Electrospinning of Poly(lactic acid) Stereocomplex Nanofibers

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The electrospinning of stereocomplex nanofibers of high-molecular-weight poly(L-lactic acid) (PLLA)/poly(D-lactic acid) (PDLA) (PLLA/PDLA = 1:1) was carried out with chloroform as the spinning solvent. The stereocomplex nanofibers with diameters of 830−1400 and 400−970 nm were successfully obtained at voltages of −12 and −25 kV, respectively. Wide-angle X-ray scattering indicated that with an increasing absolute value of voltage from 0 to 25 kV the crystallinity of homo-crystallites composed of either PLLA or PDLA decreased from 5% to 1%, whereas the crystallinity of stereocomplex crystallites increased slightly from 16% to 20%. The obtained results reveal that electrospinning is an effective method to prepare stereocomplex nanofibers with a negligibly small amount of homo-crystallites, even when high-molecular-weight PLLA and PDLA are used, and that the orientation caused by high voltage (or electrically induced high shearing force) during electrospinning enhances the formation and growth of stereocomplex crystallites and suppresses the formation of homo-crystallites.

Introduction

Poly(L-lactide) (i.e., poly(L-lactic acid) (PLLA)), a biodegradable polyester produced from renewable resources such as starch, is now widely used in commodity applications as well as biomedical and pharmaceutical applications due to reduced cost by mass production.[1−11] Recently, PLLA has been used in parts of automobiles and the housings of personal computers and mobile phones. The improvement of mechanical properties and heat resistance of poly(lactide) (i.e., poly(lactic acid) (PLA))-based materials is a matter of concern when they are used in biomedical and commodity applications. One of the most effective methods to enhance the mechanical properties and thermal stability of PLA-based materials is stereocomplex formation between PLLA and poly(D-lactide) (i.e., poly(D-lactic acid) (PDLA)).[12−14] Such stereocomplex formation is defined as stereocomplex crystallization (or racemic crystallization) between PLLA and PDLA.

Since Ikada et al.[15] found stereocomplex crystallization between enantiomeric PLLA and PDLA, intensive and numerous studies on stereocomplex crystallization have been carried out.[10−14] Stereocomplex crystallization was found to enhance not only the mechanical performance[16] and thermal stability[17] but also the hydrolysis resistance[18,19] of PLA-based materials. However, the homo-crystallization (the formation of homo-crystallites composed of either PLLA or PDLA) prevails over stereocomplex crystallization, when blends are prepared from high-molecular-weight PLLA and PDLA,[14] despite the fact that high molecular weight is indispensable for high mechanical performance. In a previous study, we prepared PLA stereocomplex fibers by solution-spinning and found that with uniaxial orientation by drawing the amount of stereocomplex crystallites increases and that of homo-crystallites decreases.[20] This exhibits that the drawing enhances the formation and growth of stereocomplex crystallites. Also, Takasaki et al. reported that the fraction of stereocomplex crystallites became higher when the melt-spinning was carried out under high tensile stress, i.e., at high take-up velocity, low throughput rate, and low extrusion temperature.[21]

Electrospinning is a powerful method to prepare versatile nanofibers from polymer solutions or melts.[22,23] This method has been utilized to prepare nanofibers of PLLA[24−42] and poly(DL-lactide) (i.e., poly(DL-lactic acid) (PDLLA)).[43,44] During electrospinning, polymer chains in a solution released from a spinneret are oriented by an electric field or by an electrically induced shearing force. Such electrical orientation during electrospinning is expected to enhance the formation and growth of stereocomplex crystallites, as in the previous studies with mechanical drawing of the blend fibers from PLLA and PDLA during spinning or thermal treatment.[20,21]

