Supporting Information: Heterogeneous Crystal Nucleation from the Melt in Polyethylene Oxide Droplets on Graphite: Kinetics and Microscopic Structure

Muhammad Tariq, Thomas Thurn-Albrecht, and Oleksandr Dolynchuk*

Institute of Physics, Martin Luther University Halle-Wittenberg, 06120, Halle, Germany

E-mail: oleksandr.dolynchuk@physik.uni-halle.de

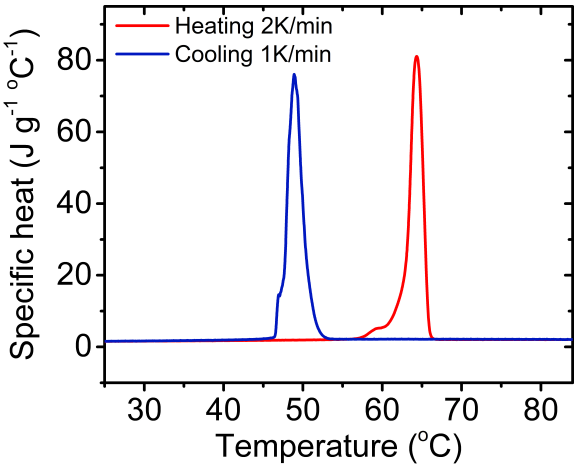

Figure S1: DSC cooling scan and subsequent heating scan of PEO at indicated rates. Measurements were performed with a UNIX DSC 7 from Perkin-Elmer (Waltham, USA).

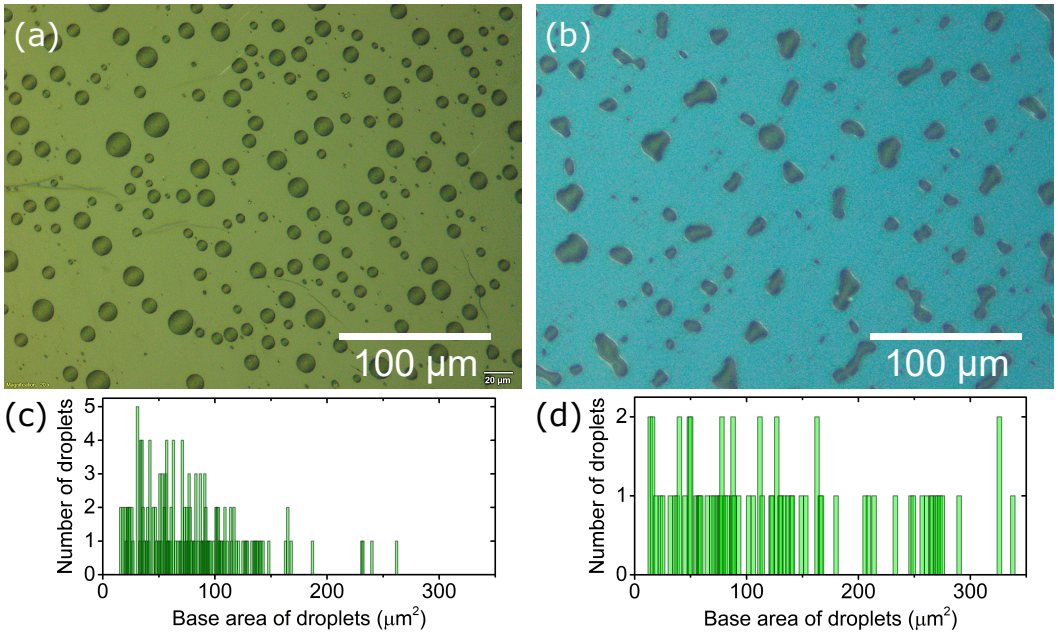

Figure S2: Comparison of length scales of PEO droplets on different substrates. (a, b) Optical microscopy images of liquid PEO droplets formed via dewetting of (a) 60 nm thin film on HOPG and (b) 80 nm thin film on PS. (c, d) Number of droplets as a function of their base area on (c) HOPG and (d) PS, as determined from the corresponding optical microscopy images (a and b) using the microscope image analysis software Stream Motion. The total number of PEO droplets in the field of view on HOPG are 194 and their base area are in the range between 16 µm^2 and 262 µm^2. On the PS substrate, there are around 86 droplets in the image with the base area ranging from 14 µm^2 to 338 µm^2. Except for only a few large droplets on PS, most of PEO droplets on PS and HOPG have similar base area, as can be seen in (c, d).

