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ARTICLE

## The Morphology and Spherulite Growth of Stereocomplex in the Linear and Branched PLLA/PDLA Blends: Effect of Molecular Weights and Structure

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The linear and three armed poly(L-lactide)/poly(D-lactide) (PLLA/PDLA, 3PLLA/3PDLA and 3PLLA/PDLA) specimens were prepared through solution mixing method, and the morphology and the spherulites growth of poly(lactide) stereocomplex crystallites (PLA sc) from the melt with various structures and molecular weights were investigated. The polarized optical microscope pictures revealed that the regular spherulites and legible frontier were developed in all the PLLA/PDLA blends with relative lower molecular weights ( $M_n < 20$  kg/mol for each branch), and irregular spherulites formed after the molecular weights of PLA polymers were higher than 60 kg/mol. The growth rate of the spherulite ( $G$ ) increased at first, and then decreased as molecular weights increasing in all the PLLA/PDLA, 3PLLA/3PDLA and 3PLLA/PDLA specimens. The highest  $G$  value in all the specimens was achieved when the average molecular weights of each branch were  $\sim 10$  kg/mol. With similar molecular weights for each branches, the  $G$  reduced gradually as the three armed PLA added in the blend (*i.e.*, PLLA/PDLA > 3PLLA/PDLA > 3PLLA/3PDLA).

### Introduction

As the oil shortage and the environmental pollution issues become bad to worse, the bio-based polymers, including the ones chemically synthesized from various naturally occurring resources and those produced by microorganisms, are attracting more and more attentions from the past two decades. Among a large number of the bio-based polymers, thermoplastic aliphatic polyester, such as poly(lactide) (PLA), has been intensively investigated and developed as an alternative to conventional non-degradable synthetic polymers because of its mechanical performances, renewable and disposable properties.<sup>1, 2</sup> However, PLA based material has its intrinsic defect, its low heat resistance temperature, which could be a major obstacle to the practical applications in a large scale. There are three types of PLAs (PLLA, PDLA and PDLLA) due to the different sequential structure of chiral carbon in the main chain of the macromolecule. For PLA with higher optical purity, *i.e.*, PLLA and PDLA, their melting temperature usually at  $\sim 180$  °C. The melting temperature of PLLA (PDLA) decreases rapidly and crystallization capacity weakens drastically after the optical purity decreasing.<sup>3, 4</sup> One interesting phenomenon of PLA is that the PLA stereocomplex crystallites (sc) form after PLLA blend with PDLA, which possess higher melting temperature, 230 °C,<sup>5</sup> and the blend

develops crystallites at a faster speed.<sup>6</sup> Thus, the PLA sc materials with higher thermal stability can be prepared and present wider application potentials. Systematic studies reveals that the PLA sc could develop from binary linear blends,<sup>6-10</sup> the di-, tri-, and multi-block copolymers,<sup>11-16</sup> and also formed in the linear/branched and branched/branched structures.<sup>17-20</sup> The crystallization and melting behaviours of PLA sc presents various regularities at different structures and conditions, and diverse morphology of PLA sc also formed in different specimens.<sup>9, 21</sup>

Different structure would present various morphology, and the morphology formed in polymer determines its usage and application field.<sup>22</sup> Although the morphology of PLLA/PDLA blends with different weight ratios and molecular weights were studied,<sup>6, 23, 24</sup> the variation of spherulite growth of PLA sc with different molecular weights are not clear yet. In addition, the melt viscosity of linear PLA reduces rapidly as temperature increasing during melting extrusion, which limits the processing temperature window of PLA, especially for the PLA sc materials as it is melted at higher temperature. Introducing branched polymers will enhance the viscosity after melting and which would in favour of the processing PLA sc materials.<sup>25, 26</sup> The stereocomplex formation between multi-armed enantiomeric PLAs has been reported in various aspects,<sup>19, 27</sup> However, the distinction of spherulite growth between linear and branched structures are still an unclear issue. These issues are critical and which could supply instruction for the process of PLA sc materials. In this study, the linear and three armed PLLA and PDLA were synthesized separately, and they were blended together to

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prepare the linear and branched PLA sc materials. After the blends were melted completely, the growth speed of the spherulites and their morphology of sc were studied. This investigation would supply instructions for the application of the PLA sc with linear and branched structures.

### Experimental Section

#### Materials and sample preparation

The L-lactide (L-LA) and D-lactide (D-LA) (optical purities  $\geq 99.5\%$ ) were bought by Purac and recrystallized in anhydrous ethyl acetate. Tin (II) 2-ethylhexanoate ( $\text{Sn}(\text{Oct})_2$ , 95%) was purchased from Aldrich and was directly used without purification. Isopropanol ( $\geq 99.5\%$ ) and propanetriol ( $\geq 99.5\%$ ) were bought from Aladdin. Linear PLLA and PDLA were synthesized by ring-opening polymerization of L-LA and D-LA, respectively, initiated by isopropanol and catalyzed by  $\text{Sn}(\text{Oct})_2$  at 120 °C in dry toluene for 24 h, and the LA/toluene ratio was 1/10 in w/v.<sup>8</sup> The three armed PLLA (3PLLA) and PDLA (3PDLA) were polymerized as the same method, and the propanetriol was used as initiator.<sup>27</sup> The molecular weights of linear and three armed PLA polymers were regulated by the LA/initiator mole ratio. The crude products were precipitated in ethanol and dissolved in dichloromethane twice to purification. The purified products were dried under vacuum at 60 °C to constant weight. Linear and three armed PLLA and PDLA used in this study were listed in **Table 1**. The linear and three armed PLLA were coded as L and 3L, separately, and the linear and three armed PDLA were abbreviated to D and 3D, respectively. The numbers after linear and branched PLLA and PDLA were their number average molecular weight, separately.