The objectives of this study were to prepare PLA stereocomplex nanofibers by electrospinning from a mixed solution of high-molecular-weight PLLA and PDLA, to investigate the effects of applied voltage on the crystalline species formed in the fibers, and to compare the properties and structures of blend and pure PLLA fibers. For these purposes, a PLLA/PDLA (1:1) blend film and a pure PLLA film were prepared by solution-casting of high-molecular-weight PLLA and PDLA, and the solutions for electrospinning were obtained by dissolving the solution-cast blend film and the pure PLLA film. This procedure was selected because of the difficulty in complete mixing of highly viscous PLLA and PDLA solutions even at low polymer concentrations around 5 g dL^{-1}. Thus prepared solutions were used for electrospinning at high voltages. The obtained blend and pure PLLA fibers were investigated by scanning electron microscopy (SEM), wide-angle X-ray scattering (WAXS), and differential scanning calorimetry (DSC). As far as we are aware, this is the first report on the electrospinning of poly(lactic acid) stereocomplex nanofibers.

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Table 1. Properties of PLLA and Blend (PLLA/PDLA = 1:1) Specimens at Different Applied Voltages.

specimen	applied voltage for spinning (kV)	diameter (nm)	T_g[a] (°C)	T_{cc}[b] (°C)	T_m(H)[c] (°C)	T_m(S)[c] (°C)	X_c(H)[d] (%)	X_c(S)[d] (%)
PLLA	0		45.0	82.0	176.6		5.2	
	−12	1700−2700	55.0	83.5	178.1		4.8	
	−25	1000−1800	58.1	83.7	178.2		4.5	
blend	0		49.8	82.9	172.0	222.0	4.9	16.4
	−12	830−1400	54.4	85.6	168.8	222.2	2.8	19.0
	−25	400−970	59.4	83.5	161.9	224.9	0.7	20.1

[a] Glass transition temperature. [b] Cold crystallization temperature. [c] T_m(H) and T_m(S) are melting temperatures of homo-crystallites and stereocomplex crystallites, respectively. [d] X_c(H) and X_c(S) are crystallinities of homo-crystallites and stereocomplex crystallites, respectively, estimated by WAXS measurements.

Experimental Section

Materials. Synthesis and purification of PLLA (number-average molecular weight (M_n) = 3.6 × 10^5 g mol^{-1}, weight-average molecular weight (M_w)/M_n = 2.3, specific optical rotation ($[\alpha]_{589}^{25}$) = −155° dm^{-1} g^{-1} cm^3) and PDLA (M_n = 3.9 × 10^5 g mol^{-1}, M_w/M_n = 1.8, $[\alpha]_{589}^{25}$ = 157° dm^{-1} g^{-1} cm^3) used in this study were described in previous papers.[15,16] Namely, ring-opening polymerization of D- and L-lactides was performed in bulk at 140 °C initiated by stannous octoate, i.e., tin(II) 2-ethylhexanoate (0.03 wt %).[45−47] D- and L-Lactide were synthesized by thermal depolymerization of low-molecular-weight PLLA and PDLA, respectively, in the presence of Sb_2O_3 and purified with repeated recrystallization using ethylacetate as a solvent.[10,15] Synthesized polymers were purified by reprecipitation using methylene chloride and methanol as solvent and nonsolvent, respectively. Blend films (50-μm-thick) used for electrospinning experiments were prepared by the method stated in previous papers.[18,19,48] Briefly, each solution of PLLA and PDLA was prepared separately to have a polymer concentration of 1.0 g dL^{-1} and then admixed with each other under vigorous stirring. Methylene chloride was used as a solvent, and the mixing ratio of PLLA and PDLA was fixed to 1:1. The solution was cast onto a Petri dish, followed by solvent evaporation at 25 °C for approximately 1 day. A pure PLLA cast film (50-μm-thick) was also prepared with the same procedure. The obtained films were dried in vacuo for at least 1 week.

