Supplementary Information

Cooperative, Selective Self-Assembly Behaviors of Diblock Copolypeptides in Nanoscale Thin Films[†]

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GIXS data analysis

The measured 2D GIXS data were quantitatively analyzed using the GIXS formulas described as follows. The intensity (I_{GIXS}) of the wave scattered from a film sample can be expressed as the following scattering formula:[1]

$$I_{GIXS}(\alpha_f, 2\theta_f) \cong \frac{1}{16\pi^2} \cdot \frac{1-e^{-2\mathrm{Im}(q_z)t}}{2\,\mathrm{Im}(q_z)} \begin{bmatrix} \left|T_iT_f\right|^2 I_1(q_\parallel, \mathrm{Re}(q_{1,z})) + \\ \left|T_iR_f\right|^2 I_1(q_\parallel, \mathrm{Re}(q_{2,z})) + \\ \left|T_fR_i\right|^2 I_1(q_\parallel, \mathrm{Re}(q_{3,z})) + \\ \left|R_iR_f\right|^2 I_1(q_\parallel, \mathrm{Re}(q_{4,z})) \end{bmatrix} \quad (1)$$

where $Im(q_z) = |Im(k_{z,f})| + |Im(k_{z,i})|$, $Re(x)$ is the real part of x, d is the film thickness, R_i and T_i are the reflected and transmitted amplitudes of the incoming X-ray beam respectively, and R_f and T_f are the reflected and transmitted amplitudes of the outgoing X-ray beam respectively. In addition, $q_{\parallel} = \sqrt{q_x^2 + q_y^2}$, $q_{1,z} = k_{z,f} - k_{z,i}$, $q_{2,z} = -k_{z,f} - k_{z,i}$, $q_{3,z} = k_{z,f} + k_{z,i}$, and $q_{4,z} = -k_{z,f} + k_{z,i}$; here, $k_{z,i}$ is the z-component of the wave vector of the incoming X-ray beam, which is given by $k_{z,i} = k_o \sqrt{n_R^2 - \cos^2 \alpha_i}$, and $k_{z,f}$ is the z-component of the wave vector of the outgoing X-ray beam, which is given by $k_{z,f} = k_o \sqrt{n_R^2 - \cos^2 \alpha_f}$, where $k_o = 2\pi / \lambda$, λ is the wavelength of the X-ray beam, n_R is the refractive index of the film given by $n_R = 1 - \delta + i\xi$ with dispersion δ and absorption ξ, α_i is the out-of-plane grazing incident angle of the incoming X-ray beam, and α_f is the out-of-plane exit angle of the outgoing X-ray beam. q_x, q_y, and q_z are the components of the scattering vector $\mathbf{q}$. I_1 is the scattering intensity of the structure in the film, which can be calculated kinematically.

In eq 1, I_1 is the scattered intensity from the certain structure in the film, and thus can be expressed by the following equation:[1,2]

$$I_1(\mathbf{q}) = P(\mathbf{q}) \cdot S(\mathbf{q}) \qquad (2)$$

where $P(\mathbf{q})$ is the form factor of the scatterers that describes the shape, size, and orientations of the scatterers, and $S(\mathbf{q})$ is the structure factor that provides information on the positions of the scatterers such as the crystal lattice parameters, orientation, dimension, and symmetry in an ordered structure and the mean-distance between the scatterers.

For a cylinder scatterer having a radius R and a length L, which can represent a homopolypeptide chain in α-helical conformation, the form factor $P(\mathbf{q})$ can be expressed by the following equation: [3,4]

$$P(\mathbf{q}) = F^2(\mathbf{q}, R, L) \qquad (3)$$

where $F(\mathbf{q}, R, L)$ is the structure amplitude of the cylindrical scatterer given by

$$F(\mathbf{q}, R, L) = 2\pi R^2 L \frac{J_1(\mathbf{q}R)}{\mathbf{q}R} \frac{\sin(\mathbf{q}L/2)}{\mathbf{q}L/2} \exp(-i\mathbf{q}L/2) \tag{4}$$
.

