

Lamella Orientation of Poly(ϵ -caprolactone) Homopolymers Confined in Cylindrical Nanodomains

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Introduction

We have recently investigated the crystallization behavior of poly(δ -valerolactone) (PVL) homopolymers confined within spherical or cylindrical nanodomains, and compared the crystallization rate with that of PVL blocks, *i.e.*, PVL with one-chain end tethered at the nanodomain interface. We found that the crystallization rate of PVL blocks at the initial stage is significantly larger than that of PVL homopolymers. However, the final crystallinity of PVL homopolymers is higher than that of PVL blocks owing to the small restriction of chain conformation.

In this study, we try to find the difference in lamella orientation between homopolymers and block chains both confined within identical cylindrical nanodomains.

Experimental Section

Sample The block copolymer used in this study is poly(ϵ -caprolactone)-*block*-polystyrene (PCL-*b*-PS) with a photocleavable *o*-nitrobenzyl group between PCL and PS blocks. The sample was subjected to the rotational shear under a dry nitrogen atmosphere at 120 °C to orient the cylindrical nanodomains. Subsequently, UV with 200 mW in intensity and wavelength longer than 300 nm was irradiated to the sample to cleave the *o*-nitrobenzyl group, and eventually we obtained PCL homopolymers confined within oriented cylindrical nanodomains.

Measurements The morphology before and after orientation was measured using 1D synchrotron small-angle X-ray scattering (SR-SAXS) and 2D conventional SAXS. SR-SAXS experiment was performed at beam line BL-10C in KEK-PF. The background scattering was taken into account, and finally the relative intensity was obtained as a function of wave number s ($= (2/\lambda)\sin \theta$, 2θ : scattering angle and $\lambda = 0.1488$ nm).

Results and Discussion

Figure 1 shows the 1D SR-SAXS curves from isotropic PCL-*b*-PS before and after crystallization of PCL blocks. We can find several scattering peaks, the angular positions of which exactly correspond to a ratio of $1:\sqrt{3}:\sqrt{4}:\sqrt{7}$, indicating that the cylindrical microdomain is formed in the system. The 2D SAXS patterns from the oriented PCL-*b*-PS are shown in Figure 2, where it is clearly found that the cylinder axis is parallel to the shear direction (Z-axis). The 2D wide-angle X-ray diffraction patterns were obtained for crystallized PCL-*b*-PS before and after photocleavage. The results are now analyzing to evaluate the relationship between the cylinder axis and the stem direction (or *c* axis) of PCL lamellae as a function of crystallization temperature.

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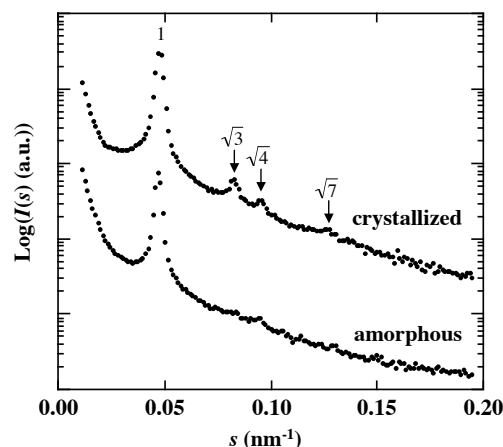


Figure 1 Static SR-SAXS curves from crystallized PCL-*b*-PS (upper) and amorphous PCL-*b*-PS (lower).

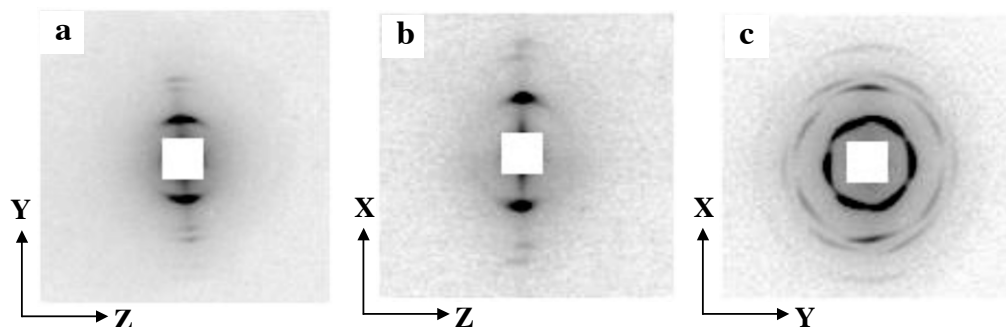


Figure 2. 2D SAXS patterns of oriented PCL-*b*-PS observed from X-axis (a), Y-axis (b), and Z-axis (shear direction) (c).