Confined and Hidden Crystallization of Poly(ethylene glycol) in Spherulites of Poly(L-lactic acid) in a PLLA/PEG Blend

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1 Introduction

Intriguing crystallization behaviors of poly(ethylene glycol) (PEG) in a blend specimen of poly(L-lactic acid) (PLLA) with PEG were studied by the polarizing optical microscopy (POM) and the differential scanning calorimetry (DSC). The PLLA/PEG (50/50) blend specimen was heated up to 180°C and kept at this temperature for 5 min to obtain complete melt without liquid-liquid phase separation. Then, a two-step temperature-jump was conducted as 180°C→ 127°C→ 45°C. It was found that PEG can crystallize only in the precedingly grown spherulites of PLLA, as no crystallization of PEG was found in the matrix of the mixed PLLA/PEG amorphous phase. This is because of the depression of the freezing temperature of PEG (T_f) due to the complete mixing of PLLA/PEG, by noting that the neat PEG can crystallize at 45°C which is lower than T_f of the neat PEG (49.8°C). Upon the PLLA crystallization at 127°C, the PEG content in the amorphous region inside of the PLLA spherulite is increased because of the formation of the pure solid phase of PLLA (crystalline phase). Namely, the PLLA content is decreased in the amorphous phase of the PLLA/PEG mixture. Then, T_f of PEG increases so that PEG can crystallize but this crystallization is only allowed inside of the preceded PLLA spherulite. Thus, the confined and hidden crystallization of PEG can be accounted for. It was further found that the ultimate degree of crystallinity (ϕ^∞) of PEG was increased and the induction period of the confined and hidden crystallization of PEG was decreased as a function of the PLLA crystallization time at 127°C because of the increase in the PEG content in the amorphous phase due to the increase of the PLLA amount crystallized, which was more clearly recognized as a function of the size of the preceded PLLA spherulite. The direct evidence of the PEG crystallization was obtained by the wide-angle X-ray scattering (WAXS). The kinetics was also studied for the confined and hidden crystallization of PEG. Based on the results of the kinetic study, the effect of the space confinement is discussed.

2 Experimental

The PLLA sample (4032D) used in this study was the product of Nature Works LLC. Its weight-average molecular weight (M_w) is 1.66×10^5 with the D content of 1.4 %. The PEG sample was purchased from Wako Pure Chemical Industries, Ltd., of which M_w is 2.0×10^4. The PLLA/PEG (50/50) blend specimen was prepared by the solution casting method. Given amounts of PLLA and PEG were dissolved in dichloromethane (DCM) at room temperature (~25°C) to obtain a solution with ca. 5 wt% of the total polymer concentration. The polymer solution was then poured into a Petri dish (diameter of 5 cm) for complete evaporation of DCM.

POM observations were conducted by using a Nikon Eclipse Ci-POL polarizing optical microscope equipped with the Linkam THMS600 hot stage (Linkam Scientific, UK). The retardation plate (of which optical retardation is 530 nm) was inserted in the optical path. The specimen was sandwiched between two cover slips with a spacer of which thickness is 20 μm. The temperature protocol for the POM observations is shown in Fig. 1. The PLLA/PEG
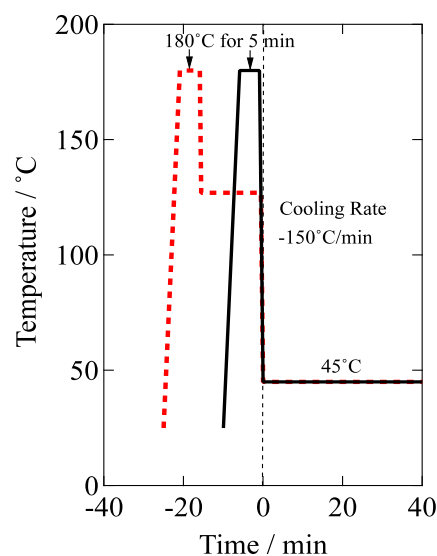

