

# Dielectric and phase behaviors of blue-phase liquid crystals

Sheng-Chieh Chen, Po-Chang Wu, and Wei Lee\*

*Institute of Imaging and Biomedical Photonics, College of Photonics, National Chiao Tung University, Guiren Dist., Tainan 71150, Taiwan*  
\*wlee@nctu.edu.tw

**Abstract:** Dielectric spectra of two pristine blue-phase liquid crystals and a polymer-stabilized counterpart were acquired at various temperatures in conjunction with simultaneous observations of their optical transmission spectra and birefringent textures. The temperature-dependent dielectric data at 5.5 kHz were specifically retrieved for further examination of the feasibility of the dielectric technique as a means to identify phase transitions. With complementary identification by optical images at specific temperatures, it is suggested that investigations of the second derivative of the real-part permittivity with respect to the temperature can be considered as one of the applicable ways to depict the phase sequence of the blue-phase liquid crystals on the cooling process from the isotropic phase through the chiral nematic phase.

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**OCIS codes:** (160.3710) Liquid crystals; (160.1585) Chiral media; (120.5050) Phase measurement; (120.6780) Temperature.

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## 1. Introduction

Blue-phase (BP) liquid crystals (LCs) as one of potential LC materials for applications in electrical and photonic devices have intensively been investigated in recent years because of their structural features and unique electro-optical responses to external stimuli. For instance, BPLCs have three-dimensional structure composed of double twist cylinders, resulting in electrically controllable Bragg diffraction in the visible spectrum and, thus, the formation of the photonic bandgap. While considering the innovation of next-generation display technology, BPLCs reveal a self-assembled lattice structure, meaning that none of alignment layer is required in the cell fabrication process. Particularly, BPLCs have sub-millisecond response time and polarization-independent optical isotropy in the absence of an applied electric field, allowing the realization of a polarizer-free and wide-viewing-angle field-sequential color LC display. Owing to the uniqueness mentioned above, most of researchers have paid their attention to practical applications of BPLCs. However, one of the crucial limits that hinders the utilization of pristine BPLCs for electro-optical devices is the narrow temperature range, typically of 0.5–2 °C. For this reason, numerous approaches, especially the polymer stabilization, have been reported to broadening the temperature range of BPs [1–4].

BPLCs are found between the isotropic (Iso) phase and the cholesteric (Ch) phase with high chirality. From the point of view of structural symmetry, BPLCs can be divided into three classifications: blue phase-I (BP I) with body-centered cubic symmetry, blue phase-II (BP II) with simple cubic symmetry, and blue phase-III (BP III) with isotropic symmetry [5–8]. To examine these BP phases, a certain number of studies concerning the identification of the mesophases as well as their phase transition temperatures have been carried out based on polarizing optical microscopy (POM), selective reflection measurement [8,9], differential scanning calorimetry (DSC) [10], thermal capacity measurement [11], refractive indices measurement [12], and Kossel-diagram observation [6].

Dielectric spectroscopy is a well-known method for investigating the polarization as well as the relaxation behaviors of a dielectric medium. Since the dielectric properties of LCs are dependent of the surrounding temperature, the behaviors of phase change between two particular LC phases have been studied based on dielectric relaxation of LC molecules. In our previous research, we have confirmed the phase sequence and transition temperatures of a LC using temperature-dependent dielectric data. According to the discontinuous variations of the dielectric function of temperature, the observed peaks in the temperature-dependent curve of the first derivative of the real-part dielectric permittivity of a LC indicate transition temperatures of two adjacent phases [13]. Considering the dielectric and phase behaviors of BPLCs, we propose in the present work a simple and useful approach to analysis of phase behaviors of BPLC samples by means of temperature-dependent dielectric spectroscopy. The first and the second derivatives of the real-part dielectric constant  $\varepsilon'$  (i.e., the dielectric function at a given frequency  $f$ ) with respect to the temperature  $T$  were derived for prompt identification of the phase transitions. With the second-order derivative of the real-part dielectric permittivity with respect to  $T$ , we clearly monitored the isotropic-to-BP II, BP II-to-BP I, and BP I-to-cholesteric phase transitions.