For a cylinder scatterer composed of two subunits where one unit has a radius R_1 and a length L_1 while the other unit has a radius R_2 and a length L_2, which can represent a diblock copolypeptide in α-helical conformation, the structure amplitude can be expressed by

$$
\begin{aligned}
F(\mathbf{q}, R, L) &= i\pi R_1^{\ 2} \frac{J_1(\mathbf{q}R_1)}{\mathbf{q}^2 R_1} \left\{1 - \cos(\mathbf{q}L_1) + i\sin(\mathbf{q}L_1)\right\} \exp(-i\mathbf{q}L_1/2) \\
&+ i\pi R_2^{\ 2} \frac{J_1(\mathbf{q}R_2)}{\mathbf{q}^2 R_2} \left\{\cos(\mathbf{q}L_2) - i\sin(\mathbf{q}L_2) - 1\right\} \exp(-i\mathbf{q}L_2/2)
\end{aligned}
\tag{5}
$$

where L is the total length of the cylinder consisted of two subunits (L_1 and L_2): $L = L_1 + L_2$. Here it is assumed that the distribution of the length L of the cylindrical scatterers follows a Gaussian distribution function $G(L)$:

$$G(L) = \frac{1}{\sqrt{2\pi}\sigma_\phi} \exp\left[-\frac{(L - \bar{L})^2}{2\sigma_L^2}\right] \tag{6}$$

where $\bar{L}$ and σ_L are the mean total length of the cylinder and a standard deviation of L from $\bar{L}$, respectively. The size distribution of the cylindrical scatterers can be taken into account by averaging the form factor $<F>$ with respect to L, yielding

$$\langle F \rangle = \frac{\int_0^\infty G(L)F(\mathbf{q}, R, L)dL}{\int_0^\infty G(L)dR} \tag{7}$$
.

    For a paracrystalline lattice consisting of these rods packed hexagonally, the structure factor $S(\mathbf{q})$ (the so-called interference function or lattice factor) can be determined from the Fourier transform of a complete set of lattice points.[5] In a paracrystal with distortion of the second kind, the positions of the

lattice points can only be described with a positional distribution function. In the simple case where the autocorrelation function of the crystal lattice is given by the convolution product of the distributions of the lattice points along three axes, and the distribution function is a Gaussian, $S(\mathbf{q})$ can be expressed by the following equation:[6]

$$S(\mathbf{q}) = \prod_{k=1}^{3} Z_k(\mathbf{q}) \tag{8}$$

$$Z_k(\mathbf{q}) = 1 + \frac{F_k(\mathbf{q})}{1 - F_k(\mathbf{q})} + \frac{F_k^*(\mathbf{q})}{1 - F_k^*(\mathbf{q})} \tag{9}$$

$$F_k(\mathbf{q}) = \left| F_k(\mathbf{q}) \right| e^{-i\mathbf{q} \cdot \mathbf{a}_k} \tag{10}$$

$$\left| F_k(\mathbf{q}) \right| = \exp\left[-\left(\frac{q_1^2 g_1^2 + q_2^2 g_2^2 + q_3^2 g_3^2}{2} \right) \right]_. \tag{11}$$

Here g_1, g_2, and g_3 are the components of the g-factor defined as

$$g_1 = \Delta\mathbf{a_1}/\mathbf{a_1} \tag{12a}$$

$$g_2 = \Delta\mathbf{a_2}/\mathbf{a_2} \tag{12b}$$

$$g_3 = \Delta\mathbf{a_3}/\mathbf{a_3} \tag{12c}$$

where $\mathbf{a_k}$ is the component of the fundamental vector $\mathbf{a}$ of the domain structure and $\Delta\mathbf{a_k}$ is the displacement of the vector $\mathbf{a_k}$. And q_1, q_2, and q_3 are the components of the scattering vector $\mathbf{q}$, which are defined as:

$$q_1 = \mathbf{a_1} \cdot \mathbf{q_x} + \mathbf{a_1} \cdot \mathbf{q_y} + \mathbf{a_1} \cdot \mathbf{q_z} \tag{13a}$$

$$q_2 = \mathbf{a_2} \cdot \mathbf{q_x} + \mathbf{a_2} \cdot \mathbf{q_y} + \mathbf{a_2} \cdot \mathbf{q_z} \tag{13b}$$

$$q_3 = \mathbf{a_3} \cdot \mathbf{q_x} + \mathbf{a_3} \cdot \mathbf{q_y} + \mathbf{a_3} \cdot \mathbf{q_z} \tag{13c}$$

From eqs 8-13 with the fundamental vectors, the structure factor $S(\mathbf{q})$ can be determined by using various g-factors, and also d-spacing values of the diffraction planes determined.

