

Supplementary Information for

Selective Dissolution as a Tool for Detecting Spatial Variations in the Metastability within Lamellar Polymer Crystals

Binghua Wang¹, Hailong Zou¹, Xuchen Wang¹, Changyu Shen¹, Jingbo Chen¹,
Günter Reiter², Bin Zhang^{1*}

¹School of Materials Science & Engineering, Zhengzhou University, Zhengzhou 450001,
People's Republic of China

²Institute of Physics, University of Freiburg, Freiburg 79104, Germany

Corresponding Author E-mail:

**binzhang@zzu.edu.cn (B. Zhang)*

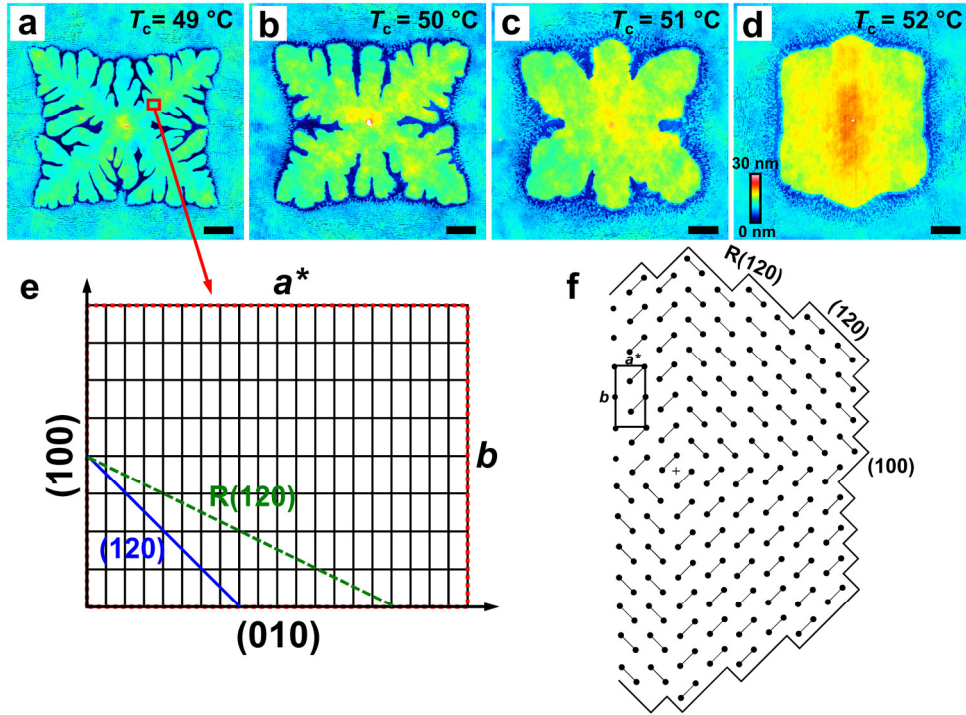


Figure S1. (a-b) Height images of initial PEO crystals grown at varying crystallization temperature T_c : (a) 49°C for 60 s; (b) 50°C for 180 s; (c) 51°C for 480 s; (d) 52°C for 780 s. (e, f) Scheme indicating the orientation of the a^* - and b -axis, as well as the bounding (100) and (010) faces, of the monoclinic crystal unit cell with $a^* = 0.805\text{ nm}$, $b = 1.304\text{ nm}$, $c = 1.948\text{ nm}$ and $\beta = 125.4^\circ$ ($a^* = a \sin \beta$). Folds are supposed to be parallel to (120) planes.

