Isothermal Crystallization Process of Poly(l-lactic acid)/Poly(d-lactic acid) Blends after Rapid Cooling from the Melt

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Supporting Information

ABSTRACT: We observed the crystallization process in poly(l-lactic acid) (PLLA) and poly(d-lactic acid) (PDLA) blends using in situ simultaneous small- and wide-angle X-ray scattering measurements with a high-speed temperature control cell. In situ X-ray scattering measurements revealed that density fluctuations larger than the long spacing periods grew during crystallization above 130 °C. In particular, the time evolution of the density fluctuations has a strong dependence on the crystallization temperature. The density fluctuations will promote the crystal nucleation and growth processes of the stereocomplex and increase with increasing crystallization temperature, which is strongly correlated with the complexation of PLLA and PDLA chains. On the other hand, below 120 °C, the kinetics of stereocomplex formation might be hindered by the decreased mobility, and no density fluctuations were observed in the case of homo crystal growth of PLLA or PDLA.

INTRODUCTION

Plant-derived poly(l-lactic acid) (PLLA) has been widely used as an alternative to petroleum-based polymers because of its superior eco-friendliness.1−6 PLLA materials are preferred for practical use and are now manufactured commercially. However, the application of PLLA materials is limited because of their high cost, inferior thermal stability, mechanical properties, and processability compared with conventional petroleum-based polymers such as isotactic polypolypropylene and polyethylene. Acceleration of crystal nucleation or the increase in crystallinity has been investigated to overcome these disadvantages. For example, cross-linking PLLA,7−9 the use of nucleating agents,10−12 and stereocomplex (Sc) crystallization13−17 were reported owing to the improvement in PLLA crystallization processes.16,19

However, the cross-linking PLLA and the use of nucleating agents might be effective but are limited to improving the properties. In particular, Sc crystallization achieved by blending PLLA with poly(d-lactic acid) (PDLA) is known to improve the mechanical performance, thermal properties, hydrolytic degradation, and gas barrier properties of PLLA.15,20 This is in part because of the higher melting temperature (Tm) of the Sc crystals (Tm = 210−230 °C) relative to the α crystalline forms of PLLA or PDLA (Tm = 160−180 °C). This elevated Tm is, in turn, attributed to the structures of the Sc crystals, which comprise equimolar l- and d-lactide unit sequences packed side by side. As a result of this packing, the interactions between the PLLA and PDLA chains are stronger than those among the PLLA or PDLA chains within the respective α crystalline forms of these materials. The growth of Sc crystals of PLLA and PDLA is much faster than that of the α crystalline form at the same crystallization temperature (Tc).

In the previous studies, Sc crystal fibers were prepared from mixed solutions of PLLA and PDLA using wet- and dry-spinning processes, and the higher-order structures and the mechanical properties of melt-spun fibers from blends of PLLA and PDLA were characterized.21,22 Polarized optical microscopy (POM) images of the fibril crystals revealed shish-kebab-like crystals of PLLA formed from the sheared melt.23 To improve the mechanical and thermal properties of polyactic acid (PLA), it is very important to enhance the overall crystallization rate. Therefore, our group previously investigated the nucleation and the crystal growth processes under shear flow using the blends of PLLA and PDLA.24 The time required

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for nucleation decreased with increasing shear rate and strain, and we observed a weak lamellar crystal orientation parallel to the shear direction rather than an oriented crystal lattice and shish-kebab structure. Because the shear rates were larger than the inverse of the estimated reptation time, convective constraint release was identified as the dominant mode. Thus, it was concluded that the crystal nucleation was enhanced by the stretched chains produced upon the disentanglement of the PLLA or PDLA chain network. Furthermore, density fluctuations before crystal nucleation were observed above 100 nm. These results suggest that the density fluctuations might form only in the mixed PLLA/PDLA phase even in the quiescent state. In the previous reports, we observed the precursor on a micron scale during the crystallization process. The precursor was formed from a stretched polymer network owing to entanglements and small crystallites under shear flow. Furthermore, the precursors, that is, the density fluctuations grown during the induction time before crystallization, were observed in poly(ethylene terephthalate) (PET), polylethylene (naphthalate), and isotactic polypropylene (iPP) crystallization. A similar time evolution of the density fluctuations before the crystallization process was observed and described as a spinodal-decomposition-type phase separation. Furthermore, Nishida et al. found that the micron-scale density fluctuations could be observed immediately after fast quenching below $T_m$ in polypropylene crystallization.

