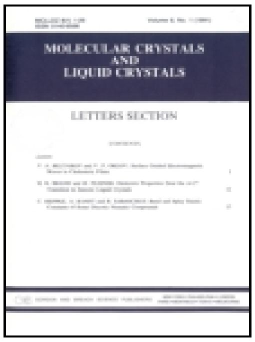

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Blue Phase in Photocurable Mesogenic Monomers for Nano-structured Materials

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Blue phase (BP) is an attractive liquid crystal because of the 3-dimensional nano-structure. We have tried to obtain the blue phase by using photocurable mesogenic monomers for nano-structured materials. In this paper, we report the dependence of the BP stability on the materials of mesogenic monomers and chiral dopants. The BP does not appear in a single monomer medium used in this research. The complex interaction between the different kinds of monomers is necessary for the appearance of BP. Furthermore, the important characteristics of chiral dopant are not only the chiral strength.

Keywords Blue phase; liquid crystal; photocurable mesogenic monomer; chiral dopant

1. Introduction

All matters are formed by atoms and molecules without any distinction of their kinds. However, biological organisms are entirely different from other matters in terms of the self-assembling nano-structure of living tissue and the high responsiveness. On the other hand, distinctive features of liquid crystal system [1–5] are also the easy self-assembly and the high responsiveness. Therefore, we can easily understand their close connection which inspires us with biological systems being not able to exist without liquid crystal systems [6]. It is a well known fact that the study of the liquid crystal started from its discovery during the research of the biological matter in 1888 [1, 2]. Therefore, we expect to fabricate materials with super-high functionalities such as biological organisms via liquid crystal states in low energy consumption due to self-assembly. In this research, we focus on blue phase (BP) which takes the 3-dimensional nano-structure like a biological structure such as a rat tooth [7–9]. We have tried to obtain the BP using photocurable mesogenic monomers and to solidify the BP structure by irradiation of ultra-violet light [10]. Furthermore, we have examined the mechanical strength of the solidified BP. In this research, we investigate the dependence of the BP stability on the materials of mesogenic monomers and chiral dopants.

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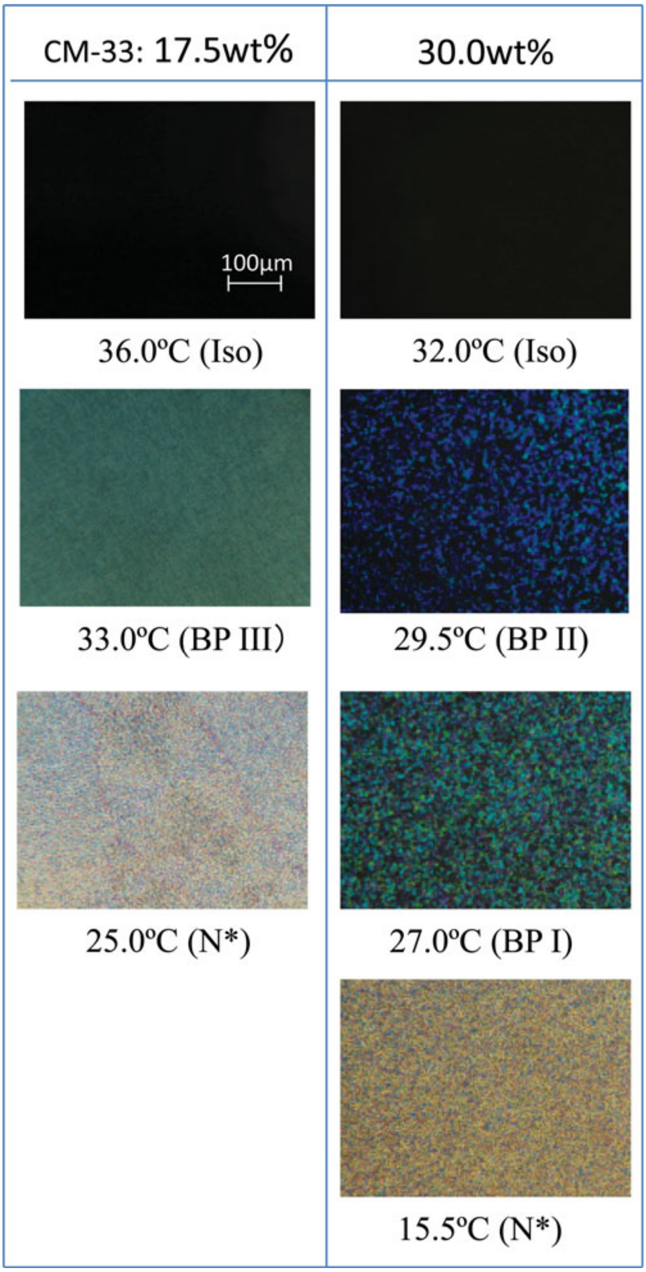

