

Blue phases induced by doping chiral nematic liquid crystals with nonchiral molecules

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The emergence of the blue phases I and II that are thought to exist in highly chiral systems has been found in chiral nematic liquid crystals (N^* LCs) when they are doped with achiral bent-core liquid crystals (banana mesogens). The same effect was also observed by adding racemic 4-(1-methylheptyl oxycarbonyl)phenyl 4'-octyloxybiphenyl-4-carboxylate (MHPOBC), while achiral terephthal-bis(*p*-butylaniline) (TBBA) was not effective. The difference was attributed to the different conformations, i.e., MHPOBC is known to have a bent shape, but not TBBA. The doping effect is more remarkable in N^* LCs with higher chiral content for both banana mesogens and MHPOBC. This unusual doping effect was attributed to selective chiral interaction between the chiral conformers of guest molecules and chiral host molecules and/or the decrease of the surface elastic constant on adding bent-shaped guest molecules.

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I. INTRODUCTION

The introduction of chirality to liquid crystal systems changes their physical properties and structures by breaking mirror symmetry. An example of such changes is the helical structure found in the chiral nematic (N^*) phase. In the achiral nematic phase, molecules have long-range orientational order with their average long axis along the nematic director n , but have only short-range positional order. The n director changes its direction by twisting along an axis perpendicular to n and forms a helix when introduction of chirality breaks the equivalence of the free energy between clockwise and counterclockwise rotation. In almost all cases, the pitch of the helix becomes shorter when the concentration of the chiral component increases or when the enantiomeric excess of the material increases. When the N^* phase appears from the isotropic phase, infinite numbers of helical axis directions are possible under the condition that the helical axis must be perpendicular to a particular molecule. Normally, one of the axes is chosen and a one-dimensional helical structure with long-range order is formed. Under a strong chiral twisting power, the system could have two helical axes perpendicular to the local n director, resulting in a three-dimensional lattice called the blue phase (BP). It is known that there exist three BPs, BPI, BPII, and BPIII, in which the molecules organize into double twisted cylinders, building up three-dimensional structures with a lattice of defects [1–6]. The detailed structures of these phases have been studied extensively using the Kossel diagram method, optical microscope observations of the crystallite morphology of single crystals of the blue phases, and electron microscopy of freeze fractures [6–8]. Two of these phases, BPI and BPII, have cubic symmetry with three-dimensional periodic orientational order and no positional order of the molecules. In the BPIII phase, the orientational order of molecules is not periodic and the symmetry of this phase is the same as that of the isotropic phase [3–8].

Theoretically, the increase in free energy due to the existence of a lattice of defects should be compensated by some interaction energy to stabilize these BPs. Several theories have suggested factors stabilizing BPs. According to the Landau theory [2,9–11], increasing the chiral parameter allows BPs to exist. On the other hand, the defect theory [12] suggests that the free energy around defects decreases on the introduction of surface elasticity. In both cases, the helical twisting power originating from the chirality of the molecules must be strong to build up the double twist cylinder in these BPs.

Experimentally, BPs are known to appear in a narrow temperature range above the N^* phase with relatively short helical pitches. Stegemeyer *et al.* studied the relation between the helical pitch in the N^* phase and the temperature range of BPs in several binary mixture systems [6] and found that in almost all cases the temperature range of BPs decreases when the helical pitch is elongated. BPs disappear when the helical twisting power decreases on adding nonchiral components or on decreasing the optical purity of the mixtures. These results have been thought to be consistent with the theoretical consideration. Here we report surprising experimental observations that BPs are induced by doping N^* liquid crystals (LCs) inherently showing no BPs with achiral or racemic molecules, although the doping slightly elongates the helical pitch in the N^* phase.

Recently, growing attention has been paid to BPs because of their potential application as photonic crystals [13,14]. The present result could suggest a direction for designing molecules that exhibit stable blue phases having capability for these applications.