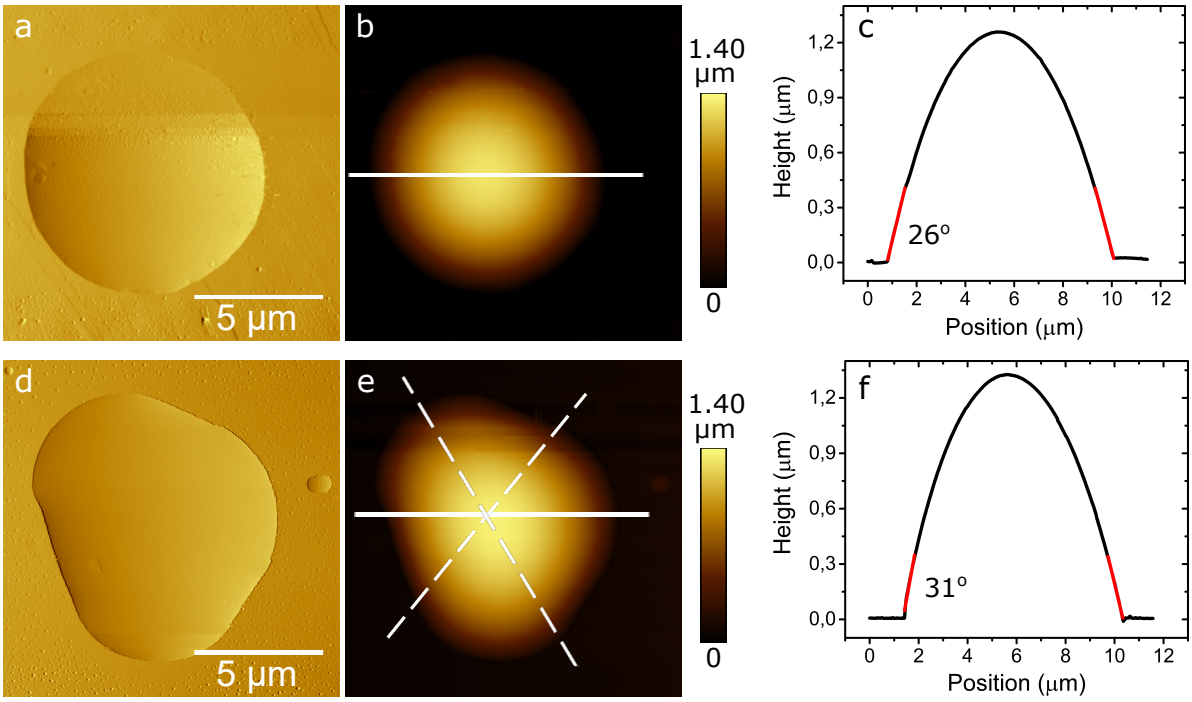

Figure S3: Determination of contact angles of molten PEO droplets on (a-c) HOPG and (d-f) PS. (a) Net-attractive AFM amplitude image and (b) the corresponding height image of a liquid PEO droplet on HOPG. (c) Height profile over the liquid PEO droplet on HOPG extracted from the position indicated by the white line in (b). (d) Net-attractive AFM amplitude image and (e) the corresponding height image of a liquid PEO droplet on PS. (f) Height profile over the liquid PEO droplet on PS extracted along the path indicated by the white solid line in (e). Measurements were performed at room temperature after cooling the samples from the melt. For both systems, the shape as well as the featureless/molten surface of the droplet can be visualized in the amplitude images, whereas the elevated surface of the droplet can be seen in the corresponding height images. To determine the contact angle of PEO droplets, height profiles were extracted from the height images. The contact angles were determined from the slope of a linear fit (red lines) to the lower part of these height profiles. Several droplets on the two substrates were used for this analysis. For PEO-HOPG, a single profile was extracted over the liquid PEO droplets from the each height image. The average value of contact angle of PEO droplets on HOPG is ca. 26°. Whereas because of asymmetric shape of the base of PEO droplets on PS, three profiles were extracted from three different positions over the droplets from the height images. This point is further demonstrated in (e), where the one position is indicated by the solid white line and the two other positions are shown by the broken white lines. The resulting average value of contact angle of PEO droplets on PS is ca. 31°, as averaged over several droplets.