Moreover, for a structure with a given orientation in a film, its fundamental vectors can be rotated and transformed by a rotation matrix. When the structure of the film is randomly oriented in the plane of the film but uniaxially oriented out of plane, the peak position vector $\mathbf{q_c}$ of a certain reciprocal lattice point $\mathbf{c}^*$ in the sample reciprocal lattice is given by

$$\mathbf{q_c} = \mathbf{R} \cdot \mathbf{c}^*$$
$$\equiv (q_{c,x}, q_{c,y}, q_{c,z})$$

(14)

where $\mathbf{R}$ is a 3×3 matrix to decide the preferred orientation of the structure in the film, and $q_{c,x}$, $q_{c,y}$, and $q_{c,z}$ are the x, y, z components of the peak position vector $\mathbf{q_c}$, respectively. Using eq 14, every peak position can be obtained. Because of cylindrical symmetry, the Debye-Scherrer ring composed of the in-plane randomly oriented $\mathbf{c}^*$ cuts an Ewald sphere at two positions in its top hemisphere: $q_{\parallel} = q_{c,\parallel} \equiv \pm\sqrt{q_{c,x}^2 + q_{c,y}^2}$ with $q_z = q_{c,z}$. Thus diffraction patterns with cylindrical symmetry are easily calculated in the $\mathbf{q}$-space. It is then convenient to determine the preferred orientation of known structures and further to analyze anisotropic X-ray scattering patterns. However, since $\mathbf{q}$-space is distorted in GIXS by refraction and reflection effects, the relation between the detector plane expressed as the Cartesian coordinate defined by two perpendicular axes (i.e., by the in-plane exit angle $2\theta_f$ and the out-of-plane exit angle α_f) and the reciprocal lattice points is needed. The two wave vectors $k_{z,i}$ and $k_{z,f}$ are corrected for refraction as $k_{z,i} = k_o\sqrt{n_R^2 - \cos^2\alpha_i}$ and $k_{z,f} = k_o\sqrt{n_R^2 - \cos^2\alpha_f}$ respectively. Therefore, the two sets of diffractions that result from the incoming and outgoing X-ray beams, and denoted by q_1 and q_3 respectively, are given at the exit angles by the following expression:

$$\alpha_f = \arccos\left(\sqrt{n_R^2 - \left(\frac{q_{c,z}}{k_o} \pm \sqrt{n_R^2 - \cos^2\alpha_i}\right)^2}\right)$$

(15)

where $q_{c,z}/k_o > \sqrt{n_R^2 - \cos^2\alpha_i}$. In eq 15, the positive sign denotes diffractions produced by the outgoing X-ray beam, and the negative sign denotes diffractions produced by the incoming X-ray beam.

The in-plane incidence angle $2\theta_i$ is usually zero, so the in-plane exit angle $2\theta_f$ can be expressed as follow:

$$2\theta_f = \arccos\left[\frac{\cos^2\alpha_i + \cos^2\alpha_f - \left(q_{c,\parallel}\, k_0^{-1}\right)^2}{2\cos\alpha_i\cos\alpha_f}\right] \tag{16}$$

Therefore, diffraction spots detected on the detector plane in GIXS measurements can be directly compared to those derived using eqs 14-16 from an appropriate model and thus analyzed in terms of the model.

To obtain information on the orientation of the paracrystal lattice of the phase separated micro domain structures from GIXS data, the distribution of the orientation vector **n** is given by a function $D(\varphi)$, where φ is the polar angle between the **n** vector and the out-of-plane of the film; for example, φ is 0° when the **n** vector in the film is oriented normal to the film plane. To calculate the 2D GIXS patterns, $D(\varphi)$ should be represented by a numerical function. In relation to the distribution of the lattice orientation, $D(\varphi)$ can generally be considered as a Gaussian distribution:

$$D(\varphi) = \frac{1}{\sqrt{2\pi}\sigma_\varphi}\exp\left[-\frac{(\varphi-\overline{\varphi})^2}{2\sigma_\varphi^2}\right] \tag{17}$$

where $\overline{\varphi}$ and σ_φ are the mean angle and standard deviation of φ from $\overline{\varphi}$, respectively. The observed scattering intensity $I_{GIXS,\varphi}(\mathbf{q})$ is obtained by integrating $I_{GIXS}(\mathbf{q})$ over possible orientations of the lattice:

$$I_{GIXS,\varphi}(\mathbf{q}) = \int_{-\pi}^{\pi} I_{GIXS}(\mathbf{q})D(\varphi)\mathrm{d}\varphi \tag{18}$$

