

The Stereocomplex Formation and Phase Separation of PLLA/PDLA Blends with Different Optical Purities and Molecular Weights^{*}

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Abstract In this study, the poly(L-lactide)/poly(D-lactide) (PLLA/PDLA) blends with different optical purities of PLLA and various molecular weights of PDLA are prepared by solution mixing, and the stereocomplex formation and phase separation behaviors of these blends are investigated. Results reveal that optical purity and molecular weight do not vary the crystal structure of PLA stereocomplex (sc) and homochiral crystallites (hc). As the optical purity increasing in the blends, the melting temperature of sc (T_{sc}) and the content of sc (ΔH_{sc}) increased, while the melting temperature of hc (T_{hm}) hardly changes, although the content of hc (ΔH_{hm}) decreased gradually. The T_{sc} and ΔH_{sc} are also enhanced as the molecular weight of PDLA reduces, and the ΔH_{hm} reduces rapidly even though the T_{hm} does not vary apparently. With lower optical purities of PLLA and higher molecular weights of PDLA, three types of crystals form in the blends, *i.e.*, PLA sc, PLLA hc and PDLA hc. As molecular weight decreases and optical purity enhances, the crystal phase decreases to two (sc and PDLA hc), and one (sc) finally. This investigation indicates that the phase separation behavior between PLLA and PDLA in the PLLA/PDLA blends not only depends on molecular weights, but also relies on the optical purities of polymers.

Keywords: Poly(L-lactide); Poly(D-lactide); Poly(lactide) stereocomplex; Homocrystallites; Phase separation.

INTRODUCTION

Poly(lactide) (PLA), a most investigated bio-plastic, which does not depend on the oil recourses and originates from the renewable resources, exhibits favorable mechanical, thermal, transparent and biodegradable properties. These performances provide numerous potential applications for PLA material in engineering, pharmaceutical and agricultural fields^[1]. For the engineering application, the application temperature largely relies on the crystal and morphology developments in the material. The melting temperature and crystallization speed of homochiral PLA, *i.e.*, poly(L-lactide) and poly(D-lactide) (PLLA and PDLA), relate tightly with its optical purity, the melting temperature and crystallization capacity reduce rapidly as the optical purity decreasing, and no PLA crystallites form when the content of isomer up to 12% in the PLLA or PDLA^[2]. Blending PLLA with PDLA, a novel PLA stereocomplex crystal forms, and most of the reports on the melting temperature of PLA stereocomplex (sc) is 230 °C^[3]. Recently, our research works reveals that the melting temperature of PLA sc in

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the linear PLLA/PDLA blend reaches to 250 °C with moderate molecular weights^[4]. Since the PLA sc shows higher melting temperature and more rapid crystallization rate than neat PLLA or PDLA specimens^[5], which provides potential for application at higher temperatures than neat PLA samples. However, when the molecular weights of PLA reach to a critical value (such as 60 kg/mol for the linear PLLA/PDLA blends), both PLA homochiral crystallites (hc) and sc would develop, and the phase separation between PLLA and PDLA occurs^[6]. The formation of hc would make the heat resist temperature of PLA sc materials similar to that of neat PLA specimens. Through elaborative research works, it is known that, apart from the molecular weights, the branched structure of PLA also has influence on the phase separate behavior of PLLA/PDLA blends^[7, 8]. Moreover, these two factors also affect the melting and crystallization behavior, such as melting temperature, crystallization temperature and their enthalpies^[9]. In addition, optical purity is another factor which has influence on the crystallization behaviors of PLLA/PDLA specimens^[10, 11]. According to previous reports, the melting temperature of PLA sc (T_{sc}) decreases with optical purity reducing^[12, 13]. However, the influence of optical purity on the phase separation behavior of PLLA/PDLA blends is still unclear. Since the PLA with 100% isotactic structure is very difficult to produce during manufacturing process or under nature circumstances. Thus, the crystallization and melting behaviors of PLA with different optical purity and its stereocomplex formation with its isomer are very important for its application. For this purpose, the PLLA/PDLA blends were prepared, and the influences of optical purity and molecular weight of PLA on the formation of PLA sc and hc were investigated in this study. This result could supply instructions for the application of PLLA/PDLA with different optical purities and molecular weights.