The stereocomplexed PLLA/PDLA blends were prepared from the linear and three armed PLLA and PDLA as follows.<sup>28</sup> Firstly, PLLA, PDLA, 3PLLA and 3PDLA were dissolved separately in dichloromethane as a concentration of 10.0 g/l. And then, the PLLA and PDLA, 3PLLA and 3PDLA, 3PLLA and PDLA were admixed together respectively under vigorous stirring for 3 h, and the proportion of PLLA:PDLA in the blends were maintained at 1:1 by weight. Finally, these solutions were poured into petri dishes for evaporation at room temperature to obtain the PLLA/PDLA, 3PLLA/3PDLA and 3PLLA/PDLA blending films. All these casted films were dried at room temperature for 24 h, and were dried to constant weight at 50 °C prior to measurements.

#### Gel permeation chromatography (GPC)

The molecular parameters of obtained PLAs were characterized by Waters GPC (USA) at 35 °C, equipped with two styragel HR gel columns (HR2 and HR4). It was calibrated with polystyrene standards that covered the range of molecular weight 1000–600,000 kg/mol. Chloroform was used as the eluent at a flow rate of 1.0 ml/min.

#### Differential Scanning Calorimetry (DSC)

Thermal properties of PLLA/PDLA, 3PLLA/3PDLA and 3PLLA/PDLA samples were investigated on a differential scanning calorimeter (DSC, Q100, TA Instrument) in nitrogen atmosphere. The specimens were scanned at a constant rate of 10 °C/min over the temperature

range of 30 to 255 °C, and the first heating of the specimens were recorded.

**Table 1.** The characterization of linear and three armed PLA

| Code <sup>a</sup> | $M_{n(\text{GPC})}$ (kg/mol) | PDI | $T_m$ (°C) |
|-------------------|------------------------------|-----|------------|
| L4                | 4                            | 1.2 | 133.8      |
| L8                | 8                            | 1.2 | 158.1      |
| L15               | 15                           | 1.2 | 165.6      |
| L32               | 32                           | 1.5 | 174.1      |
| L50               | 50                           | 1.4 | 176.3      |
| L70               | 70                           | 1.7 | 175.8      |
| D5                | 5                            | 1.3 | 145.8      |
| D7                | 7                            | 1.1 | 157.6      |
| D11               | 11                           | 1.3 | 160.8      |
| D14               | 14                           | 1.3 | 166.8      |
| D22               | 22                           | 1.4 | 170.3      |
| D31               | 31                           | 1.1 | 173.5      |
| D42               | 42                           | 1.1 | 174.9      |
| D52               | 52                           | 1.5 | 175.2      |
| D68               | 68                           | 1.8 | 176.9      |
| 3L10              | 10                           | 1.4 | 150.2      |
| 3L35              | 35                           | 1.4 | 162.1      |
| 3L60              | 60                           | 1.4 | 171.5      |
| 3L95              | 95                           | 1.5 | 173.4      |
| 3L130             | 130                          | 1.3 | 175.1      |
| 3D9               | 9                            | 1.1 | 145.8      |
| 3D33              | 33                           | 1.1 | 163.9      |
| 3D57              | 57                           | 1.4 | 170.8      |
| 3D105             | 105                          | 1.6 | 175.8      |

<sup>a</sup> The PLLA was coded as L and PDLA was abbreviated as D, the three armed PLLA and three armed PDLA were code as 3L and 3D, respectively. The numbers after L or D were their number-average molecular weights.

#### Polarized Optical Microscopy (POM)

The morphology and growth rate of PLA sc spherulite in the films was observed using a Carl Zeiss Axio Imager A2m (Germany) polarized optical microscope, which equipped with a heating cooling stage and a temperature controller (THMS-600, Linkam Scientific Instruments, UK). A small piece of sample was squeezed between two microscope slides, then inserted in the hot stage. The films were heated from 30 to 260 °C at a rate of 30 °C/min, held at this temperature for 1 min, then cooled to a desired isothermal crystallization temperature ( $T_c$ ) at 100 °C/min, and then held at the  $T_c$  and observed the spherulite growth here. The radii of growing crystals were monitored during solidification by taking photomicrographs at appropriate intervals of time. Spherulite radii were measured with the software Image-Pro Plus 3.0. Dry nitrogen gas was purged throughout the hot stage during all the measurements and thermal treatments.