II. EXPERIMENT

Mixtures of a nematic liquid crystal (NLC) ZLI-2293 (Merck) and a chiral dopant MLC6248 (Merck) were prepared as host materials for the following experiments. Four host mixtures with various concentrations of the chiral dopant were prepared: 25.03% (YR25), 23.00% (YR23), 21.04% (YR21), and 18.01% (YR18). The N^* phase of all these host materials melts to isotropic at 82 °C. As nonchiral guest ma-

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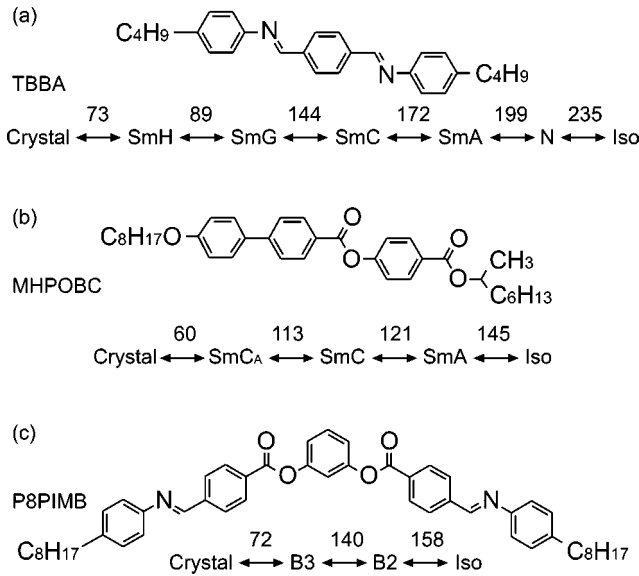


FIG. 1. Chemical structures and transition temperatures of non-chiral guest materials: (a) TBBA, (b) MHPOBC, and (c) P8PIMB

terial, the rodlike nematic liquid crystal TBBA, the bent-core liquid crystal P8PIMB [15], and the rodlike racemic liquid crystal MHPOBC [16] were mixed into the host materials. The chemical structures and transition temperatures of these materials are shown in Fig. 1.

To determine the helical pitch in the N^* phase, selective reflection wavelengths (p_{op}) from planar-aligned liquid crystal cells were measured using a visible light spectrometer with a microscope (ORC TFM-120AFT). Transition temperatures and phase sequences were obtained by optical microscope (Nikon OPTIPHOTO2) observations using a hot stage (Mettler FP-90).

III. RESULTS

The selective reflection wavelength (p_{op}) of the host materials was measured in the N^* phase at 25 °C and at $T - T_{I-N} = -5$ K, where T_{I-N} is the transition temperature between isotropic and N^* phases. The inverse of p_{op} , which is proportional to the twisting power, is plotted as a function of concentration of the chiral component in Fig. 2. The data clearly show a straight line passing through the origin, indicating that the twisting power is proportional to the concentration of the chiral component. At a temperature close to T_{I-N} , a focal-conic texture with a lattice of point disclinations was observed, as shown in Fig. 3, where textures in a wedge cell of YR25 are shown. This figure also indicates that no BPs emerge between the isotropic and N^* phases. It was also confirmed that all of the host materials with the chiral component lower than 26 wt % did not exhibit any BPs.

As the first nonchiral dopant, we chose an achiral liquid crystal TBBA which exhibits the N phase with T_{I-N} higher than that of the host materials. Figure 4 shows the phase diagrams of the mixtures with different weight% of TBBA molecules. The selective reflection wavelength in the N^* phase at $T - T_{I-N} = -5$ K is also shown. The phase diagrams show that no additional phases emerge and only a shift of

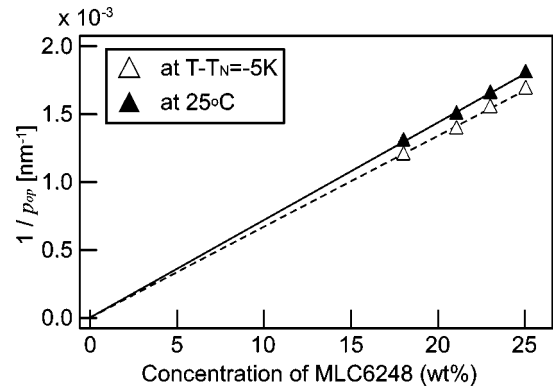


FIG. 2. The inverse of the selective reflection wavelength of host materials with different concentration's of chiral dopant measured at 25 °C and $T - T_{I-N} = -5$ K.