Figure 1. Microscopic textures of UCL-001+LC-1 doped with CM-33.

2. Experimentals

The materials used in this research were as follows: the photocurable mesogenic monoacrylate monomers were UCL-001 (DIC) [11], LC-1 [11] and LC-19 (Nissan Chemical Industries) which were doped 1wt% photoinitiator; and the chiral dopants were CM-33 (Chisso), ZLI-4572 (Merck) and PCM-104 (DIC). Although LC-1 and LC-19 have alkyl spacer between the main chain and the mesogenic side chain, UCL-001 does not. Further, the

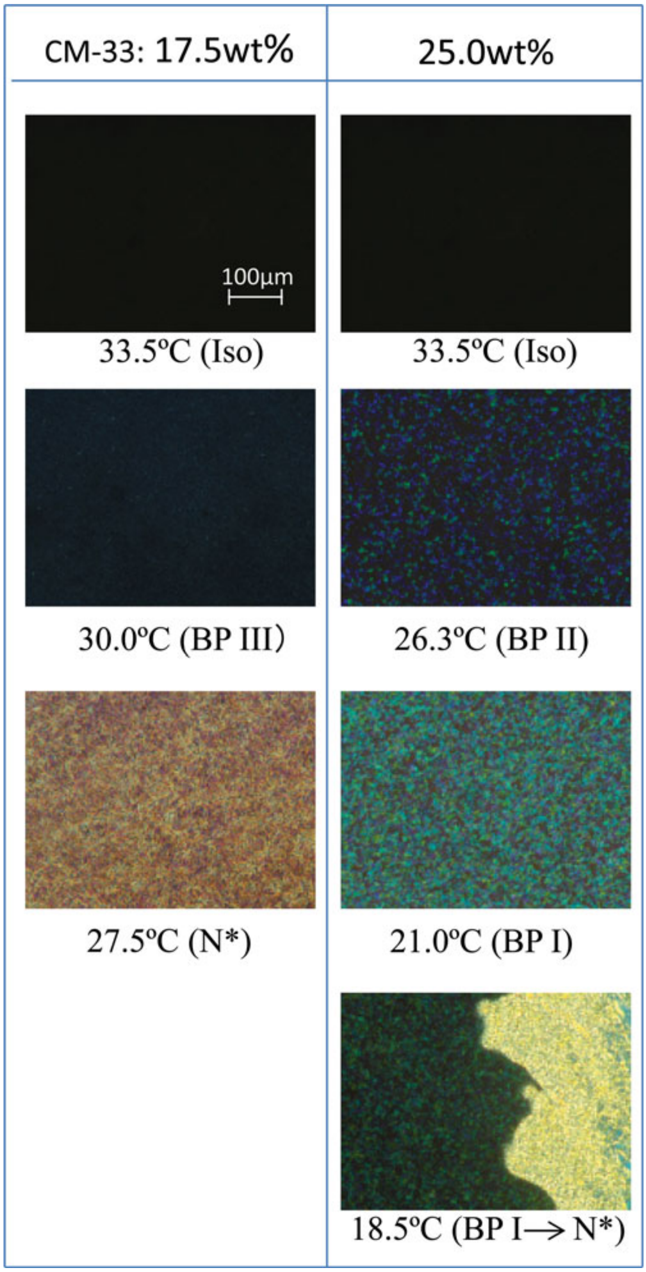

Figure 2. Microscopic textures of UCL-001+LC-19 doped with CM-33.

dielectric anisotropy of UCL-001 and LC-1 is positive, and that of LC-19 is negative. Moreover, LC-1 has a cyano group at the molecular terminal. In the chiral dopants, CM-33 and ZLI-4572 are conventional chiral dopants without photocurability, but PCM-104 is photocurable.