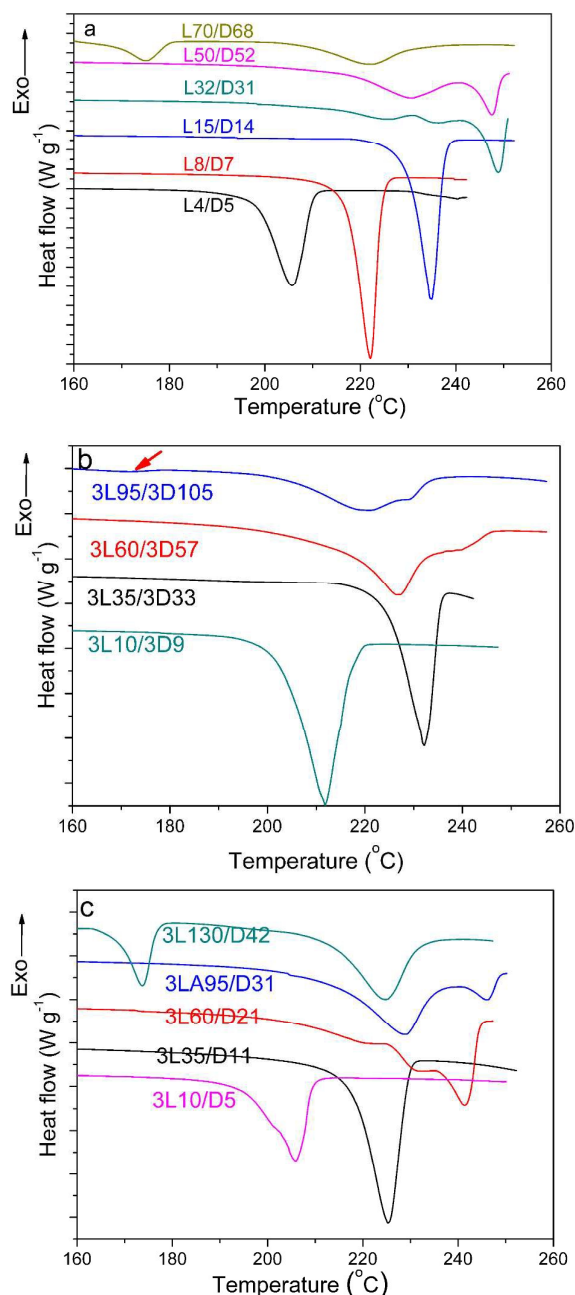
## Results and discussion

### The DSC of linear and three armed PLLA/PDLA blends

The DSC results of linear PLLA/PDLA specimens were shown in Fig. 1a. Endothermic signals were observed above 200 °C in all the specimens, which should be ascribed to the melting peak of PLA sc. An additional endothermic signal was found around 175 °C in the L70/D68 specimen, which should be due to the melting of PLA homochiral crystallites (hc). In the DSC curve of 3PLLA/3PDLA (Fig. 1b) and 3PLLA/PDLA (Fig. 1c) specimens, the signals around 220 °C were obviously observed in all the specimens. Besides, signals assigned to PLA hc were also found around 170 °C in the 3L95/3D105 and 3L130/D42 specimens. From Fig. 1a to 1c, it found that the PLA hc appeared when the total number average molecular weight of linear PLLA/PDLA was 138 kg/mol ( $M_{n,PLLA} + M_{n,PDLA}$ ), and this value was 200 and 172 kg/mol, respectively, for the 3PLLA/3PDLA and 3PLLA/PDLA blends. The total molecular weight, which developed PLA hc, increased as three armed PLA added in the specimens. However, the number average molecular weight for each branch, 69 kg/mol in PLLA/PDLA, 43 kg/mol in 3PLLA/PDLA and 33 kg/mol in 3PLLA/3PDLA, reduced as the three armed PLA added in the blends. In addition, the melting temperatures of PLA sc in all the specimens were not higher than 250 °C. And according to the reported literature, the highest melting temperature of PLA sc also did not exceed to 250 °C.<sup>8, 18, 27, 29, 30</sup> Thus, all the specimens were heated to 260 °C and held for 1 min, which could ensure that all the PLA sc are melted completely and the heat history are eliminated thoroughly. On the other hand, both the PLA sc and hc crystallites would form at relative lower crystallization temperature in the specimens with higher molecular weights.<sup>31, 32</sup> Thus, all the crystallization temperatures of specimens were selected at 180 and 190 °C, respectively, which were higher than the melting temperature of PLA hc. Accordingly, it is reasonable to assume that only PLA sc formed in all the linear and branched blends.

### The morphology and spherulite growth of PLLA/PDLA blends

Fig. 2 presented the morphology of linear PLLA/PDLA blends annealed at 180 °C for 5 min with various molecular weights. In the L4/D5 specimen, the spherulite with obvious Maltese crosses was



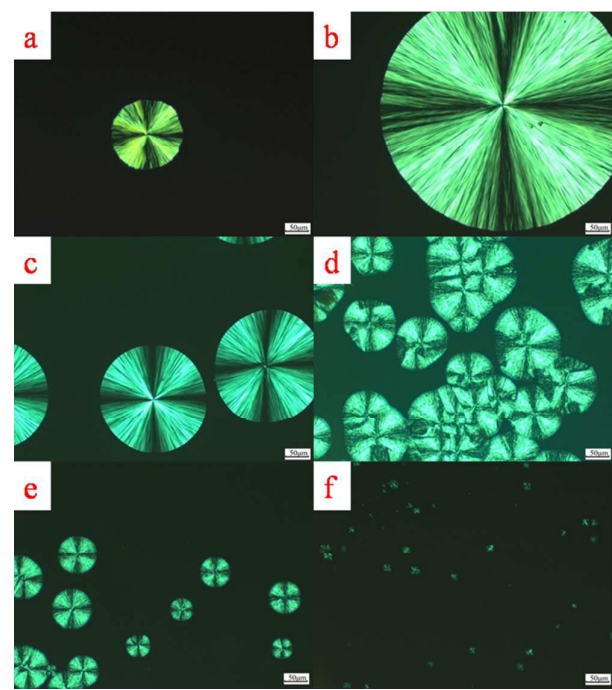
**Fig. 1** The DSC of PLLA/PDLA (a), 3PLLA/3PDLA (b) and 3PLLA/PDLA (c) blends.

