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Improvements of thermal property and crystallization behavior of PLLA based multiblock copolymer by forming stereocomplex with PDLA oligomer

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Abstract

Although poly(L-lactic acid) (PLLA) can be greatly toughened by copolymerization, its lower melting temperature and lower ability of crystallization limit its widespread application as commodity. In order to improve the melting point and ability of crystallization of PLLA based multiblock copolymers, Poly (D-lactic acid) (PDLA) oligomer was used to complex with PLLA–bisphenol A epoxy resin multiblock copolymer (PLLA-*co*-bis A) to form a stereocomplex. Differential scanning calorimeter (DSC), X-ray diffraction (XRD) and polarized optical microscopy (POM) were used to characterize the thermal properties and crystallization behavior of the stereocomplexes. The results indicated that the stereocomplex of PLLA-*co*-bis A and PDLA was formed. The formed stereocomplexes with good thermal properties (high T_m) and good crystallization properties (high crystallization rate and more stable crystals) are convinced to have high potential as high performance biodegradable polymers.

Keywords: PLLA based multiblock copolymer; Poly(D-lactic acid); Stereocomplexes

1. Introduction

Poly(lactic acid) (PLA) is a biodegradable aliphatic polyester derived from renewable resources that has gained much interest in recent years [1–6]. PLA could become a competitive alternative to traditional commodity plastics for everyday applications from an environmental standpoint. Unfortunately, currently, PLA is primarily used for biomedical applications such as sutures and drug delivery devices [7,8], broad substitution of PLA is mainly thwarted by its brittle behavior under impact loads. It is quite reasonable to expect that the copolymerizaion may bring improved flexibility. Therefore, the syntheses of PLLA copolymers have been widely studied [9–11]. Although PLLA can be greatly toughened by copolymerization, its lower melting temperature and lower ability of crystallization limit its widespread application as commodity.

A few studies have focused on the heterogeneous nucleation of PLLA. Urayama et al. [12] tested an assortment of nucleating agents and found talc, a common nucleating agent for polymers, was the most effective on PLLA. Ogato and co-workers [13] observed a nucleation effect in PLLA–clay blends and suggested that clay functioned as a heterogeneous nucleation site, allowing the PLLA to crystallize at a higher temperature upon cooling from the melt. Although the addition of a nucleating agent can be beneficial to the rate of polymer crystallization, it should not detract from the ultimate physical properties of the material. For example, while talc was shown to increase the crystallization rate in isotactic-polypropylene/polyethylene blends, it also reduced the overall toughness of the system [14].

One interesting attribute of PLA is the ability of enantiomeric blends of PLLA and isotactic PDLA to form a stereocomplex with high crystal stability and crystalline ability [15]. The most stable crystalline unit cell of isotactic PLA has been proposed to consist of a pair of 10-3-helices, whereas the chains in the stereocomplex have been shown to exist as 3-1-helices of the opposite configuration [16–18]. It is presumed that the packing of the stereocomplex 3-1-helices is stabilized by strong van der Waals interactions leading to the observed increase in melting temperature [18]. Ikada et al. [15] first reported that the 1/1 blend of PLLA and PDLA which produce a stereocomplex with T_m around 230 °C, 50 °C higher than the melting point of enantiomeric polymers. The formations of stereocomplexes have also been reported for PLLA–PCL and

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PDLA–PCL [PCL = poly(ε-caprolactone)] copolymer blends [19,20], branched PLLA (or linear PLLA) and branched PDLA [21], and triblock copolymers of poly(ethylene glycol) and PLLA or PDLA [22]. Yamane et al. [23] studied the effect of the addition of PDLA on the thermal property of PLLA and found that a small amount of PDLA added in PLLA could significantly enhance the crystallization of PLLA by forming stereocomplex crystallites in the PLLA matrix.

In this paper, we use PDLA oligomers to complex with PLLA-*co*-bis A. There are no reports on forming stereocomplex for PLLA based multiblock copolymer. Unlike in diblock or triblock copolymer, the lactic acid segments were separated/disrupted by other backbone chains in the PLLA based multiblock copolymer. Can this multiblock copolymer form the stereocomplex with PDLA? In this report, DSC, XRD and POM were used to characterize the thermal properties and crystallization behavior of the stereocomplexes and the results indicated that the stereocomplex of PLLA-*co*-bis A and PDLA was formed. The formed stereocomplexes had good thermal properties (high T_m) and good crystallization properties (high crystallization rate and more stable crystals).