## 2. Experiment

In this study, three BPLC mixtures, including two pristine BPLCs and a polymer-stabilized (PS)-BPLC, were concocted. Samples A and C are pristine BPLCs composed of a nematic liquid crystal (NLC) host (HTG135200, HCCH) doped with 3.5 wt.% of the right-hand chiral agent R-5011 and 30 wt.% of left-hand chiral dopant S-811, respectively. The NLC has physical properties of birefringence  $\Delta n = 0.2$  at wavelength  $\lambda = 633$  nm, dielectric anisotropy

$\Delta\epsilon = 96$  at  $f = 1$  kHz and  $22$  °C, and clearing point  $T_c = 97$  °C. On the other hand, the PS-BPLC designated sample B was prepared by mixing the mixture of sample A with 8-wt.% monomers [4.8-wt.% RM257 (Merck) and 3.2-wt.% TMPTA (1,1,1-Trimethylolpropane Triacrylate, Sigma–Aldrich)] and 0.6-wt.% photoinitiator (Irg 184). Each BP sample was injected into a  $4.5$   $\mu\text{m}$ -thick cell by capillary action in isotropic phase. Note that the cell was fabricated without any alignment film and surface treatment. As determined preliminarily by the observation of POM images on the cooling process, the phase sequences of samples A and C are Ch–(85.2 °C)–BP I–(86.9 °C)–BP II–(88.3 °C)–Iso and SmA\*–(37.1 °C)–Ch–(85.2 °C)–BP I–(41.5 °C)–BP II–(59.1 °C)–Iso, respectively. Furthermore, sample B was exposed to ultraviolet light ( $\lambda = 365$  nm) with an irradiance of  $2$  mW/cm<sup>2</sup> in the BP I phase for 30 min to carry out photopolymerization. A PS-BPLC characterized by a widened BP temperature range was thus fabricated in comparison with its pristine BPLC counterpart (without polymer stabilization).

Temperature-dependent dielectric data were measured with a high-precision LCR meter (Agilent E4980A) in the frequency range of 100 Hz–100 kHz. The probe voltage was  $0.1 V_{\text{rms}}$  in the sinusoidal waveform, which was smaller than the Fréedericksz-transition voltage of the BPLCs. The temperature range for dielectric measurement was set between 20 and 95 °C with an accuracy of  $\pm 0.01$  °C using a temperature controller (Linkam T95-PE). Two other methods, POM observation and the selective reflection measurement, were also performed in this study to ascertain the transition temperature of two adjacent phases of the BPLCs. The textures of BPLCs at some selective temperatures were observed using a polarizing optical microscope (Olympus BX51) with crossed polarizers while the polarizer-free transmission spectra of both BPLCs in the wavelength range from 380 to 800 nm were measured with a high-speed fiber-optic spectrometer (Ocean Optics HR2000 +) in conjunction with a halogen light source (Ocean Optics HL2000).

### 3. Results and discussion

Figure 1 shows an example of the complex dielectric spectrum of a BPLC (sample A) in the frequency range of  $10^2$ – $10^5$  Hz. Since the polarization in a material does not respond instantaneously to an applied field, the resulting dielectric loss causes the permittivity to be complex and depends generally on the frequency. Consequently, the complex dielectric function can be expressed as  $\epsilon^* = \epsilon' - i\epsilon''$ , where  $\epsilon'$  as the real-part and  $\epsilon''$  as the imaginary-part permittivities, respectively, denote the energy-storage and energy-dissipation within the dielectric medium. Based on the frequency-dependent dielectric properties, the technique of dielectric spectroscopy has been extensively investigated to clarify the polarization and orientation process of the material in designated frequency regimes. In this work, as presented in Fig. 1, the complex dielectric function in the low-frequency regime ( $10^2$ – $10^3$  Hz) is dominated by the ionic effect (or space-charge polarization) in which the dependences of  $\epsilon'$  and  $\epsilon''$  behave as  $f^{-3/2}$  and  $f^{-1}$ , respectively. On the other hand, the constant value of  $\epsilon'$  in the frequency range between  $10^3$  and  $10^4$  Hz is attributable to the dipole orientation of LC molecules. Because the molecular ordering depends strongly on  $T$ , the phase transition can be clarified by the variation of  $\epsilon'$  with  $T$  in this frequency regime. Accordingly, the temperature-dependent dielectric permittivity at the frequency of  $f = 5.5$  kHz is established to study phase behaviors of BPLCs in this work. Note that the dielectric data beyond  $10^4$  Hz as shown in Fig. 1 should not be used for analysis owing to the pseudo-relaxation fundamentally caused by the cell geometry [14].