observed, but the frontier of spherulite in the L4/D5 was not as ordered as the L8/D7 and L15/D14 specimens. The contrast between the bright and dark regions of Maltese cross was legible and the orientation of the crystals along the radius direction was distinct when the molecular weights of PLAs were not higher than 15 kg/mol. However, this contrast reduced for the specimens which molecular weights were 32 kg/mol or higher, and the orientation of the crystals along the radius direction was disturbed. Such structural disorder should be attributable to the decreased

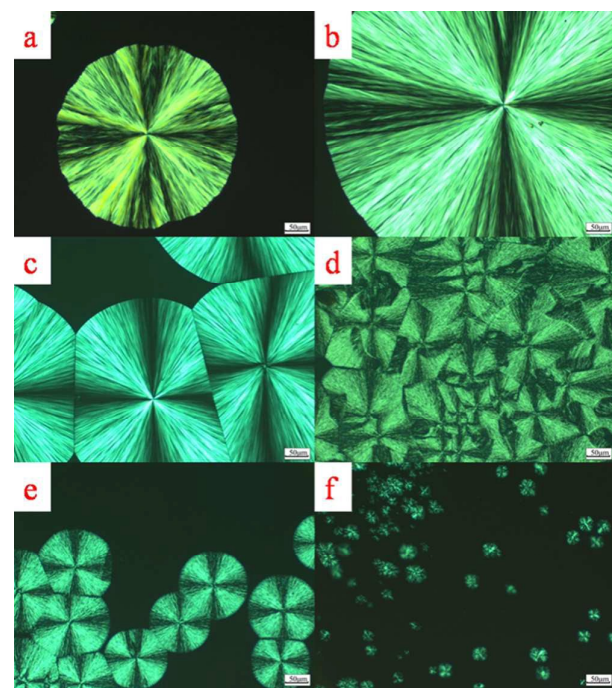
orientation of lamellae, because the entanglement increased as molecular weight increasing.<sup>33</sup> At the same time, the interdiffusion of PLLA and PDLA molecular chains would also embarrass the enantiomeric PLAs rearrange side by side alternately. The number of nucleus increased notably when the molecular weights of PLA polymers were higher than 30 kg/mol, and the Maltese crosses was not distinctly observed in the L70/D68 specimen. The radius of the spherulite increased at first, and was highest in the L8/D7 specimen, then decreased as the molecular weight of PLAs increasing from 4 to 70 kg/mol. After these specimens were annealed at 180 °C for 10 min, The POM of these specimens were shown in Fig. 3. It found that the size of spherulites in all the specimens became larger. In L8/D7, the only one spherulite covered almost the observed picture even annealed for 7.7 min. The racemic crystallites fulfilled the whole horizon in the L32/D31 after annealed for 10 min, which should be ascribed to more nucleation points were produced in this specimen as its higher degree of supercooling ( $\Delta T = T_m - T_c$ ). In the case of L70/D68 specimen, no discernable orientation of the crystals along the radius of spherulites were observed even annealed for a longer time, which should be interpreted that the viscosity and chain entanglement at this molecular weights were grievous, the orientation of the crystal along the radius was impeded, and resulted to the crystals arranged in an irregular shape.

When the specimen were annealed at 190 °C for 5 min, the pictures were presented in Fig. 4. The L4/D5 did not form any spherulites even annealed for a longer time (60 min), which should be due to the formation of PLA sc became very difficult under that supercooling condition ( $\Delta T \approx 15$  °C), and its picture did not show here. Compared to the Fig. 2, the diameter of the spherulites which annealed at 190 °C were obviously smaller than that of corresponding specimens annealed at 180 °C, which was ascribed to the lower speed of spherulites growth at the higher annealing temperature (lower degree of the  $\Delta T$ ). The size of the spherulites decreased as molecular weight increasing from 8 to 70 kg/mol, but the number of the nucleus tended to increase as molecular weight increasing, which should be ascribed to the viscosity enhanced as molecular weight enlarging, and which in favor of generating more nucleating points. In the L70/D68 specimen, no obvious spherulites were observed after annealing for 5 min, but spherulites appeared after annealing for longer time, and the pictures annealing for longer time were exhibited in Fig. 5. After annealed at 190 °C for longer time, the radius of spherulites increased in all the specimens (shown in Fig. 5). A small amount of additional spherulites developed in the L50/D52 specimen, and a large number of new spherulites appeared in the L70/D68 specimen.

