Stereocomplexation and Morphology of Enantiomeric Poly(lactic acid)s with Moderate-Molecular-Weight

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ABSTRACT: The thermal behavior and spherulitic morphologies of poly(L-lactic acid) (PLLA)/poly(D-lactic acid) (PDLA) 1/1 blend with weight-molecular-weight of 10^5 order, together with those of pure PLLA and PDLA, were investigated using differential scanning calorimetry and polarized optical microscopy. It was found that in the blend, stereocomplex crystallites could be formed exclusively or coexisted with homocrystallites depending on thermal history. Banded to nonbanded spherulitic morphological transition occurred for melt-crystallized PLLA and PDLA, while the blend presented exclusively nonbanded spherulitic morphologies in the temperature range investigated. The spherulite growth of the blend occurred within a wider temperature range ($\leq 180°C$) compared with that of homopolymers ($\leq 150°C$), while the spherulite growth rates were comparable for both the blend and homopolymers. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 1621–1627, 2008

Key words: blends; polyesters; biodegradable; crystallization; spherulites

INTRODUCTION

Poly(L-lactic acid) (PLLA) has wide applications as surgical implant materials and drug delivery systems as well as ecological materials because of its biocompatibility and biodegradability to nontoxic products.[1–3] It was found that PLLA could form stereocomplex crystallites with poly(D-lactic acid) (PDLA) in solution or during crystallization from the melt, which could enhance the mechanical performance, thermal stability, and hydrolysis-resistance of poly(lactic acid)-based materials, and therefore widen its applications as an alternative of commercial polymers and drug delivery systems.[4,5]

In the context of stereocomplexation from the melt, the effects of various parameters, including the mixing ratio and the molecular weight of the isomers, and the annealing temperature and time, on the stereocomplexation of PLLA and PDLA have been reported by several authors.[6–10] It was presented that equimolar blending of D-lactide and L-lactide units, and low molecular weight for both the isomeric polymers are in favor of exclusive formation of stereocomplex crystallites without homocrystallites.[6–10] Furthermore, an intensive investigation on the spherulite growth of stereocomplex crystallites in a PLLA/PDLA (1/1) blend with relatively low-molecular-weight PLLA and PDLA (in the order of 10^4 g/mol), where solely stereocomplex crystallization took place, was reported by Tsuji and Tezuka.[11]

In this study, we will examine more deeply the stereocomplexation in a PLLA/PDLA (1/1) blend with moderate-molecular-weights from the melt state. One reason is that the information obtained should be interesting since it is generally favorable to employ high molecular weight polymers to get high-strength polymeric materials, although the blend at this molecular weight range is more complicate since it may contain both racemic crystallites and homocrystallites.[6] Another reason is that banded spherulites were clearly observed in this molecular weight range for PLLA,[12] which provides a model system for checking possible morphological difference between homopolymer and stereocomplex spherulites, since it was reported that the homopolymer chains form 10_3 helices (where PLLA is left-handed and PDLA is right-handed) while the stereocomplex chain conformation is rather a 3_1 helix (where PDLA and PLLA chains are packed side by side with a D monomer unit to L monomer unit ratio of 1 : 1).[13–15]

EXPERIMENTAL

The PLLA and PDLA materials were supplied by Purac Biochem (Netherlands), with the specific rotation (chloroform, 20°C) of PLLA and PDLA are $-157.9°$ and $155.2°$, respectively. The average
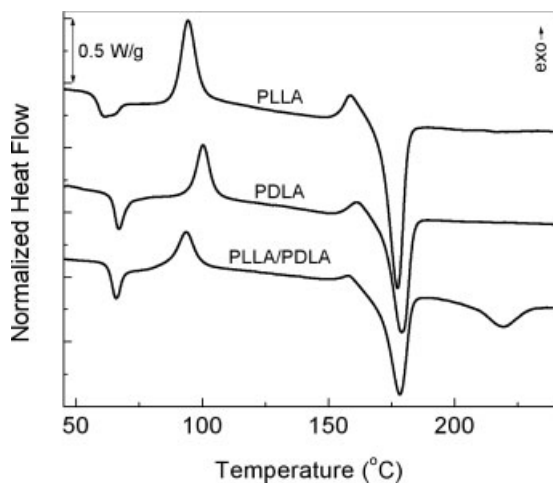
Figure 1 DSC traces of as-cast PLLA, PDLA, and their blend at a heating rate of 10°C/min.

molecular weights, M_n and M_w, of the polymers were evaluated from gel permeation chromatography (Shimadzu, LC 10A, Japan) using polystyrene as standard and chloroform as solvent. For PLLA, M_n and M_w are 59,256 and 149,197, respectively, and for PDLA, M_n and M_w are 31,753 and 100,051, respectively.

