Supporting Information

Nonbirefringent bands in thin films of a copolymer melt: rapidly rhythmic crystal growth with an unusual crystal-melt interface

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1. Experimental Section

1.1. Materials. $PCL_{11.0k}$-*b*-$PEO_{5.0k}$ (Product ID: P3128-EOCL) with the number average molecular weights of PCL and PEO blocks of 11.0 and 5.0 kg/mol (ω_{PEO}= 0.31) respectively and a polydispersity index (PDI) of 1.3 was purchased from Polymer Source, Inc., and used without further purifying. Homopolymer $PCL_{10.0k}$ (Aldrich Inc., PDI= 1.4) was also employed for comparison. The subscript in polymer abbreviation denotes its number average molecular weight. According to the product parameters offered by Polymer Source, Inc., $PCL_{11.0k}$-*b*-$PEO_{5.0k}$ possesses a single glass transition temperature T_g of -63 °C, a single crystallization temperature T_c of 23 °C, and double melting temperatures T_m of 49 and 60 °C, respectively (the thermal analysis was conducted on a TA Q100 differential scanning calorimeter at a scanning rate of 20 °C/min).

1.2. Preparation of Polymer Thin Films. Polymers were dissolved in toluene to prepare solution, and a drop of ca. 10 μL solution was cast onto silicon wafers to fabricate initial thin films. The as-cast films were first dried at ambient conditions for 2 days and then treated inside a vacuum oven at 50 °C for another 3 days to remove the solvent completely. The thickness of dried films lies in a range of 300~600 nm, depending on the distance away from the edge.

1.3. Melt Crystallization Procedure. The isothermal melt crystallization of resultant dried polymer films was carried out by using a Linkam hot-stage. First, the system was heated (10 °C/min) to an erase temperature of 80 °C, which is above both the equilibrium melting points of PCL and PEO, and held for 5 minutes to completely melt the existed crystals and erase thermal histories. A rapid cooling (50 °C/min) was then applied to reach a desired crystallization temperature T_c to perform isothermal melt crystallization. Note that the crystal patterns are independent upon the employed solvents (toluene, tetrahydrofuran or chloroform) and substrates (glass or silicon wafer).

1.4. Equipment. Optical microscopy (OM) experiments were carried out by using a Carl Zeiss A2m microscope equipped with a CCD camera at reflectance mode, and a continued shooting mode with time intervals of 2~10 s, depending on the isothermal T_c, was employed to capture the structural formation and morphological evolution processes. A tapping mode atomic force microscope (AFM) (Keysight 5500 AFM/SPM System) was employed to examine both the height profiles and lamellar organizations of resultant spherulites by using silicon cantilevers (Nanosensors, PPP-NCL). Wide angle X-ray diffraction (WAXD) was captured via the Xuess System (Xenocs Company, France, λ=1.54 Å). Here each real time pattern in isothermal crystallization process was collected with a time of 10 min.