However, in the case of PLLA/PDLA blend, it is not clear whether these density fluctuations were observed. Then, it is necessary to observe the structure formation processes before nucleation even below $T_m$ of the homo crystal. In the case of PLLA, melting and reorganization of the $\delta$-phase have been analyzed as a function of heating rate for heating rates between 10$^{-1}$ and 10$^3$ °C/s. The reorganization from the $\delta$-phase to the $\alpha$-phase occurs when the heating rate is lower than 30 °C/s and under isothermal annealing at 150–160 °C. Therefore, we investigate the crystallization of PLLA/PDLA blends under high-speed quenching, which is similar to polymer processing, with a high-speed temperature jump hot stage. The cell developed by Nishida et al. was installed in a synchrotron radiation X-ray scattering apparatus. This hot stage enabled the observation of very fast structural formations, similar to those in polymer processing. Furthermore, the formation of mesophase iPP was observed by a fast differential scanning calorimetry (fast DSC). In this study, to analyze the structure formation from nanometers to microns in PLLA/PDLA blends during isothermal crystallization from the melt, we performed in situ POM and synchrotron X-ray scattering measurements using a high-speed temperature jump hot stage.

**EXPERIMENTAL PROCEDURE**

**Materials.** PLLA and PDLA samples with weight average molecular masses $M_w$ of 1.66 × 10$^5$ and 1.79 × 10$^5$, respectively, and a polydispersity $M_w/M_n$ of 2.0 were provided by Teijin Ltd. (Tokyo, Japan). A PLLA/PDLA blend with a 1:1 weight ratio was extruded for 3 min at 240 °C and pelletized. The pellets were melted in a vacuum oven at 240 °C for 2 min and then quenched to 0 °C using a cooling gas to obtain amorphous blend films. Subsequently, the amorphous films were dried for 1 day in a vacuum oven at room temperature to remove water. We confirmed the amorphous nature of the quenched samples using wide-angle X-ray scattering (WAXS).

**High-Speed Temperature Jump Stage.** The temperature jump stage consists of two thermally separated heat blocks developed by Nishida et al. The temperature of each heat block was regulated independently. The sample cell consisted of a spacer rim and a pair of window materials (aluminum foil for X-ray scattering measurements and glass for optical microscopy). The sample films were cooled from the molten state to various $T_c$ values using the temperature jump stage and annealed within the sample stage according to the protocol depicted in Figure 1. The sample thickness in the cell was 200 μm for all experiments. The temperatures used in the analysis were the temperatures calibrated using the actual temperatures measured at the sample position.

**Simultaneous Small- and Wide-Angle X-ray Scattering Measurements.** Simultaneous time-resolved small-angle X-ray scattering (SAXS) and WAXS measurements were performed at the BL40B2 beam lines at Spring-8 in Nishihara, Japan. The wavelength of the incident X-ray beams was 0.10 nm. Time-resolved SAXS profiles were recorded using charge-coupled device cameras (C4742-98, Hamamatsu Photonics KK, Hamamatsu, Japan), and an image intensifier was used for time-resolved WAXS measurements (C9728DK-10, Hamamatsu Photonics KK). The sample-to-detector lengths for SAXS and WAXS profiles were 1765 and 75 mm, respectively. The lengths of the scattering vector $q$ in the SAXS and WAXS measurements were 0.07–1.5 and 5–22 nm$^{-1}$, respectively, where $q = 4\pi \sin \Theta/\lambda$ (where $2\Theta$ and $\lambda$ are the scattering angle and the wavelength, respectively). The scattered X-ray beams were detected at 3 s intervals.

**Crystallinity Evaluation.** The fractions of S$c$ and homo crystals in the isothermally crystallized samples were estimated using WAXS. The time evolution of the crystallinities of the S$c$ and homo crystals [$X_{S,c}(t)$ and $X_{H}(t)$, respectively] was determined from the WAXS profiles. In particular, for a $q$-range of 5.0–18.0 nm$^{-1}$, $X_{S,c}$ and $X_{H}$ were calculated using the area of the diffraction peaks for the corresponding crystals relative to the total area between the diffraction profile and the baseline. These peaks were located at $q = 8.5, 14.9$, and 17.0 nm$^{-1}$ for the S$c$ crystals and $q = 8.9, 10.6, 12.1, 13.5, 15.9$, and 16.6 nm$^{-1}$ for the homo crystals. These calculations were conducted using the following equations:

$$X_{S,c}(t) = \frac{I_{S,c}}{I_{S,c} + I_{H} + I_{A}} \times 100$$

$$X_{H}(t) = \frac{I_{H}}{I_{S,c} + I_{H} + I_{A}} \times 100$$

where $I_{S,c}$, $I_{H}$, and $I_{A}$ are the peak area factors for the S$c$ crystal, homo crystal, and amorphous fraction, respectively.

