

Liquid Crystals



ISSN: 0267-8292 (Print) 1366-5855 (Online) Journal homepage: http://www.tandfonline.com/loi/tlct20

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To cite this article: Igor Gvozdovskyy (2015) 'Blue phases' of highly chiral thermotropic liquid crystals with a wide range of near-room temperature, Liquid Crystals, 42:10, 1391-1404, DOI: 10.1080/02678292.2015.1053001

To link to this article: http://dx.doi.org/10.1080/02678292.2015.1053001



Published online: 30 Jun 2015.



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'Blue phases' of highly chiral thermotropic liquid crystals with a wide range of near-room temperature

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The phase transitions of pure cholesteric liquid crystals, based on right- or left-handed chiral dopants (ChDs) (enantiomers R-811 and S-811, Merck, Darmstadt, Germany) with various concentrations dissolving in the nematic liquid crystal mixture CHCA (ZhK-805, Russia, NIOPIK) were experimentally studied. For the first time, blue phases of cholesterics were found at the concentration range of ChDs 32–36 wt.%. Experimentally it was observed that during the cooling process the blue phase of cholesterics is stable over a wide temperature range about ~15°C including human body and near-room temperatures. Thermal phase transitions, spectral characteristics and electro-optical features of blue phases were examined. Planar and homeotropic alignment layers were used to study the influence of various boundary conditions on platelet textures of blue phases.

Keywords: blue phases; cholesteric liquid crystals; chirality; phase transitions

Introduction

It is known that for certain chiral liquid crystals (CLCs) and their mixtures the transition between the regular (helical) cholesteric phase (Ch) and the isotropic phase (Iso) occurs through a series of additional transitions well known as 'blue' phases (BPs), [1–9] which in most cases can exist only for cholesterics with pitch P < 5000 Å.[5,10] Within a narrow temperature range three thermodynamically stable blue phases (BP-III, BP-II and BP-I) exist, which can be usually observed on cooling from Iso to Ch, but sometimes on heating from Ch to Iso [3,9,11] and vice versa with thermal hysteresis.[11–13]

The so-called 'fog' blue phase (BP-III) is amorphous with a local cubic lattice structure in the director field, which appears over a very narrow temperature range between BP-II and the Iso,[3,14–17] while BP-II and BP-I have a fluid three-dimensional periodic structure in the director field with simple cubic and body-centred cubic symmetry, respectively.[6–8,15,16,18] For BP-I the elementary cell (lattice) size changes with temperature; while for BP-II there is not temperature change in the lattice size.[19]

According to the theory,[19] structures of BPs can be described as 'double twist' cylinders (in which the director twists simultaneously in two independent directions), filling up large volumes and disclinations. The fact that the periods of lattices of BP-II and BP-I are of the order of the visible wavelength region, leads to the observation of the selective Bragg diffraction. In addition, BPs are optically active but, unlike Ch, they are optically isotropic and are not birefringent. [5-8,20,21]

Because of thermal stability within a very narrow temperature range (usually it is few degrees Celsius [7,8,20,21]) blue phases of pure CLCs were always difficult for experimental observations and studies. In addition, there were usage limits of threedimensional periodic structures of BP-II and BP-I (because of the selective reflection of light (Bragg diffraction)) of pure cholesterics and their mixtures for practical applications, such as displays, optical filtres and 3D lasers. Therefore, searches and creation of new classes of the CLC systems with a wide temperature range of BPs [22-44] are very important to apply these materials in different fields. In this case the fabrication of materials with certain features based on CLCs and polymers (so-called polymer-stabilised blue phase liquid crystals (PS-BPLC) [22,25-27,33]), the search of new LC molecules, such as bimesogens, [23] or the creation of BP polymer-templated nematic (BPTN) [39] are of increasing interest for different applications: solution of the storage problems, [25–27] existence of BPs at room temperature [22,23,28,29] and essential increase of BPs thermal range.[29,33,40-45] A new class of BPs of the CLCs, which are stable over a wide temperature range -16-60°C, was recently reported in, [23] that potentially opens up new possibilities for their photonic applications. It was also shown that the usage of PS-BPLCs is promising for photonics including 3D lasers, [24,30-32] tunable gratings [34] and displays.[33,35–38,44] A fast switching broad-temperature range electro-

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optical material was demonstrated in [39] for BPTN (by using available nematic LC MLC2048 and chiral dopant (ChD) S-811, further this template was filled with nematic E7). In addition, as shown in,[43,46] the doping of pure CLC CE6 (or CE8 [46]) with hydrophobic surface-treated CdSe nanoparticles can lead to an essentially stabilised BP-III (*i.e.* about 20°C) [46]). It can be useful for application especially if the usage of LCs, which have BPs close to room temperature, is needed.

However, there are articles related to BPs with a wide temperature range and a fast response time based on pure CLC mixtures without stabilisation with polymers or nanoparticles. Thermodynamically stable BPs within a wide temperature range have been created on the basis of conventional rod-like nematogen [40] or chiral nematic LCs [41,42,47] mixed with a bent-core molecules. The phase-transition behaviour of the blue phase was discussed from viewpoint of the molecular shapes [45,48] and structures (stereochemical restraints and conformations). [47] In [45] a T-shaped chiral compound was prepared, possessing a molecular biaxiality and, due to a double twist structure, formed by this compound. can stabilise BPs with a wide range of near-room temperature about 13°C during the cooling process. BPs with a wide temperature range (about 30°C) and electric-field-induced transitions for binaphthyl derivative was studied in.[48] As shown in,[49] the usage of the rod-like low-molecular weight cyano homologue chiral nematic LCs with various core groups and concentrations of ChD lead to the stable BP temperature range (more than 13.5°C) on heating and cooling and fast response (less than 1 ms). The influence of number chiral mesogenic units and spatial arrangement on BP induction and stability, by using benzene derivatives possessing various helical twisting power (HTP), was investigated in.[50] When characteristics of blue phases of the pure cholesterics, based on 5CB and OBOP compared, authors concluded that the choice and screening of nematic LCs (taking into account the thermal range of the mesophase) are also important in order to

increase the temperature ranges of BPs. In addition, the correlation between the stability of BPs and value of HTP of ChDs adding to a non-chiral bent-core LC was studied in.[51,52] As was discussed in [53] chirality (*i.e.* value of HTP) and handedness have also a key role for exhibition of BPs in hydrohen-bonded (H-bonded) LC complexes between chiral donor and achiral acceptor with further formation of dimer.