2. Supporting Figures

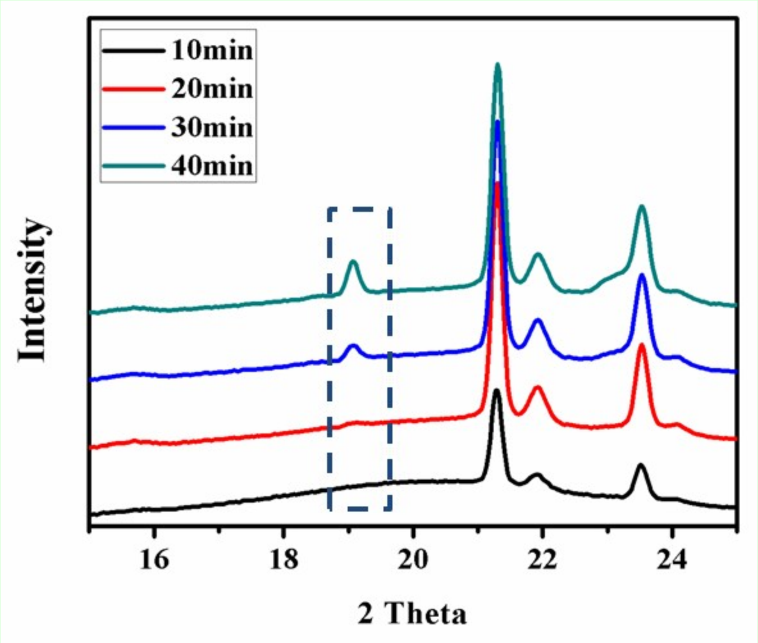

Figure S1. In-situ WAXD patterns of PCL$_{11.0k}$-*b*-PEO$_{5.0k}$ as a function of elapsed time during the isothermal crystallization process under 45 °C. The later emergence of the (120) diffraction (2θ = 19.2°) of PEO crystals indicates the first crystallization of the major PCL block at 45 °C in the PCL$_{11.0k}$-*b*-PEO$_{5.0k}$, as denoted by the dashed rectangle. Furthermore, a coupling between the disappearance of (120) diffraction of PEO crystals during the former 20 minutes and the nearly invariant intensifies of the two representative diffractions, (110) (2θ = 21.3°) and (200) (2θ = 23.5°), of PCL crystals with the crystallization time of 20, 30, and 40 min seems to further implicate that the PEO crystals even begin to appear after the complete development of PCL crystals. It is therefore reasonable that the long PCL chains dominate the developing of rhythmic growth into such periodic banding. The present findings are in good agreement with previous literatures.

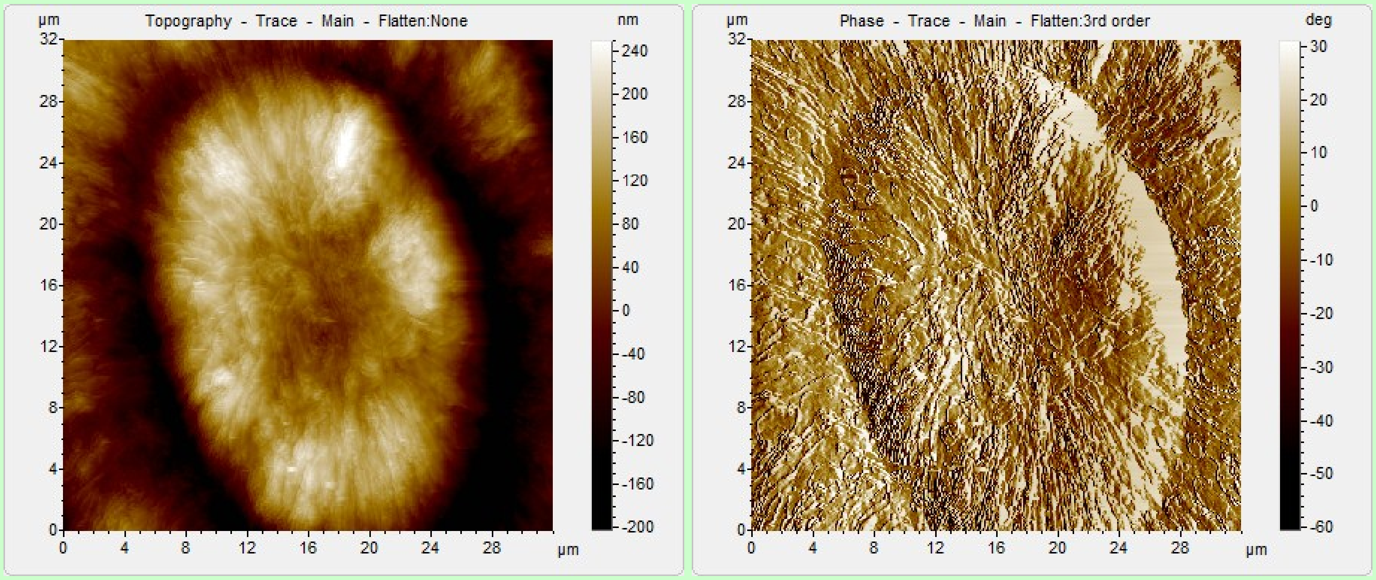

Figure S2. AFM height and phase images of the elongated hexagonal core shows that it also consists of mainly flat-on lamellae.