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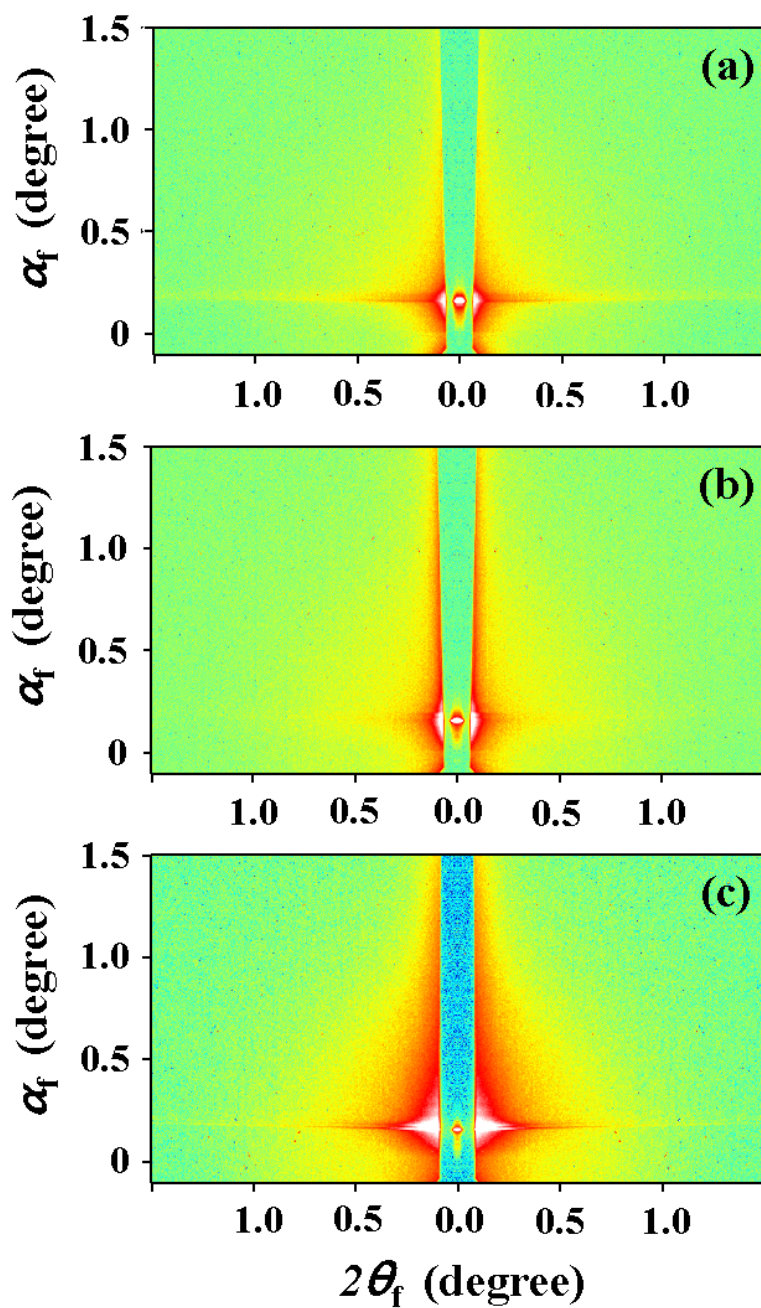6 G. Kim, J. Yoon, J.-S. Kim, H. Kim, M. Ree, *J. Phys. Chem. B*, 2008, **112**, 8868.

