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Giant Polymer Lattice in a Polymer-stabilized Blue Phase Liquid Crystal

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Ultrasmall-angle synchrotron X-ray scattering measurements showed that a three-dimensional polymer lattice of a few 100 nm order with body-centered cubic O^{8-} symmetry was formed in polymer-stabilized blue phase liquid crystals. We obtained a clear experimental evidence that the polymer chains condensed selectively in the disclinations within the blue phase during photo-polymerization of monomers in the blue phase.

Blue phase liquid crystals uniquely have giant three-dimensional (3D) cubic structures with lattice periods of several hundred nanometers with periodically aligned disclination lines due to frustration between the helical twisting power in the molecular alignment and the 3D packing topology[1, 2]. Formerly, the blue phase was believed to only exist within a very small temperature range, typically less than a couple of degrees K. About a dozen years ago, we found that the temperature range for a stable blue phase could be greatly extended to several tens of degrees K by in-situ photopolymerization of an appropriate amount of monomers in the blue phase; this material is referred to as the polymer-stabilized blue phase (PSBP)[3]. PSBPs and blue phases have drawn considerable attention for their possible use in photonic and electro-optic devices, especially LC displays, due to their fast Kerr-effect-like switching between optically isotropic and anisotropic states by electric field without any surface orientation pretreatment[4-8]. However, the fundamental scientific question of why the blue phase is stabilized in PSBP has not been answered adequately. We have speculated that the formation of polymers along the disclinations within the blue phase lattice could cause the stabilization of the blue phase[3]. Theoretical simulations[9, 10] indicate that colloidal particles can self-assemble into stable 3D periodic structures in the blue phase, and the blue phase must be stabilized through the replacement of the disclination regions with other guest substances; this strongly supports our speculation. However, experimental evidence that polymers condense selectively into disclinations has been lacking. Here, we present a clear experimental evidence of the condensation of polymers in 3D-aligned disclinations in PSBP by measuring synchrotron ultrasmall-angle X-ray diffraction.

To evaluate the polymer aggregation structure in PSBPs using X-ray scattering, the tagged polymer method[11] was applied. The main atomic components of polymers in PSBP are similar to those of the host liquid crystal: hydrogen, carbon, oxygen, and nitrogen, which all have atomic numbers Z less than 9. Therefore, it is difficult to

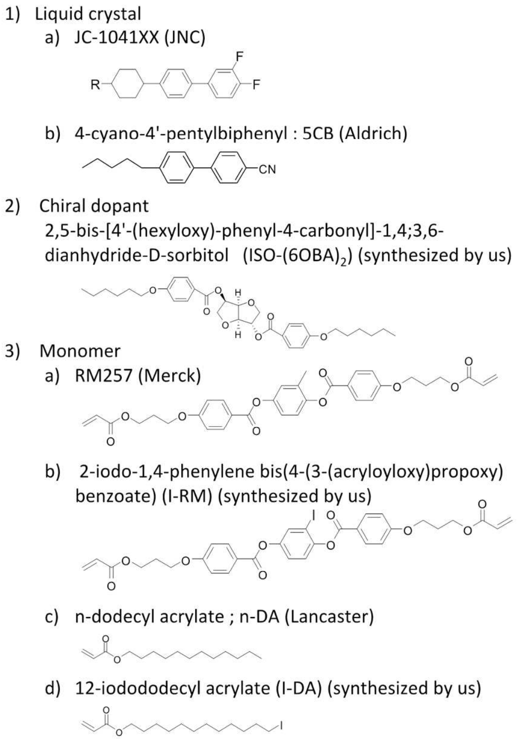

Fig. 1 Chemical structures of materials used to prepare the polymer-stabilized blue phase liquid crystal.

