

Research Article

Thermal and Mechanical Properties of Biodegradable Star-Shaped/Linear Polylactide Stereocomplexes

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The 6-arm star-shaped poly(L-lactide) (6PLL)/linear poly(D-lactide) (1PDL) stereocomplex films were prepared by the solvent casting method. The influences of the 6PLL/1PDL blend ratios (75/25, 50/50, and 25/75 w/w) and 1PDL molecular weights (15,000, 30,000, and 60,000 g/mol) on the thermal and mechanical properties of the stereocomplex films were investigated. The 6PLL and 1PDLs had a single melting temperature (T_m) of homocrystallites at 174°C and 167°C, respectively. The 6PLL/1PDL blends had two T_m s: a lower T_m of homocrystallites (160–173°C) and a higher T_m of stereocomplex crystallites (219–228°C). The stereocomplex crystallinity and mechanical properties of the 6PLL/1PDL blend films were higher than those of 6PLL and 1PDL and were the highest in the 50/50 (w/w) blend ratio. However, the stereocomplex crystallinity of the 50/50 (w/w) 6PLL/1PDL blend films decreased and the mechanical properties increased as the molecular weight of 1PDL increased.

1. Introduction

Poly lactides are interesting nontoxic, biodegradable, and renewable polymers for use in biomedical, pharmaceutical, and packaging applications that are usually synthesized from lactide monomer by ring-opening polymerization. The lactide monomers have three different stereochemistries: L-lactide, D-lactide, and D,L-lactide [1]. Poly(L-lactide) (PLL) and poly(D-lactide) (PDL) are semicrystalline, while poly(D,L-lactide) (PDLL) is amorphous [2]. PLL has received much interest because of its low-cost production and possible use instead of oil-based commodity plastics such as polyethylene and polypropylene. However, the major limitations of PLL products are their poor mechanical properties, nonheat resistance, and slow crystallization. There have been many developments to improve the properties of PLL by blending with fillers [3–5] and other polymers [6, 7] as well as stereocomplex formation [2].

The polylactide stereocomplexes obtained from linear PLL and linear PDL blending have been extensively studied in the past few decades [2]. The cocrystallization of linear PLL

and linear PDL molecules leads to a stereocomplex crystalline structure that is different from a homocrystalline structure. The melting temperature (T_m) of the polylactide stereocomplex ($T_m \approx 230^\circ\text{C}$) is approximately 50°C higher than the T_m of either original PLL or PDL, due to the strong van der Waals forces in the stereocomplex crystalline structure [8–10]. The stereocomplex formation enhances the thermal resistance, the mechanical properties, and the hydrolysis resistance of the polylactides [2, 11–13]. However, precise adjustments of the polylactide stereocomplex properties are still required for each process and application.

Polylactide stereocomplexes have also been prepared from block polylactides [14] and star-shaped polylactides [15–18]. The star-shaped polymers have a lower melt viscosity than linear polymers with the same molecular weight [19]. The star-shaped polylactide stereocomplexes with adjustable melt viscosity may be appropriate for each melting process. Some properties, such as thermal and mechanical ones, of the star-shaped/linear polylactide stereocomplexes are still not clear.

In the present work, the thermal and mechanical properties of star-shaped/linear polylactide blend films prepared

with different blend ratios and molecular weights of linear polylactide were studied. For this purpose, linear polylactides with molecular weights of 15,000, 30,000, and 60,000 g/mol were synthesized. The results were also compared to neat star-shaped and linear polylactides.

2. Materials and Methods

2.1. Materials. L-Lactide and D-lactide monomers were synthesized using well-established procedures, polycondensation followed by thermal decomposition, from L-lactic acid (88%, Purac, Thailand) and D-lactic acid (90%, Haihang Industry Co., Ltd., China), respectively. The lactide monomers were purified by repeated recrystallization from ethyl acetate (four times) before drying in a vacuum oven at 55°C for 48 h. 1-Dodecanol (98%, Fluka, Switzerland) containing one-hydroxyl end group was purified by distillation under reduced pressure before use. Dipentaerythritol (99%, Aldrich, USA) was dried in a vacuum oven at 55°C for 48 h before use as the initiators contained 6-hydroxyl end groups. Stannous octoate (95%, Sigma, USA), Sn(Oct)₂, was used without further purification. All reagents used were analytical grade.

2.2. Synthesis of Star-Shaped and Linear Polylactides. The 6-arm star-shaped poly(L-lactide) (6PLL) and 1-arm linear polylactide (1PDL) were synthesized by single step ring-opening polymerization in bulk at 165°C for 2 h under a nitrogen atmosphere using dipentaerythritol and 1-dodecanol as initiators, respectively. Stannous octoate was used as a catalyst that was maintained at 0.01 mol%. The obtained polylactide was purified via dissolution in chloroform before being precipitated in cool *n*-hexane and dried to a constant weight in a vacuum oven at 50°C.

The 6PLL with a theoretical number-average molecular weight of 120,000 g/mol and the 1PDL with theoretical number-average molecular weights of 15,000 (1PDL15K), 30,000 (1PDL30K), and 60,000 (1PDL60K) g/mol were synthesized. A 0.12 mol% dipentaerythritol initiator was used for 6PLL synthesis. 1-Dodecanol initiators at 0.96, 0.48, and 0.24 mol% were used to synthesis the 1PDL15K, 1PDL30K, and 1PDL60K, respectively.