T_{I-N} is observed, although miscibility becomes worse, or becomes lower in YR23 with higher weight% of TBBA. The measurable range of the selective reflection wavelength was shorter than 800 nm, which makes the measurements possible only for YR23 and YR21. Nevertheless, it is clear in Fig. 4 that the helical pitch in the N^* phase is elongated by adding TBBA. Thus, all the results of doping experiments in the TBBA/YR systems mentioned above are just as expected.

The second dopant we chose is an achiral bent-core liquid crystal P8PIMB. The phase diagrams and pitch changes in the P8PIMB/YR(23,21,18) systems are shown in Fig. 5. Quite surprisingly, a BP emerges in all the mixtures when P8PIMB molecules are added. In YR23, 2 wt % of P8PIMB

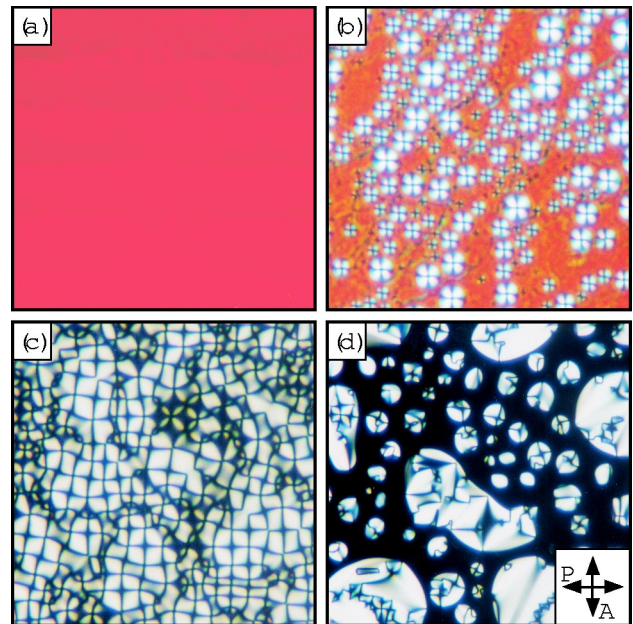


FIG. 3. (Color online) Photomicrographs of Grandjan texture and focal-conic texture of pure host material YR25. (a) Grandjan texture in a wedge cell at 75 °C, (b) nucleation of focal-conic domains at 80 °C, (c) focal-conic texture (also called polygonal texture) at 80.5 °C, and (d) transition from N^* to isotropic phase at 81 °C.

