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# Benign Fabrication of Fully Stereocomplex Polylactide with High Molecular Weights via a Thermally Induced Technique

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**ABSTRACT:** A reproducible and environmentally friendly method for the preparation of high molecular-weight stereocomplex polylactide (HMW SCPLA) is achieved. Poly(L-lactide) and poly(D-lactide) were simply dissolved in an environmentally friendly solvent, dibasic ester (DBE), at 110 °C. Then, the two solutions were mixed and cooled to room temperature, and the HMW SCPLA spontaneously precipitated in the form of fine powder consequently. The presence of the DBE reduced the reaction temperature and improved the molecular mobility of the polymers; thus, the degradation problems and the molecular diffusion issue in the process of the formation of the stereocomplex could be overcome. The relationship among the concentration of the mixture, degree of stereo-complexation, and thermal properties of SCPLA powders was also established. Moreover, porous membrane and film SCPLA material with good thermal properties were also obtained using this thermally induced technique. This method could be a good approach to expand the SCPLA applications.



## 1. INTRODUCTION

Poly lactides [poly L-lactide (PLLA) and poly D-lactide (PDLA)] are biodegradable, compostable, and producible from renewable resources. They have been widely used in medical applications because of their excellent biocompatibility and biodegradability.<sup>1</sup> However, the widespread application of homopolylactide (HCPLA) has been limited by its poor thermal stability and hydrolysis resistance.<sup>2</sup> Stereocomplex polylactide (SCPLA) has been proven to possess more excellent properties than HCPLA.<sup>3</sup> The stereocomplex has a melting temperature ( $T_m$ ) of approximately 50 °C higher than the  $T_m$  of HCPLA.<sup>4</sup>

Many strategies, such as crystallization of block copolymers,<sup>5</sup> casting of films from concentrated solutions,<sup>6,7</sup> melt blending processes,<sup>8,9</sup> supercritical fluid technology,<sup>10</sup> layer-by-layer deposition,<sup>11,12</sup> electrospinning,<sup>13</sup> gelation in an ionic liquid,<sup>14</sup> and spray-drying technology<sup>15</sup> have been developed to prepare SCPLA. Collectively, these methods have produced SCPLA successfully. However, generally, while these methods provide some advantages such as scalability and high degree of SCPLA formation, they still suffer from drawbacks including high cost, low throughput, significant degradation, and time consuming. Therefore, a simple, scalable, inexpensive, and high-throughput method of fabricating SCPLA remains a challenge. Furthermore, similar to cellulose,<sup>16</sup> searching for systems with an environmentally friendly process is very important for advancement of the SCPLA industries.

In this paper, we reported the preparation of complete high molecular-weight (HMW) SCPLA using the thermally induced technology with dibasic ester (DBE) as medium. DBE is known as a low-risk green solvent that is derived from biomass which is biodegradable.<sup>17,18</sup> DBE solution provides an environment beneficial to the formation of stereocomplex crystals. On the basis of previous studies, the thermally induced technique is reported to be an easy scalable method, which separates the mixture solution into two phases (polymer-rich/polymer-lean phase) either by exposing the solution to an immiscible solvent or by cooling the solution below its solubility temperature.<sup>19–21</sup> This whole system reduced the temperature of preparation of SCPLA, which effectively inhibited the PLA degradation and reduced the energy consumption. Moreover, this method of solution crystallization was more conducive to the formation of fully HMW SCPLA. The difficulties in low-chain diffusion ability and restricted intermolecular crystal growth of HMW PLA, which have profound influence in the degree of stereo-complexation, could be overcome.<sup>22</sup> By using the thermally induced phase separation technique in DBE solution, this fabrication approach might be sustainable, reproducible, scalable, and economical to prepare SCPLA materials.

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## 2. EXPERIMENTAL SECTION

**2.1. Materials and Reagents.** DBE and  $\text{Sn}(\text{Oct})_2$  were purchased from Sigma-Aldrich. DBE was distilled over  $\text{CaH}_2$  before use. Lactide (D- and L-) with an optical purity of 98% was supplied by Musashino Chemical (China) Co., Ltd.