In this paper new pure CLCs, based on right- or left-handed ChDs dissolving in the thermotropic nematic liquid crystal (NLC) mixture, that have BPs within a wide temperature range during the cooling process, including near-room and human body temperatures, will be described. The detailed investigations of phase transitions, spectral characteristics of BPs, influence of the boundary conditions of substrates of the LC cell and electro-optical studies will be also conducted.

Experiment

Two non-mesogen enantiomers ZLI-3786 (R-811) and ZLI-0811 (S-811), obtained by Licrystal (Merck, Darmstadt, Germany), were used as ChDs to prepare the right-handed and left-handed CLCs, respectively. The phase diagram for ChDs is Cr 48°C Iso.[54] Right- or left-handed ChDs were dissolved at various concentrations in (1:1) the mixture of 4-n-butyl- and 4-n-hexyl-trans-cyclohexancarboxylic acids, forming hexancarboxylic acid dimers, representing thermotropic NLC CHCA (ZhK-805, Russia, NIOPIK). The temperature range of the LC phase of CHCA is -27 to +95°C and index of refraction is $n_e = 1.491$, $n_o = 1.456, \ \Delta n = 0.035 \ (\Delta n_{\rm max} = 0.053).[55,56]$ The value of the dielectric anisotropy of the nematic CHCA is $\Delta \varepsilon = + 0.17.55$ The molecular structure of ChDs and NLC are shown in Figure 1.

To observe the selective Bragg diffraction (selective reflection of the maximum wavelength of light, λ_{max}) in the visible region, concentrations of ChDs in NLC were 18, 25, 33 and 36 wt.%.



Figure 1. Molecular structures of ChDs (a): (1) – ZLI-3786 (R-811) and (2) – ZLI-0811 (S-811); and (b) nematic LC CHCA, consisting of: (3) – 4-*n*-butyl-*trans*-cyclohexancarboxylic acid and (4) – 4-*n*-hexyl-*trans*-cyclohexancarboxylic acid dimers.

Liquid Crystals 1393

In our experiments three types of LC cells were made. To record the transmission spectra of various phases the quartz substrates without any surface alignment layers were used. To investigate the influence of boundary conditions on textures of BPs, LC cells with glass substrates, covered with films for the planar or homeotropic alignment were created. In order to study electro-optical effects (EOEs) of BPs, glass substrates, covered with transparent indium tin oxide (ITO) electrodes, were used.

To obtain the planar alignment of CLCs the solution of polymer oxidianiline-polyimide (ODAPI) (Kapton synthesised by I. Gerus, Institute of Bioorganic Chemistry and Petrochemistry, NASU) was spin-coated (7000 rpm, 5 s) on glass substrates and further annealed for 90 min at temperature 240°C, as was described in.[57] Thereafter thin films were unidirectionally rubbed.

For the homeotropic alignment treatment the polyimide SE1211 (Nissan, Japan) was deposited on glass substrates by spin-coating method (3000 rpm, 30 s), and then annealed at temperature 180°C for 30 min and unidirectionally rubbed, as was described in.[58] In this case the planar alignment of CLCs with high concentrations of ChDs was also observed. It should be also noted that for non-rubbed SE1211 films the planar alignment of CLCs was also found.

The LC cells were assembled, using two substrates with opposite rubbing directions and dimensions $20 \times 15 \text{ mm}^2$. The cell thickness *d* was set to 13–30 µm by Mylar spacers and controlled by the interference method measuring the transmission spectra of empty cells.

The phase diagrams of CLCs with various concentrations of ChDs were studied for both heating and cooling of LC cells by using polarisation microscopy. The LC textures were viewed through a polarising microscope BioLar (PZO, Warszawa, Poland) equipped with a digital camera Nikon D80 (Japan). The cells with CLCs were placed in the thermostable heater, based on a temperature regulator MikRa 603 (LLD 'MikRa', Kyiv, Ukraine). The accuracy of the temperature measurement was \pm 0.1°C. Temperature was measured with a thermocouple type L (chromelcopel: *chomel* – 90% nickel and 10% chromium, *copel* – 43–44% nickel, 2–3% iron and everything else is copper). The speed of the temperature change was 0.1–0.2°C per 5 min (*i.e.* 0.02–0.04°C/min).

Transmission spectra were recorded at a constant temperature using a spectrophotometer (made at the Institute of Physics, Ukraine), based on a CCD line sensor ILX-544 B-UV (Sony, Japan). In order to avoid the scattering of light and to record further a transmission spectra (selective Bragg diffraction) of the planar texture of CLCs, the LC cell with focal conic Ch, obtained after the cooling process of the supercooled BP-I, has undergone 100 g-weight pressure with value about \sim 3300 N/m².

To demonstrate EOEs, AC voltage (f = 1 kHz) between 0 and 110 V was applied to the sample by using a frequency generator GZ-109 (Pskov Region, Russia) equipped with an amplifier (made at the Institute of Physics, Ukraine). Higher voltages were not applied to avoid dielectric breakdown of LC cells.