EXPERIMENTAL

Materials

The tin(II) 2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$, 95%) was bought from Sigma-Aldrich, and it was used as received. D-Lactide (D-LA) (optical purity $\geq 99.5\%$) was supplied by Changchun Sino Biomaterials Co., Ltd. (China), and was re-crystallized in dry ethyl acetate for three times. Isopropanol ($\geq 99.5\%$) was purchased from Aladdin, and was dehydrated under calcium hydride (CaH_2) for 24 before distillation. The toluene was refluxed with sodium and distilled under nitrogen prior to use.

The Synthesis of PLLA and PDLA

The PLLA samples with different optical purities were kindly supplied by Hisun Biomaterials Co., Ltd. (China), and which were polymerized from L-Lactide (L-LA) in bulk with the catalyst of $\text{Sn}(\text{Oct})_2$. The PDLA with different molecular weights were synthesized by ring-opening polymerization of D-LA, catalyzed by $\text{Sn}(\text{Oct})_2$ and initiated by isopropanol at 120 °C in anhydrous toluene, the molecular weight was regulated by the D-LA/isopropanol ratio^[14, 15]. The PLLA and PDLA polymers were purified by repeated precipitation, the dichloromethane was used as solvent and ethanol as the non-solvent. The products were dried at 60 °C in vacuum to constant weight before use. The physical properties of PLLA and PDLA used in this study were list in Table 1. The numbers after PLLA were their melting temperatures separately. In this study, all the weight average molecular weights of PLLA specimens were larger than 100 kg/mol, which could ignore the end group effect on their melting temperatures. The numbers after PDLA were their number average molecular weights, respectively.

Preparation of the PLLA/PDLA Cast Films

The PLLA/PDLA cast films were prepared according to literatures^[14, 15]. The given amount of PLLA (0.25 g) and PDLA (0.25 g) were separately dissolved in dichloromethane at a concentration of 10 g/L. After the specimens were dissolved completely, the solutions were admixed together, and the mixed solutions were vigorously stirred for 3 h immediately. Finally, the mixed solutions were poured onto petri-dishes ($d = 90$ mm) and the solvent was evaporated under room temperature for one day. The weight ratios of PLLA: PDLA in this study were fixed at 1:1. All the cast films were dried under vacuum condition to constant weight at 50 °C before use.

Table 1. The characterization of PLLA and PDLA

Code	PLLA149 ^a	PLLA156	PLLA161	PLLA173	PLLA177	PDLA21 ^b	PDLA42	PDLA67
M_n (kg/mol)	75.5	105.0	102.4	133.8	64.7	21.2	42.4	67.4
PDI	1.5	1.4	1.5	1.3	1.7	1.4	1.1	1.8
$[\alpha]_{20}$ (deg·cm ³ /dm·g)	−134.0 ^c	−139.0	−141.6	−151.4	−155.7	152.6	153.6	158.6
X_D (%)	8.4 ^a	6.8	6.0	3.0	1.6	97.4	97.7	99.3
T_m (°C)	148.6	155.5	161.2	173.1	176.2	169.7	175.2	176.9

^a The numbers after PLLA were their melting temperatures; ^b The numbers after PDLA were their number average molecular weights; ^c The optical rotation of PLLA with 100% L content was −161 deg·cm³/dm·g.

Characterization Methods

The number average molecular weights (M_n) and molecular weight distributions (PDI) were evaluated by a Waters gel permeation chromatography system (GPC) equipped with two Styragel HR gel columns *i.e.*, HR3 and HR4. Chloroform (CHCl₃) was used as the mobile phase, and the flow rate of mobile phase was fixed at 1 mL/min. The measurement was carried out at 35 °C. Monodispersed polystyrene standards purchased from Waters Co. with molecular weight ranging from 1790 g/mol to 2.0×10^5 g/mol were used to generate the calibration curve.

The specific optical rotation was measured in CHCl₃ solution at a concentration of 1.0 g/L at 20 °C, using a 341LC polarimeter (Perkin Elmer) equipped with a sodium lamp at a wave length of 589 nm. The D content in the specimens was calculated by the following equation:

$$X_D (\%) = 100 \times [([\alpha]_{20} - (-161)) / (161 - (-161))] \quad (1)$$

where −161 was the optical rotation value for PLLA with 100% L content^[16], and the $[\alpha]_{20}$ values were the optical rotations of PLLA and PDLA polymers.