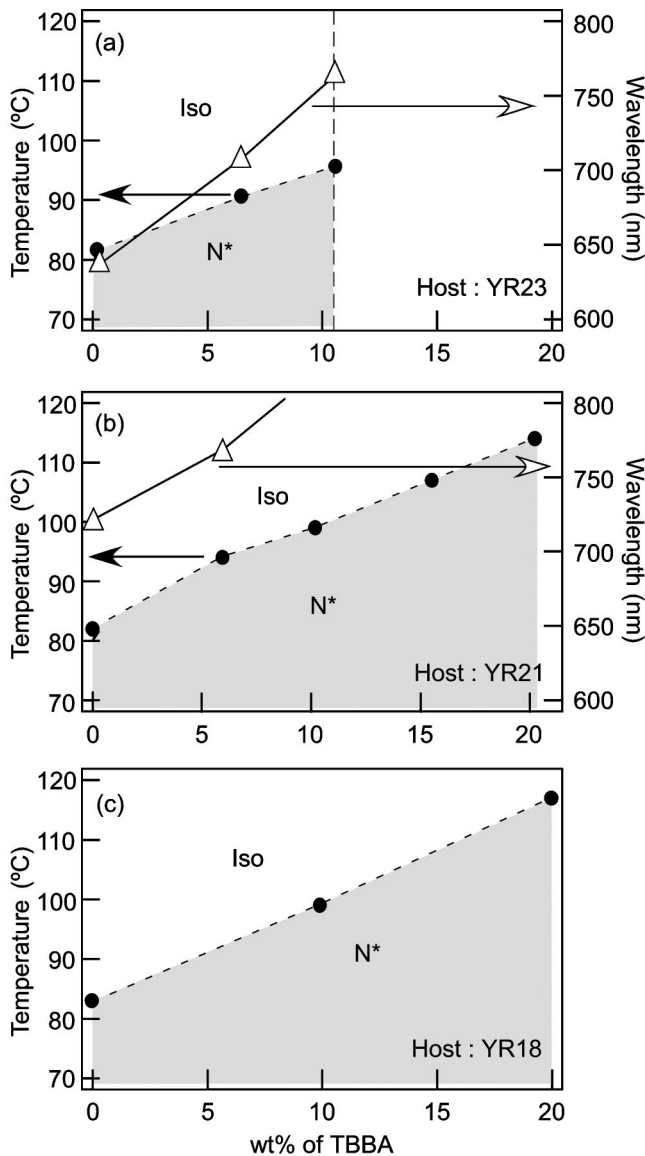


FIG. 4. Phase diagram and selective reflection wavelength of mixtures with TBBA: (a) TBBA/YR23, (b) TBBA/YR21, and (c) TBBA/YR18

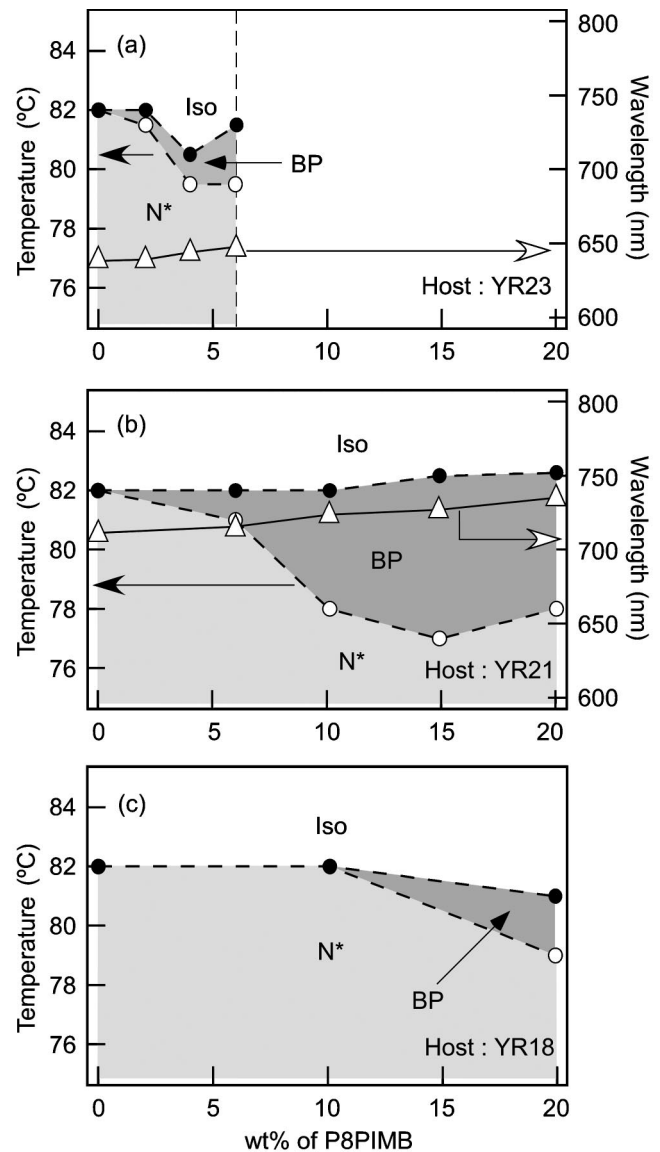


FIG. 5. Phase diagram and selective reflection wavelength of mixtures with P8PIMB; (a) P8PIMB/YR23, (b) P8PIMB/YR21, and (c) P8PIMB/YR18.