Each solution of PLLA and PDLA was prepared separately by dissolving them in methylene dichloride at a concentration of 1.0 g/dL under stirring (400 mg PLLA or PDLA in 40 mL methylene dichloride, respectively). PLLA/PDLA blend in 1/1 molar ratio was prepared by admixing the solution of PLLA (200 mg PLLA in 20 mL methylene dichloride) and PDLA (200 mg PDLA in 20 mL methylene dichloride) with each other under vigorous stirring. Each solution of PLLA, PDLA, and their blend was cast separately on a petri dish at room temperature, followed by evaporating in a controlled air stream for 2 days, and further dried in vacuum at 40°C for 2 days. The thickness of the as-cast films was ca. 40 μm.

Differential scanning calorimetry (DSC) measurements were conducted with a Setaram DSC 131 using nitrogen as a purge gas. Calibration for the temperature and energy scale was carried out using a pure indium standard. Each sample (about 5.6 mg) was cut from the obtained films and then packed in a DSC aluminum cell. All the measurements were performed at a heating rate of 10°C/min. Some of the films, called as-cast films, were scanned without any prior thermal treatment. Others were melted and then subjected to various thermal treatments, including:

1. *Isothermal cold-crystallization.* The films were melted 3 min at 210°C (for pure PLLA or PDLA) or at 250°C (for PLLA/PDLA blend), quenched to room temperature through air, and then held in a tube oven at the chosen crystallization temperatures (T_c) for 6 h.

2. *Nonisothermal melt-crystallization.* The films of the blend were melted 3 min at 250°C, followed by cooling at 10 or 5°C/min down to room temperature in the DSC.

3. *Isothermal melt-crystallization.* The films of the blend were melted 3 min at 250°C and isothermally crystallized 3 h at various T_c after fast cooling from the melting temperature.

The morphologies of the samples were investigated using an Olympus BH-2 polarizing microscope equipped with and a digital camera system. The samples were melted between two glass slides at 210°C (for PLLA or PDLA) or 250°C (for the blend), and a gentle pressure was applied to the upper glass to squeeze the melt into a very thin film (ca. 10 μm). The prepared slides were moved onto a Mettler hot-stage (FP80) and kept at 210°C (for PLLA or PDLA) or 250°C (for the blend) for 3 min under a nitrogen atmosphere, cooled fast down to the designated T_c, and held at that temperature for isothermal crystallization.

RESULTS AND DISCUSSION

DSC analysis

The DSC traces of as-cast PLLA, PDLA, and their 1 : 1 blend are shown in Figure 1. The transitions observed around 60, 95, and 180°C are due to the glass transition, homocrystallization, and melting of homocrystallites, respectively.[8,15] Evidently, one additional melting peak around 220°C is found for the blend, because of the fusion of stereocomplex crystallites.[4,8]

Figure 2 shows the DSC scans obtained during heating of PLLA/PDLA 1 : 1 blend, after quenching, or cooling from the melt. The quenched sample presents a cold crystallization peak at around 109°C, and two
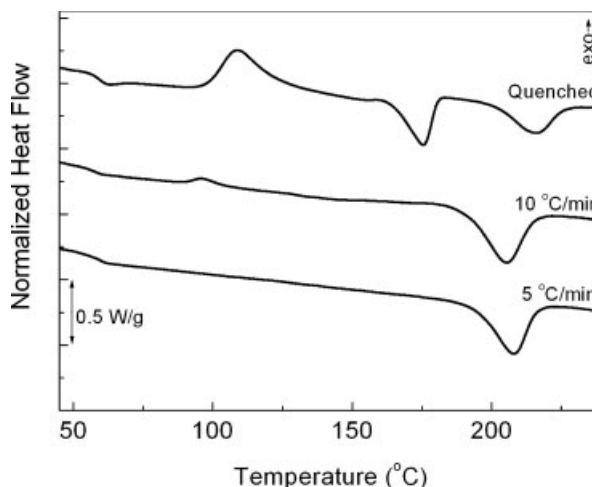