**2.2. Fabrication of SCPLA Powder, Porous Membrane, and Film.** PLLA and PDLA were synthesized by ring-opening polymerization according to the literature.<sup>23</sup> The following were the specific steps: lactide (D- and L-) was reacted in the ampoule bottle in  $137\text{ }^\circ\text{C}$  under 50 Pa after being dried in vacuum for 24 h at room temperature, and 0.05 wt %  $\text{Sn}(\text{Oct})_2$  was added as the catalyst. The resulting polymers were purified by reprecipitation using dichloromethane as the solvent and methanol as the precipitant. The purified products were dried to constant mass in a vacuum oven at  $40\text{ }^\circ\text{C}$ .

The fabrication of SCPLA via a thermally induced process was carried out as illustrated in Scheme 1.

**Scheme 1. Preparation Process of the SCPLA**



PLLA ( $M_n = 111.5\text{ kg/mol}$ ,  $M_w/M_n = 1.4$ ) and PDLA ( $M_n = 100.4\text{ kg/mol}$ ,  $M_w/M_n = 1.3$ ) were dissolved separately in DBE solutions and then mixed together with a 1:1 ratio by weight at the same temperature ( $110\text{ }^\circ\text{C}$ ). HMW PLLA and PDLA are almost insoluble in DBE at room temperature but could be totally dissolved in DBE equal to or higher than  $110\text{ }^\circ\text{C}$ . In terms of reducing energy consumption, the polylactide dissolve

experiment was carried out at  $110\text{ }^\circ\text{C}$ . The solutions were mixed under the concentration of 25, 50, and  $100\text{ mg/mL}$  accordingly which are successively named as SC25, SC50, and SC100, respectively. After stirring for ca. 15 min, glass bottles containing the mixed solutions were cooled down to room temperature at the rate of ca.  $10\text{ }^\circ\text{C/min}$ . When the temperature dropped to ca.  $95\text{ }^\circ\text{C}$ , the solution became turbid and the precipitates could be observed. The picture of the cooling process is shown in Figure 1. The solution was left statically for 1 h, and after that the formed precipitates were separated from the suspensions by centrifugation and washed twice with ethanol at room temperature to remove the residual DBE. The obtained white powder was dried in vacuum at  $40\text{ }^\circ\text{C}$  for ca. 24 h.

The porous membrane of SCPLA was prepared using the following procedures: the solution of SC50 was cast on a clean tinfoil substrate under  $110\text{ }^\circ\text{C}$ . After the solvents were evaporated completely, the microporous film was formed.

The films of PLLA, PDLA, and SCPLA are prepared in the compression moulding machine (Carver, Wabash, IN). The powder was spread on the aluminum foils and placed in the compression mold at a pressure of approximately 15 MPa and a set temperature of  $190\text{ }^\circ\text{C}$  for 5 min.

**2.3. Characterization.** The molecular weight and polymer dispersity index of PLLA, PDLA, and SCPLA were determined using gel permeation chromatography (GPC; Malvern Viscotek 270 max UK). Hexafluoroisopropanol was used as the mobile phase and the polystyrene was used as the standard.

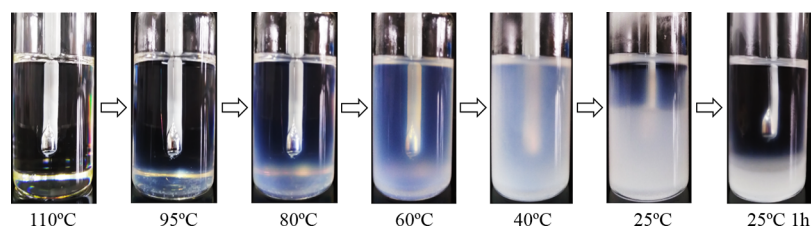
Differential scanning calorimetry (DSC) was carried out with Netzsch DSC 204 F1 Germany. Specimens (powders and films) weighing around 5 mg were heated at the rate of  $10\text{ }^\circ\text{C/min}$  and cooled at the rate of  $10\text{ }^\circ\text{C/min}$ . All tests were under the nitrogen atmosphere.

