

Crystallization Behavior of Poly(β -propiolactone) *-block-*Polyethylene Diblock Copolymers with Varying Polyethylene Crystallinity

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1 Introduction

The crystallization behavior of crystalline-crystalline diblock copolymers has been extensively examined because it is driven by two kinds of crystallization to yield the complicated morphology formation. In this study, we investigate the crystallization behavior and final morphology of poly(β -propiolactone)-*block*-polyethylene (PPL-*b*-PE) copolymers with the wide PE crystallinity χ_{PE} ranging from 0 to 0.33. The crystallization ability of PE blocks is expected to increase significantly with increasing χ_{PE} , which might affect the crystallization behavior of PE and PPL blocks and the resulting morphology after the crystallization of both blocks.

2 Experiment

Samples Several PPL-*b*-PE copolymers with different χ_{PE} were synthesized. In these systems, the PE block crystallized first on quenching, and subsequently the PPL block crystallized. Therefore, the crystallization of PPL blocks started from some morphology formed by the advance crystallization of PE blocks.

Measurements The melting behavior of crystallized PPL-*b*-PE copolymers was examined by differential scanning calorimetry (DSC) with a heating rate of 10 °C/min to evaluate χ_{PE} . The crystallization behavior was pursued using synchrotron small-angle X-ray scattering (SR-SAXS) and Fourier transform infrared spectroscopy (FTIR). The SR-SAXS experiment was performed at beam line BL-10C in KEK-PF.

3 Results and Discussion

Figure shows time-resolved SR-SAXS curves during isothermal crystallization at 60 °C when quenched from the microphase-separated melt for PPL-*b*-PE copolymers

with $\chi_{PE} = 0.33$ (a) and $\chi_{PE} = 0$ (b). In Figure a, the crystallization of PE blocks replaces the existing lamellar microdomain structure with a crystalline lamellar morphology, and subsequently PPL blocks crystallize within this morphology. In Figure b, on the other hand, the PE block does not crystallize, and the crystallization of PPL blocks destroys the lamellar microdomain structure to result in a crystalline lamellar morphology. For PPL-*b*-PE copolymers with $0 < \chi_{PE} < 0.26$ (SR-SAXS curves are not shown), the crystallization ability of PE blocks is not strong, so that the crystallization of PE blocks does not destroy the lamellar microdomain structure but reinforces it against the subsequent crystallization of PPL blocks. As a result, a crystalline lamellar microdomain structure is formed after the crystallization of both blocks.

Based on the SR-SAXS results, together with FTIR results, it is possible to classify the morphology formation occurring in PPL-*b*-PE copolymers into three groups according to χ_{PE} . When $\chi_{PE} > 0.30$, the crystallization of PE blocks yields the morphological transition and then the PPL block crystallizes to yield the crystalline lamellar morphology in which both blocks crystallize. When $0 < \chi_{PE} < 0.26$, the crystallization of PE blocks reinforces the lamellar microdomain structure and the PPL block crystallizes within it to form the crystalline lamellar microdomain structure. When $\chi_{PE} = 0$, the PE block does not crystallize and the crystallization of PPL blocks leads to the crystalline lamellar morphology in which only PPL blocks crystallize.

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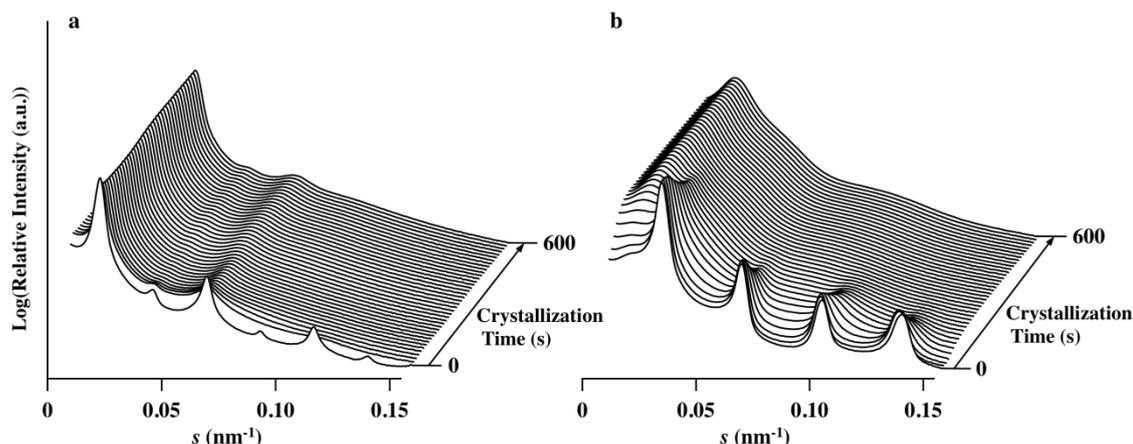


Figure. SR-SAXS curves during crystallization at 60 °C for PPL-*b*-PE copolymers with $\chi_{PE} = 0.33$ (a) and $\chi_{PE} = 0$ (b).