Chinese Journal of
POLYMER SCIENCE

ARTICLE

https://doi.org/10.1007/s10118-021-2588-x
Chinese J. Polym. Sci. **2021**, *39*, 1470–1480

Mixing of Racemic Poly(L-lactide)/Poly(D-lactide) Blend with Miscible Poly(D,L-lactide): Toward All Stereocomplex-type Polylactide with Strikingly Enhanced SC Crystallizability

Yi-Long Ju, Xiang-Li Li, Xing-Yuan Diao, Hong-Wei Bai*, Qin Zhang, and Qiang Fu*

College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, China

Electronic Supplementary Information

Abstract Stereocomplex-type polylactide (SC-PLA) consisting of alternatively arranged poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) chains has gained a good reputation as a sustainable engineering plastic with outstanding heat resistance and durability, however its practical applications have been considerably hindered by the weak SC crystallizability. Current methods used to enhance the SC crystallizability are generally achieved at the expense of the precious bio-renewability and/or bio-degradability of PLAs. Herein, we demonstrate a feasible method to address these challenges by incorporating small amounts of poly(D,L-lactide) (PDLLA) into linear high-molecular-weight PLLA/PDLA blends. The results show that the incorporation of the atactic PDLLA leads to a significant enhancement in the SC crystallizability because its good miscibility with the isotactic PLAs makes it possible to greatly improve the chain mixing between PLLA and PDLA as an effective compatibilizer. Meanwhile, the melt stability (*i.e.*, the stability of PLLA/PDLA chain assemblies upon melting) could also be improved substantially. Very intriguingly, SC crystallites are predominantly formed with increasing content and molecular weight of PDLLA. More notably, exclusive SC crystallization can be obtained in the racemic blends with 20 wt% PDLLA having weight-average molecular weight of above 1×10^5 g/mol, where the chain mixing level and intermolecular interactions between the PLA enantiomers could be strikingly enhanced. Overall, our work could not only open a promising horizon for the development of all SC-PLA-based engineering plastic with exceptional SC crystallizability but also give a fundamental insight into the crucial role of PDLLA in improving the SC crystallizability of PLLA/PDLA blends.

Keywords Polylactide; Stereocomplex; Crystallization; Melt stability; Melt memory

Citation: Ju, Y. L.; Li, X. L.; Diao, X. Y.; Bai, H. W.; Zhang, Q.; Fu, Q. Mixing of racemic poly(L-lactide)/poly(D-lactide) blend with miscible poly(D,L-lactide): toward all stereocomplex-type polylactide with strikingly enhanced SC crystallizability. *Chinese J. Polym. Sci.* **2021**, *39*, 1470–1480.

INTRODUCTION

In response to the petroleum resource shortage and environmental pollution issues aggravated by the excessive consumption and careless disposal of traditional synthetic plastics, scientists and engineers worldwide have geared continuous efforts to engineer fully biodegradable alternatives derived from 100% biorenewable resources over the past decades.[1−3] Polylactide (PLA) has emerged as an increasingly popular sustainable polyester that can compete with existing commodity plastics in performance (*e.g.*, biocompatibility, mechanical strength, nontoxicity, transparency and processability).[4−6] To data, with the continuous plunge in production cost, PLA has enjoyed great success in some commercial applications, such as biomedicine, packaging and other disposable commodities.[7,8] Unfortunately, the competitive edge of PLA over the common engineering plastics (*e.g.*, poly(butylene terephthalate) (PBT) and nylon) has been considerably hindered by its insufficient heat resistance and durability (associated with the hydrolysis during its service life).[9−12] Owing to the chiral nature of lactic acid used for polymerization, PLA exists as three stereochemical forms including poly(L-lactide) (PLLA), poly(D-lactide) (PDLA), and poly(D,L-lactide) (PDLLA). Fascinatingly, the blending of PLLA and PDLA can form unique stereocomplex crystallites (SCs) by compact side-by-side co-crystallization between the two PLA enantiomers.[13−19] In comparison with enantiopure PLA homocrystals (HCs), the SCs consisting of more compactly packed PLLA/PDLA chains exhibit much higher resistances to heat deformation and hydrolytic degradation.[20−25] Particularly, the melting temperature of SCs (T_m, 220–240 °C) is around 50–60 °C higher than that of HCs, which enables PLA to withstand elevated temperatures of nearly 200 °C.[13] Beyond that, the stereocomplexation is verified to endow the PLLA/PDLA blends with superior mechanical strength and modulus, toughness, and chemical resistance.[26−29] Thus, SC-type PLA (SC-PLA) has attracted growing interests recently due

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* Corresponding authors, E-mail: hongweibai@scu.edu.cn, bhw_168@163.com (H.W.B.)
E-mail: qiangfu@scu.edu.cn (Q.F.)

Received March 2, 2021; Accepted April 11, 2021; Published online June 15, 2021

to its tremendous application potential as a next-generation engineering plastic possessing exceptional sustainability and physicochemical properties.