The wide-angle X-ray diffraction (WXR) analyses were performed on Rigaku D/max-2550 PC (Japan).  $\text{Cu K}\alpha$  radiation with wavelength  $\lambda = 0.1542\text{ nm}$  was used.

The Fourier transform infrared (FTIR) spectra of PLLA, PDLA, and SCPLA were obtained by the attenuated total reflection method using a PerkinElmer Spectrum II FTIR spectrometer.

Scanning electron microscopy (SEM) images were obtained with Hitachi S-4800 equipped with an SE detector at  $\text{HV} = 5\text{ kV}$ .

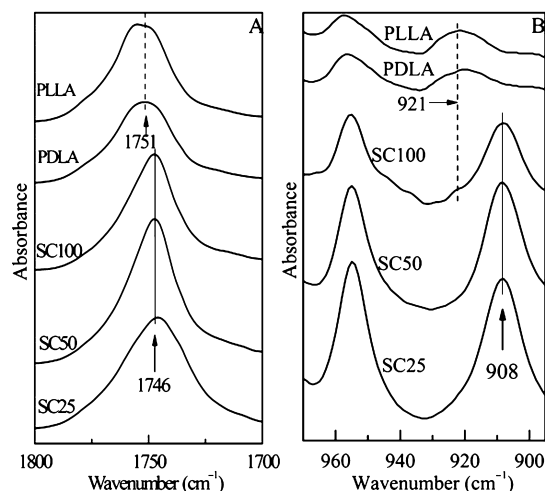
The mechanical properties of PLLA, PDLA, and SCPLA films were measured on a Universal Material Tester (H5 K-S, Hounsfield, UK) operating with an extension rate of  $50\text{ mm/min}$  according to ASTM D5034. The reported Young's modulus, tensile strength at yield, and elongation at break were evaluated from five repeats for each sample.



**Figure 1.** Precipitates observed in different temperatures.

### 3. RESULTS AND DISCUSSION

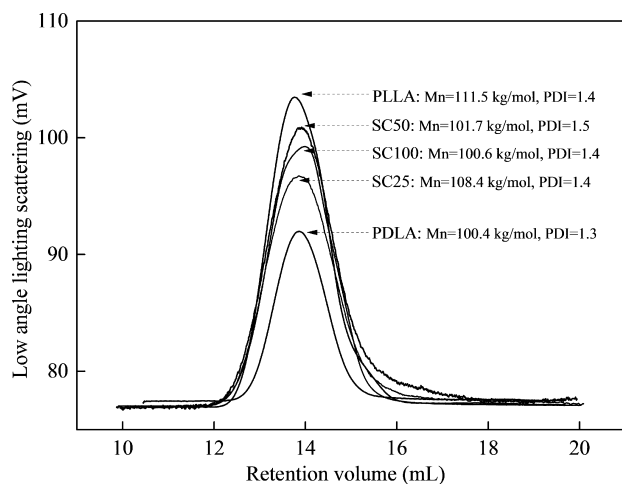
FTIR spectroscopy is a powerful tool for distinguishing a stereocomplex from a homocrystal. The  $\text{CH}_3\cdots\text{O}=\text{C}$  intermolecular interaction is revealed as the driving force for SCPLA formation.<sup>24</sup> The band of  $\nu(\text{C}=\text{O})$  migrated from  $1751\text{ cm}^{-1}$  for HCPLA to  $1746\text{ cm}^{-1}$  for SCPLA (Figure 2A).



**Figure 2.** FTIR spectra of PLLA, PDLA, SC25, SC50, and SC100 [(A) absorption peak of C=O, (B) absorption peak of SC crystallites].