The glass cells were fabricated without alignment films, and then the mesogenic monomers, which were doped with the chiral dopants, were injected into empty cells in the

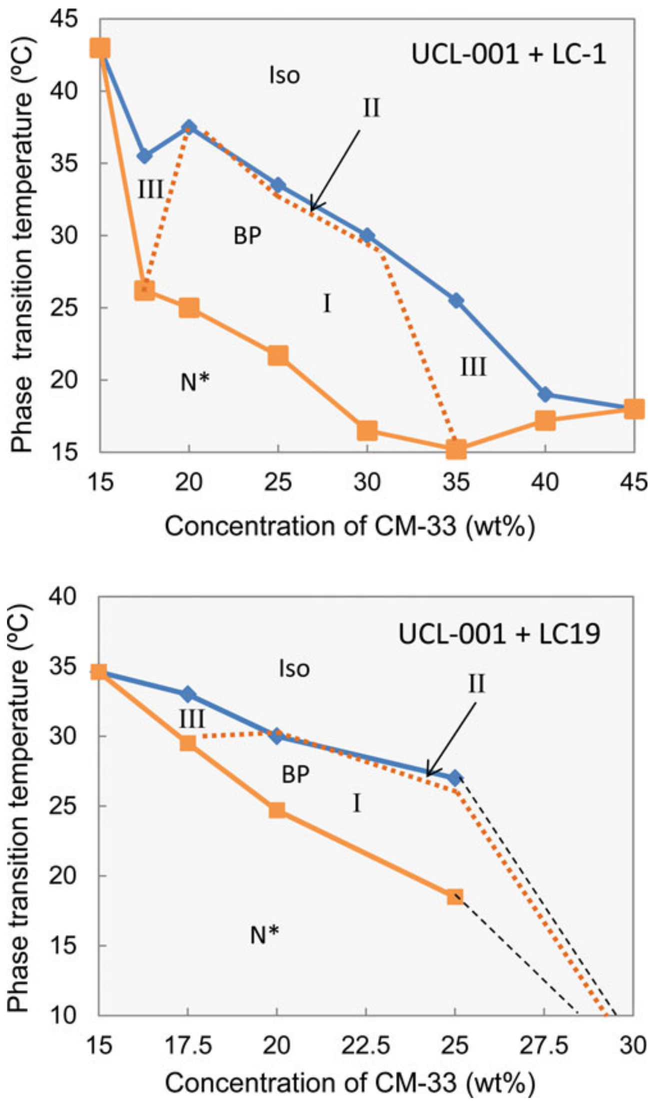

Figure 3. Phase diagrams of UCL-001+LC-1 and +19 doped with CM-33.

isotropic phase via capillary action. The cell gap was set 10μm. The textures in the cells fabricated by above method were observed with a conventional polarizing microscope, and the phase transition temperature was measured. In order to know the chiral strength of the chiral dopants used in this research, the helical pitch was measured with Grandjean-Cano wedge method by addition of the chiral dopant to 5CB liquid crystal.

3. Results and Discussion

First, it was confirmed that BP does not appear in a single monomer medium used in this research for any concentration of the chiral dopant. Therefore, mixing plural mesogenic monomer materials is necessary for obtaining BP.