SC-PLA can be easily prepared by either solution or melt mixing of equimolar PLLA and PDLA.[14,15] However, it is extremely challenging to attain useful SC-PLA products through melt-processing of well-stereocomplexed PLLA/PDLA blends possessing high molecular weights (typically M_w≥10^5 g/mol, which is an essential prerequisite for achieving favorable thermomechanical properties and processability)[30,31] because their SC crystallizability is too weak to stimulate the excusive SC formation during melt-crystallization. In general, large amounts of HCs are preferentially formed in melt-processed products along with the SCs, which undoubtedly gives rise to significantly impaired properties.[31−37] It means that the high performance of SC-PLA materials can hardly be transferred into final products. As such, enhancing the SC crystallizability becomes a vital issue to fully exploit the potential of SC-PLA.[38−40] The weak SC crystallizability has been believed to arise from the insufficient chain mixing between the PLA enantiomers[14,41−45] and inadequate melt stability (*i.e.*, the PLLA/PDLA chain clusters cannot preserve their steteoselective interactions upon melting and then the PLAs chains separated from the clusters could distribute randomly or even demix into PLLA- and PDLA-rich domains).[34−36,46−49] When compared with the blend melts consisting of phase-separated or randomly-distributed PLLA and PDLA chains, the existence of abundant PLLA/PDLA chain clusters makes it easier for the melt to exclusively crystallize into SCs because of the much shorter chain diffusion pathway and lower kinetic barrier.[35,41−50] In this scenario, many strategies have been proposed to enhance the SC crystallizability of SC-PLA by improving the chain mixing degree and/or melt stability, such as stereoblock copolymerization,[51,52] synthesis of special PLAs with complex molecular architectures (*e.g.*, star-shaped and comblike PLAs),[34,50,53−57] selective cross-linking[35] and use of processing additives (*i.e.*, compatibilizers,[47,58] nucleators,[59−62] and plasticizers).[63,64] Most of these approaches involve complicated chain modification reactions or tedious synthesis procedures. Meanwhile, some toxic reactants (*e.g.*, isocyanate) are frequently used. By contrast, the addition of highly efficient compatibilizers into commercial linear high-M_w PLLA/PDLA blends is a simpler, greener and more cost-effective way toward SC-PLA materials with exceptional SC crystallizability. Unfortunately, despite several compatibilizers have been proved to be effective in enhancing the SC crystallizability, their compatibilizing efficiency is rather low. For instance, Pan *et al.*[50,58] have successfully used the miscible poly(vinyl phenol) (PVPh) and poly(vinyl acetate) (PVAc) to enhance the SC crystallizability of PLLA and PDLA by constructing plentiful hydrogen bonds in the blends, respectively, but at least 30 wt% PVPh or 75 wt% PVAc is needed for the exclusive SC crystallization. Besides, Samuel *et al.*[65] found that the sole formation of SCs in PLLA/PDLA blends under non-isothermal crystallization conditions can only be realized when the content of miscible poly(methyl methacrylate) (PMMA) is higher than 30 wt%−40 wt%. More seriously, in the current compatibilization strategy for PLLA/PDLA blends, the precious sustainable attributes of PLA are substantially impaired with the incorporation of these petroleum-derived and non-biodegradable compatibilizers. It is therefore highly desirable to develop bio-derived and biodegradable compatibilizers capable of efficiently enhancing the SC crystallizability so as to meet the growing demand for full sustainable SC-PLA products.

Inspired by the compatibilization of immiscible polymer blends using A-B type block copolymers, Fukushima *et al.*[47] have attempted to use the stereoblock PLA (sb-PLA) as a compatibilizer to enhance the SC formation in racemic PLLA/PDLA blends. It was found that the sb-PLA can markedly suppress the homocrystallization and simultaneously promote the SC crystallization in a certain extent, especially for those with low molecular weights (*e.g.*, M_w=3.9×10^4 g/mol), indicating a feasible route to prepare all SC-PLA with essentially enhanced SC crystallizability. However, the compatibilizing efficiency of the sb-PLA is also unsatisfactory (the added amount is as high as 30 wt%) probably because the preferential stereocomplexation between adjacent L- and D-blocks makes it difficult for many enantiomeric blocks to collaborate with PLLA and PDLA chains. Moreover, both the melt-processability and end-use properties of SC-PLA could be remarkably deteriorated with the incorporation of large amounts of low-M_w sb-PLA.

To address these challenges, in this work, PDLLA was selected as a potential compatibilizer in the preparation of all SC-PLA with strikingly enhanced SC crystallizability from linear high-M_w PLLA/PDLA blends. It has been verified that the PDLLA is miscible with PLLA or PDLA over the whole composition range,[66] and thereby the intermolecular interactions between the two enantiomers were excepted to be notably enhanced by the PDLLA. Meanwhile, the PDLLA is completely amorphous due to the random distribution of L- and D-lactic acid units,[67,68] which could interact more efficiently with the enantiomeric PLLA/PDLA chains as compared to the sb-PLA possessing strong crystallizability. Both of them are favorable to the enhancement in the melt stability of SC-PLA. Furthermore, the incorporation of PDLLA could facilitate the homogeneous mixing of high-M_w PLLA and PDLA chains during the melt mixing. The isothermal and non-isothermal crystallization behaviors of PLLA/PDLA blends with different contents of PDLLA were examined, with a special attention on the competitive homocrystallization and SC crystallization. The plausible mechanism for the PDLLA-promoted SC crystallization at molecular level is discussed. Also, the important role of the PDLLA molecular weight in tailoring the SC crystallizability of the racemic blends has been highlighted for the first time.

EXPERIMENTAL

Materials

PLLA (M_w=1.7×10^5 g/mol, PDI=1.7, D-lactic acid content=1.5%) and PDLA (M_w=1.3×10^5 g/mol, PDI=1.6, L-lactic acid content=0.7%) were purchased from NatureWorks LLC (USA) and Zhejiang Hisun Biomaterial Co., Ltd. (China), respectively. PDLLA with different M_ws (between 0.1×10^5 and 1.5×10^5 g/mol), synthesized by ring-opening polymerization of D,L-lactide cyclic dimers, was obtained from Jinan Daigang Biomaterial Co., Ltd. (China). Because the sequence distribution of L- and D-lactic acid units is random in the backbones (as confirmed by the exclusive existence of syndiotactic L/D hexads (iisii, isiii, iisis, sisii, sisis, and isisi[36,69,70]) in the ^{13}C-NMR spectra in Fig. 1a),

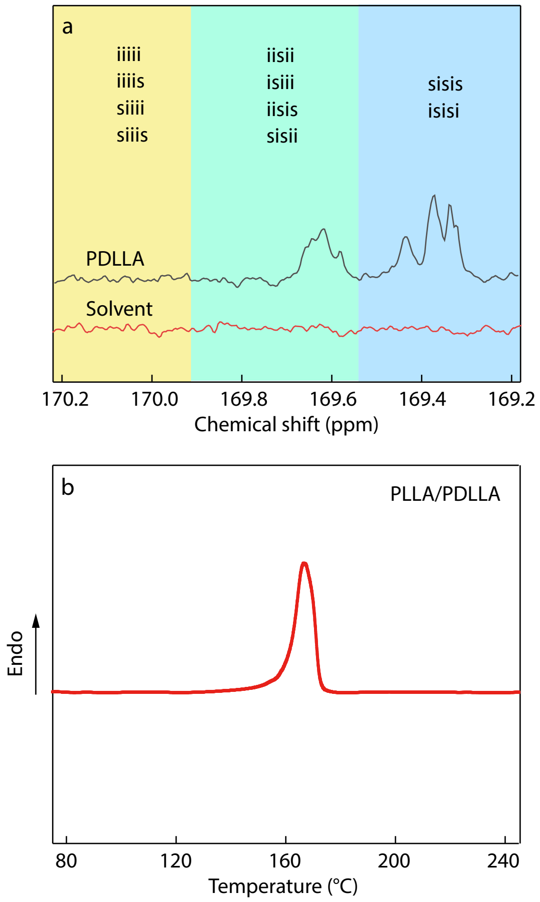

Fig. 1 (a) Carbonyl carbon resonances in the ^{13}C-NMR spectra of PDLLA, and (b) DSC heating curve of PLLA/PDLLA (50/50) blend melt-crystallized at a cooling rate of 5 °C/min. The M_w of the PDLA used is 1.5×10^5 g/mol.