2.3. Preparation of Star-Shaped/Linear Polylactide Stereocomplexes. The stereocomplexes of the 6PLL/1PDL blends were obtained via solution blending before film casting. The 6PLL and 1PDL were dissolved separately in chloroform at a concentration of 1 g/dL at room temperature and then mixed together at the same temperature under vigorous stirring for 30 min. The blend solution was then cast onto a Petri dish followed by solvent evaporation at 40°C in an air oven for 24 h. The film was then dried in a vacuum oven at 70°C for 48 h to remove any residue solvent. The blended films with 6PLL/1PDL blend ratios of 75/25, 50/50, and 25/75 (w/w) were investigated. The 6PLL and 1PDL films were also prepared by the same method for comparison.

2.4. Characterization of Polylactides and Their Stereocomplexes. The intrinsic viscosities, $[\eta]$, of 6PLL and 1PDL were measured by flow-time measurements from a diluted series of solutions in chloroform, as the solvent, at 25°C using an Ubbelohde viscometer.

The number-average molecular weight (M_n) and molecular weight distribution (MWD) of the 6PLL and 1PDLs were determined by Gel Permeation Chromatography (GPC) with a Waters e2695 separations module equipped with PLgel 10 μ m mixed B 2 columns operating at 40°C and employing a refractive index (RI) detector. Tetrahydrofuran was used as the solvent at a flow rate of 1.0 mL/min.

The thermal transition properties of the 6PLL, 1PDL, and their stereocomplexes were determined with a Perkin-Elmer Pyris Diamond differential scanning calorimeter (DSC) under a nitrogen flow. For DSC, samples of 5–10 mg in weight were heated at 10°C/min over a temperature range of 0 to 250°C (the 1st heating scan) to observe their melting temperature (T_m). Then the samples were quenched to 0°C according to the DSC instrument's own default cooling mode before heating from 0 to 250°C (the 2nd heating scan) to observe their glass transition (T_g) and crystallizing (T_c) temperatures. The homocrystallinity (χ_{hc}) and stereocomplex crystallinity (χ_{sc}) of polylactides were determined from the heats of melting of the homocrystallites (ΔH_m of hc) and stereocomplex crystallites (ΔH_m of sc) using (1) and (2), respectively. Consider the following:

$$\chi_{hc} (\%) = \left[\frac{\Delta H_m \text{ of hc}}{93.7} \right] \times 100, \quad (1)$$

$$\chi_{sc} (\%) = \left[\frac{\Delta H_m \text{ of sc}}{142} \right] \times 100, \quad (2)$$

where 93.7 J/g and 142 J/g are the theoretical heats of melting for 100% homocrystallinity and 100% stereocomplex crystallinity, respectively [4, 20].

The wide angle X-ray diffraction (WAXD) spectra the 6PLL, 1PDL, and their stereocomplex films were recorded with a Bruker D8 Advance wide-angle X-ray diffractometer at 25°C using CuK α radiation at 40 kV and 40 mA. For XRD, the scanning angle range of $2\theta = 5^\circ - 30^\circ$ at a scan speed of 3°/min was chosen to determine the homocrystalline and stereocomplex crystalline structures of the polylactides.

The thermal stability of the 6PLL, 1PDL, and their stereocomplexes was determined with a TA-Instrument SDT Q600 thermogravimetric analyzer (TGA) in a nonisothermal mode. For TGA analysis, samples of 5–10 mg in weight were heated at 20°C/min under a nitrogen atmosphere over the temperature range 50 to 800°C to assess their temperature of maximum decomposition rate ($T_{d,max}$).

Mechanical properties including stress at break, elongation at break, and initial Young's modulus, of the 6PLL, 1PDL, and their stereocomplex films, were determined at 25°C and 65% relative humidity with a Lloyds LRX+ Universal Mechanical Testing Machine. The film samples (80 \times 10 mm) were tested with a gauge length of 25 mm and a crosshead speed of 10 mm/min. The mechanical properties

TABLE 1: Thermal transition properties of 6PLL, 1PDL, and 6PLL/1PDL stereocomplexes.

6PLL/1PDL blend ratio (w/w)	T_m of hc ^a (°C)	T_m of sc ^a (°C)	T_g ^b (°C)	T_c ^b (°C)	ΔH_c ^b (J/g)
6PLL/1PDL15K					
100/0	167	—	57	92	32.5
75/25	160	226	59	101	27.2
50/50	—	228	60	96	14.5
25/75	170	226	58	95	29.4
0/100	174	—	58	97	33.3
6PLL/1PDL30K					
100/0	167	—	57	92	32.5
75/25	163	224	59	104	29.2
50/50	—	227	59	99	13.0
25/75	171	226	58	99	32.0
0/100	176	—	58	98	35.4
6PLL/1PDL60K					
100/0	167	—	57	92	32.5
75/25	173	219	57	104	32.9
50/50	161	219	56	100	32.9
25/75	165	220	58	100	37.0
0/100	167	—	57	99	36.7

^aobtained from 1st heating scan DSC thermograms.

^bobtained from 2nd heating scan DSC thermograms.

were determined from the average of three measurements for each sample.

The data were expressed as mean \pm SD. Statistical analysis was performed using a one-way analysis of variance (ANOVA).