2. Experimental

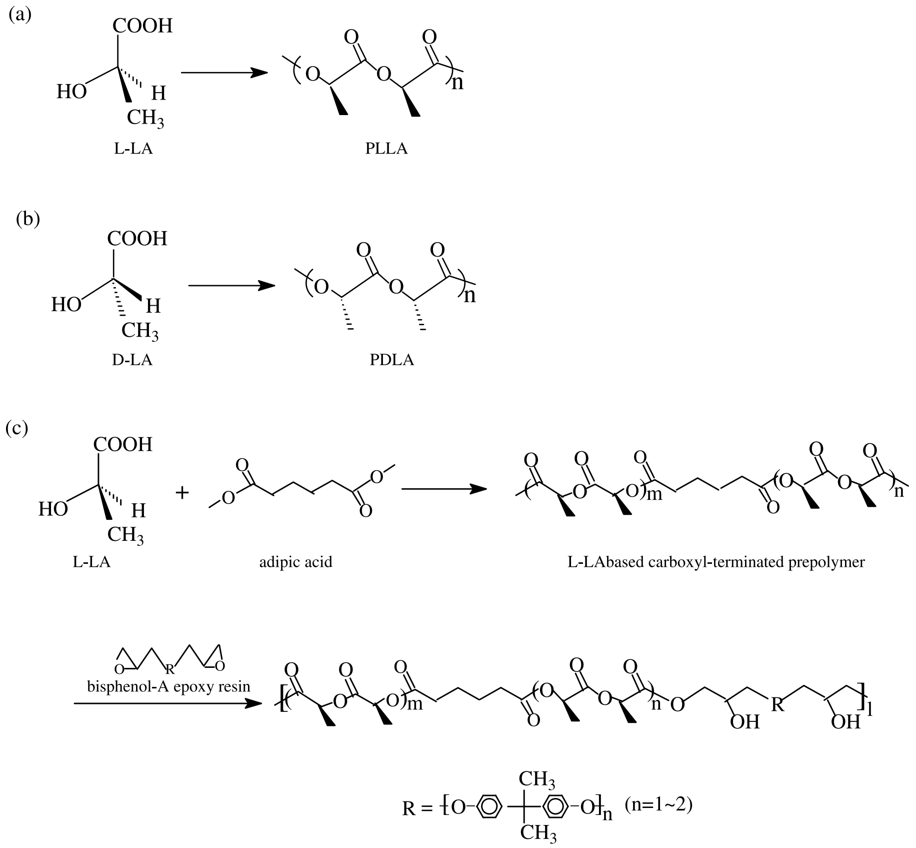
2.1. Materials

L-Lactic acid (L-LA) and D-lactic acid (D-LA) purchased from Jiangxi Musashino Bio-chem. Co. Ltd (China) were 90 wt% aqueous solution of the monomer, 99% optically pure according to the manufacturer. The excess water was removed before use by distillation under reduced pressure at 130 °C. Bisphenol-A epoxy resin with molecular weight of 450 was supplied by Shanghai Resin Factory (China). Tin II chloride dihydrate ($SnCl_2 \cdot 2H_2O$), adipic acid and methylene chloride were purchased from Shanghai Chemical Reagent Company, China Medicine (Group). All materials above were analytical-grade.

2.2. Synthesis of PLLA, PDLA and PLLA-co-bis A

PLLA oligomer was synthesized by direct melt polycondensation of L-LA using $SnCl_2 \cdot 2H_2O$ (0.5% based on the mass of L-LA) as catalyst. The polycondensation was carried out at 170 °C for 10 h under vacuum (Scheme 1(a)). PDLA oligomer was also synthesized by direct melt polycondensation of D-LA under the same reaction condition (Scheme 1(b)). The weight average molecular weight of PLLA and PDLA were about 3.0×10^4.

The synthesis of PLLA-*co*-bis A with weight average molecular weight of 1.7×10^5 was performed by the reaction between carboxyl-terminated PLLA prepolymer and bisphenol-A epoxy resin at 180 °C (Scheme 1(c)). The molar ratio of bisphenol-A epoxy resin to carboxyl-terminated PLLA prepolymer was 1.2. The carboxyl-terminated PLLA prepolymer used above was synthesized by direct polycondensation of L-LA and 0.75 mol% adipic acid at 170 °C for 10 h using



Scheme 1. Synthesis and molecular structures of PLLA (a), PDLA (b), and PLLA-*co*-bis A (c).