The wide angle X-ray diffraction (WAXD) measurements were carried out on a Bruker D8 Advance X-ray diffractometer equipped with a Cu K α radiation, and the scanning angle ran at a speed of 3 (°)/min from 10° to 30°.

The thermal properties of specimens were performed on a differential scanning calorimeter (DSC, Q100, TA) under the nitrogen atmosphere. The specimens were heated at a constant rate of 10 K/min. The temperature and heat flow were calibrated with standard indium. The first heating of all the neat PLA specimens and PLLA/PDLA blends was recorded.

RESULTS AND DISCUSSION

The PLLA/PDLA67 Specimens

The WAXD profiles of the PLLA/PDLA67 specimens are shown in Fig. 1(a), it was found that the diffraction peaks at 14.8°, 16.9°, 19.1° and 22.5° were assigned to the α crystal of PLA hc. And the signals around 12.0°, 21.0° and 24.0° were ascribed to the diffraction of PLA sc^[3, 4, 17]. Both the diffraction peaks assigned to PLA hc and sc were observed in all the PLLA/PDLA67 blends, and all of them tended to enhance as optical purity increased, indicating that more content of PLA hc and sc formed in the specimens and the crystallization capacity enhanced with the optical purity of PLLA.

The DSC curves of PLLA/PDLA67 specimens with different optical purities of PLLA are presented in Fig. 1(b), and the thermal data calculated from the DSC curves are listed in Table 2. In all the specimens, the T_g appeared at 60–70 °C, and it increased gradually as the optical purity of PLLA enhanced. Weak and wide cold crystallization peaks were observed at 80–140 °C. The signals ranged from 140 °C to 180 °C should be assigned to the melting peaks of PLA hc. Between 140 and 180 °C, two endothermic signals were detected in most of the specimens, the lower one should be assigned to the melting signal of PLLA crystallites, because the lower melting peak increased as the optical purity improved, at the same time, the temperature at the peak (T_{hm1}) was similar to that values of PLLA list in Table 1. The higher one (T_{hm2}) could be attributed to the melting temperature of PDLA67 since it hardly changed in different specimens although the melting enthalpy varied in

different specimens. In addition, the endothermic signal at 200–230 °C could be ascribed to the melting of PLA sc, the T_{sc} increased gradually as the optical purity of PLLA increased. As the optical purity of PLLA increased, the sequence structure of PLLA became more uniform, and the capacity of stereocomplex formation between PLLA and PDLA was enhanced. Consequently, the T_{sc} increased and the content of sc (ΔH_{sc}) improved.

