

Interactive Crystallization Behavior of Double Crystalline Block Copolymers with Close Crystallizable Temperatures

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1 Introduction

Morphology formation in double crystalline diblock copolymers is extremely complicated due to an 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 work¹, we investigated the non-isothermal crystallization behavior of crystalline-crystalline diblock copolymers with close crystallizable temperatures, poly(β -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 Experiment

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 for all copolymers

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 microdomain structure is formed in the melt and the lamellar morphology after crystallization. Fig.1 shows the time (t) dependence of the primary peak intensity (black) and long period (blue) for PL-PE10 and PL-PE51 when isothermally crystallized at 55 °C. For PL-PE10, the long period is almost constant (41 - 42 nm) irrespective of t , indicating that the lamellar microdomain is preserved during the crystallization of PPL blocks. This fact suggests that the advance crystallization of PE blocks makes the microdomain structure stable against the subsequent crystallization of PPL blocks. In addition, the primary peak intensity increases monotonously with increasing t at small t (< 230 s).

The long period of PL-PE51 increases significantly at the early stage of crystallization of PPL blocks. That is, it increases from 42 nm to 47 nm, as shown in Fig.1-b. It is interesting to find that the crystallization time when the long period sharply increases corresponds to the peak intensity minimum for PL-PE51 (arrow). We can successfully explain this fact by considering that lamellar microdomains are replaced with the crystallized lamellar morphology by the crystallization of PPL blocks.

We concluded from these results that the prompt crystallization of PE blocks coupled with the strong block incompatibility reinforced the lamellar microdomain structure and made it stable against the subsequent crystallization of PPL blocks to result in double crystallized lamellar microdomains.

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

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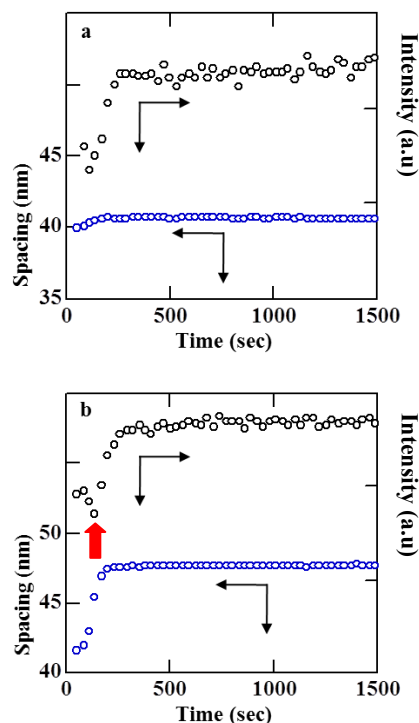


Fig. 1: Long period and primary peak intensity plotted against crystallization time for PL-PE10 (a) and PL-PE51 (b) isothermally crystallized at 55 °C.