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From a Chiral Molecule to Blue Phases

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Abstract

Chiral molecules play an important role in a wide range from biological structures of plants and animals to chemical systems and liquid crystal display technologies. These molecules were used in different research fields due to their opaqueness and iridescent colors changes as a function of the variation in temperature after their discovery by Lehman in 1889. The iridescent colors and different optical textures of cholesterol make it attractive for the new study field of cholesteric liquid crystals. The direction of the cholesteric liquid crystals generates a periodic helical structure depending on the chirality of molecules. This helical structure might be right or left handed configuration and it is very sensitive to the external conditions, such as chiral dopant concentration and temperature. The variation in a helical structure, which was induced by these external conditions, had a great attraction for the scientists working on the chirality in liquid crystals and their applications. This chapter will provide a general introduction not only about the chirality in nature and its application in liquid crystals, especially in blue phases but also about the trends in the stabilization of blue phases and the investigation of their electro-optical properties for advanced applications in display, photonic devices.

Keywords: chiral molecule, chirality, cholesteric liquid crystal, blue phase liquid crystal, Bragg reflection, polymer stabilization

1. Introduction

Chiral molecules play an important role in a wide range from biological structures of plants and animals to chemical systems and liquid crystal display technologies. The chiral molecules as liquid crystals in the form of cholesterol in the biological substances were discovered by the biologist Friedel in 1922 [1, 2]. After cholesterol was extracted from plants, cholesteryl esters were obtained by treating cholesterol with fatty acids and Reinitzer observed that cholesterol has two different melting points during heating from the crystalline phase or upon cooling

from the isotropic liquid [3]. The cholesteryl esters were examined with the help of a polarizing optical microscope by chemist Reinitzer in 1888 [3], biologists Planer in 1861 [4] and physicist Lehman in 1889 [5] and they noticed that these esters showed an opaqueness and iridescent colors with the changes in temperature. Therefore, the structure and optical behavior of cholesterol were explained with the contribution of biologist, physicist, chemist and the iridescent colors and different optical textures of cholesterol make it attractive for the new study field of cholesteric liquid crystals. The cholesteric liquid crystals are generally derivatives of the cholesterol which exhibit in organic compounds of elongated molecules (like nematic liquid crystal) without mirror symmetry [6–8]. They can be formed using pure chiral compounds or the mixture of the chiral and achiral compounds [9–13]. The direction of the cholesteric liquid crystals generates a periodic helical structure depending on the chirality of molecules. This helical structure might be right or left handed configuration and it is very sensitive to the external conditions, such as chiral dopant concentration and temperature [14]. The variation in a helical structure, which was induced by these external conditions, had a great attraction for the scientists working on the chirality in liquid crystals and their applications.

Moreover, recent studies showed that the reduction of the pitch of the helical structure of the cholesteric liquid crystal by adding chiral dopants generates different phases, such as blue phase [15, 16]. Blue phases are mesophases with double-twisted cylinders of cholesteric liquid crystals and they come into existence in a self-organized three-dimensional (3D) structures in the narrow temperature range between the cholesteric and isotropic phases [3–17]. Recent studies showed the trends in the stabilization of blue phase in order to expand its narrow temperature range using different stabilization methods, such as photopolymerization [18–22], nanoparticles doping [23–27], polymer-modified carbon nanotubes (CNTs) [28, 29]. Specifically, the temperature range of blue phase was broadened up to 60 K by using a polymerized polymer network, called as the polymer-stabilized blue phase (PSBP) [18] whereas blue phase was stabilized over a range of about 50°C by using a mixture nematic bimesogenic liquid crystals [30]. Furthermore, blue phase has some advantageous in the display applications due to its outstanding electro-optical properties. Blue phases have field-induced birefringence (Kerr effect) and their response time is in the level of submillisecond. Additionally, blue phases do not need any surface modification which leads simplicity in the fabrication process and they have wide and symmetric viewing angle.

This chapter will be focused on the stabilization and electro-optical properties of blue phases and their potentials for advanced applications in display as well as photonic devices [18–22, 31, 32]. The chapter concludes with the studies related to the recent novel studies on the encapsulation of blue phases [33], the stabilization of the encapsulated blue phases [34] and polymerization-induced polymer-stabilized blue phase [35–37].

2. Cholesteric liquid crystals

2.1. Chirality

The word of chirality originates from Greek as a meaning of hand and chirality was discovered by Lord Kelvin in 1894 [38]. It was described as a property of a molecule that cannot be

superimposed over its own mirror image. The main feature that gives rise to chirality at a molecular scale is the presence of an asymmetric ally handed carbon atom. A chiral molecule typically has a carbon atom in the center of the molecule surrounded by four different substituents and these molecules cannot be transformed into their mirror image by rotations [39–41]. Moreover, all these different groups are not in the same plane, although the positions of these groups form the corners of a tetrahedron with a central carbon atom (**Figure 1**). The configuration of these molecules can be classified into two different group, such as 'R' (for Latin rectus, right) or 'S' (for Latin sinister, left). In that case, handedness can be defined as right hand or left hand for a chiral molecule [42]. In order to define handedness of the molecule, the four groups are arranged in a priority list. Groups with the higher atomic number take precedence of the groups of lower atomic number. Each chiral center is labeled as R or S related to the priority of the substituents of the molecule based on their atomic numbers. To determine the handedness of the molecule, first the chiral center is determined according to the lowest priority of the four substituents. If the priority of the other three substituents decreases in clockwise direction, it is called R (right handed), if it decreases in counterclockwise direction, it is called S (left handed). **Table 1** summarizes a list for the enantiomers of chiral materials. Moreover, an enantiomer can be named by its ability to rotate the plane of plane-polarized light (+/–). The enantiomer is labeled (+), if it rotates light in a clockwise direction. If it rotates the light counterclockwise direction, it is labeled as (–). Liquid crystals may have multiple chiral centers with handedness and configuration. Moreover, the chirality of atoms can be detected by optical experiments [43], which shows that the broken mirror symmetry in stable atoms as a function of absorption of light.