Fig. 1 Temperature protocol for the POM observation for the PLLA/PEG (50/50) blend specimens isothermally crystallized by the two-step T-jump. The solid (black) and broken (red) lines are the protocols for the PEG crystallization after the PLLA crystallization at 127°C for 0 min (one-step T-jump directly from 180°C) and for 15 min (as an example of the two-step T-jump via 127°C for 15 min), respectively.
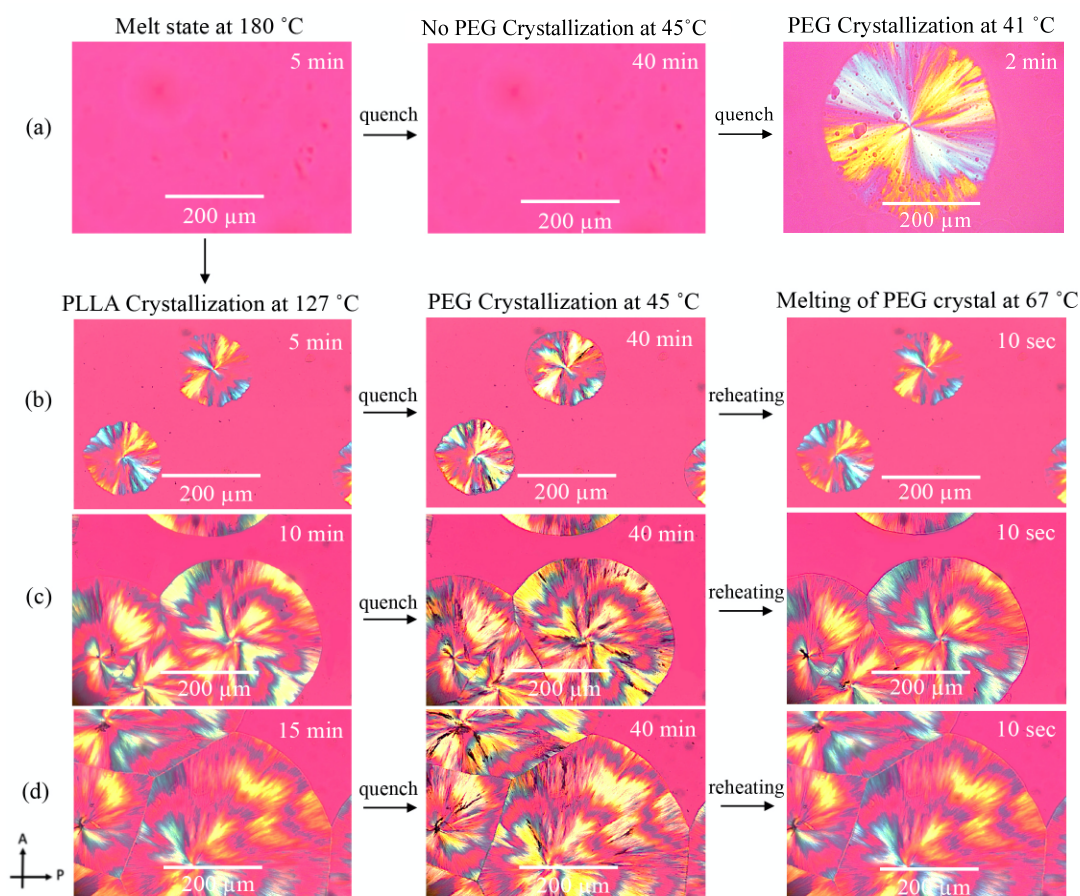
Fig. 2   POM micrographs showing the crystallization processes of PLLA/PEG (50/50) blend specimens at 45°C (40 min) after the temperature jump from 127°C crystallization of PLLA for (a) 0, (b) 5, (c) 10, and (d) 15 min. Subsequently, the specimens were subjected to reheating with 50°C/min up to 67°C. POM images shown at the right column were taken after 10 sec of the temperature equilibrium at 67°C.

(50/50) blend specimen was heated up to 180°C and kept at this temperature for 5 min to obtain complete melt without liquid-liquid phase separation. Then, two-step T-jump was conducted as 180°C → 127°C → 45°C. The isothermal crystallization time at 127°C was controlled as 0, 5, 10, and 15 min where the PLLA spherulite grew. After that, the specimen was quenched to 45°C and kept at this temperature for 40 min to induce the crystallization of PEG.