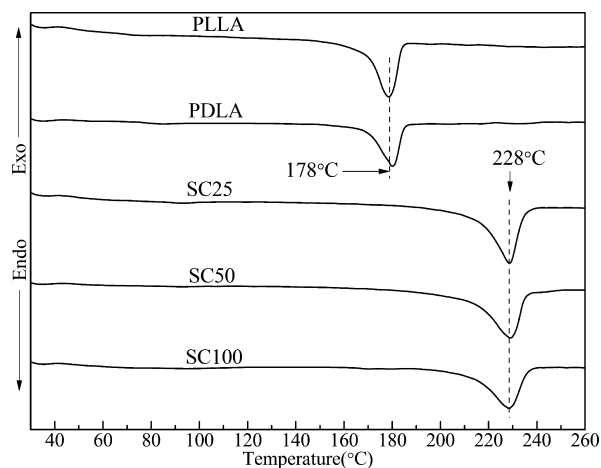
The absorbance peaks of  $921\text{ cm}^{-1}$  and  $908\text{ cm}^{-1}$  are the characteristic peaks of HCPLA and SCPLA, respectively.<sup>25</sup> As shown in Figure 2B, the FTIR absorption of SC crystallites ( $908\text{ cm}^{-1}$ ) became prominent for SC100, and the band of HCPLA crystallites ( $921\text{ cm}^{-1}$ ) vanished completely for SC50 and SC25.

The relative molecular weights of PLA are usually reduced during the hot procedure at elevated temperature. The molecular weights of the SCPLA, PLLA, and PDLA were determined after stereocomplexation by a GPC light scattering detector. The results are shown in Figure 3. The molecular weights of the SCPLA and PLLA/PDLA were almost the same, indicating no significant polymer degradation during the preparation process.



**Figure 3.** GPC curves and molecular characteristic of PLLA, PDLA, SC25, SC50, and SC100.

To investigate the formation of the stereocomplex of PLA in the DBE, DSC measurements were also conducted. Figure 4

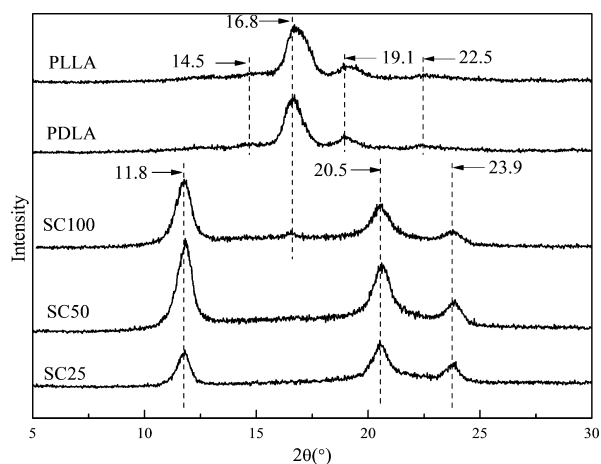


**Figure 4.** DSC thermograms of the first heating scan of PLLA, PDLA, SC25, SC50, and SC100.

shows the DSC heating traces of PLLA, PDLA, SC25, SC50, and SC100. Obviously, SCPLA crystallites generated in the precipitates from all the solutions studied here. Either the pure PDLA or PLLA gave a peak at  $178\text{ }^\circ\text{C}$ , which corresponded to the melting point of the homocrystal of PLLA and PDLA. For the SC25, SC50, and SC100, the melting points were around  $228\text{ }^\circ\text{C}$ , whereas the endothermic peaks related to the homocrystal were not observed, indicating that stereocomplex crystallites existed solely. These observations coincided well with the FTIR results. The enthalpies of SCPLA were estimated by DSC, and the values were  $88.0$ ,  $82.9$ , and  $70.3\text{ J/g}$  for SC25, SC50, and SC100, respectively. Crystallinities ( $X_c$ ) of SCPLA crystallites were estimated by normalizing their enthalpy to the equilibrium enthalpy of perfect crystals, taken as  $142\text{ J/g}$  for SCPLA crystallites.<sup>26</sup> Consequently, the  $X_c$  were  $62$ ,  $58$ , and  $50\%$  for SC25, SC50, and SC100, respectively. It was noticeable that  $X_c$  became smaller as the polymer concentration increased, which might be attributed to the more difficult molecular chain movement with the higher concentration. The presence of DBE could improve the molecular chain mobility and mutual diffusion of PLLA and PDLA, leading to reduction of the kinetic barrier for stereocomplex formation to a certain extent.

