

## Isothermal Crystallization of Double Crystalline Diblock Copolymers with Close Crystallizable Temperatures

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### 1 Introduction

Morphology formation in double 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 behavior. In our previous work<sup>1</sup>, we investigated the non-isothermal crystallization behavior of crystalline-crystalline diblock copolymers with close crystallizable temperatures, poly ( $\beta$ -propiolactone)-*block*-polyethylene (PPL-*b*-PE), and found that when the crystallization rate of one block was large, that of the other block was small, suggesting simultaneous crystallization. In this study, we investigate the isothermal crystallization behavior of PPL-*b*-PE.

### 2 Experimental

**Samples** Four PPL-*b*-PE copolymers were synthesized using anion polymerization. The samples were named as PL-PE10, PL-PE15, PL-PE20, and PL-PE51, where the numeral in the sample code represents the mole% of 1,2-addition for ethylene monomers in PE blocks. The volume fraction of PPL blocks was around 0.5.

**Measurements** The microdomain structure was investigated using small-angle X-ray scattering with synchrotron radiation (SR-SAXS), which was performed at beam line BL-10C in KEK-PF. The isothermal crystallization behavior was also observed using time-resolved SR-SAXS, and independently using Fourier transform infrared spectroscopy (FT-IR).

### 3 Results and Discussion

The SR-SAXS curves from molten and crystallized samples have several scattering peaks, the angular positions of which exactly correspond to a ratio of 1: 2: 3. This indicates that the lamellar morphology is formed in all samples at both amorphous and crystallized states. Fig. 1 shows the time-resolved SR-SAXS curves for PL-PE10 and PL-PE51 isothermally crystallized at 55°C. The SR-SAXS curves for PL-PE10 show the monotonous increase in the primary peak intensity with increasing crystallization time  $t$  except at the initial period ( $< 50$  s). It is successfully explained by considering that the PE blocks crystallize promptly during quenching to form the crystallized lamellar microdomains, which are rigid and stable against subsequent crystallization of PPL blocks. Therefore, the crystallization of PPL blocks occurs within this crystallized microdomain. The SR-SAXS curves for PL-PE51 have the minimum of the primary peak intensity (indicated by an arrow) during isothermal crystallization,

suggesting the morphological transition from the molten lamellar microdomain structure into crystallized lamellar morphology. That is, the scattering peak intensity arising from the microdomain structure steadily decreases and simultaneously that from the crystallized lamellar morphology increases with increasing  $t$  to yield the peak intensity minimum during the course of crystallization.

The results of isothermal crystallization behavior for PL-PE10 and PL-PE51 obtained using FT-IR are consistent with those obtained by SR-SAXS measurements. In addition, we found from FT-IR results that PE blocks in PL-PE51 do not crystallize during isothermal crystallization. On the contrary, the PE blocks in PL-PE10 crystallize. We conclude that the difference in crystallization behavior between PL-PE10 and PL-PE51 mainly arises from the rigidity of the lamellar microdomain structure existing just before the crystallization of PPL blocks.

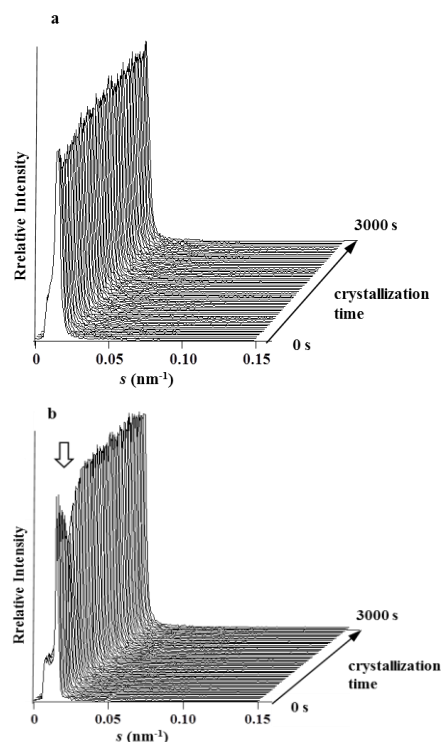


Fig. 1: Time-resolved SR-SAXS curves of PL-PE10 (a) and PL-PE51 (b) isothermally crystallized at 55 °C.

1 J. Matsumoto *et al.*, *Photon Factory Activity Report* 2010, **28**, 162 (2011).

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