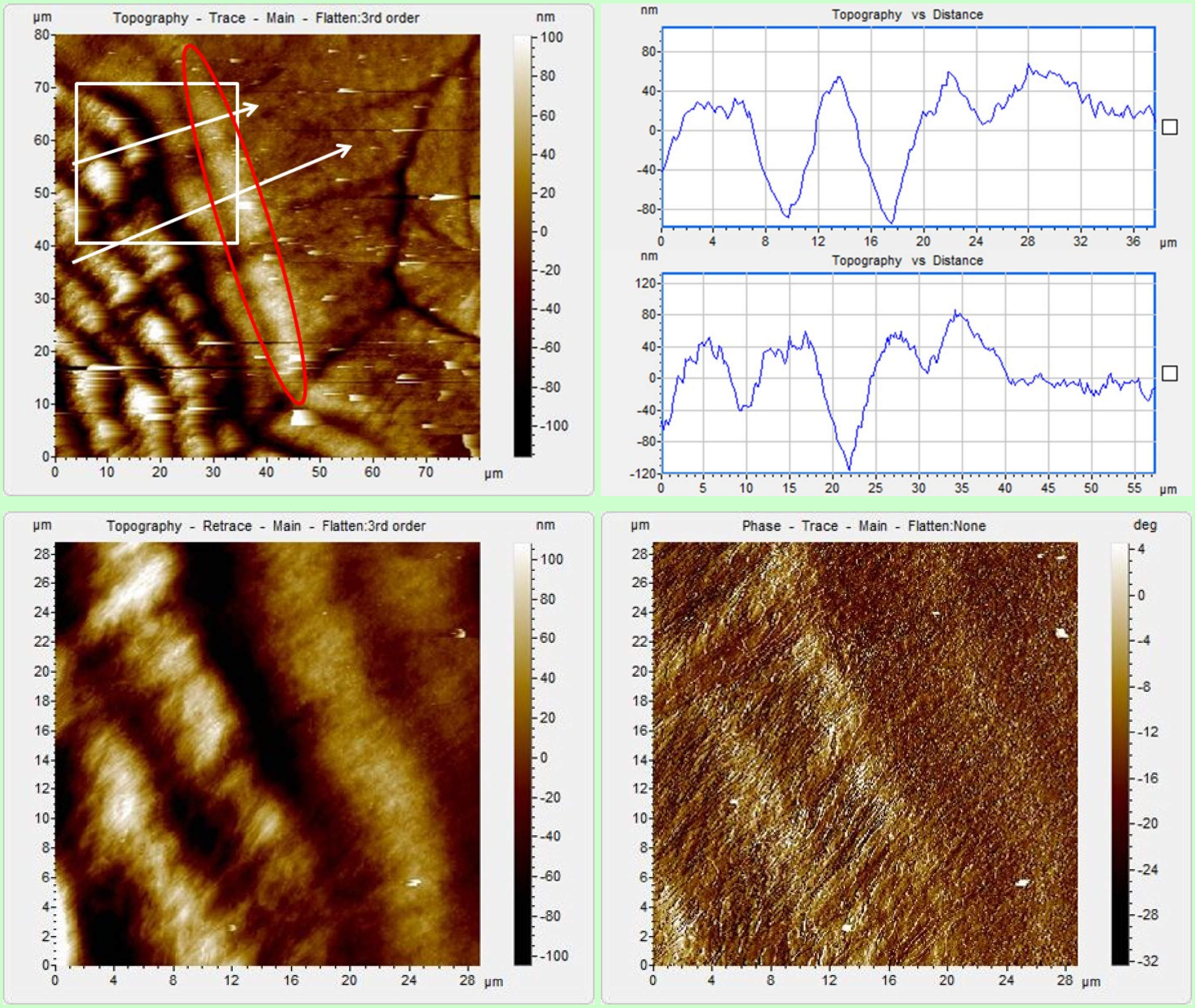

Figure S3. The sample was first crystallized at 45 °C for 20 min and then rapid cooled to room temperature (about 20 °C). (Up) AFM height and corresponding height profiles along the added white arrows reflecting the features of halo zone appeared in real time OM micrographs (Figure 3). It is evident from the red oval-shaped region and corresponding height profiles that the thickness of halo zone is changed, and it can higher, equal or lower than the neighboring continued crystals, implying that the amount of polymer in this zone can alter during the rhythmic growth process. (Down) The enlarged topography and relevant phase image further illustrate that the height of periodic banding is higher than the molten film, and that the former rhythmic growth and the latter continued growth results in periodic packing of large-sized flat-on and compact stacking of small-sized lamellae respectively.

3. Supporting Video

Video S1. The growth process of $PCL_{11.0k}$-*b*-$PEO_{5.0k}$ periodic crystals formed at 45 °C. The video was produced using 500 photos captured with a time interval of 3s (i.e., total time of 25min) by in situ optical microscopy experiment.