WAXS measurements were conducted to obtain the direct evidence of the PEG crystallization at 45°C by using the synchrotron radiation as an X-ray source at the beamline BL-6A of Photon Factory at the KEK (Hight Energy Accelerator Research Organization) in Tsukuba, Japan. The wavelength of the incident X-ray beam was 0.150 nm. The PLLA/PEG blend specimen was packed into an aluminum cell with a diameter of 4 mm and thickness of 1 mm and was sandwiched by a couple of pieces of the polyimide (Kapton) film, obtained from DuPont-Toray Co., Ltd., Tokyo, Japan [1,2]. In the WAXS measurement, a specimen was heated up to 180°C and kept at this temperature for 5 min to completely melt the specimen and then the sample cell was quickly moved to another heater block which was maintained at 127°C.

The specimen was annealed at this temperature for 15 min to grow the PLLA spherulite and then the sample cell was quickly transferred into the heater block settled at the sample position for the WAXS measurement where the incident X-ray beam was irradiated. This heater block temperature was maintained at 45°C to detect the PEG crystallization. Time-dependent WAXS patterns were measured with a step of 15s by using PILATUS 100K (Dectris, Switzerland) as a two-dimensional detector. Note here that this two-step T-jump was conducted according to the same temperature protocol for the POM observation and for the DSC measurement, which was shown in Fig. 1. The 1d-WAXS profiles were extracted from the 2d-WAXS patterns.

3 Results and Discussion

Fig. 2a shows the POM result showing no PEG crystallization at 45°C due to the depression of the $T_{f,PEG}$ in the complete mixture of the PLLA/PEG (50/50) blend specimen. Fig. 2a also confirms the formation of the PEG spherulite at 41°C, where PLLA cannot crystallize because of its extraordinarily slow crystallization rate. In Figs. 2b-d, the PLLA spherulites in the first-step of T-jump to 127°C (for 5, 10, and 15 min) were clearly observed. Interestingly, at the secondary T-jump in Figs.

2b-d, POM images in the middle column suggest that the colors changed into more brilliant ones in the interior of all PLLA spherulites. Moreover, the POM images shown in the right column being taken at 67°C, which is above $T_{m,PEG}$, clearly indicated almost the same images of spherulites observed at 127°C. These results imply the PEG crystallization in the PLLA spherulites at 45°C.

The direct evidence of the PEG crystallization was provided by the time-resolved WAXS measurement. The change in the WAXS profiles during the isothermal crystallization at 45°C after the PLLA crystallization for 15 min at 127°C was show in Fig. 3a. Here, q denotes the magnitude of the scattering vector, as defined by $q = (4\pi/\lambda) \sin(\theta/2)$ whit λ and θ being the wavelength of X-ray and the scattering angle, respectively. The WAXS profiles measured at $t = 315$ s to $t = 405$ s with a step of 15 s (in total 6 profiles) are shown in Fig. 3a and those for the neat PLLA (crystallized isothermally at 127°C) and for the neat PEG (crystallized isothermally at 45°C) are shown in Fig. 3b for comparison. In Fig. 3a, there were no PEG crystalline reflection peaks in the first profile at $t = 315$ s, which shows only the PLLA crystalline reflection peaks at $q = 11.95$, 13.43, and 15.45 nm^{-1} for the (200)/(110), (203), and (210) plane reflections, respectively [3]. As time goes on, the PEG crystalline reflection peaks appeared at $q = 13.56$, 15.94, 16.12, 16.30 nm^{-1} with increasing their intensity. From the lattice parameters for PEG [2] which are $a = 0.805$ nm, b

$= 1.304$ nm, $c = 1.948$ nm, and $\beta = 125.4°$ of the monoclinic crystal with 7/2 helix conformation of the polymer chains, it is confirmed that those reflections are assigned to (120), (20-2), (12-4)/(-124), and (112)/(1-12)/(-204) of PEG, respectively, although the q range of from 15.8 to 16.4 nm^{-1} is very crowded with a bunch of PEG crystalline reflection peaks [4]. The evolution of those reflection peaks is the clear evidence of the PEG crystallization.

We conducted peak decomposition to determine the peak area. Although the peak area for PLLA seems to slightly decrease as a function of time, we found that the intensity level due to the amorphous halo decreased with time along the progress in the PEG crystallization. This explains the apparently decreasing tendency of the PLLA reflections. As a matter of fact, the peak area stays constant as plotted in Fig. 4. On the contrary, the peak area of all of the PEG reflections shows the similar increasing tendency in Fig. 4. The onset time of the peak evolution can be considered as the induction period which was about 5 min for this particular case. This value is in good accord with the differential scanning calorimetry (DSC) results. The termination of the PEG crystallization where the curves in Fig. 4 leveled off was evaluated to be 6.5 min. Therefore, the total crystallization time is about 1.5 min, which is also in good accord with the DSC results.

