# Characterization of Martensitic Phase Transformations in Blue Phase Liquid Crystals Using In-situ Small Angle Scattering

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## 1. Introduction

Blue phase liquid crystals can spontaneously form cubic lattice with the unit cell of few hundreds nanometer length scale.(*1*) Directed self-assembly (DSA) of blue phase liquid crystals (BP LCs) on chemically patterned surface enables to form single crystal of BP LCs into arbitrary large area (*2*) and provides us the unique opportunity to observe the martensitic transformation in the soft crystal, which further enriches and extends our understanding of such diffusionless phase transformation.(*3*) Based on the optical crosshatched structure that was previously captured during the phase transition, here, relying on in-situ resonant soft X-ray scattering (RSoXS),(*4*) we conduct more in-depth quantitative study of such soft crystal martensitic transformation.

## 2. Methods and Results

### *2.1 Materials*

MLC 2142 and S-811 were purchased from Merck. Octadecyltrichlorosilane (OTS), heptane, toluene, chlorobenzene, 1-methyl-2-pyrrolidinone (NMP), anisole, n-amyl acetate, isopropyl alcohol (IPA) and dichloromethane (DCM) were purchased from Sigma-Aldrich and used without further purification. Glass microscope slides were purchased from Fisher Scientific in the finest premium grade.

### *2.2 Preparation of BP LC materials*

The 36.32 wt% 4-(1-methylheptyloxycarbonyl) phenyl-4-hexyloxybenzoate (S-811) in MLC 2142mixtures were prepared by using toluene as a co-solvent. After mixing with an ultrasonic cleaner, toluene was evaporated overnight under vacuum at 50 °C.

### *2.3 RSoXS*

RSoXS was measured with transmission geometry at beamline 11.0.1.2 at the Advanced Light Source (ALS) of Lawrence Berkeley National Laboratory. The BP LC was measured in the SiN sandwich membrane cell. All the measurement was conducted at 284.5 eV. A post carbon K-edge of 284.5 eV was selected to obtain an enhanced scattering intensity and to minimize an absorption for preventing a sample damage. The beam was circular shape with diameter of approximately 300 μm and collecting time was varied from 0.1 to 10 s. The in-situ RSoXS measurement of BP LC phase transformation during heating was measured using temperature controlled stage. Heating rates were 0.45 °C/min. A modified version of the NIKA software package was used for calibration and data reduction. (*5*)

### *2.4 In-situ RSoXS during BP LC phase transformation*

Upon heating, the texture of the LC within the chemically-patterned sandwich cell, observed by polarized optical microscopy (POM), and shows considerable changes (Fig. 1). Upon heating from 39.19 °C, the texture changes from that associated with a cholesteric (Chol.) LC phase, to that associated with the BPI (green domains; 40.83 °C), BPII (blue domains; 41.23 °C), and, finally, the isotropic (Iso.) (black; 42.80 °C) LC phase. Based on the color spectra of the textures, the out-of-plane orientation could be identified as the (110) axis for the BPI (i.e. $BPI_{(110)}$), and the (100) axis for the BPII (i.e. $BPII_{(100)}$). In all cases, poly-crystals with random in-plane orientations are observed. (Crystallinity of the BP LCs is sensitive to the heating rate: the rate here, ≈ 0.5 °C/min, results in poly-crystals of $BPII_{(100)}$ but a slower rate, e.g. ~ 0.2 °C/min, would have resulted in a single domain.(*3*)) During the transition from $BPI_{(110)}$ to $BPII_{(100)}$, a mixture of green $BPI_{(110)}$ and blue $BPII_{(100)}$ domains are observed (e.g. at 41.01 °C).

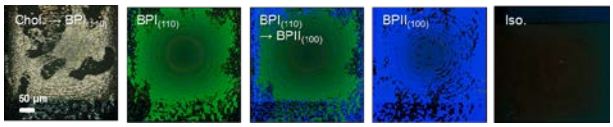


Fig. 1. Optical microscopy images during phase transformations (Chol.→BPI→ BPII→Iso.) upon heating.

Two distinct scattering patterns may be observed during heating of the LC sandwich cells (Fig. 2). When the LC is at a temperature of 41.0 °C, rings are observed at *q*-values corresponding to the {110}, {200}, {211}, and {220} planes of a 250.3 nm unit cell size BPI LC with the (110) orientation out-of-plane (Fig. 2a). The

intensity of the rings varies as a function of azimuthal angle due to the polarization of the incident soft X-rays, the electric field of which oscillates in the horizontal direction. At 42.8 °C, the RSoXS scattering pattern again consists of rings but at *q*-values corresponding to the {100}, {110}, {200}, and {210} planes of a 141.7 nm unit cell size BPII LC with the (100) orientation out-of-plane (Fig. 2b). The observation of rings, rather than distinct peaks, in the RSoXS scattering patterns of the $BPI_{(110)}$ and $BPII_{(100)}$ LC phases confirms that the samples indeed consist of small poly-crystals with random in-plane orientation, as observed optically (cf. Fig. 1a).

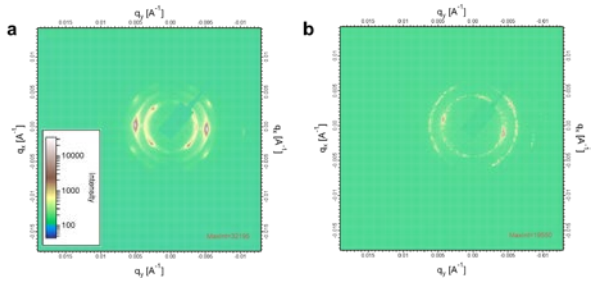


Fig. 2. Representative RSoXS pattern of (a) $BPI_{(110)}$ at 41.0 °C and (b) $BPII_{(100)}$ at 42.7 °C during heating.

### 3. Conclusions

In conclusion, we directly visualized the phase transformation of BP LC during heating using optical microscopy and RSoXS measurement. The understanding of the phase transformation principle between the two fluid lattices will provide important insight for designing various applications including optical switching device.(*6*, *7*) Above all, RSoXS using single crystalline BP LC will provide a fertile platform to study the behavior of fluidic LC in the crystalline soft matter system.

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