Results and discussion

Thermal and optical features of CLCs and their BPs

To study concentration dependencies of the cholesteric pitch *P* CLCs, based on ChD R-811 (or S-811) with various concentrations C = 18, 25, 33 and 36 wt. %, doped with NLC CHCA, were used. As can be seen from Figure 1(b) CHCA molecule is composed of two identical acids and owing to their weak interaction by the H-bond (- C = O...H – O -) can form rod-like dimers (3, 4; or combination between carboxylic acids), which can be flexible.[55]

Dependencies of λ_{max} on various concentrations of ChDs are shown in Figure 2(a). As can be seen from Figure 2(a), the increase in concentration of ChD results in a shift of λ_{max} to shorter wavelengths (so-called 'blue' shift), related to the cholesteric pitch *P* by equation:[59]

$$\lambda_{\max} = n \cdot P, \tag{1}$$

where *n* is the refractive index of NLC. The value of λ_{max} is also called the 'optical pitch'.[60] Therefore, in consideration of Equation (1), dependence of changes of $1/\lambda_{\text{max}}$ on concentration of ChD is shown in Figure 2(b). Dependencies of the reciprocal 'optical pitch' ($1/\lambda_{\text{max}}$) are linear functions of concentration of ChDs, although concentrations of ChDs in NLC CHCA are high.

Temperature dependencies of λ_{max} for ChDs with various concentrations of ChDs (R-811 or S-811) in CHCA, filling in the LC cell with glass substrates and thickness $d \approx 13 \,\mu\text{m}$, are shown in Figure 3. It is seen that on heating the sample (solid symbols) the 'blue' shift of λ_{max} was observed for all concentrations of ChDs. But in case of high concentrations of ChDs (C = 33 and 36 wt.%) the essential 'blue' shift (~ 150 nm) of λ_{max} were found. As can be seen from Figure 3, on cooling (open symbols) the 'red' shift of λ_{max} was observed.

In addition, the increasing concentration of ChDs results in a decrease of the clearing temperature T_c of CLCs. For cholesterics, containing 18 and 25 wt.% of ChDs, Ch \rightarrow Iso transitions were only observed.



Figure 2. (colour online) Dependencies of the: (a) maximum of the selective reflection λ_{max} (circle symbols) and (b) reciprocal optical pitch $1/\lambda_{max}$ (square symbols) on concentrations of ChD R-811 (solid symbols) and S-811 (open symbols) added to NLC CHCA. The calculated dependencies are depicted by dashed curves (lines).



Figure 3. (colour online) Selective reflection of maximum λ_{max} for Ch (curves 1–4) and BPs (curves 3 and 4) as a function of temperature of LC cells with thickness $d = 13 \pm 0.5 \,\mu\text{m}$, filled with CLCs, based on nematic CHCA doped by R-811 or S-811 with concentration: (1) 18 wt.%; (2) 25 wt.%; (3) 33 wt.% and (4) 36 wt.% on cooling (solid symbols) and on heating (open symbols).

Schematically, phase diagrams are shown in Figure 4 (a) and (b), respectively. The phenomenon of hysteresis of the cholesteric pitch P was observed on heating and cooling of samples.

Firstly, BPs, existing at certain temperatures between Ch and Iso, were found for CLCs, based on 32–36 wt.% of ChDs added to CHCA. Schematically, phase diagrams for both concentrations are shown in Figure 5 (a) and (b), respectively.

Thermal hysteresis is observed during the phase transition $Ch \rightarrow BPs$ and vice versa at low rates of temperature changes (*i.e.* 0.02–0.04°C/min). As can be seen from Figure 5, both Ch and BPs can exist at near-room and human body temperatures.

It was experimentally found that during the cooling, for concentration of ChDs C = 33 wt.%, the temperature range of BPs was about ~15°C, which is wider than for pure CLCs under discussion in. [3,5,17,19,39] It is obvious that in case of the highly chiral mixture, owing to flexibility of LC molecules,



Figure 4. (colour online) Schematic diagrams of transitions between Ch and Iso on heating and cooling of CLCs, containing 18 wt.% (a) and 25 wt.% (b) ChDs.



Figure 5. (colour online) Schematic diagrams of the sequence of Ch transitions on heating and cooling of CLCs, containing 33 wt.% (a) and 36 wt.% (b) ChDs. (a) During the heating process BPs exist within a temperature range $T = (39.8-41.5^{\circ}C)$; during the cooling process: BP-III within a range of $T = (41.3-41^{\circ}C)$, BP-II within a range of $T = (40.9-34.9^{\circ}C)$ and BP-I within a range of $T = (45.5-44.9^{\circ}C)$, (b) On heating BPs exist within a range of $T = (46.2-45.1^{\circ}C)$; on cooling: BP-III within a range of $T = (45.5-44.9^{\circ}C)$, BP-II within a range of $T = (44.8-42.7^{\circ}C)$ and BP-I within a range of $T (42.6-36.7^{\circ}C)$. The rates of the temperature change during the heating/cooling process were $0.04^{\circ}C/min$ and $0.02^{\circ}C/min$, respectively.

the hexancarboxylic acids molecules could easily combine with ChDs (R-811 or S-811) molecules through a relatively stronger H-bond, similarly to as was deal with in [53] for chiral donor (S)-2-fluoro-4-(2-octyloxy) benzoic acid (SFBA) and achiral acceptor 4-(4-trans-propylcyclohexyl)phenyl isonicotinate (PPI). The complex of CHCA – R-811 (or – S-811) molecules and hexancarboxylic acids dimers formed the elementary cell (lattice) of BPs, which appear due to competition between the chiral twisting force and packing topology according to.[1,7,19] It should be noted that the increasing of the concentration of ChDs (R-811 or S-811) to C = 33 wt.% leads to the increase of the chiral twisting force, which is account for widening the temperature range of BPs.