Figure 2 DSC traces of PLLA/PDLA blends after quenching or cooling at indicated rates, recorded during heating at 10°C/min.
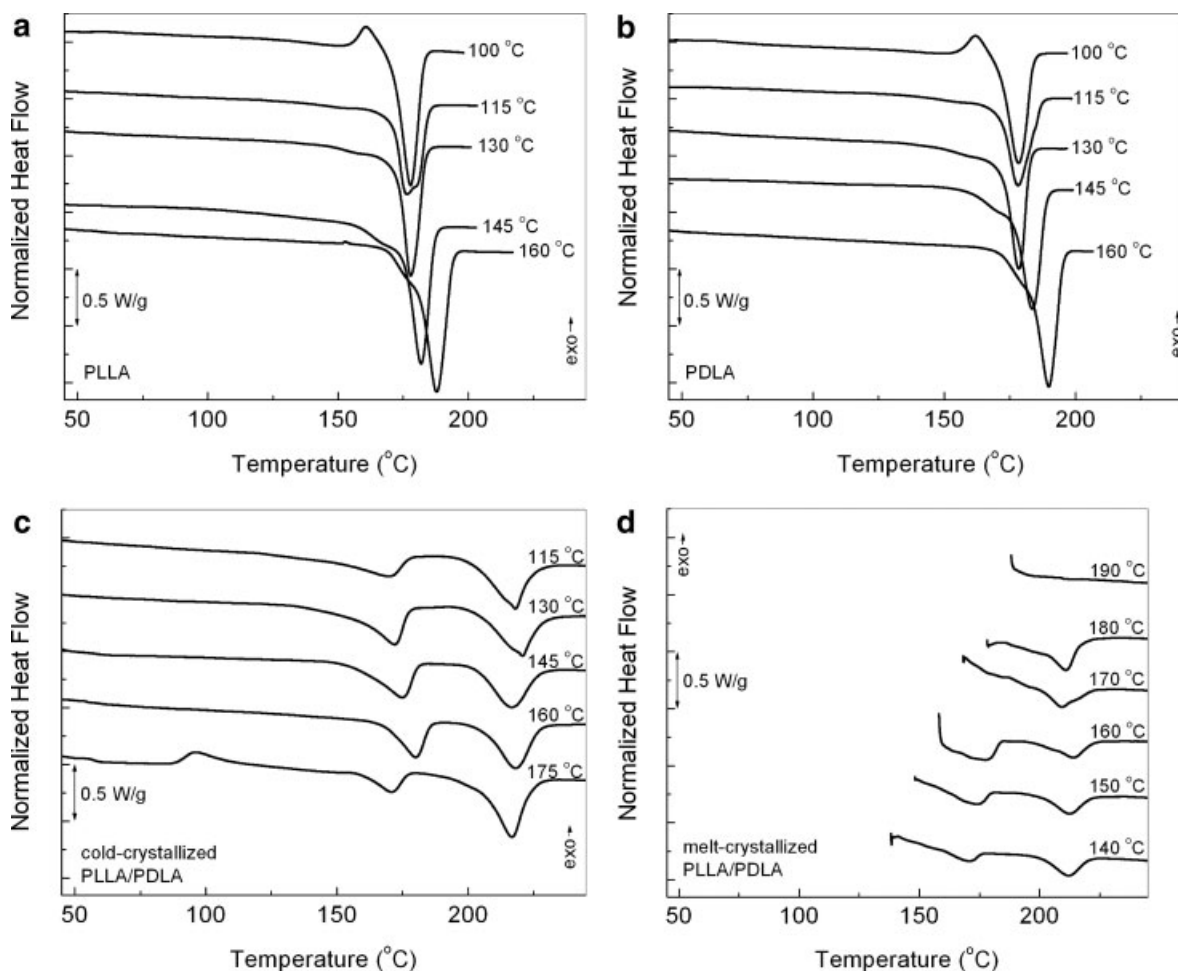
Figure 3 DSC traces of the films after isothermally crystallized at indicated temperatures, recorded during heating at 10°C/min: (a) PLLA cold-crystallized for 6 h; (b) PDLA cold-crystallized for 6 h; (c) PLLA/PDLA blend cold-crystallized for 6 h; (d) PLLA/PDLA blend melt-crystallized for 3 h.

melting peaks of homocrystallites and racemic crystallites around 175 and 216°C, respectively. For the blend of 10°C/min cooling rate, a weak crystallization peak around 96°C and a melting peak at 205°C are observed, while for the blend of 5°C/min cooling rate, only a melting peak at 208°C is found. These results suggest that cooling from the melt at low rates favors formation of stereocomplex. It can also be concluded that, by controlling adequate thermal history, exclusively stereocomplex could be formed in PLLA/PDLA blend with moderate-molecular-weight.

