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Supplementary Information

Investigation on the Influence of Fold Conformation on PLLA Lamellar Splaying by Film Crystallization in Supercritical CO_2

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In order to further illustrate the relationship between lamellar splaying and lamellar thickness, we performed the other three groups of experiments, the experimental details are as follows: PLLA2 and PLLA3 were used as samples, the method mentioned in section 2.2 of manuscript was adopted to treat Si substrate, the PLLA/Dichloromethane solution with a concentration of 10 mg/ml was dropped on the treated Si substrate to prepare PLLA film. The isothermal crystallization processing methods were same with that mentioned in section 2.3, the specific process parameters are listed in table S1.

Table S1 main process parameters of crystallization process in supercritical CO_2

Sample No.	T_c (°C)	T_p (°C)	T_m (°C)	P_c (MPa)
PLLA2	90	120	180	10
PLLA2	90	130	180	12
PLLA3	100	135	180	12

Figure R1 shows the AFM images and altitude data of the above three samples. According to figure 9 in the manuscript, the crystal form in the film sample prepared by PLLA2 solution with a concentration of 10 mg/ml is trigonal crystal. The PLLA molecular chains in the crystal present $P3_1$ helical conformation, and the length of the monomer unit is 0.3 nm. According to the calculation formula of the length of the helix chain in the crystal: the length of the helix chain = (degree of polymerization + 1) × length of the single unit, it can be calculated that the length of the extended PLLA2 chain (degree of polymerization: 72) is 21.9 nm, and the length of a once-folded chain is about 10.9 nm. These two lengths are close to the lamellar thickness given in figure S1(c) and (f). Thus, it can be judged that the molecular chain in the crystal shown in figure S1(a)-(c) is a once-folded chain, which is tight fold. While the molecular chain in the crystal given in figure S1(d)-(f) is an extended chain. The treatment process of the PLLA3 sample shown in figure S1(g)-(i) is same with that of the PLLA3 sample shown in figure 10(g)-(i). Under the same crystallization treatment condition, the crystal form and molecular chain conformation of the PLLA3 crystal shown in figure S1(g)-(i) were consistent with the that of PLLA3 crystal shown in figure 10(g)-(i). The crystal form is orthorhombic crystal, and the chain conformation is a once-folded chain whose fold is loose, as shown in figure S1(i).