Electrospinning. A PLLA/PDLA (1:1) solution and a pure PLLA solution both with concentrations of 4 g dL^{-1} were prepared for electrospinning by dissolving the cast films in chloroform. Chloroform was selected as the spinning solvent because of its appropriate evaporation rate during electrospinning. The polymer solution was placed into a syringe with a needle (inner diameter of 0.5 mm), and the polymer solution was pumped continuously at a rate of 0.1 mL min^{-1}. During electrospinning, a voltage of −12 or −25 kV was applied to the tip of the needle by the use of a high-voltage regulated direct current power supply, model 502 (Pulse Electronic Engineering Co., Ltd., Chiba, Japan), while the collecting drum was grounded. Similarly, Casper et al. applied a negative voltage (−12 kV) to the tip of a needle for the electrospinning of poly(lactide-*co*-glycolide).[49] The gap between the tip of the needle and the surface of the collecting drum was 10 cm. The surface of the collecting drum was covered with aluminum foil. During electrospinning, the collecting drum, which was 10 cm in diameter rotated, at a surface speed of 20 cm min^{-1}. Without a voltage (0 kV), the fiber-form specimens were not obtained, and the polymer solution from the tip of the needle was collected with a Petri dish. The collected specimens were dried in vacuo for at least 7 days, and then the measurements and observations stated below were performed.

Physical Measurements and Observations. The M_w and M_n of polymers were evaluated in chloroform at 40 °C using a Tosoh (Tokyo, Japan) gel permeation chromatography (GPC) system with two TSK gel columns (GMH_{XL}) and polystyrene standards. Therefore, the M_w and M_n values are given relative to polystyrene. The $[\alpha]_{589}^{25}$ values of the polymers were measured in chloroform at a concentration of 1 g dL^{-1} and 25 °C using a JASCO DIP-140 polarimeter at a wave length of 589 nm.

The glass transition temperature (T_g), cold crystallization temperature (T_{cc}), and melting temperatures of homo-crystallites (T_m(H)) and stereocomplex crystallites (T_m(S)) of the specimens were determined with a Shimadzu (Kyoto, Japan) DSC-50 differential scanning calorimeter. The specimens were heated at a rate of 10 °C min^{-1} under a nitrogen gas flow for DSC measurements. WAXS measurements were carried out at 25 °C using a RINT-2500 (Rigaku Co., Tokyo, Japan) equipped with a Cu Kα source (λ = 0.154 nm). The crystallinity values of the homo-crystallites (X_c(H)) and stereocomplex crystallites (X_c(S)) were determined by a simplified method using WAXS profiles.[50] Namely, for a 2θ range of 10−25°, the crystalline peak areas for stereocomplex crystallites at 2θ values of 12°, 21°, and 24° and for homo-crystallites at 2θ values of 17° relative to the total area between a diffraction profile and a baseline were used to estimate X_c(H) and X_c(S), respectively.[15,51−53] The diffraction profiles at a 2θ range of 10−25° were used for crystallinity estimation because the diffraction profiles became horizontal outside this 2θ range. The properties of the PLLA and blend specimens are summarized in Table 1. The morphology of the fibers was studied with a Hitachi (Tokyo, Japan) scanning electron microscope (S-2300). The fibers for SEM observation were coated with carbon to a thickness of approximately 10 nm.

Results and Discussion

Morphology. Figure 1 shows the SEM photographs of electrospun fibers. Here, only the SEM photographs for the electrospun fibers at the applied voltages of −12 and −25 kV are shown, because the fiber-form specimens were not obtained at 0 kV. In this study, only the results for PLLA are shown, because it is expected that the results for PDLA should be very similar to those of PLLA, which has similar molecular characteristics. It is seen that the PLLA fibers with diameters of 1.7−2.7 and 1.0−1.8 μm were formed at voltages of −12 and −25 kV, respectively, whereas the blend fibers with nano-order diameters of 800 nm−1.4 μm and 400−970 nm were successfully obtained at the applied voltages of −12 and −25 kV (Table 1). The fiber diameter was reduced by blending and increasing the absolute value of applied voltage. The blend fiber diameters were 2 orders of magnitude smaller than those of PLLA/PDLA fibers prepared by a conventional solution-spinning method (60−180 μm (Tsuji et al.[20])) and a melt-spinning method (20−500 μm (Takasaki et al.[21])). Therefore, electrospinning is an effective method to prepare nano-order PLLA/PDLA blend fibers. Numerous pores with maximum diameters of approximately 1 μm were noticed for the PLLA fibers. Such pore formation is consistent with the morphology reported for PLLA nanofibers prepared with a spinning solvent of methylene chloride (Kwon et al.[36] and Dersch et al.[37]) and is indicative of the fact that the electrospinning conditions (polymer concentration, solvent type, distance to the collector, or other conditions) were not optimum for the spinning of PLLA. In contrast, the surfaces of the blend fibers were smooth. The

