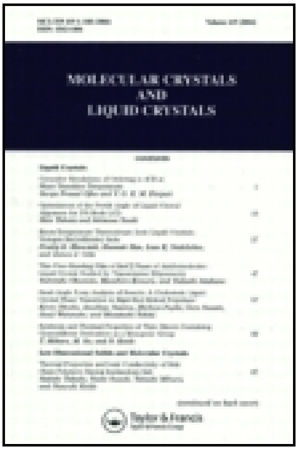

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Confocal Laser Scanning Microscopic Observation of Polymer-Stabilized Blue Phase I

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The structure of the polymer-stabilized blue phase I with a cubic structure of the order of optical wavelength was observed by the confocal laser scanning microscope. The spacing of a striped pattern observed in the (110) plane of the polymer-stabilized blue phase I was a couple of hundred nm, which agreed to the interval of the ordered double twisted cylinders estimated based on a well-known model of blue phase I with O^8 symmetry.

Keywords: confocal laser scanning microscopy; polymer-stabilized blue phase

INTRODUCTION

The blue phases (BP) have unusual structures formed by short-pitched chiral nematic liquid crystals, typically in a small temperature range between the chiral nematic phase and the isotropic one [1]. It is well known that in BP I and BP II, the director is ordered in double-twisted arrangements having the symmetries of cubic lattices, body-centered

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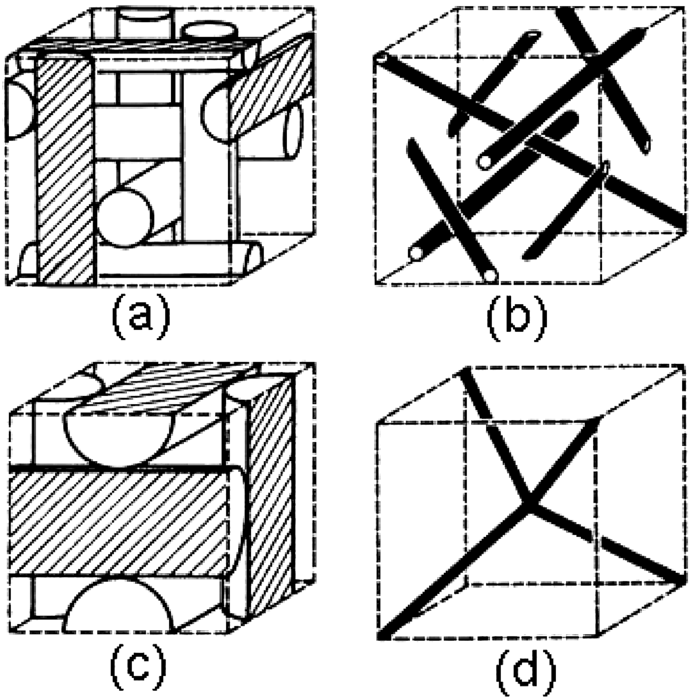

FIGURE 1 Schematic illustration of blue phase structure. (a) Arrangement of double twist cylinders of BP I. (b) Corresponding unit cell of disclinations for BP I. (c) Arrangement of double twist cylinders of BP II. (d) Corresponding unit cell of disclinations for BP II. From reference [1].

cubic and simple cubic, respectively. The structures of BP I and BP II as shown in Figure 1 were proposed by Meiboom and coworkers [2]. The models have been supported theoretically and experimentally [1]. Direct observations of the BP lattice structure have been attempted by freeze-fracture electron microscopy and atomic force microscopy for quenched BPs [3–5]. However, more detailed investigation of the structural analysis is required without fracture and quenching. Here we report the direct observation of a polymer-stabilized blue phase [6–8] in a liquid crystalline state by using confocal laser scanning microscopy technique without fracture and quenching.

EXPERIMENTAL

The liquid-crystal materials used in this study consisted of a nematic mixture (JC-1041XX, Chisso Co.) and 4-cyano-4′-pentylbiphenyl

(5CB). We used a chiral dopant, 2,5-bis-[4′-(hexyloxy)-phenyl-4-carbonyl]-1,4;3,6-dianhydride-D-sorbitol (ISO-(6OBA)2), to induce blue phases. The acrylate monomers were dodecyl acrylate (12A, Aldrich) and diacrylate (RM257, Merck). The photoinitiator was 2,2-dimethoxy-2-phenyl acetophenone (DMPAP, Aldrich). The constituent fractions of the samples are liquid crystals/chiral dopant/monomers/photo-initiator = 86.5/5.5/7.7/0.3 (wt.%). The mixture showed the phase sequence on cooling and heating at 1 Kmin^{-1}as follows.