However, experimentally it was found that the increasing of the concentration ChDs to C = 36 wt. % leads to the decrease of the temperature range of BPs. On cooling of the sample the temperature range of BPs was about ~9°C, as can be seen from Figure 5 (b). As in,[53] here it can be also supposed that higher concentrations of non-mesogenic ChDs are not useful in the formation of mesophases. As can be seen from the phase diagrams, BPs can exist in a narrow concentration range of ChDs (a few weight percents).

Typical platelet textures of Iso \rightarrow BP transitions during the cooling process of CLC, based on 33 wt.% of S-811 and filled into the LC cell, assembled with quartz substrates without any alignment layers are shown in Figure 6. In this case, polydomain platelets were forming domains of a size ~50 µm. It is in a good agreement with results founded in,[19] for LC cells formed with quartz substrates without any special treatment with surfactants and filled with the mixture of cholesteryl nonanoate (CN) and cholesteryl cloride (CC) with the concentration ratio (90:10).

As shown below, any alignment treatments (planar and homeotropically alignment layers) lead to changes in a size of platelets. It was found that transmission spectra of the LC cell, prepared with quartz substrates without any alignment treatment/with planar alignment ODAPI films are alike.

The sequence changes of the transmission spectrum, when one phase changes into another for CLC, based on 33 wt.% of S-811 added to CHCA, are shown in Figure 7. Spectra were recorded by a spectrophotometer as a function of wavelength over a range of 350–800 nm, during slow cooling with rate 0.02°C/min, starting from Iso just above T_c and finishing to Chs with selective reflection in the visible region.

As can be seen from Figure 7(a) the transmission spectrum 1 in Iso is a horizontal line. The transmittance value is ~95% at temperature T = 42°C. At temperature T = 41.3°C the sample transmission spectrum 2 is changed in a range 350–530 nm. It is like the typical spectrum of the fog blue phase, observed during Iso \rightarrow BP-III transition for CN and mixtures.[1,3,17]

As mentioned, the viewing of the BP-III texture for the planar alignment of CLCs with 33 and 36-wt. % of ChDs through a polarisation microscope is difficult. Beforehand it is noted, that for homeotropic boundary conditions the texture of BP-III was welldefined. For tangential boundary conditions (Figure 8 (b)), BP-III is observed within a narrow temperature range about ~0.3°C. It should be noted that BP-II with much larger domains is often contacted with BP-III (Figure 8(c)).

Further cooling of the sample leads to BP-III \rightarrow BP-II transition. Typical microphotographs of textures for BP-II are shown in Figure 8(d), (e). By analogy with,[49] using a slow cooling rate (about 0.1°C per 30 min), large single crystals of the simple cubic BP-II (T = 40.9°C) could be observed (Figure 8 (d)). Cooling of the LC sample to T = 40.1°C results in well-defined larger domains of BP-II, as can be seen from Figure 8(e). In this case the selective reflection is observed in the blue region with $\lambda_{max} = 470$ nm. The transmission spectrum 3 of BP-II is shown in Figure 7(a).



Figure 6. Sequential phase transitions between Iso and BPs on cooling of CLC, based on 33 wt.% of S-811, dissolved in NLC CHCA. In the microphotographs: (a) Iso at 42°C; (b) BP-II together with the 'fog' phase at 41°C; (c) platelet texture of BP-II at 39.8°C; platelet textures of BP-I: (d) at 32.1°C and (e) at 27.8°C. The 30 µm LC cell, assembled with quartz substrates without any alignment layers. During the cooling process the rate of the temperature change was 0.02°C/min.



Figure 7. Transmission spectra of CLC formed with 33 wt.% of S-811 added to NLC CHCA at various values of the sample temperature. (a) Transmission spectra are corresponding to: (1) Iso at 42°C; (2) 'fog' phase (BP-III) at 41.3°C and (3) BP-II at 40.1°C. (b) Transmission spectra of BP-I at various temperatures: (4) T = 34.5°C; (5) T = 32.3°; (6) T = 31.2°C. (c) Transmission spectra of supercooled BP-I: (7) at 28.3°C; (8) after storage ~ 2 min at T = 28.3°C and (9) focal conic texture of Ch at 26.7°C. (d) Transmission spectra of the planar texture of Ch at various temperatures after a slight pressure (~3300 N/m²): (10) at 26.3°C; (11) at 25.4°C; (12) at 24.5°C; (13) at 23.7°C. LC cell was prepared with quartz substrates with the planar alignment of layers (unidirectionally rubbed ODAPI films). The rate of cooling of the sample was 0.02°C/min. Thickness of the LC cell is 30 µm. The insets depict transmission spectra in the enlarged scale.



Figure 8. Sequential phase transitions between Iso and Ch during the process of cooling of the planar aligned CLC, containing 33 wt.% of S-811. In the microphotographs: (a) Iso at 42°C; (b) BP-III at 41.3°C; (c) BP-II together with BP-III at 41°C; (d) single crystal of the simple cubic BP-II at 40.9°C for low cooling rate 0.003° C/min; (e) platelet texture of BP-II at 40.1°C; platelet textures of the body-centre cubic symmetry BP-I: (f) at 34.5°C, (g) at 32.3°C and (h) BP-I at 28.3°C; (i) supercooled BP-I together with Ch (in the centre of the photography the arrow points to the growth of the focal conic texture) at 26.7°C; (j) Ch (focal conic texture) at 26.5°C. The 30 µm LC cell is assembled with quartz substrates with the planar alignment of layers (unidirectionally rubbed thin films of ODAPI). Except (d), a cooling rate was 0.02° C/min.