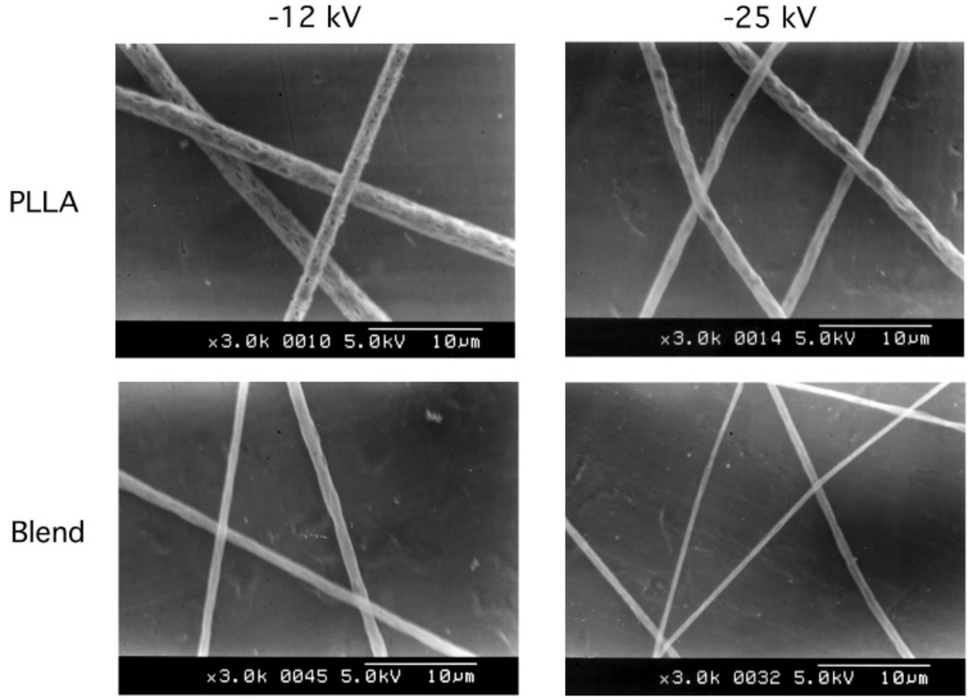

Figure 1. SEM photographs of PLLA and blend (PLLA/PDLA = 1:1) fibers electrospun at applied voltages of −12 and −25 kV.

porous structure of the PLLA fibers should have elevated the apparent diameters compared with those of blend fibers.

Wide-Angle X-ray Scattering. The WAXS profiles of PLLA and blend specimens obtained at different voltages are shown in Figure 2. For all of the PLLA specimens, a weak diffraction was observed at a 2θ value of 17°. This is the most intense diffraction observed for the α-form of PLLA crystallized in a pseudo-orthorhombic unit cell of dimensions $a = 1.07$ nm, $b = 0.595$ nm, and $c = 2.78$ nm, which contains two 10_3 helices.[51] Therefore, the α-form was formed in the PLLA specimens during solvent evaporation or electrospinning. These peak areas of PLLA specimens at 17° were similar to each other, and the X_c(H) value estimated by WAXS measurements was constant around 5%, irrespective of the applied voltage (Table 1). This reflects the fact that the crystallinity or crystallization behavior was not influenced by the applied voltage. WAXS measurements have been performed for PLLA nanofibers electrospun with solvents of chloroform/acetone (2:1) (Zeng et al.[28]), methylene chloride/dimethylformamide (65:35) (Kwon et al.[36]), and chloroform or 1,1,1,3,3,3-hexafluoro-2-propanol (You et al.[41]). However, reported diffraction profiles contain no crystalline peak, in contrast to those in the present study. The difference between our results and reported results can be ascribed to the difference in polymer molecular weight or concentration, solvent type, or electrospinning conditions. However, we could not specify the main factor for the difference in the results.

