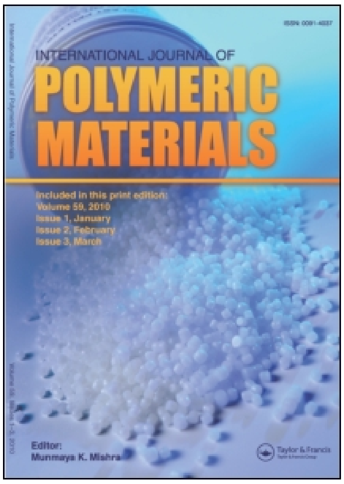

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Influence of Temperature and Time on Isothermal Crystallization of Poly-L-lactide

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The thermal behavior of poly-L-lactide (PLLA) isothermal crystallization upon cooling from the melt was investigated using differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD) and polarizing microscope (POM) by changing the crystallization temperature and time. It was indicated that 110°C should be a critical temperature for PLLA melting crystallization. The melting point of crystallized PLLA discontinuously changed with crystallization temperature, increased with temperature, but decreased at about 110°C, and thereafter again increased with higher crystallization temperatures. At 110°C a multiple endothermic peak was observed. PLLA crystals of higher perfection form when crystallized under higher temperature, which reflects the effects of high chain mobility in higher temperatures. During isothermal crystallization, PLLA crystallites become increasingly perfect, and thicken with prolonged time, leading to an increasing melting point.

Keywords: isothermally melting crystallization, poly-L-lactide, temperature, time

INTRODUCTION

Poly-L-lactide (PLLA) has been studied intensively, because it is producible from renewable resources, nontoxic in natural environments,

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biodegradable, and compostable. Moreover, PLLA has a high mechanical performance comparable to that of commercial polymers such as polyethylene, polypropylene, and polystyrene [1,2].

The physical and mechanical properties of stereoregular polymers, like isotactic PLLA, largely depend on solid-state morphology and degree of crystallinity [3]. Due to its rather low crystallization rate, compared to other thermoplastics, it is rather easy to define processing conditions to obtain PLLA products with a wide range of degrees of crystallinity, thus varying product properties. A key factor in both medical and industrial applications of polylactides may lay in a full establishment of degradation rate, which, in turn, strongly depends on crystallinity degree, as crystalline lamellar organization plays a crucial role in the degradation mechanism [4,5]. Therefore, an intense research work is needed to correlate the thermal history imparted during processing to the final microstructure.

The crystallization behavior of PLLA has been largely investigated [6–12]. It is well-known that crystallization temperature (T_c) is a key factor for the crystallization process of polymers. The change of T_c-induced crystalline order or perfection affects the crystalline morphology to some extent however, in this case the crystalline morphology usually changes gradually with the variation of T_c. Nevertheless, in the T_c-induced polymorphic crystallization of polymers, generally, there is a critical T_c or an exact temperature region for the transition of the different crystal modifications [13]. On the other hand, the crystallization time has an important effect on crystallinity and the thermal behavior of PLLA. Wang and Mano [14,15] reported that the appearance of double melting peaks in PLLA is strongly dependent on the prior melting conditions, such as melting temperature and time. They attributed this double melting behavior of PLLA to the thermal degradation of PLLA in the melt and the recrystallization mechanism.

Although the melting behavior of PLLA has been reported in several publications, controversy on the complex thermal behavior in PLLA still exists. Especially, it is important to elucidate how the discrete change in the preceding crystallization process affects the melting behavior. We performed differential scanning calorimeter (DSC), wide-angle X-ray diffraction (WAXD) and polarizing microscope (POM) studies to clarify fundamental aspects of the melting process, using isothermal crystallization upon cooling down from the melt. Particularly the effects of the crystallization condition, crystallization temperature and crystallization time on the melting behavior were investigated in this work.

EXPERIMENTAL

Preparation of PLLA Samples

PLLA was prepared by using ring-opening polymerization [16] and purified by the dissolution/precipitation method using dichloromethane as solvent and ethanol as nonsolvent. Purified PLLA was dissolved in chloroform with a polymer concentration of 0.05 $g \cdot mL^{-1}$, cast onto a flat glass plate, and evaporated at room temperature to obtain PLLA films.

