Supporting Information

for

Formation of Stacked Three-Dimensional Polymer "Single Crystals"

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1. Morphology of iPS "3D single crystals" after short crystallization times

Before washing, the shape of "3D single crystals" visible in optical micrographs was fuzzy (see Figure 1b of the main text), mainly because they were hidden under a layer of molten polymers. Interestingly, after removing the amorphous polymer chains, a clear hexagonal shape appeared (shown in Figure S1a). The comparison of Figure S1a with Figure 1b demonstrates that through a proper washing procedure amorphous chains can be removed, but crystals can be completely retained. Figure 1 and Figure S1 show the evolution of a stack of uniquely oriented polymer lamellae, demonstrating the preservation of the unique hexagonal shape of the stack and that all lamellar crystals shared the same orientation as the basal crystal. Details of the morphology of such stacks are provided through AFM images. However, due to the large size (many micrometers) of these stacks, it is not easily possible to show the overall shape and details on the nanometer scale simultaneously (examples are shown in Figure S5). Thus, we have added here additional small-scale AFM image that provide information only on parts of such large stacks.



Figure S1. Details of the structure of iPS "3D single crystals" obtained by isothermal crystallization at 205 °C for 15 h and made visible by an appropriate washing procedure. (a) Contrast enhanced optical micrograph with a size of 35 μ m × 40 μ m (same picture with Figure 2b). (b) AFM height micrographs zoomed-in on the dotted green box shown in (a).

2. Observation of "3D single crystals" by polarized optical microscopy

In order to demonstrate the orientation of polymer chains within stacks of lamellar crystals, polarized optical microscopy was employed (results are shown in Figure S2b). There, no birefringence was observed. Thus, we inferred that the "3D single crystals" were composed flat-on lamellar crystals rather than spherulites composed of radially growing edge-on lamellar crystals. This assumption was proved by AFM images shown in Figures 1f, S1 and S3.

The crystalline structures shown in Figure S2a demonstrate clearly the hexagonal symmetry of the objects. With the images shown in Figure S2a, although cracks are slightly irregular after washing when compared with cracks before washing, we

emphasize that cracks prefer to develop in the three principal directions of these hexagons. Before washing, the edges of these hexagonal crystals do not appear as sharp lines in optical microscope, mostly because of the layer of non-crystalline polymers on top. However, as shown in Figure S2a, after washing, the edges of these hexagonal crystal became sharper. Of course, optical microscopy cannot resolve morphological features smaller than the optical resolution limit. The provided AFM images (Figure 1f, Figure S1and Figure S3) allow to see how crystalline lamellae were arranged in the stacks.

The size of "3D single crystals" in Figure S2a was 95 μ m. If transport problems and supply of molecules are well controlled, even much larger crystal can be obtained.



Figure S2. Observation of iPS "3D single crystals" after washing in cyclohexanone for 6 min at room temperature. (a) Bright field optical microscopy, (b) Polarized optical microscopy. The red dotted hexagon indicates the boundary of the crystal, the white arrows in (b) represent the directions of the crossed polarizers. The size of the images is 140 μ m × 120 μ m.

3. Stacking structure after different crystallization times

In order to demonstrate that crystals grown for different times $t_{\rm C}$ were always flat-on oriented, we performed AFM measurements on washed crystals obtained after different $t_{\rm C}$. The boundaries of all lamellar crystals were parallel to each other. As crystals grew, height reached several micrometers, they also maintained the orientation of the hexagonal basal lamellar crystal. A characteristic feature of single crystals is the existence of unique long-range order represented in terms of multiples of the parameters of the unit cell. In our stacks of uniquely oriented polymer lamellae, the long-range order of unique orientation is preserved despite the amorphous interlayers which separated the individual lamellar crystals. That's why we named such three-dimensional stacks of uniquely oriented polymer lamellae "3D single crystals" (the quotation marks indicate that amorphous fold layers separate the crystalline layers).

We admit that there are small changes in orientation of the lamellae in Figure S3a. We do not exactly know what caused the slight deviations in orientation of the different layers. Two possible sources come to mind. As has been shown in computer simulations and corresponding experiments, small foreign particles can change the growth direction.¹ As a second possibility, a lack or difference in supply of polymers may cause

distortions of the "perfect" hexagons and accordingly lead to the impression of a "splaying angle".²

We also note that even after washing, our "3D single crystals" have a slightly "fuzzy" or "blurred" surface topography. In many cases, inhomogeneous transport processes or a consequence of crystallization kinetics are causing such an uneven surface topography.³



Figure S3. Stacked lamellar structure of iPS "3D single crystals" observed by AFM after washing the crystals, grown isothermally at 205 °C for (a) $t_c = 5 h$ (b) $t_c = 15 h$ (c) $t_c = 25 h$. The images of the top and bottom row represent phase and height images obtained by tapping-mode AFM, respectively.

4. Surface contour scans

To demonstrate the reproducibility and validity of the surface contours shown in the main text, we provide additional surface contour lines for determining the average height and average lateral size. Results from different surface contour lines from various crystals were averaged for calculating the average height and average lateral size of "3D single crystals" shown in Figure 2 of the main text as a function crystallization time $t_{\rm C}$.



Figure S4. Characteristic surface contour lines (measured by AFM) for washed "3D single crystals" grown at 205 °C for different crystallization times t_c similar to the one shown in Figure 2a of the main text. Different colors represent different crystallization times as indicated in the legends. The

dotted lines indicate the average height. These surface contour lines demonstrate the synchronous increase of height and lateral size of iPS "3D single crystals" at 205 °C with $t_{\rm C}$.

5. Increase of the 3D structure of "single crystals" with crystallization time

Before washing, crystals were covered by amorphous polymer chains and for higher stacks, their height was larger than the focal depth of objective lens in optical microscope. At the same time, the resolution of optical microscopy is low. Therefore, the evolution of the morphology of "3D single crystals" could not be observed clearly in optical micrograph. A clearer perspective for crystal growth in three-dimensions, is provided through three-dimensional AFM height images for different crystallization times t_c . As t_c increased, the height of the "3D single crystals" increased as well.



Figure S5. Typical 3D AFM height images of iPS "3D single crystals". Samples were isothermally crystallized at 205 °C for (top) $t_{\rm C} = 5$ h, (middle) $t_{\rm C} = 15$ h, and (bottom) $t_{\rm C} = 25$ h. All samples were washed in cyclohexanone at room temperature for 6 min. The size of the image is (top) $10 \times 10 \,\mu\text{m}$, (middle) $30 \,\mu\text{m} \times 30 \,\mu\text{m}$ and (bottom) $50 \,\mu\text{m} \times 50 \,\mu\text{m}$, respectively.

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