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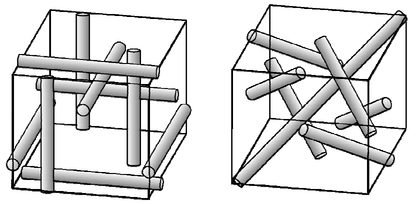
distinguish scattering by the polymers from background scattering by the liquid crystal. Thus, the monomers used to make the polymers in the blue phase were chemically modified and tagged with iodine (Z = 53), which scatters more strongly than the main component atoms of the liquid crystal molecules and polymer, since the atomic scattering factor in small-angle X-ray scattering is nearly equal to Z. The chemical structures of the materials used to prepare PSBPs are shown in Figure 1. The synthesis procedure and characterization data of both iodine-tagged monomers are described in the Supplementary Information 1. A well-mixed solution of JC-1041XX/5CB/ISO-$(6OBA)_2$/I-RM/I-DA=40.5/40.5/6.2/5.7/7.1 (wt%) and a small amount of photoinitiator 2,2-dimethoxy-2-phenylacetophenone (Aldrich) were sandwiched between polyethylene terephthalate film substrates, and thicknesses were fixed by 75- or 100-μm-thick film spacers to make the sample cells for X-ray measurements. The cells were irradiated with UV light of 365 nm to photopolymerize the monomers within the solutions, which were on a hot plate.

The small-angle X-ray scattering measurements were performed using the BL40B2 beamline at the synchrotron radiation facility of SPring-8(Hyogo, Japan). The camera length L was 2–4.31 m and the X-ray wavelength was 0.15 nm.

The structures of blue phases I and II are body-centred cubic (BCC) with space group symmetry $I4_132$ (O^8) and simple cubic with $P4_232$ (O^2), respectively[1, 12]. Each structure is composed of two overlapping lattices of double-twist cylinders and disclinations. In the case of blue phase I, which we focused on in this study, the lattice symmetries of the double-twist cylinders and disclinations are O^{8+} and O^{8-}, respectively[2]. We calculated the structure factors for the X-ray scattering of O^{8+} and O^{8-} and found that they can be expressed by equations 1 and 2, respectively, when only the alignments of the axes of the double-twist cylinders and disclinations are considered as shown in Figure 2 (Supplementary Information 2). This simplification is valid when the analyses are focused on diffracting directions of the X-rays, as in this study.

$$F_{hkl}^{O8+}=f\left\{\left(1+e^{(k+l)\pi i}\right)e^{\frac{1}{2}k\pi i}\frac{e^{2h\pi i}-1}{2h\pi i}+\left(1+e^{(h+l)\pi i}\right)e^{\frac{1}{2}l\pi i}\frac{e^{2k\pi i}-1}{2k\pi i}\right.$$
$$\left.+\left(1+e^{(h+k)\pi i}\right)e^{\frac{1}{2}h\pi i}\frac{e^{2l\pi i}-1}{2l\pi i}\right\} \quad (1)$$

$$F_{hkl}^{O8-}=f\left\{\frac{e^{2(h+k+l)\pi i}}{(h+k+l)\pi i}+\left(e^{l\pi i}+e^{(h+k)\pi i}\right)\frac{e^{(h-k-l)\pi i}}{(h-k-l)\pi i}\right.$$
$$\left.+\left(e^{h\pi i}+e^{(k+l)\pi i}\right)\frac{e^{(h-k+l)\pi i}}{(h-k+l)\pi i}+\left(e^{k\pi i}+e^{(h+l)\pi i}\right)\frac{e^{(h+k-l)\pi i}}{(h+k-l)\pi i}\right\} \quad (2)$$



O^{8+} O^{8-}

Fig. 2 Schematic illustration of O^{8+} and O^{8-} alignments.

where h, k, l are Miller indices and i is imaginary. Both structure factors are zero except for cases in which $h+k+l$ = even number, which is consistent with the BCC symmetry of the blue phase I lattice. For the lattice planes with smaller spacing satisfying $h+k+l$ = even number, i.e., {110}, {200}, {211}, and {220}, the magnitude of the structure factors can be calculated, as shown in Table 1. The spacing d_{hkl} is expressed by equation (3) using the lattice constant a for the blue phase cubic lattice.

$$d_{hkl}=\frac{a}{\sqrt{h^2+k^2+l^2}} \quad (3)$$

Table 1 indicates that X-ray diffraction for larger d_{hkl} occurs, i.e., $F^2P \neq 0$, only from the {110}, {220}, {310}, {400}, {330}, and {420} planes for O^{8+} (double-twist cylinder lattice) and from {211}, {220}, {321}, and {422} for O^{8-} (disclination lattice) due to the extinction rule. Therefore, it is easy to distinguish whether X-ray diffractions from PSBP originate from O^{8+} or O^{8-} because their extinction rules differ.