$SnCl_2 \cdot 2H_2O$ (0.5% based on the mass of L-LA) as catalyst. All polymerizations were carried out under vacuum.

2.3. Preparation of stereocomplexes

All stereocomplexes were prepared with a solution blending method. PLLA-*co*-bis A or PLLA (1 g) and PDLA (1 g) were dissolved separately in methylene chloride (20 mL), and then the solutions were mixed with vigorous stirring for approximately 2 h. The ratio of PLLA-*co*-bis A to PDLA or PLLA to PDLA was just 1:1. The solutions were cast onto dishes and evaporated at room temperature, which took approximately 3 days. The resulting films were dried in vacuo for 3 days and stored at room temperature for more than 7 days to obtain stereocomplexes.

2.4. Measurements

Thermal properties of the stereocomplexes and enantiomeric polymers were measured with a Mettler 822^e differential scanning calorimeter. The heating and cooling rates were 10 °C/min in a nitrogen stream. The crystallinities derived from PLLA crystalline residues ($X_{c\ PLA}$) were calculated with the following equation: $X_{c\ PLA}(\%) = 100\Delta H_m/135$ [20]. $X_{c\ PLA}$ values of the copolymers and stereocomplexes samples were also roughly estimated with the same equation. Isothermal crystallization behavior at different temperatures was observed with an Olympus model BX51 polarized optical microscope. X-ray diffraction powder patterns were recorded with a Rigaku Model RU200 X-ray apparatus equipped with a rotating anode generator. Diffraction angles reported are for Cu Kα radiation.

3. Results and discussion

3.1. DSC analysis

DSC thermograms of the stereocomplexes and the enantiomeric polymers are presented in Fig. 1, and the data of fusion and crystallization are listed in Table 1. Table 1 and Fig. 1 indicated the T_m values increased by about 60 °C for all the stereocomplexes, and the ΔH_m values for both PLLA/PDLA and PLLA-*co*-bis A/PDLA stereocomplexes increased remarkably, and which reflected the high crystallinity. In addition, in cooling processing, no exothermic peaks corresponding to enantiomeric polymers were observed because of their too slow crystallization rates, but one exothermic crystallization peak appeared on the DSC curve of stereocomplexes of PLLA/

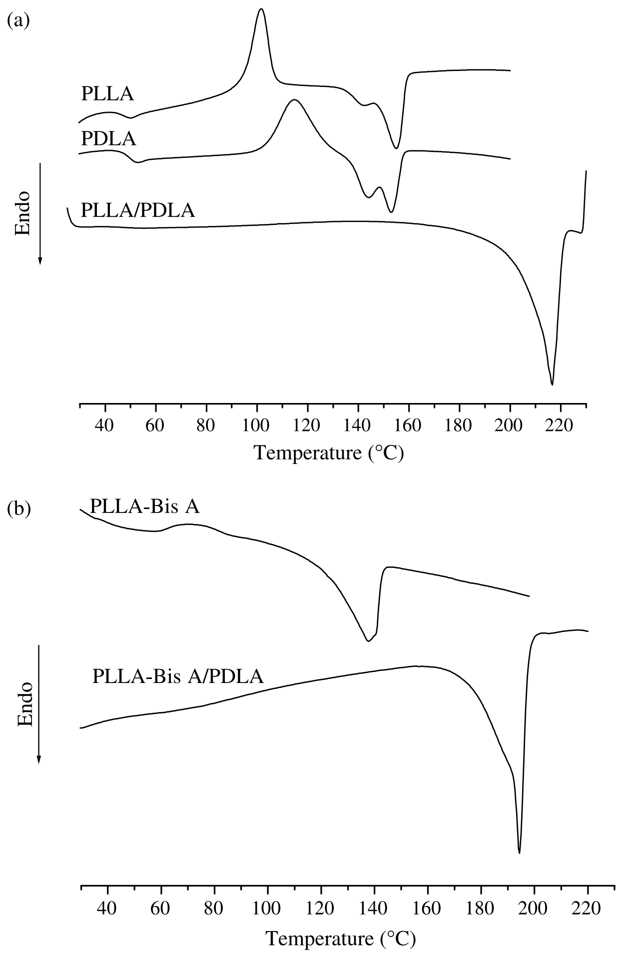


Fig. 1. DSC thermograms of the stereocomplexes and the enantiomeric polymers: (a) PLLA/PDLA stereocomplex and the enantiomeric polymers; (b) PLLA-*co*-bis A/PDLA stereocomplex and the enantiomeric polymer.

