

Electronic Supplementary Information

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

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1. Syntheses and Measurements

1.1 Materials and General Methods

12-iodododecyl acrylate,¹ 2-iodobenzene-1,4-diol,²⁻⁴ and 4-(3-acryloyloxypropoxy)benzoic acid⁵ were synthesized according to references.

Reagents and solvents were purchased from Wako Pure Chemical Industries, Ltd., Tokyo Chemical Industry Co., Ltd., and Kanto Chemical Co., Inc. and used without purification. Thin layer chromatography was conducted on SiO₂-layered glass plate (60 F254; Merck). The chromatographic separations were carried out on SiO₂ 60 N (particle size 0.063-0.210 mm; Kanto Chemical Co., Inc.). ¹H NMR spectra were measured on JEOL JNM-LA400 (400 MHz) using CDCl₃ as a solvent at 25 °C. Chemical shifts are reported in ppm relative to the signal of tetramethylsilane. Residual solvent signals in the ¹H NMR spectra were used as an internal reference. Mass spectra (MS) and elemental analyses were performed at Kyushu University.

1.2 Synthesis of 2-iodo-1,4-phenylene bis(4-(3-(acryloyloxy)propoxy)benzoate)

A mixture of 2-iodobenzene-1,4-diol (0.47 g, 1.99 mmol) and 4-(3-acryloyloxypropoxy)benzoic acid (1.00 g, 3.99 mmol) in CH₂Cl₂ (55 mL) was cooled with an ice bath. *N,N'*-dicyclohexylcarbodiimide (3.96 g, 19.2 mmol) and *N,N*-dimethyl-4-aminopyridine (1.66 g, 13.6 mmol) was added to the solution. The reaction mixture was stirred magnetically for 24 hours at room temperature. The solvent was removed in vacuo after filtration. The residue was purified by silica gel column chromatography (AcOEt/toluene = 5:95) and recrystallization from AcOEt/EtOH in 47% yield.

¹H NMR (400 MHz, CDCl₃): δ = 8.22 (dd, *J* = 7.0, 1.9 Hz, 2H), 8.13 (dd, *J* = 7.0, 1.9 Hz, 2H), 7.74 (d, *J* = 1.0 Hz, 1H), 7.30-7.28 (m, 2H), 7.02-6.98 (m, 4H), 6.43 (dd, *J* = 17.3, 1.3 Hz, 2H), 6.14 (dd, *J* = 17.3, 10.4 Hz, 2H), 5.86 (dd, *J* = 10.4, 1.3 Hz, 2H), 4.39 (t, *J* = 6.3 Hz, 4H), 4.17 (td, *J* = 6.3, 3.2 Hz, 4H), 2.23 ppm (quin, *J* = 6.3 Hz, 4H); MS (FAB⁺): *m/z* (%): 154 (100) [matrix: 3-nitrobenzyl alcohol], 233 (59) [M⁺-C₂₆H₂₆O₈], 412 (5) [M⁺-C₁₆H₁₆O₅], 700 (0.7) [M⁺], 701 (1) [M⁺+1]; elemental analysis calcd (%) for C₃₂H₂₉IO₁₀: C 54.87, H 4.17; found: C 54.87, H 4.19.

2. Derivation of equations 1 and 2

The amplitude and phase of X-ray diffracted from crystal lattice planes characterized by Miller indices h, k, l are described by the structure factor F_{hkl} .

$$F_{hkl} = \sum_{j=1}^N f_j e^{2\pi i(\mathbf{H}\mathbf{r}_j)} = \sum_{j=1}^N f_j e^{2\pi i(hu_j + kv_j + lw_j)}$$

where the sum is over all atoms in the unit cell, \mathbf{H} is the reciprocal lattice vector, u_j, v_j, w_j are positional coordinates of the j th atom, f_j is the scattering factor of the j th atom. In the case of the X-ray diffraction of the polymer-stabilized blue phases as in this study, the contrast of electron density to give a structure factor should be made by not points but lines unlike normal crystals. We calculated the structural factors of O^{8+} and O^{8-} lattices when X-ray scattering occurred from the axes of double twist cylinders and the disclinations, respectively, in blue phase I (BP I). A straight line \mathbf{r}_j passing through two points \mathbf{p}_j and \mathbf{q}_j in the unit cell of BP I can be expressed using a parameter t by

$$\begin{aligned} \mathbf{r}_j &= (1-t)\mathbf{p}_j + \mathbf{q}_j t \\ &= \mathbf{p}_j + (\mathbf{q}_j - \mathbf{p}_j)t \end{aligned}$$