Figure 2 demonstrates the temperature dependence of the real-part dielectric permittivity  $\epsilon'(T)$  as well as the first and second derivatives of  $\epsilon'$  with respect to  $T$  of sample A. The orientation of LC molecules and the physical properties of LC phases reveal distinct dependencies of the temperature; thus, one can simply estimate the phase transition temperature between two LC phases in accordance with the discontinuous variation in  $\epsilon'(T)$ . For BPLCs, the discontinuous points in the data of  $\epsilon'(T)$  as shown in Fig. 2(a) can hardly be found for mesophases between BP and isotropic phase due to the fact of either the weakly

first order or second order phase transition [12,15]. Since the curve of the first derivative of  $\epsilon'$  with respect to  $T$ ,  $d\epsilon'/dT$ , has previously been proposed as a sensitive probe for determination of the phase transition temperature [13], the phase sequence of a BPLC can briefly be depicted by means of the data of  $d\epsilon'/dT$ . As displayed in Fig. 2(b), five regions separated by the jumps in  $d\epsilon'/dT$  can be identified, briefly representing the existing phases and their temperature ranges.

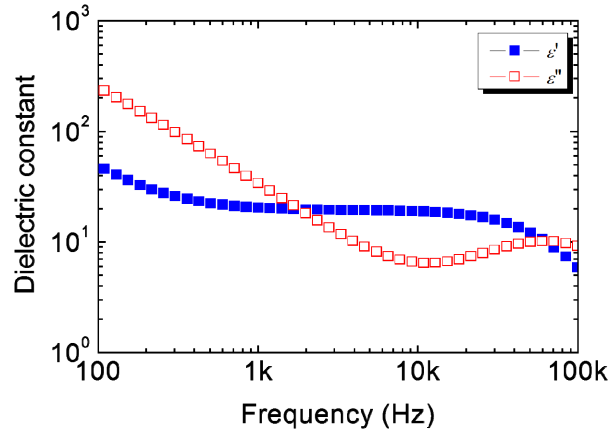


Fig. 1. Dielectric spectra of sample A at 87.5 °C.  $\epsilon'$  and  $\epsilon''$  are the real and imaginary parts of the complex dielectric function.

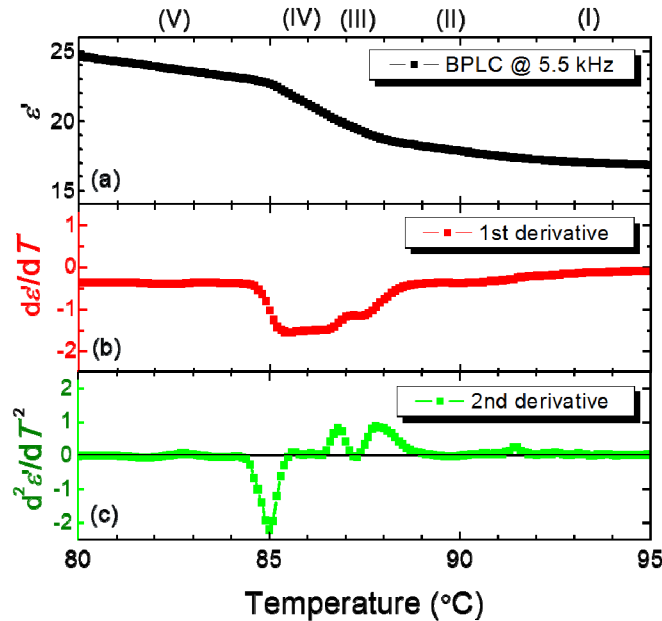


Fig. 2. (a) Temperature-dependent real-part dielectric permittivity, and (b) the first- and (c) second derivative of the real-part dielectric constant of sample A at 5.5 kHz on the cooling process with a rate of 0.1 °C/min.

