at 47.8 °C (red trace) and 48.7 °C (green trace). (b) Lattice constants of BP I (red squares) and BP II (green circles) as a function of temperature.

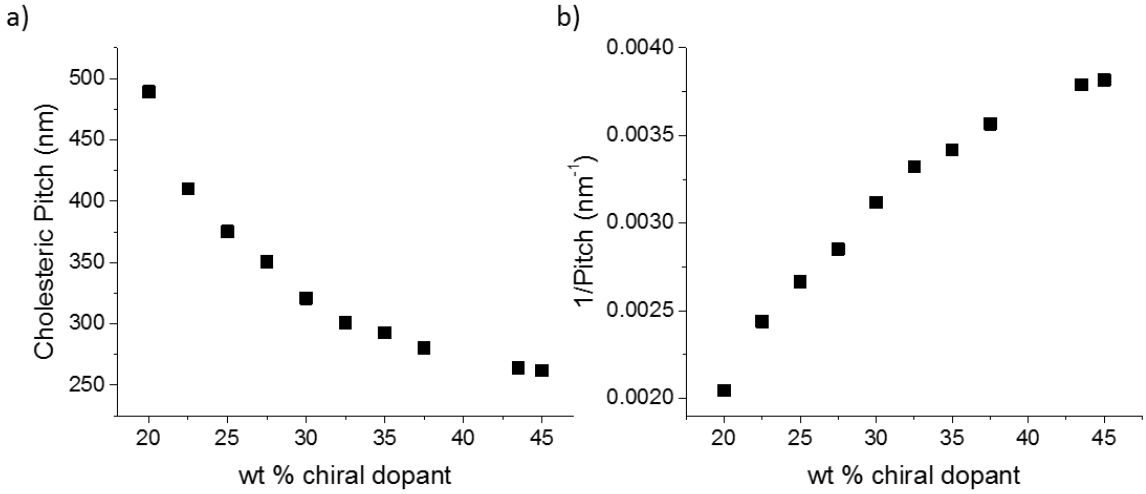

Figure S4. (a) Pitch of cholesteric LCs as a function of the weight percent of the chiral dopant (S-811). Data obtained at room temperature (26 °C). (b) Plot of inverse of the pitch against the concentration of chiral dopant in the LC.

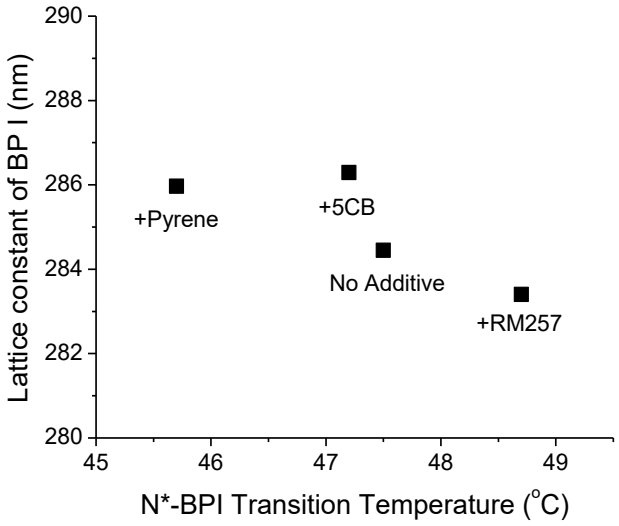

Figure S5. Lattice constant of BP I at the N*-BP I transition temperature of BPs 1 wt. % of containing various additives.

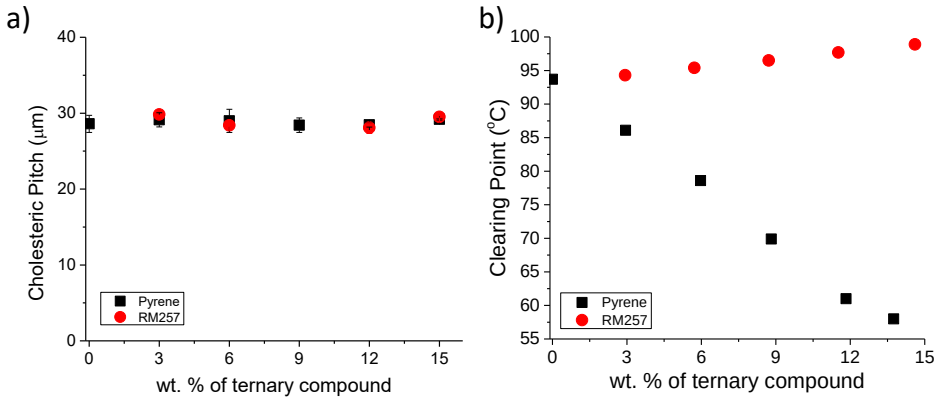

Figure S6. (a) Pitch and (b) clearing point of a cholesteric LC containing various amounts of pyrene or RM257. Cholesteric LC contained 0.3 wt. % of S-811. Characterization of the pitch was performed at room temperature.