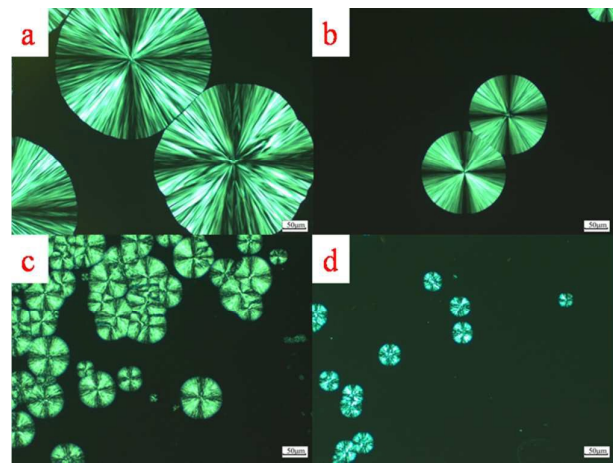
The diameters of spherulites at different time of the specimens which annealed at 180 °C were presented in Fig. 6. In L4/D5 and L8/D7, only one line was presented in the graph, which indicated that only one spherulite was observed and calculated. In other specimens, more spherulites were observed and calculated, and they were plotted as different colored lines in the graph. It could be seen that the diameters of spherulites increased linearly with time in most of the specimens except the L70/D68. The deviation of the diameter in L70/D68 should be due to the fact that, the entanglement and the interdiffusion between isomer polymers were grievous in the melting state, and the crystals which located



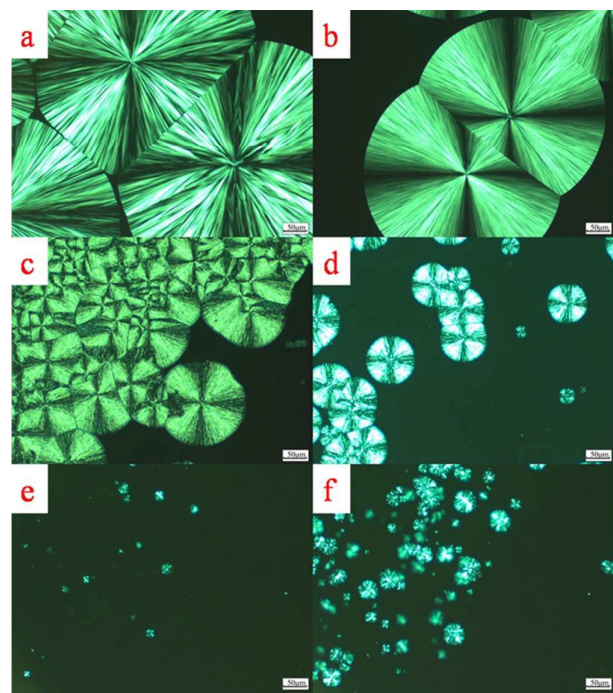
**Fig. 2** The morphology of linear PLLA/PDLA blends at 180 °C for 5min. (a) L4/D5, (b) L8/D7, (c) L15/D14, (d) L32/D31, (e) L50/D52 and (f) L70/D68.



**Fig. 3** The morphology of PLLA/PDLA blends at 180 °C for 10 min. (a) L4/D5, (b) L8/D7 for 7.7 min, (c) L15/D14, (d) L32/D31, (e) L50/D52 and (f) L70/D68.



**Fig. 4** The morphology of linear PLLA/PDLA blends at 190 °C for 5 min. (a) L8/D7, (b) L15/D14, (c) L32/D31 and (d) L50/D52.

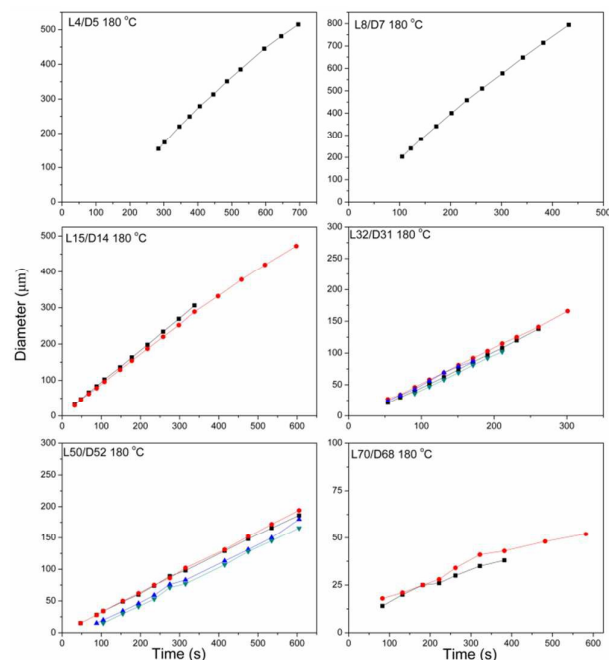


**Fig. 5** The morphology of linear PLLA/PDLA blends at 190 °C. (a) L8/D7 for 8 min 9 s, (b) L15/D14, (c) L32/D31, (d) L50/D52 and (e) L70/D68 for 10 min, (f) L70/D68 for 20 min.

nearby the entanglement point would not exclude the entangled molecular chains, which resulted to the spherulites presented in an irregular shape. Thus, the calculation of the diameter could not as precise as other specimens.

The growth of spherulites in the linear PLLA/PDLA specimens which annealed at 190 °C were similar to the Fig. 6, and were not presented here, whereas, the diameter was much smaller than the corresponding specimens annealed at 180 °C. The radius growth

rates of spherulites ( $G$ ) with different specimens were plotted in Fig. 7. Here, the  $G$  values were estimated from the slopes of spherulite diameter plotted in Fig. 6. When the specimens were annealed at 180 °C, the  $G$  value increased at first, then decreased as molecular weights enlarging from 4 to 70 kg/mol. When the molecular weights of PLA polymers were  $\sim 8$  kg/mol, the  $G$  value reached the highest value. It is known that, the polymers with lower molecular weight exhibited higher mobility. However, the higher mobility would not in favour of nucleating. As molecular weight increasing, the chain entanglement and viscosity enhanced, and which would be convenient for nucleating. Notwithstanding, the improvement of chain entanglement and viscosity of the specimens would limit the migration of molecular chain, and depressed the growth rate of spherulites. Accordingly, the biggest  $G$  value appeared in the blends with moderate molecular weight. After the specimens were annealed at 190 °C, the  $G$  value decreased as molecular weight increased from 8 to 70 kg/mol, which exhibit similar regularity as the specimens annealed at 180 °C. Furthermore, all the  $G$  value reduced as the temperature elevated from 180 to 190 °C, which should be due to the nucleation became difficult at that higher annealed temperature.



