

Crystallization of Poly(ϵ -caprolactone) Chains Confined in Lamellar Nanodomains

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1 Introduction

The crystalline block in crystalline-amorphous diblock copolymers crystallizes within nanodomains formed by microphase-separation when the amorphous block is vitrified. In such cases, the crystallization behavior is affected not only by the spatial confinement imposed by the nanodomains, but also by the chain-end tethered onto nanodomain interface (chain-end tethering). Our previous studies revealed that the effects of chain-end tethering in cylindrical nanodomains depended significantly on the nanodomain diameter [1]. Therefore, different effects of chain-end tethering can be expected in the nanodomains with different shapes.

In the present study, we investigate the crystallization behavior of the block and homopolymer chains both confined in identical lamellar nanodomains.

2 Experiment

Samples. We synthesized two lamella-forming poly(ϵ -caprolactone)-*block*-polystyrene (PCL-*b*-PS) diblock copolymers with an *o*-nitrobenzyl group between two blocks, and cleaved them by irradiating ultraviolet light (UV) to yield PCL and PS homopolymers (denoted as PCL/PS). The microphase-separated structures in PCL-*b*-PS copolymers were essentially preserved by the vitrification of PS matrices even after the UV irradiation (Fig. 1a). Thus it is possible to directly observe the effects of chain-end tethering on the crystallization by comparing the samples before and after the UV irradiation.

Measurements. The size and shape of the microphase-separated structures were determined by synchrotron small-angle X-ray scattering (SR-SAXS) conducted at beam line BL-10C in KEK-PF. The crystallization behavior was investigated by time-resolved SR-SAXS and differential scanning calorimetry (DSC).

3 Results and Discussion

The SR-SAXS curves of the samples are shown in Fig. 1b, where several scattering peaks can be observed. The positions of these peaks relative to that of the primary peak are 1, 2, 3, and 4, indicating the formation of lamellar microphase-separated structures. The scattering curves are unchanged after the UV irradiation, indicating the preservation of these structures. The PCL layer thickness d in two PCL-*b*-PS copolymers was calculated from the primary peak position and volume fraction of PCL to be 8.7 and 15.8 nm.

Fig. 2 shows the time development of PCL crystallinity during the isothermal crystallization. PCL-*b*-PS with $d = 8.7$ nm (Fig. 2a) shows an exponential time evolution of PCL crystallinity at a considerably low temperature,

whereas PCL/PS with the same d shows a sigmoidal curve at an ambient temperature, suggesting that the nucleation mechanism is changed by the chain-end tethering. For $d = 15.8$ nm (Fig. 2b), the crystallization proceeds sigmoidally in both PCL-*b*-PS and PCL/PS, though the crystallization of PCL-*b*-PS is slower than that of PCL/PS. These results suggest that the chain-end tethering reduces the crystal growth rate, which is more significant in smaller lamellar nanodomains.

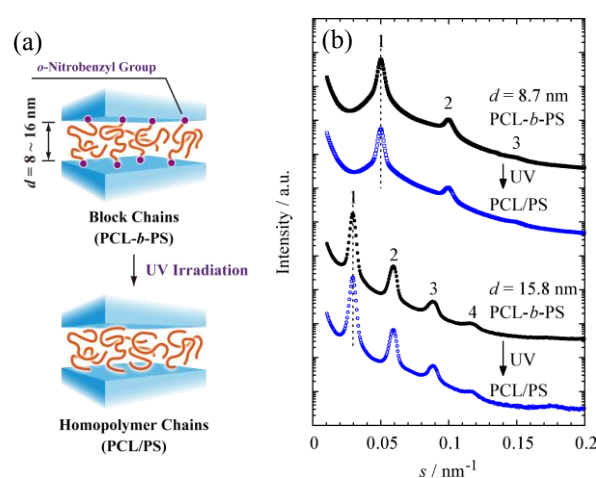


Fig. 1: (a) Schematic illustration of the sample preparation method used in the present study. (b) SR-SAXS curves of the crystallized samples.

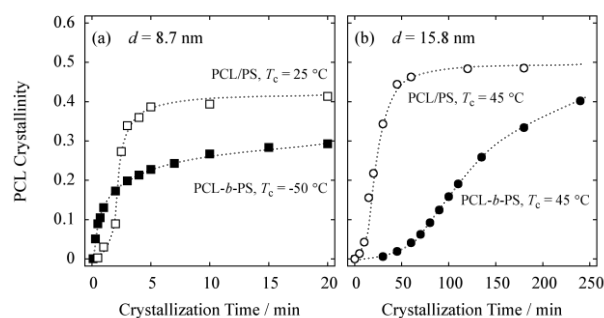


Fig. 2: Time development of crystallinity during the isothermal crystallization of the samples at the selected crystallization temperature (T_c) indicated.

References

[1] S. Nakagawa *et al.*, *Macromolecules* **29**, 172 (2012).

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