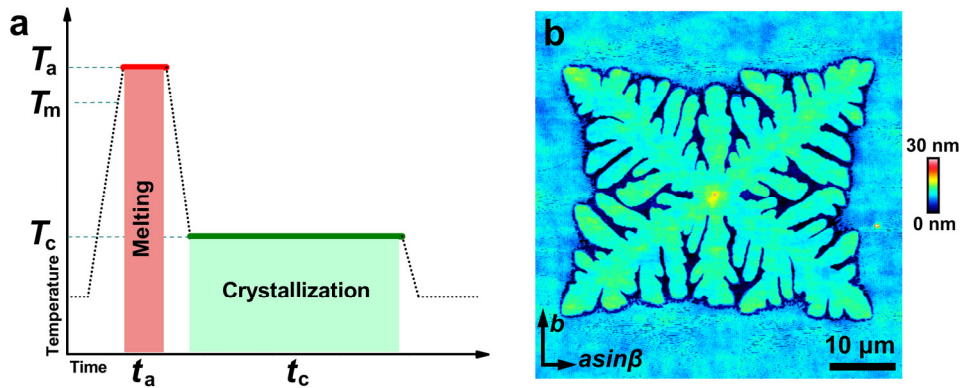


Figure S2. (a) Schematic diagram showing the temperature as a function of time protocols applied for crystallizing ultrathin polyethylene oxide (PEO) films from the melt. (b) AFM height image of a typical dendritic PEO crystal grown at $[(\text{crystallization temperature } T_c, \text{ crystallization time } t_c) = (49^\circ\text{C}, 120\text{ s})]$.

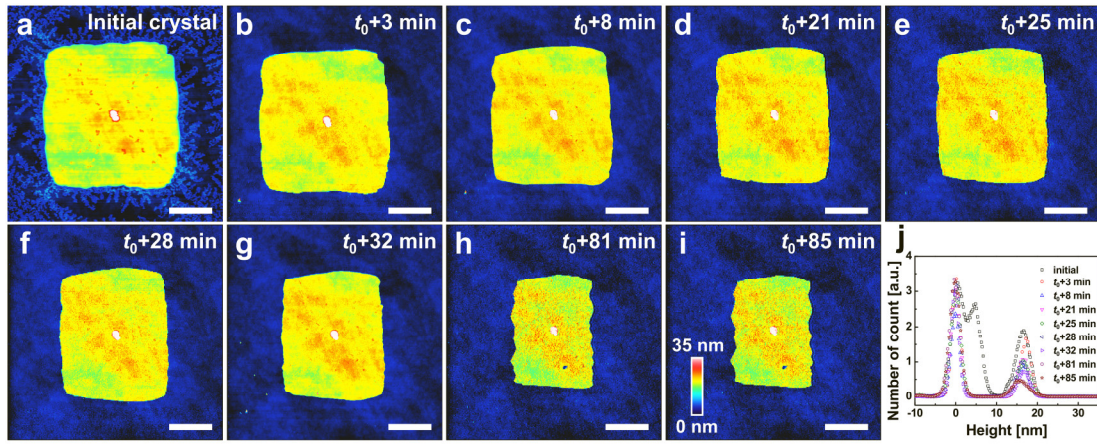


Figure S3. Temporal evolution of changes in morphology in faceted PEO crystals, which were induced by selective dissolution. (a) Height image of typical faceted PEO crystal grown at $[(T_c, t_c) = (54\text{ }^{\circ}\text{C}, 25\text{ min})]$. (b-i) Successive AFM height images measured *in situ*, showing the surface topography of this PEO crystal after selective dissolution in toluene at $T_d = 25\text{ }^{\circ}\text{C}$ for different times (t_d), indicated in each panel. (j) Height histogram of the PEO single crystal after different times of selective dissolution. The scale bars represent $5\text{ }\mu\text{m}$.

