Creation of Large Size Monodomains of Polymer–stabilized Cholesteric Blue Phases

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Cholesteric blue phases (BPs) are kinds of liquid crystal phase, which exist in a very narrow temperature range between an isotropic phase and a cholesteric phase. Since they have a three dimensional periodic structure of several hundreds nanometers, BPs are applicable as a three–dimensional photonic crystal. In our previous study, the temperature range of BP was extended to more than 60 K in polymer-stabilized cholesteric blue phases. In this study, preparation method to create large size monodomains of polymer-stabilized cholesteric blue phases were investigated because a large single monodomain is required for applying to various optical devices such as a photonic crystal. The sizes of BP platelets became larger as the cooling rate from an isotropic phase was slower. Furthermore, BP platelets of sub-mm^2 in area were obtained by applying an electric field during cooling.

Key words: liquid crystal, blue phase, monodomain, photonic crystal, polymer-stabilized blue phase

1. INTRODUCTION

Photonic crystals, which have periodic refractive indices, can control the spontaneous emission of light and photon localization[1,2]. Therefore, photonic crystals behave as an insulator to the light of specific wavelength. As for photonic crystals, the application to many optical devices is expected, such as low-threshold laser[3] and waveguide[4]. Such effects are more effective in case of higher dimensional of periodic structures. Then, various structures of a three-dimensional (3D) photonic crystal have been proposed, for example, woodpile structure[5], autocloned structure[6], colloidal crystal (opal)[7], and so on.

Cholesteric blue phases (BPs) are kinds of liquid crystal phases, which exist in a very narrow temperature range between an isotropic phase and a cholesteric phase[8,9]. Fig.1 shows shematic illustration of the structures of BP. In the cholesteric liquid crystal with small helical pitches, the energy can be lowered by allowing twist in all directions perpendicular to the molecular long axis. This configuration is called double twist. Double twist cylinder consisting of double twist alignment stack into the 3D cubic lattice with lattice period of several hundreds nanometers. Recently lasing from BP including dye was demonstrated in the three axes of the cubic lattice, indicated a 3D photonic band in BP[10]. Since BPs can respond to the change of temperature and electric field[11], BPs can be applicable for a tunable photonic crystal[12]. However, owing to the narrow temperature range of BP, it is difficult to put into practical application for optical devices based on photonic crystal.

The BPs with unique structures occur by a delicate balance between a structure with a local energetic minimum and defects[13]. Because these defects tend to make the global structure less stable, BPs are energetically favorable only in a narrow temperature range. Recently, the temperature range of BPs has been successfully extended to more than 60 K in the polymer-stabilized cholesteric blue phases[14]. The
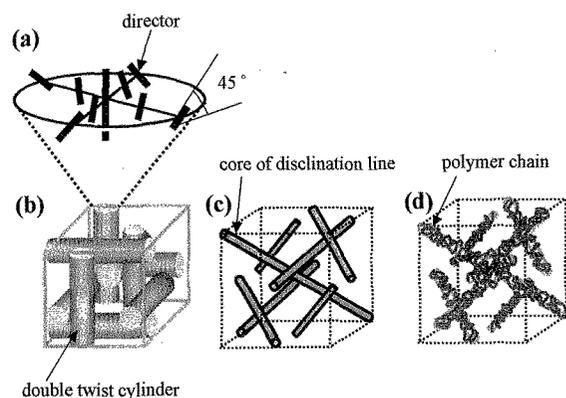

Fig.1 Structures of Polymer-stabilized BP; (a) the orientation of the director field of double twist (b) the arrangement of double twist cylinder (c) disclination lattices (d) the aggregation state of polymer chain in polymer-stabilized BP

remarkable stabilization of the polymer-stabilized BP might be resulted from the stabilization of the defects, disclination lines, by a polymer which is expected to be concentrated in the disclination lines rather than in the double twist cylinder. However, in this system reported so far, the problems involve the segregation of a part of constituent materials after allowing to stand for a long time and the difficulty to create large size monodomains of BP.

In this study, the chemical structures of the constituents molecules in the polymer-stabilized BP was adjusted so that no segregation occurred and the BP platelets of sub-mm^2 in area was created by controlling the kinetics of domain size.

