

Crystallization Behavior of Crystalline-Crystalline Diblock Copolymers with Close Crystallizable Temperatures

Jun MATSUMOTO, Yoshimasa FUKAGAWA, Richard LABRADOR,
Chang GONG, 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

Introduction

Morphology formation in crystalline-crystalline diblock copolymers is extremely complicated due to the interplay between two kinds of crystallization starting from the molten microdomain structure. The relative position of crystallizable temperatures of two blocks is an important factor to control the crystallization process. In our previous work [1], we investigated the non-isothermal crystallization of a crystalline-crystalline diblock copolymer with close crystallizable temperatures, polyethylene-*block*-poly(β -propiolactone) (PE-*b*-PPL), and found both blocks crystallized simultaneously when the cooling rate was slow. In this study, we investigate the simultaneous crystallization of both blocks in more detail using new PE-*b*-PPL with closer crystallizable temperatures.

Experimental Section

Sample The total molecular weight of PE-*b*-PPL is 18,400 and the volume fraction of PE blocks is 0.45. The crystallizable temperature for PE blocks is 70 °C and that for PPL blocks is 61 °C when the sample is cooled at -1 °C/min.

Measurements The microdomain structure was investigated using small-angle X-ray scattering with synchrotron radiation (SR-SAXS). The SR-SAXS experiment was performed at beam line BL-10C in KEK-PF. The crystallization behavior during cooling from the melt at -1 °C/min was investigated using differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FT-IR).

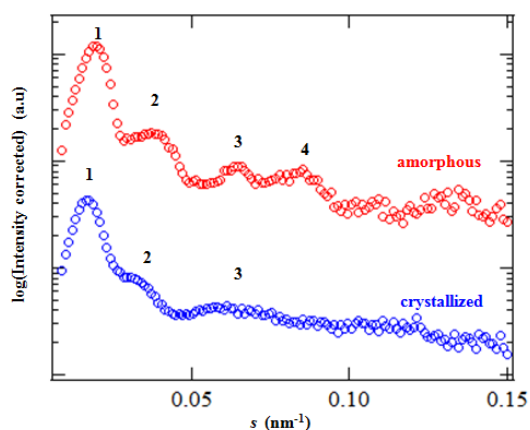


Figure 1. SR-SAXS curves for amorphous (top) and crystallized (bottom) PE-*b*-PPL.

Results and Discussion

Figure 1 shows SR-SAXS curves for amorphous and crystallized PE-*b*-PPL. The SR-SAXS curve from the molten PE-*b*-PPL has several scattering peaks, the angular positions of which exactly correspond to a ratio of 1 : 2 : 3 : 4, indicating that the lamellar microdomain structure is formed in the melt. The SR-SAXS curve from the crystallized PE-*b*-PPL has several scattering peaks, which also correspond to a ratio of 1 : 2 : 3. This indicates that the lamellar morphology is formed in the crystallized state. In addition, the long period of the lamellar morphology, evaluated from the primary peak position, changes continuously with changing temperature. These results indicate that PE and PPL blocks crystallize within each lamellar microdomain without any morphological transformation.

The time evolution of crystallinity for each block was mainly evaluated from FT-IR measurements. When PE-*b*-PPL was cooled from the melt at -1 °C/min, the normalized crystallinity of PE blocks and PPL blocks plotted against temperature showed the distorted sigmoidal curve, which reflects the interactive crystallization of both blocks. Figure 2 shows the temperature dependence of the crystallization rate of both blocks evaluated from the above plot. We can find that when the crystallization rate of one block is large, that of the other block is small, suggesting that crystallization of one block significantly affected that of the other in simultaneous crystallization.

Reference

[1] S. Nojima et al., *Macromolecules*, **42**, 9515 (2009).

* snojima@polymer.titech.ac.jp

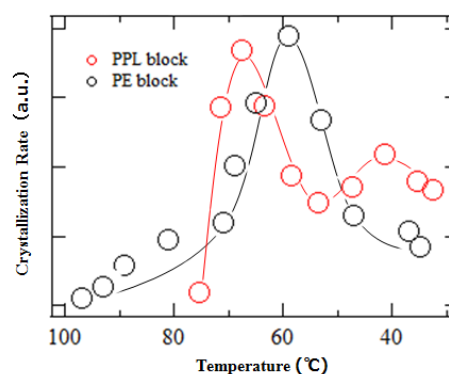


Figure 2. Crystallization rate of PE blocks (black) and PPL blocks (red) plotted against temperature during cooling at -1 °C/min.