While further performing the second derivation of  $\epsilon'$ , four peaks located at temperatures of 91.5, 87.9, 86.8 and 85 °C can be found in Fig. 2(c). This suggests that each peak corresponding to the change in tangent in the  $T$ - $\epsilon'$  curve precisely identifies the phase transition temperature of two adjacent phases. With the known Iso-BP-Ch phase sequence in conventional BPLCs, the adjacent phases, separated by a peak in Fig. 2(c), can be defined

according to the type of the phase change. In addition to the first-order transition between the cholesteric and blue phase, the Iso-to-BP II and BP II-to-BP I are carried out via second order and weakly first order transitions, respectively. Therefore, it is reasonable to say that the highest and lowest values of local maximum and minimum peaks at temperatures of 91.5 and 85 °C in Fig. 2(c) are transition temperatures of Iso-to-BP II and BP I-to-Ch, respectively. The peak at 87.9 °C thus corresponds to the transition temperature of BP II-to-BP I. The undefined peak at 86.8 °C is presumably dominated by the BP I to the BP I/Ch coexisting phase since the two-phase state always occurs in the first-order transition [16].

Combined with the results of the POM images and the transmission spectra, as shown in Fig. 3, the phase behavior of the investigated BPLC can be divided into five regions, (I) Iso, (II) BP II, (III) BP I, (IV) BP I + Ch, and (V) Ch phases, classified as the following three parts:

- (1) In the case of region I where temperatures are higher than 91.5°C ( $T > 91.5$  °C), the value of  $\epsilon'$  approximately preserves as a constant due to the random orientation of LC molecules in the isotropic phase. The confirmation of isotropic phase in this temperature regime can further be checked by the results in Fig. 3(a) in which the POM image exhibits complete dark appearance and the transmission spectrum of the BPLC cell shows an identical optical profile to that of the reference signal.
- (2) With further decrease in temperature, regions II and III constitute the temperature regimes of  $91.5$  °C  $> T > 87.9$  °C and  $87.9$  °C  $> T > 86.8$  °C, which correspond to the temperature ranges of BP II and BP I, respectively. The observed peaks at  $T = 91.5$  and  $87.9$  °C in the second derivative curve imply the Iso-to-BP II and BP II-to-BP I phase transition temperatures, believed to be caused by the structural changes from the isotropic orientation to double twisting cylinders and from the simple cubic lattice to body-centered cubic, respectively. For the POM images and transmission spectra of the cell, two temperature points of 89.7 and 87.8 °C were chosen which are highly closed to that of BP II-to-BP I phase transition. As shown in Figs. 3(b) and 3(c), the resulting platelet textures of the cell preliminarily confirm the existence of BP phases. Specifically, the appearance of the reflection peak (in the transmittance spectrum) at approximately 540–550 nm corresponds to the (1 1 0) diffraction of BP I. This implies that there is a phase change between two adjacent BP phases at 89.7 and 87.8 °C.
- (3) As the temperature decreases below 86.8 °C, the LC phase starts transferring from BP to cholesteric phase which leads to a considerable increase in  $\epsilon'$  with decreasing temperature. Results shown in Fig. 3(d) on the POM and the transmission spectrum of the cell at 85.8 °C suggest coexistence of the BP phase and cholesteric phase in the focal conic state within temperature regime IV of  $86.8$  °C  $> T > 85.0$  °C. In region V where temperatures are lower than 85.0 °C, the POM image at 83.0 °C reveals completely the focal conic texture of a typical cholesteric phase and the peak corresponding to BP I vanishes in the transmission spectrum, as shown in Fig. 3(e).