was enough to induce a BP, although doping much above 6 wt % was not possible, because of the low miscibility of P8PIMB and YR23. A small increase (YR21) or even a decrease (YR18) of the transition temperature between isotropic phase and BP was observed, indicating low miscibility of the host and dopant. In YR21, the BP emerges in a wide range of P8PIMB content, at least from 5 to 20 wt %. In the mixture of lower concentration of P8PIMB, only one BP (assignable to BPII by texture observation) was induced. In the mixture of higher concentration of P8PIMB, at least two BPs, i.e., BPI and BPII, were confirmed. In YR18, the BP is also induced by adding P8PIMB at more than 10 wt %.

The selective reflection wavelength at $T - T_{I-N} = -5$ K or at $T - T_{BP-N} = -5$ K increases but the rate of increase is less pronounced compared with the TBBA/YR system. In the mixtures with the host YR18, the helical pitch in the N^* phase was longer than 850 nm.

The identification of BPs was made by texture observations as shown in Fig. 6, where the textures of 15 wt % P8PIMB/YR21 are shown. The texture under a temperature gradient (left around 77 °C and right around 83 °C) shown in Fig. 6(a) clearly reveals the existence of BPII and BPI between the isotropic and N^* phases. The textures of BPII and BPI are respectively shown in Figs. 6(b) and 6(c). A platelet texture with various colors was observed in the BPII phase [Fig. 6(b)] and fine stripes appeared in the plate after the transition to BPI [Fig. 6(c)]. The temperature range of the BPs was over 4 K in the 15% P8PIMB/YR21 mixture.

The third dopant we chose was racemic MHPOBC. It is also surprising that BPs were induced by adding a racemic liquid crystal material MHPOBC to the host materials, as shown in Fig. 7. As in the phase diagrams in P8PIMB/YR mixtures, a BP is easily induced in the mixture with high chiral content; YR23 exhibits a BP at least at 4 wt % of

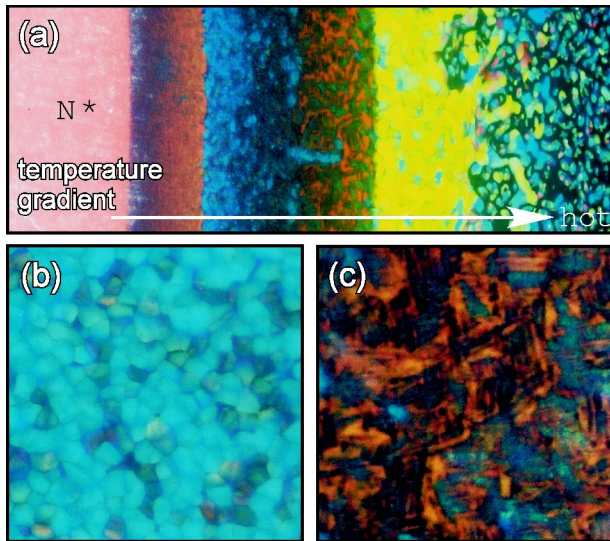


FIG. 6. (Color online) Photomicrographs of the BPII and BPI phases in the mixture of 15 wt% P8PIMB/YR21. (a) Texture under a temperature gradient covering the transition between N^* and the blue phases. Left side (around 77 °C) of the cell is cooler than right side (around 83 °C). (b) BPII phase (at 81 °C) obtained by cooling from isotropic and (c) BPI phase (at 79 °C) obtained by cooling from (b).

MHPOBC, 10 wt% in YR21, and more than 10 wt% in YR18. The BP temperature range becomes wider with increasing dopant ratio. It is also noted that T_{I-BP} or T_{I-N} increases when the concentration of racemic MHPOBC increases, indicating that the racemic MHPOBC has better miscibility with the host than does P8PIMB. The helical pitch in the N^* phase at $T - T_{I-N} = -5$ K or at $T - T_{BP-N} = -5$ K was elongated, as shown in Fig. 7. In the mixtures with the host YR18, the helical pitch in the N^* phase was longer than 850 nm. Photomicrographs of BPs are shown in Fig. 8. The texture under a temperature gradient shown in Fig. 8(a) clearly shows the existence of at least two BPs, BPI and BPII. The respective textures are shown in Figs. 8(c) and 8(b).