Cooling: Iso – 314.3 K – BP I – 304.2 K – N*

Heating: N* – 312.5 K – BP I – 314.3 K – Iso

A glass cell was filled with a homogeneous mixture and irradiated with UV light (365 nm, L2859-01, Hamamatsu Photonics) of 1.5 mWcm^{-2} intensity. The cell gap was maintained with a spacer of 7 μm thickness. During photoirradiation, we monitored the optical texture of the blue phases with a polarizing optical microscope. After photoirradiation, the blue phase was kept in a broad temperature range including room temperature as reported in references [6] and [7].

UV-visible reflection spectra of BPs were measured by UV-visible microspectrophotometer (MSV-350, JASCO).

Confocal laser scanning microscopic observation was conducted by LSM510 (Carl Zeiss Co., Ltd.) using 458 nm Ar laser at 295 K.

RESULTS AND DISCUSSION

Well-aligned striped pattern was observed by using CLSM in the polymer-stabilized blue phase I as shown in Figure 2. The spacing of the stripe was 221 ± 6 nm. For the observed area, the (110) plane of the bcc lattice of polymer-stabilized blue phase I was confirmed to be parallel to the sample surface from the UV-visible reflection microspectrophotometry. The BP is known to show reflection peaks in UV-visible regions originating from the Bragg diffraction of light from the cubic lattice. A peak corresponding to the Bragg diffraction from the (110) plane was observed at around 660 nm for our sample as shown in Figure 3. The relationship between the peak wavelength, λ and the lattice constant, a was expressed by equation (1).

$$\lambda = \frac{2na}{\sqrt{h^2 + k^2 + l^2}} \tag{1}$$

where n is the refractive index of the substance and h, k, l are Miller indices. The n was estimated to be 1.561 with the Abbe refractometer. Inputting data of microspectrophotometry, (hkl) = (110) and $n = 1.561$ to equation (1) the a was determined to be 299 ± 12 nm.

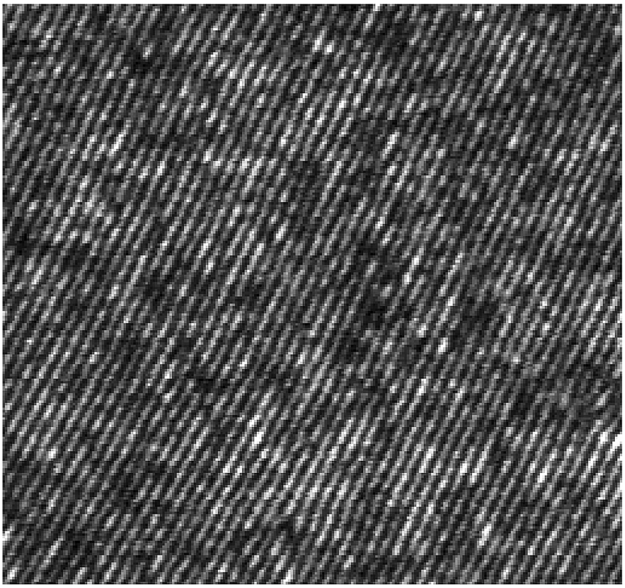

FIGURE 2 Observed confocal laser scanning micrograph for polymer-stabilized blue phase I.

The question is what the stripped pattern observed by CLSM corresponds to. In order to investigate the origin of the stripped pattern, we checked up the sectional structure of the (110) plane of BP I based on

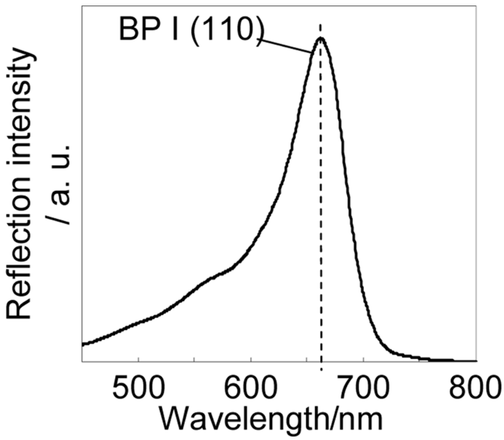

FIGURE 3 The reflection spectra of the area observed by the confocal laser scanning microscope.