Figure 3(a–c) shows the DSC melting curves of PLLA, PDLA, and their blend, after cold-crystallization for 6 h at various crystallization temperatures, T_c. For comparison, melting curves of the blend after melt-crystallization for 3 h are also presented [Fig. 3(d)]. The values of the melting peak temperatures of the homocrystallites and racemic crystallites (T_{m1} and T_{m2}) estimated from the DSC thermograms are plotted in Figure 4 as a function of T_c. As is seen, T_{m2} of the blend remains constant around (218.4 ± 1.3)°C for cold-crystallized samples or (211.3 ± 1.3)°C for melt-crystallized samples,

independent of T_c. In contrast, T_{m1} of the blend increases linearly with an increase in T_c, and extrapolation of the experimental data to $T_m = T_c$ gives around 186°C as the equilibrium melting point of the homocrystallites (T_{m1}^0) for either cold-crystallized or melt-crystallized samples. In this procedure the data for T_c lower than 130°C were neglected because it was apparent from DSC curves that recrystallization of the homocrystallites occurred during scanning, resulting in a higher T_{m1} than the true value. The estimated T_{m1}^0 for the blend is significant lower than that of pure homopolymers, in consistence with the observation in literature[6] for PLLA/PDLA (1/1) blend with viscosity-average molecular weights of 4.2–4.5 × 10⁴ obtained by melt-crystallization. It is interesting to note that the T_{m2} of the cold-crystallized blend is close to the value of the as-cast blend but significantly higher than that of the melt-crystallized blend.

Morphology

Crystallization from the melt is in favor of the formation of larger spherulites, being helpful to an improve-
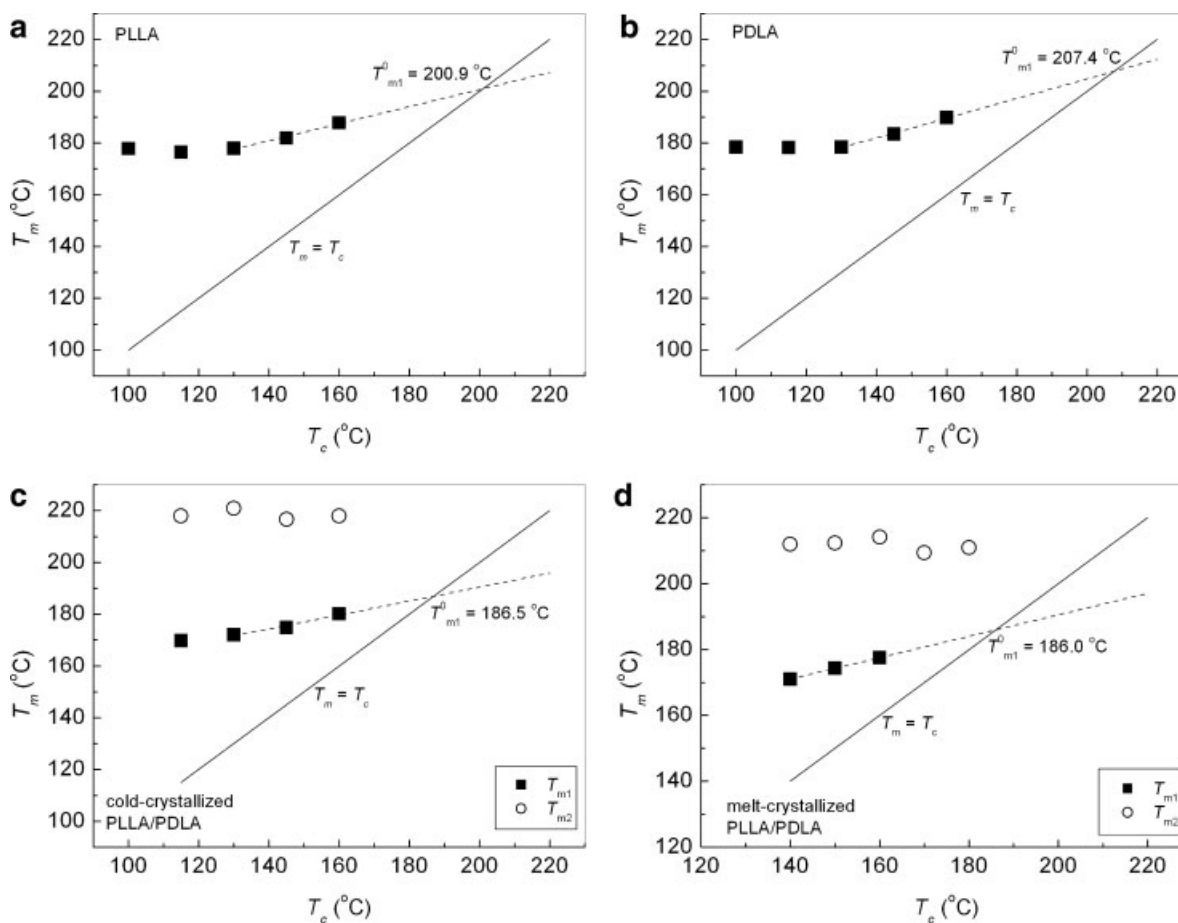
Figure 4 T_{m1} and T_{m2} evaluated from DSC thermograms of PLLA, PDLA, and their blend films as a function of T_c: (a) PLLA cold-crystallized for 6 h; (b) PDLA cold-crystallized for 6 h; (c) PLLA/PDLA blend cold-crystallized for 6 h; (d) PLLA/PDLA blend melt-crystallized for 3 h.