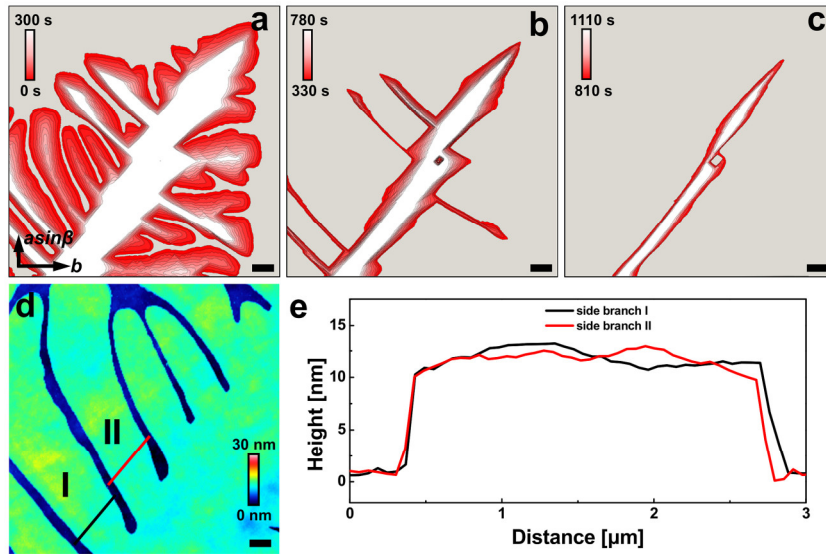


Figure S4. (a-c) A false-colour overlay of the contours of a PEO crystal derived from AFM images, taken in the course of selective dissolution at $T_d = 20.5\text{ }^{\circ}\text{C}$ for different times. The bare substrate is represented in a grey colour. (d) AFM height image of a part of the initial dendritic PEO crystal grown at $[(T_c, t_c) = (49\text{ }^{\circ}\text{C}, 120\text{ s})]$. The scale bars in (a-d) represent $2\text{ }\mu\text{m}$. (e) Cross sectional profiles along the black and red lines in (d).

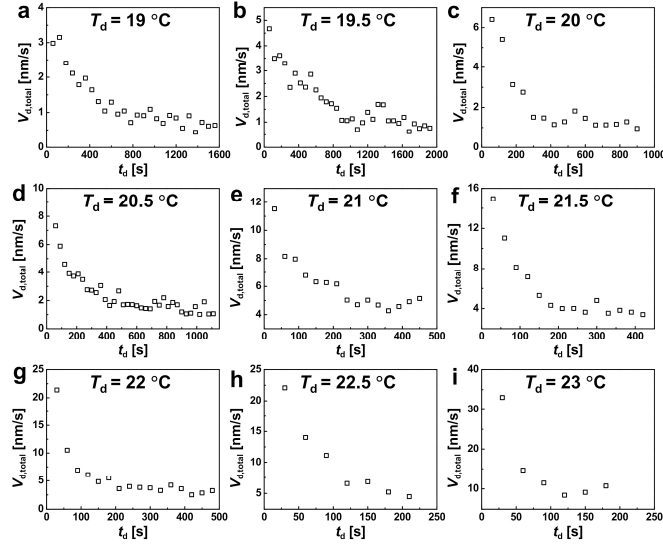


Figure S5. Plots of the overall dissolution velocity ($V_{d,\text{total}}$) as a function of dissolution time (t_d) in the course of dissolution in toluene at different temperatures (T_d): (a) 19 °C, (b) 19.5 °C, (c) 20 °C, (d) 20.5 °C, (e) 21 °C, (f) 21.5 °C, (g) 22 °C, (h) 22.5 °C, and (i) 23 °C. The initial PEO crystals were grown at $[(T_c, t_c) = (49 \text{ °C}, 120 \text{ s})]$.