3. Results and Discussion

The intrinsic viscosities ($[\eta]$) of the 6PLL, 1PDL15K, 1PDL30K, and 1PDL60K measured in chloroform at 25°C were 1.05, 0.63, 1.03, and 1.57 dL/g, respectively. The $[\eta]$ of 6PLL with a theoretical number-average molecular weight (M_n) of 120,000 g/mol was nearly the same as 1PDL30K and lower than the 1PDL60K. The $[\eta]$ of the polymer solution was directly related to the hydrodynamic volume of the polymer molecules in solution. The 6-arm star-shaped PLL exhibited a smaller hydrodynamic volume than the linear PLL for a similar molecular weight [21, 22].

The number-average molecular weights (M_n) from GPC curves were 88,400, 13,800, 24,800, and 53,600 g/mol for the 6PLL, 1PDL15K, 1PDL30K, and 1PDL60K, respectively. These M_n values obtained from GPC curves were nearly the same as those obtained from the feed ratio, except the 6PLL. This may be explained by the hydrodynamic volume of the star-shaped molecules in solution being smaller than that of the linear molecules, as well as linear polystyrene being used for GPC calibration [21, 22]. All the GPC curves were of the unimodal type. The molecular weight distributions (MWD) of the 6PLL, 1PDL15K, 1PDL30K, and 1PDL60K obtained from GPC curves were 2.2, 1.8, 2.2, and 2.5, respectively.

3.1. Thermal Transition Properties. The thermal transition properties of the 6PLL, 1PDL, and their stereocomplexes were determined from their 1st and 2nd heating scan DSC thermograms, examples of which are shown in Figure 1 for the 6PLL, 1PDL15K, and 6PLL/1PDL15K blends. The melting temperatures of the homocrystallites (T_m of hc) and stereocomplex crystallites (T_m of sc) were detected from the 1st heating scan DSC thermograms. The glass transition (T_g) and crystallizing (T_c) temperatures were obtained from the 2nd heating scan DSC thermograms. The DSC results are summarized in Table 1.

It can be seen that the 6PLL and 1PDLs gave a single T_m of hc at 167°C and 167–176°C, respectively. The 6PLL/1PDL stereocomplexes showed that the T_m of hc and T_m of sc were in the ranges 160–173°C and 219–228°C, respectively. The strong van der Waals interactions between PLL and PDL chains lead to the formation of stereocomplex crystallites, which significantly increased in the T_m of the PLL/PDL blends [10]. The broad shoulders of the melting peaks of the stereocomplex crystallites in Figure 1 indicated that the sizes of the stereocomplex crystallites in each 6PLL/1PDL blend sample were different.

All the 6PLL/1PDL stereocomplexes have both T_m of hc and T_m of sc, excepted for the 50/50 (w/w) 6PLL/1PDL15K and 50/50 (w/w) 6PLL/1PDL30K stereocomplexes that gave only the T_m of sc. This suggests that the 1PDL with low (1PDL15K) and medium (1PDL30K) molecular weights induced complete stereocomplex formation by blending with 6PLL, but the 1PDL with a high molecular weight (1PDL60K)

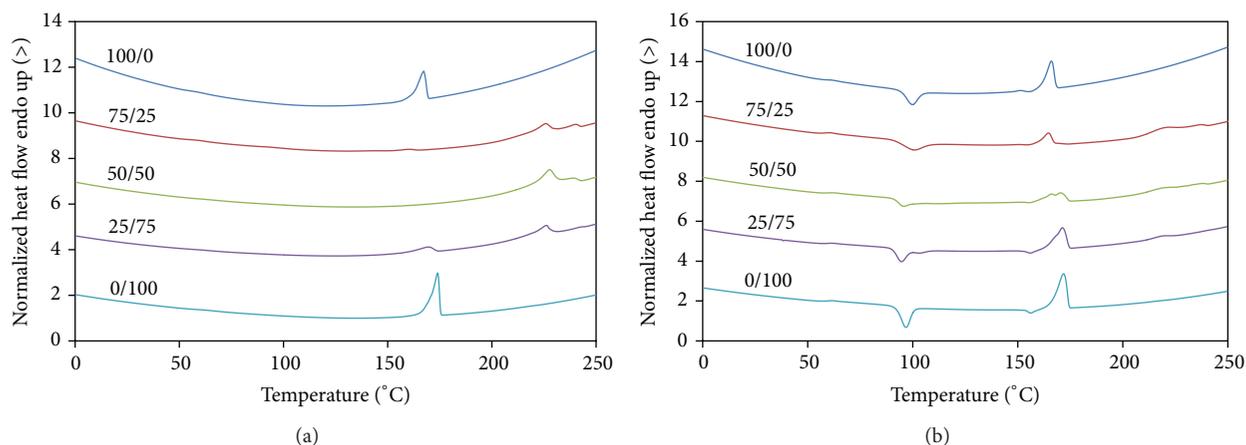


FIGURE 1: DSC thermograms of (a) 1st and (b) 2nd heating scans of 6PLL, 1PDL15K, and poly lactide stereocomplexes prepared with different 6PLL/1PDL15K blend ratios.