With further decrease in temperature at low cooling rate (*i.e.* 0.02°C/min), λ_{max} is shifted to longer wavelengths of the visible spectrum, which results from the appearance of a new form of the blue phase (BP-I). Transmission spectra of BP-I for various temperatures are shown in Figure 7(b). On cooling of the LC sample, the decrease of temperature between values 35–31°C gives rise to sequential shifts of minima of spectra ($\lambda = 510, 523, 532$ nm), indicated with numbers 4, 5 and 6 (Figure 7(b)). Platelet textures of the body-centre cubic symmetry BP-I are shown in Figure 8 (f)–(h).

The continued cooling of BP-I to $T = 28.3^{\circ}C$ results in the appearance of a supercooled BP-I. In this case certain platelets of the texture can change into the red colour, as can be seen from Figure 8(h). At the beginning of the supercooled BP-I, due to the different orientation of planes of the cubic BP-I three minima of the transmission spectrum 7 at $\lambda \sim 410$, 510 and 610 nm were observed (Figure 7(c)). From the comparison of spectrum 7 and the similar spectrum of the mixture CN:CC with ratio (90:10),[17] obtained for BP-I (at $T = 85.97^{\circ}$ C) it can be concluded that diffraction patterns of BP-I phase is observed on [110], [200] and [211] planes. After $\sim 2 \text{ min storage}$ of the LC cell at the constant temperature $T = 28.3^{\circ}$ C, spectrum 7 transforms to 8. As can be seen from Figure 7(c), the position of the minimum of transmittance is observed in the long-wavelength diffraction line at $\lambda = 622$ nm.

When temperature reaches a value $T = 26.7^{\circ}$ C, then the supercooled BP-I changes to Ch. BP-I \rightarrow Ch transition starts from one platelet of the supercooled BP (Figure 8(i)), and after a certain time ($t \approx 3$ min) the platelet texture entirely changes to the focal conic texture (Figure 8(j)). Transmission spectrum 9 of the focal conic texture of Ch is shown in Figure 7(c). Due to the high scattering of focal conic textures of Ch the transmittance of the sample was about 55–58%. After a slight pressure of the sample (~3300 N/m²) the scattering is decreased owing to the fact that the focal conic texture changes to the planar texture of CLC. In this case, the transmittance of the sample is increased to ~ 60 – 70%, and intensity of the selective Bragg reflection is also increasing.

On further cooling of the planar texture of Ch, the maximum of Bragg reflection is shifting to the region of longer wavelengths. At temperatures 26.3°C, 25.4°C, 24.5°C and 23.7°C, transmission spectra, indicated with numbers 10–13 respectively, are shown in Figure 7(d).

In comparison with the usage of tangential boundary conditions (Figure 8), some differences of the BP transitions for the LC cell with homeotropic alignment layers were observed (Figure 9).



Figure 9. (colour online) Sequential phase transitions between Iso and Ch on cooling of CLC, based on 33 wt.% of R-811 dissolved in NLC CHCA. The 13 μ m LC cell was assembled with two glass substrates, covered with homeotropic alignment layers (SE1211). In the microphotographs: (a) Iso at 42°C; (b) 'fog' blue haze phase (BP-III) at 41.9°C; (c) texture of 'islands' of BP-III at 41.4°C. Platelet textures are observed for: (d) BP-II at 40.1°C and (e) BP-I at 28.5°C. (f) The supercooled BP-I \rightarrow Ch (focal conic texture) transition at 26.6°C. The temperature ranges of the existence of BPs: BP-III (41.9–40.2°C), BP-II (40.1– 35.6°C) and BP-I (35.5–26.8°C). During the cooling process the rate of the temperature change was 0.02°C/min.

For the homeotropically aligned treatment, the cooling of Iso ($T = 42^{\circ}$ C, Figure 9(a)) produced a well-defined BP-III (Figure 9(b), (c)), which is rather like a texture previously observed for BP of the discotic LC in.[61] It is found that the amorphous blue haze phase appears at $T = 41.9^{\circ}$ C (Figure 9(b)). The slow cooling of the sample results in the appearance of BP-III, by forming the texture of 'islands', as shown in Figure 9(c). In comparison with tangential boundary conditions, for homeotropically aligned layers BP-III exists over a sufficiently wide temperature range about ~ 1.7^{\circ}C. It should be mentioned that during the usage of tangential boundary conditions BP-III exists over a narrow temperature range about ~ 0.3^{\circ}C.

The continued cooling of BP-III leads to the appearance of BP-II (at 40.1°C) and BP-I (at 28.5°C), which usually appeared as a polycrystalline sample with fairly small domains (platelets) and weak hues of colours (blue, green, red), as shown in Figure 9(d) and (e), respectively. In addition, for homeotropically aligned conditions intensity of the Bragg diffraction peak decreases. It can be explained as deterioration of the cell orientation with respect to the incident light. Further BP-I \rightarrow Ch transition is shown in Figure 9(f).

Illumination of the polycrystalline sample with BP-I at $T = 29^{\circ}$ C, by using light-emitting diodes (LEDs) with different wavelengths in a narrow region



Figure 10. Photographs of the platelet texture of BP-I at $T = 29^{\circ}$ C and radiation spectra of different LEDs. The 19 µm LC cell with tangential boundary conditions, filled with CLC, based on 33 wt.% of S-811, during illumination of the sample by: (a) cold white LED with the radiation spectrum (e); (b) blue LED with the radiation spectrum (f) and $\lambda_{max} = 465$ nm; (c) green LED with the radiation spectrum (g) and $\lambda_{max} = 520$ nm and (d) red LED with the radiation spectrum (h) and $\lambda_{max} = 635$ nm. Illumination of the LC cell was carried out at the fixed angle 45 degrees to the plane of the sample.

of the visible spectrum (blue, green and red), leads to the selective Bragg reflection from some small domains (platelets) with the definite orientation, as can be seen from Figure 10.