**Fig. 6** The diameter of spherulites with different time in the PLLA/PDLA specimens (180 °C).

### The morphology and $G$ value of 3PLLA/3PDLA blends

After melted and subsequently annealed at 180 °C for 5 min, the morphologies of 3PLLA/3PDLA blends with different molecular weights were shown at Fig. 8. Obvious spherulites formed in all the specimens but the 3L95/3D105 sample. Ordered spherulites morphology was observed when the molecular weights were not higher than 35 kg/mol, and disordered spherulites developed when

the molecular weight was 95 kg/mol. After annealed for 10 min (Fig. 9), all the size of spherulites became larger, and more spherulites formed in all the specimens but the 3L10/3D9. The number of nucleus tended to increase as molecular weights increasing, especially for the 3L95/3D105 specimens. This should be due to the melt viscosity improved as molecular weight increasing, and which made the nucleation at the favourable condition.

When these specimens were annealed at 190 °C for 30 min (Fig. 10), the spherulites developed were similar to 180 °C, but the speed of spherulites growth was much slower than that annealed at 180 °C. According to the spherulites growth at 180 °C in different specimens, the diameters of the 3PLLA/3PDLA specimens plotted with time were shown in Fig. 11. The diameter of spherulites in most specimens grew linearly as time but the 3L95/3D105, which should be due to the same reason explained in the linear PLLA/PDLA specimens.

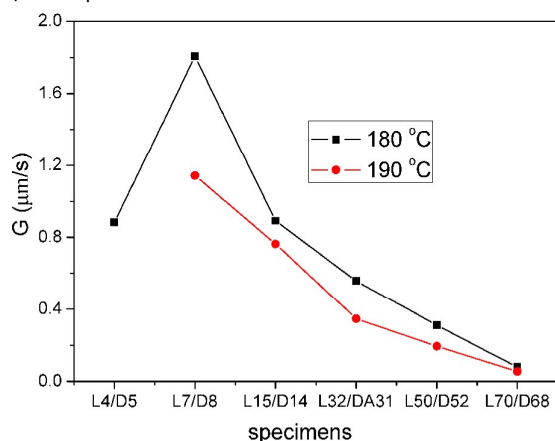


Fig. 7 The G values in the linear PLLA/PDLA blends.

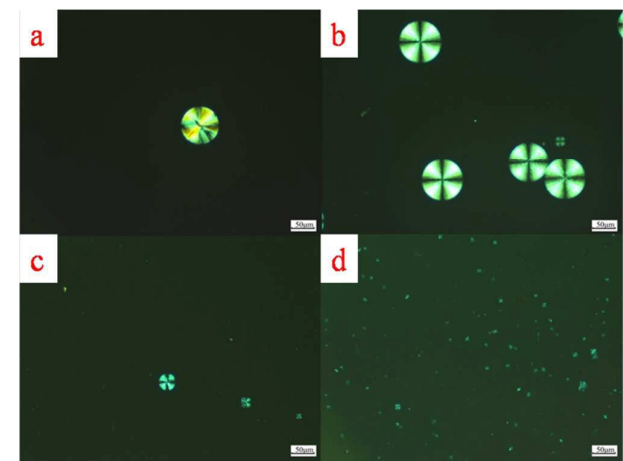


Fig. 8 The morphology of 3PLLA/3PDLA blends at 180 °C for 5 min. (a) 3L10/3D9, (b) 3L35/3D33, (c) 3L60/3D57 and (d) 3L95/3D105.

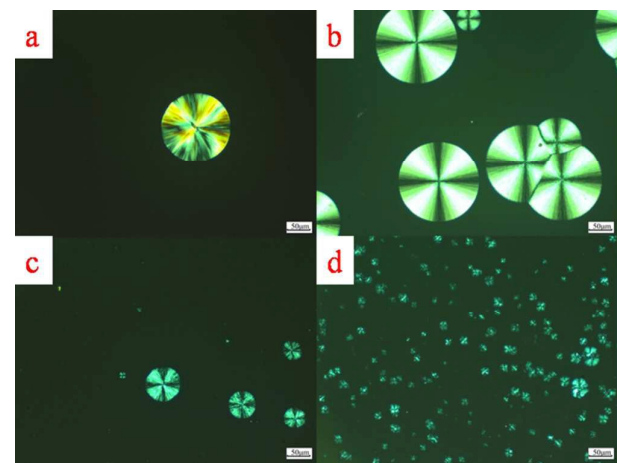


Fig. 9 The morphology of 3PLLA/3PDLA blends at 180 °C for 10 min. (a) 3L10/3D9, (b) 3L35/3D33, (c) 3L60/3D57 and (d) 3L95/3D105.