Chiral molecules may give rise to an intrinsic helical structure of the director in liquid crystals inducing chirality [44–49]. The liquid crystal state is a mesophase between solid and liquid which is characterized by the alignment of rod-like molecules which has two aromatic rings

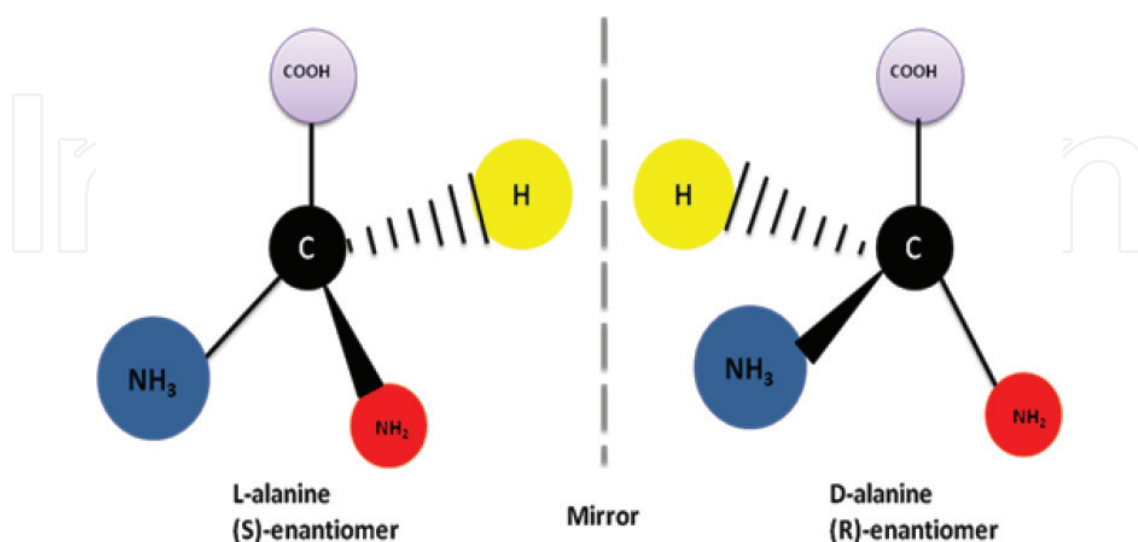
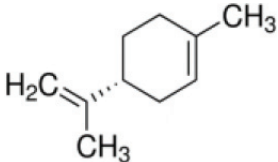
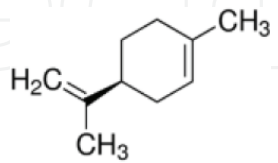
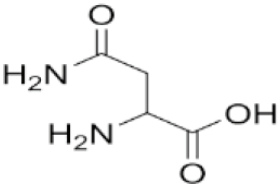
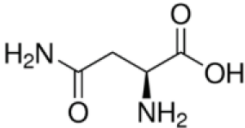
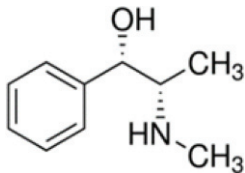
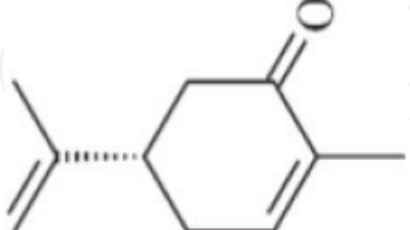
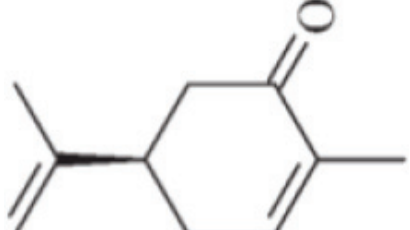


Figure 1. Simulation of a chiral molecule which cannot be superimposed with its mirror image [53].

Name of an enantiomer	Chemical structure of an enantiomer	Properties of enantiomers
(R) Limonene		Orange smell
(S) Limonene		Lemon smell
(S) Asparagine		Sweet taste
(R) Asparagine		Bitter taste
Pseudoephedrine		Active ingredients in over-the-counter nasal decongestants
(S) Carvone		Caraway flavor
(R) Carvone		Spearmint flavor

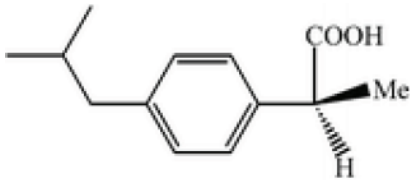
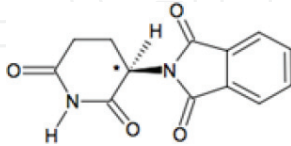
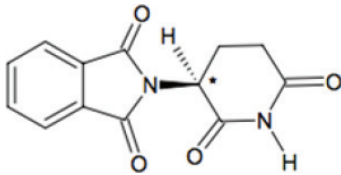
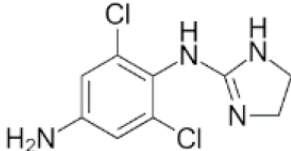
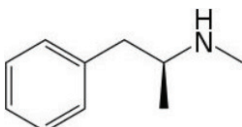
Name of an enantiomer	Chemical structure of an enantiomer	Properties of enantiomers
(S) Ibuprofen		The over-the-counter painkiller
(R) Thalidomid		Sedative and antinausea
(S) Thalidomid		Teratogen
Cloramphenicol		It is an antibiotic and it works to treat serious infections induced by certain bacteria
Levomethamphetamine		Active ingredients in over-the-counter nasal decongestants

Table 1. Enantiomers and their properties.

with the aliphatic chains. These rod-like shaped molecules are usually formed liquid crystal materials by aligning along a certain direction and this certain direction forms a helical structure with the addition of chiral molecules. In that case, the liquid crystal phase is called chiral nematic (cholesteric) phase which is one of the several additional phases in the temperature range between the crystalline and the isotropic liquid state (**Figure 2**). Moreover, chirality can be induced in smectic and columnar phases which are a quasi-long range positional order in less than three dimensions. In contrast to thermotropic liquid crystals, chiral columnar liquid crystals are formed by amphiphilic molecules in lyotropic liquid crystals. However, these amphiphilic molecules can be arranged in an anisotropic structure as in thermotropic liquid crystals, when the concentration of these molecules in a solvent is enough. Recently, Takezoe et al. induced a molecular chirality in the bent-core molecules which do not have molecular handednesses. They successfully induced a chirality in these achiral molecules based on the packing of the bent-core molecules [15, 17].