Figure S1. 2D GISAXS patterns measured with an incidence angle α_i of 0.160° at 25°C for diblock copolypeptide and blend thin films (approx. 100 nm thick): (a) GL1; (b) GL3; (c) Blend2 (PBLG/PBCL = 1/1, wt/wt).
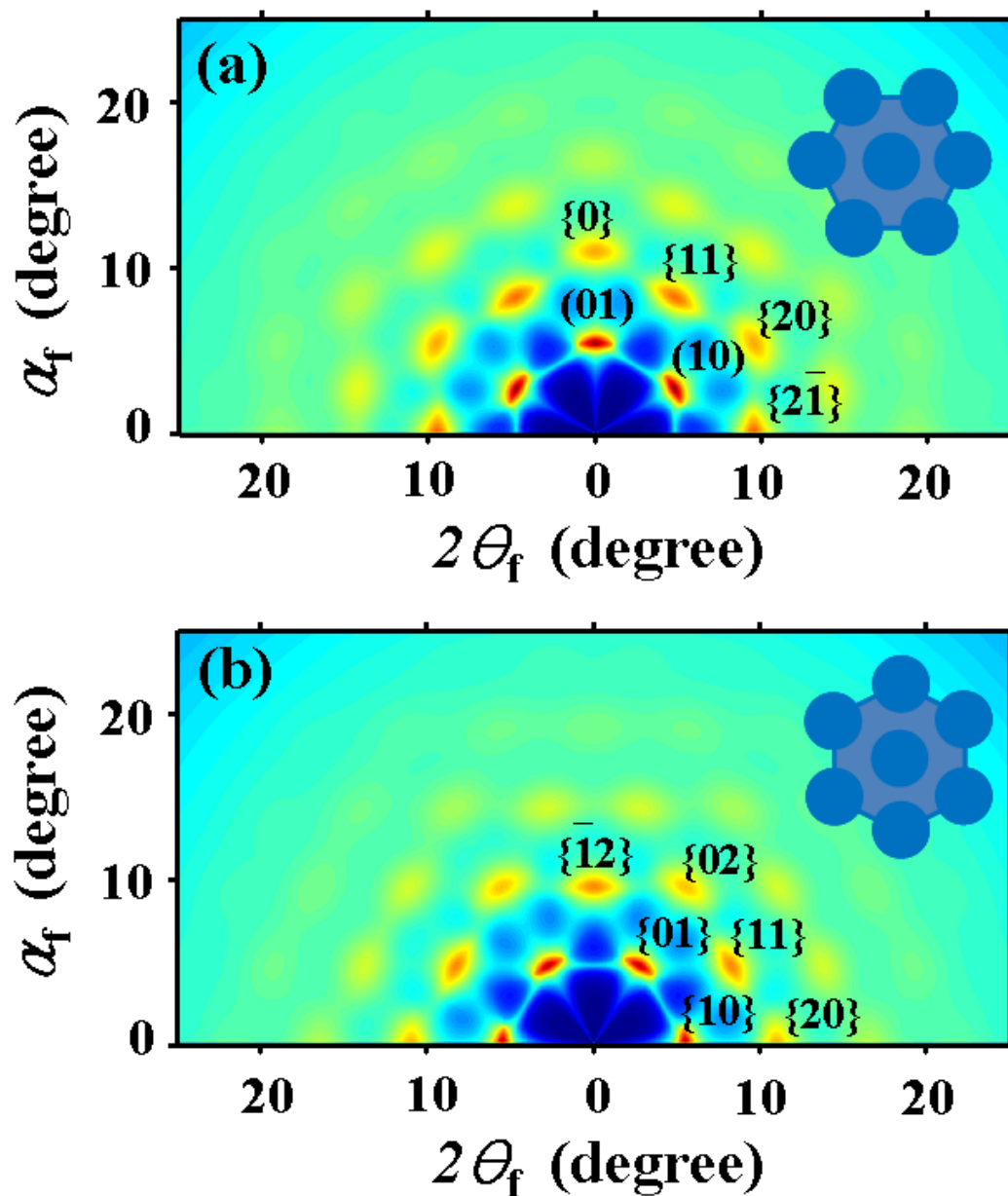
Figure S2. Two models (type-I and II) of HEX-structured PBCL molecules in thin film, as shown Figure 7b, and their 2D GIWAXS images: (a) type-I HEX cylinder structure (inset) and its scattering pattern; (b) type-II HEX cylinder structure (inset) and its scattering pattern. The scattering images were constructed with $\alpha_i = 0.150°$ from the structural parameters of the PBCL film in Table 1 by using the GIXS formula described in the GIXS Data Analysis.