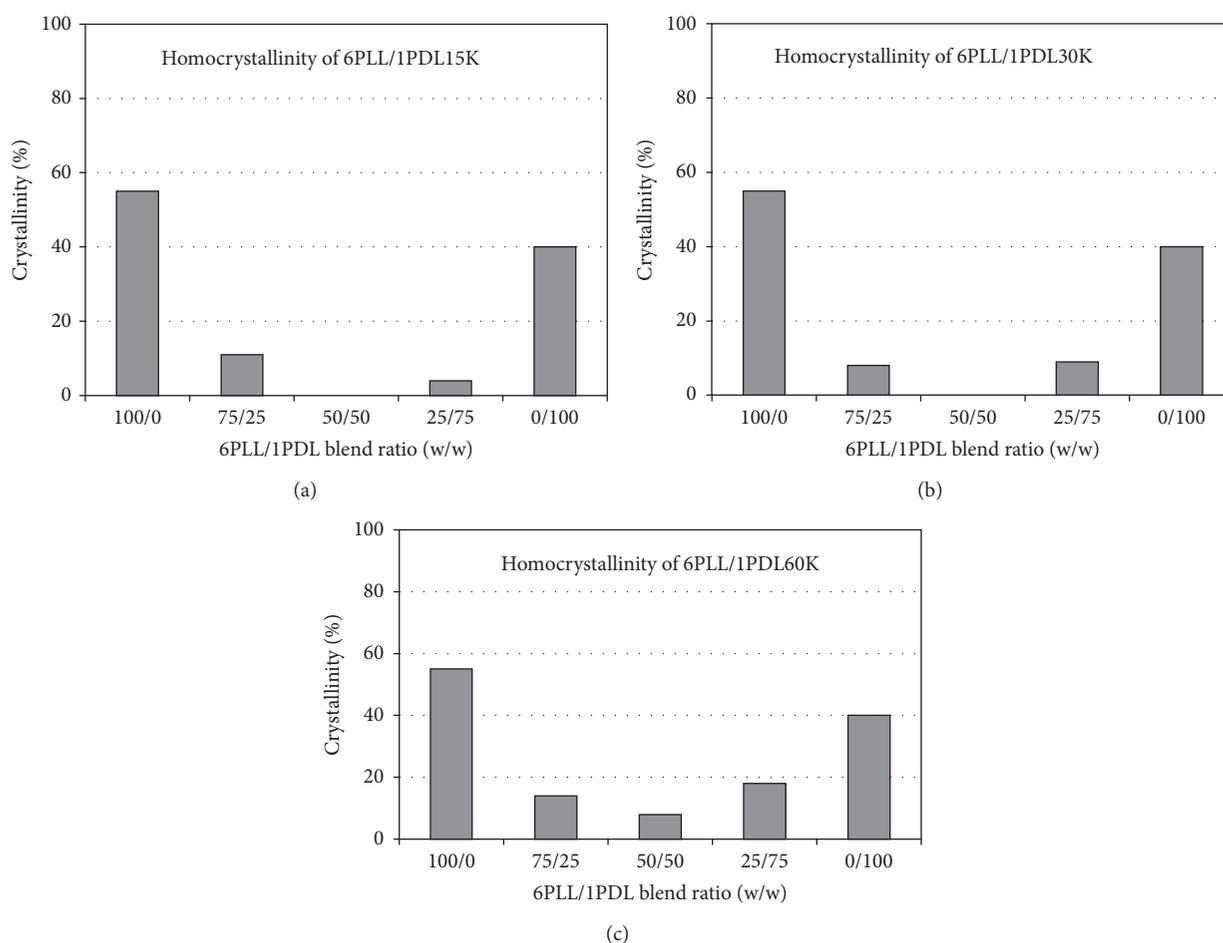


FIGURE 2: Homocrystallinity of 6PLL, 1PDL, and their poly lactide stereocomplexes prepared with different 1PDL molecular weights and 6PLL/1PDL blend ratios.

did not. These results are similar to the stereocomplexation and melting behaviors of linear PLL/linear PDL stereocomplexes prepared with different molecular weights [2].

The homocrystallinity (χ_{hc}) and stereocomplex crystallinity (χ_{sc}) of the poly lactides calculated from (1) and (2)

are compared in Figures 2 and 3, respectively. The χ_{hc} of the 6PLL/1PDL stereocomplexes were lower than those of the 6PLL and 1PDL (see Figure 2). This is due to the poly lactide crystallites being formed as stereocomplex crystallites instead of homocrystallites. The χ_{hc} begins to reduce when 6PLL