Although the peak positions of the PEG reflections in the second-step of T-jump of the blend specimen is the same as those for the neat PEG, it is specific to recognize the tremendous suppression of the (12-4)/(-124) reflection peak for the blend specimen as compared to that for the neat PEG. This may indicate the effect of the space confinement that the direction of the PEG crystal growth is suppressed, which is the [12-4]/[-124] direction almost parallel to the c-axis, in turn, the polymer chain direction. On the other hand, the (120) reflection peak is not suppressed, indicating that the PEG crystal growth in the direction perpendicular to the polymer chains was not affected. Assuming the folded-chain crystal of the PEG crystalline lamella, these results suggest the suppression of the lamellar thickening due to the space confinement in
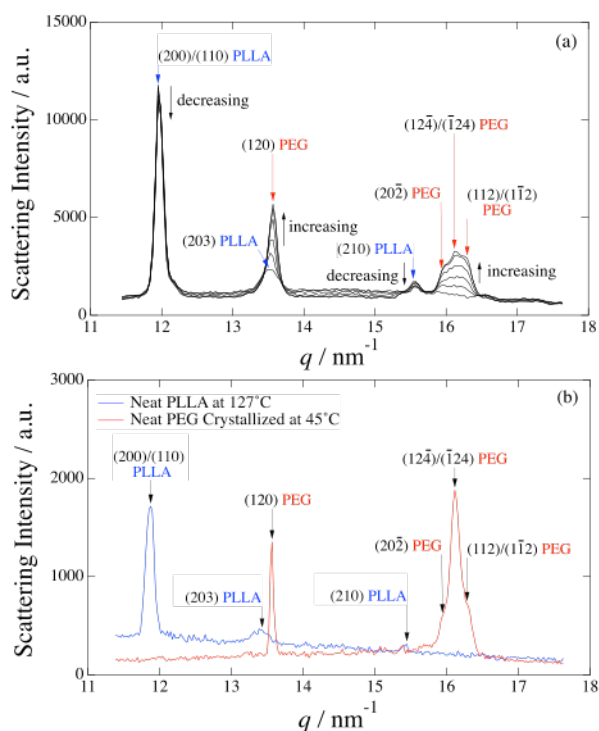

Fig. 3 (a) Time-resolved 1d-WAXS profiles along the PEG crystallization at 45°C in the PLLA/PEG (50/50) blend specimen after PLLA crystallized at 127°C for 15 min and (b) 1d-WAXS profiles for the neat PLLA and PEG crystallized at 127°C and 45°C, respectively.
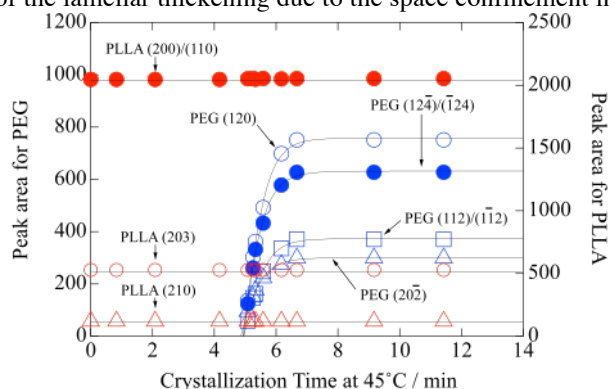

Fig. 4 Plots of the area of the crystalline peaks as a function of time, which was evaluated from WAXS results shown in Fig. 3(a) after the peak decomposition.

the amorphous phase sandwiched by the PLLA crystalline lamellae. This further suggests the orientation of the PEG lamellae parallel to those of PLLA. Huang et al. have reported this kind of the crystal orientation for the PEG confined crystallization in the PEG-*b*-PS (polystyrene) diblock copolymer forming the lamellar microdomains at the isothermal crystallization temperature higher than 20°C for $M_{n,PEG} = 2.31 \times 10^4$ [5], which is close to our PEG specimen's M_w used in the current study. Thus, our result implying the parallel orientation of the PEG lamellae (parallel to the preceding PLLA crystalline lamellae) as a consequence of the space confinement can be explained by the previous work of Huang, et al. [5].

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