The structure factor of each line is calculated by following equation.

$$\begin{aligned} \int_0^1 e^{2\pi i(\mathbf{H}\mathbf{r}_j)} dt &= \int_0^1 e^{2\pi i[\mathbf{H}\cdot\{\mathbf{p}_j + (\mathbf{q}_j - \mathbf{p}_j)t\}]} dt \\ &= e^{2\pi i(\mathbf{H}\mathbf{p}_j)} \int_0^1 e^{2\pi i[\mathbf{H}\cdot(\mathbf{q}_j - \mathbf{p}_j)t]} dt \\ &= \frac{e^{2\pi i(\mathbf{H}\mathbf{p}_j)}}{2\pi i[\mathbf{H}\cdot(\mathbf{q}_j - \mathbf{p}_j)]} \left(e^{2\pi i[\mathbf{H}\cdot(\mathbf{q}_j - \mathbf{p}_j)]} - 1 \right) \end{aligned}$$

The structure factor of unit cell in which N lines are involved is calculated by

$$\begin{aligned} F_{hkl} &= \sum_{j=1}^N F_j = \sum_{j=1}^N f_j L_j \int_0^1 e^{2\pi i(\mathbf{H}\mathbf{r}_j)} dt \\ &= \sum_{j=1}^N f_j L_j \frac{e^{2\pi i(\mathbf{H}\mathbf{p}_j)}}{2\pi i[\mathbf{H}\cdot(\mathbf{q}_j - \mathbf{p}_j)]} \left(e^{2\pi i[\mathbf{H}\cdot(\mathbf{q}_j - \mathbf{p}_j)]} - 1 \right) \end{aligned}$$

where f_j and L_j are the scattering factor per unit and the length of the j th line.

2.1 O^{8+} structure

Taking positional coordinates of 8 corners of the cubic unit cell with lattice constant a to be $(0, 0, 0)$, $(a, 0, 0)$, $(0, 0, a)$, $(a, a, 0)$, $(a, 0, a)$, $(0, a, a)$ and (a, a, a) , the 9 double twist cylinder axes in BP I unit cell are expressed by following 9 lines which link between 2 points \mathbf{p}/a to \mathbf{q}/a ; i) $(0, 0, 1/4)$ to $(0, 1, 1/4)$, ii) $(1/2, 0, 3/4)$ to $(1/2, 1, 3/4)$, iii) $(1, 0, 1/4)$ to $(1, 1, 1/4)$, iv) $(1/4, 0, 0)$ to $(1/4, 0, 1)$, v) $(1/4, 1, 0)$ to $(1/4, 1, 1)$, vi) $(3/4, 1/2, 0)$ to $(3/4, 1/2, 1)$, vii) $(0, 1/4, 0)$ to $(1, 1/4, 0)$, viii) $(0, 3/4, 1/2)$ to $(1, 3/4, 1/2)$, ix) $(0, 1/4, 1)$ to $(1, 1/4, 1)$ as shown in Fig. SI-1. It should be noted that the diffraction intensities of lines i), ii), iv), v) and ix) are half of iii), vi) and viii) to avoid double counting because the cores of the lines i), ii), iv), v) and ix) are in the boundary planes. All the lengths of line are equal in this cell, then we take $L_j=1$. The structure factors of each line are

$$\text{i) } F_1 = \frac{\frac{1}{2} f e^{\frac{1}{2} l \pi i}}{2 k \pi i} (e^{2 k \pi i} - 1)$$

$$\text{ii) } F_2 = \frac{f e^{\frac{(h+\frac{3}{2}) \pi i}{2}}}{2 k \pi i} (e^{2 k \pi i} - 1)$$

$$\text{iii) } F_3 = \frac{\frac{1}{2} f e^{\frac{(2h+\frac{1}{2}) \pi i}{2}}}{2 k \pi i} (e^{2 k \pi i} - 1) = \frac{\frac{1}{2} f e^{\frac{1}{2} l \pi i}}{2 k \pi i} (e^{2 k \pi i} - 1)$$

$$\text{iv) } F_4 = \frac{\frac{1}{2} f e^{\frac{1}{2} h \pi i}}{2 l \pi i} (e^{2 l \pi i} - 1)$$