EOEs of BPs

To study EOEs of BPs, the LC cell with the average thickness 30 μ m, constructed with glass substrates with ITO and rubbing ODAPI films, was used. For these studies CLC, containing 36 wt.% of R-811 in NLC CHCA, was used. EOEs were investigated at various temperatures of the existence of BPs.

At $T = 44.8^{\circ}$ C (BP-II), which is approximate to temperature of BP-III (Figure 5(b), EOE is shown in Figure 11. At the beginning U = 0 V the minimum of the transmission spectrum 1 of BP-II is at $\lambda_{\min} = 440$ nm. The increase of voltage to 80 V leads to the 'blue' shift of λ_{\min} to 434 nm (spectrum 2, Figure 11). In case, when voltage is turned off the minimum of transmittance returns to the initial state, as shown by spectrum 4 with $\lambda_{\min} \sim 443$ nm. This process is cyclic and depict in Figure 11(b). The further step-up of voltage to 90 V can result in the disappearance of the selective reflection (*i.e.* the minimum vanishes, spectrum 3), as can be seen from Figure 11(a).



Figure 11. Transmission spectra (a) of the 30 µm LC cell, filled with CLC based on 36 wt.% R-811, at a constant temperature of $T = 44.8^{\circ}$ C (BP-II) for various values of the applied voltage: (1) the initial spectrum for U = 0 V; (2) for $U_{on} = 80$ V; (3) BP-II \rightarrow BP-III transition for $U_{on} = 90$ V and (4) after switching off voltage $U_{off} = 0$ V. (b) Dependence λ_{max} of Bragg reflection on the applied voltage under switched on–switched off conditions. In each cycle, the applied voltage was changed from 0 to 80 V and further voltage was switched off.

At a constant temperature of BP-I $T = 42.6^{\circ}$ C. dependence of sequential changes of the minimum of wavelength of the transmission spectrum on step-up of the applied voltage $(\lambda_{\min} (U))$ is analogous to the previous temperature. At the beginning, when voltage is turned off (U = 0 V), the transmission spectrum 1 with $\lambda_{\min} \approx 484$ nm was observed (Figure 12). Step-up of voltage to values 80, 90 and 100 V results in successive 'blue' shifts of the minimum of the transmission spectrum of CLC to values $\lambda_{\min} \sim 460, 451$ and 446 nm, depicted by number 2, 3 and 4, respectively (Figure 12(a)). When voltage of the sample is turned off, the minimum of transmittance returns to the initial state (spectrum 5 with $\lambda_{\min} \sim 481$ nm) and the so-called 'red' shift is observed. This is a cyclic process, as shown in Figure 12(b). It should be noted that the increase of the applied voltage to values 105 V gives rise to the BP-I \rightarrow BP-III transition (spectrum 6, Figure 12(a)) with the disappearance of the selective reflection.

For BP-I at $T = 40.5^{\circ}$ C, dependence of sequential changes of λ_{\min} (U) is insignificant, as can be seen from Figure 13. At the beginning, when U = 0 V, the transmission spectrum 1 with $\lambda_{\min} \approx 495$ nm is observed. The sufficient step-up of voltage results in the small value of the 'red' shift of λ_{\min} (spectrum 2 and 3), as shown in Figure 13(a). When voltage is turned off, the spectrum 3 transforms to 4, which corresponds to the beginning of spectrum 1. This is one cycle of dependence of $\lambda_{\min}(U)$.

At the threshold value of voltage $U_{\rm on} = 110$ V, the BP-I \rightarrow Ch transition is observed. If voltage of the applied field is changed in the range about 0–100 V, then successive cyclic processes of 'red' (when voltage is switched on) and 'blue' shifts (when voltage is turned off) are observed (Figure 13(b)). The transmission spectrum 5 of Ch (at $T = 40.5^{\circ}$ C, $U_{\rm on} = 110$ V) is shown in Figure 13(a). If the electric field is turned off, no reversible 'blue' shift of $\lambda_{\rm min}$ (U) is observed. When voltage reaches 110 V, the process is not cyclic



Figure 12. (colour online) Transmission spectra (a) of the 30 μ m LC cell, filled with CLC with 36 wt.% R-811, at a constant temperature of $T = 42.6^{\circ}$ C (BP-I) for various values of the applied voltage: (1) the initial spectrum for U = 0 V; (2) for $U_{on} = 80$ V; (3) for $U_{on} = 90$ V; (4) for $U_{on} = 100$ V; (5) after switching off voltage $U_{off} = 0$ V and (6) for $U_{on} = 105$ V BP-I \rightarrow BP-III transition with the disappearance of the selective reflection was observed. (b) Dependence of the maximum wavelength of Bragg reflection on the applied voltage under switched on–switched off conditions. In each cycle, the applied voltage was changed from 0 to 100 V and further voltage was switched off.



Figure 13. (colour online) Transmission spectra (a) of the 30 μ m LC cell, filled with CLC with 36 wt.% R-811, at a constant temperature of $T = 40.5^{\circ}$ C (BP-I) for various values of the applied voltage: (1) the initial spectrum for U = 0 V; (2) for $U_{\rm on} = 80$ V; (3) for $U_{\rm on} = 100$ V; (4) after switching off voltage $U_{\rm off} = 0$ V and (5) for $U_{\rm on} = 110$ V the BP-I \rightarrow Ch transition was observed. (b) Dependence of the maximum wavelength of Bragg reflection on the applied voltage under switched on-switched off conditions. In each cycle, the applied voltage was changed from 0 to 100 V and further voltage was switched off.



