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Periodic Surface Morphology by Solvent-mediated Crystallization of Polymer Brushes

Shintaro Nakagawa[1,*] and Naoko Yoshie[1]
[1] Institute of Industrial Science, The University of Tokyo
4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan

1 Introduction

It is well known that crystallization of polymers is quite different from that of low-molar-mass substances. The most prominent feature of polymer crystallization may be the complexity of the resultant morphology. Usually, an elementary crystal lattice builds up into a folded chain crystal lamella, which then is incorporated into an alternating stack of the crystal lamella and an amorphous layer. This further assembles into higher-order structure such as spherulites. Control of such crystal morphology is essential in many applications, although it is generally difficult to suppress the formation of complex hierarchical morphology. In this study, we aimed to control polymer crystallization by a combination of spatial confinement and mobility control by solvents.

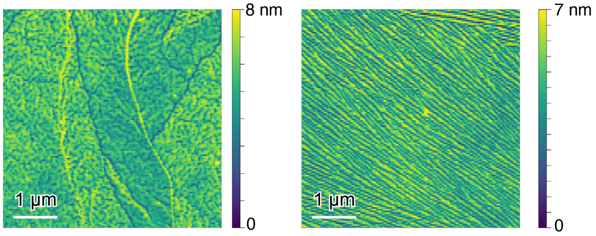
2 Experiment

We created a model crystalline polymer brushes on a solid substrate to impose spatial confinement to polymer chains. We used poly(ε-caprolactone) (PCL) as the crystalline polymer. PCL chains were grown from a glass substrate by surface initiated ring opening polymerization of ε-caprolactone. One end of PCL chain is covalently attached to the substrate. The PCL brush were immersed in tetrahydrofuran (THF, a good solvent for PCL) and then in a poor solvent kept at a prescribed temperature to crystallize PCL in the poor solvent. The poor solvents used were water, methanol, ethanol, 1-propanol, and *n*-hexane. Crystallized PCL brushes were dried and the surface morphology was observed by atomic force microscopy (AFM) in the dynamic force mode. Crystal orientation and the periodicity of meso-scale morphology were investigated by grazing incidence small-angle/wide angle X-ray scattering (GISAXS/WAXD) at BL-10C, KEK-PF.

3 Results and Discussion

Fig. 1 shows the representative AFM height images of the PCL brushes crystallized in air or methanol. The one crystallized in air shows quite complex morphology, while that in methanol mainly consists of a regularly spaced line-like structure. Quantitative analysis of the height image showed that the pitch between adjacent lines was ~ 100 nm and the height of the line was ~ 4 nm. The pitch and height could be tuned through the crystallization temperature and/or the thickness of the PCL brush layer. Similar periodic structure was also observed when the PCL brushes were crystallized in ethanol, propanol, and hexane. Crystallization in water resulted in a complex morphology resembling the one obtained by crystallization in air. These results suggest that the formation of periodic morphology requires the presence of a moderately poor solvent.

The PCL brushes crystallized in methanol were further examine by GISAXS/WAXD, the experimental geometry of which is illustrated in Fig. 2a. The GISAXS pattern shown in Fig. 2b clearly exhibit a peak in the in-plane direction. The spacing corresponding to this peak, estimated by $2\pi/q^*$, was ~ 100 nm. This confirms the periodic structure observed by AFM. Since GISAXS provides the averaged information over the beam footprint, the observation of the peak suggests the presence of the nanoscale periodic structure in a large area. Fig. 2c shows the GIWAXD pattern of the same sample. Two diffractions are identified at the equator, which are assigned to be (110) and (200) reflections from the orthorhombic lattice of PCL crystal. These reflections are observed only in the in-plane direction, indicating that the *c* axis (= chain direction) predominantly orients perpendicular to the substrate surface. From this result, we can conclude that the periodic line pattern was created by the lateral growth of a PCL crystal lamella with "flat-on" orientation.



(a) Crystallized in air (b) Crystallized in methanol

Fig. 1: AFM height images of the PCL brushes crystallized in air or methanol.

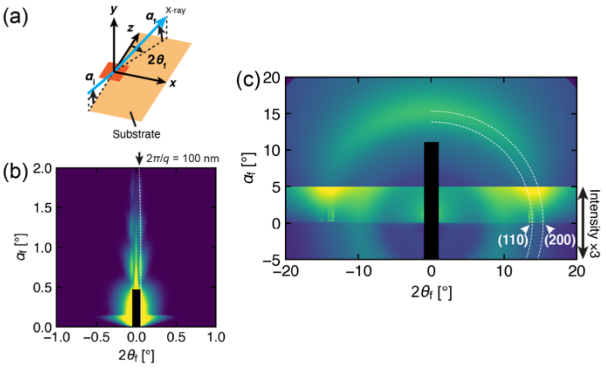


Fig. 2: GISAXS/WAXD results of the PCL brushes crystallized in methanol at 15°C. (a) Geometry of the experiment. (b) GISAXS pattern. (c) GIWAXD pattern.

References

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* snaka@iis.u-tokyo.ac.jp