Heating and Cooling Conditions

In the present experiment, PLLA samples were held in a molten state (200°C) for 10 min to remove any crystal nuclei in the samples. The melted samples were cooled to a predetermined crystallization temperature (T_c) at a rate of 10°C·min^{-1}, and the isothermal crystallization was conducted at various crystallization temperatures ranging from 80 to 150°C during various crystallization times. After the isothermal crystallization, the sample was rapidly cooled to 30°C at a rate of 20°C·min^{-1} to prevent additional crystallization during cooling from T_c and held for 10 min at 30°C.

Methods

GPC was performed on a Waters 510 with Shodex KF-800 columns; the data processing software was Waters Millennium 32. Samples were measured at 35°C with chloroform as eluent at a flow rate of 1.0 mL·min^{-1}. The molecular weight was calibrated relative to polystyrene standards. The number average molecular (M_n) of PLLA was 1.65×10^5 Da, and the weight average molecular weight (M_w) was 2.56×10^5 Da.

Spherulite structures of the thin films were observed using POM (Olympus BX50) equipped with a Japan Hightech hot-stage RH-350, and photographed using a digital camera. Thin films were placed on slide glasses and the thickness of the samples was less than 10 μm. Each PLLA sample was heated on the hot-stage from room temperature to 200°C at a heating rate of 10°C·min^{-1}, held at 200°C for 10 min for completion of the polymer melting, and cooled from 200°C at a rate of 10°C·min^{-1} to a temperature where the growing of spherulites start. For each of the specimens, the average size of spherulites was then measured from the digital image.

The crystallization experiments of the PLLA specimens were determined by DSC analysis using DSC-60 (Shimadzu Co., Ltd) equipped with a TA-60WS thermal analysis system. Samples of about 5–10 mg were placed in aluminum cells, and heated from room temperature to 210°C at a rate of $10^\circ C \cdot min^{-1}$ in nitrogen atmosphere, where they were held for 10 min to ensure complete melting. The crystallinity (X_c) of the films was evaluated according to the following equation [11]:

$$X_c(\%) = 100 \times (\Delta H_m + \Delta H_c)/93 \qquad (1)$$

where ΔH_m and ΔH_c are the enthalpies of melting and crystallization of the PLLA samples respectively, and 93 (J/g of polymer) is the enthalpy of fusion of PLLA crystals having infinite crystal thickness.

Wide-angle X-ray diffraction (WAXD) patterns were obtained at room temperature with a WAXD measurement system. Monochromatized Cu Kα radiation was used as an incident X-ray beam. The diffracted X-ray intensity was detected with a position-sensitive proportional counter system.

RESULTS AND DISCUSSION

Influence of Temperature on Crystallization from the Melt

The DSC curves of PLLA isothermal crystallization for 1 h at different temperatures are presented in Figure 1. As shown in Figure 1, the crystallization of PLLA-140 and 150 is not complete within 1 h, as indicated in the broad “cold-crystallization” peak, T_{cI}, due to the fewer nuclei existing in these samples, which results in slow crystallization kinetics at high temperatures.

The DSC curves of PLLA-80, 140, 150 exhibit two exothermic peaks and one endothermic peak. For convenience, we designate the exothermic peak at lower temperature as T_{cI} due to cold crystallization, and a second exothermic crystallization peak, T_{cII}, just prior to the final melting, and the endothermic peak, T_m, due to melting point. It is interesting to note that although ΔH_{cI} of PLLA-80 is smaller than that of others, its ΔH_{cII} is actually larger. This confirms that temperature plays an important role in the crystallization of PLLA. Even when less crystallization took place at higher treatment temperatures, the resultant crystals are more perfect due to high chain mobility and less recrystallization in the subsequent heating scans [11]. Although the samples crystallized at 140 and 150°C in regime II are different from that crystallized at 80°C in regime III (see below), the melting crystallization of PLLA-80, 140 and 150 do not complete in 1 h, and the crystallinity is only 12.9, 5.0, and 1.4%, respectively. Therefore, the

