

## Crystallization Behavior of a Double Crystalline Block Copolymer

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### Introduction

When a crystalline-crystalline diblock copolymer, poly( $\epsilon$ -caprolactone)-*block*-polyethylene (PCL-*b*-PE), is heated, we usually observe a sudden decrease in the long period (LP), an alternating distance of the morphology, by the melting of PCL blocks [1]. This characteristic melting behavior might be caused by a long-time crystallization of both blocks before heating. In this study, we have investigated the crystallization behavior of PCL-*b*-PE over a long time (~3days) by synchrotron small-angle X-ray scattering (SR-SAXS), conventional SAXS (C-SAXS), differential scanning calorimetry (DSC), and Fourier transform infrared spectroscopy (FTIR) to reveal structural changes during crystallization.

### Experimental Section

#### Sample

PCL-*b*-PE was obtained by the hydrogenation of PCL-*block*-polybutadiene anionically synthesized. The molecular weight of PCL-*b*-PE is 14,000 g/mol, the molecular weight distribution is 1.16, the volume fraction of PCL blocks is 64 vol.%, the melting temperature of the PCL blocks is *ca.* 56 °C, and that of PE blocks is *ca.* 95 °C.

#### SAXS Measurements

The sample was annealed at 120 °C for 10 min and subsequently quenched into crystallization temperature  $T_c$  (= 25~50 °C below melting temperature of PCL blocks), where PE blocks crystallized first followed by the crystallization of PCL blocks. In order to pursue the early stage crystallization (< 40 min) we used SR-SAXS while the late stage crystallization was observed by C-SAXS. The SR-SAXS experiment was performed at beam line BL-10C. The background scattering and Lorentz factor were taken into account, and the relative intensity was

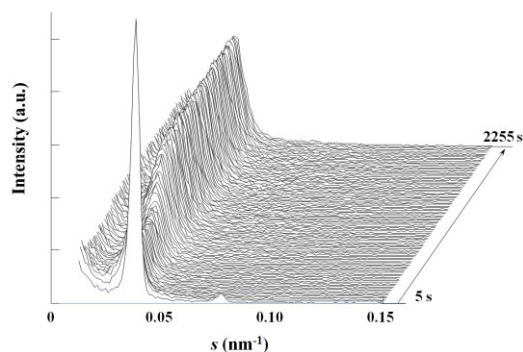


Fig. 1 SR-SAXS profiles of PCL-*b*-PE quenched from 120 °C into 40 °C.

obtained as a function of wave number  $s$  ( $= (2/\lambda)\sin\theta$ ,  $2\theta$  is scattering angle and  $\lambda = 0.1488$  nm). The peak position (or LP) was finally evaluated as a function of crystallization time  $t_c$ .

### Results and Discussion

Fig. 1 shows the typical SR-SAXS profiles during crystallization of PCL-*b*-PE at 40 °C. We can observe a sharp diffraction arising from the microdomain structure just after quenching, which turns quickly into a small scattering peak with a considerable shift of the peak position, indicating that the microdomain structure is completely transformed into the lamellae morphology by the crystallization of PE blocks.

Fig. 2 shows the plot of LP against  $t_c$  for PCL-*b*-PE crystallized at  $T_c = 25$  °C (squares) and 40 °C (circles). At the early stage of crystallization ( $t_c < 10$  min) we can observe the significant increase of LP caused by the crystallization of PE and PCL blocks, but at the late stage of crystallization ( $t_c > 10$  min) no change in LP can be observed, that is, the morphology remains unchanged at the late stage crystallization. However, the results of DSC and FTIR measurements, which carried out with the same thermal history of SAXS measurements, clearly indicate that the crystallinity of PCL blocks increases and simultaneously that of PE blocks decreases slightly at the late stage of crystallization. From these results we conclude that the partial melting of PE crystals, which is facilitated by further crystallization of PCL blocks, yields the constant LP during the late stage crystallization.

[1] S. Nojima, et al., *Macromolecules*, **40**, 7566 (2007).

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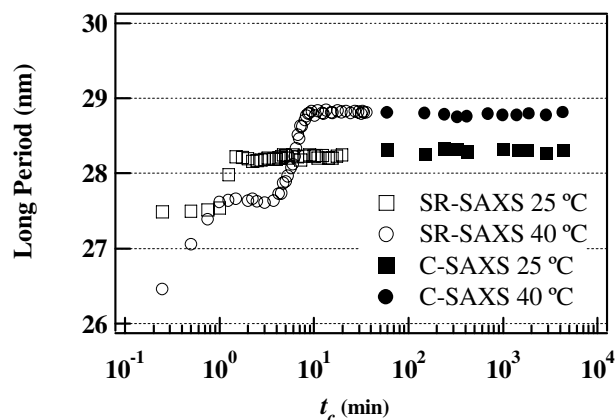


Fig. 2 LP plotted against  $t_c$  for PCL-*b*-PE crystallized at  $T_c = 25$  °C (squares) and 40 °C (circles). Open symbols are measured by SR-SAXS and closed symbols by C-SAXS.