

# Crystallization Behavior of Poly( $\epsilon$ -caprolactone) Blocks Confined in Crystalline Lamellar Morphology of Poly( $\epsilon$ -caprolactone)-*block*-Polyethylene Copolymers

Takuya SAKURAI, Satoru GONDO, 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

We have recently reported on the crystal orientation of poly( $\epsilon$ -caprolactone) (PCL) blocks in PCL-*block*-polyethylene (PCL-*b*-PE) copolymers as a function of the crystallinity of PE blocks  $\chi_{PE}$  and the layer thickness of PCL blocks  $d_{PCL}$ , where the amorphous PCL blocks were confined within the lamellar morphology formed by the crystallization of PE blocks (PE lamellar morphology) [1]. In this report, we examined the crystallization behavior of PCL blocks spatially confined in the PE lamellar morphology as a function of  $\chi_{PE}$  and  $d_{PCL}$ .

## 2 Experiment

**Samples** Four PCL-*b*-PE copolymers with different  $\chi_{PE}$  and  $d_{PCL}$  (denoted E07, E16, E23, and E24) were prepared. In these systems, the PE blocks crystallized first on quenching to form the PE lamellar morphology, in which the PCL blocks were completely confined. Therefore, the PCL blocks crystallized within the PE lamellar morphology on further quenching.

**Measurements** The morphology formed at each temperature was examined using synchrotron small-angle X-ray scattering (SR-SAXS). The SR-SAXS experiment was performed at beam line BL-10C in KEK-PF. The crystallization time dependence of crystallinity for PCL blocks  $\chi_{PCL}$  was pursued using differential scanning calorimetry (DSC) at a heating rate of 10 °C/min.

## 3 Results and Discussion

Figure shows the SR-SAXS curves from the samples at

each temperature, where both blocks are amorphous at 120 °C, only the PE block are crystallized at 70 °C, and both blocks are crystallized at 25 °C. We find a series of scattering peaks at 120 °C, indicating that a cylindrical microdomain is formed in E07 and E23 and a lamellar microdomain in E16 and E24. When only PE blocks crystallize at 70 °C, the higher-order peaks disappear and the primary and second peaks become diffuse and shift appreciably to lower angles, suggesting that both microdomain structures are replaced with the PE lamellar morphology by the crystallization of PE blocks. The PCL blocks crystallize on further quenching into 25 °C, but the SR-SAXS curves are similar to those observed at 70 °C, suggesting that the PCL blocks crystallize in the existing PE lamellar morphology.

The time evolution of  $\chi_{PCL}$  (isothermal crystallization behavior) depends significantly on  $\chi_{PE}$  and  $d_{PCL}$ . That is, when  $d_{PCL}$  is smaller and  $\chi_{PE}$  is higher, the crystallization behavior is largely different from that of other copolymers. For example, the Avrami index  $n$  is moderately small and the half time of crystallization is extremely long. These facts indicate that the PE lamellar morphology with higher  $\chi_{PE}$  and smaller  $d_{PCL}$  works as a hard confinement against the crystallization of PCL blocks, which is similar to the confinement due to glassy microdomains.

[1] T. Sakurai, H. Nagakura, S. Gondo, and S. Nojima, *Photon Factory Activity Report 2011*, **29**, 174 (2012).

\* snojima@polymer.titech.ac.jp

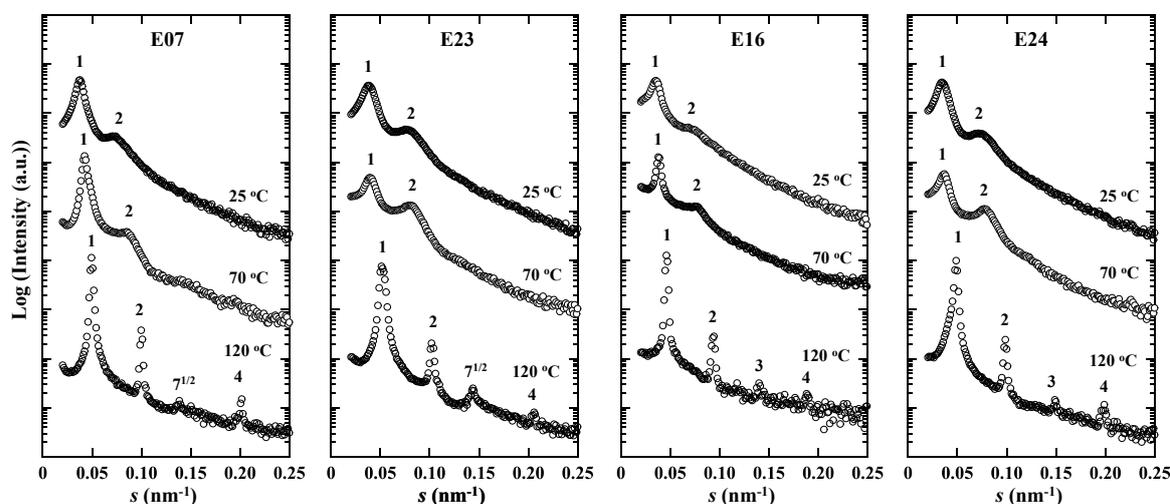


Figure. SR-SAXS curves from different samples at 120 °C (bottom), 70 °C (middle), and 25 °C (top).