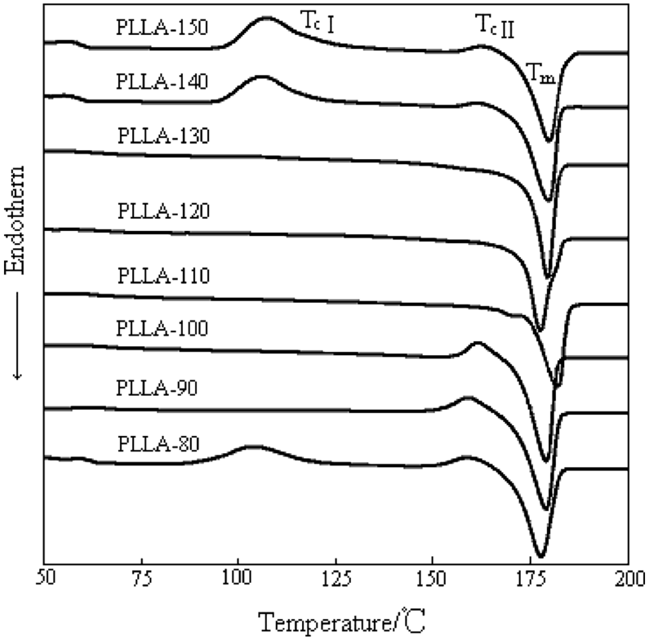

FIGURE 1 DSC curves of PLLA isothermal crystallization for 1 h at different temperatures.

curves for 140 and 150°C are similar to the curve for 80°C, exhibiting two exothermic peaks (cold crystallization and melting recrystallization) and one endothermic peak.

The DSC scans of PLLA-90 and 100 also reveal crystallization peak T_{cII} although the absence of T_{cI}, suggests the completion of crystallization before the heating scan. This observation further supports what we found before in the samples obtained through nonisothermal crystallization at slow cooling rates like 0.5°C·min^{-1}, 1°C·min^{-1}, and 2°C·min^{-1}. That is, no matter whether the crystallization is completed or not under the treatment conditions, as long as the crystals formed retain a certain extent of imperfection, T_{cII} will by all means show up during the subsequent heating scan as a result of the emergence of a continuous recrystallization process [12].

In the curve of PLLA-110 double melting is clearly observed, with T_{mI} and T_{mII} at 169.1°C and 180.9°C, respectively. Also ΔH_{mII} is significantly larger than ΔH_{mI}. At 110°C, due to the enhancement of crystal perfection at this temperature, smaller amount of reorganization is needed.

For the sample of PLLA-120, the crystallization upon cooling is largely limited at 10°C·min^{-1} heating rate due to the perfection of original crystals, so that only a broad melting peak is visible. As treatment temperature reaches 130°C, only a sharp single melting temperature is detected where the recrystallization can be considered as finally suppressed. Melting temperature of samples crystallized from 120°C to 150°C increases, which indicates the resultant crystals are more perfect due to high chain mobility in higher temperature.

The isothermal crystallization studies showed that crystallization was not completed within 60 min for samples crystallized at 80°C or above 130°C as indicated in the broad cold crystallization peak, T_{cI}. Thus, the features observed in the subsequent DSC scans depended strongly on the isothermal treatment temperature. Table 1 illustrated the overall crystallinity of PLLA isothermal crystallization at different temperatures for 1 h. The crystallinity increased with higher temperature, but decreased at above 140°C, where regime II is characterized by multiple secondary nucleation process. At low degrees of supercooling, crystal growth is faster than nucleation, leading to the formation of a smaller number of larger crystals and lower crystal-nuclei density.