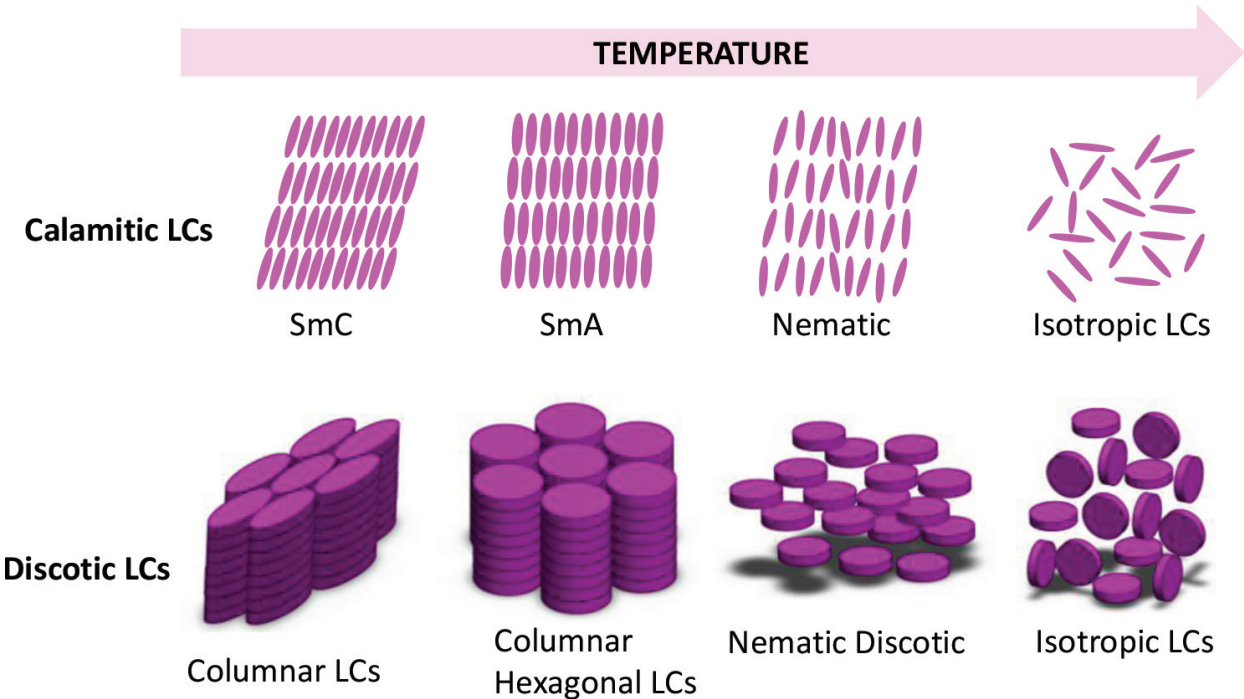


Figure 2. Phase sequence in thermotropic liquid crystals.

2.2. Cholesteric liquid crystals

The cholesteric phase is a mesophase which exhibits between the smectic and isotropic phases in thermotropic liquid crystals. Chiral nematic liquid crystals are a type of liquid crystal which has a helical structure based on the molecular chirality of its components (Figure 3). This phase can be formed using the chiral dopants in an achiral nematic forms new chiral materials with specific helical pitches (Figure 4) [50–52].

Cholesteric liquid crystals arrange within layer without any positional ordering in the layer whereas the director axis rotates with the layers as shown in Figure 5. The rotation of the director axis is periodic and its full rotation of 360° is called the pitch, p. The value of the pitch may change as a function of enantiomeric excess in an ideal mixture containing chiral and racemic.

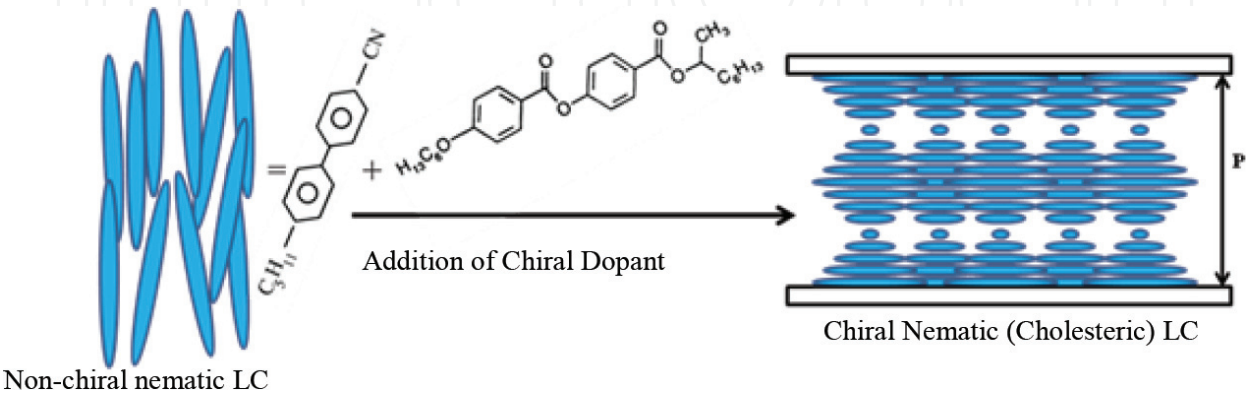


Figure 3. Simulation of formation of the helical structure of a chiral nematic (cholesteric) phase.

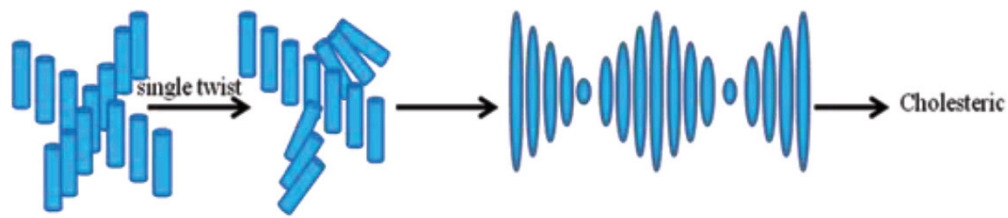


Figure 4. Formation of helical chiral nematic phase using chiral dopant.

