Electronic Supplementary Material (ESI) for Soft Matter

Supplmentary Information for :

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

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Fddd phase in bulk

Transmission small-angle X-ray scattering (TSAXS) experiment was conducted at the 4C1 beam line of the Pohang Accelerator Laboratory, Pohang, Korea.[1] 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.[2] At 144^{o}C, the HPL phase is fully developed. And, at 160^{o}C, the regularly spaced reflections, a characteristic of lamellar structure, disappear and a complex scattering profile corresponding to *Fddd* phase is developed. Reflection peaks appear at q/q* (q^{*} = 0.293 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 *Fddd* space group was calculated as a : b : c = 24.6 nm : 50.0 nm : 89.8 nm. At a higher temperature, *Fddd* phase is converted to double gyroid phase showing two familiar peaks appearing at q/q* of √6 and √8 before going into the disordered state.

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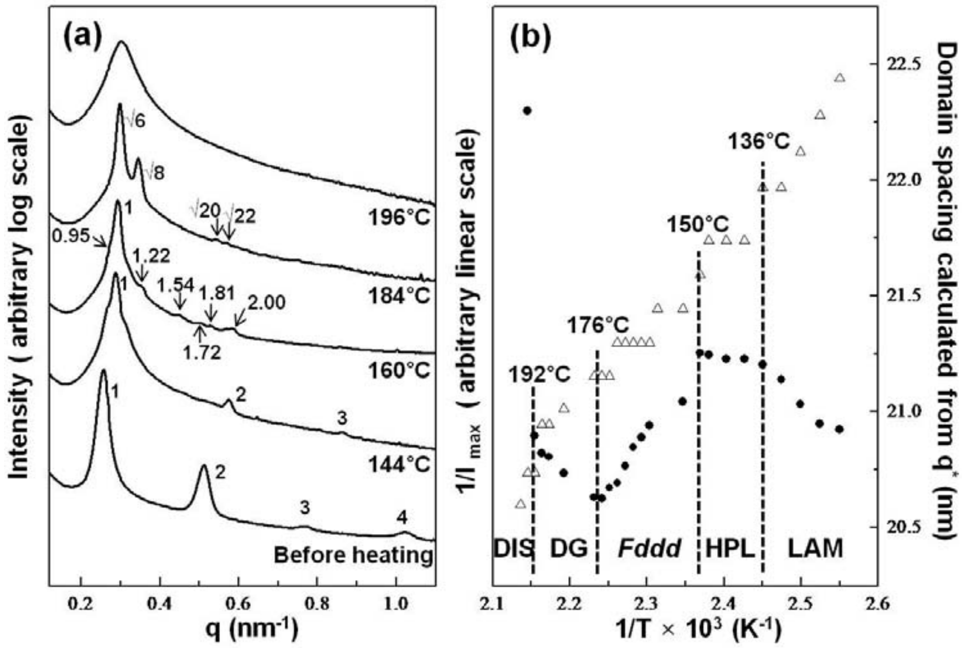

Figure S1. (a) Representative TSAXS profile of each phases obtained at different temperatures in the PS-*b*-PI bulk. Each peak is labeled with the ratio (q/q^*) relative to the principal peak (q^*). (b) The plot of the change of inverse intensity of primary peak and domain spacing ($d = 2\pi/q^*$) against 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[a)]**
0.278	0.948	004
0.293 (q*)	1.00	111
0.358	1.22	113
0.451	1.54	115
0.503	1.72	040
0.531	1.81	202
0.587	2.00	222

[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

1. J. Bolze, J. Kim, J. Y. Huang, S. Rah, H. S. Youn, B. Lee, T. J. Shin, M. Ree, *Macromol. Res.* **2002**, *10*, 2-12.

2. Y. L. Loo, R. A. Register, D. H. Adamson, A. J. Ryan, *Macromolecules* **2005**, *38*, 4947-4949.