As shown in Figure 1, the crystallization temperature of 110°C produces double melting peak. This behavior can be related to the transition from regime II to regime III occurring during the isothermal crystal growth. The crystallization kinetics are discontinuous in the temperature around 110°C, that is, the curve of the half time in the melt crystallization ($t_{1/2}$) versus crystallization temperature (T_c) is discontinuous and the profile of spherulite radius growth rate (G) versus T_c shows two peaks. Hoffmann et al. [17] recognized that the mechanism of crystallization from melts is a function of the degree of undercooling ΔT. Regime I, which usually occurs at low ΔT, is characterized by a growth rate G that is proportional to the surface nucleation rate i. At lower temperatures, multiple surface nuclei begin to occur on the substrate because of the rapid increase of i associated with the large undercooling, and G becoming proportional to $i^{1/2}$, and the crystallization mechanism is indicated as regime II. Regime III is entered when G is proportional to i. On the basis of the Hoffman–Lauritzen theory, crystallization regimes were investigated for PLLA,

TABLE 1 Crystallinity of PLLA Isothermally Crystallized for 1 h at Different Temperatures

Crystallization temperature/°C	80	90	100	110	120	130	140	150
Crystallinity/%	12.9	39.7	47.9	53.2	55.1	58.9	5.0	1.4

and regime II to regime III transition was detected at 115°C by Iannace et al. [18], at 118°C by Zhou et al. [19] and at 130°C by Di Lorenzo [9].

As shown in Figure 1, it can be seen that when PLLA isothermally crystallized at the temperature range from 80°C and 110°C, it happened predominantly under regime III. Thin lamellar crystals developed at high undercooling in regime III, characterized by irregular surface. At the temperature range from 110°C and 150°C, the crystallization covered regime II, leading to thicker and more regular lamellae. Thicker and more regular lamellae may give rise to a higher melting temperature.

As illustrated in Figure 2 it is obvious that the T_c value shows a distinct effect on the WAXD patterns. PLLA-150 is almost amorphous from the XRD patterns, which is consistent with their low crystallinity values estimated from DSC. Notable differences in WAXD patterns are observed between the PLLA samples crystallized at low T_c ($T_c < 110°C$) and high T_c ($T_c > 110°C$). The major differences are as follows: (1) Compared with the samples crystallized at $T_c > 110°C$,

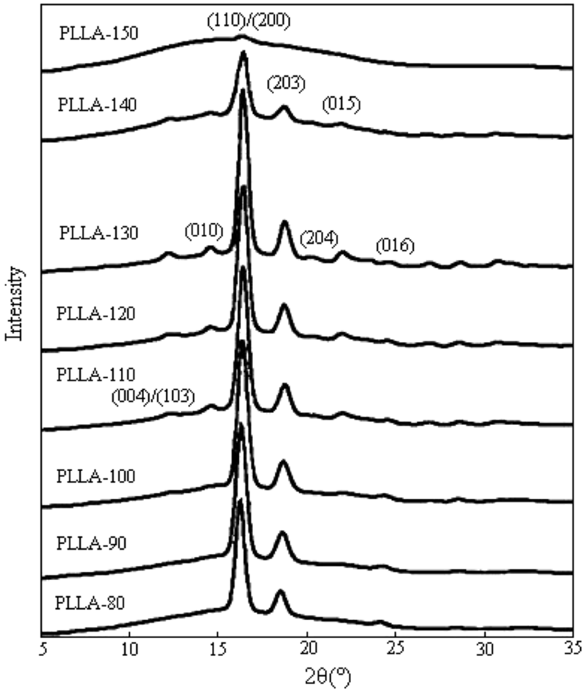

FIGURE 2 WAXD of PLLA isothermal crystallization for 1 h at different temperatures.