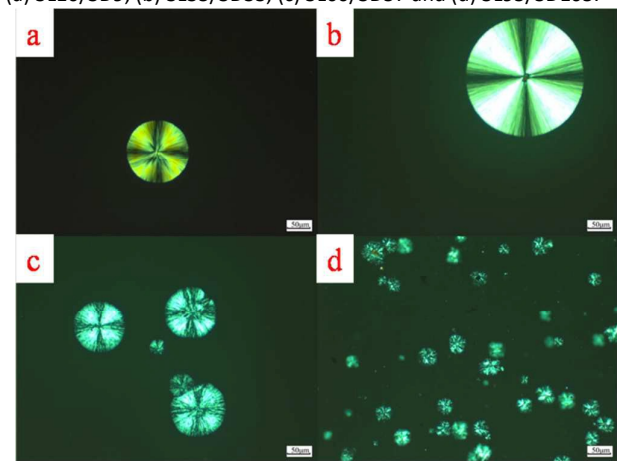


Fig. 10 Morphology of 3PLLA/3PDLA blends at 190 °C for 30 min. (a) 3L10/3D9, (b) 3L35/3D33, (c) 3L60/3D57 and (d) 3L95/3D105.

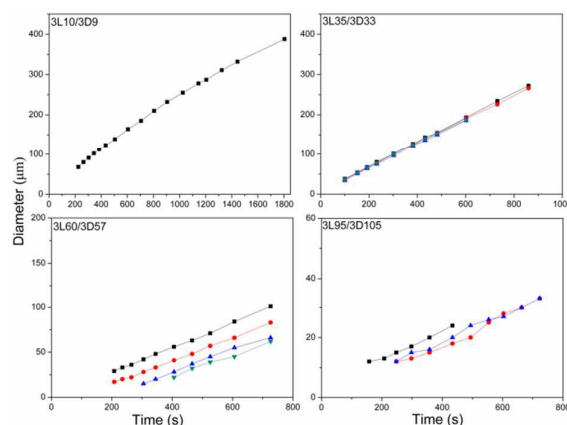
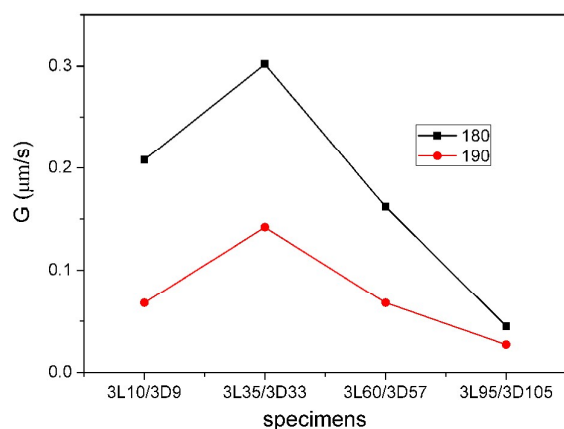


Fig. 11 The diameter of spherulites growth in the 3PLLA/3PDLA blends with different molecular weight (180 °C).



**Fig. 12** The  $G$  value in 3PLLA/3PDLA blends with different molecular weights.

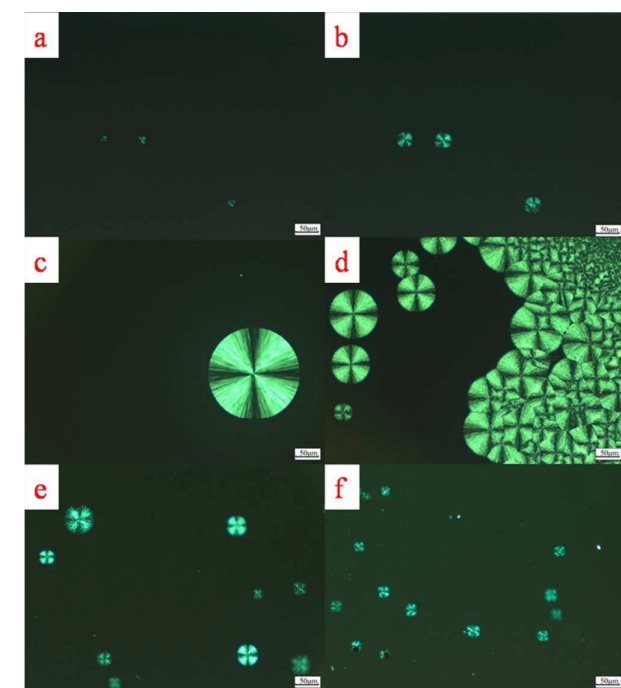
The  $G$  values in 3PLLA/3PDLA blends with different molecular weights were presented at **Fig. 12**. Similar to the linear PLLA/PDLA blends, the  $G$  increased at first, and then decreased as molecular weight increasing. When the molecular weights of 3PLAs were *c.a.* 35 kg/mol, and the molecular weights for each branch were  $\sim$ 11 kg/mol, the  $G$  value was highest.