Figure 14. (colour online) Dependence of minimum of the transmittance on the applied voltage (a) at the constant temperature of BPs: (1) $T = 36.5^{\circ}$ C (BP-I), (2) $T = 37.3^{\circ}$ C (BP-I), (3) $T = 40.5^{\circ}$ C (BP-I), 4) $T = 41.5^{\circ}$ C (BP-I), (5) $T = 42.6^{\circ}$ C (BP-I), (6) $T = 43.9^{\circ}$ C (BP-I) and (7) $T = 44.8^{\circ}$ C (BP-II). (b) Dependence of the threshold voltage of the transition: BP-I \rightarrow Ch (solid squares), BP-II \rightarrow BP-III (solid triangle) and BP-I \rightarrow BP-III (solid circles) on various constant temperatures of BPs. Open circle denotes a case when measurement of the threshold voltage of BP-I \rightarrow BP-III transition was not carried out to avoid the dielectric breakdown of the LC cell. The 30 µm LC cell was filled with CLC, based on 36 wt.% of R-811 dissolved in CHCA.

and Ch with λ_{max} of Bragg reflection in the green range is observed.

As can be seen for BP-I at $T = 40.5^{\circ}$ C, when voltage is raised, the 'red' shift of the λ_{max} is observed. It is noted, that for EOEs, described above for BP-I at temperatures of $T = 44.8^{\circ}$ C and 42.6° C, the 'blue' shifts are observed.

In addition, if voltage is turned off, the peak with maximum of Bragg reflection returns to its initial position but in case of BP-II (Figure 11(a)), the intensity is higher, than one at the beginning. It can be explained by the conservation of a better cell orientation after switching off voltage. For BPs-I with temperatures T = 42.6°C and 40.5°C the intensities of peaks have much of the same value, as can be seen from Figure 12(a), (spectrum 5) and Figure 13(a), (spectrum 4), respectively. The low temperature and higher viscosity of BP-I are likely to restrict the cell reorientation that results in weak changes of intensity after turning off the applied voltage.

As described by theory, [62, 63] distortion of a size and shape of the elementary cell (lattice) of BP-I and BP-II can be induced in the electric field. The shifts of Bragg reflection under switching on–switching off the applied voltage could be explained by the theory, [62-65] when the electric field is applied along the certain direction (*e.g.* [011]), then BP-I and BP-II undergo an expansion of the lattice parallel to the field; and transition between BPs can be observed under larger field strengths.

In the past it was assumed, that when the electrical field is applied to a sample with BPs, then temperature of BP could change at the small value, that is enough to observe transitions between different BPs. [66] In accordance with this assumption, the increase of voltage should lead to the weak increase in the sample temperature that will become a reason of the 'blue' shift of λ_{max} of Bragg reflection. Below two different cases will be described, one is not in a good agreement with the conclusion in [66] and should be explained by.[62–65]

The wavelength of maximum of Bragg reflection as a function of the applied voltage for different temperatures of BPs is shown in Figure 14. It is seen that dependencies $\lambda_{\min}(U)$ shows a positive slope (*i.e.* the increase of voltage gives rise to the 'red' shift of λ_{\max} of Bragg reflection) at temperatures $T = 36.5^{\circ}$ C, 37.3° C and 40.5°C, denoted by numbers 1, 2 and 3, respectively. Maximal values of the shift of the wavelength are about 5–7 nm.

For a rough analysis, let consider as an example on the one hand, the temperature dependence of the transmission spectra of BPs (Figure 7(b)) and on the other hand dependence λ_{\min} of transmittance on the applied voltage at the constant temperature of BPs (Figure 14(a)). Firstly, on cooling the change of temperature of BP from $T = 32.3^{\circ}$ C to $T = 31.2^{\circ}$ C results in the change of λ_{\min} from 525 to 532 nm, as can be seen from spectrum 5 and 6 (Figure 7(b)), respectively. Consequently, differences between maxima of wavelengths of Bragg reflection and temperatures are $|\Delta\lambda| = 7.2$ nm and $\Delta T = 1.1$ °C, respectively. Secondly, it can be seen from Figure 14(a), for BP-I at the constant temperature of T = 37.3°C (curve 2), the value of the shift λ_{max} during increasing voltage is $\Delta \lambda = 7.1$ nm. By comparing two differences between λ_{\min} , on the one hand during the change of temperature (Figure 7(b)) and on the other hand the applied voltage (Figure 14(a)) it can be concluded that the increase of the applied voltage leads to the shift of λ_{\min} as though it was the change of temperature at ΔT ~ 1°C. It is noted that dependence of $\lambda_{\min}(U)$ was carried out at the constant temperature of BPs, by using a thermostability heater with accuracy $\pm 0.1^{\circ}$ C. Thereby, it can be concluded that the increase of voltage cannot give rise to essential changes of the sample temperature till $\Delta T \sim 1^{\circ}$, in order to observe the shift of λ_{\min} on the value $\Delta \lambda = 7.1$ nm or more, as can be seen from curves 5 and 6 in Figure 14(a).

In addition as can be seen from Figure 14(b), for each constant value of temperature of BP-I ($T = 36.5^{\circ}$ C, 37.3° C and 40.5° C) the transition of BP-I \rightarrow Ch is observed under various values of voltage: 70 V, 90 V and 110 V, respectively. Therefore, for the sample with the supercooled BP-I ($T = 36.5^{\circ}$ C and 37.3° C), the transition of BP-I \rightarrow Ch is observed for a lower value of the applied voltage 70 V and 90 V, respectively, than for a sample with BP-I at $T = 40.5^{\circ}$ C.