**RESULTS AND DISCUSSION**

We observed the linear growth of spherulites above 140 °C using polarized optical microscopy [VHX-900 digital microscope manufactured by Keyence Corp. (Osaka, Japan)]. The
morphologies of spherulites of the homo and Sc crystals were the same as shown in Figures S1 and S2. Therefore, it is difficult to discuss whether the spherulites consist of Sc and/or homo crystals only from the results of POM images. We conducted simultaneous WAXS and SAXS measurements to analyze the crystal growth and nucleation processes in more detail.

The time evolution of the WAXS profiles of the samples crystallized from the melt at various temperatures is shown in Figure 2. At 190 °C, which is above the $T_m$ of homo crystals, the most intense peak is observed at $q = 8.5$ nm$^{-1}$, which is attributed to the (110) plane. In the cases of $T_c$ values above the $T_m$ of homo crystals, the profiles are assigned to the $\beta$-form of Sc crystals, which is triclinic with parameters $a = 0.916$ nm, $b = 0.916$ nm, $c$ (fiber axis) $= 0.870$ nm, $\alpha = 109.2^\circ$, $\beta = 109.2^\circ$, and $\gamma = 109.8^\circ$, where the molecules are assumed to have a 3/1 helical conformation. By contrast, at 150 °C, which is just below the $T_m$ of homo crystals, the most intense peak was observed at $q = 8.5$ nm$^{-1}$, which is attributed to the (110) plane. The weak peaks at $q = 10.6$ nm$^{-1}$ are assigned to the (110) and/or (200) planes of the PLLA homo crystals. For $T_c$ values between the $T_m$ of the homo crystals and 120 °C, the profiles comprise both the $\beta$-form of the Sc crystals and the $\alpha$-form of the homo crystals, which is orthorhombic with parameters $a = 1.07$ nm, $b = 0.645$ nm, and $c$ (fiber axis) $= 2.78$ nm, where the molecules are assumed to have a 10/3 helical conformation. \textsuperscript{33} Furthermore, at 110 °C, the most intense peak is attributed to the (200) and/or (110) planes of the PLLA (or PDLA) homo crystals. The profiles comprise both Sc crystals and the $\alpha$'-form of the homo crystals, which is pseudohexagonal with $a = b = 0.62$ nm, and $c$ (fiber axis) $= 2.78$ nm, where the molecules are assumed to have a 3/1 helical conformation.\textsuperscript{6}

Figure 3a–c shows the time evolution of $X_{\text{Sc}}$, $X_{\text{H}}$, and the fraction of the amorphous region $A_m$ [$A_m(t) = 1 - (X_{\text{Sc}}(t) + X_{\text{H}}(t))$] for samples crystallized at 190, 150, and 110 °C, respectively. At 190 °C (Figure 3a), $X_{\text{Sc}}$ increases with crystallization time after an induction period of 30 s. The induction period is defined as the onset time of increasing crystallinity from the baseline. Under this temperature condition, (110) and (030)/(300) diffraction peaks are observed at 8.5 and 14.9 nm$^{-1}$, respectively, as shown in Figure 2a. After 1000 s of crystallization, only the $\beta$-form of the Sc crystals is observed because the temperature is above the $T_m$ of the homo crystals. At this time, $X_{\text{Sc}}$ is approximately 0.20. Figure 3b shows that the Sc crystallization starts after an induction period of 30 s and that the homo crystallization of PLLA or PDLA starts after 200 s. The growth of Sc crystals begins much sooner than the growth of homo crystals because the quenching depth of the Sc crystal is much larger than that of the homo crystal. $X_{\text{Sc}}$ is larger than $X_{\text{H}}$ for the first 400 s; however, the growth rate of the homo crystal increases after this point. Thus, $X_{\text{Sc}}$ (0.20) is smaller than $X_{\text{H}}$ (0.33) after 1800 s. This finding suggests that Sc crystals could accelerate the growth of homo crystal under this condition. Even in the deeper quenching case at 110 °C, as shown in Figure 3c, we observe strong diffraction peaks for homo crystals in the induction period of 60 s. After homo crystallization, the growth of Sc crystals is observed for 200 s. Under these low $T_c$ conditions, the crystal growth of Sc was prevented. In general, the growth rate and the nucleation rate of crystals depend on the quenching depth, that is, $T_c$. The highest crystallization rate occurs between $T_m$ and the glass transition temperature ($T_g = 63.0$ °C), whereas the rates near $T_g$ and $T_m$ are quite slow. Even after 1200 s of crystallization at 110 °C, $X_{\text{Sc}}$ is only 0.03. In this case, Sc crystallization was inhibited because $T_c$ was too close to the $T_m$ of PLLA/PDLA blends.