Figure 4 depicts the temperature-dependent dielectric data of the PSBP cell (i.e., sample B). In contrast to the result of Fig. 3(c) for pristine BPLC, here, by performing the second derivative of  $\epsilon'$  with respect to  $T$ , only an oscillating signal having local maximum and minimum values at 88 and 84 °C, respectively, is obtained within the temperature regime from 95 to 35 °C. Because the photopolymerization process for sample B was carried out in BP I phase, the BP II phase is expected to be suppressed and the detected signal in  $d^2\epsilon'/dT^2$  is thus attributable to the phase change from the isotropic to BP I phase. On the other hand, since the intensity of signal for the Iso-to-BP phase transition is the smallest among phase change points in the BPLC, the small variations in  $d^2\epsilon'/dT^2$  at temperatures below 85 °C are simply noises. By checking the optical images, it is confirmed that sample B in the temperature range between 86 and 35 °C exhibits entirely the BP I phase. This outcome

results from the use of the polymer stabilization method in sample B, which is a well-known approach for widening the temperature range of BPLCs. Our results indicate that the behavior of phase transition can precisely be monitored using the dielectric data for both the BPLCs with and without polymer stabilization.

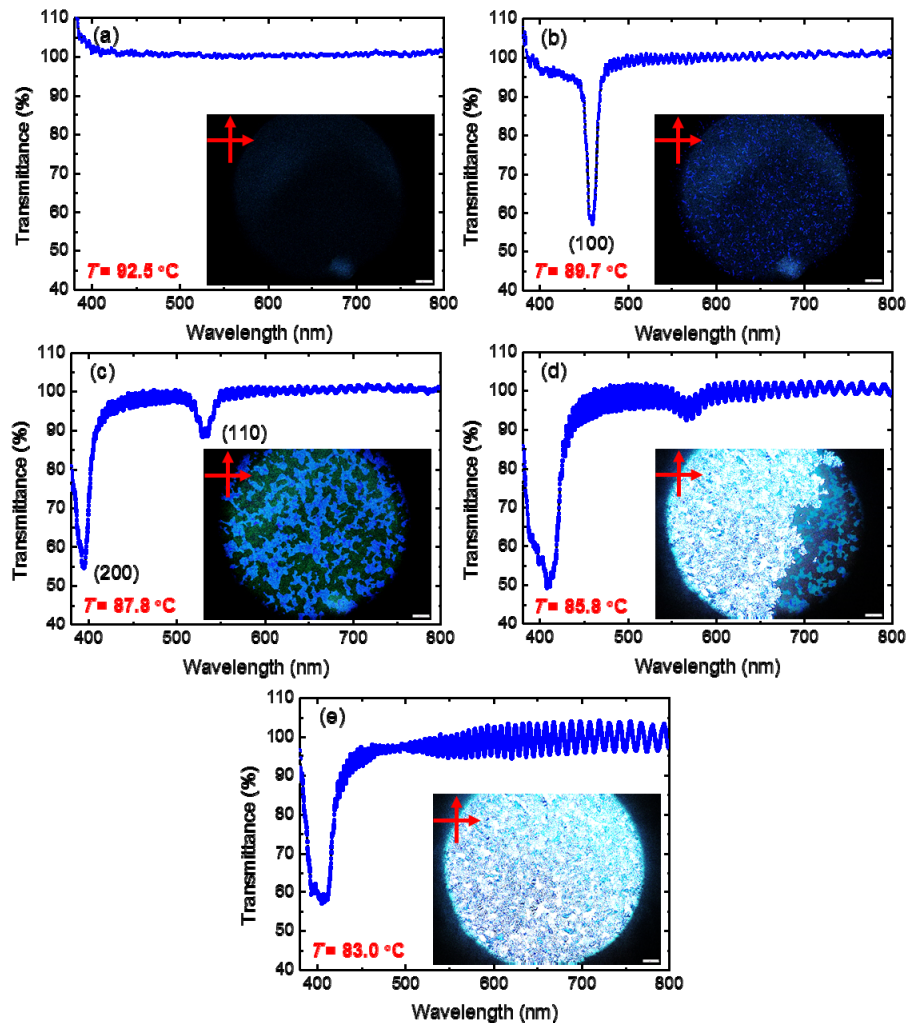


Fig. 3. Transmission spectra and POM images of the BPLC sample A in (a) the isotropic phase (92.5 °C), (b) BP II (89.7 °C), (c) BP I (87.8 °C), (d) the mixed BP and cholesteric phases (85.8 °C), and (e) the cholesteric phase (83.0 °C).

