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Small- and Wide-Angle X-ray Scattering Studies on Confined Crystallization of Poly(ethylene glycol) in Poly(L-lactic acid) Spherulite in a PLLA/PEG Blend

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1 Introduction

We have reported in our previous publication that the PEG crystalline lamellae were considered to be confined in between preformed PLLA crystalline lamellae when the PLLA/PEG (50/50) blend specimen was subjected to the two-step T-jump at 45.0˚C via the first-step crystallization at 127.0˚C (T_1 = 127.0˚C and T_2 = 45.0˚C) [1]. Note that the polarized optical microscope (POM) showed that the PEG crystallization occurred only inside the preformed PLLA spherulite. Important point is that we set the crystallization temperature slightly above the freezing temperature (T_f) of PEG in the PLLA/PEG (50/50) blend specimen, i.e., $T_f \approx$ 45˚C. This is the reason of no PEG crystallization in the amorphous mixture of the blend with the content of PEG (w_{PEG}) = 0.5 at 45˚C. However, once the PLLA crystallizes in the amorphous mixture of PLLA/PEG (50/50), the accumulation of the PEG content is resulted in the vicinity of the PLLA crystalline phase so that T_f of PEG is increased only in the region close to the PLLA crystalline phase, which is inside the PLLA spherulite. Due to this increase, if T_f becomes higher than 45˚C, the PEG becomes able to crystallize. This event occurs exclusively inside the PLLA spherulite and nothing happens outside the PLLA spherulite because of no accumulation of the PEG content far from the PLLA crystalline phase. In this report, we provide experimental evidence of the confined crystallization of the PEG lamellae in a stack of the preformed PLLA lamellae by conducting simultaneous SAXS and WAXS measurements along with the two-step T-jump as 180.0˚C→127.0˚C→45.0˚C.

2 Experiment

The PLLA sample (4032D; Nature Works LLC, USA) having a weight-average molecular weight (M_w) of 1.66 × 10^5 with the D content of 1.4% was used in this study. The PEG sample (M_w = 20000) was purchased from Wako Pure Chemical Industries, Ltd, Japan.

Given amounts of PLLA and PEG were dissolved in dichloromethane (DCM) to make a clear polymer solution with a polymer concentration of 5 wt% by stirring for 24 h at room temperature. Then, the solution was poured into a Petri dish with a diameter of 5.0 cm to allow complete evaporation of DCM at room temperature for 60 h.

The SWAXS (small- and wide-angle X-ray scattering) measurements were conducted at the BL–6A beamline of PF, using X-ray with λ = 0.150 nm. The sample-to-detector distance was 2.184m, which was calibrated using a chicken tendon collagen having a d-spacing of 65.3nm. The beam size was measured at the detector position as 0.245mm (an FWHM value) in the vertical direction and 0.498mm (an FWHM value) in the horizontal direction. A PILATUS3-1M (DECTRIS Ltd., Baden, Switzerland) was used as a two-dimensional detector.

3 Results and Discussion

Confined crystallization of PEG in the stack of the preformed PLLA lamellae was studied by conducting the time-resolved simultaneous SAXS/WAXS measurements upon the two-step T-jump experiment from 180.0˚C to 45.0˚C (T_2) via 127˚C (T_1) for the PLLA/PEG (50/50) blend specimen. The WAXS results showed much suppression of (12-4)/(1-24) crystalline reflection for the blend specimen as compared to the neat PEG, as well as much wider peak width for the same reflection. These results indicate the suppression of the growth of the PEG lamellae due to the space confinement owing to the preformed PLLA lamellae. The SAXS results also confirmed the confined crystallization of PEG in the amorphous layer sandwiched by the preformed PLLA crystalline lamellae. Nevertheless, more regular stacking was formed due to the PEG crystallization as the neat PEG has the ability of forming very regular stacking of the crystalline lamellae, as evidenced by observing second-order peak in the SAXS profile for the blend specimen.

Reference

1. Apisit Banpean, Shinichi Sakurai, “Confined crystallization of Poly(ethylene glycol) in spherulites of Poly(L-lactic acid) in a PLLA/PEG blend”, Polymer, 215, 123370 (2021).

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