To further confirm the formation of the stereocomplex in the DBE, WXR measurements were conducted. As shown in Figure 5, the neat PLLA and PDLA have characteristic diffractions at  $2\theta$  of about  $14.5^\circ$ ,  $16.8^\circ$ ,  $19.1^\circ$ , and  $22.5^\circ$ , which is in agreement with the peaks reported at  $15^\circ$ ,  $16^\circ$ ,  $18.5^\circ$ , and  $22.5^\circ$  by Ikada and co-workers.<sup>4</sup> Meanwhile, the SCPLA has the diffraction peaks appearing at  $2\theta$  of around  $11.8^\circ$ ,  $20.5^\circ$ , and  $23.9^\circ$ , which is in agreement with the peaks reported at  $12^\circ$ ,  $21^\circ$ , and  $24^\circ$  by Ikada and co-workers.<sup>4</sup> However, for SC100, a very small diffraction peak at  $2\theta$  of about  $16.8^\circ$  can be observed, which might be a symbol of residual homo-PLA crystallites. When the concentration reached  $100\text{ mg/mL}$ , chains should be intensively entangled and their mobility might be constrained relatively, leading to the more difficult formation of SCPLA. In combination with SC50 and SC25, this result further confirmed that the higher the concentration,



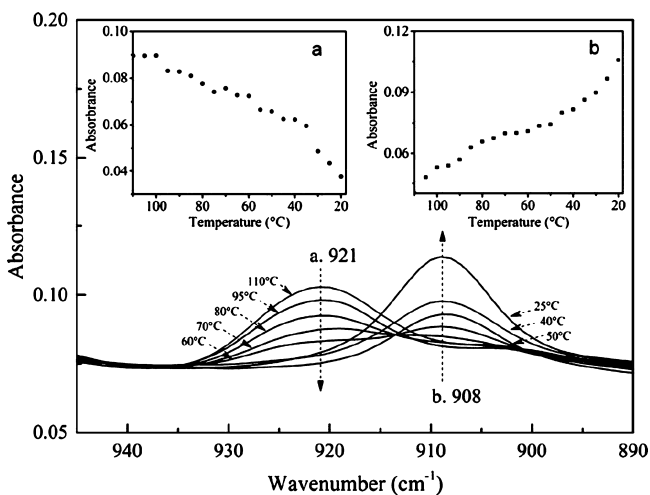


**Figure 5.** WAXRD patterns of PLLA, PDLA, SC25, SC50, and SC100.

the lower mobility of the molecular chain, which is consistent with the DSC results.

In summary, the abovementioned results demonstrated that the HMW enantiomeric polylactides could form a high degree stereocomplexation upon cooling in the solvent of DBE. In addition, the relative molecular weight mass was not decreased in production.

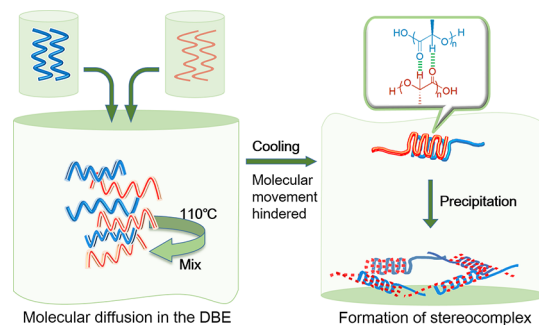
To further understand the enhanced molecular mobility and mutual diffusion of the enantiomeric polylactides in DBE, in situ FTIR measurements of the mixtures upon cooling were carried out. The results are shown in Figure 6. As it shown,



**Figure 6.** FTIR spectra of 50 mg/mL SCPLA solution during the cooling process. The absorbance changes of the peaks at (a) 921 and (b) 908  $\text{cm}^{-1}$  at different temperatures.