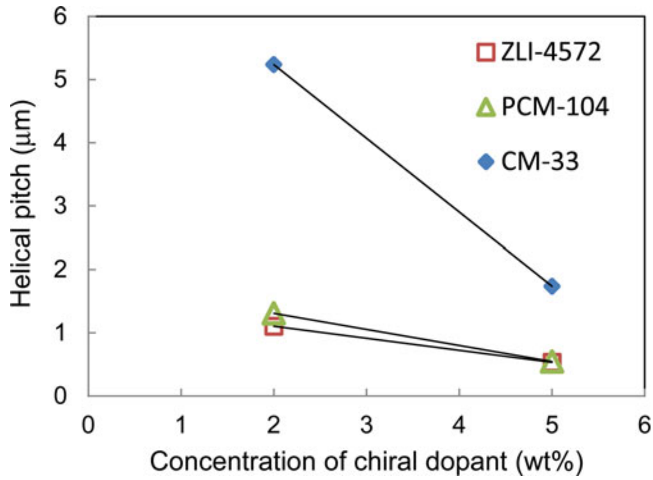

Figure 4. Helical pitch of 5CB doped with chiral dopants used in this research.

Figure 1 shows the samples of microscopic textures observed in UCL-001+LC-1 (1:1 in weight) doped with CM-33 under cooling process. In 17.5wt% of CM-33 concentration, since a fog texture appears, BP III which takes a sponge or amorphous structure can be obtained. On the other hand, in 30wt% CM-33, since two types of platelet textures appear, BP I and BP II, which take a body-centered and a simple cubic structure, respectively, can be obtained. Figure 2 shows the samples of microscopic textures observed in UCL-001+LC-19 (1:1 in weight) doped with CM-33 under cooling process. It is found that the BPs can be obtained similarly to the media of UCL-001+LC-1. Thus, the complex interactions between the different kinds of monomers are necessary for the appearance of BP. Figure 3 shows the phase diagrams of UCL-001+LC-1 and UCL-001+LC-19 (1:1 in weight) doped with CM-33. It is found that BP in the case of LC-1 is more stable than that of LC-19. The large difference is the dielectric anisotropy between LC-1 ($\Delta\varepsilon > 0$) and LC-19 ($\Delta\varepsilon < 0$). Moreover, the molecule of LC-1 has a strong polar group of cyano at molecular terminal. It is guessed that since BPs form the higher-order structures containing defects of molecular alignment, the balance of the complex interactions between constituent molecules is important for the appearance and stability of BP. Furthermore, as seen in the phase diagrams of Fig. 3, BP III appears in the lower or higher concentration of the chiral dopant than the concentration in which BP I and II appear. Therefore, it is thought that BP III has a collapsed cubic structure due to the unsuitable chiral strength for the formation of complete cubic structure of BP I and II.

Figure 4 shows the helical pitch of 5CB doped with the chiral dopants used in this research. It is found that the helical twisting power of ZLI-4572 and PCM-104 is almost same each other, but is about three times as strong as that of CM-33. Figure 5 shows the phase diagram of UCL-001+LC-1 (1:1 in weight) doped with ZLI-4572. It is found that BPs can be obtained by one third of the chiral dopant concentration in the case of CM-33. Therefore, the total value of chiral strength to obtain BP is constant in the UCL-001+LC-1 medium. However, the stability of BP is large different between the cases using CM-33 and ZLI-4572. Furthermore, the BP cannot be obtained in UCL-001+LC-1 (1:1 in weight) doped with PCM-104, as shown in Fig. 6. Therefore, it is concluded that the important characteristics of chiral dopant for the appearance and stability of BP are not only the

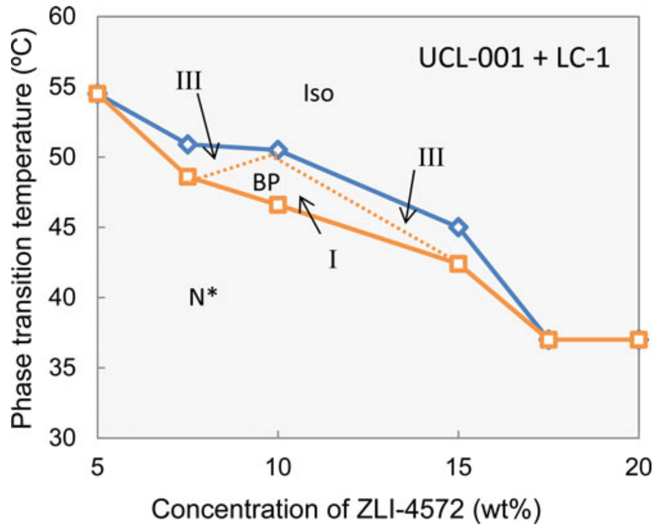

Figure 5. Phase diagram of UCL-001+LC-1 doped with ZLI-4572.