The phase behaviour of the sample solution was investigated using a polarizing optical microscope. The JC-1041XX/5CB/ISO-$(6OBA)_2$/I-RM/I-DA=0.5/40.5/6.2/5.7/7.1 (wt%) solution without polymerization exhibited the phase transitions of chiral nematic-blue phase I at 303.0 K and blue phase I-isotropic at 306.8 K. PSBP prepared using the above solution showed a blue phase–isotropic phase transition at approximately 322 K. The blue phase of PSBP was stable at around room temperature.

Figure 3 shows small-angle X-ray scattering two-dimensional (2D) images from an imaging plate taken at 298 K for solutions of JC-1041XX/5CB/ISO-$(6OBA)_2$/I-RM/I-DA=40.5/40.5/6.2/5.7/7.1 (wt%) photopolymerized at temperatures of (a) 294.8 K (chiral nematic phase, N*), (b) 303.5 K (blue phase I, BP I), and (c) 311.0 K (isotropic phase, Iso), respectively. The sample photopolymerized at 303.5 K,

Table 1. Magnitudes of the structure factors for O^{8+} and O^{8-}.

O^{8+}				O^{8-}				
hkl	F^2	*P*	F^2P	*hkl*	F^2	*P*	F^2P	d_{hkl}/a
110	4	12	48	110	0	12	0	0.707
200	0	6	0	200	0	6	0	0.500
211	0	24	0	211	4	24	96	0.408
220	4	12	48	220	16	12	192	0.354
310	4	24	96	310	0	24	0	0.316
222	0	8	0	222	0	8	0	0.289
321	0	48	0	321	4	48	192	0.267
400	16	6	96	400	0	6	0	0.250
330	4	12	48	330	0	12	0	0.236
411	0	24	0	411	0	24	0	0.236
420	4	24	96	420	0	24	0	0.224
332	0	24	0	332	0	24	0	0.213
422	0	24	0	422	4	24	96	0.204

F: structure factor, *P*: multiplicity factor, and d_{hkl}/a: spacing of (*hkl*) normalized by the lattice constant. The intensity of X-ray diffraction is proportional to F^2P for random orientation.

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as shown in Figure 3b, was PSBP, and the other two samples showed no blue phase at a measuring temperature of 298 K. The 2D images of Figure 3 were magnified about the small-angle region just around the direct beam. The circular shape at the centre of each image was the shadow of the 2-mm-diameter beam stopper. Clear Debye-Scherrer rings are observable in Figure 3b, while no clear diffractions are seen in Figures 3a and c, indicating that the sample photopolymerized at BP I temperature forming PSBP had a periodic structure, while the samples photopolymerized in states other than BP I did not have periodic structures in the observed small-angle region. In addition, we confirmed that no diffractions were observed for the blue phase with iodized monomers without photopolymerization (see Supplementary Information 3), and PSBP prepared with monomers with no iodine showed very weak diffractions at the same angles as Figure 3b. These results clearly indicate that the observed diffraction patterns in Figure 3b were due to PSBP with polymers tagged with iodine photopolymerized in a solution in the blue phase. When we used a solution in which only one of the two monomers had iodine, similar diffraction patterns were observed. This means that both monomers were incorporated in the periodic polymer structure in PSBP.

Figure 4 shows a) the X-ray diffraction intensity profile after subtracting the background scattering and b) the 2D image trimmed in a small-angle region for well-oriented PSBP prepared from JC-1041XX/5CB/ISO-(6OBA)$_2$/I-RM/n-DA=43.4/43.4/6.5/2.4/4.3 (wt%). At least four diffraction peaks are observable. From the Bragg angles of the diffraction peaks and the Bragg equation, each spacing *d* can be calculated, with d_1 = 109, d_2 = 96, d_3 = 72, and d_4 = 54 nm in order of ascending angle. The ratios of the spacings, as normalized by d_1, are 1 : 0.88 : 0.66 : 0.49 for $d_1 : d_2 : d_3 : d_4$. The expected normalized ratios of spacing for O^{8+} and O^{8-} lattices, as calculated from Table 1, are $d_{110} : d_{220} : d_{310} : d_{400}$ = 1 : 0.5 : 0.45 : 0.35 for O^{8+} and $d_{211} : d_{220} : d_{321} : d_{422}$ = 1 : 0.87 : 0.66 : 0.50 for O^{8-}. Comparing our experimental results with the theoretical calculations, the structure of polymers tagged with iodine in PSBP is clearly consistent with an O^{8-} structure, that is, the alignment of the disclinations in BP I. Thus, it is reasonable to attribute d_1, d_2, d_3, and d_4 observed in this study to d_{211}, d_{220}, d_{321}, and d_{422}, respectively, for O^{8-}. The intensity of the diffraction peaks decreased with increasing Bragg angle and the intensity ratio of observed peaks is different from expected one from the theory. This could be due to the disordering and fluctuation of the lattice because the blue phase is a fluid crystal and to the deviation of the lattice orientation from a complete random while the theory is assumed to be completely random.