PDLLA does not have the ability to crystallize (Fig. S1 in the electronic supplementary information, ESI). Prior to use, all PLA pellets were dried overnight at 50 °C under vacuum.

Sample Preparation

The PLLA/PDLA (50/50) blends with different amounts of PDLLA (0 wt%–25 wt%) were prepared by solution mixing using dichloromethane (DCM) as a solvent, according to the following protocol. Briefly, the pre-weighted PLLA, PDLA and PDLLA were separately dissolved in DCM (about 20 g/L in concentration) at room temperature and subsequently mixed together under vigorous stirring for at least 1 h. The mixed solution was poured into an excess amount of methanol (used as a precipitation solvent) to give a white flocculent precipitate, followed by the vacuum filtration and vacuum-drying at 50 °C to completely remove the residual solvents. For convenience, the obtained PLLA/PDLA/PDLLA blends were denoted as LD-*x*, in which *x* represents the weight fraction of PDLLA. In order to analyze the SC crystallizability between PDLLA and PLLA (or PDLA), PLLA/PDLLA (50/50) binary blends were also prepared using the same mixing procedure.

Characterization

Differential scanning calorimetry (DSC)

DSC analysis was performed on a DSC 8000 calorimeter (PerkinElmer, USA) under a dry nitrogen flow (20 mL/min). The thermal protocols used in different melt-crystallization processes are presented as follows. In the non-isothermal crystallization, the specimens (5–6 mg) were first heated from 30 °C to 250 °C at a scan rate of 10 °C/min and persisted at this temperature for 3 min to erase any thermal history. Then, they were cooled to 30 °C at a rate of 5 °C/min, followed by another heating to 250 °C at 10 °C/min. Specially, this DSC cycle was repeated for three times to examine the melt stability of the blends. In the case of isothermal crystallization, the specimens were quenched (at 150 °C/min) to a pre-determined temperature (100–160 °C) after being melted at 250 °C for 3 min and persisted at this temperature until the crystallization finished. Then, they were reheated to 250 °C at 10 °C/min to analyze the melting behaviors.

The crystallinity values of homocrystallites ($X_{c,HC}$) and SCs ($X_{c,SC}$) were estimated from the second DSC heating curves, based on the following equations:

$$X_{c,HC} = \frac{\Delta H_{m,HC}}{W \times \Delta H^0_{m,HC}} \tag{1}$$

$$X_{c,SC} = \frac{\Delta H_{m,SC}}{W \times \Delta H^0_{m,SC}} \tag{2}$$

$$X_c = X_{c,HC} + X_{c,SC} \tag{3}$$

where $\Delta H_{m,HC}$ and $\Delta H_{m,SC}$ are the measured melting enthalpies of homocrystallites and SCs, respectively; $\Delta H^0_{m,HC}$ and $\Delta H^0_{m,SC}$ are the melting enthalpies of infinitely sized homocrystallites (92 J/g[30]) and SCs (142 J/g[30]), respectively; and *W* is the weight fraction of PLLA/PDLA component in the blends.

The relative fraction of SCs (f_{SC}) in total crystal phase (*i.e.*, homocrystallites and SCs) of the blends was calculated according to the following equation:

$$f_{SC} = \frac{X_{c,SC}}{X_{c,SC} + X_{c,HC}} \times 100\% \tag{4}$$

Wide angle X-ray diffraction (WAXD)

WAXD measurements were carried out on a X'Pert pro MPD X-ray diffractometer (PANalytical, Holland), which was equipped with a Cu K*α* radiation (*λ*=0.154 nm, 40 kV and 40 mA). The WAXD patterns were recorded in a 2*θ* range of 5°–40°.

^{13}C nuclear magnetic resonance (^{13}C-NMR)

^{13}C-NMR spectrum (400 MHz) was recorded on a Bruker Avance II-400 MHz NMR spectrometer (Germany) at room temperature, using $CDCl_3$ as solvent.

RESULTS AND DISCUSSION

Miscibility

It has been reported that the stereoregularity of PLA has a significant effect on its glass transition temperature (T_g) and the T_g value of PDLLA is much lower than that of PLLA or PDLA,[5,66] so the miscibility between the PDLLA and PLLA/PDLA blend component can be checked by the change of their T_g values upon mixing. Herein, DSC was used as a highly sensitive tool to distinguish the T_g values of the high-M_w blend components. Fig. 2(a) shows the DSC heating curves of amorphous PLLA/PDLA blends with different contents of PDLLA (its M_w is around 1.5×10^5 g/mol) obtained by complete melting and

https://doi.org/10.1007/s10118-021-2588-x

subsequent ice-water quenching. As expected, all blends exhibit a single and composition-dependent T_g that is located between the T_g values of PDLLA (52.5 °C) and PLLA/PDLA component (60.9 °C), vividly indicating the intermolecular interaction between the PLAs chains is strong and the PLLA/PDLA/PDLLA blends are miscible over the composition range investigated. Meanwhile, the T_g of the blends is found to gradually shift to lower temperature with increasing PDLLA content up to 20 wt% (Fig. 2b). The decreased T_g suggests that the presence of miscible PDLLA could behave as plasticizer to enhance the chain mobility of PLLA and PDLA.