2. EXPERIMENTAL

In order to form a polymer network in the BPs, 2-ethylhexyl acrylate (EHA, Aldrich) and a diacrylate monomer (RM257, Merck) were dissolved in a liquid crystal mixture. For the liquid crystal material, nematic mixture (JC1041-XX, Chisso), 4-cyano 4'-pentylbiphenyl (5CB, Aldrich), 4-cyano 4'-pentylterphenyl (5CT, Fuji Pigment) and 4-cyano 4'-octyloxybiphenyl (8OCB, Aldrich) were used at various concentration. ZLI4572 (Merck) or 4-cyano 4'(2-methyl)buthyl-biphenyl (CB15, Merck) were used as a chiral dopant. 2,2-dimethoxy-2-phenyl-acetophenon (DMPAP, Aldrich) was added to the solution as a photoinitiator.

The glass cell of which inner surfaces were coated with indium tin oxide (ITO) was filled with the mixture solution by capillary action. The cell thickness was 13 μm. The optical textures and the BP domain size were observed by polarizing optical microscope (POM, Nikon OPTIPHOTO2-POL) equipped with a hot stage (Linkam LK-600PM). Polymer-stabilized BP was fabricated by photopolymerization. The light source used for polymerization was UV light of 1.5 mWcm^{-2}. Each sample was irradiated with UV light at the temperature range of BP, while checking the optical texture with a POM (Fig.2).
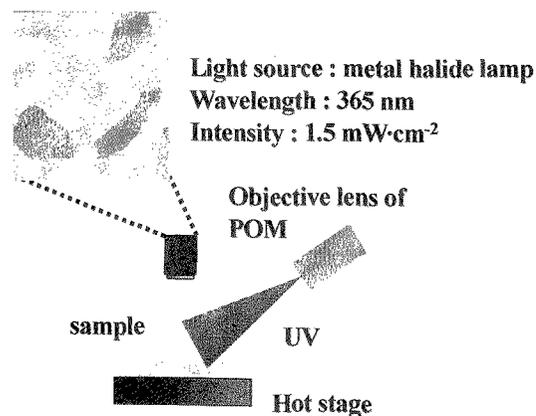
X-ray diffraction measurements (Rigaku RINT2500V) were performed to identify the component segregated in the material. Ultraviolet and visible spectrophotometer (JASCO MSV-350) was used to measure the reflection wavelength of BP.

3. RESULTS AND DISUCUSSION
3.1 Creation of large size BP monodomain

BP domains emerge by cooling from the isotropic phase. The domain size is responsible for the cooling condition like general crystal growth from the melt. The cooling rate dependence of BP domain size for (JC1041-XX/5CB/ZlI4572:47.5/47.5/5 mol %) mixture was investigated by polarizing optical microscopic observation. The platelet texture is a typical optical texture of BP. Each colored platelet observed could be assumed to correspond to a BP single domain. Different colors of platelet are due to different orientation of cubic lattice. In this system, observed color was mainly blue and green, which could be assigned to (200) and (110) lattice plane, respectively. When the cooling rate was 1 K· min^{-1}, a lot of small platelets appeared, that is, the BP domain size was small, ranging 10 to several 10 μm in width. As the cooling rate was slower, the larger BP platelets were formed. For the cooling rate of 0.01 K· min^{-1}, the platelets size was about 100 μm. This is because that slower molecular diffusion and lattice construction allowed to form a uniform domain in a large scale, like a single crystal growth. A remarkably effective method to form a large BP domain was applying an electric field. When an electric field of 2 V· μm^{-1} was applied in the direction perpendicular to the substrate surface simultaneously with cooling from an isotropic state, a large platelet of about sub-mm^2 area was obtained. From the color of the platelet, the (110)
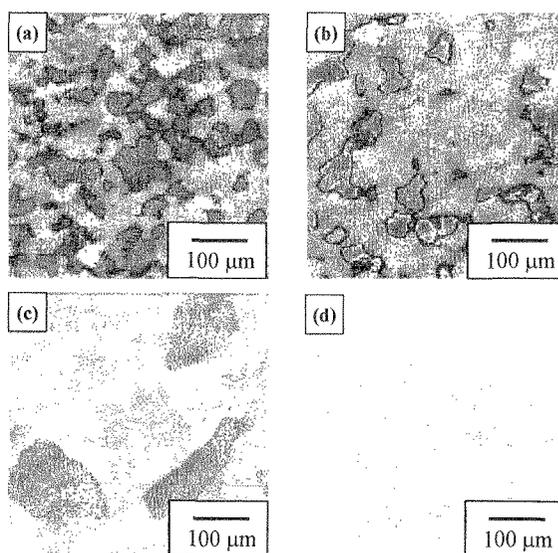