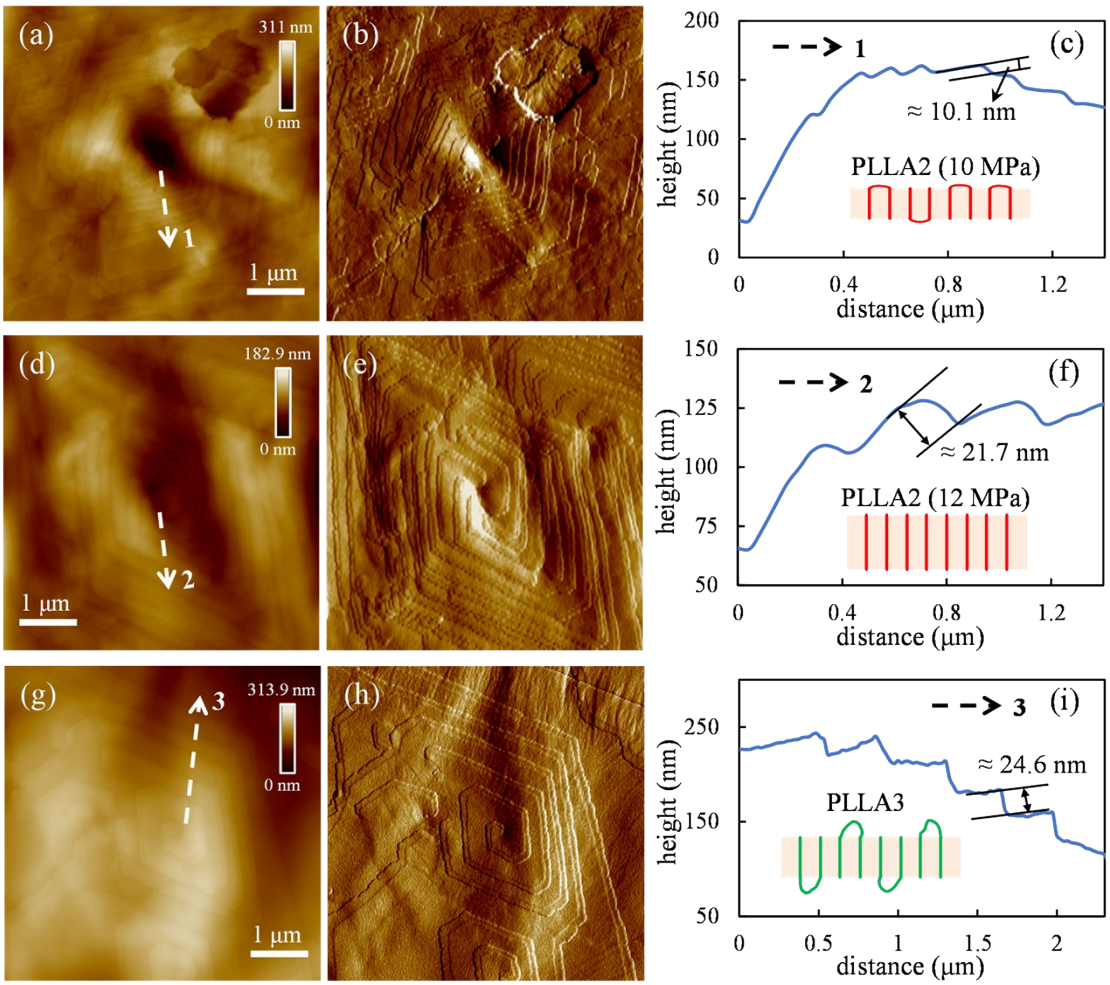

Figure S1 AFM images of multilayer screw terrace crystals found in treated PLLA2 and PLLA3 sample, (a) height image of PLLA2 crystal formed in 10 MPa CO_2, (b) PFE image of (a), (c) altitude curve along line 1 in (a); (d) height image of PLLA2 crystal formed in 12 MPa CO_2, (e) PFE image of (d), (f) altitude curve along line 2 in (d); (g) height image of PLLA3 crystal, (h) PFE image of (g), (i) altitude curve along line 3 in (g).

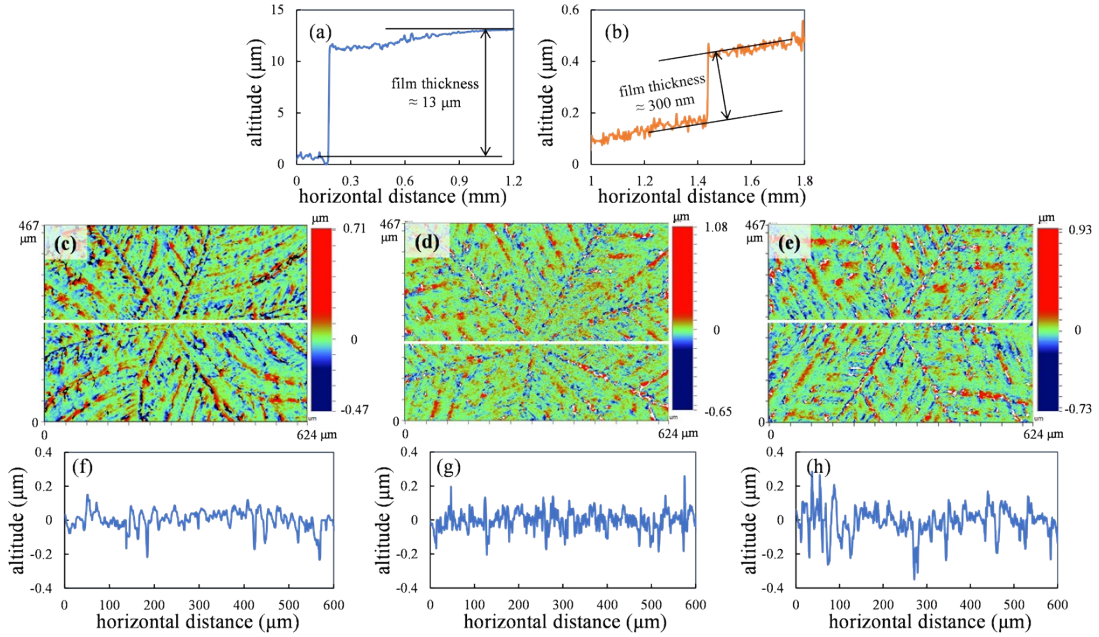

Figure S2 the altitude data of PLLA film sample, curves in (a) and (b) represent the height change curve of the film edge of two samples measured by the white light interferometer, the step height is the film thickness. (c)-(e) show the three-dimensional height isochromatic cloud map of the film sample after crystallization. (f)-(h) are the change curve of crystal surface height on the white horizontal line in (c)-(e), respectively.

The thickness of dendritic crystal shown in figure S2 is not uniform. The screw terrace with fewer layers can be found on the edge of crystal branch with a small thickness, while the multilayer screw terrace can be found in the center of crystal branch with a larger thickness.