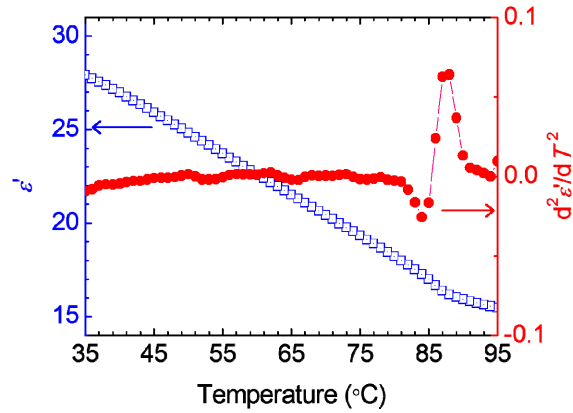
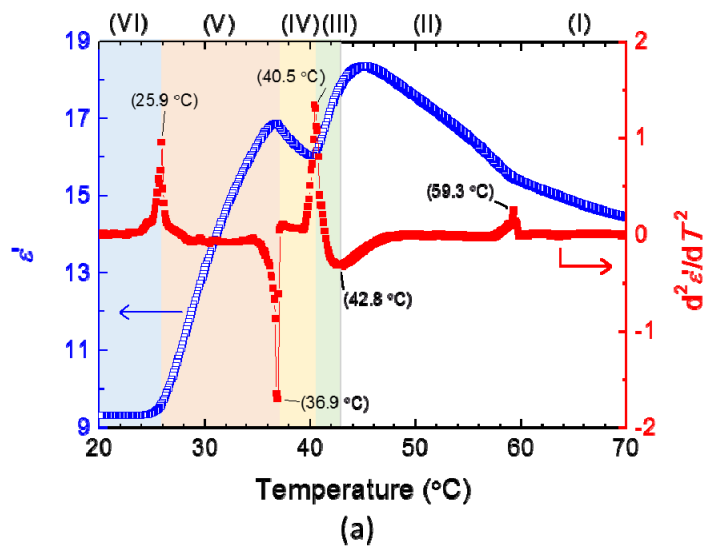
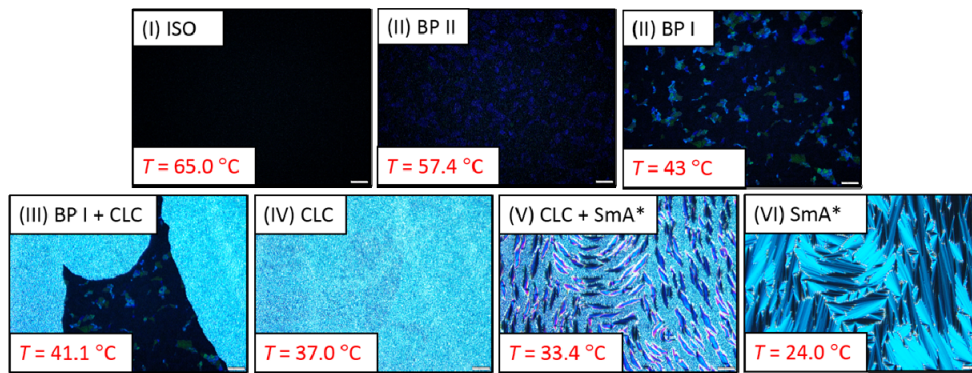


Fig. 4. Temperature-dependent dielectric permittivity and its second derivative with respect to temperature of the PS-BPLC (sample B) at  $f = 5.5$  kHz.



(a)



(b)

Fig. 5. (a) Temperature dependence of the real-part dielectric permittivity  $\epsilon'(T)$  and the second derivative of  $\epsilon'$  with respect to  $T$  at 5.5 kHz and (b) POM images at some given temperatures in various phase regions of the pristine BPLC (sample C) on the cooling process with a rate of 0.1 °C/min.