ment in the morphological analysis, compared with cold-crystallization in PLLA.[16] Figures 5–7 show a series of polarized optical micrographs for PLLA, PDLA, and their blend isothermally crystallized from the melt state at various T_c. In PLLA (Fig. 5), banded spherulites appear at 135–145°C, while at lower T_c (130 and 125°C) nonbanded spherulites appear. At higher T_c (150°C) slightly deformed spherulites without clear Maltese cross extinction appear. In PDLA (Fig. 6), banded spherulites appear at 130–145°C, while at lower T_c (125°C) nonbanded spherulites appear. At higher T_c (150°C) slightly deformed spherulites with clear banding appear. These banded to nonbanded spherulitic morphological transition is similar to a previous study for PLLA ($M_n = 86,000$) where the film were prepared by melting raw materials directly.[12] It is noteworthy that no spherulites were observed for pure PLLA and PDLA at $T_c = 160$°C and above, as expected. In contrast, in PLLA/PDLA film (Fig. 7), well-defined spherulites are observed even at 180°C. The spherulite density of the blend is higher at 130°C than at 180°C, being in line with the trends of pure PLLA and PDLA. Interestingly, the blend show

exclusively nonbanded spherulitic morphologies in the temperature range investigated. One possible reason is PLLA (or PDLA) has well-defined chirality (where PLLA is left-handed and PDLA is right-handed), being in favor of the formation of banded spherulites,[17] while the stereocomplex chain conformation is rather a 3_1 helix (where PDLA and PLLA chains are packed side by side with a D monomer unit to L monomer unit ration of 1 : 1).[13–15] However, it could not be excluded that the apparent nonbanded spherulites might actually contain crystals that twist with a period larger than the spherulite radius or with a too short period.