IV. DISCUSSION

It is known that BPs appear above the N^* phase with relatively short helical pitch ($< \sim 500$ nm), and disappear when the helical twisting power is decreased by adding non-chiral components or decreasing the optical purity of the mixture. We found, however, that BPs are induced by adding nonchiral mesogens to N^* liquid crystals that do not exhibit any BPs. The key to interpreting the phenomenon is that bent-core achiral P8PIMB and racemic MHPOBC are effective in showing the phenomenon, but not achiral TBBA. These dopants can be classified from the two viewpoints of molecular chirality and molecular shape.

It is important to note that the bent-core achiral molecules, i.e., the so called banana mesogens; are known to take chiral conformations [17–19] and to be segregated into two chiral domains [20–22]. In this sense, we could say that achiral bent-core mesogens are inherently racemic with equal

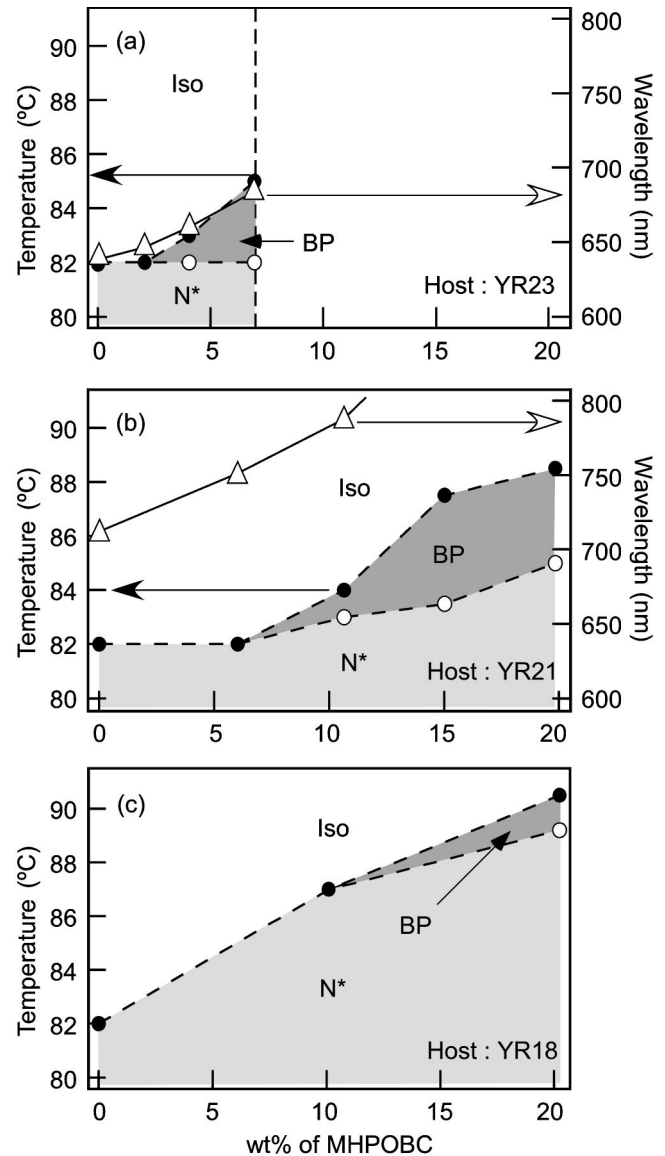


FIG. 7. Phase diagram and selective reflection wavelength of mixtures with racemic MHPOBC: (a) MHPOBC/YR23, (b) MHPOBC/YR21, and (c) MHPOBC/YR18.

numbers of R and S molecules. The MHPOBC used in the present experiments is also racemic. This point is definitely different from TBBA, which is an achiral molecule and has no chiral conformers.