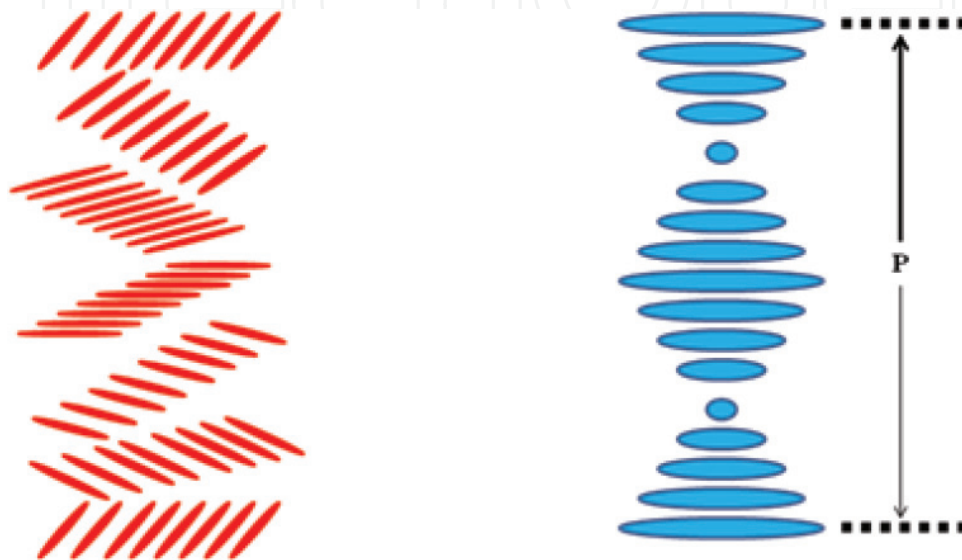


Figure 5. An illustration of cholesteric liquid crystal with a pitch p . Pitch plays an important role in the reflection of the wavelength of the incident light, as a result of the periodic structure of cholesteric liquid crystals [53].

Pitch plays an important role in the reflection of the wavelength of the incident light, as a result of the periodic structure of cholesteric liquid crystals [53]. Cholesteric liquid crystals have the ability to reflect a handedness of circularly polarized light when the pitch has the same wavelength of visible light [53]. The light will be circularly reflected if it is the same handedness as that of the cholesteric liquid crystal, whereas it will be circularly transmitted with opposite handedness as that of the cholesteric liquid crystal [44]. This selective reflection of circularly polarized light exhibits an iridescent color depending on the angular deviation. This property of selective refraction may practically be used in the application of liquid crystals, such as thermometers, polarizing mirrors, refractive electro-optic displays and optical storage [53–58].

Furthermore, chirality in liquid crystals can be described related to inverse of the pitch of the material and a shorter helical pitch has a higher chirality. The normalized reciprocal of the pitch (p^{-1}) is described as the helical twisting power (HTP) of a molecule and it can be defined as the chiral dopant's ability to induce helicity in the molecule [17].

$$HTP = 1/c * p \quad (1)$$

where p is helical pitch in microns and c is concentration of chiral dopant in the cholesteric liquid crystal mixture.

However, q_0 is the pitch in the ground state given by Eq. (2) and it is induced in nematic liquid crystal where there are long-range distortions

$$q_0 = 2\pi/p \quad (2)$$

and the pitch introduces in a scalar quantity of the free energy of cholesteric phases [44]:

$$F = \frac{1}{2} \left[K_{11}(\nabla \cdot n)^2 + K_{22}(n \cdot \nabla \times n + q_0)^2 + K_{33}(n \times \nabla \times n)^2 \right] \quad (3)$$

where n is the director, K_{11} is splay elastic constant, K_{22} twist elastic constant and K_{33} is bend elastic constant. When the chirality of a material is high enough, in other words the pitch of the molecule is around 100 nm, another phase becomes energetically favorable, which is called blue phase with self-organized three-dimensional double twist structure [17].

3. Blue phases

Blue phases were first observed in 1888 by Reinitzer who noticed a brief hazy blue color that exhibited in the narrow temperature range between the chiral nematic (cholesteric) and the isotropic phases [17]. Blue phases are locally isotropic fluids. Moreover, the molecules are self-organized and complex three-dimensional (3D) structures and characterized by crystallographic space group symmetry in this kind of liquid crystal phase. The blue phases are generated by double-twisted cylinders separated by defect lines (**Figure 6**). Effectively, blue phase is classified by the network of the defect line and three network states are known as BPI, II and III as a function of increasing temperature. The Bravais lattice is body-centered and simple cubic for BPI and BP II, respectively, as shown in **Figure 7** [59]. The BPI and BP II have soft, frequently coagulating platelet-small domains in a size of micrometer to submillimeter. The lattice constant which is around 100 nm depends on the radius of double-twisted helix and photonic band. This constant is mostly in the blue wavelength range and has the same order of magnitude as the cholesteric pitch. Additionally, the BP III is called 'blue fog' since it has a cloudy and an amorphous appearance.

Moreover, Bragg scattering of BP which is the characteristics of the selective reflections of BPs have been comprehensively investigated since 1980 [59, 60]. Because of the exhibition of the BPs in a narrow temperature range, studies on BPs have been a challenge to the experimentalists

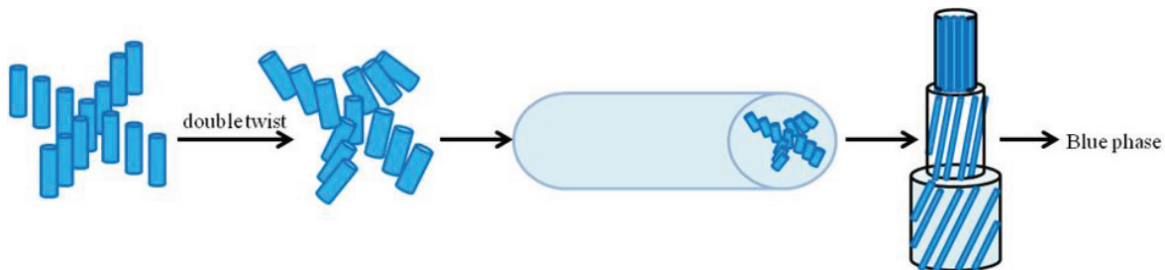


Figure 6. The simulation of a double twist cylinder structure of blue phase.