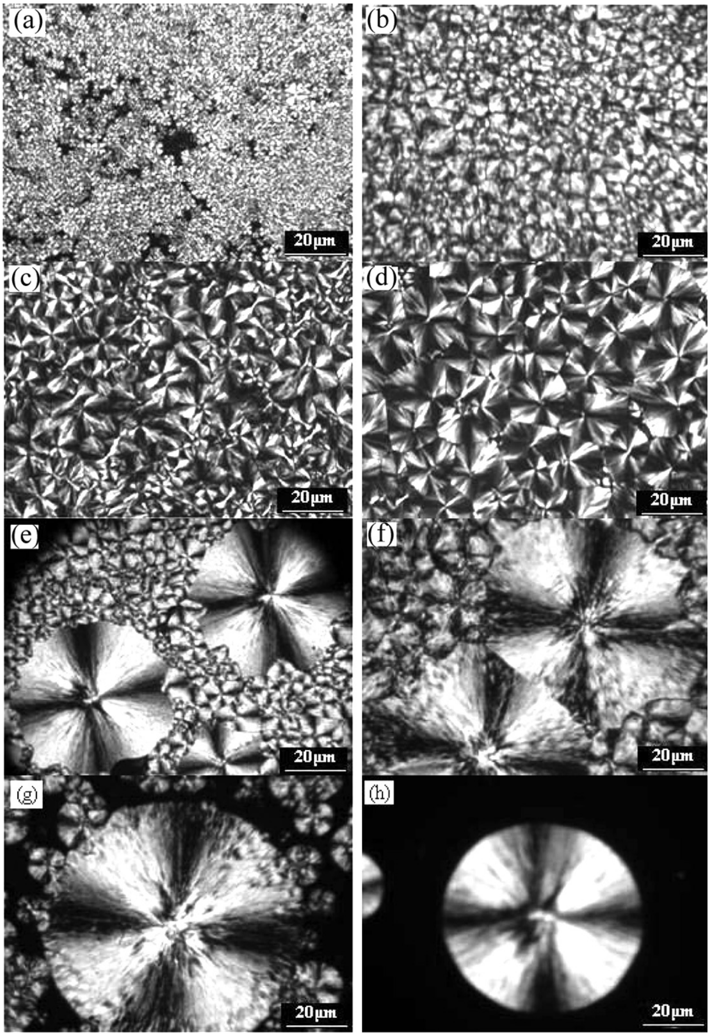

FIGURE 3 Polarizing micrographs for PLLA samples isothermally crystallized for 1 h at (a) 80°C; (b) 90°C; (c) 100°C; (d) 110°C; (e) 120°C; (f) 130°C; (g) 140°C; (h) 150°C.

the samples crystallized at $T_c < 110°C$ show that the two dominant diffraction peaks, the 110/200 and 203 reflections, appear at lower 2θ; (2) It can be seen that at $T_c > 110°C$, both the 010 and 015 reflections are more distinct; (3) At $T_c > 110°C$, some small diffraction peaks, locating at $2\theta = 12.49$, 20.81 and 24.15, which have been assigned to the reflections of 004/103, 204 and 016 planes, respectively, are present, whereas they are absent at $T_c < 110^\circ C$. Interestingly, it was found that the temperature 110°C is a critical temperature in the T_c-dependent WAXD patterns. The WAXD patterns of the PLLA samples crystallized at $T_c < 110^\circ C$ distinctly differ from those of the PLLA samples crystallized at $T_c > 110^\circ C$. The result of WAXD of PLLA is consistent with that of DSC analysis.

Although the patterns of PLLA-140 and 80 have similar crystallinity values reflected in DSC, PLLA-140 actually shows a bit trace of (004)/(103), (010), (015) peaks, while PLLA-80 shows none. This indicates the perfection of crystals is better when formed at higher temperature.

As shown in Figure 2, the WAXD curve for 150°C is nearly amorphous, and the crystallinity is only 1.4%. We do find that DSC curve for 150°C in Figure 1 shows cold crystallization. However, this cold crystallization is not reflected in the WAXD pattern, which can be explained by the appearance of cold crystallization, attributed to the subsequent heating scan of the PLLA sample for DSC measurement.

The morphology of the PLLA samples during isothermal crystallization was studied in a temperature range between 80°C and 150°C under the polarizing microscope. Figure 3 showed optical micrographs for 1 h at different crystallization temperatures. In the isothermal crystallization process at 80°C, a lot of spherulites uniformly appear in the whole view field of the microscope. These spherulites grew at a slow growth rate. The morphology of this sample showed granular appearance as observed in Figure 3(a). In contrast, spherulites did not uniformly appear in the temperature range of T_c between 90°C and 110°C. Then, sparsely distributed spherulites grew. The dimension of the spherulites in 1 h is irregular as observed in Figures 3(b)–(c). When T_c increased to 110°C, the dimension of the resulting spherulites and the uniformity of the dimension evidently increased as observed in Figure 3(d).