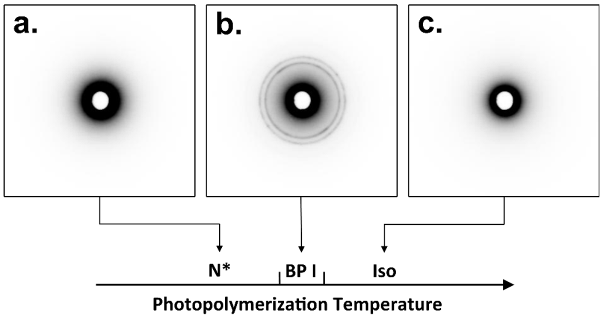

Fig. 3 Small-angle X-ray scattering 2D images trimmed in a small-angle region taken at 298 K by an imaging plate for solutions of JC1041XX/5CB/ISO-(6OBA)2/I-RM/I-DA=40.5/40.5/6.2/5.7/7.1 (wt%) photopolymerized at temperatures of **a.** 294.8 K (chiral nematic phase), **b.** 303.5 K (blue phase I), and **c.** 311.0 K (isotropic phase). Wavelength of X-ray: 0.15 nm and camera length: 4.31 m.

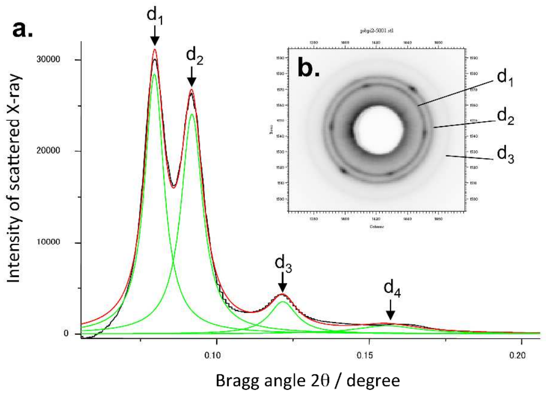

Fig. 4 **a**. X-ray diffraction intensity profile after subtracting the background scattering and **b.** the 2D image trimmed in a small-angle region for a well-oriented PSBP. Wavelength of X-ray: 0.15 nm and camera length: 2.13 m.

Figure 5 is an illustration of the diffraction pattern of Figure 4b. The four spots along the Debye-Scherrer ring of {211} and the two spots along {220} are indicated. The in-plane angles of the spots are 110° and 55°, as schematically shown in Figure 5. The angle between spots reflects the angle between the different planes diffracting the X-rays. This angle *δ* is expressed by the following formula:

$$\delta = \cos^{-1}\left(\frac{\mathbf{H}_{hkl}\cdot\mathbf{H}_{h'k'l'}}{\left|\mathbf{H}_{hkl}\right|\cdot\left|\mathbf{H}_{h'k'l'}\right|}\right) \qquad (4)$$

where $\mathbf{H}_{\mathrm{hkl}}$ is the reciprocal lattice vector of the (*hkl*) plane. We investigated all possible values of *δ* for the {211} and {220} spots and found that *δ* between (112) and $(11\bar{2})$ was 109.5° and δ between (220) and (112) or $(11\bar{2})$ was 54.7°, which corresponds to possible diffractions when the X-ray is incident perpendicular to the $(\bar{1}10)$ plane. The observed angles involving the {211} and {220} spots back up the validity of our assignment of the diffraction spots. From the above results, we can conclude that the polymers in PSBP condensed selectively into the disclinations within the blue phase lattice. In addition, because the blue phase before the photopolymerization of iodized monomers showed no diffraction, we can deduce that the monomers were dispersed randomly in the blue phase before photopolymerization and then the growing polymers drifted, segregated, or grew selectively along the disclination cores during in-situ photopolymerization in the blue

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phase. Particles and molecules in a liquid crystal tend to be attracted and trapped by disclinations or disordered places[10, 13, 14].

