BL-10C/2016G652

Effects of Bulky End-groups on the Crystallization Rate of Poly(ε-caprolactone) Homopolymers Confined in a Cylindrical Nanodomain

Koshun Kawazu[1], Shintaro Nakagawa[2], Hironori Marubayashi[1], and Shuichi Nojima[1,*]
[1]Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-1552, Japan
[2]The University of Tokyo, 4-61-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan

1 Introduction

The crystallization of polymer chains spatially confined in nanodomains is interesting because of their unique features. [1] In this study, we prepare several poly(ε-caprolactone) (PCL) homopolymers with various end-groups all confined in an identical nanocylinder provided by the microphase separation of PCL-*block*-polystyrene (PCL-*b*-PS), where the chain mobility of confined PCL chains is expected to change continuously (**Fig. 1**). The crystallization rate of these PCL homopolymers is examined as a function of the molecular weight of end-groups M_E (or overall mobility of confined chains).

2 Experiment

A PCL-*b*-PS with a photocleavable *o*-nitrobenzyl group (ONB) at block junctions was prepared. The PCL block confined in nanocylinders was converted into PCL homopolymers by cleaving ONB with UV light. The T_m of PCL blocks was lower than T_g of PS blocks, so the nanocylinder was preserved after the photocleavage of ONB owing to the vitrification of PS matrices. The chain-end of PCL blocks was replaced with various bulky groups. That is, an acetyl group with M_E = 43 g/mol (denoted 0-PCL) in the original PCL block was replaced with adamantine (M_E = 163, A-PCL), cholesterol(M_E = 386, C-PCL), methyl 2,3,6-tri-o-benzyl-α-D-galactopyranside (M_E = 506, M-PCL), and glassy PS (i.e., original PCL-*b*-PS) (M_E = ∞, PS-PCL).

The microdomain structure was confirmed by small-angle X-ray scattering (SR-SAXS) at BL-10C, KEK-PF. The crystallization rate of each confined PCL was obtained by differential scanning calorimetry (DSC).

3 Results and Discussion

The SR-SAXS curves from crystallized samples after irradiating UV light (denoted X-PCL/PS) are shown in **Fig. 2.** Every curve has several intensity peaks, the positions of which exactly correspond to a ratio of $1 : \sqrt{3} : 2 : \sqrt{7}$, indicating the cylindrical microdomain structure is formed. The primary peak position does not change before and after irradiating UV light, suggesting the microdomain structure is completely preserved after photocleavage, and eventually the PCL homopolymers are successfully confined in the nanocylinder. The nanocylinder diameter D was evaluated to be 12.9 nm from the interdomain distance derived from the primary peak position and the volume fraction of PCL chains.

The inverse of half-time of crystallization $1/\tau_{1/2}$ (a measure of crystallization rates) is obtained as a function of M_E for confined PCL homopolymers. Surprisingly, $1/\tau_{1/2}$ of PCL homopolymers with bulky end-groups (i.e., A-PCL, C-PCL, and M-PCL) is significantly larger than that of 0-PCL (with largest chain mobility) and PS-PCL (smallest chain mobility). This result indicates that the crystallization of confined homopolymers depends complicatedly on their chain mobility as well as D.

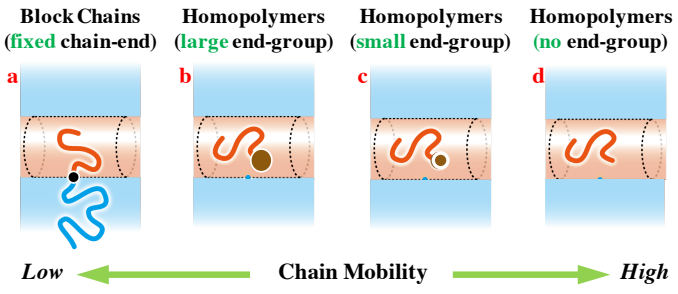

Fig. 1. Schematic illustration showing the crystalline block (a) and crystalline homopolymers (b - d) confined in an identical nanocylinder. The chain mobility of confined polymers is expected to increase gradually from a to d.

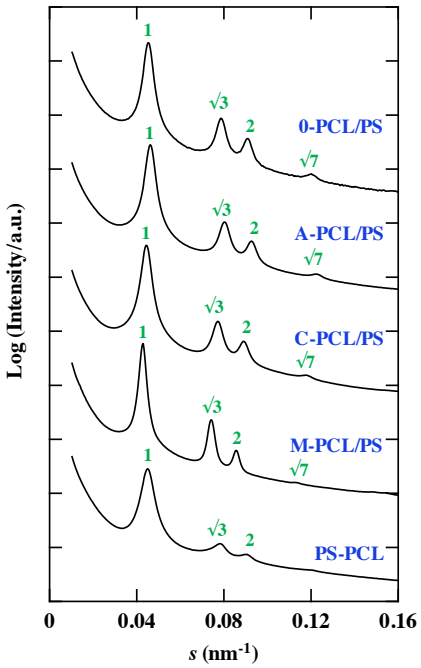

Fig. 2. SR-SAXS curves from crystallized samples indicated on each curve after irradiating UV light.

References

[1] S. Nakagawa *et al.*, *Eur. Polym. J.* **70**, 262 (2015).

* snojima@polymer.titech.ac.jp