The melting behavior of the obtained spherulites has also been examined. In all the homopolymers of PLLA and PDLA, the birefringence vanishes immediately when the samples are brought to 180°C (not shown). In contrast, the melting behavior of the spherulites in blend of PLLA/PDLA is more complicate as shown in Figure 8. For the blends crystallized at 130 and 145°C, a significant decrease of birefringence could be observed when the samples are brought to 180°C, which should be ascribed to the fusion of the
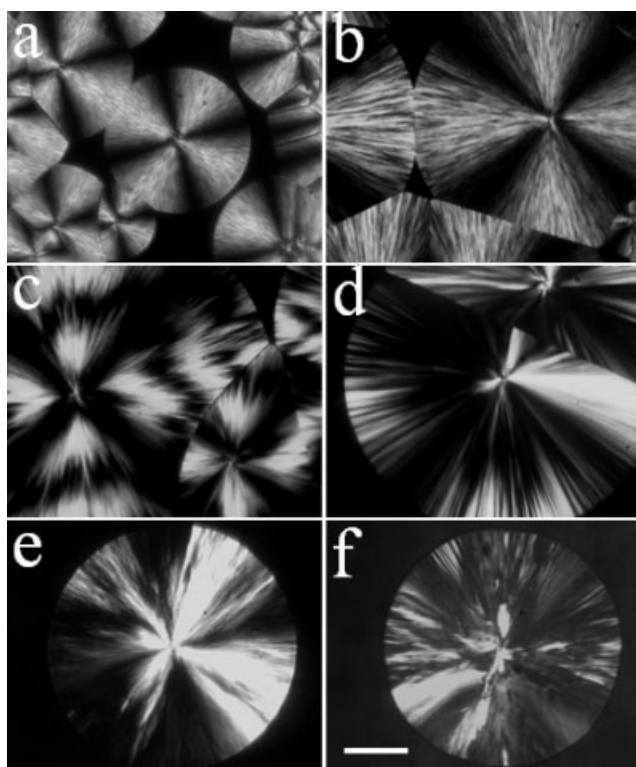
Figure 5 Polarized optical micrographs of PLLA films crystallized at various temperatures from the melt. (a) 125°C; (b) 130°C; (c) 135°C; (d) 140°C; (e) 145°C; (f) 150°C. The scales for all the graphs are the same as image (f), which represents 100 µm.
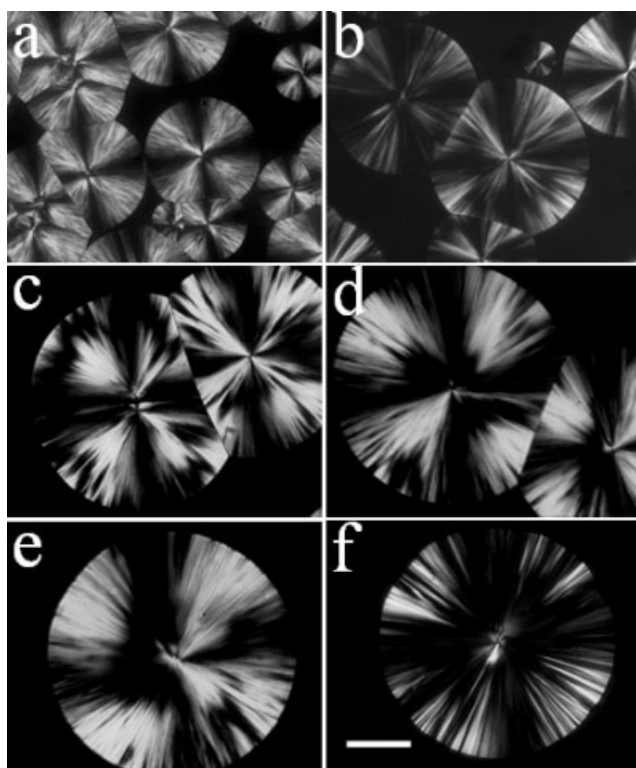

Figure 6 Polarized optical micrographs of PDLA melt-crystallized at various temperatures. (a) 125°C; (b) 130°C; (c) 135°C; (d) 140°C; (e) 145°C; (f) 150°C. The scales for all the graphs are the same as image (f), which represents 100 µm.

homocrystallites of PLLA and PDLA. It is noteworthy that the fusion of the homocrystallites of PLLA and PDLA does not induce any noticeable change in the sample morphology, that is, most of the spherulites keep their initial shape and aspect. When the samples are brought further to 200°C, the birefringence vanishes very soon (not shown), which should be ascribed to the fusion of the stereocomplex crystallites. For the blend crystallized at 170°C, no change of birefringence is observed when the sample is kept at 180°C for 10 min and then at 190°C for 5 min, and finally most of the spherulites disappears when the sample is further brought to 200°C, and all the spherulites disappear when the sample is kept at 200°C for 8 min.