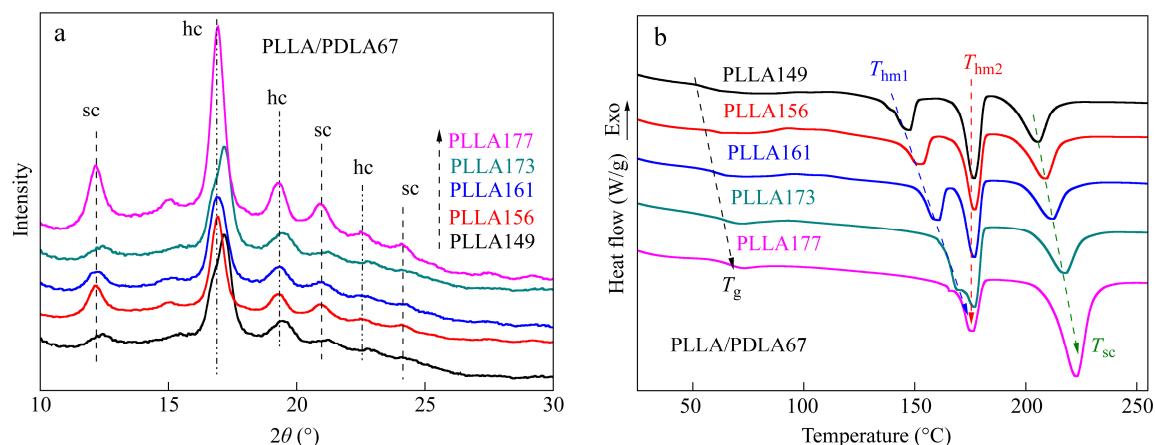


Fig. 1 The WAXD (a) and DSC (b) measurements of PLLA/PDLA67 specimens

Table 2. The thermal data of PLLA/PDLA specimens

		PLLA149	PLLA156	PLLA161	PLLA173	PLLA177
PDLA67	T_{hm1} (°C)	147.7	152.5	160.5	170.1	— ^a
	ΔH_{hm1} (J/g)	8.2	8.7	9.4	— ^a	— ^a
	T_{hm2} (°C)	176.7	176.9	176.5	176.9	176.0
	ΔH_{hm2} (J/g)	16.7	16.8	17.1	39.1 ^a	17.4 ^b
	T_{sc} (°C)	205.6	209.2	212.2	217.7	222.7
	ΔH_{sc} (J/g)	15.8	17.4	18.4	22.3	42.2
PDLA42	T_{hm1} (°C)	145.2	151.7	—	—	—
	ΔH_{hm1} (J/g)	1.7	1.3	—	—	—
	T_{hm2} (°C)	175.0	174.9	174.2	173.7	—
	ΔH_{hm2} (J/g)	16.4	12.5	3.8	4.3	—
	T_{sc} (°C)	209.7	212.6	216.6	222.6	228.5
	ΔH_{sc} (J/g)	37.2	39.9	57.4	60.3	86.5
PDLA21	T_{hm1} (°C)	—	—	—	—	—
	ΔH_{hm1} (J/g)	—	—	—	—	—
	T_{hm2} (°C)	169.0	168.7	168.6	—	—
	ΔH_{hm2} (J/g)	1.0	0.7	0.4	—	—
	T_{sc} (°C)	209.5	213.9	217.6	224.0	228.5
	ΔH_{sc} (J/g)	56.2	68.2	74.3	81.7	93.3

^a The peak is partially overlapped with that peak at 176 °C, and the ΔH_{hm1} could not be calculated accurately, then total ΔH_{hm} was calculated as 39.1 J/g; ^b In the PLLA177/PDLA67 specimen, the T_{hm} of PLLA177 was almost identical with that of PDLA67, thus, the total ΔH_{hm} was calculated as 17.4 J/g.

In the WAXD profiles of the PLLA/PDLA67 blends, the diffraction intensities of PLA sc were much lower than those of PLA hc. However, in the DSC thermogram, the signals assigned to PLA sc were more obvious, which should be explained from two aspects. On the one hand, the PLA sc could form after the PLLA and PDLA hc were melted. On the other hand, the PLA sc was not formed efficiently in the cast films due to the higher molecular weights, and the PLA sc formation proceeded again during heating (see the broad exothermic peaks at 80–140 °C in Fig. 1b). In these PLLA/PDLA67 blends, the stereocomplex formation was due to the hydrogen

bond interaction of the $\text{CH}_3\cdots\text{O}=\text{C}$ between enantiomeric PLAs^[18]. However, in the case of the PLA hc, the PLLA and PDLA should form homocrystallites, respectively, because if the PLLA and PDLA formed homocrystallites together, the PLA sc would form, rather than hc. Thus, it is rational to thought that parts of PLLA and PDLA molecular chains participated in stereocomplex formation, and some of others aggregated by themselves and formed homochiral crystallites, respectively, and they were respectively melted at different temperatures during heating. This result implied that parts of PLLA and PDLA67 molecular chains involved in the stereocomplex formation and produced PLA sc, and some other parts formed PLLA hc and PDLA hc, respectively. Thus, the phase separation between PLLA and PDLA67 partially took place and were evidently observed in the blends.

The PLLA/PDLA42 Specimens

The WAXD patterns of PLLA/PDLA42 blends are presented at Fig. 2(a). It was found that the diffractions assigned to PLA sc (12.0° , 21.0° , 24.0°) were obviously observed, and the diffraction peaks assigned to PLA hc crystallites were found at 14.8 , 16.9 and 19.1° . Additionally, the intensity of diffractions assigned to PLA hc was weaker than that of sc in these PLLA/PDLA42 blends, indicating that more content of sc than hc formed in the specimens. As the molecular weight of PDLA decreased from 67 to 42 kg/mol, the entanglement and viscosity decreased and the mobility of chain segments increased. Thus, the stereocomplex formation in the solution became effective, and the molecular chains which did not participate in the stereocomplex formation reduced and the formation of hc was depressed. As the optical purity of PLLA increased, the diffraction peaks assigned to PLA hc declined sharply in the blends, and these diffraction peaks disappeared in the PLLA177/PDLA42. On the contrary, the diffractions ascribed to PLA sc strengthened continuously as optical purity enhanced, which suggested that more sc formed with optical purity increasing.