To analyze the crystal nucleation process, we focused on the time at which $X_{\text{Sc}}(t)$ and $X_{\text{H}}(t)$ began to increase under various crystallization temperatures. Figure 4a shows the dependence of the onset time on $T_c$. At high temperatures (above 180 °C), the onset time of the growth of Sc crystals increases with temperature because of a reduction in the quenching depth. Between 180 and 120 °C, the onset time of the growth of Sc crystals is almost independent of $T_c$ within error bars. These results suggest that Sc nucleation is quite slow even when the quenching is deep; this highly unexpected phenomenon is discussed below using the SAXS profiles recorded. By contrast, the homo crystal nucleation became faster with the increasing quenching depth of the homo crystals. Below 110 °C, the onset of homo crystallization occurs sooner...
than that of Sc crystallization. Tsuji found that the T_g value of Sc crystals for a PLLA/PDLA blend is higher than that for pure PLLA or PDLA samples. This might be one of the possible reasons for the homo crystallization process that takes place sooner than the Sc crystallization process.

We investigated the time evolution of the nano- and submicron-scale structures via in situ SAXS measurements for a more detailed analysis of the crystal nucleation process. Figure 4b shows X_c,Sc and X_c,H after 1800 s. Between 210 and 180 °C, only the diffraction pattern for Sc crystals could be observed because T_c is higher than the T_m of the homo crystals. Below 170 °C, diffraction patterns were observed for both Sc and homo crystals. In general, PLLA (or PDLA) crystallization is quite slow, and it is difficult to observe homo crystals at T_c above 170 °C because of the shallow quenching depth. In our measurement of this PLLA sample, crystallization at 150 °C begins after 300 s of annealing, and no crystal growth occurs above 160 °C. These results suggest that the Sc crystal could act as a nucleating agent for the homo crystals. In the case of crystallization near T_g, both crystallinity values decreased rapidly with the decreasing temperature. In particular, the Sc crystallinity is less than 2%, the homo crystallinity is above 10%, and the onset of homo crystallization occurs sooner than Sc crystallization below 120 °C. On the basis of these results, homo crystals do not seem to act as nucleating agents for Sc crystallization because of the proximity of T_c and T_g. In these cases, the polymer chains undergo a less diffusive motion.

Figure 5 shows the time evolution of the SAXS profiles for samples crystallized at 190 (a), 150 (b), and 110 °C (c). After crystallization, the long spacing period can be observed around q = 0.2−0.3 nm⁻¹. The long spacing period L was evaluated from the peak positions q_peak using the relation L = 2π/q_peak. In general, L increases with T_c because of the increasing thickness of the lamellar structure and the amorphous region. Furthermore, very-large-scale fluctuations were noted during the crystal growth below q = 0.1 nm⁻¹, as shown by arrows in Figure 5a,b. Such large-scale fluctuations were previously observed in the crystallization of PLLA/PDLA blends under shear flow. By contrast, no increasing intensity in the low-q region was observed after crystallization (Figure 5c); therefore, the large density fluctuations could not grow. On the basis of these results, these large fluctuations might be observed only in the case of the nucleation of Sc crystals. We subtracted the SAXS profiles of the molten state from each SAXS profile to clarify the growth process from the molten state. Figure 6 shows the time evolution of the subtracted intensity...
immediately after quenching to $T_c$ at 190 °C (Figure 6a) and 150 °C (Figure 6b). The onset of crystallization occurs at 30 s for these crystallization temperatures. Even before nucleation, the difference in intensity increases with time, especially below $q = 0.10 \text{ nm}^{-1}$; therefore, the submicron-scale density fluctuations increased with time. The intensity continues to grow after crystal nucleation because of the growth of the lamellar structure. Of course, the subtracted intensity in the case of 110 °C crystallization is approximately zero after crystallization below $q = 0.10 \text{ nm}^{-1}$; then there are no density fluctuations before the nucleation of homo crystals.