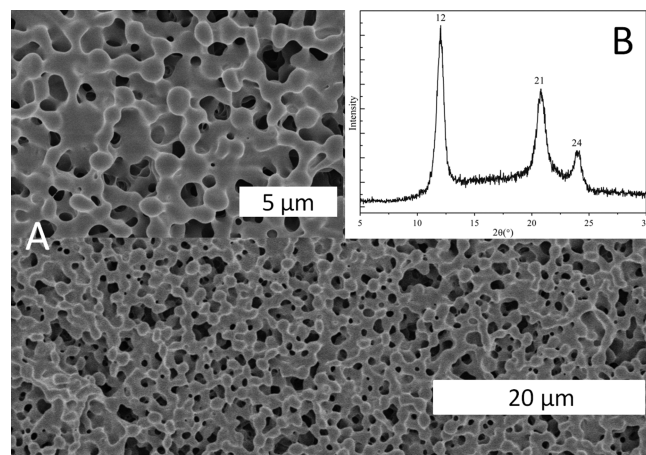
when the mixture cooled down from 110 to 20  $^{\circ}\text{C}$ , the intensity of the peaks at 921  $\text{cm}^{-1}$  became weak gradually (Figure 6a), but the intensity of the peaks at 908  $\text{cm}^{-1}$  became strong gradually (Figure 6b). Finally, the peak at 921  $\text{cm}^{-1}$  vanished. These results demonstrated that the enantiomers tended to form stereocomplex crystals, not homocrystals, during the cooling process. In other words, the driving force for stereocomplexation was stronger than the driving force for homocrystallization.<sup>14</sup> The stronger driving force probably came from the hydrogen bond of SCPLA (as shown in Figure

7). Therefore, the stereocomplexation was predominant during the crystallization process.



**Figure 7.** Schematic of the crystallization process of SCPLA.

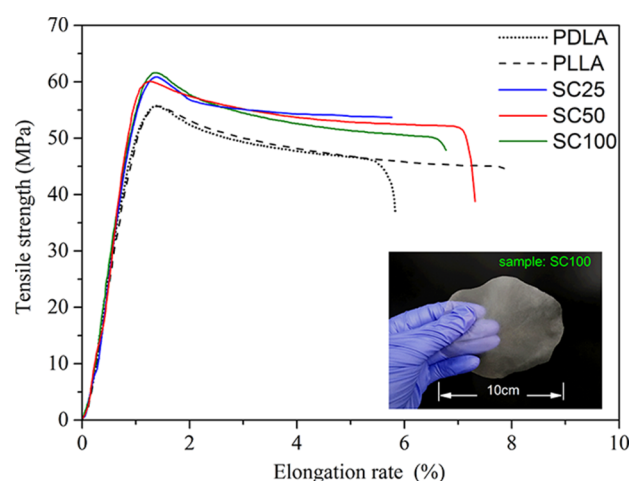
In practical applications, polylactide not only need to be made SCPLA but also need to be SCPLA materials with certain morphology, usage or function, such as fiber, film, particle, and so on. Here, the thermally induced method could be used to generate porous SCPLA materials. Figure 8 presents



**Figure 8.** (A) SEM image of the SC50 porous film and (B) WAXRD pattern of the SC50 porous film.

SEM images and the WAXRD pattern of a typical porous membrane of SC50. From Figure 8A, the pores are circular-like, micro-well structures with a diameter of about 1–2  $\mu\text{m}$ . Figure 8B shows that the membrane has the diffraction peaks appearing at  $2\theta$  of around 12 $^{\circ}$ , 21 $^{\circ}$ , and 24 $^{\circ}$ , confirming the formation of the stereocomplex. The reason for forming porous structures is probably the phase separation induced thermally.<sup>27</sup>

Additionally, SCPLA films were made by hot press molding, and the appearance is shown in Figure 9. Tensile tests were carried out and the stress–strain curves of PLLA, PDLA, and SCPLA films are also presented in Figure 9. The tensile properties are summarized in Table 1. The tensile strength and the Young's modulus of SCPLA films were enhanced slightly compared to the neat PLLA/PDLA. The SCPLA films were not only stronger but also stiffer than the neat PLA films slightly. The elongation at break values of PLLA, PDLA, and SCPLAs were nearly the same, around 6–7%. The improved tensile modulus and strength of the SCPLA films are probably due to enhanced intermolecular forces resulted from the more close arrangement of molecules after stereocomplexation.