Table 1
Thermal properties of the stereocomplexes and the enantiomeric polymers determined by DSC

Samples	T_m (°C)	$-\Delta H_m$ (J/g)	$T_c{}^a$ (°C)	$\Delta H_c{}^a$ (J/g)	X_c (%)
PLLA	155.1	37.6	–	–	27.9
PDLA	153.2	36.4	–	–	27.0
PLLA/PDLA[a]	216.1	81.8	133.8	65.8	60.6
PLLA-*co*-bis A	137.5	27.6	–	–	20.5
PLLA-*co*-bis A/PDLA[a]	193.3	55.6	101.4	4.1	41.2

[a] The data of T_c and ΔH_c are come from the cooling processing.

PDLA and PLLA-*co*-bis A/PDLA, respectively, which indicated the crystallization rates of stereocomplexes were fast.

The T_m and ΔH_m values of PLLA-*co*-bis A/PDLA were lower than those of PLLA/PDLA because of the lack of regular rearrangements of each component.

3.2. X-ray diffractometry

The X-ray diffraction (XRD) analyses of the stereocomplexes and the enantiomeric polymers are illustrated in Fig. 2. The diffraction profile for the homopolymer of PDLA is not shown in Fig. 2, because it is identical with the pattern of PLLA. Homo-PLLA revealed the presence of peaks at 14.9, 16.8,19.1, and 22.4° (Fig. 2(a)), which consistent with the peaks at 15, 16, 18.5, and 22.5° reported by Ikada et al [15]. For the α form of the optically pure PLLA crystallizing in a pseudo-orthorhombic unit cell of dimensions $a=1.07$ nm, $b=0.595$ nm, and $c=2.78$ nm, which contains two 10_3 helices. However, the blended polymer of PLLA and PDLA showed a quite different pattern; that is, the peaks were observed at 12.0, 20.9, and 24.0° (Fig. 2(b)), in excellent agreement with the reported results [15] for PLA stereocomplex crystallized in a triclinic unit cell of dimensions: $a=0.916$ nm, $b=0.916$ nm, $c=0.870$ nm, $\alpha=109.2°$, $\beta=109.2°$, and $\gamma=109.8°$, in which L-lactic acid and D-lactic acid segments were packed parallel taking 3_1 helical conformation [16].

Fig. 2(c) shows that PLLA-*co*-bis A had one broad reflection, whereas the blend of PLLA-*co*-bis A and PDLA showed a quite different pattern; that is, the peaks were observed at 12.0, 20.9, and 24.0° (Fig. 2(d)), in good agreement with Fig. 2(b), which indicated that PLLA-*co*-bis A/PDLA stereocomplex was formed and the stereocomplex was of high crystallinity. It is presumed that PLLA-*co*-bis A/PDLA stereocomplex can be formed by strong van der Waals interactions between PDLA molecular chains and PLLA segments of PLLA-*co*-bis A. This X-ray diffraction study also supports the formation of a polymer complex with a crystalline structure entirely different from that of enantiomeric polymers.

These results are in good agreement with those obtained by DSC measurements. This reveals that stereocomplex crystallites were formed in PLLA/PDLA and PLLA-*co*-bis A/PDLA