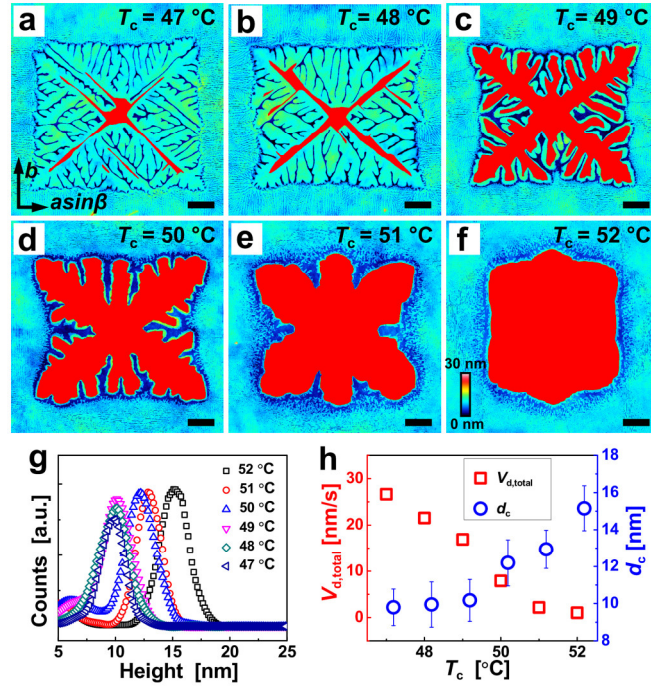


Figure S6. Dependence of the dissolution velocity (V_d) on the crystallization temperature (T_c) of PEO crystals. Height images of initial PEO crystals grown at varying T_c : (a) 47 °C for 10 s; (b) 48 °C for 20 s; (c) 49 °C for 60 s; (d) 50 °C for 180 s; (e) 51 °C for 480 s; (f) 52 °C for 780 s. The remaining crystalline structures after selective dissolution in toluene at $[(T_d, t_d) = (22 \text{ °C}, 30 \text{ s})]$ also shown in (a-f) in bright red colour. The scale bars represent 10 μm . (g) Height histograms for the initial PEO crystals shown in (a-f). (h) The overall dissolution velocity [$V_{d,\text{total}}(T_d, t_d)$] and mean lamellar thickness (d_c) as a function of T_c . The error bars indicate standard deviation of the replicate measurements.

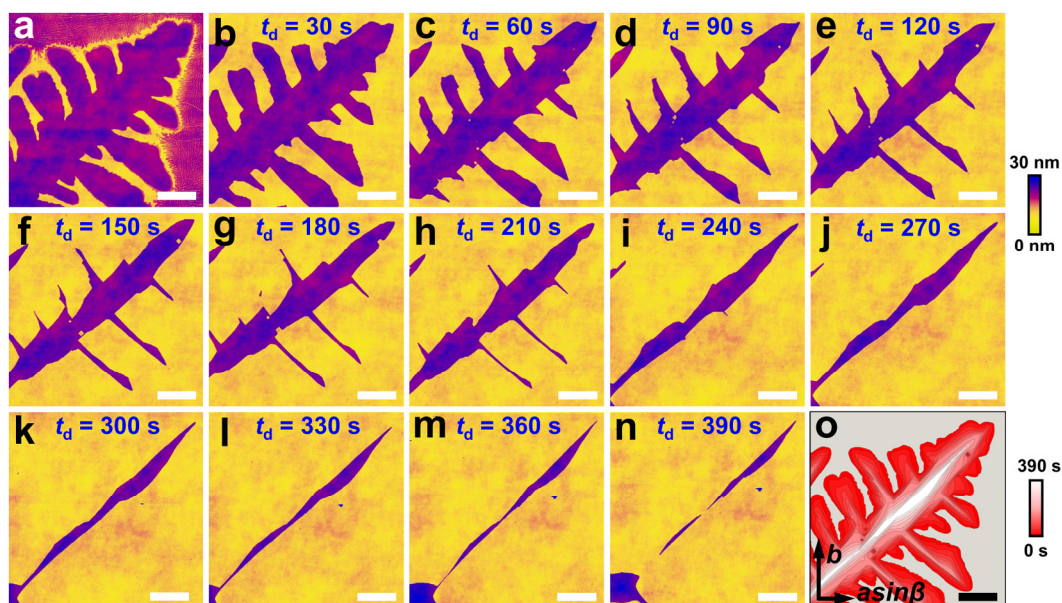


Figure S7. Temporal evolution of changes in morphology in PEO crystals, which were induced by selective dissolution. (a) Height image of the initial dendritic PEO crystal grown at $[(T_c, t_c) = (49\text{ }^{\circ}\text{C}, 120\text{ s})]$. (b-n) Successive AFM height images showing the surface topographies of the PEO crystal (a) after selective dissolution in toluene at the dissolution temperature $T_d = 21\text{ }^{\circ}\text{C}$ for different times (t_d). (o) A false-colour overlay of the contours of the crystals derived from AFM images, which depicts the changes in morphology of the same PEO crystal in the course of selective dissolution. The scale bars represent $5\text{ }\mu\text{m}$.