The DSC thermograms of PLLA/PDLA42 specimens are exhibited in Fig. 2(b). On the whole, as the optical purity of PLLA increased, the signals at 60°C , which indicated the glass transition, weakened. The endothermic signals ranged from 140 – 180°C , which should be assigned to PLA hc, reduced gradually and disappeared finally. While the melting peak of PLA sc became larger and appeared at higher temperatures. Two endothermic peaks observed between 140 and 180°C in the PLLA149/PDLA42 and PLLA156/PDLA42 specimens, the lower one should be assigned to the melting of PLLA and the higher one was the melting peak of PDLA42 (Table 2). However, only one melting peak was detected at 175°C in PLLA161/PDLA42 and PLLA173/PDLA42 specimens, which would be ascribed to the melting peak from PDLA42. In the case of PLLA177/PDLA42, none obvious endothermic signal was observed at that temperature range, and only one endothermic signal observed around 230°C , which suggested that the PLA sc exclusively formed in this blend.

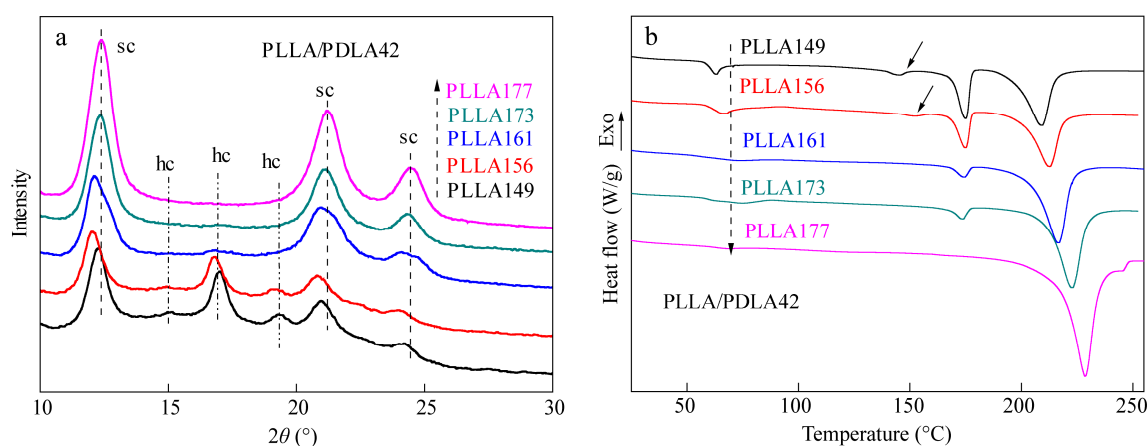


Fig. 2 The WAXD (a) and DSC (b) measurements of PLLA/PDLA42 specimens

The WAXD and DSC results of PLLA/PDLA42 specimens revealed that, beside the formation of PLA sc, the PDLA hc and PLLA hc respectively formed in the PLLA149/PDLA42 and PLLA156/PDLA42 specimens. While both the PLA sc and the PDLA hc formed in the PLLA161/PDLA42 and PLLA173/PDLA42 specimens. And only PLA sc formed in the PLLA177/PDLA42 blend. These results suggested that the phase separation was obviously observed in the PLLA/PDLA42 blends with relative lower optical purities (PLLA149/PDLA42 and PLLA156/PDLA42), and PLA sc, PLLA hc and PDLA hc formed. This phase separation behavior weakened as the optical purity of PLLA increasing (PLLA161/PDLA42 and PLLA171/PDLA42) and PLA sc and PDLA hc formed. And the separation behavior disappeared in the highest optical purity specimen (PLLA177/PDLA42) since PLA sc formed solely. These results implied that the phase separation behavior in the PLLA/PDLA42 specimens was influenced by the optical purity of PLLA.