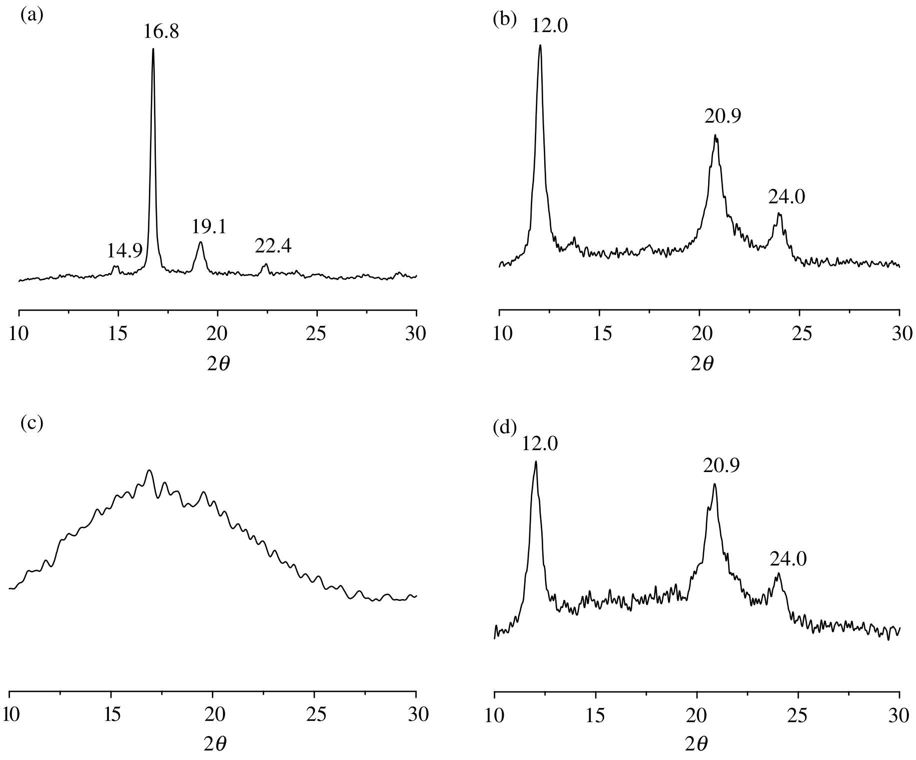


Fig. 2. XRD profiles of (a) homo-PLLA, (b) PLLA/PDLA stereocomplex, (c) homo-PLLA-*co*-bis A, and (d) PLLA-*co*-bis A/PDLA stereocomplex.

during solvent evaporation but not during heating in DSC measurements.

3.3. Polarized optical microscopy

Fig. 3 shows the polarization photomicrographs of stereocomplexes and enantiomeric polymers. At 120 °C, isolated and deformed spherulites in PLLA were observed (Fig. 3(a)), whereas spherulite growth occurred in PLLA below this temperature. At T_c exceeding 120 °C, spherulite could not be formed in PLLA. On the other hand, the spherulites of stereocomplexes crystallites covered PLLA/PDLA stereocomplex films in a very short period at 130 °C (Fig. 3(b)), and the well-defined spherulites of stereocomplex crystallites were observed in the PLLA/PDLA film even at 180 °C (Fig. 3(c)).

As seen from Fig. 3(d) that PLLA-*co*-bis A could hardly crystallize even at 115 °C for 20 min, while the microcrystallites were observed in PLLA-*co*-bis A/PDLA stereocomplex at 130 °C for only 0.5 min (Fig. 3(e)). The well-defined spherulites of stereocomplex crystallites were also observed in PLLA-*co*-bis A/PDLA film at 170 °C (Fig. 3(f)).

Fig. 4 gives the spherulite diameter of stereocomplexes and enantiomeric polymers as a function of crystallization time (t_c). Evidently, the spherulites of stereocomplexes and enantiomeric polymers grew linearly with t_c, irrespective of T_c. The spherulites of stereocomplex crystallites can grow at a temperature below 130 °C, but too high of a density and rapid growth completion of the spherulites disturbed the evaluation of time change of the diameter. The diameter growth rates of the spherulites (G) were estimated from the slope of spherulite diameter in Fig. 4. The obtained G is plotted in Fig. 5 as a function of T_c.

As seen in Fig. 5, the G of PLLA gave maximum value of 12.6 μm/min at 110 °C. The G of the stereocomplex crystallites in the PLLA/PDLA films decreased monotonically with T_c from 44.5 μm/min at 130 °C to 3.2 μm/min at 180 °C. Surprisingly, at 130 °C, the G value (44.5 μm/min) of stereocomplex crystallites is 3.6 times that of homo-crystallites in PLLA films (12.6 μm/min). On the other