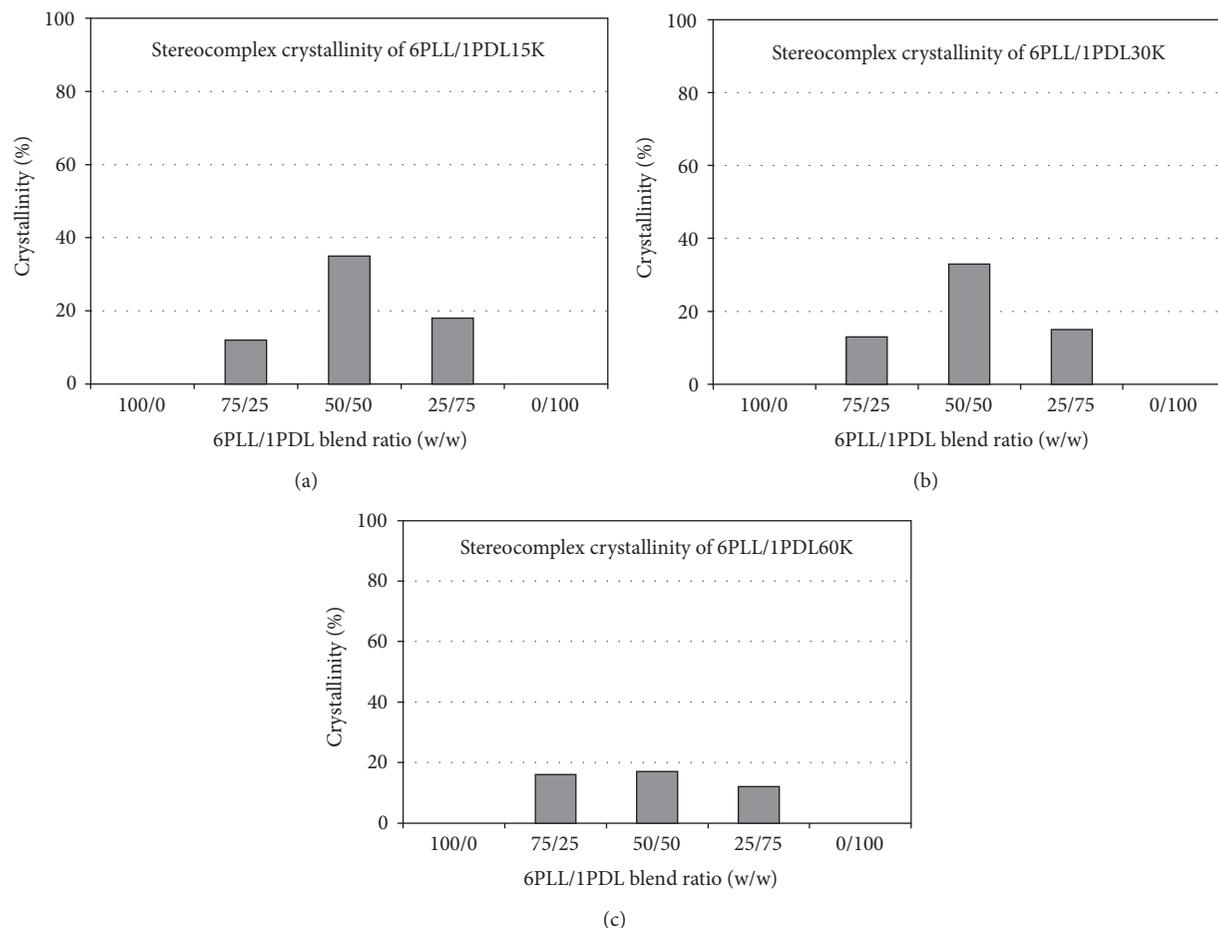


FIGURE 3: Stereocomplex crystallinity of 6PLL, 1PDL, and their polylactide stereocomplexes prepared with different 1PDL molecular weights and 6PLL/1PDL blend ratios.

and 1PDL were blended together and finally disappeared at a 50/50 (w/w) blend ratio for the 6PLL/1PDL15K and 6PLL/1PDL30K blends. The χ_{sc} appeared when the 6PLL and 1PDL were blended (see Figure 3). The χ_{sc} of the polylactide blends with a 50/50 (w/w) 6PLL/1PDL blend ratio was the highest for all the 1PDL molecular weights.

It should be noted that the χ_{sc} of the 50/50 (w/w) 6PLL/1PDL stereocomplexes largely decreased as the 1PDL molecular weight increased from 30,000 (1PDL30K) to 60,000 (1PDL60K) g/mol. This may be explained by the racemic or stereocomplex crystallization preferentially taking place when the 6PLL was blended with low (15K) or medium (30K) molecular weight 1PDL; therefore more perfect stereocomplex crystallites can be obtained. For the high molecular weight 1PDL (1PDL60K), the 1PDL molecules aggregate by themselves from homocrystallization to form as homocrystallites.

The T_g s and T_c s of 6PLL, 1PDL, and their stereocomplexes are also reported in Table 1 and are in the ranges 56–60°C and 92–104°C, respectively. This indicates that the stereocomplex formation did not clearly affect the T_g and T_c . In addition, the heats of crystallization (ΔH_c) of the 6PLL/1PDL15K and

6PLL/1PDL30K blends was lower than those of the 6PLL and 1PDL, excepted for the 6PLL/1PDL60K. This may be due to the stereocomplex formation of 6PLL/1PDL60K being too low, as shown in Figure 3 for the results of the stereocomplex crystallinity. The enhancement of crystallization for stereocomplex formation has been reported in previous work [9, 14].

3.2. Crystalline Structures. Figure 4 shows that the WAXD diffraction peaks of 6PLL (100/0) and 1PDL (0/100) are $2\theta = 15^\circ, 17^\circ,$ and 19° , which can be attributed to the homocrystallites of 6PLL and 1PDL [2]. The WAXD diffraction peaks of $2\theta = 12^\circ, 21^\circ,$ and 24° can be ascribed to the stereocomplex crystallites of the 6PLL/1PDL blends [2]. Only the 50/50 6PLL/1PDL15K and 50/50 6PLL/1PDL30K blends exhibited perfect stereocomplex crystallites without any homocrystallites. The diffraction peaks of the 50/50 6PLL/1PDL60K blend showed both the characteristic peaks of homocrystallites and stereocomplex crystallites; however, the 1PDL60K blending did not give perfect stereocomplex crystallites. The 75/25 and 25/75 6PLL/1PDL blends contained both homocrystallites and stereocomplex crystallites. This shows that the WAXD