The above observations can be explained as follows, as suggested by Brochu et al.[7] for PLLA/PDLA with low-molecular-weight and various compositions. When the temperature is decreased from the melt to a temperature above the crystallization of the homopolymers, only stereocomplexation occurs, as can be deduced from Figure 8(e–h) for the blend crystallized at 170°C. This behavior is in agreement with DSC results [Fig. 3(d)], showing only the melting of stereocomplex for the blends crystallized at 170°C and above. However, when the temperature is decreased from the molten state to a temperature where the crys-
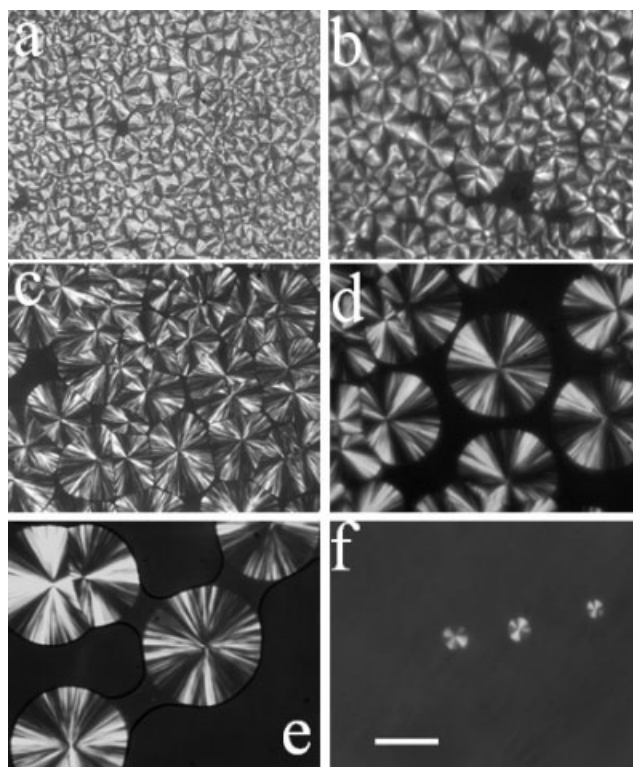

Figure 7 Polarized optical micrographs of PLLA/PDLA blend melt-crystallized at various temperatures. (a) 130°C; (b) 140°C; (c) 145°C; (d) 160°C; (e) 170°C; (f) 180°C. The scales for all the graphs are the same as image (f), which represents 100 µm.

tallization of the homopolymers could also occur, the stereocomplex formation is preferred to the homopolymer crystallization and the stereocomplex controls the morphology of the blend over a wide range of crystallization temperature. The chains of homopolymers in excess are then trapped between the stereocomplex lamellae inside the spherulites but can also form crystalline lamellae between the stereocomplex lamellae, as shown in Figure 8(a–d). This behavior is in agreement with DSC results [Fig. 3(d)], showing the coexistence of homocrystallites and stereocomplex crystallites for the blends crystallized at 140, 150, and 160°C. Since the homocrystallites are formed inside the stereocomplex lamellae, they should be less per-
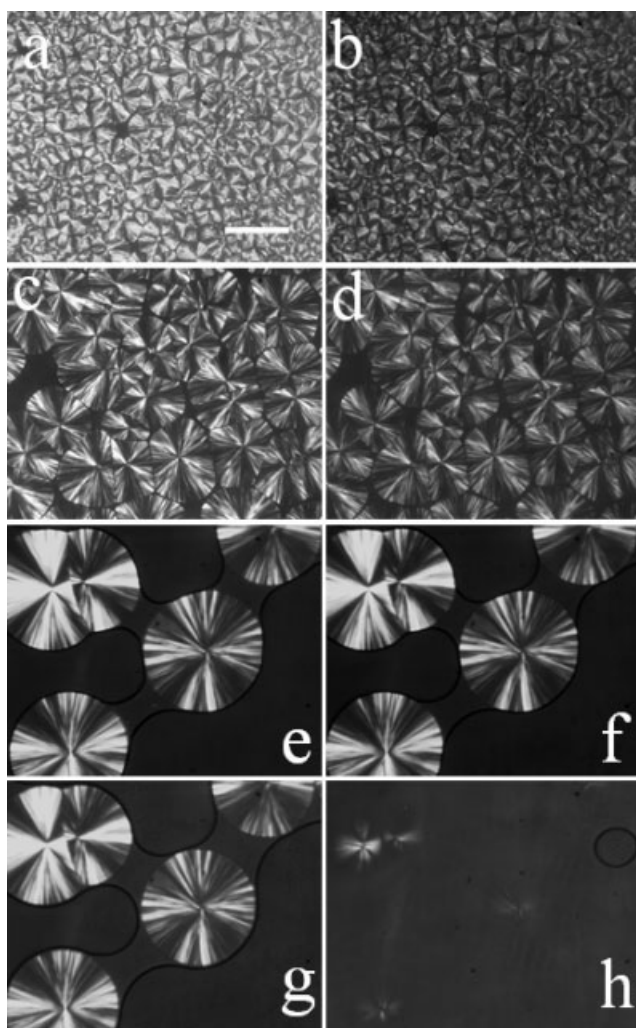