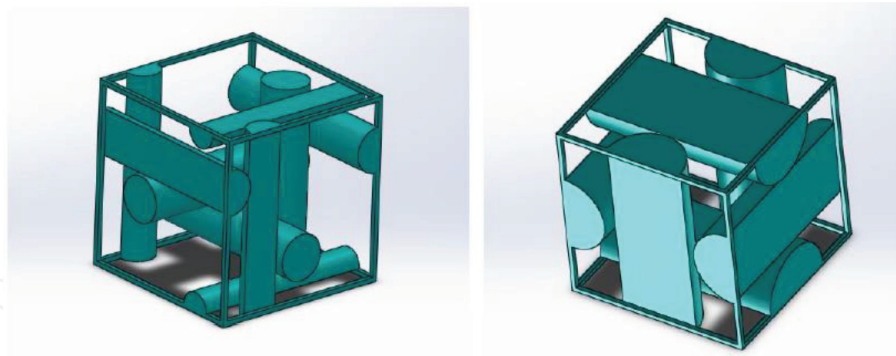


Figure 7. Blue phase structures in (a) BPI and (b) BPII.

[61, 62]. Recently, it became possible to observe BPs in wide temperature range via the stabilization method. The thermodynamic stability of BPs which were composed of chiral nematic liquid crystal with a low chirality have been predicted using Landau theory [63] and it was proved that the instability of cholesteric phase increases at the temperature near the transition point depending on the increment in the planar helix structure. Alternatively, the temperature of the blue phase liquid crystal can be determined by the help of Meiboom's defect model depending on the Oseen-Frank elasticity equation [64]. The presence of the defect lines is essential for entity of the lattice structure in blue phase liquid crystals and the energy cost of the defects should be low enough to stabilize the entire phase for narrow range temperatures. Moreover, the free energy per unit length for the disclination line in BPs can be described as in Eq. (4):

$$F_{\text{discl}} = F_{\text{core}} + F_{\text{int}}F_{\text{surf}} + F_{\text{el}}, \quad (4)$$

where F_{discl} is the total free energy per unit length of the disclination, F_{el} is the elastic energy related the defect, F_{surf} is the free energy at the disclination surface and F_{int} is the energy related to melting of area to the isotropic core. For blue phase double-twist cylinder lattices, the free energy calculations of Meiboom et al. comprise F_{core} as the only temperature-dependent term:

$$F_{\text{core}} = \alpha(T_{\text{iso}} - T) \pi R_o^2 \quad (5)$$

where T_{iso} is the isotropic transition temperature, R_o is the defect core radius size and the difference in free energies of the isotropic and ordered phases at temperature T is represented by $\alpha(T_{\text{iso}} - T)$.

The surface energy at the interface between core and cholesteric is characterized by a surface tension, σ (Eq. (6));

$$F_{\text{interface}} = 2\sigma\pi R_o \quad (6)$$

F_{surf} can be turned into a surface integral and it is negligible and ignored, since surface terms do not scale competitively with the bulk terms. In that case the interior surface of the

disclination must be taken into consideration and the solution covers the energy per unit length of the disclination line (Eq. (7)):

$$F_{\text{surf}} = -\pi(K_{22} + K_{24}) = -\pi K \quad (7)$$

F_{el} is the elastic energy where K is the elastic constant and R_{max} is the radius of the double twist cylinder and R_0 is the defect core radius.

$$F_{\text{el}} = \frac{1}{4} \pi K l n \left(\frac{R_{\text{max}}}{R_0} \right) \quad (8)$$

According to Eq. (8), one parameter in this equation must minimize the energy of cost of the disclination line in BPs to expand the BP temperature range. It is expected to move the isotropic particles, such as nanoparticles or monomers, towards isotropic areas of liquid crystals in order to minimize the core energy. The addition of these nanoparticles into an isotropic phase of sample and cooling to the BP give rise to an aggregation of these nanoparticles in the defect lines. These nanoparticles will interrupt any inclination towards orientational order inside the core when temperatures decreased into the blue phase. However, the surface energy at the interface between core and cholesteric was assumed zero during the energy minimization of the system [53].

3.1. Stabilization of blue phases

Blue phase liquid crystals have a great potential for various applications due to their electro-optical properties, such as fast response time, wide and symmetric viewing angle and lack of requirement of any surface alignment layer. However, BPs have limited usage in the practical applications because of their narrow temperature range [18, 65, 66]. Recently, two independently reported methods to expand the BP temperature range have a great attraction to blue phase materials, which have become a hot topic of comprehensive research in exploiting applications in new optics, photonics and information displays based on the outstanding electro-optical properties of BPLCs. The first reported approach uses a tiny amount of monomer for polymerization and it has been reported polymer stabilization which helps to expand the BP temperature range to more than 60 K including room temperature with an ultrafast response time [18]. Kikuchi et al. [67–69] developed a technique to extent the BP temperature range with a polymerized polymer network, denoted as the polymer-stabilized blue phase (PSBP). The synchrotron small angle X-ray scattering measurements exhibited that polymers are selectively concentrated in the disclination cores and a remarkably unique accumulation structure in the PSBP [70]. This result evidently conforms the mechanism of the stabilizing effect of BPI originating from the immobilization of the disclination in the blue phase by polymers. The first method proposed that the polymer network which is concentrated not only in the isotropic defect core but also in the disclination core of BP causes an increment in the temperature range of BP. Therefore, cross-linked network of the polymer which was produced by the process of in-situ polymerization blocked the molecular reorientation of liquid crystal directors [18]. The latter approach reported the usage of the nematic bimesogenic liquid crystal mixtures to stabilize the defect structures in the blue phase. This method provided a

successfully polymerization of BPs in a wide temperature range [71] which is more than 50°C [30]. Recently, Coles' group reported a study about the stabilization benefitted from the flexoelectric coupling between polar order and curvature of the director. Unfortunately, the report does not address the question of whether BPI appears at 16.5°C on heating from the smectic phase. Therefore, thermodynamic stability of BPI were not clearly indicated [53, 72, 73].

Alternatively, Yoshizawa et al. [74] successfully manage to extent the temperature range of the BPs more than 10°C using chiral T-shaped compounds. Yelamaggad et al. [75] were able to stabilize the BP more than 20°C using chemically linked bent core molecules.