In contrast, for the blend specimens, in addition to the diffraction of the α-form at 17°, other diffractions were observed at 2θ values of 12°, 21°, and 24°. The 2θ values of latter peaks are in excellent agreement with the reported values[15,52,53] for the PLA stereocomplex crystallized in a triclinic unit cell of dimensions $a = 0.916$ nm, $b = 0.916$ nm, $c = 0.870$ nm, $\alpha = 109.2°$, $\beta = 109.2°$, and $\gamma = 109.8°$, in which L-lactide and D-lactide segments are packed parallel taking a 3_1 helical conformation.[51] Interestingly, the diffraction peak for the α-form became smaller with an increasing absolute value of the applied voltage and almost disappeared at −25 kV. Correspondingly, the X_c(H) value estimated by WAXS measurements decreased from 5% to 1%, when the absolute value of the applied voltage was increased from 0 to 25 kV (Table 1). This means that the high voltage is effective to suppress the formation of homo-crystallites and to obtain stereocomplex fibers with a negligibly small amount of homo-crystallites. The X_c(S) value estimated by WAXS measurements increased slightly from 16% to 20% with an increasing absolute value of the applied voltage from 0 to 25 kV (Table 1), suggesting that the orientation induced by high voltage enhanced the formation and growth of stereocomplex crystallites. This is in good agreement with the reported results that the orientation of PLLA/PDLA fibers caused by thermal drawing elevated the amount of stereocomplex crystallites.[20,21]

WAXS measurements indicated that stereocomplex crystallization occurs in PLLA/PDLA materials during heating as in DSC measurements without an explicit cold crystallization peak at approximately 200 °C.[54] Therefore, the crystallinity values obtained with WAXS measurements in the present study were not compared with the reported values estimated with DSC measurements. However, it should be noted that although high-molecular-weight PLLA and PDLA were used for electrospinning stereocomplex crystallites were the dominant crystalline species in the blend fibers and negligibly small amounts of homo-crystallites were formed. This is in marked contrast with the results for conventional solution-casting or solution-spinning methods, where homo-crystallites were the main crystalline species or large amounts of homo-crystallites were formed.[16,20] This can be attributed partly to the chain orientation caused by the high voltage or the electrically induced high shearing force, which increased the surface area of the molecular chains and thereby elevated the interaction between PLLA and PDLA chains, resulting in rapid stereocomplex crystallization. Moreover, it seems probable that the stereocomplex crystallite nuclei or microcrystallites formed during solution-casting for film preparation, whose solubility is very low compared with that of homo-crystallites, remained insoluble in solution for electrospinning and enhanced the