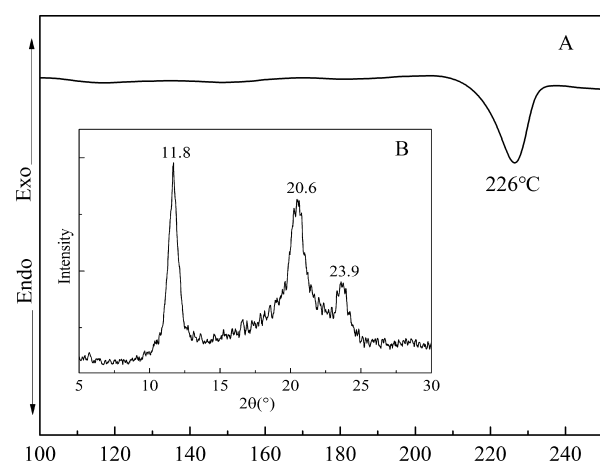


**Figure 9.** Stress–strain curves of SCPLAs, PLLA, and PDLA.

**Table 1. Mechanical Properties of SCPLAs, PLLA, and PDLA**

| sample name | Young's modulus (GPa) | tensile strength (MPa) | elongation at break (%) |
|-------------|-----------------------|------------------------|-------------------------|
| PLLA        | 3.89 ± 0.14           | 54.71 ± 3.72           | 7.94 ± 1.17             |
| PDLA        | 4.09 ± 0.40           | 55.04 ± 3.40           | 5.90 ± 2.31             |
| SC25        | 5.04 ± 0.19           | 60.89 ± 2.41           | 5.77 ± 1.88             |
| SC50        | 5.21 ± 0.11           | 60.18 ± 1.87           | 7.31 ± 2.14             |
| SC100       | 4.96 ± 0.28           | 61.65 ± 1.72           | 6.78 ± 2.55             |

When considering the crystal stability of the SCPLA after hot pressing, DSC analysis of the SC100 film (Figure 10A)



**Figure 10.** (A) DSC trace of the SC100 film made by hot press molding and (B) WXR D pattern of the SC100 film.

revealed that the melting point of the heating processes was around 226 °C, which is slightly lower than that of SCPLA powder (228 °C). The enthalpy of the SC100 film was 74.7 J/g ( $X_c = 52.6\%$ ). There was no homocrystal endothermic peak observed, and the degree of crystallinity of the SC100 film was higher than that of SC100 powder. This might be attributed to the role of the hot pressing temperature and pressure, and 190 °C was selected as the hot pressing temperature, which was higher than the end set melting temperature of neat PLA and lower than the stereocomplex melting point. Therefore, the crystals of HCPLA will be melted, but the stereocomplex crystals still existed and acted as nucleation sites to induce

crystallization in the molten PLA phase.<sup>28,29</sup> The earlier research reported that when cooling from temperatures below the stereocomplex melting point, the crystalline fraction of the stereocomplex became larger than the stereocomplex without heat treatment, implying that the nucleating effect of stereocomplex crystals help increase the spherulite density.<sup>30</sup>

WXR D analysis (Figure 10B) was carried out for the further confirmation of the stereocomplex structure of the SC100 film. It should be noticed that the small diffraction peak at  $2\theta$  of 16.8° was vanished compared to the WXR D pattern in Figure 4. Similarly, the SC100 film had the diffraction peaks appearing at  $2\theta$  of around 11.8°, 20.0°, and 23.9°, confirming the formation of the stereocomplex. This might suggest the enhanced organization of PLA molecular chains and more perfect crystals within the stereocomplex.<sup>31,32</sup>

## 4. CONCLUSIONS

In conclusion, an efficient and reproducible thermally induced method for the preparation of SCPLA with HMW is proposed. The approach is environmentally friendly, easy to implement, and can easily be scaled up. Using this technique, various forms of stereocomplex poly(lactides) materials which exhibit good thermal properties might be obtained, such as powder, membrane, and film. Further research on SCPLA materials to other forms using the thermally induced method in DBE and other alternative solvents are now in progress.

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### Notes

The authors declare no competing financial interest.

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