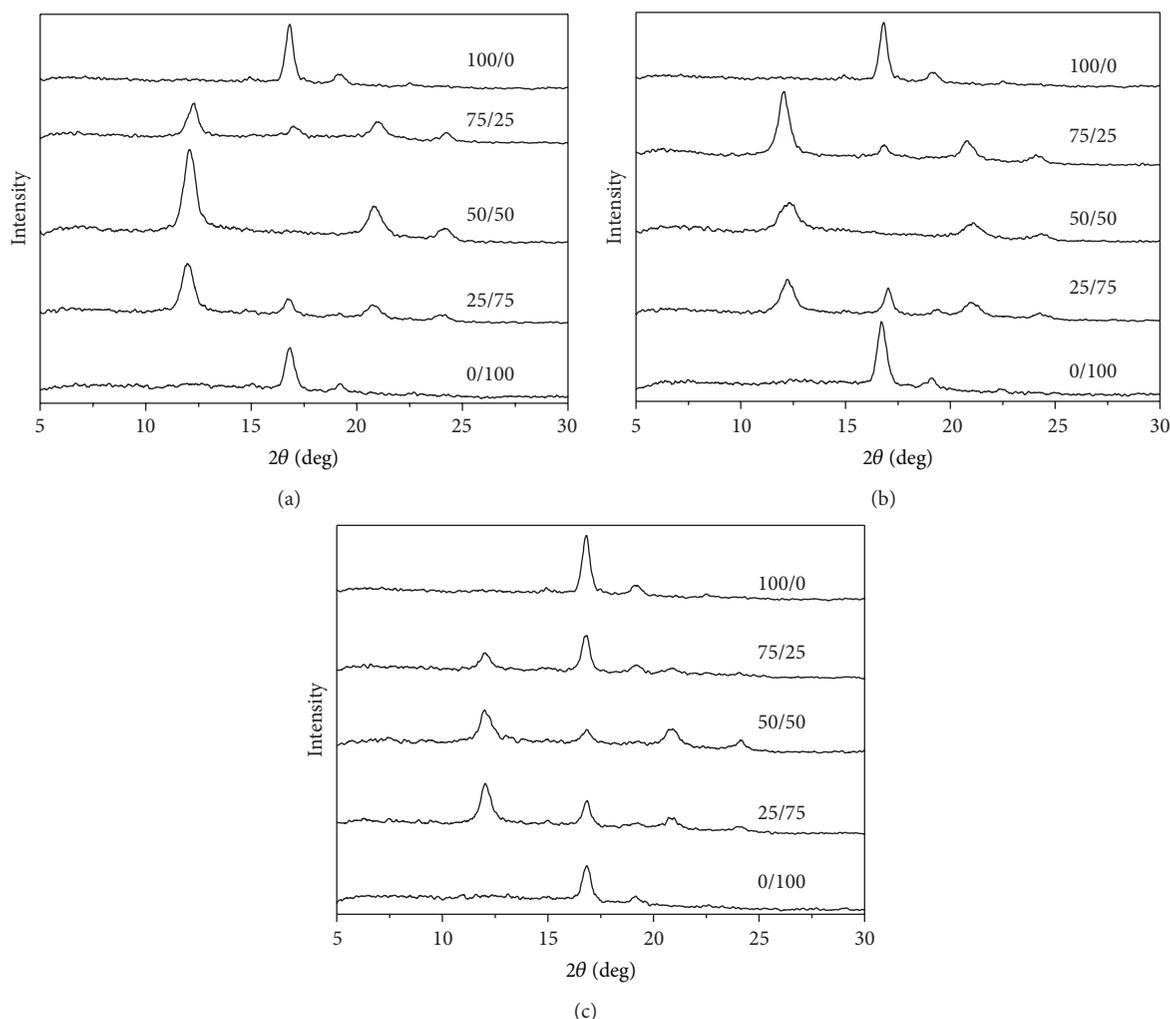


FIGURE 4: WAXD patterns of (a) 6PLL/1PDL15K, (b) 6PLL/1PDL30K, and (c) 6PLL/1PDL60K stereocomplexes prepared with different 6PLL/1PDL blend ratios.

results are entirely consistent with the DSC results described above.

3.3. Thermal Stability. The thermal stabilities of 6PLL, 1PDL, and their stereocomplexes were determined from their differential thermogravimetric (DTG) thermograms. The peak in the DTG thermogram gives the temperature of maximum decomposition rate ($T_{d,max}$), as summarized in Table 2. It can be seen that the $T_{d,max}$ values of the 50/50 (w/w) 6PLL/1PDL15K and 50/50 (w/w) 6PLL/1PDL30K blends were slightly higher than those of the 6PLL and 1PDL. This may be due to the stronger van der Waals interactions between the PLL and PDL chains in the molten state that enhanced their thermal stability. However, the $T_{d,max}$ value of the 50/50 (w/w) 6PLL/1PDL60K was similar to the 6PLL. This suggests that the higher molecular weight PDL chains reduced the van der Waals interactions in the stereocomplexation, according to the results of the stereocomplex crystallinity in Figure 3.

3.4. Tensile Properties. The tensile test was used to examine the mechanical properties of polylactide films. The tensile

strength and elongation at break of 6PLL, 1PDLs, and their stereocomplex films prepared with different molecular weights of 1PDL are plotted as a function of the 6PLL/1PDL blend ratio in Figures 5 and 6, respectively. The 25/75 6PLL/1PDL15K stereocomplex and 1PDL15K films could not be prepared due to the molecular weight of 1PDL15K being too low for film formation; therefore, there are no tensile test results for them.

