

Crystallization Behavior of Poly(ϵ -caprolactone) Homopolymers Confined in Nanocylinders : Effects of Nanocylinder Dimension

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Introduction

We have reported the crystallization behavior of poly(δ -valerolactone) (PVL) homopolymers and PVL blocks both confined in spherical or cylindrical nanodomains, and found that the tethering effect of PVL chain ends, as well as the spatially confined effect, significantly controls the crystallization behavior [1]. In this report, we investigate the crystallization behavior of poly(ϵ -caprolactone) (PCL) blocks and PCL homopolymers confined in identical nanocylinders as a function of the cylinder diameter, and try to elucidate the effects of chain tethering on the crystallization of PCL chains at various confined dimensions.

Experimental Section

Samples We synthesized four poly(ϵ -caprolactone)-*block*-polystyrene (PCL-*b*-PS) diblock copolymers with a photocleavable *o*-nitrobenzyl group between PCL and PS blocks (denoted PCL-PS1 ~ PCL-PS4). The diameter of nanocylinders was in the range between 13.0 ~ 27.0 nm. After forming the cylindrical microdomain by microphase separation of block copolymers, the block junction was cleaved by irradiating UV to prepare PCL homopolymers confined in nanocylinders (PCL/PS1 ~ PCL/PS4).

Measurements The morphology formed was measured using small-angle X-ray scattering with synchrotron radiation (SR-SAXS). The SR-SAXS experiment was performed at beam line BL-10C in KEK-PF. The melting temperature T_m , crystallinity χ , and crystallization behavior of PCL blocks and PCL homopolymers were obtained using differential scanning calorimetry (DSC).

Results and Discussion

Figure 1 shows the typical SR-SAXS curves from amorphous PCL-PS, crystallized PCL-PS, and photocleaved PCL/PS. The SAXS curves of crystallized PCL-*b*-PS and PCL/PS have several scattering peaks, the angular positions of which exactly correspond to a ratio of $1:\sqrt{3}:2:(\sqrt{7})$, indicating the formation of cylindrical microdomain. It is found from Figure 1 that the primary peak position does not change substantially before and after crystallization of PCL blocks, suggesting that the molten cylindrical microdomain is completely preserved after PCL crystallization (confined crystallization). The cylinder diameter d is estimated from the peak position in the SAXS curves and the block ratio in the copolymers to

be 14.9 nm for PCL-PS2 and 17.9 nm for PCL-PS3 (and also 13.0 nm for PCL-PS1, 27.0 nm for PCL-PS4).

Figure 2 shows T_m and χ plotted against d , where both values increase steadily with increasing d , suggesting that the effect of spatial confinement substantially control the crystallization of PCL chains. In addition, T_m and χ of PCL homopolymers are always higher than those of PCL copolymers, indicating that the chain tethering significantly affects the crystallization of PCL chains. The crystallization behavior, *i.e.*, the time evolution of χ , is also driven by the combined effect of d (confined effect) and the tethering effect.

[1] S. Nojima et. al., *Macromolecules*, **41**, 1915 (2008).

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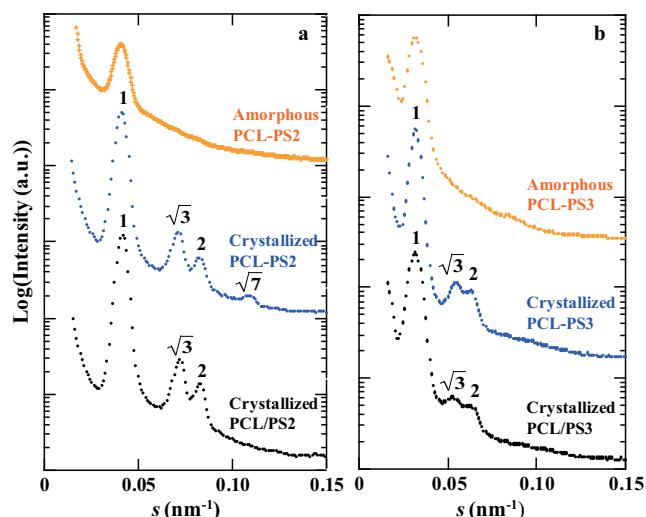


Fig. 1. SR-SAXS curves from PCL-PS2 (a) and PCL-PS3 (b) at various states indicated.

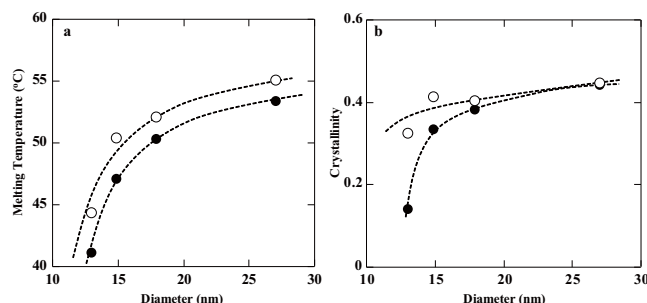


Fig. 2. Melting temperature (a) and crystallinity (b) of PCL blocks (closed circle) and PCL homopolymers (open circle) plotted against cylinder diameter.