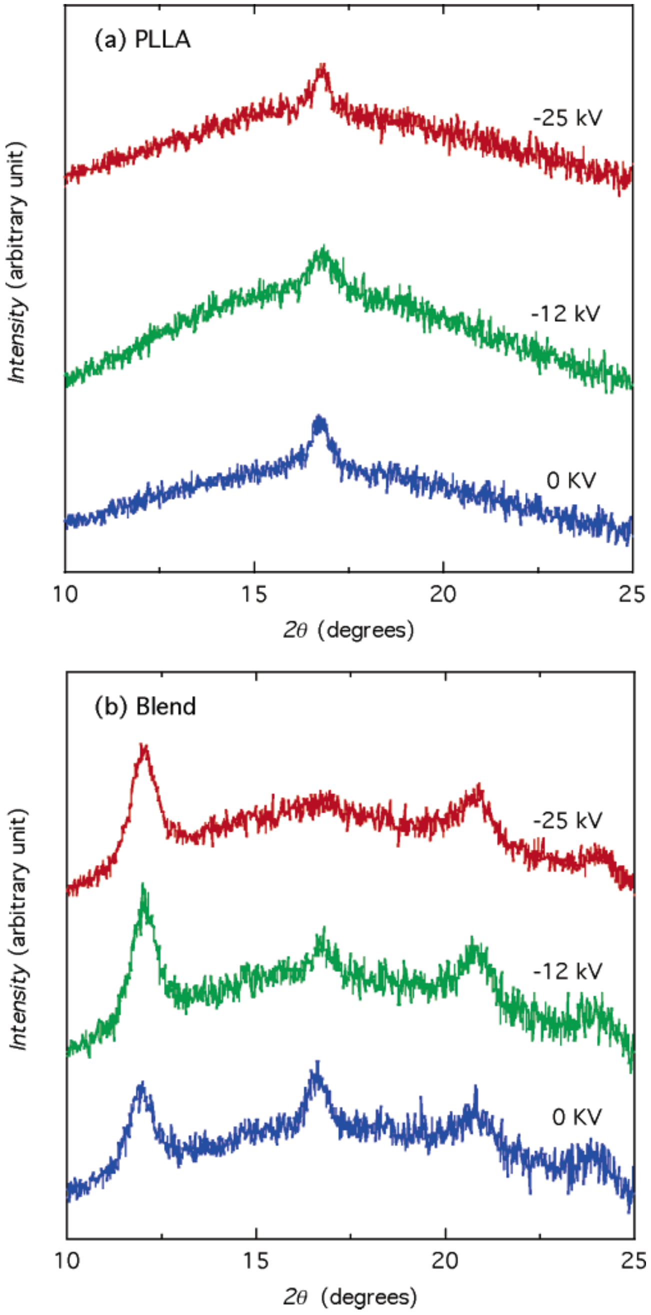

Figure 2. WAXS profiles of (a) PLLA and (b) blend (PLLA/PDLA = 1:1) specimens obtained at different applied voltages.

formation and growth of stereocomplex crystallites during electrospinning.