Non-isothermal Crystallization

In order to explore the SC crystallizability of high-M_w PLLA/PDLA/PDLLA blends, their melt-crystallization behaviors and kinetics were analyzed under both non-isothermal and isothermal conditions by using DSC and WAXD. Figs. 3(a) and 3(b) present the DSC cooling and subsequent heating curves of PLLA/PDLA blends with different contents of PDLLA, respectively. Based on these DSC results, some important thermal

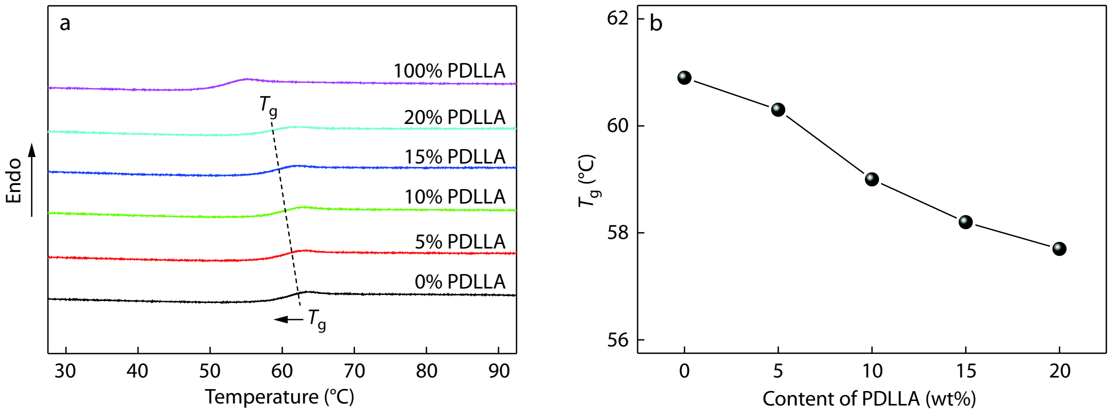

Fig. 2 (a) DSC heating curves of amorphous PLLA/PDLA blends with various amounts of high-M_w PDLLA in the glass transition region; (b) Plot of T_g values determined from the DSC heating curves as a function of PDLLA amount.

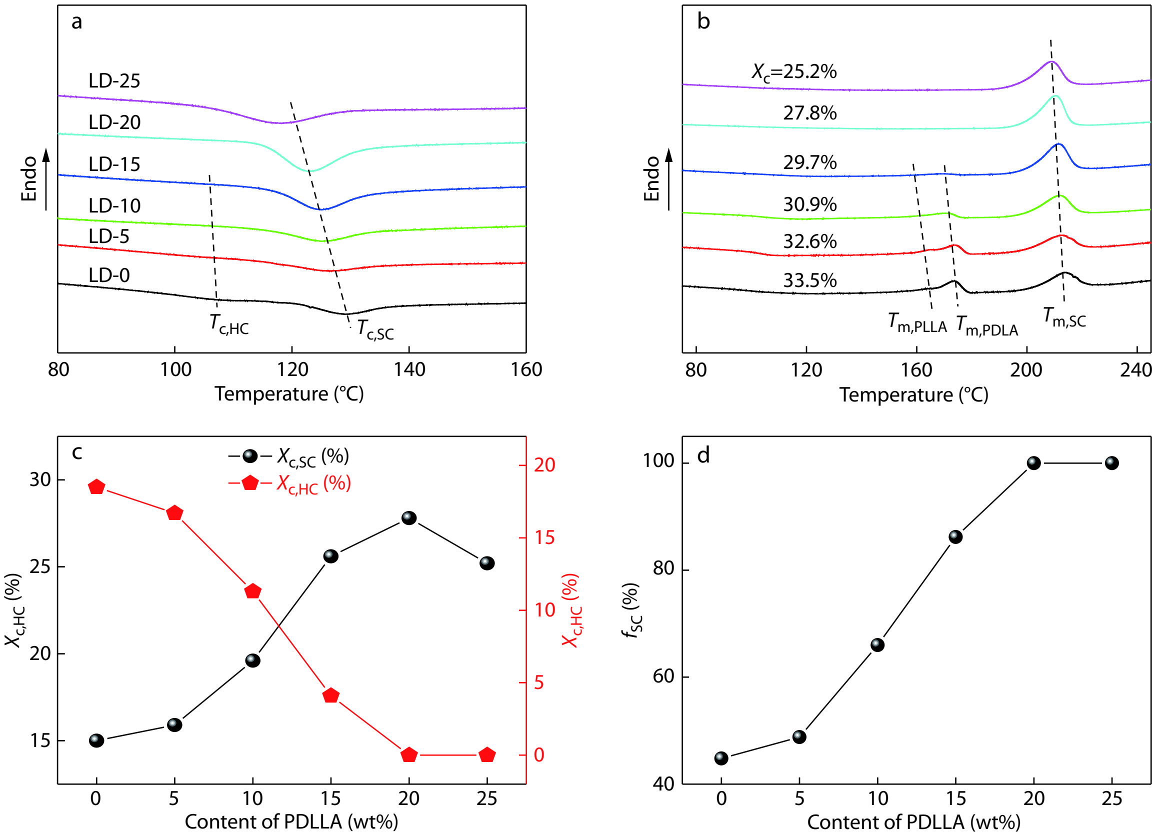

Fig. 3 DSC thermograms of PLLA/PDLA blends with various amounts of high-M_w PDLLA recorded during (a) non-isothermal melt-crystallization at a rate 10 °C/min and (b) subsequent heating processes at a rate of 5 °C/min. (c) Crsytallinity and (d) f_{SC} values as a function of PDLLA amount.

parameters including crystallinity of homocrystallites ($X_{c,HC}$), crystallinity of SCs ($X_{c,SC}$), and the relative fraction of SCs (f_{SC}) were calculated, as plotted in Figs. 3(c) and 3(d). As presented in Fig. 3(a), the presence of PDLLA has a remarkable influence on the non-isothermal melt-crystallization of the PLLA/PDLA component. For the PLLA/PDLA blend, two exothermic crystallization peaks are observed at around 130 and 105 °C upon cooling, which should be assigned to the SC crystallization ($T_{c,SC}$) and homocrystallization ($T_{c,HC}$), respectively.[16] Moreover, the melting endothermic peak of SCs appearing at 200–220 °C is weaker than that of HCs at 160–180 °C upon subsequent heating (Fig. 3b) and the $X_{c,HC}$ is about twice of $X_{c,SC}$ (Fig. 3c), proving that the HCs are predominantly formed in the non-isothermal crystallization of the high-M_w PLLA/PDLA blend (the f_{SC} is only about 42%, Fig. 3d). It should be mentioned that the T_m of PLLA HCs is evidently lower than that of PDLA ones due to its lower optical purity (Fig. S2 in ESI). However, with the increasing PDLLA content, the melting peak area of SCs increases while that of HCs decreases significantly (Fig. 3c), indicating that the addition of high-M_w PDLLA can efficiently promote the SC crystallization and also suppress the homocrystallization in racemic PLLA/PDLA blends. Interestingly, when the PDLLA content increases to 20 wt%, the melting peak of HCs vanishes completely and thereby only the stronger melting peak of SCs can be seen in the subsequent heating curve (Fig. 3b), which is indicative of the exclusive formation of large amount of SCs. In this case, the $X_{c,SC}$ and f_{sc} are increased from 15.0% to 27.8% and 42% to 100%, respectively. It should be noted that further increment of PDLLA content (*e.g.*, 25 wt%) is detrimental to the SC formation, as evidenced by the obviously decreased $X_{c,SC}$. It implies that, although PDLLA can facilitate the exclusive formation of SCs in PLLA/PDLA blends, the presence of excess PDLLA chains could also disturb the SC crystallization. Besides, a continuous decrease in the $T_{c,SC}$ (from 130 °C to 117 °C) is clearly observed with increasing high-M_w PDLLA content from 0 wt% to 25 wt% (Fig. 3a), which should be ascribed to the dilution effect of non-crystallizable PDLLA on the PLLA/PDLA component because the PDLLA cannot participate in SC crystallization (no melting endothermic peak of SCs can be identified in the DSC heating curve of PLLA/PDLLA blend, Fig. 1b) and then higher energy is required for the diffusion of PLLA and PDLA chains from miscible blend melts to the growth sites of SCs during the melt-crystallization process.[16]