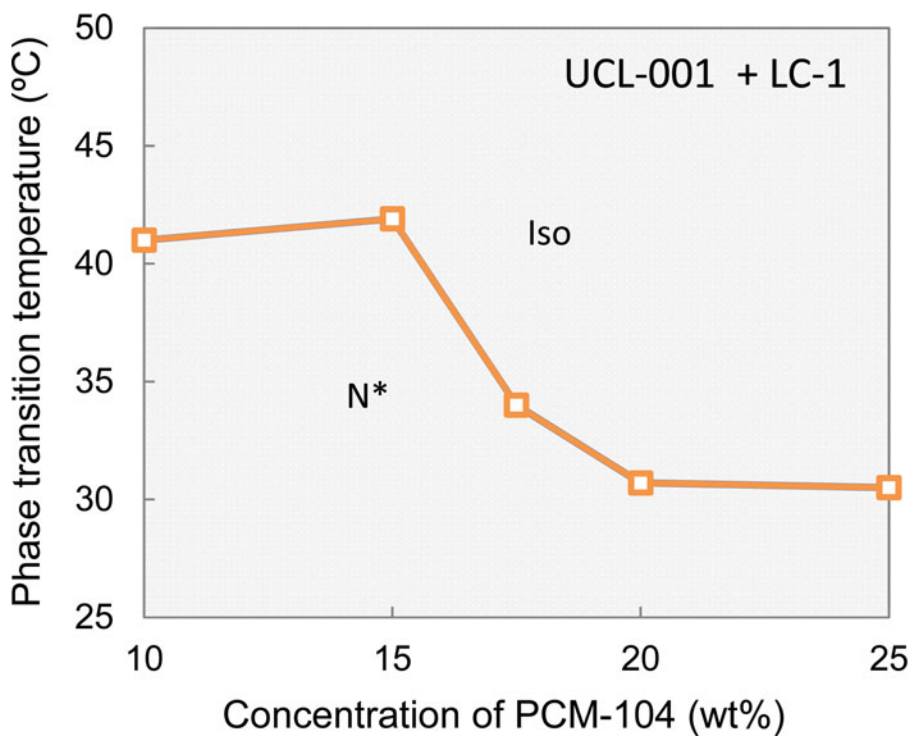

Figure 6. Phase diagram of UCL-001+LC-1 doped with PCM-104.

macroscopic chiral strength but also the microscopic molecular interaction between LC monomer and chiral dopant. Although BP cannot be obtained in this research using PCM-104, PCM-104 is attractive for solidified nano-strucure materials because of a photocurable monomer. The realization of BP utilized PCM-104 is currently being researched by the variation of the mixing ratio of UCL-001 and LC-1.

4. Conclusions

We tried to obtain BP by using photocurable mesogenic monomers for nano-structured materials, and researched the dependence of the BP stability on the materials of mesogenic monomers and chiral dopants. As a result, BP does not appear in a single monomer medium used in this research. On the other hand, BP can be obtained in the mixture of mesogenic monomer materials. Thus, the complex interaction between the different kinds of monomers is necessary for the appearance of BP. Furthermore, the stability of BP is large different between the mixtures fabricated in this research. Therefore, the balance of the complex interactions between constituent molecules is important for the appearance and stability of BP. Moreover, BP III appears in the lower or higher concentration of the chiral dopant than the concentration in which BP I and II appear. Therefore, it is thought that BP III has a collapsed cubic structure due to the unsuitable chiral strength for the formation of complete cubic structure of BP I and II.

From the investigation of chiral dopants, it is found that although the total value of chiral strength to obtain BP is constant in any chiral dopant, the stability of BP strongly depends on the chiral dopant materials. Therefore, the important characteristics of chiral dopant for the appearance and stability of BP are not only the macroscopic chiral strength but also the microscopic molecular interaction between mesogenic monomer and chiral dopant.

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