

# Crystallization of Both-ends-tethered, One-end-tethered, and Untethered Polymer Chains Confined in Lamellar Nanodomains

Shintaro Nakagawa, Koshun Kawazu, and Shuichi Nojima\*

Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, H-125, 2-12-1 Ookayama, Meguro-ku Tokyo 152-8552, Japan

## 1 Introduction

Block copolymers consisting of a crystalline block and a glassy amorphous block exhibit interesting crystallization behavior since the crystalline blocks are spatially confined in nanodomains formed by microphase separation of block copolymers. Crystallization behavior in such cases is significantly affected not only by the shape and size of nanodomains but also by the chain-ends fixed at nanodomain interfaces (chain-end tethering). We have recently studied the effect of chain-end tethering on crystallization by comparing one-end-tethered (OT) and untethered (UT) chains both spatially confined in identical nanodomains [1]. In the present study, we investigate the crystallization behavior of both-ends-tethered (BT) chains as well as OT and UT chains to comprehensively understand the effects of chain-end tethering on the crystallization under spatial confinement.

## 2 Experiment

**Samples.** We synthesized two lamella-forming polystyrene-*block*-poly( $\epsilon$ -caprolactone)-*block*-polystyrene (PS-*b*-PCL-*b*-PS) triblock copolymers having identical composition and molecular weight (SCS and SC'S in Fig. 1a). SCS has two photocleavable *o*-nitrobenzyl groups (ONBs) in interblock junctions while SC'S has only one ONB. SCS and SC'S both have BT PCL chains confined in lamellar nanodomains. Upon photocleaving ONBs by UV irradiation, BT chains in SCS and SC'S are converted to UT and OT chains, respectively (S/C/S and S/C'S in Fig. 1a). It is then possible to directly compare the crystallization behavior of BT, OT, and UT chains confined in identical lamellar nanodomains.

**Measurements.** The size and shape of nanodomains were determined by SAXS at BL-10C in PF-KEK using PILATUS3 2M detector. The isothermal crystallization behavior was investigated using time-resolved infrared spectroscopy (TR-IR) and differential scanning calorimetry (DSC).

## 3 Results and Discussion

SAXS curves of SCS, SC'S, S/C/S, and S/C'S in crystallized state are shown in Fig. 1b. All the samples exhibit multiple scattering peaks whose relative positions are 1:2:3, indicating the presence of well-ordered lamellar nanodomains. It is also clear that all the samples before and after UV irradiation have identical nanodomains since their primary peak positions are completely matched. From the primary peak position and the volume fraction of PCL chains, the thickness of lamellar

nanodomains containing PCL chains was calculated to be ca. 11 nm for all the samples.

Fig. 2 shows the crystallization half-time  $t_{1/2}$  of the PCL chains in the samples evaluated from TR-IR and DSC results, where larger  $t_{1/2}$  means the lower crystallization rate. It can be seen that the temperatures at which  $t_{1/2}$  is 10 min follow the relation SCS = SC'S  $\ll$  S/C'S < S/C/S, indicating that chain-end tethering moderately retards the crystallization, though the effect of one-end-tethering is not as profound as that of both-ends-tethering.

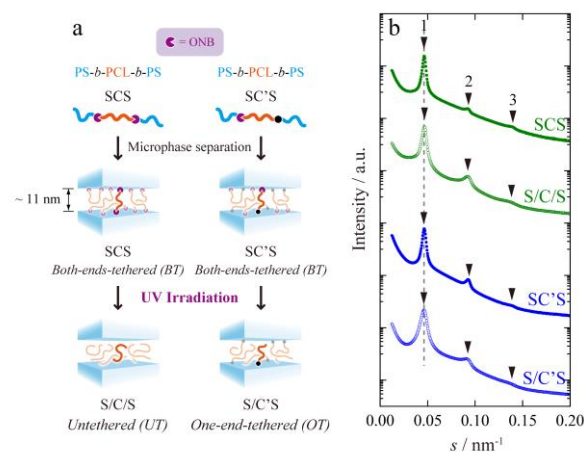


Fig. 1: (a) Schematic illustration showing the sample preparation method used in this study. (b) SAXS curves of the crystallized samples.

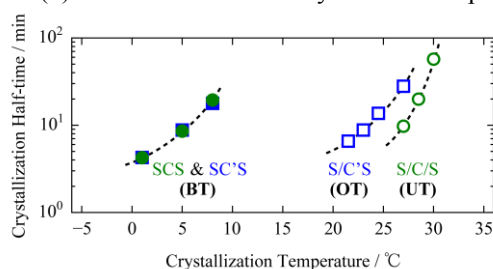


Fig. 2: Crystallization half-time plotted against crystallization temperature.

## Acknowledgment

Authors thank Prof. T. Ishizone at Tokyo Tech and Profs. K. Yamaguchi and S. Nakahama at Kanagawa Uni. for their help in synthesizing the samples.

## References

[1] S. Nakagawa *et al.*, *Polymer* **55**, 4394-4400 (2014).

\* snojima@polymer.titech.ac.jp