The crystalline composition of PLLA/PDLA/PDLLA blends crystallized under the same non-isothermal condition (*i.e.*, cooling from 250 °C to 50 °C at a rate of 10 °C/min, which was performed by using a Linkam THMS 600 hot stage), was further analyzed by WAXD, and the results are depicted in Fig. 4. In the WAXD patterns, the characteristic diffraction peaks of HCs appear at around 16.9°, 19.0° and 22.3°, while those of SCs locate at around 12.0°, 20.8° and 23.9°.[16] Expectedly, the strong characteristic peaks of HCs as well as the weak peaks of SCs can be observed in the WAXD pattern of the PLLA/PDLA blend without PDLLA, confirming the preferential formation of HCs over SCs. With the increasing PDLA content, the characteristic peak area of HCs decreases sharply and that of SCs increases evidently, which further demonstrates that the HC formation is suppressed and the SC formation is facilitated by the incorporated PDLLA chains at the same time. When the PDLLA content reaches 20 wt%, the characteristic peaks of HCs disappear completely, indicating that the SCs are exclusively formed during the crystallization of the blend. These results are well consistent with the DSC data shown in Fig. 3.

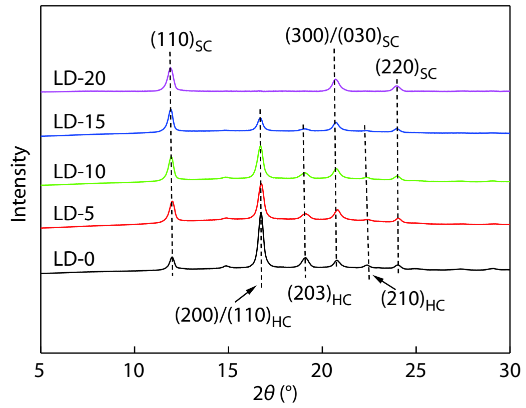

Fig. 4 WAXD patterns of PLLA/PDLA/PDLLA blends after non-isothermal crystallization (from 250 °C to 50 °C at a cooling rate of 10 °C/min).

On basis of the above non-isothermal crystallization results, it can be tentatively concluded that incorporating sufficient amounts (*e.g.*, 20 wt%) of high-M_w PDLLA into racemic PLLA/PDLA blends can substantially enhance the SC crystallizability between PLLA and PDLA chains. It also implies that these blends could have good melt stability under non-isotheral crystallization conditions, which can be verified by applying continuous DSC heating/cooling/heating cycles of the PLLA/PDLA blend with 20 wt% PDLLA. As displayed in Fig. 5, the exclusive SC formation is found to be completely reversible during the successive melting and recrystallization processes. More notably, the $T_{c,SC}$, $T_{c,HC}$ and $X_{c,SC}$ do not compromise significantly in three thermal cycles, suggesting that the blend melt consisting of PLLA/PDLA chain clusters could be sufficiently stable to survive upon melting. This intriguing finding demonstrates that mixing of PLLA/PDLA blends with miscible PDLLA can give all SC-PLA with exceptional melt stability.

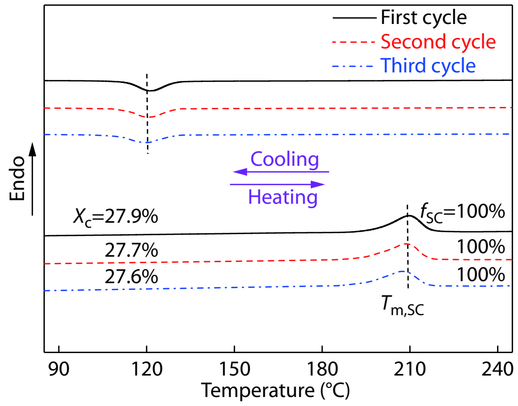

Fig. 5 DSC thermograms of PLLA/PDLA blend with 20 wt% PDLLA recorded during multiple heating-cooling-heating cycles. The heating and cooling rates were set as 10 and 5 °C/min, respectively.

Isothermal Crystallization

Considering that the crystallization temperature (T_c) of PLLA/PDLA/PDLLA blends varies with the PDLLA content in the non-isothermal crystallization process (Fig. 3a), their isothermal crystallization behaviors were also studied in a wide T_c range of 120–160 °C by using DSC so as to further explore the SC crystallizability and melt stability. Fig. 6 shows the DSC curves of some representative blends collected during isothermal crystallization at various T_cs and subsequent heating scans. In some isothermal crystallization curves, two exothermic peaks (the headmost one is associated with the SC crystallization and the other one is related to the homocrystallization[48]) can be observed, as highlighted by the arrows. Clearly, the PLLA/PDLA binary blend exhibits not only the characteristic crystallization peaks (Fig. 6a) but also the melting peaks (Fig. 6b) of both HCs and SCs. Moreover, the f_{SC} values are found to be lower than 32% after isothermal crystallization at all T_cs, indicating the preferential formation of HCs due to the poor melt stability. Fascinatingly, with the incorporation of 20 wt% PDLLA into the blend, the SC crystallization is decelerated slightly (as evidenced by the increased peak-time (t_p) for SC crystallization) but SCs are predominantly formed (Figs. 6c and 6d). Especially, when T_c is above 140 °C, the exclusive SC formation can be triggered, revealing that the incorporation of PDLLA chains does not evidently restrict the crystallization of the enantiomeric PLA chains but endow the racemic blends with substantially enhanced melt stability and SC crystallizability. Furthermore, it should be noted that the formation of a small amount of HCs during the isothermal crystallization at a low T_c of 120 °C implies that there are still some PLLA- and PDLA-rich domains in the blend because the optimum crystallization temperature for SC crystallization is higher than that for homocrystallization (Fig. 3a), the exclusive formation of SCs in the non-isothermal crystallization and isothermal crystallization at high T_c (*e.g.*, 140–160 °C) can be reasonably explained by the strong suppressing effect of the precedingly formed SCs on the homocrystallization in PLLA- and PDLA-rich domains.