Wang et al. [76] both introduced BPs in a wide temperature range using ZnS nanoparticles and showed the stability of the cubic structures against the electrical field. Recent studies on BPs with an broadened temperature range make them more attractive for applications because of some specific electro-optical (E-O) properties of BPs, such as fast response time [31], wide viewing angle and also any surface treatments are not necessary for the BPs. Moreover, Kemiklioglu et al. stabilized the cholesteric blue phases using polymerizable silicon-based nanoparticles to expand the temperature range of BPS. They showed that these polymerizable nanoparticles help to modify the interfacial properties of disclination cores broadening the blue phase temperature range and also the polymer concentration plays an important role in the thermodynamic stability of modulated liquid crystal blue phases. They also reported inorganic polymer leads to significant reduction in the switching voltage from about 140 to 40 V in corresponding device as a result of the low surface energy property of the inorganic polymers [72, 73, 77, 20].

3.2. Carbon nanotubes doping for the stabilization of blue phases

Nanoparticles [63, 64, 30, 72, 73] and polymer-modified carbon nanotubes (CNTs) [67] are emerging as new classes of nanoscaled materials and have become the subjects of extensive research because of their potential in improving the mechanical, electrical and thermal features of composite materials. Recently, with new approaches, such as doping MgO [68], ZnS [69] and CNTs into LCs, it has been possible to overcome the limitations of the transition temperature range and physical properties of LCs [53].

Carbon nanotubes are not only anisotropic but also metallic or semiconducting nanoparticles based on the diameter and helicity of the carbon rings [78]. Moreover, they categorized into two different morphologies namely, single-wall carbon nanotubes (SWCNTs) and multi-wall carbon nanotubes (MWCNTs). Moreover, the typical length of SWCNT which changes from submicron to microns is an important parameter for the determination of tensile strength of SWCNTs since they show exceptional tensile strength depending on their high aspect ratio and rigidity. In addition, the diameter in the range from 0.5 to 2 nm leads a high aspect ratio of tubes [53, 79]. Besides, MWCNTs show the similar electronic behaviors with those of SWCNTs due to weak coupling between cylinders of them.

Carbon nanotubes have become an important research topic for the liquid crystal scientists after their discovery by Iijima in 1991 [80] because of the extraordinary electrical properties and strong interactions of the CNTs with the mesogenic units of liquid crystals [81]. Recently, different groups have reported studies on the alignment and characterization of CNTs in

nematic liquid crystals [82–86] as well as on the dielectric [87–89] and electro-optical properties [90, 91] of CNTs [93]. Different textures of CNTs were observed when the nematic LC droplets were embedded in a polymer matrix medium [53, 80, 92]. However, carbon nanotubes have been studied in blue phase liquid crystals to expand the temperature range of the blue phases depending on thermal stability of carbon nanotubes. Another group studied CNT-doped polymer-stabilized blue phase (PSBP) LC. The CNT-doped PSBP mixtures exhibit a good thermal stability in a wide BP temperature range which is more than 40°C. They reported that BP temperature range and electro-optical properties, such as Kerr constant, switching voltages and response times of the PSBP LCs were able to improved when a mixture of monomer and BPLCs doped with CNT [93].

Moreover, the electro-optical behaviors of liquid crystals were studied as a function of the addition of carbon nanotubes. Several liquid crystal textures were observed in the CNT-doped liquid crystal mixture based on the field-induced movement of CNTs inside nematic liquid crystal by applying a high electric field [94–96]. Furthermore, it has also been demonstrated that the rising time of CNT-doped nematic liquid crystals leads a decrement in the threshold voltage both of the twisted nematic and in-plane switching cells with the dispersion of a very small concentration of CNT dopant [90, 91, 97, 98]. The addition of CNTs in the optical controlled birefringence cells lead to a fast response time due to the increment in anchoring energy of the alignment layer by CNT doping [53, 99].

3.3. Polymer stabilization of blue phases

Although BPLCs have the potential for various applications because of their electro-optical properties, such as fast response time, wide and symmetric viewing angle, the narrow temperature range of BPs is still one of the main limitations for their practical applications [18, 65, 66]. Therefore, stabilization of blue phase (PSBP) liquid crystals via polymerization have been studied commonly for two decades [18, 19, 32, 100–105] because of their great potential for use in display devices or as an optical modulator.

Recently, many studies on the increment in the BP temperature range via polymer stabilization methods have drawn attention to blue phase materials, which have thereafter become a subject of extensive research in exploiting applications in new optics, photonics and information displays because of the outstanding electro-optical properties of BPLCs [53]. One of these studies include a method which uses a small amount of polymer for polymerization that is phase-separated to the defects of the blue phase based on the concept of the polymer-stabilized liquid crystal the orientation of liquid crystal directors can be stabilized by a crosslinked network dispersed in a liquid crystal [18]. Moreover, the polymer network plays a fundamental role in the increment of temperature range, causing the thermodynamic stabilization of BP [18, 19, 32, 100]. Furthermore, another study explored that the stabilization of cholesteric blue phases using polymerizable silicon-based nanoparticles to modify the interfacial properties of disclination cores and broaden the blue phase temperature range. This study showed that the polymer concentration has an important effect on the thermodynamic stability behaviors of modulated liquid crystal blue phases. There was a significant reduction in the switching voltage of the device as a result of the low surface energy property of the inorganic polymer used in the

experiments. This low surface energy leads a significant decrement in the switching voltage from 140 to 40 V [19, 20, 72, 73]. The significant reduction in the switching voltage and widening of blue phase temperature range are useful for new electro-optical applications [22, 53]. Besides, Coles et al. reported that they managed to expand the blue phase temperature range to over 50°C by using the nematic bimesogenic liquid crystal mixtures to stabilize the defect structures of the blue phase [30]. However, a three-dimensional polymer network is formed by the reaction of benzoyl radicals with the double bonds of the diacrylate monomer through a chain reaction [53, 101]. Furthermore, molecular mobility of the network polymers obtained in the PSBP affects the stability of PSBP [53, 102]. Additionally, the electro-optic properties can be improved due to the variation of the flexibility of the molecule, the length of the rigid core and the polymerizable functional group of reactive monomer [53, 103]. All these studies showed that either thermally polymerizable [101] or photopolymerizable [18, 19, 32, 100–105] monomers can be used in the polymer stabilization of BP liquid crystals and PSBP liquid crystals have some advantages [31, 104–111]. PSBP liquid crystals become an attractive material as a next generation display technology [109–111] since, these materials have submillisecond response time, and wide viewing angle and also they do not need any surface alignment [53]. On the other hand, high operating voltage, and a low-contrast ratio due to residual birefringence and hysteresis [107, 108] are some disadvantages of PSBP liquid crystals which limits the wide-spread applications of them. There are two common approaches in order to overcome the issue of high operating voltage, there are two common approaches. One of these approaches is using a small electrode gap to produce a strong electric field [53, 110, 111]. The second approach is electric-field-induced birefringence known as the Kerr effect [53, 71]. Kerr effect is an electro-optical behavior of blue phases. Blue phase liquid crystals not have birefringence in the absence of the electric field and Kerr effect can be explained as the induced birefringence occurrence in the presence of the electrical field. PSBP liquid crystal with large Kerr constant was reported by Kikuchi et al. [107] and Wu et al. [111, 112–114]. Kerr effect can be calculated using Eq. (9)