With increasing T_c in the temperature range above 110°C, the number of spherulite in the view field largely decreased. However, the size of the spherulites considerably increased with increasing T_c. The spherulites evidently showed negative birefringence as reported by many authors [11,19]. As mentioned above, number of spherulites in the view field and the growth rate of spherulites drastically decreased with increasing T_c. The polarizing micrographs also prove that the resultant crystals are more perfect at the higher temperature.

Influence of Time on Behavior of Melting Crystallization

A series of DSC curves of PLLA isothermally crystallized at 140°C for different periods of time are presented in Figure 4. The area of peak

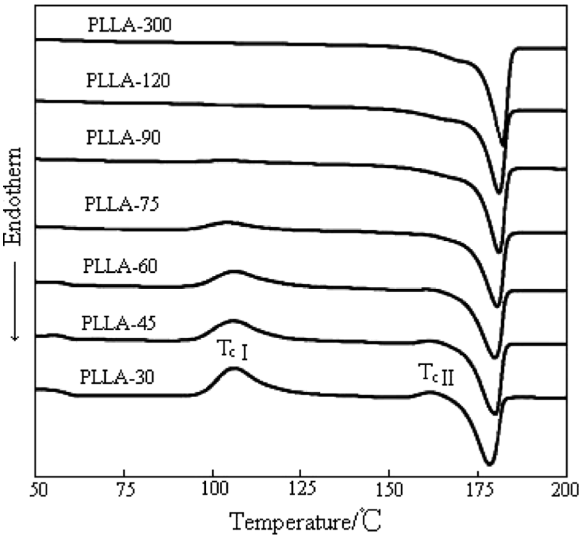

FIGURE 4 DSC curves of PLLA crystallized at 140°C for different periods of time (min).

T_{cI} decreases with an increase of crystallization time, and eventually disappears after isothermal crystallization for 90 min. The crystallization does not complete if the time is less than 90 min, as indicated in the broad "cold-crystallization" peak, T_{cI}, in Figure 4. It is to be noted, however, that the area of exothermic peak T_{cII} also decreases in parallel, and disappears in samples crystallized from the melt for 75 min. This implies that the crystallites reorganization causing peak T_{cII} takes place at 140°C, as the isothermally melting crystallization proceeds. In DSC measurements, the exothermic peak T_{cII} is observed in the temperature range of 160 to 165°C in Figures 1 and 4. This implies that when the samples crystallized at a high temperature were heated at a rate of $10°C{\cdot}min^{-1}$, the crystallites reorganization proceeded at a rate comparable to the heating rate in the temperature range from 160 to 165°C. In addition, the curves in Figure 4 differ from those in Figure 1 in that the peak temperature T_m, i.e., the melting point increases gradually with increasing time. The crystallinity of isothermally melt-crystallized at 140°C for different times is presented in Table 2. The crystallinity increases with the increasing time. It is well known that when polymer crystallites are subjected to isothermal crystallization, or isothermal annealing, they become increasingly perfect, and thicken with time, leading to an increasing melting point.

TABLE 2 Crystallinity of PLLA Isothermally Crystallized at 140°C for Different Times

Crystallization time/min	30	45	60	75	90	120	300
Crystallinity/%	2.6	7.8	17.3	24.7	47.6	57.4	69.6

On isothermal crystallization at 140°C, the long period remained constant with time throughout the crystallization process, suggesting that the crystallization temperature strongly influences the long period. During the initial development of crystallinity, the crystal thickness first increases but soon achieves a constant value that appears to be determined by the temperature of crystallization.