Light source : metal halide lamp
Wavelength : 365 nm
Intensity : 1.5 mW·cm^{-2}

Objective lens of POM

sample   **UV**

Hot stage

Fig.2   The method of fabrication of polymer-stabilized BP

Fig.3 POM image of BP at various cooling rate ; (a)1 K· min^{-1} (b)0.1 K· min^{-1} (c)0.01 K· min^{-1} (d)Applied voltage at 2 V·μm^{-1}

lattice plane of the BP oriented along the substrate surface normal, that is, along the electric field. Though the physical mechanism of the electric field-mediated orientation effect is still unclear, this could be practically very useful to create large monodomains of BPs.

3.2 Preparation of polymer-stabilized BP composed of new chemical constituents

It has been found that the a segregation takes place after being allowed to stand for a long time at room temperature for the conventional polymer-stabilized BP ((EHA/RM257:6/4)/ (JC1041-XX/5CB:1/1)/ZLI4572:7/88/5). Figs.4(a) and (b) show the POM images of polymer-stabilized BP before and after the segregation. Some needles appeared after standing as shown in Fig.4(b). In order to solve this problem, the chemical component of the segregated crystallites was evaluated by X-ray measurements. Fig.5 shows X-ray diffraction profiles of the polymer-stabilized BP after occurring segregation (line 1) and the crystalline powder of ZLI4572 (line 2). The sharp peaks in line 1 should be resulted from the segregation, because those peaks were not observed before segregation. The diffraction angles of the peaks are in good agreement with those of line 2. Thus, the segregated substance is conclusively identified to be ZLI4572 added as a chiral dopant. The segregation could be due to insufficient

miscibility between LCs and ZLI4572. Therefore, ZLI4572 was replaced by CB15 which is expected to show better miscibility to LCs than ZLI4572 because the chemical structure is similar to 5CB and the melting point is lower than ambient temperature.

The phase transition behavior and the lattice constant are dependent on the kind of chiral dopant. In general, BPs appeared in a temperature range between an isotropic phase and a cholesteric phase of which pitch length is smaller than 500 nm. The pitch length is determined by the helical twist power and the concentration of a chiral dopant dissolved in LC. A change in concentration of a chiral dopant brings about a change in phase transition temperature. Therefore, it is necessary to know the dependence of the chiral dopant concentration on the lattice
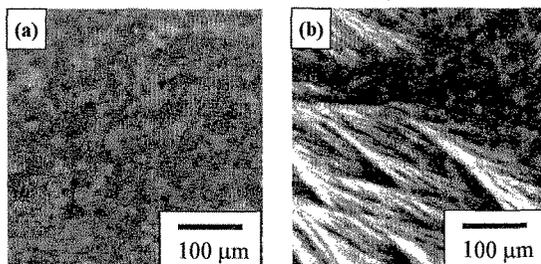

Fig.4 POM image of polymer-stabilized BP; (a) before the segregation (b) after the segregation
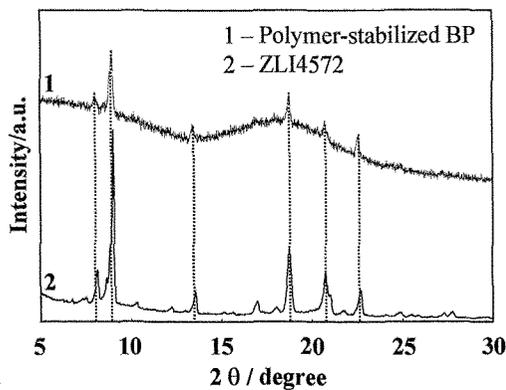