At higher temperatures of BPs (41.5°C, 42.6°C, 43.9°C and 44.8°C), the behaviour of dependencies $\lambda_{\min}(U)$, denoted by numbers 4, 5, 6 and 7, respectively, is identical and shows a negative slope, that is directly opposite to dependencies at low temperatures. As can be seen from Figure 14(a), the increase of the applied voltage at the higher constant temperature results in the 'blue' shift of the maximum of Bragg reflection (BP-II \rightarrow BP-III or BP-I \rightarrow BP-III transitions). The maximal values of the 'blue' shifts are observed in a range 6–38 nm and depend on the sample temperature.

In addition, at each constant higher temperatures of the sample, BP-II (or BP-I) \rightarrow BP-III transitions are observed under the certain threshold value of the applied voltage, as can be seen from Figure 14(b). At $T = 44.8^{\circ}$ C the threshold value of the applied voltage to observe BP-II \rightarrow BP-III transition is ~ 90 V. The decrease of temperature of BP results in the increase of the threshold value of voltage. Thus at temperatures of 43.9°C, 42.6°C and 41.5°C the threshold value of voltage for BP-I \rightarrow BP-III transition is equal 100 V, 110 V and more than 110 V (higher voltages were not applied to avoid the dielectric breakdown of the LC cell), respectively.

From Figure 14 it can be concluded that the increase of the applied voltage to the LC cell has a mixed influence on changes of the shifts of Bragg reflection at the constant sample temperature and could be agreed with the theory in.[62–65] For example, from Figure 14 can be seen, that with increase of voltage applied to the LC cell, BPs transitions are observed at times – for higher temperature ('blue' shift of the maximum of Bragg reflection, negative slopes – curves 1, 2, 3 and 4) and at other times – for lower temperature of BPs ('red' shift, positive slopes – curves 5, 6 and 7) and does not support a key assumption to the effect that the increase of the applied voltage leads exclusively to the increase of

temperature of BPs.[66] It is obvious that obtained results need detailed studies, but they could be explained by various reasons. For instance, in the electric field the process of the unwinding ('red' shift of the maximum of Bragg reflection) and BP-I \rightarrow Ch transition are always observed with minimisation of the free energy F.[59,63] It may be supposed that the process of the winding (*i.e.* 'blue' shift) and BP-II (BP-I) \rightarrow BP-III transitions could be explained by the increasing of the flexibility of molecular complexes at the higher temperature and the usage of the electric field should lead to the change of a size and shape of the elementary lattice of BP-I and BP-II with the subsequent appearance of BP-III, which provides minimum of the free energy.[7–9,63]

Conclusion

The phase transitions of highly chiral thermotropic liquid crystals were studied. For the first time, it is found that BPs are observed at near-room temperature both on cooling and heating of the sample. In addition, the phenomenon of hysteresis of $Ch \rightarrow BPs$ \rightarrow Iso transitions was experimentally observed when temperature changes in the opposite direction. It is experimentally found that during cooling the existence of BPs has been observed in a wide temperature range about (9-15°C). This positive property can enable application of BPs in practice (for instance, for studies of colloidal particles in BPs [67] at nearroom temperature), as compared to the most wellknown pure thermotropic cholesterics and their mixtures, possessing BPs in narrow temperature ranges (0.5-2°C), that recently leaded to searches of new classes of the CLCs, possessing on the one hand, a wide temperature range of the blue phase, [40-53] in particular bimesogens, PS-BPLC or BPTN, [23,25-29,33,39] and on the other hand CLCs, having BPs at low temperatures (*i.e.* at near-room temperature).

It is found experimentally that transitions of BPs occurred for various concentrations of ChDs and for different boundary conditions at substrates of LC cells that well agree with.[19] As it was determined that the usage of homeotropically aligned layers leads to the increase of the temperature range of the existence of BP-III to about ~ 1.7° C, in comparison with tangential boundary conditions (*i.e.*, BP-III exists over a narrow temperature range about ~ 0.3° C), but spectral characteristics of the sample with BPs are better for tangential boundary conditions and vice versa.

Experimentally it was found that the size of platelets forming on cooling of Iso depends on boundary conditions of the alignment of layers. The maximal value of the platelet size ~ 50 μ m was observed for substrates without any special alignment treatment of layers. For the planar alignment of thin films the value of the platelet size was ~ 20 μ m and the minimal value was ~ 10 μ m in a case of homeotropically aligned layers.

In addition, it was shown that a very weak EOEs of BPs are observed at the high voltage. The reason is the usage of the NLC mixture with a very small value of the dielectric anisotropy.[55] Hence, in order to receive BPs with a strong EOE other nematics should be applied or non-mesomorphic dopants should be added into CHCA, that will increase the value of the dielectric anisotropy, as described in.[55]

Acknowledgements

Author I.G. thanks W. Becker (Merck) for his generous gift of chiral dopants R-811 and S-811, Prof. I. Gerus (Institute of Bio-organic Chemistry and Petrochemistry, NAS of Ukraine) for the kind provision of ODAPI polymer, Leading Researcher L. Vorobyov (Institute of Engineering Thermophysics, NAS of Ukraine) for the provision of thermocouple type L and the idea of true measurements and stabilisation of temperature, Dr. O. Shumeluk (Institute of Physics, NAS of Ukraine) for the help during EOE studies and Leading Engineer V. Chmil' (Institute of Applied Physics, NAS of Ukraine) for the technical help.

Disclosure statement

No potential conflict of interest was reported by the author.

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