Fig. 7 shows the effect of PDLLA content on the isothermal crystallization behaviors of PLLA/PDLA/PDLLA blends. Obviously, although increasing PDLLA content leads to a slightly decelerated SC crystallization of the blends (the t_p is increased from 3.0 min to 5.5 min, Fig. 7a), the f_{SC} is found to remarkably increase without compromising the $X_{c,SC}$ and $T_{m,SC}$ (Figs. 7b–7d). More interestingly, the critical content of PDLLA required for triggering excusive SC formation in the melt-crystallization of high-M_w PLLA/PDLA blends is *ca.* 20 wt%, which is much lower than those of the other polymer additives (*e.g.*, 75 wt% for PVAc and 40 wt% for PMMA) reported in literature (Table 1). These results highlight the superiority of the PDLLA in compatibilizing PLLA/PDLA blends efficiently.

Strong Dependence of the SC Crystallizability on PDLLA Molecular Weight

Previous studies have proposed that introducing some flexible polymers (*e.g.*, poly(ethylene glycol) (PEG)) can facilitate the SC

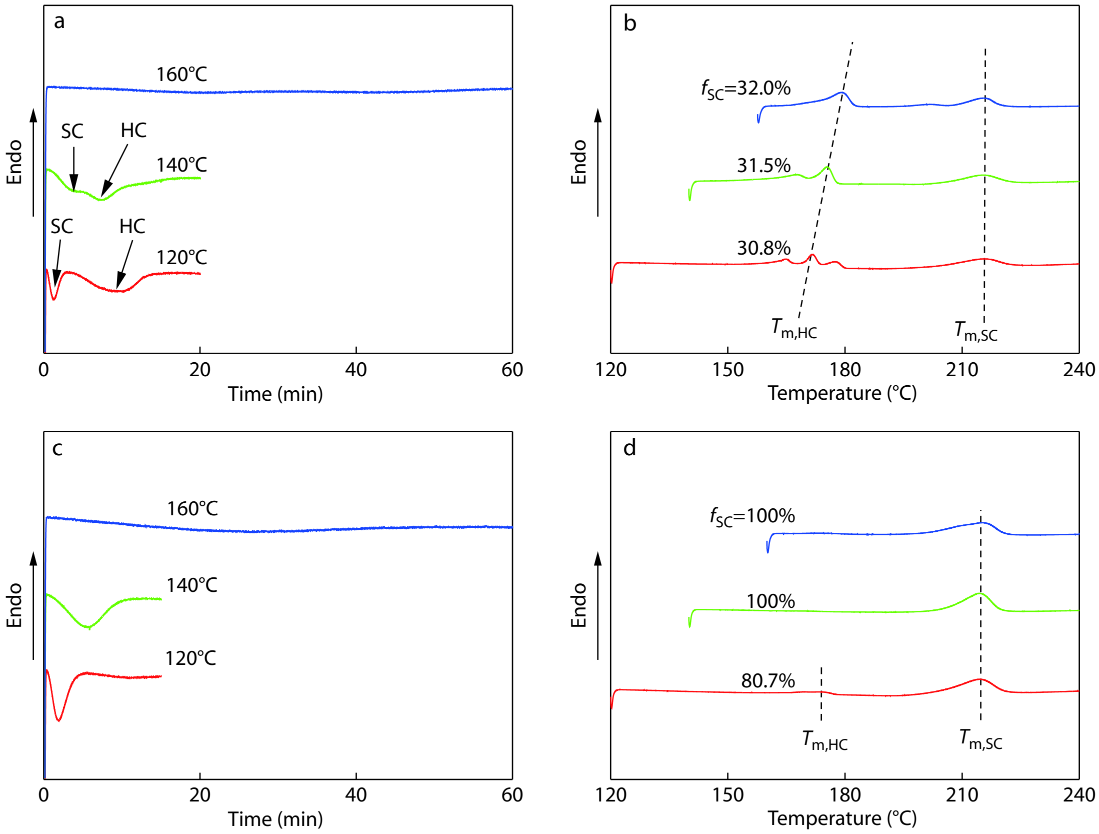

Fig. 6 DSC thermograms recorded during (a, c) isothermal crystallization at different temperatures and (b, d) subsequent heating processes for PLLA/PDLA blends (a, b) without and (c, d) with 20 wt% PDLLA.

