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Crystallization Behavior of Homopolymer/Block Chain Blends Confined in Nanocylinders with Different Diameters

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1 Introduction

Crystalline blocks in crystalline-amorphous diblock copolymers crystallize within nanodomains formed by microphase separation if the amorphous block is vitrified. Our previous investigation on crystallization of homopolymers and block chains confined in nanodomains suggested that the chain-end tethering accelerated nucleation upon crystallization [1]. It was also revealed that the effect of chain-end tethering depended significantly on nanodomain size and crystallization temperature [2].

In the present study, we investigate the isothermal crystallization behavior of binary blends consisting of homopolymers and block chains confined in cylindrical nanodomains (nanocylinders) as a function of both blend composition and nanocylinder size to understand how the confinement diameter affects the crystallization behavior of crystalline chains through the chain-end tethering.

2 Experiment

Samples Two Poly(ε-caprolactone)-*block*-polystyrene (PCL-*b*-PS) diblock copolymers, PCL-PS2 and PCL-PS5, with different molecular weights and similar compositions were synthesized. These PCL-*b*-PS copolymers have a photocleavable *o*-nitrobenzyl group between PCL and PS blocks that allows them to separate into PCL and PS homopolymers when irradiated with ultraviolet light (UV). The binary blends of PCL homopolymers and PCL blocks were prepared using controlled UV irradiation after the formation of cylindrical microphase-separated structure. Here we define f_h as the weight fraction of PCL homopolymers against all PCL chains (i.e., PCL homopolymers + PCL blocks) existing in the system.

Measurements The diameter of nanocylinders was evaluated from the volume fraction of each block and the primary peak position in synchrotron small-angle X-ray scattering (SR-SAXS) curves, which were obtained at beam line BL-10C in KEK-PF. Differential scanning calorimetry (DSC) was utilized to observe the isothermal crystallization behavior of the blends.

3 Results and Discussion

Fig. 1(a) shows the SAXS profiles of crystallized PCL-PS2 and PCL-PS5 with f_h = 0 (neat PCL blocks) and maximum f_h (almost PCL homopolymers). All crystallized samples have a couple of scattering peaks, the positions of which exactly correspond to a ratio of $1{:}3^{1/2}{:}2({:}7^{1/2})$, indicating the formation of well-ordered nanocylinders. The diameters of nanocylinders existing in PCL-PS2 and PCL-PS5 were evaluated from Fig. 1(a) to be 14.9 nm and 17.2 nm, respectively.

Crystallization kinetics of both systems was analyzed using crystallization halftime $t_{1/2}$, where $t_{1/2}^{-1}$ is a measure for the crystallization rate of PCL chains. Fig. 1(b) shows the plot of $t_{1/2}^{-1}$ against f_h for each sample at the same crystallization temperature T_c (= -40 ℃). $t_{1/2}^{-1}$ increases monotonously with increasing f_h in PCL-PS2 whereas it decreases with increasing f_h in PCL-PS5. From Fig. 1(b), we suppose two distinct effects of chain-end tethering on the crystallization behavior. One is the acceleration of nucleation rates at the tethering points and the other the deceleration of nucleus growth rates by reduced chain mobility. The relative magnitudes of these two opposite effects vary with the confinement size to yield the marked difference in the f_h dependence of crystallization rates between PCL-PS2 and PCL-PS5.

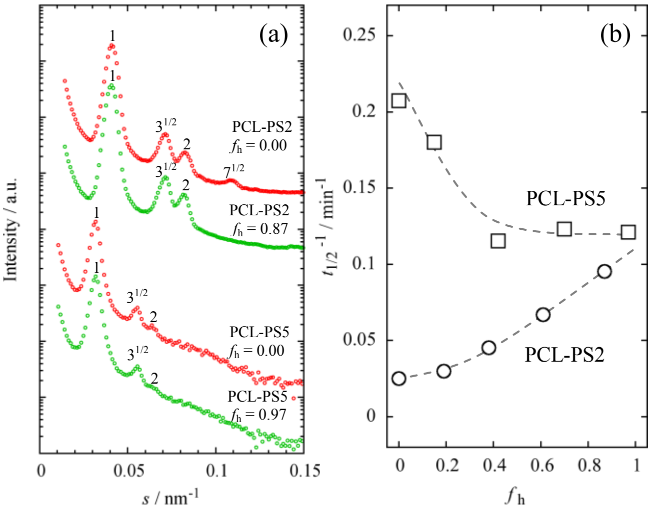

Fig. 1: (a) SR-SAXS curves of crystallized PCL-PS2 and PCL-PS5 with different f_h indicated. (b) $t_{1/2}^{-1}$ plotted against f_h for PCL-PS2 and PCL-PS5 crystallized at T_c = -40 ℃.

References

[1] Nojima, S. *et al.*, *Macromolecules* **41**, 1915 (2008).
[2] Nakagawa, S. *et al.*, *Macromolecules* **45**, 1892 (2012).

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