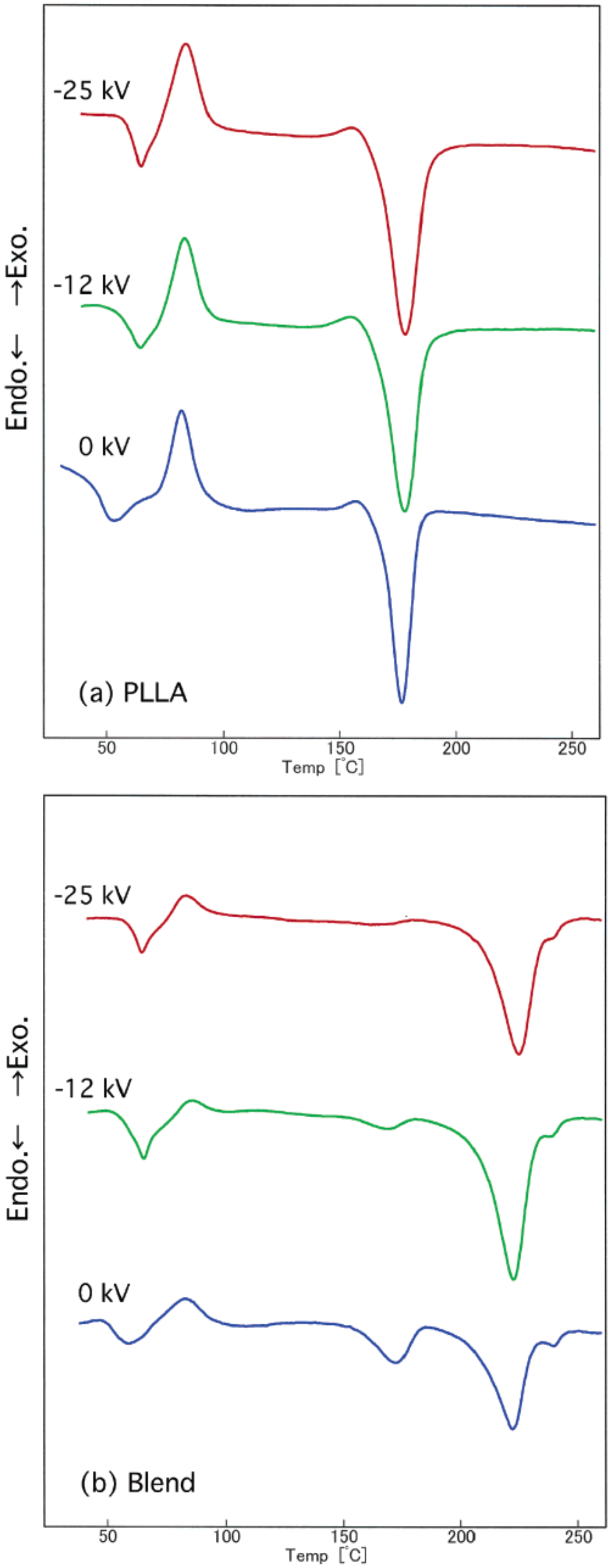

Figure 3. DSC thermograms of (a) PLLA and (b) blend (PLLA/PDLA = 1:1) specimens obtained at different applied voltages.

Differential Scanning Calorimetry. Figure 3 shows the DSC thermograms of PLLA and blend specimens. The shapes of the thermograms for PLLA specimens are very similar to the reported ones.[24,38,39,41] That is, glass transition, cold crystallization, and melting peaks are clearly observed, and the cold crystallization peak is adjacent to or slightly overlaps the glass transition peak. The latter finding is in contrast with the results for melt-quenched amorphous PLLA specimens, where glass transition and cold crystallization peaks are located separately, and the cold crystallization peak appears at a higher temperature around 100 °C.[55] A relatively low cold crystallization temperature for all of the blend and PLLA specimens means that the crystallization was frozen before completion by the removal of solvent from the spun fibers. Also, the fact that the cold crystallization peak at approximately 85 °C was noticed for all the blend and PLLA specimens reflects the fact that all of the specimens contain crystallizable free amorphous regions. The cold crystallization peak was higher for PLLA specimens than that for the blend specimens, indicating that the PLLA specimens contained a larger amount of crystallizable free amorphous regions.

As stated above, we did not estimate the X_c(H) and X_c(S) values from the DSC thermograms, because of the slight overlapping of the glass transition and cold crystallization peaks, of the difficulty in dividing the enthalpy of the cold crystallization peak at around 85 °C into those of stereocomplex crystallites and stereocomplex crystallites, and of the stereocomplex crystallization during heating without explicit cold crystallization peak at around 200 °C. However, the dependence of the ratio of the melting peak height of homo-crystallites to the melting peak height of stereocomplex crystallites on the applied voltage (34.8, 7.2, and 2.5 for 0, −12, and −25 kV) is consistent with that of the ratio of X_c(H) to X_c(S) (30.0, 14.7, and 3.5 for 0, −12, and −25 kV). This strongly suggests that the melting peak height ratio can be used as an index for the ratio of two crystalline species.

In conclusion, this study reveals that electrospinning is an effective method to prepare stereocomplex nanofibers with a negligibly small amount of homo-crystallites, even when high-molecular-weight PLLA and PDLA are used, and that the orientation caused by high voltage during electrospinning enhances the formation and growth of stereocomplex crystallites and suppresses the formation homo-crystallites.

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