$$\text{v) } F_5 = \frac{\frac{1}{2} f e^{\frac{(\frac{1}{2} h + 2k) \pi i}{2}}}{2 l \pi i} (e^{2 l \pi i} - 1) = \frac{\frac{1}{2} f e^{\frac{1}{2} h \pi i}}{2 l \pi i} (e^{2 l \pi i} - 1)$$

$$\text{vi) } F_6 = \frac{f e^{\frac{(\frac{3}{2} h + k) \pi i}{2}}}{2 l \pi i} (e^{2 l \pi i} - 1)$$

$$\text{vii) } F_7 = \frac{\frac{1}{2} f e^{\frac{1}{2} k \pi i}}{2 h \pi i} (e^{2 h \pi i} - 1)$$

$$\text{viii) } F_8 = \frac{f e^{\frac{(\frac{3}{2} k + l) \pi i}{2}}}{2 h \pi i} (e^{2 h \pi i} - 1)$$

$$\text{ix) } F_9 = \frac{1}{2} f e^{\frac{1}{2}(k+l)\pi i} \left(e^{2h\pi i} - 1 \right)$$

Then the equation (1) in the manuscript is derived by sum of above 9 equations.

2.2 O^{δ^-} structure

7 disclinations in BP I unit cell are expressed by following 7 lines which link between 2 points \mathbf{p}_j/a to \mathbf{q}_j/a ; i) (0, 0, 0) to (1, 1, 1), ii) (0, 1, 1/2) to (1/2, 1/2, 0), iii) (1/2, 1/2, 1) to (1, 0, 1/2), iv) (0, 1/2, 1/2) to (1/2, 0, 1), v) (1/2, 1, 0) to (1, 1/2, 1/2), vi) (0, 1/2, 1) to (1/2, 1, 1/2), vii) (1/2, 0, 1/2) to (1, 1/2, 0) as shown in Fig. SI-2. The line length of i) is twice of the other 6 lines. The structure factors of each line are

$$\begin{aligned} \text{i) } F_1 &= \frac{2f}{2(h+k+l)\pi i} \left(e^{2(h+k+l)\pi i} - 1 \right) \\ \text{ii) } F_2 &= \frac{f e^{(2k+l)\pi i}}{(h-k-l)\pi i} \left(e^{2(h-k-l)\pi i} - 1 \right) = \frac{f e^{l\pi i}}{(h-k-l)\pi i} \left(e^{2(h-k-l)\pi i} - 1 \right) \\ \text{iii) } F_3 &= \frac{f e^{(h+k+2l)\pi i}}{(h-k-l)\pi i} \left(e^{2(h-k-l)\pi i} - 1 \right) = \frac{f e^{(h+k)\pi i}}{(h-k-l)\pi i} \left(e^{2(h-k-l)\pi i} - 1 \right) \\ \text{iv) } F_4 &= \frac{f e^{(k+l)\pi i}}{(h-k+l)\pi i} \left(e^{2(h-k+l)\pi i} - 1 \right) \\ \text{v) } F_5 &= \frac{f e^{(h+2k)\pi i}}{(h-k+l)\pi i} \left(e^{2(h-k+l)\pi i} - 1 \right) = \frac{f e^{h\pi i}}{(h-k+l)\pi i} \left(e^{2(h-k+l)\pi i} - 1 \right) \\ \text{vi) } F_6 &= \frac{f e^{(k+2l)\pi i}}{(h+k-l)\pi i} \left(e^{2(h+k-l)\pi i} - 1 \right) = \frac{f e^{k\pi i}}{(h+k-l)\pi i} \left(e^{2(h+k-l)\pi i} - 1 \right) \\ \text{vii) } F_7 &= \frac{f e^{(h+l)\pi i}}{(h+k-l)\pi i} \left(e^{2(h+k-l)\pi i} - 1 \right) \end{aligned}$$

Then the equation (2) in the manuscript is derived by sum of above 7 equations.

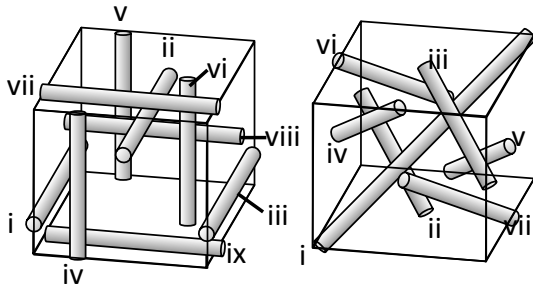


Fig. SI-1

Fig. SI-2

3. SAXD images



SAXD image of a blue phase with iodized monomer without photopolymerization. The camera length was 4.305 m.

4. References

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