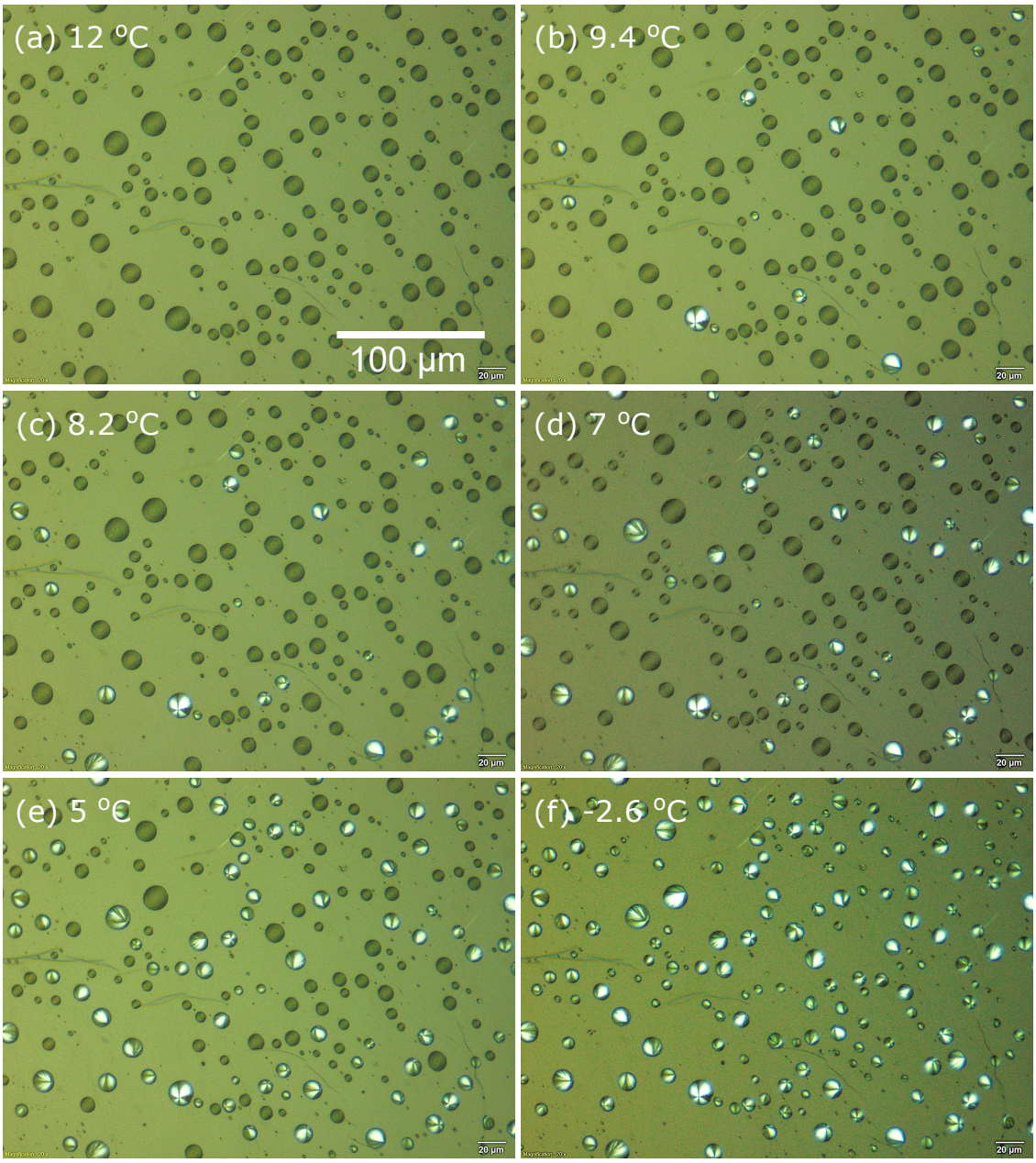

Figure S4: Selected optical microscopy images of PEO droplets on HOPG at indicated temperatures during cooling from the melt at a fixed cooling rate of 0.4 °C min^{-1}. The position of the polarizers was kept nearly-crossed. Images correspond to the same series of measurement as that presented in the main article.