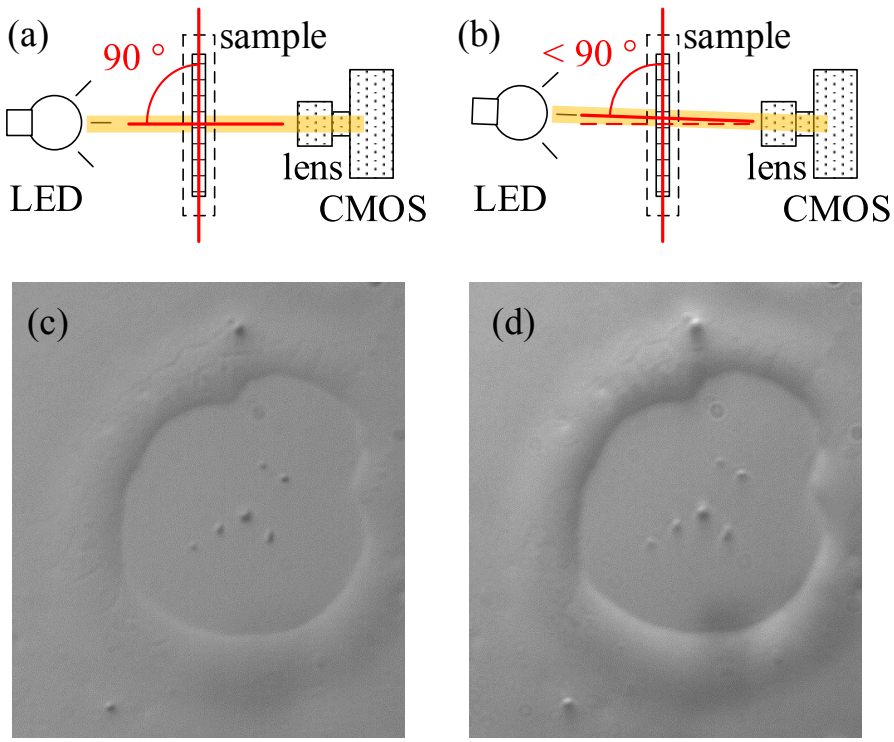

Figure S3 The imaging method of microscopic pictures shown in figure 4 (c)-(k), (a) The angle between beam and sample plane is 90 °, (b) The angle between beam and sample plane is slightly smaller than 90 °, (c) and (d) are two sample picture imaged by the method of (a) and (b), respectively.

The sample is a thin film sample. If the beam is 100% perpendicular to the sample plane, the sample will almost appear transparent and it is difficult to present the uneven surface of the sample, as shown as figure S3 (a) and (c). We inclined the light path slightly and let the light pass through the sample plane at an angle of slightly less than 90 °, as shown as figure S3 (b). As a result, the two sides of the convex surface or the concave surface of the sample surface present different brightness, as shown as figure S3 (d). In this way, the picture can present the uneven surface of the sample more clearly.

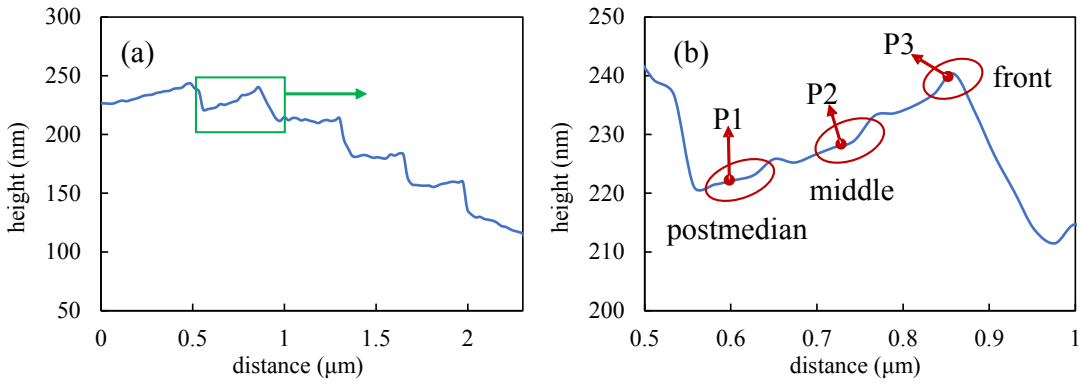

Figure S4 The selecting scheme of the three points used to calculate the lamellar curvature, (b) is the partial enlarged drawing of (a).

The coordinates of the three points are: P1 ($x1$, $y1$), P2 ($x2$, $y2$) and P3 ($x3$, $y3$). In order to clearly present the morphology of lamellar step, the point located at the postmedian of step is selected as P1, the point located at the middle of step is selected as P2, and the point located on the front of step is selected as P3. Figure S4 gives an example to show the selection scheme of the three points used to calculate the lamellar curvature.