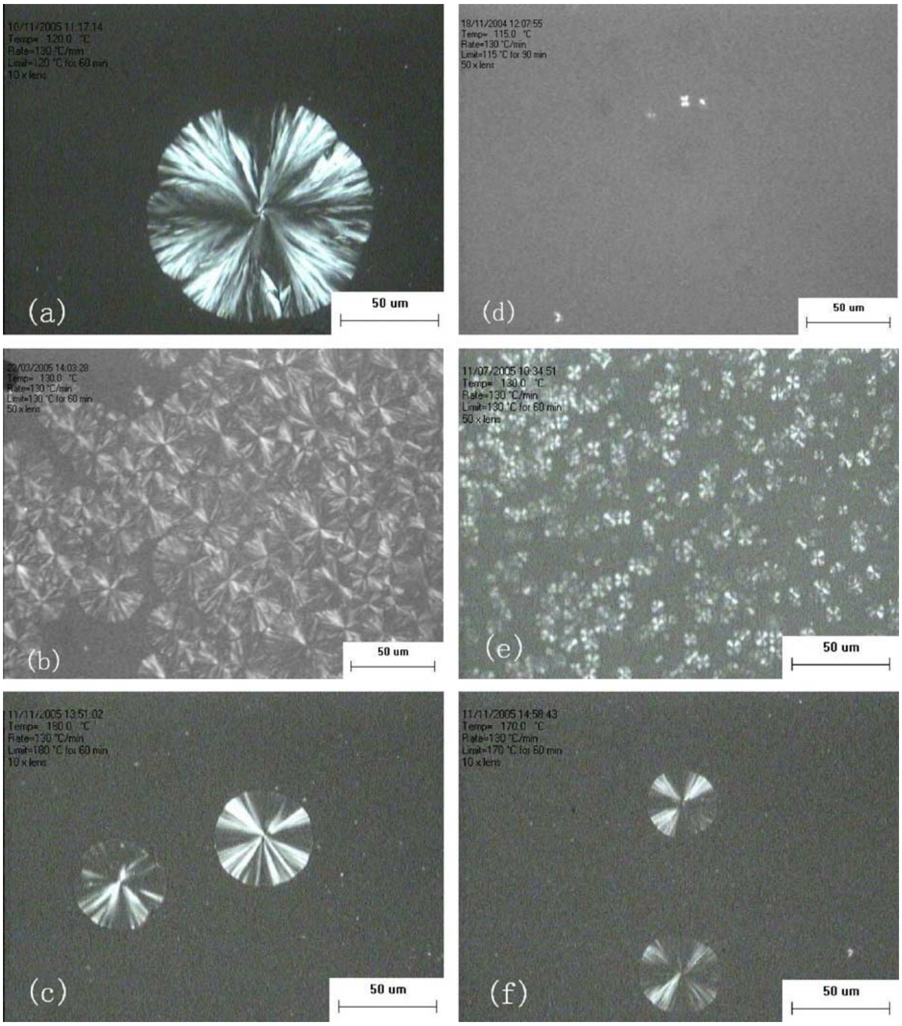


Fig. 3. Polarized optical micrographs during isothermal crystallization: (a) homo-PLLA, at 120 °C for 9 min; (b) PLLA/PDLA, at 130 °C for 0.5 min; (c) PLLA/PDLA, at 180 °C for 14 min; (d) homo-PLLA-*co*-bis A, at 115 °C for 20 min; (e) PLLA-*co*-bis A/PDLA, at 130 °C for 0.5 min; (f) PLLA-*co*-bis A/PDLA, at 170 °C for 20 min.