The PLLA/PDLA21 Specimens

In the WAXD of the PLLA/PDLA21 specimens (Fig. 3a), the diffraction peaks assigned to PLA sc were obviously observed in all the specimens. In the PLLA/PDLA21 specimens with relative lower optical purity, besides the diffractions of PLA sc, a very weak diffraction at 16.9° appeared, and which should be due to the formation of PLA hc, indicating that tiny amount of PLA hc formed, and the weak phase separation occurred. As optical purity of PLLA increasing, the diffraction peaks belonged to PLA sc strengthened and the diffractions assigned to PLA hc disappeared finally.

The DSC thermograms of the different PLLA/PDLA21 cast films are shown in Fig. 3(b), and the DSC data are listed in Table 2. In the PLLA149/PDLA21, PLL156/PDLA21 and PLLA161/PDLA21 blends, apart from a major endothermic peak $\sim 210^\circ\text{C}$, a weak peak appeared at *ca.* 169°C . In the other specimens, only one endothermic signal appeared around 220°C . The signals at *ca.* 169°C should be assigned to the melting of hc from PDLA21, because it was similar to the melting temperature of neat PDLA21 listed in Table 1, and the signals above 200°C were ascribed to the melting of PLA sc. The T_{sc} increased as the optical purity of PLLA increased. The WAXD and DSC results hinted that a large amount of PLA sc formed and few hc developed in the PLLA/PDLA21 blends, and the phase separation behaviors between PLLA and PDLA21 were not obvious.

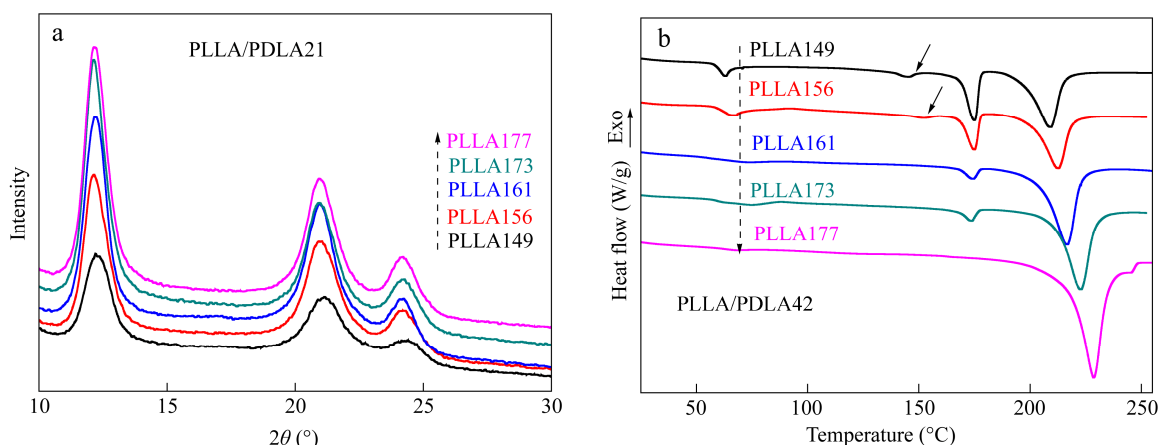


Fig. 3 The WAXD (a) and DSC (b) measurements of PLLA/PDLA21 specimens

All the above WAXD and DSC results heralded that, PLA sc formed in all the blends regardless of the molecular weights of PDLA and optical purity of PLLA. However, the PLA hc formed in the PLLA/PDLA specimens with lower optical purity of PLLA or higher molecular weight of PDLA. The contents of PLA hc and sc calculated from DSC are schemed as Fig. 4 and listed in Table 2. In the PLLA/PDLA67 specimens, because of both the molecular weights of PLLA and PDLA were higher than 60 kg/mol , apart from the PLA sc, most of the samples presented two melting signals of PLA hc, which indicated that the obvious phase separation happened in all the specimens. In the PLLA/PDLA42 specimens with lower optical purities, two endothermic

signals were observed at 140–180 °C as well as the signals around at 210 °C, this phenomenon indicated that the PLLA and PDLA42 formed hc separately, and phase separation between PLLA and PDLA42 happened. As optical purity increased, the signal assigned to PLLA hc reduced and disappeared, but PDLA hc and PLA sc still formed. Finally, only PLA sc observed in the PLLA/PDLA42 specimens with the highest optical purity, which suggested that the phase separation behaviors between PLLA and PDLA were not only influenced by the molecular weights of PLLA and PDLA samples, but also affected by the optical purity of polymers. In the PLLA/PDLA21 blends with lower optical purities, after the stereocomplex formed between PLLA and PDLA, a small amount of PDLA hc formed in the blends with relatively lower optical purities. As the optical purity increased, only PLA sc was detected, and the phase separation was not obvious in all the PLLA/PDLA21 blends.