$$\Delta n(E) = \lambda K E^2 \quad (9)$$

where K is the Kerr constant, λ is the probe wavelength, and $E (= V/l$, where V is the applied voltage and l is the distance between electrodes) is the applied electric field. Induced birefringence is linearly proportional to E^2 , where E is the electric field and this linear relationship is valid only in the low field region [53, 111, 112].

3.4. Polymer dispersion of blue phases

Polymer-dispersed liquid crystals (PDLCs) have become the topic of considerable interest during the last decades, because of their potential applications such a smart windows, flexible displays, projection displays and holographic gratings [115–119]. The PDLC films have been widely studied as a candidate for the large area display because of the simplification of the preparation process and because their light transmittance is higher than conventional LCs in the absence of polarizer by the reason of their light scattering nature [120–126]. PDLC films are a mixed phase of micron-sized liquid crystal droplets, which are randomly dispersed inside a polymer matrix [127]. In general, the polymer weight concentration is between 30 and 60%

[127]. However, it was known four different methods for the fabrication of PDLCs. The first one of these four methods is encapsulation (emulsification) which includes the liquid crystal inside an aqueous solution of film-forming polymer. The second one is called the solvent-induced phase separation (SIPS) which is used to dissolve the liquid crystal and thermoplastic polymer and forms a single phase by evaporating the solvent at a certain rate. The third method is known as thermally induced phase separation (TIPS) which includes the heating of the liquid crystal and thermoplastic polymer to obtain a single phase. After heating procedure, the liquid crystal phase separates into droplets with the cooling of mixture at a controlled rate. The fourth method is polymerization-induced phase separation (PIPS). This method contains the liquid crystal that is dissolved into the monomer [93] and uses ultraviolet radiation to initiate the free radical polymerization of monomers [127]. One of the main advantages of this method is the possibility to form a composite directly between two glass substrates coated with indium-tin-oxide (ITO) without any requirement of laminating procedure. The above methods produce a wide size distribution of liquid crystal domain size [127]. PDLCs are operated based on the micron-sized LC droplet dispersion inside the polymer matrix and the scattering performance of the PDLC film is determined by the LC droplet size. The operation principle of the PDLC films—electrically switchable between light scattering and transparent states or vice versa depends on the refractive indices matching between guest and host materials [128, 129]. The PDLC films normally seems milky since the randomly orientation of LC molecules inside the droplets causes a scattered light at zero voltage. As a function of an applying a voltage across the PDLC film, the LC directors align in the direction parallel to the applied field. Due to matching in indices of refraction between polymer and liquid crystal molecules under the electric field, PDLC film becomes transparent at normal viewing direction. Additionally, H-PDLC, which is the another type of PDLC, includes liquid crystal droplets smaller than that of PDLC [130] and they are staged in varying planes in accordance with the polymer. There are two modes of H-PDLCs, which are called transmissive and reflective. In the transmissive mode, diffraction occurs by an applying voltage and light is reflected in the absence of electric field. In the reflective mode, light is reflected in the absence of electric field, with the applying voltage it transmits through the display.

Polymer-dispersed liquid crystals (PDLCs) which are a class of important electro-optical (E-O) materials comprise of dispersions of micron-sized LC droplets inside a polymer matrix which were discovered by Fergason [127, 130]. The PDLC films were fabricated by using different methods, such as solvent evaporation, thermal induction or polymerization-induced phase separation [131]. The first method used in the preparation of PDLC films is the encapsulation (emulsification) of the liquid crystal inside an aqueous solution of film-forming polymer [130]. After water evaporated at a certain rate to induce phase separation, the film is laminated between two conductive electrode coated substrates. The second method which is called the solvent-induced phase separation (SIPS) includes solvent which is used to dissolve the liquid crystal and thermoplastic polymer and create a single phase. The certain solvent evaporation rate induces the phase separation. The third method is the thermally induced phase separation (TIPS). This method uses liquid crystal and thermoplastic polymer. These two phases are heated to obtain a melting and then mixed to form a single phase. Liquid crystal phase separates into droplets with cooling of the mixture at a controlled rate. The fourth method is

known as polymerization-induced phase separation (PIPS) containing the liquid crystal, monomer and a small amount of catalyst. After exposing the prepolymer mixture to an external stimulus, for example, light or heat, the monomer gels into a polymer matrix and liquid crystal phase separates into droplets.

The operation principle of the PDLC films based on the electrical switching between light scattering and transparent states due to index matching between guest and host materials [115, 132, 127]. The PDLC films normally appear milky and scatter incident ambient light because the LC molecules orient randomly inside of the droplets in the absence of voltage. With the applying a voltage across the PDLC film, the LC directors align in the direction parallel to the applied field. As a result of index matching between polymer and LC molecules in the presence of the electric field, the PDLC film becomes transparent when viewed along the normal direction. These PDLC films have significant advantages for electro-optical device applications, since PDLCs do not require any polarizers also PDLCs have the property of high light transmittance [127]. A number of reports have appeared recently suggested application areas for PDLCs ranging from switchable light modulators [71, 133], smart windows [127], information displays [134] and holographically formed optical elements and devices [127–135].