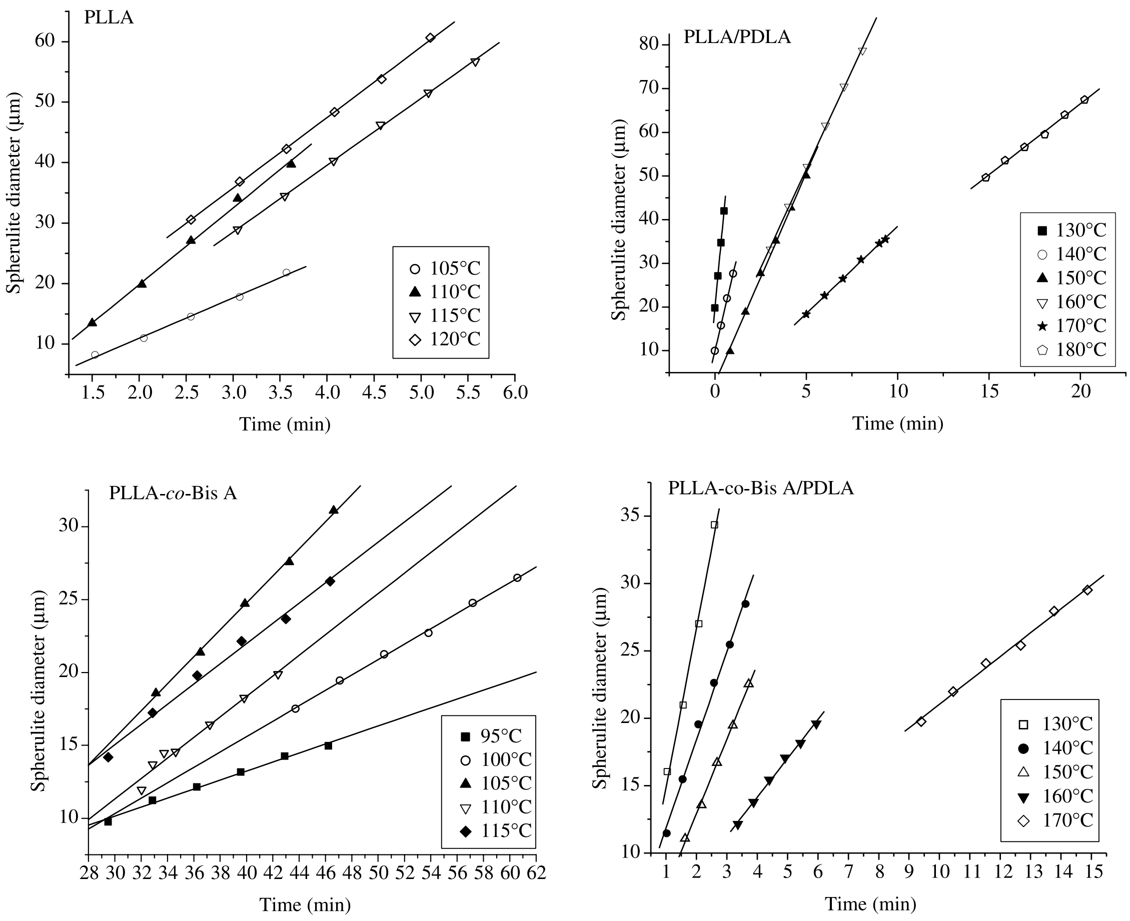


Fig. 4. Growth of spherulite in sterecomplexes and enantiomeric polymers.

hand, the maximum value of G of PLLA-*co*-bis A was 0.9 μm/min at 105 °C. The G of the stereocomplex crystallites in the PLLA-*co*-bis A/PDLA films decreased with T_c from 11.8 μm/min at 130 °C to 1.8 μm/min at 170 °C. And, at 130 °C, the G value (11.8 μm/min) of stereocomplex crystallites is 13.1 times that of PLLA-*co*-bis A crystallites (0.9 μm/min). Moreover, it is interesting to note that the spherulites of stereocomplexes crystallites can grow at the T_c exceeding 130 °C, at which no spherulite of enantiomeric polymer crystallites was formed in PLLA, PDLA and PLLA-*co*-bis A films, and even at a T_c exceeding 170 °C, which is higher than the T_m values of enantiomeric polymers. In other words, the stereocomplex crystallites and their nuclei must be stable at a wide temperature range below 170 °C.

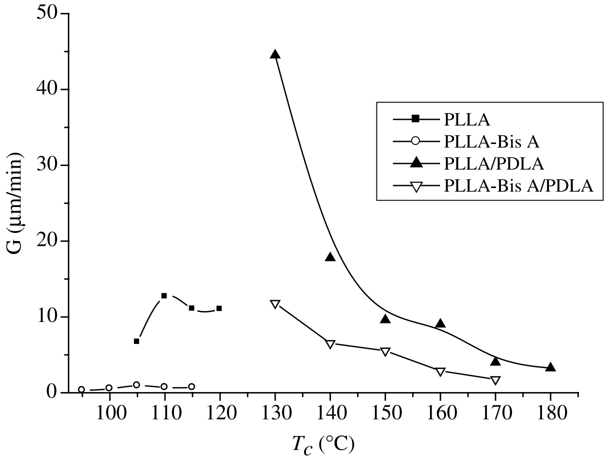


Fig. 5. Diameter growth rate of spherulites (G) of stereocomplexes and enantiomeric polymers as a function of crystallization temperature (T_c).

4. Conclusion

Stereocomplexes of PLLA-*co*-bis A/PDLA can be formed with a solution blending method. The formed stereocomplexes with good thermal properties (high T_m) and good crystallization properties (high crystallization rate and more stable crystals) are convinced to have high potential as improvement of melt temperature and crystallization ability of PLLA based multiblock copolymer.

Acknowledgements

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