Crystal Orientation in Nano-confined Lamellae of Strongly-segregated PLLA-b-PE and PLDA-b-PE Diblock Copolymers

Ming-Champ Lin (林明昌)[1], Yi-Chin Wang (王怡今)[1], Hsin-Lung Chen (陳信龍)[1], Alejandro J. Müller[2], Chun-Jen Su (蘇群仁)[3], U-Ser Jeng (鄭有舜)[3], and Marc A. Hillmyer[4]

[1]Department of Chemical Engineering, National Tsing Hua University, Hsinchu, Taiwan
[2]Departamento de Ciencia de los Materiales, Grupo de Polímeros USB, Caracas, Venezuela
[3]National Synchrotron Radiation Research Center, Hsinchu, Taiwan
[4]Department of Chemistry, University of Minnesota, Minneapolis, USA

Crystal orientation in strongly-segregated poly(lactide)-*block*-polyethylene (PLA-*b*-PE) diblock copolymers has been investigated by combination of 2D small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD). The systems included an amorphous-crystalline PLDA-*b*-PE (in which the PLA block is racemic) and a double-crystalline PLLA-*b*-PE. Due to the large segregation strength and approximate 50/50 composition in these two diblocks, the crystallization took place within one-dimensionally (1D)-confined lamellar microdomains without forming spherulites. In amorphous-crystalline PLDA-*b*-PE system, homogeneous crystal orientation with the PE crystalline stems oriented perpendicular to the lamellar normal was observed for the crystallization temperature (T_c) higher than 60 ^{o}C. Once the sample was directly quenched into liquid nitrogen from the melt, the isotropic WAXD pattern indicated that the PE crystallites became randomly oriented. In the case of double-crystalline PLLA-*b*-PE system, two kinds of crystallization history were imposed. The first type is called “two-stage crystallization”, where the PLLA block crystallized first followed by PE crystallization. The other is called “one-stage crystallization”, where the PLLA and PE blocks completed to crystallize. For the crystal orientation of PLLA, homeotropic crystal orientation always preserved with the crystalline stems lying parallel to the lamellar normal regardless of the crystallization history and T_c. On the other hand, the crystal orientation of PE in PLLA-*b*-PE was essentially identical to that in PLDA-*b*-PE. Our results hence demonstrated that the orientation of PE crystals was mainly dependent on T_c, but independent of the competitive crystallization and characteristics (racemic vs. L-form) of PLA block. This is a consequence of the strong segregation for these two systems that led the two blocks to crystallize independently within their respective microdomains.

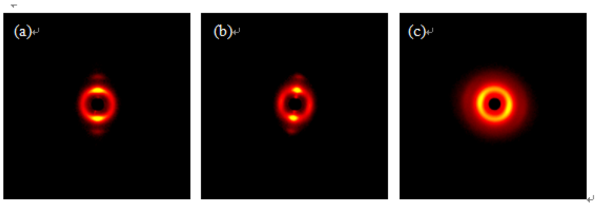

Fig. 1: (conducted at BL 23A1). The 2D SAXS patterns of shear-aligned PLLA-*b*-PE subjected to a two-stage crystallization process. The system was cooled from 190 to 120 °C to allow PLLA crystallization followed by cooling to 80 °C to induce PE crystallization. (a) tangential-view (the X-ray beam is travelling along $\hat{x}$); (b) radial-view (the X-ray beam is along $\hat{y}$); (c) top-view (the X-ray beam is along $\hat{z}$).

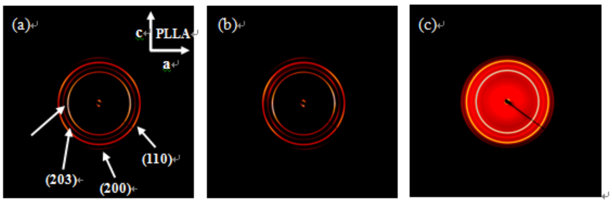

Fig. 2: (conducted at BL 17A1). The 2D WAXD patterns of shear-aligned PLLA-*b*-PE subjected to a two-stage crystallization process. The system was cooled from 190 to 120 °C to allow PLLA crystallization followed by cooling to 80 °C to induce PE crystallization. (a) tangential-view (the X-ray beam is travelling along $\hat{x}$); (b) radial-view (the X-ray beam is along $\hat{y}$); (c) top-view (the X-ray beam is along $\hat{z}$).