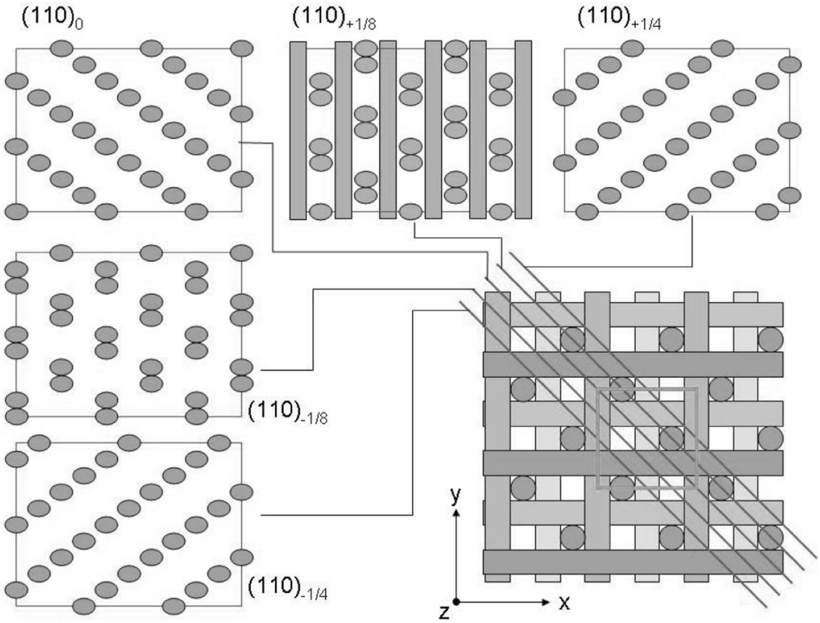

FIGURE 4 Arrangements of sections of double twist cylinder at the (110) plane of BP I.

the model with O^8 symmetry shown in Figure 1(a). Figure 4 shows possible sectional structures of the (110) plane of BP I. In Figure 4 the arrangement of the cut-surfaces of the double twist cylinder at (110) plane was illustrated. The ellipses in Figure 4 correspond to the obliquely cut surface at an angle of 45 degree of the double twist cylinder. The straps aligned in parallel to each other in $(110)_{+1/8}$ plane in Figure 4 correspond to the longitudinal section of the double twist cylinder. From a geometrical consideration, the spacing, d, of the longitudinal section of the double twist cylinder in $(110)_{+1/8}$ plane is calculated to be

$$d = \frac{a}{\sqrt{2}} \tag{2}$$

Inputting the result of reflection spectra, $a = 299 \pm 12\,\text{nm}$ to equation (2), we get $d = 211 \pm 8\,\text{nm}$, which is in good agreement with the spacing of the stripped pattern observed by CLSM, $221 \pm 6\,\text{nm}$. In the double twist cylinder, the director twists along any radius from the center. At the center, the director is parallel to the central axis of the cylinder, but rotates by 45 degree. Therefore, at the longitudinal section of the double twist cylinder, the director is parallel to the sectional plane at the center and 45 degree oblique at the edge of each cylinder. The effective refractive index, n_{eff} of the liquid crystals is expressed by equation (3) depending on the angle, θ between the incident light direction and the director.

$$n_{eff} = \frac{n_{\perp} n_{/\!/}}{\sqrt{(n_{\perp} sin\theta)^2 + (n_{/\!/} \cos\theta)^2}} \tag{3}$$

where $n_{\perp}$ and $n_{/\!/}$ are refractive indices for lights polarized parallel and perpendicular, respectively, to the director, and $n_{/\!/} > n_{\perp}$. In the CLSM observation, the scanning laser beam was incident normal to the (110) plane. The reflectance of the beam is dependent on the effective refractive index of the liquid crystal at the interface with the covered glass and the refractive index of the glass is smaller than both $n_{\perp}$ and $n_{/\!/}$. Therefore, the reflectance shows maximum at $\theta = \pi/2$ and minimum at $\theta = 0$. Then CLSM observes the refractive index map of the sample. In the case of the $(110)_{+1/8}$ plane, the center axis regions of the double twist cylinder, where $\theta = \pi/2$, have maximum effective refractive index, that is, highest reflectance for incident light. Thus, it is reasonable to consider that the striped pattern observed by CLSM for the polymer-stabilized blue phase I corresponded to the aligned arrays of the double twisted cylinders at the $(110)_{+1/8}$ plane.

Although not only the striped pattern but also many other types of image were observed for polymer-stabilized blue phase I by means of CLSM, the results of the structural analyses of those images will be reported elsewhere.

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