As shown in Figure 5, the WAXD patterns of these samples show almost no crystalline peaks when treated less than 45 min. The crystals start to develop when treated over 60 min. It seems the longer the time the more perfect the crystals get, judging from the development of peaks like (004)/(103), (010) and (203). One important observation is that, at 75 min time, even though crystallization is not completed, the crystals are perfect enough to give sharp WAXD peaks and most of all, showing no T_{cII}. It is indicated that the crystallization is not completed within time allowed. However, the crystals are perfect enough not to undergo a reorganization process during heating.

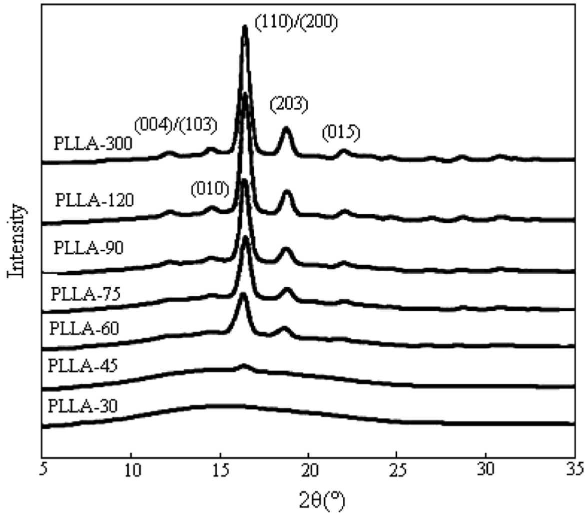

FIGURE 5 WAXD of PLLA isothermally crystallized at 140°C for different times (min).

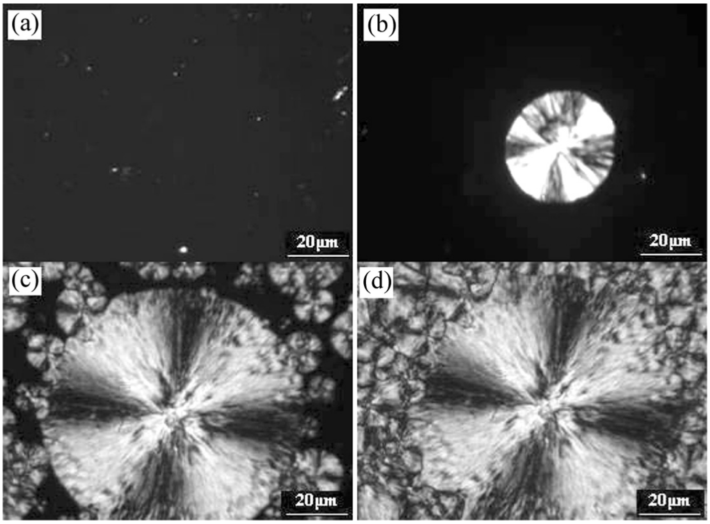

FIGURE 6 Polarizing micrographs for PLLA samples isothermally crystallized at 140°C for different time: (a) 5 min; (b) 20 min; (c) 60 min; (d) 300 min.

After 2.5 h crystallization, the crystallinity of PLLA reaches 69.6% according to the X-ray patterns.

Figure 6 shows optical micrographs of PLLA crystallized at 140°C for different times. The spherulites are formed after about 5 min, which is the apparent induction period. The radius of spherulites increases with increasing crystallization time. Thicker and more regular lamellae develop under regime II with increasing crystallization time, and 300 min later, a lot of spherulites have covered the whole surface of the sample.

CONCLUSIONS

According to the present study, the following points are clarified. 110°C is a critical crystallization temperature for the crystalline structure and crystallization behavior of PLLA. At 110°C, the PLLA sample has double melting point, and the melting point discontinuously changed, which can be related to the transition from regime II to regime III occurring during the isothermal crystal growth. The WAXD patterns of the PLLA samples crystallized at $T_c < 110°C$ distinctly differ from those of the PLLA samples crystallized at $T_c > 110°C$. Crystals of higher perfection form when PLLA crystallizes under higher temperature and prolonged time. The melting point increases gradually with increasing time, and the crystallites become more perfect.

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