To ensure that the above-mentioned dielectric technique is nonspecific and can be applicable to identification of multimorphic phases beyond BPs, we examined another BPLC containing the left-handed chiral dopant S-811 instead of R-5011. Figure 5 shows the temperature dependence of the real-part dielectric permittivity ( $\epsilon'(T)$ ) and the second derivatives of  $\epsilon'$  with respect to  $T$  of sample C in the temperature regime between 20 and 70 °C. The helical twisting power of S-811 is much lower than that of R-5011, resulting in a higher dopant concentration of S-811 for realizing a BPLC. This leads to notable modification of the phase transition temperature and physical properties of sample C, as compared with those of samples A and B. According to the data of  $d^2\epsilon'/dT^2$  along with the POM images at specific temperatures, the phase sequence of sample C can be clearly determined, giving six temperature or phase regions: (I) Iso, (II) BP II and BP I, (III) BP I + cholesteric, (IV) cholesteric, (V) cholesteric + SmA\*, and (VI) SmA\*. The phase transition temperatures of isotropic to BP II (Iso-to-BP II) and BP I to cholesteric (BP I-to-Ch) in sample C appeared at 59.3 °C and 40.5 °C, respectively, which are much lower than those in sample A and B. Especially in region II, the BP II-to-BP I phase transition temperature in sample C cannot be confidently identified by our proposed approach whereas the BP II and BP I images are clear based on the POM observation. In view of the limitations of the measuring system, such as the signal-to-noise ratio of the LCR meter and the stability of the temperature controller, the vanished feature signaling the BP II-to-BP I phase transition in the data of  $d^2\epsilon'/dT^2$  for sample C is presumably due to the weak variation in dielectric permittivity with temperature between BP II and BP I phases that is undetectable by our instrument. Other possibilities in association with the used chiral agent and the resulting mixture are the strong temperature-dependent helical twisting power (HTP) of S-811 and the serve modification of physical properties of the BPLC mixture. It has been reported that the HTP of S-811 in a helical LC system increases with decreasing temperature [17]. This might suppress the discontinuity in  $\epsilon'(T)$  between BP I and BP II, as both of them show highly twisting helical structure. As for the further decrease in dielectric permittivity in the BPLC dominated by the high content of S-811, it is suggested that the variation of  $\epsilon'(T)$  in the BPLC with S-811 is too small for the dielectric technique to identify the signal of BP II-to-BP I phase change. As a result, our purposed dielectric approach for phase identification of BPLCs seems to have the limit on the used chiral dopant as well as its concentration in the mixture, which should be considered as a critical viewpoint for further analysis. On the other hand, the signal of cholesteric-to-SmA\* transition temperature is unambiguously detected at the temperature of 25.9 °C in sample C. It has previously been reported that the SmA\* is presented in the binary mixture containing S-811 and NLC when the dopant concentration is high enough [18]. The above-mentioned results imply that the proposed dielectric technique with high precision and reliability provides a useful pathway for determination of phase sequences of BPLC mixtures in general.

#### 4. Concluding remarks

This study investigates the phase behaviors of BPLCs by means of temperature-dependent dielectric data at a specific frequency. The temperature-dependent dielectric data reveals temperature ranges of blue phases for LC cells with and without polymer stabilization on cooling process from the isotropic phase downward. Notably, the second derivative of the real-part permittivity with respect to the temperature derived from the experimental results clearly identifies the BP II and BP I phases and their phase transition temperatures in BPLC cells investigated. Such results are in good agreement with data of POM images and transmission spectra. In view of the nature of measuring tools and experimental setups, one should keep in mind that the POM provides direct information on phase transitions only in a very limited area of the LC bulk whereas the dielectric technique enables the instantaneous and precise detection of the collective behavior during the phase transition in the whole electrode area. As such, the POM and dielectric techniques are complementary for LC phase identification. While the BPLC is emerging as one of the fascinating research topics in



academia and display industry, this work provides a feasible and precise approach for the determination of dielectric and phase properties of optically isotropic mesogens.

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