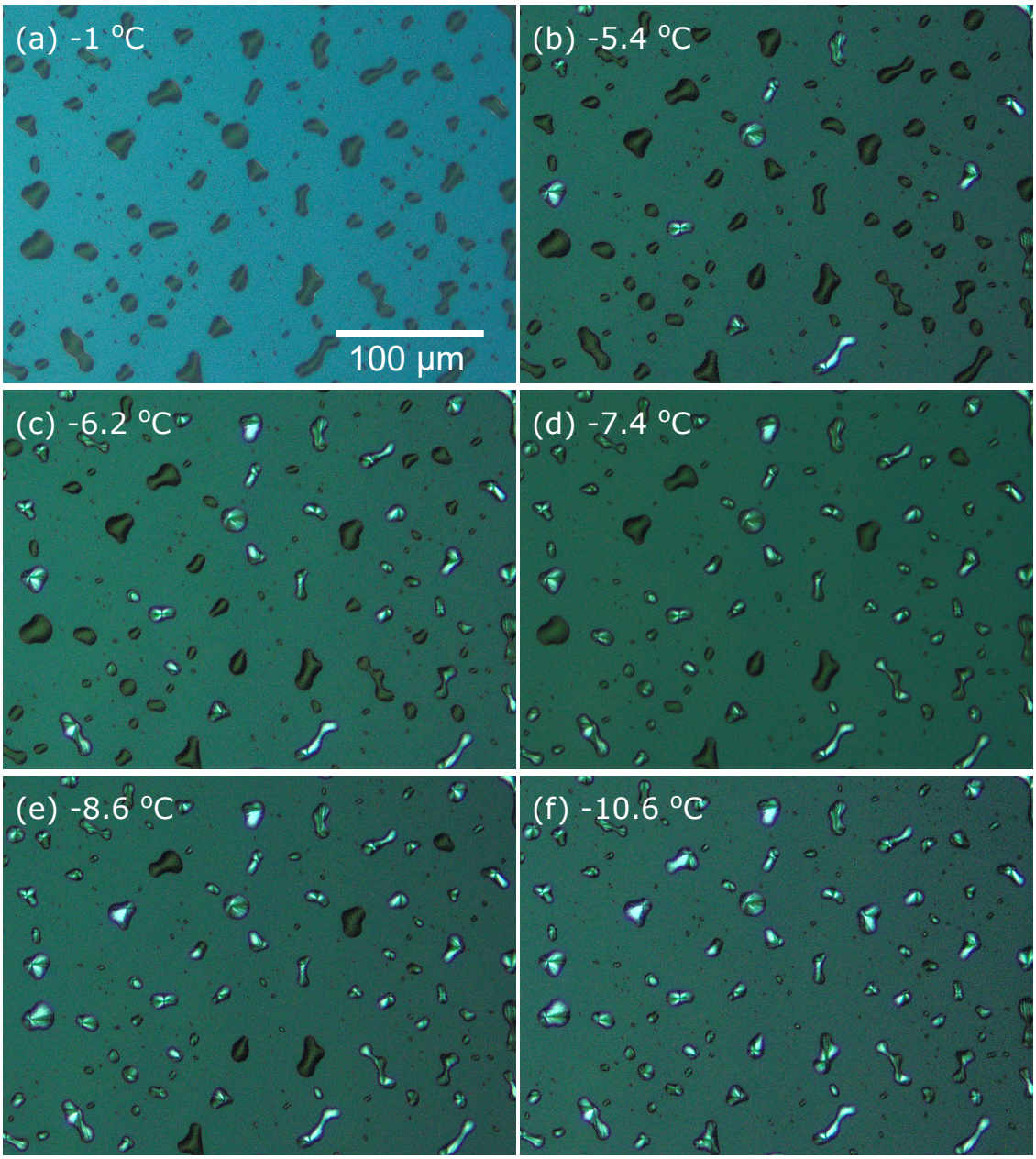

Figure S5: Selected optical microscopy images of PEO droplets on a PS substrate at indicated temperatures during cooling from the melt at a fixed cooling rate of $0.4\,^{\circ}\mathrm{C\,min^{-1}}$. The position of the polarizers was kept nearly-crossed. Images correspond to the same series of measurement as that presented in the main article.