We should also note the difference of the shape. P8PIMB molecules are clearly of bent shape because of the chemical structure of the molecule. Chiral MHPOBC, the first antiferroelectric LC [15,16], has been extensively studied from many viewpoints. Related to the origin of the appearance of the anticlinic molecular orientation in adjacent smectic layers, stable molecular conformations were examined. Several experiments such as Fourier transform IR [23] and NMR [24] spectroscopy suggested that the chiral end is greatly bent with respect to the core direction of MHPOBC, and a MOPAC calculation [25,26] also supports the stable bent conformation. Hence, not only P8PIMB but also racemic MHPOBC might have bent shapes, while TBBA is a straight (rodlike) molecule.

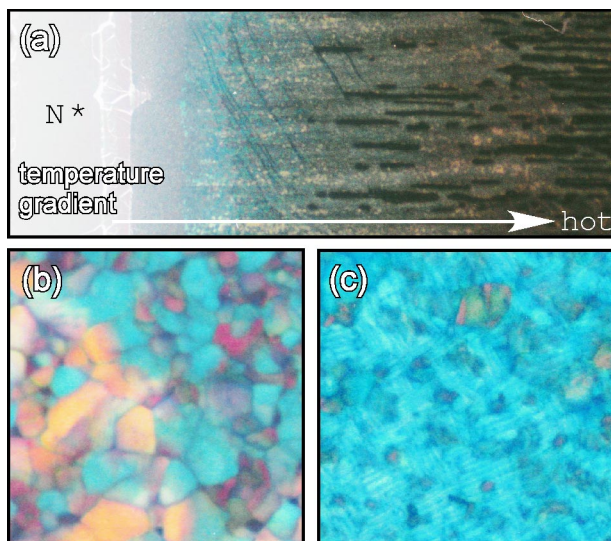


FIG. 8. (Color online) Photomicrographs of the BPII and BPI phases in the mixture of 15 wt% MHPOBC/YR21. (a) Texture under a temperature gradient covering the transition between N^* and the blue phases. Left side (around 82 °C) of the cell is cooler than right side (around 88 °C). (b) BPII phase (at 86 °C) obtained by cooling from isotropic and (c) BPI phase (at 84 °C) obtained by cooling from (b).

Then is it the chirality, the shape, or both, that plays a role in the present surprising phenomenon, induced BPs by adding nonchiral mesogens? Before the detailed discussion, we have to point out an interesting doping effect of bent-core mesogens, namely, the enhancement of twisting power (shortening of helical pitch) by doping a chiral host with achiral bent-core mesogens. The effect was observed in both N^* [27] and chiral smectic phases (SmC^* and SmC_A^*) [28]. In the former case, cholesteryl 4-formylbenzoate was used as a host N^* material. The doping of bent-core mesogens induced shortening of their helical pitch, although TBBA lengthened the pitch [27]. A qualitative explanation of this enhanced chirality is that one of the chiral conformations is preferentially realized in chiral systems and acts as chiral dopant. In the latter case, shortening of helical pitch in SmC^* and SmC_A^* was also observed on adding achiral bent-core mesogens [28]. There is a theoretical treatment to explain the phenomenon; the essence of the interpretation is chirality transfer between host and bent-core mesogen, the same as in the N^* system. Achiral bent-shaped molecules become structurally chiral due to the interactions with the chiral host, which induces tilt and polar order of bent-core molecules. The induced chirality is then transferred back to the host. In this theoretical interpretation, the importance of the bent shape is included in addition to the chiral conformation.

