Supplementary Information for:

Structural Characterization of Fddd phase in Diblock Copolymer Thin Film
by Electron Microtomography

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Transmission small-angle X-ray scattering (TSAXS) experiment was conducted at the 4C1 beam line of the Pohang Accelerator Laboratory, Pohang, Korea. Wavelength of the X-ray beam was 1.21 Å and sample-to-detector distance was 2.1 m. The TSAXS specimen was prepared in a cell consisting of a 1 mm thick Al spacer and Kapton® film windows. Prior to in-situ heating experiment, the bulk specimen was annealed at 120°C for 24 h in vacuo. The TSAXS profiles were obtained as the sample was heated from 120°C to 200°C at a rate of 1°C/min and the beam exposure time to obtain each pattern was 50 sec.

Upon heating, the PS-b-PI sample exhibited various order-order transitions. Figure S1(a) displays representative TSAXS profile of each phase obtained during heating. These profiles are plotted as a function of wave vector \( q = (4\pi/\lambda)\sin(\theta/2) \) and circular-averaged intensity. Reflection peaks are labeled with the value of \( q/q^* \) where \( q^* \) is the wave vector of the principal peak. The initial specimen before heating exhibits LAM showing peaks at the integer multiple wave-vector positions of the primary peak. As the temperature rises, the first order peak becomes broader due to the reflections from \{101\}_HPL and \{102\}_HPL in ABC stack type HPL phase. At 144°C, the HPL phase is fully developed. And, at 160°C, the regularly spaced reflections, a characteristic of lamellar structure, disappear and a complex scattering profile corresponding to \textit{Fddd} phase is developed. Reflection peaks appear at \( q/q^* \) (\( q^* = 0.293 \text{ nm}^{-1} \)) of 0.94, 1, 1.22, 1.55, 1.72, 1.81, 1.95, 2.00. These wave vectors of observed reflections are indicated by the arrows in Figure S1, and their miller indices are listed in Table S1. From the data, lattice parameters for the \textit{Fddd} space group was calculated as \( a : b : c = 24.6 \text{ nm} : 50.0 \text{ nm} : 89.8 \text{ nm} \). At a higher temperature, \textit{Fddd} phase is converted to double gyroid phase showing two familiar peaks appearing at \( q/q^* \) of \( \sqrt{6} \) and \( \sqrt{8} \) before going into the disordered state.
Figure S1. (a) Representative TSAXS profile of each phases obtained at different temperatures in the PS-b-PI bulk. Each peak is labeled with the ratio ($q/q^*$) relative to the principal peak ($q^*$).

(b) The plot of the change of inverse intensity of primary peak and domain spacing ($d = 2\pi/q^*$) against the reciprocal of the absolute temperature.
Table S1. Wave vectors of the observed reflections and their Miller indices of the reflection planes from Fddd TSAXS profile obtained at 160°C.

| q (nm⁻¹) | q/q* | hkl
<table>
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<tr>
<td>0.278</td>
<td>0.948</td>
<td>004</td>
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<tr>
<td>0.293 (q*)</td>
<td>1.00</td>
<td>111</td>
</tr>
<tr>
<td>0.358</td>
<td>1.22</td>
<td>113</td>
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<tr>
<td>0.451</td>
<td>1.54</td>
<td>115</td>
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<tr>
<td>0.503</td>
<td>1.72</td>
<td>040</td>
</tr>
<tr>
<td>0.531</td>
<td>1.81</td>
<td>202</td>
</tr>
<tr>
<td>0.587</td>
<td>2.00</td>
<td>222</td>
</tr>
</tbody>
</table>

a) Miller indices corresponding to the observed reflections.

To estimate the temperature windows of stable phases, the reciprocal intensity of the primary peak and the domain spacing (d = 2π/q*) are plotted against the reciprocal temperature as shown in Figure S1 (b). Three order-order transitions takes place at 136°C (LAM-HPL), 150°C (HPL-Fddd) and 176°C (Fddd-DG). And order to disorder transition from DG phase occurs at 192°C.

Electronic supplementary information (ESI) available:
3D movie of Figure 3 is attached as MPEG video.

References