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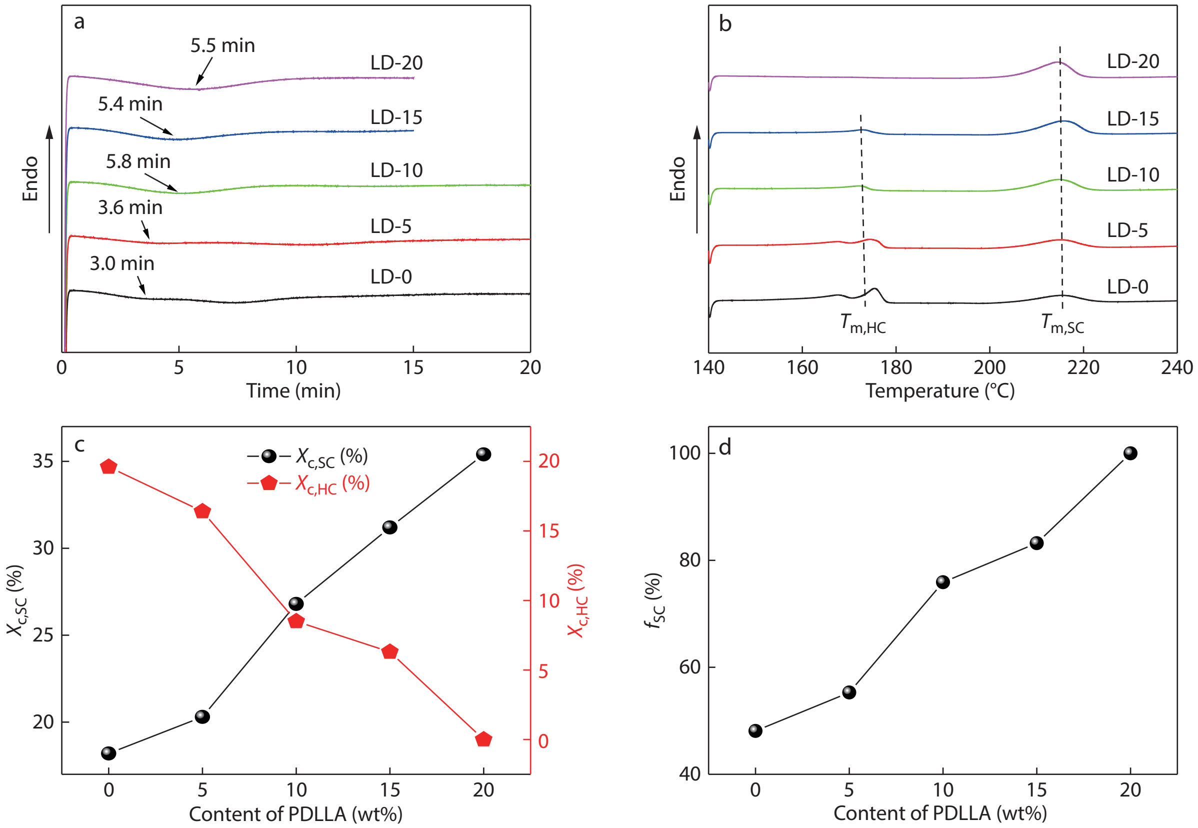

Fig. 7 DSC thermograms of PLLA/PDLA blends with various amounts of PDLLA recorded during (a) isothermal crystallization at 140 °C and (b) subsequent heating processes; (c) Crsytallinity and (d) f_{SC} values as a function of PDLLA amount.

Table 1 Comparison of the critical contents between different polymer additives for obtaining excusive SC formation during melt-crystallization of PLLA/PDLA blends.

Polymer additive	Critical content required (wt%)
PVAc[50]	75
PMMA[65]	40
PVPh[58]	30
PDLLA (this work)	20

formation in the melt-crystallization of PLLA/PDLA blends due to the increase in chain mobility.[64] In our blends, the PDLLA induced decrease in the T_g of PLLA/PDLA component (Fig. 2) could be an indicator of the increased chain mobility. In this case, a question arises whether the chain mobility is the main molecular mechanism for the substantially enhanced SC crystallizability and melt stability. Therefore, it is crucial to clarify whether the PDLLA can effectively plasticize the PLLA/PDLA component to reveal the possible mechanisms for the preferred SC crystallization in PLLA/PDLA/PDLLA blends.

It is generally believed that lowering molecular weight of plasticizers is conductive to the plasticizing effect on various polymer matrices.[5] Recently, Yang *et al.*[64] reported that the enhancement in the SC crystallizability of PLLA/PDLA blends becomes more significant with lowering the M_w of PEG due to the greatly increased segmental mobility of PLAs chains. It is thus natural to think that decreasing PDLLA molecular weight may facilitate the SC crystallization in PLLA/PDLA/PDLLA blends. Fig. 8 presents the strong molecular weight effect on the SC crystallizability during non-isothermal melt-crystallization of the blends containing 20 wt% PDLLA. It is quite unexpected to observe that the SC formation in the melt-crystallization is promoted with increasing M_w of PDLLA and the preferred SC formation can only be achieved when the M_w is higher than 1.0×10^5 g/mol (Figs. 8a and 8b). More importantly, increasing M_w of PDLLA leads to an evident reduction in the T_g of PLLA/PDLA component (Fig. 8c) and there is a linear relationship between T_g and f_{SC} values (Fig. 8d). These findings suggest that the PDLLA is most likely to enhance SC crystallizability by increasing the intermolecular interactions and chain mobility because only the high-M_w PDLLA chains could form physical entanglements with PLLA and PDLA chains.

Molecular Mechanism for the PDLLA Induced Substantial Enhancement in SC Crystallizability

Based on the aforementioned results, it is clear that the incorporation of high-M_w PDLLA can substantially facilitate the SC crystallizability and melt stability of PLLA/PDLA blends due to the increased intermolecular interactions. Fig. 9 illustrates a plausible molecular mechanism for the PDLLA-promoted SC crystallization of high-M_w PLLA/PDLA/PDLLA blends. The intermolecular ordering plays an important role in the crystallization of PLLA/PDLA blends because it can stimulate preferred nucleation and growth of SCs than those of homocrystallites.[71] For the PLLA/PDLA blend without PDLLA, the ordered PLLA/PDLA chain assemblies could be dissociated upon melting, resulting in randomly distributed PLAs chains or