It can be seen that the tensile strength and elongation at break of the polylactide stereocomplex films were higher than those of the 6PLL and 1PDL films. This was due to the stereocomplex crystalline structure of the polylactides having stronger van der Waals interactions than the homocrystalline structure [8–10]. The 50/50 (w/w) 6PLL/1PDL stereocomplex films showed the highest tensile strength and elongation at break, which were similar to the linear PLL/linear PDL stereocomplex films [2]. This may be due to the 50/50 (w/w) 6PLL/1PDL stereocomplexes having the highest stereocomplex crystallinity, as described in the previous DSC results. In addition, the tensile strength and elongation at break of

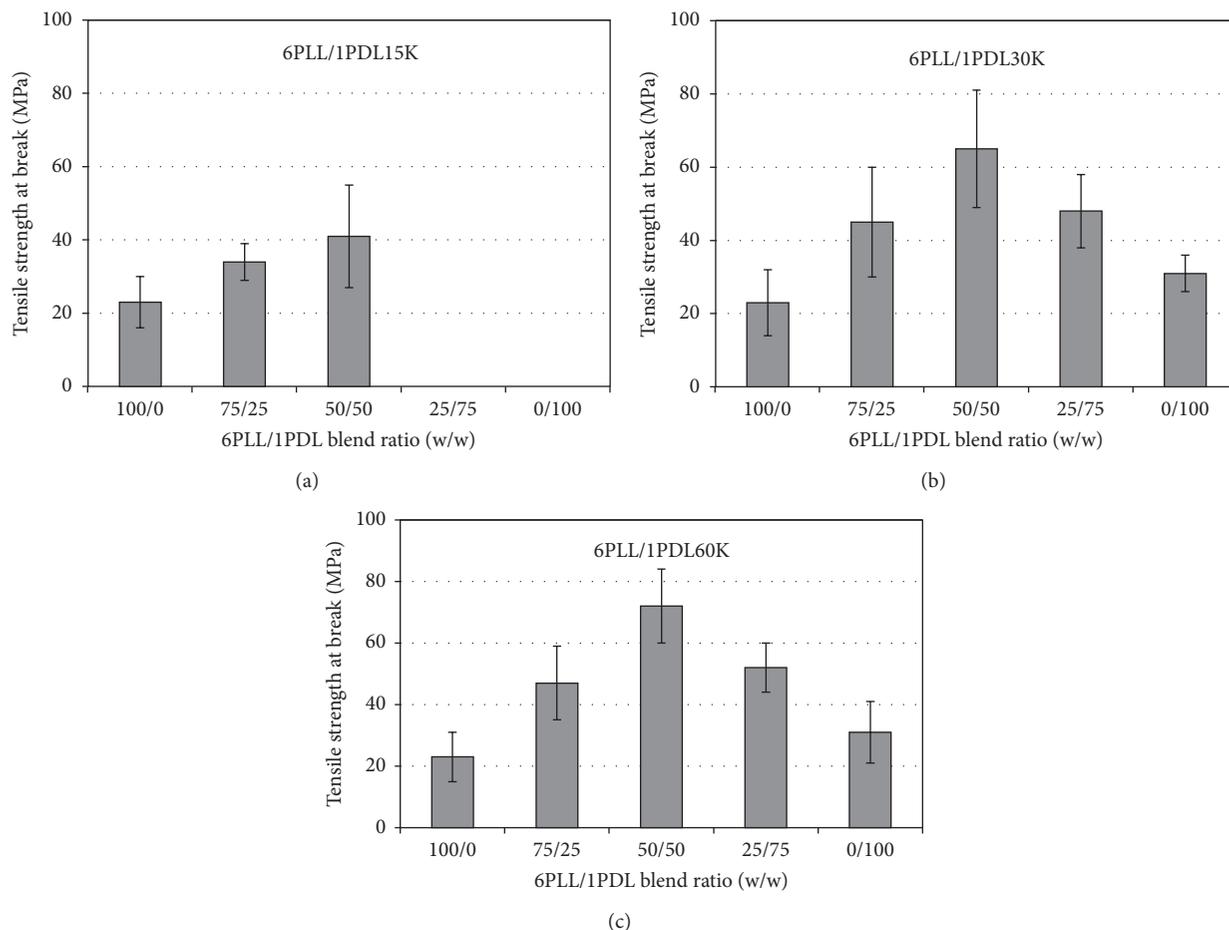


FIGURE 5: Tensile strength at break of 6PLL, 1PDL, and 6PLL/1PDL stereocomplex films prepared with different 1PDL molecular weights and 6PLL/1PDL blend ratios.

TABLE 2: $T_{d,max}$ of 6PLL, 1PDL, and 6PLL/1PDL stereocomplexes.

6PLL/1PDL blend ratio (w/w)	$T_{d,max}$ ($^{\circ}$ C)
6PLL/1PDL15K	
100/0	367
75/25	368
50/50	373
25/75	363
0/100	362
6PLL/1PDL30K	
100/0	367
75/25	369
50/50	372
25/75	369
0/100	362
6PLL/1PDL60K	
100/0	367
75/25	368
50/50	368
25/75	365
0/100	362

the polylactide stereocomplex films increased slightly as the molecular weight of 1PDL increased. The density of the tie chain, which connects the homocrystallites or stereocomplex crystallites with each other, may increase as the molecular weight of the polylactide increases [23]. However, Young's modulus values of 6PLL, 1PDL, and their stereocomplexes were similar. They were in range 987–1108, 940–1138, and 952–1152 MPa for the 6PLL/1PDL15K, 6PLL/1PDL30K, and 6PLL/1PDL60K stereocomplex films, respectively.