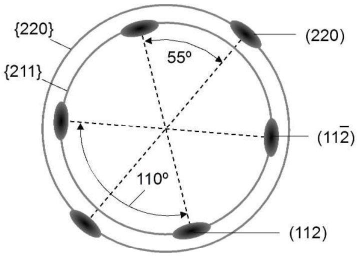

Figure 5. Schematic illustration of the diffraction pattern of Figure 4b.

Therefore, it is plausible and reasonable that polymers generated in the blue phase are attracted and trapped by the disclinations inside the blue phase, and then polymer networks with same alignment as the disclination lattice in the blue phase can form as shown in Figure 6. Interestingly, PSBP still diffracted even after heating to the isotropic state, which indicates that the polymer networks were tough enough to withstand phase transition, presumably because of chemical cross-linking through I-RM and were not destroyed even when the molecular alignment of the blue phase was lost. This result explains why the blue phase state of PSBP was recoverable even after heating to the isotropic phase temperature followed by cooling back down to the blue phase temperature again.

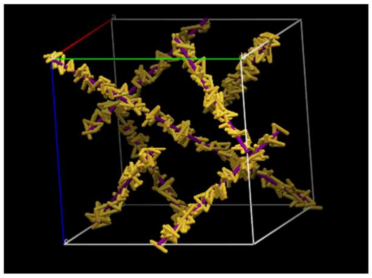

Figure 6. A possible polymer aggregation structure with body-centered cubic O^{8-} symmetry formed in polymer-stabilized blue phase I liquid crystal.

Conclusions

Clear Debye-Scherrer rings and/or spots were observed in an ultrasmall-angle region of synchrotron X-ray scattering by polymer-stabilized blue phase liquid crystals when monomers tagged with iodine were polymerized in the blue phase. The results indicate the polymers had three-dimensional lattice structure with body-centered cubic O^{8-} symmetry of a few 100 nm order periodicity, which is consistent with the disclination lattice structure of blue phase I. We conclude that during polymerization in the blue phase, the polymer chains condensed selectively into the disclinations within the blue phase. Our experimental results greatly contribute to understanding of the mechanism why the blue phase is stabilized in the polymer-stabilized blue phases.

Acknowledgements

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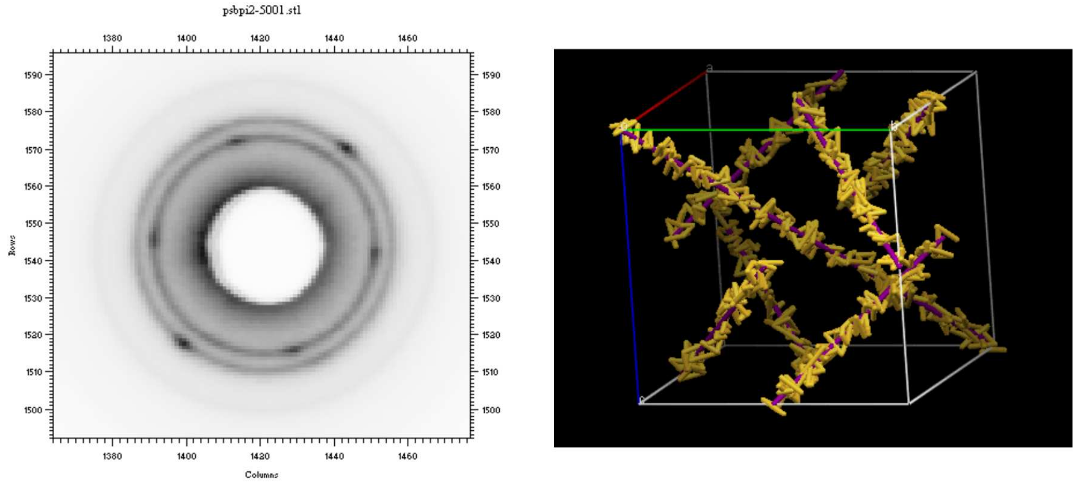

Ultra-small angle X-ray diffraction pattern of polymer-stabilized blue phase liquid crystals and a possible three-dimensional giant polymer lattice with body-centered cubic O^{8-} symmetry formed in them.

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