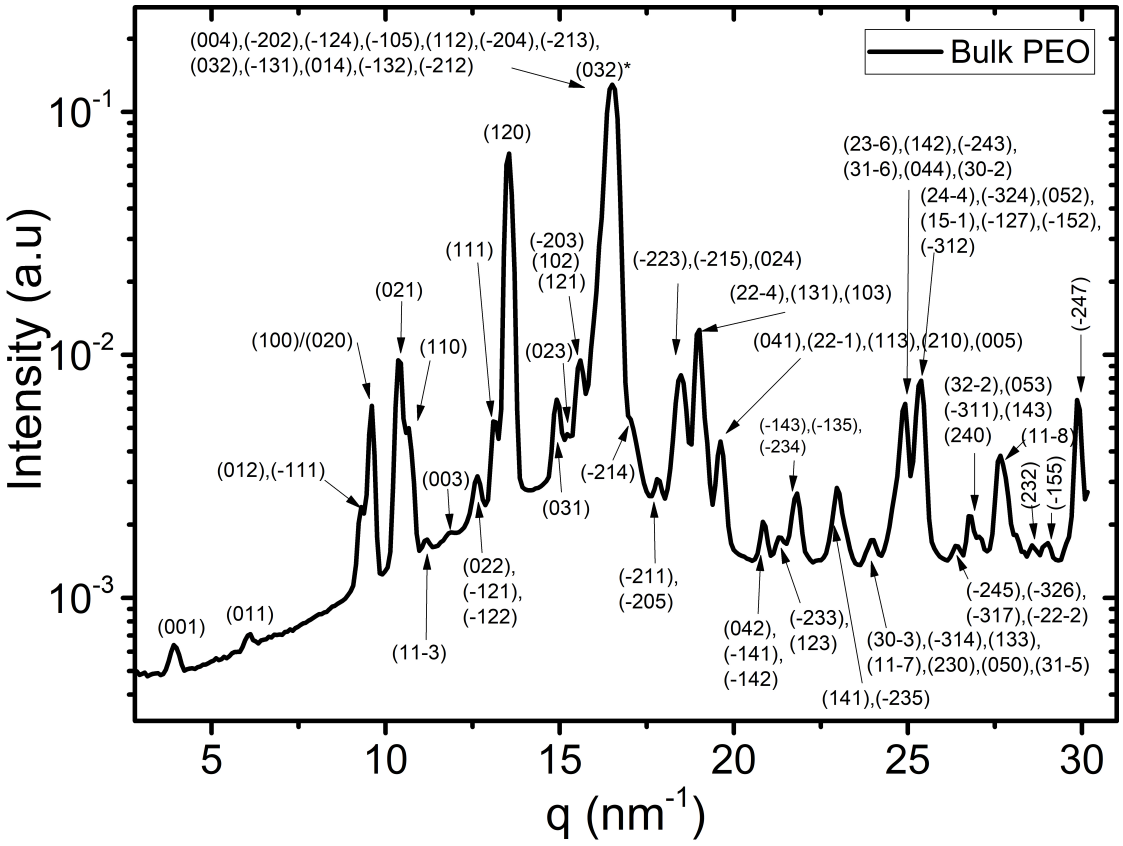

Figure S6: Wide angle X-ray scattering pattern of bulk PEO sample measured in transmission mode at room temperature after cooling from the melt. The miller indices of all reflections were calculated using the lattice parameters of monoclinic unit cell of PEO ($a = 8.05\,\text{Å}$, $b = 13.04\,\text{Å}$, $c = 19.48\,\text{Å}$, $\beta = 125.4°$).[S1] Measurement was performed on SAXSLAB laboratory setup (Retro-F).

Reference

(S1) Takahashi, Y.; Tadokoro, H. Structural Studies of Polyethers, (-(CH2)m-O-)n X. Crystal Structure of Poly(ethylene oxide). *Macromolecules* **1973**, *6*, 672–675.