The electro-optic properties of PDLC devices, such as displays and smart windows can be improved by using BPLCs. The polymer dispersed or encapsulated blue phase liquid crystal films have many advantages when compared to that of polymer dispersed or encapsulated nematic liquid crystals [33–35, 53]. One of these advantages of BPLCs is field-induced birefringence due to their submillisecond response time, which is at least one order of magnitude faster than the present nematic LC-based displays [53]. BPLCs do not require any surface alignment layer; thus, the device fabrication process is greatly simplified [53]. Another significant advantage of BPLCs is their wide and symmetric viewing angle due to the fact that their 'voltage off' state is optically isotropic and the 'voltage on' state forms multidomain structures [53, 108, 109]. Moreover, BPLC can be a substantial candidate for polymer encapsulated LC films due to their fast switching properties [53]. Due to all these advantages of BPLCs, polymer encapsulated blue phase liquid crystal films are a strong candidate for the next generation of displays and spatial light modulators due to their optical properties [22, 31, 32] and also these films have potential for advanced applications in displays and photonic devices [53].

3.5. Polymer encapsulated blue phase liquid crystals

Encapsulation is one of the major methods used in the fabrication of PDLC films [53]. This method includes emulsion-based PDLC films which are formed of small liquid crystal droplets inside the aqueous solution of water soluble polymer [136, 137] or a colloidal suspension of a water insoluble polymer [130, 138]. Moreover, the energy is required to form the encapsulated droplets. This required energy which generally arises from the chemical potential of components or from mechanical devices break-up the droplets. The emulsion system is obtained by high shear; for example, by ultrasonication or high-pressure homogenizers and the rate of solidification and polymer solubility play a role in the yield. Microspheres formed by rapid solidification of the polymer may give a higher yield due to encapsulation of some of the soluble fractions in the matrix [53, 140, 141]. Besides, the emulsion is coated on a conductive

substrate before allowing the water to evaporate to produce thin polymer films containing liquid crystal droplets dispersed in a matrix. Evaporation process is one of the key factors for the droplet shape deformation which affects the alignment of LC inside the film cavities, which has a significant effect on the physical properties of PDLC films. Droplets become spherical or oblate in the polymer film [71, 120, 127, 132–145] depending on the evaporation process. However, the size distribution of the liquid crystal droplets in the emulsion can be modified by the preparation process and materials used to produce the emulsion, for example, the stirring time and speed, viscosities of polymer and liquid crystal. With increase in time of mixing in an ultrasonic cleaner, the droplet size of emulsion decreases [53, 146]. Moreover, surfactant type and concentration are the other key factors which affect the size, stability, and polydispersity of the droplets. The droplet size and polydispersity index decreased with increase in surfactant concentration [53]. The size and size distribution of encapsulated LC droplets can have a significant effect on the electro-optical properties of the films. Large area applicability of the emulsion system enhances the range of useful applications of PDLCs, ranging from switchable light modulators [71, 133], smart Windows [127] and information displays [134], as well as holographically formed optical elements and devices [135, 137, 142–144]. In PDLC systems, LC droplets are dispersed in a polymer film and these LCs can be oriented in the polymer droplets leading a switching from scattering to transparent states or vice versa with an applying electric field. There is a mismatching of refractive indices in the field-off state and these refractive indices of LC and the polymer match in the field-on state [53, 115, 127, 132–134, 146]. This phenomenon gives the electro-optical performance of the corresponding device. This electro-optical performance of displays and smart windows can be improved by replacing the nematic LCs with BPLCs, and the dispersed or encapsulated BPLCs leads a development in the original optical and E-O properties with an external electrical field [53].

A recent study has appeared recently demonstrating polymer-encapsulated blue phase (PEBP) liquid crystal films were prepared via solvent evaporation-induced phase separation of a mixture of blue phase liquid crystal (BPLC) and polymer latex [33]. It was observed that the PEBP films induced the birefringence between crossed polarizers at low switching voltage and with fast response time. PEBP samples generated considerably large Kerr constants, in the range of 1.83×10^8 – $20 \times 10^8 \text{ V}^{-2} \text{ m}$ (at 633 nm), which are about 10 times higher than those of the reported PSBPs [139]. Therefore, PEBP liquid crystal films are strong candidates for next-generation displays as a result of the outstanding E-O properties of blue phases [33].

3.6. Polymer stabilization of polymer encapsulated blue phase liquid crystals

A novel report has appeared recently suggesting the stabilization of encapsulated BPLC droplets is useful technique to expand their wide temperature range and improve the E-O properties of PDLCs using BPLCs [33]. Besides, polymer stabilization is one of the most effective methods to expand the thermal stability of BPLCs. However, liquid crystal/polymer composites can be classified into two distinct groups as polymer-dispersed liquid crystal (PDLC) and polymer-stabilized liquid crystal (PSLC). Both PDLC and PSLC methods are usually operated between a transparent state and an opaque state [53]. In the PDLC systems, droplets of liquid crystal are dispersed in a polymer film, which can be switched from scattering state to transparent state or vice versa with an applied electric field. In the reported study,

composite materials of polymer-dispersed blue phase (PDBP) LCs were studied by combining PDLC films and BPLCs using two preparation methods, that is, polymer encapsulation and polymer stabilization in order to fabricate polymer encapsulated–polymer-stabilized blue-phase (PEPSBP) LC droplets[33]. Encapsulated droplets were stabilized via the polymerization of reactive monomers after they were produced in a polyvinyl alcohol solution by emulsification. It was reported that polymer stabilized droplets caused an expansion of the BP temperature range from 53 to below 0°C. Moreover, this study concluded that low switching voltage and fast response time based on the decrement in the interfacial energy of polymer encapsulated and stabilized BPLC droplets. Furthermore, stabilization and positions of droplets in the aqueous phase have a great attraction for the researchers [142–146].

Kemiklioglu et al. firstly demonstrated the polymer-dispersed blue-phase liquid-crystal films between two indium-tin-oxide-coated conductive substrates by switching between light scattering and transparent states with applying an electric field across the films [35].

They experimentally investigated the photoinitiator effect on the electro-optical properties of the polymer-dispersed blue phase liquid crystals as well as the ratio between the crosslinking agent and the monomer. They showed that the increasing monomer concentration reduces the switching voltage of the corresponding device. Moreover, the increment of the monomer concentration in the polymer-dispersed blue phase liquid crystal samples leads an increment in the contrast ratio. All these significant improvements in the electro-optical properties of polymer-dispersed blue-phase liquid crystal devices are promising for new electro-optical applications [35].

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