#### The morphology and $G$ value of 3PLLA/PDLA specimens

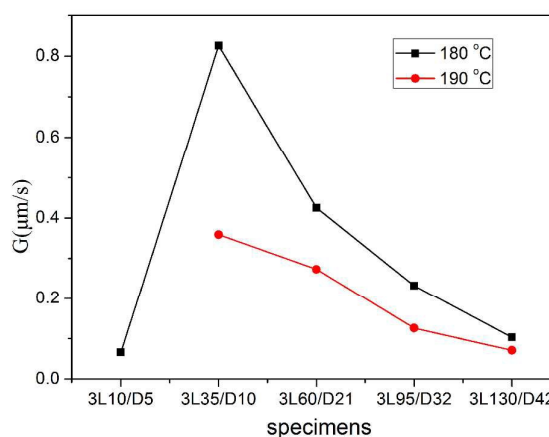
In the 3PLLA/PDLA specimens, the molecular weight of PDLA was similar with the branch of 3PLLA in each specimen. **Fig. 13** exhibited the morphology of 3PLLA/PDLA specimens annealed at 180 °C. It could be seen that normal spherulite formed in the specimens with relative lower molecular weights, and the size of the spherulites formed in the blends increased at first, and then decreased as the molecular weight increasing. In the  $G$  value of 3PLLA/PDLA blends with different molecular weights (**Fig. 14**), it also found that the  $G$  value increased at first then decreased as molecular weights increasing, and the highest  $G$  value was received in the 3L35/D10, where the molecular weight for each branch was  $\sim$ 10 kg/mol.

Combined with the results of  $G$  values presented in **Fig. 7**, **Fig. 12**, and **Fig. 14**, it could be confirmed that the growth rate of spherulites with different molecular weights displayed identical regularity, *i.e.*, the  $G$  value increased at first, and then decreased as molecular weight increasing. In the linear PLLA/PDLA blends, the highest  $G$  value observed when the molecular weight was  $\sim$ 8 kg/mol. For the 3PLLA/3PDLA specimens, this highest value was found when the number average molecular weights of each branch was *c.a.* 11 kg/mol. In the case of 3PLLA/PDLA, that value of molecular weight was  $\sim$ 10 kg/mol for each branch. It is interesting to find that this molecular weight for each branch was almost at the same in all the specimens. According to the reported literature, the critical entanglement molecule weight of PLLA is  $\sim$ 8 kg/mol.<sup>34</sup> When the molecular weights of PLA polymers are lower than this critical molecular weight, the motion capacity of molecular chain and chain segment is high, the PLLA and PDLA could move freely after melted and no chain entanglement between inter or intra molecular weight happens. However, this high mobility make the nucleation become difficult, and the degree of the supercooling (compared to the

annealing temperature adopted in this investigation) is low, due to its lower melting temperature of PLA *sc.* When the molecular weight were much higher than this critical molecular weight, the chain entanglement happens and aggravates, and which would be convenient for the nucleation, but higher molecular weights decrease the mobility of chain segments. at the same time, the PLLA and PDLA would interdiffuse with each other and form entanglement point, which would impede the enantiomeric PLA arrange side by side. Consequently, the highest  $G$  value was received when the molecular weights of PLAs were around this critical entanglement molecule weight.



**Fig. 13** the morphology of 3PLLA/PDLA blends at 180 °C (a) 3L10/D5, (c) 3L35/D10, (d) 3L60/D21, (e) 3L95/D31 and (f) 3L130/D42 for 5 min, (b) 3L10/D5 for 10 min.



**Fig. 14** The  $G$  value in 3PLLA/PDLA blends with different molecular weights.



During crystallization from the melt, lots of factors could restrict the molecular chains discharging into the lattices, such as, the end group, viscosity, the core limitation and steric hindrance from the branch structures, etc. In the linear PLLA/PDLA blends, both the end group and viscosity have influences on the rearrangements of molecular chains. Thus, it could form PLA sc in a facilitated environment. However, in the case of 3PLLA/3PDLA and 3PLLA/PDLA blends, lots of effects, such as, the core inside the 3PLAs, the end group, the steric hindrance of branched structure and higher melt viscosity compared to corresponding linear polymers, could restrict the mobility of 3PLA molecules synergistically. Thus, the *G* value decreases gradually as the content of three armed polymer increased in the PLLA/PDLA blends, *i.e.*, linear/linear blends > three armed/linear blends > three armed/three armed blends.

## Conclusions

In this study, the linear and three armed PLLA and PDLA were synthesized, and the PLLA/PDLA, 3PLLA/3PDLA and 3PLLA/PDLA binary casted films with various molecular weights were prepared. The effect of branched structures and molecular weights on the morphology and the spherulites growth of the PLA sc were investigated. The POM results indicated that regular spherulites formed in the specimens with relative lower molecular weights, after the molecular weight for each branch was higher than 30 kg/mol, the morphology of spherulites became disordered gradually as molecular weight increasing, which should be due to the higher viscosity and entanglement restricted the arrangement of molecular chain. The *G* values increased at first, and then decreased as molecular weight increased in all the three kinds of blends, and the highest *G* value were observed when the number average molecular weight for each branch was ~10 kg/mol. With similar molecular weights, the *G* value reduced gradually as the content of three armed polymer increased in the blends, *i.e.*, PLLA/PDLA > 3PLLA/PDLA > 3PLLA/3PDLA.

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**The graphical abstract for The morphology and spherulite growth of stereocomplex in the linear and branched PLLA/PDLA blends: effect of molecular weights and structure**

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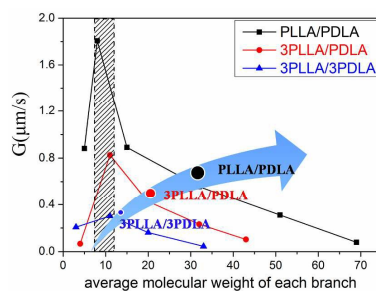
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**For graphical abstract**

$G$  increased firstly, then decreased as  $M_{n, \text{PLA}}$  increased in the blends, and  $G$  reduced as three armed PLAs added.