To evaluate the time evolution of the submicron-scale density fluctuations on Sc crystallization excluding the growth of the lamellar crystal, we calculated the integrated intensity of the SAXS profiles in the region of $q = 0.072−0.18 \text{ nm}^{-1}$ measured at different times during crystallization at 190 (a) and 150 °C (b).

![Figure 5. SAXS profiles recorded at various times during crystallization at 190 (a), 150 (b), and 110 °C (c). The arrows show the very-large-scale fluctuations in (a) and (b).](image)

![Figure 6. Difference in intensity in the low-q region ($q = 0.072−0.18 \text{ nm}^{-1}$) measured at different times during crystallization at 190 (a) and 150 °C (b).](image)

![Figure 7. Time evolution of the integrated intensity of the SAXS profiles at $q = 0.072−0.1 \text{ nm}^{-1}$ for various $T_c$ values.](image)

above 180 °C, only the growth of Sc crystals was observed because this temperature is above the $T_m$ of the homo crystals. A previous study insisted that density fluctuations before nucleation were present only in the case of Sc crystallization at 190 °C. Additionally, in this study, density fluctuations could be observed before the nucleation of Sc crystals for $T_c$ even below the $T_m$ of the homo crystal. The integrated intensity decreases with decreasing $T_c$. Below 120 °C, we could not note any growth of the submicron-scale density fluctuations; however, above 130 °C, the density fluctuations increased with crystallization time even before nucleation. There are two
possible reasons for such a growth of density fluctuations before crystallization. One reason is that these fluctuations might be due to incomplete mixing of the PLLA and PDLA chains in the molten state of the sample blended above 240 °C.²⁴ The melting temperatures of homo and Sc crystals were observed using DSC measurements even in the case of both melt-pressed and cast films mixed in a dilute solution because of the incomplete mixing of these chains. However, it is quite strange due to the same chemical structural formulas between PLLA and PDLA; therefore, the interaction parameter (i.e., the χ parameter) between PLLA and PDLA will be zero, and it looks inconsistent. The other reason is that Sc nucleation and growth processes induce the submicron-scale density fluctuations.²⁴,³⁸

Figure 7 shows that the density fluctuations increase with $T_c$. Furthermore, the crystallinity of Sc increases with $T_c$ until just below 200 °C in Figure 4b. From these results, the submicron-scale density fluctuations have a strong correlation with the formation of Sc crystals and/or Sc nucleation. Furthermore, even before crystal nucleation, we could observe the density fluctuations. Some research groups suggest density fluctuation-assisted crystallization,³⁹−⁴¹ especially before nucleation. However, the density fluctuations of PLLA/PDLA blends might be different from density-fluctuation-assisted crystallization because of the absence of phase separation processes in PLLA/PDLA blends. In our previous study on the crystallization of PLLA/PDLA blend samples under shear flow, we found that the scale of the density fluctuations ranged from several tens to hundreds of nanometers.²⁴ From Figure 7, the density fluctuations above 60 nm ($q = 0.1$ nm$^{-1}$) might depend on the crystallinity of Sc shown in Figure 4b. However, it is difficult to discuss the growth process of these density fluctuations because of observation of only the tails of peaks. These results suggest that the submicron-scale density fluctuations are strongly correlated with the complexation process composed of PLLA and PDLA chains. In other words, the nucleation process of Sc crystals was accelerated by density fluctuations above 60 nm. In the case of low $T_c$, the kinetics of Sc crystals might be hindered by the decreased mobility; then no density fluctuations were observed, especially in the case of the homo crystal growth of PLLA or PDLA.

## CONCLUSIONS

During the PLLA/PDLA blend crystallization, density fluctuations larger than the long spacing period grow over time, even before the nucleation of Sc crystals. We could observe the very large density fluctuations above 130 °C. The density fluctuations will promote the crystal nucleation and growth processes of Sc crystals and increase with increasing $T_c$. Especially, the time evolution of the density fluctuations has a strong dependence on $T_c$. The nucleation processes of Sc crystals were accelerated by the submicron-scale density fluctuations. In the case of low $T_c$, the kinetics of Sc might be hindered by the decreased mobility; then no density fluctuations were observed, especially in the case of the homo crystal growth of PLLA or PDLA.

## ASSOCIATED CONTENT

1. Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.6b00098.

Optical micrographs during spherulite growth, time evolution of radius of spherulites, and crystallization temperature dependence of nuclear density and growth rate, curve fitting of WAXS profile, and Avrami exponent at various crystallization temperatures (PDF)

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Notes
The authors declare no competing financial interest.

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