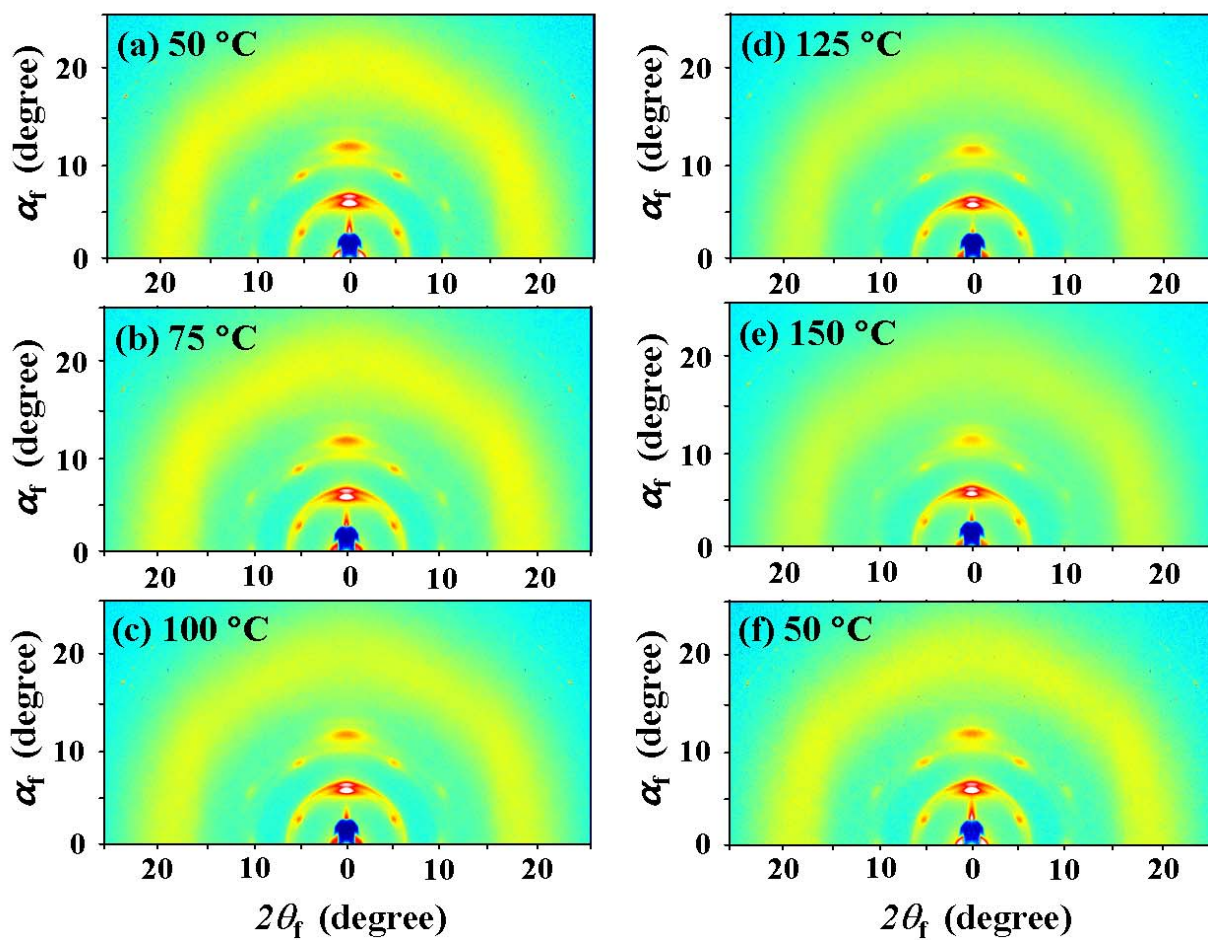**Figure S3.** 2D GIWAXS patterns of a GL3 thin film measured with $\alpha_i = 0.160°$ during heating up to 150 °C and subsequent cooling: (a)−(e), measured during heating run; (f), measured during cooling from 150 °C.