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Significant Increase in Melting Temperature of Constituent Blocks Confined in Crystallized Lamellar Morphology of Crystalline-Crystalline Copolymers

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Introduction

We have reported the melting process of poly (ε-caprolactone) (PCL) blocks in PCL-*block*-polyethylene (PCL-*b*-PE) diblock copolymers, where PCL blocks crystallized within the crystallized PE lamellar morphology (PE lamellar morphology) [1]. In this report, we analyze the experimental results and discuss the effect of the PE morphology on the melting behavior of PCL blocks.

Experimental section

Samples The copolymers used are PCL-*b*-PE, which were obtained by the hydrogenation of PCL-*block*-polybutadiene (PCL-*b*-PB) anionically synthesized (denoted C51 ~ C91). The PE block is a minor component in these samples, *i.e.*, the PE composition is in the range between 9 ~ 49 vol. %.

Morphology of PCL-b-PE The morphology formed was measured using small-angle X-ray scattering with synchrotron radiation (SR-SAXS), which was performed at beam line BL-10C in KEK-PF.

Melting process of PCL blocks The melting process was investigated using differential scanning calorimetry (DSC) with a heating rate of 10 °Cmin^{-1}. We first crystallized PE blocks at 70 °C and then annealed at 45 °C to crystallize PCL blocks. We also measured the melting process of PCL-*b*-PB, and evaluated the melting temperature difference ΔT_m between PCL blocks in PCL-*b*-PE and those in PCL-*b*-PB.

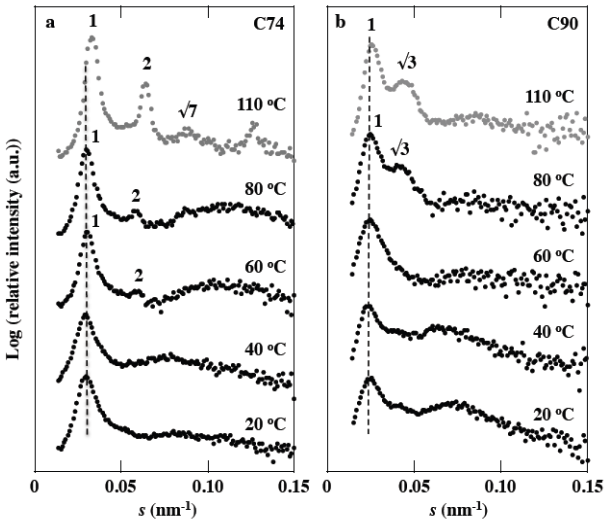

Figure 1. SR-SAXS curves for C74 (a) and C90 (b) at each temperature indicated.

Results and discussion

The SR-SAXS curve at 110 °C has several scattering peaks for the sample with 74 vol. % PCL blocks (C74), indicating the cylindrical microdomain structure is formed in melt (Figure 1-a). The primary peak position of the SR-SAXS curves below 80 °C is significantly different from that at 110 °C, suggesting the morphological transition occurs by the crystallization of PE blocks. We obtained similar results for the samples with 51 ~ 84 vol. % PCL blocks, and also the sample with 91 vol. % PCL blocks, where PE blocks was crystallized at higher temperature to form the PE lamellar morphology. For the sample with 90 vol. % PCL blocks (C90), however, the SR-SAXS curve at 110 °C is similar to those below 80°C with the primary peak position being unchanged, suggesting that PE blocks crystallize within the microdomain structure existing in the melt (Figure 1-b). Similar results were obtained for the sample with 91 vol. % PCL blocks and also the sample with 84 vol. % PCL, where it was quenched into liquid nitrogen for rapid crystallization.

Figure 2 shows ΔT_m plotted against the volume fraction of PCL blocks (Φ_{PCL}). We find ΔT_m for the PE lamellar morphology (open circle) increases steadily with increasing Φ_{PCL} but that for the crystallized microdomain structure (closed circle) is very small. This difference in ΔT_m can arise mainly from the difference in conformation of amorphous PCL blocks, which originates from the difference in the morphology after PE crystallization.

Reference

[1] T. Sakurai and S. Nojima, *Polym. J.*, **43**, 370 (2011)

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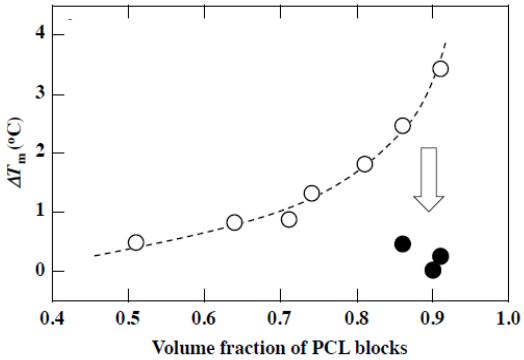

Figure 2. The difference in melting temperature ΔT_m between PCL blocks in PCL-*b*-PE and those in PCL-*b*-PB plotted against Φ_{PCL}.