In the present experiments, slight elongation of the helical pitch was observed even when the banana mesogen was chosen as a nonchiral dopant in contradiction to the previous results mentioned above. We tested another pure chiral host material, cholesteryl decanoate, having a similar chemical structure to that used in [27]. By mixing bent-shaped molecules P8PIMB, the helical pitch was slightly shortened, as

in the case reported in Ref. [27] but BPs were not induced in this system even though the selective reflection wavelength was shorter than 400 nm. The following three explanations are possible to account for the opposite pitch changes in the present and previous works. (1) The use of different host molecules. The host materials used in the previous work [27,28] are purely chiral systems, while those in the present study are mixtures with chiral dopants. This brings about fewer chiral interactions between the host and bent-shaped molecules because the number of chiral molecules in the system is small. (2) Different ability of chiral transfer. It is known that racemic domains and/or equal fractions of chiral domains are usually formed in achiral banana phases [29], and chiral dopants sometimes can produce an imbalance of chirality [21,30], i.e., chiral transfer from guest to host. We found that chiral analogs of PnOPIMB, chiral MHPOBC, cholesteryl 4-formylbenzoate, and cholesteryl decanoate have a strong ability for chiral transfer, while MLC6248 does not, when achiral PnPIMB is doped with these chiral dopants. (3) Different miscibility between chiral molecules and bent-shaped molecules. The cholesteryl derivatives showed better miscibility with bent-shaped molecules than MLC6248. This could be explained by the chemical structure; namely, the chiral material MLC6248 used in our experiments has two phenyl rings and a cyclohexane ring connected to each other in a straight line in its mesogenic part, while cholesteryl derivatives could form a slightly bent conformation because of the chemical structure of their mesogenic core. The differences in the three above points brings about less chiral interaction between MLC6248 (chiral dopant) and the chiral conformers of the present nonchiral dopants, resulting in weaker chiral enhancement. From these results, we conclude the following points. (1) The ability of chiral transfer would be high between a host and a guest material with high miscibility. (2) A host chiral material showing better miscibility with an achiral dopant could have better ability to transfer chirality, but no blue phase was induced. On the other hand, a host showing lower miscibility with a nonchiral dopant could have lower ability to transfer chirality but blue phases were induced. Thus, it is clear that the “chirality” of the nonchiral dopant which is transferred from the chiral host has little influence in inducing blue phases, and some factors other than the transferred chirality play a role in inducing the blue phases. However, the effect of the bent core might show up even in the present result, as clearly seen by the weaker pitch changes with increased P8PIMB content.

Let us consider the origin of induced BPs from the chirality viewpoint; namely we consider the hypothesis as a strong prerequisite that BPs emerge only in highly chiral systems. As mentioned above, P8PIMB and MHPOBC might have chiral conformations, although the ratio of plus and minus chirality is 50/50. Hence these dopant molecules decrease the chirality of the system as a whole. However, if the same conformer as the host interacts with the host more strongly than does the opposite conformer, the chiral parameter that governs the emergence of BPs in the Landau theory might effectively increase by elongation of the coherence length, which compensates the increase of the helical pitch. In the

case of TBBA, no chiral conformation exists, so that no effect results.

Another viewpoint that we should examine is the shape of the molecules. Doped molecules could be segregated from the host and could make defect cores stable. Also, decrease of the bend-elastic constant in a NLC system on adding bent-core molecules was reported by Dodge *et al.* [31] Thus, it is necessary to consider a reduction in the free energy cost for defects and double twist cylinders for stabilizing BPs. As described in the defect theory, surface elastic constants are not canceled out around the double twist cylinders in BPs, while they should be equal to zero in bulk systems. There is a possibility that doped molecules make the surface elastic constant K_{24} lower or stabilize defect cores because of their bent molecular shape in P8PIMB and MHPOBC, while a straight molecule, TBBA, does not induce any BPs.

V. CONCLUSION

It was found that cholesteric BPs are induced by doping N^* LCs having no BPs with nonchiral molecules that have

inherently chiral conformers and bent shape. In order to interpret the phenomenon, the chirality and shape of the dopant molecules were examined. Both the bent-core mesogen P8PIMB and racemic MHPOBC have chiral conformations and a bent shape, in contrast to straight-shaped achiral TBBA. Therefore, both or either of them must play a role in inducing BPs in N^* LCs; namely, chiral molecular interaction among molecules with the same chirality in host and dopant and/or the decrease of the K_{24} surface elastic constant by adding bent-shaped molecules may play a major role in the present surprising phenomenon.

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