In the same PLLA specimens, as the molecular weight of the PDLA decreased, the ΔH_{sc} and T_{sc} increased (Table 2 and Fig. 4), while the ΔH_{hm} decreased as the molecular weight of PDLA decreased, and T_{hm} did not vary obviously. As the molecular weight decreased, the chain entanglement decreased, and the mobility of chain segments increased, more molecular chains participated in the stereocomplex formation. Thus, the interaction between enantiomeric PLAs was enhanced, and the stereocomplex formed efficiently, and the lamellar thickness of sc also improved. Then, less chain segments were left to form hc, and the content of hc reduced.

In the same PDLA specimens, as the optical purity of PLLA increased, the ΔH_{sc} and T_{sc} increased progressively. In contrast, the ΔH_{hm} reduced in the PLLA/PDLA21 and PLLA/PDLA42 specimens, although the T_{hm} did not change apparently. As the optical purity was enhanced, the sequential structure of the molecular chain improved, and the intensity of hydrogen bond between isomers intensified, as a result, the stereocomplex formation was enhanced. However, in the PLLA/PDLA67 specimens, because both the molecular weights of PLLA and PDLA were larger than 60 kg/mol, the phase separation obviously occurred between PLLA and PDLA, and the crystallization capacity was enhanced as optical purity increased. Accordingly, both the ΔH_{sc} and ΔH_{hm} tended to increase in most of specimens.

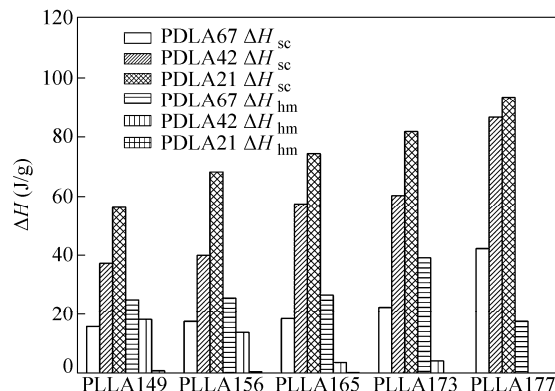


Fig. 4 The content of ΔH_{sc} and ΔH_{hm} in the PLLA/PDLA blends with different optical purities and molecular weights (The ΔH_{hm} was the total melting enthalpy of the ΔH_{hm1} and ΔH_{hm2} .)

CONCLUSIONS

In this study, the PLLA/PDLA blends were investigated through varying optical purities of PLLA and the molecular weights of PDLA. WAXD and DSC results suggested that, the molecular weights and optical purities did not vary the structure of PLA homochiral and stereocomplex crystals, and the stereocomplex crystallites preferentially formed in all the blends. As the molecular weight of PDLA decreased from 67 kg/mol to 21 kg/mol, the formation of PLA stereocomplex became more efficient and the melting temperature of PLA stereocomplex increased, while the content of homochiral crystallites reduced. The melting temperature and content of PLA stereocomplex crystallites increased as the optical purity of PLLA was enhanced. Compared to the neat PLLA and PDLA specimens, the melting temperature of PLA hc did not vary evidently in the

PLLA/PDLA blends although the melting enthalpy of PLA homocrystallites varied intensively. As the molecular weight decreased and the optical purity increased, the total number of crystal phases of the PLLA/PDLA specimens decreased from three (PLA sc, PLLA hc and PDLA hc) to two (PLA sc and PDLA hc) and one (PLA sc) at last. This investigation indicated that the phase separation behavior of the PLLA/PDLA blend was not only influenced by the molecular weights, but also affected by the optical purities of PLA. This study would provide a deeper understanding of the phase separation behaviors of the PLLA/PDLA blends.

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