4. Conclusions

In conclusion, the 6-arm star-shaped PLL and linear PDL were successfully synthesized using 6-OH (dipentaerythritol) and 1-OH (1-dodecanol) end-group compounds, respectively, as the initiators. The DSC and WAXD results revealed that the solvent cast films of the 6PLL/1PDL blends preferentially formed stereocomplex crystallites when the 1PDL molecular weights were low (15,000 g/mol) and medium (30,000 g/mol), and the 6PLL/1PDL blend ratio was 50/50 (w/w). The thermal stabilities of the 6PLL/1PDL15K and 6PLL/1PDL30K stereocomplexes with the 50/50 (w/w) blend

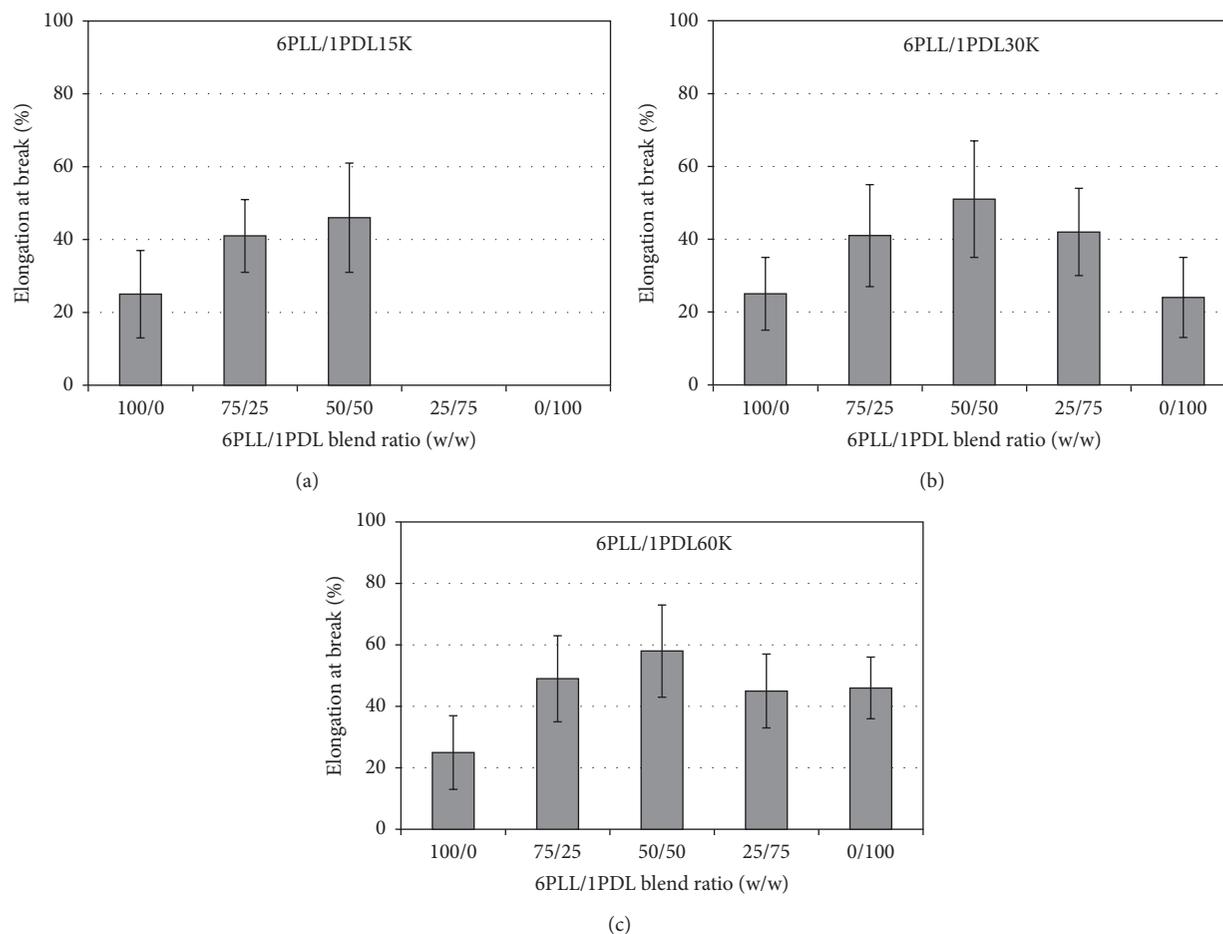


FIGURE 6: Elongation at break of 6PLL, 1PDL, and 6PLL/1PDL stereocomplex films prepared with different 1PDL molecular weights and 6PLL/1PDL blend ratios.

ratio were slightly higher than those of the original 6PLL and 1PDL. The tensile strength and elongation at break of the 6PLL/1PDL were better than both the 6PLL and 1PDL and increased as the molecular weight of 1PDL also increased. The 50/50 (w/w) 6PLL/1PDL stereocomplexes showed the highest mechanical properties. These star-shaped/linear polylactide stereocomplexes are promising renewable bioplastics with tuneable thermal and mechanical properties to replace oil-based commodity plastics for various applications.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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