Figure 9 Radius growth rates of spherulites (G) of PLLA, PDLA, and their blend as a function of crystallization temperature (T_c).

fect than those from the pure homopolymers, as a result, the estimated T_{m1}^0 for the blend is significantly lower than that of pure homopolymers (Fig. 4).

The spherulites of PLLA, PDLA, and PLLA/PDLA films grow linearly with crystallization time, irrespectively of T_c, and their radius growth rates (G) can therefore be easily determined from the slope of the spherulite radii. Figure 9 shows a summary of growth rate data as a function of T_c. The G of PLLA and PDLA gives maximum values of 5.0 and 6.2 μm/min, respectively, at around 130°C. These G_{max} values in the present study are in comparable with the values for PLLA with M_w in the order of 10^5,[18–23] while significantly lower than 37.8 (or 36.1) μm/min for PLLA with M_w of 1.0×10^4 (or PDLA with M_w of 2.2×10^4).[11] Except a higher value of 8.8 μm/min at 125°C, the G values of PLLA/PDLA are quite similar with those of pure PLLA and PDLA at temperature range from 120 to 150°C. This observation is completely different from the results reported by Tsuji and Tezuka[11] that the G of PLLA/PDLA was an order of magnitude higher than those of homocrystallites of PLLA and PDLA with M_w in the order of 10^4. The possible reason is that the spherulite growth becomes complicated when both stereocomplex crystallites and homocrystallites are formed simultaneously in the spherulites. It is interesting to note that the spherulites of stereocomplex crystallites can grow even at T_c exceeding 150°C, at which no spherulite of homocrystallites was formed in PLLA and PDLA films, being in consistent with the observation by Tsuji and Tezuka.[11]

Figure 8 Polarized optical micrographs of PLLA/PDLA blend melt-crystallized at 130°C (a, b), 145°C (c, d), and 170°C (e–h), respectively. Images (a, b) were taken at 130°C and after held at 180°C for 5 min, respectively; images (c, d) were taken at 145°C and after held at 180°C for 5 min, respectively; images (e–h) were taken at 170°C, then held at 180°C for 10 min, then held at 190°C, and then held at 200°C for 1 min, respectively. The scales for all the graphs are the same as image (a), which represents 100 μm.
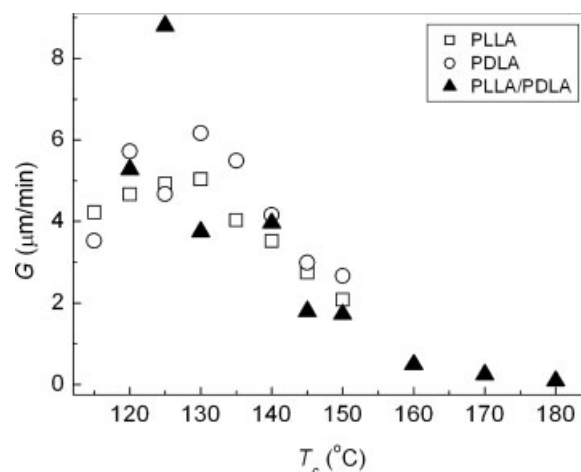
CONCLUSIONS

This study investigated the stereocomplexation and morphology of PLLA/PDLA equimolar blend with moderate-molecular weight. Banded to nonbanded

spherulitic morphological transition occurs for melt-crystallized PLLA and PDLA, while the blend presents exclusively nonbanded spherulitic morphologies in the temperature range investigated. The spherulite growth of the blend occurs at a wider temperature range ($\leq 180°C$) compared with that of homopolymers ($\leq 150°C$), while the spherulite growth rates are comparable for both the blend and homopolymers.

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