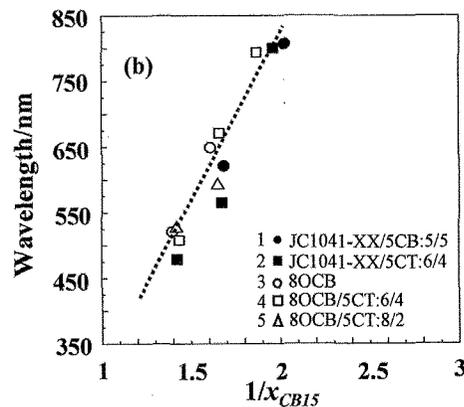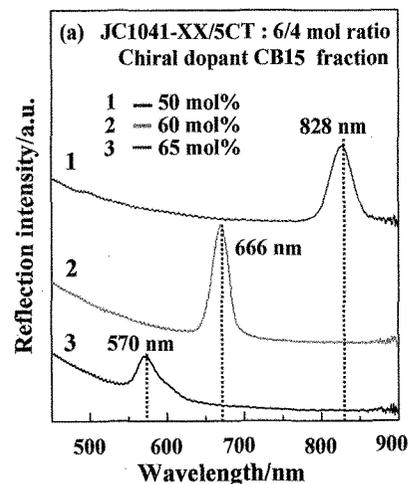Fig.5 X-ray diffraction spectra of polymer-stabilized BP and ZLI4572

Fig.6 The diffraction wavelength dependence of CB15 concentrations; (a) the mixture containing JC1041-XX/5CT 6:4 mol ratio with various CB15 concentrations (b) the diffraction wavelength of various mixture dependence of CB15 concentrations

constant of BP and the isotropic-BP transition temperature. Fig.6(a) shows the CB15 concentration dependence of the reflection spectra of (JC1041-XX/5CT:6/4 mol rate) mixture in BP. The observed peak could be assigned to the Bragg diffraction from (110) lattice plane. The peak shifted to smaller wavelength with increasing CB15 concentration. The relation between the (110) diffraction wavelength and the CB15 concentration is shown in Fig.6(b). Clearly, the reciprocal of the CB15 concentration is proportional to the (110) diffraction wavelength of BP. This is similar to the relationship between a chiral dopant concentration and a helical pitch length of a cholesteric phase.

Fig.7 shows the dependence of the isotropic-LC (nematic or BP) phase transition temperature on CB15 concentration in 8OCB/5CT mixture. Generally the additive property is known to hold for the LC-isotropic transition temperature of nematic mixture. In this case, an additivity is recognized between the isotropic-nematic transition temperature for the 8OCB/5CT mixture without 5CB and the isotropic-crystal (Iso-K) transition temperature (277 K) for pure CB15.
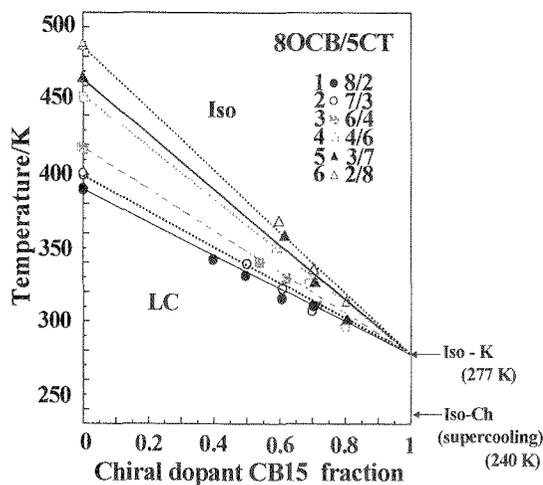

Fig.7 The transition temperature dependence of CB15 concentration

Based on the results of Figs.6 and 7, the chemical components of BP are able to adjust so as to exhibit a desired lattice constant and a phase transition temperature.

Finally we successfully prepared the polymer-stabilized BP containing CB15 instead of ZLI4572. In this system, no segregation occurs even after allowing to stand at room temperature for long time, at least longer than one year.

4. CONCLUSIONS

Large size BP monodomains were created through gradual growth of platelets by cooling slowly from the isotropic phase. A simultaneous

application of an electric field during cooling gave a distinguishing effect of forming large monodomain of BP. The (110) lattice plane of BP faced substrate surface when an electric field was applied in the direction perpendicular to the substrate surface. The dependence of chiral dopant concentration in BP on the phase behavior and the lattice constant was investigated in detail. The reciprocal of the CB15 concentration was proportional to the lattice constant of BP. The additive property was hold for the isotropic-BP transition temperature for a variation of chiral dopant concentration. High stabilization of polymer-stabilized BP was achieved by using a chiral dopant which shows a good miscibility with LC and a melting point lower than ambient temperature.

6. REFERENCES
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