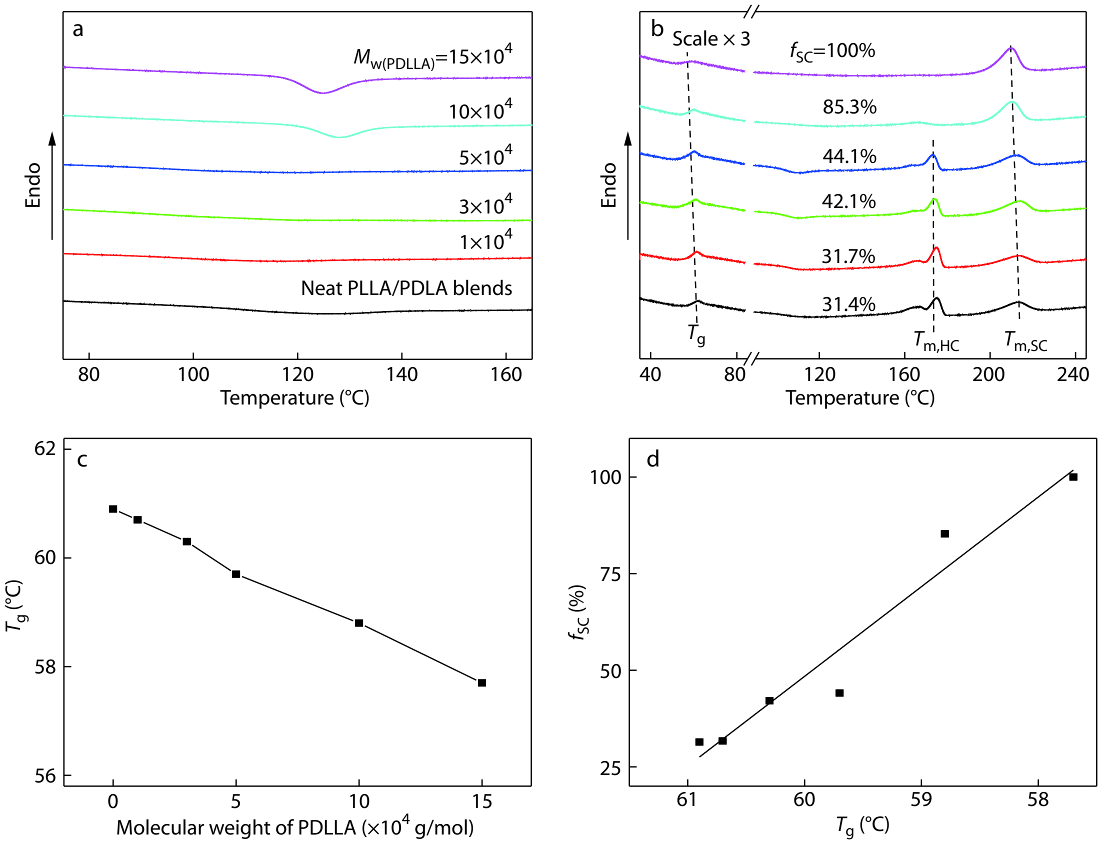

Fig. 8 DSC thermograms of PLLA/PDLA blends with various molecular weights of PDLLA (the weight fraction is 20 wt%) recorded (a) upon cooling at a rate 10 °C/min, and (b) subsequent heating at a rate of 5 °C/min; DSC heating curves of these blends in the glass transition region, (c) plots of T_g values obtained from the DSC heating curves as a function of PDLLA molecular weight, and (d) plots of the f_{SC} values as a function of T_g.

even PLLA- and PDLA-rich domains in the blend (Fig. 9a). In this case, the SC crystallization between PLLA and PDLA chains is kinetically limited by the prolonged diffusion pathway from the homogeneous or phase-separated melt to the crystal growth sites upon subsequent crystallization. However, the high-M_w PDLLA can readily entangle with both PLLA and PDLA chains, which is favorable to enhance the intermolecular interactions and improve the stability of the chain assemblies, and thus the heterogeneous blend melts tend to preferentially crystallize into SCs (Fig. 9b). Meanwhile, although the PDLLA does not co-crystallize with PLLA and PDLA, the formation of chain entanglements could also increase the amount of trapped PDLLA chains within amorphous regions of PLLA/PDLA blends and thus facilitate the SC formation in the blends by enhancing chain mobility. In addition, the compatibilizing effect of PDLLA could improve the mixing level between PLLA and PDLA chains,

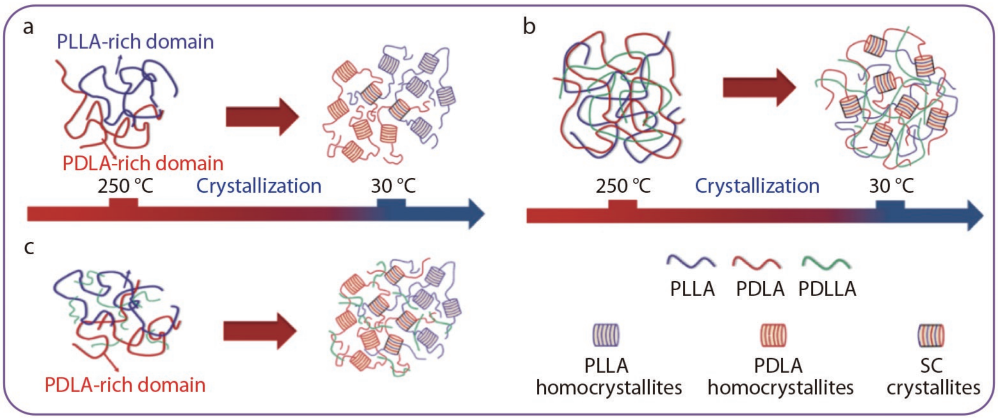

Fig. 9 Schematic illustration showing the possible crystallization process of PLLA/PDLA blends (a) without PDLLA, (b) with a sufficient amount of high-M_w PDLLA, and (c) with low-M_w PDLLA.

which can shorten the diffusion pathway of the enantiomeric chains in SC formation. With regard to the incorporation of low-M_w PDLLA, the low chain entangleability makes PDLLA difficult to form strong interactions with the enantiomeric PLA chains, which induces a weak promoting effect on SC formation (Fig. 9c).

CONCLUSIONS

In conclusion, a simple-yet-effective strategy has been devised to engineer all SC-PLA with excellent SC crystallizability by incorporating PDLLA into commercial linear high-M_w PLLA/PDLA blends. The single and composition-dependent T_g of the blends suggests that PDLLA has good miscibility with the PLLA/PDLA component. Even though the overall crystallinity is slightly decreased after mixing with PDLLA, the amount of SCs formed in the racemic blends is found to increase remarkably along with the suppression of the homocrystallization under both the non-isothermal and isothermal melt-crystallizations, vividly indicating that the PDLLA can behave as an effective compatibilizer to endow the blends with a much superior SC crystallizability by enhancing the mixing level and intermolecular interactions between PLLA and PDLA chains. More intriguingly, the promoting effect of the PDLLA on SC crystallizability is strongly dependent on its content and molecular weight, and increasing weight fraction and M_w are beneficial to the preferential SC crystallization. In particular, the blends can exclusively crystallize into SCs when the content of high-M_w PDLLA (*e.g.*, M_w=1.5×10^5) reaches 20 wt%. The higher efficiency of the high-M_w PDLLA in enhancing the SC crystallizability can be reasonably explained by its stronger intermolecular interaction with the PLLA/PDLA chains and the greatly improved chain mixing degree. We believe that these findings could not only provide a valuable way to prepare all SC-PLA engineering plastic suitable for melt processing but also shed light on the fundamental understanding of PDLLA-promoted stereocomplexation between enantiomeric PLAs.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://doi.org/10.1007/s10118-021-2588-x.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (No. 51873129).

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