

Self-Nucleation Efficiency of PDLA in PLAs: Crystallization Behavior and Morphology¹

Guoxiang Zou, Xin Qu, Caixia Zhao, Yingjie He, and Jinchun Li*

Jiangsu Key Laboratory of Materials Surface Science and Technology, Changzhou University,
Changzhou, Jiangsu, 213164 China

*e-mail: lijinchun88@163.com

Received December 12, 2016;

Revised Manuscript Received August 28, 2017

Abstract—Crystallization behavior and morphology of PLA blended with 0.05–1.00 wt % loadings of poly(*D*-lactic acid) (PDLA) forming stereocomplex crystallites as in-situ nucleating agents, were studied using wide-angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), and polarizing-light optical microscopy (POM). Blending PLA with small amount of PDLA does lead to formation of PLA stereocomplex (SC), although the PLA is a random copolymer. The in-situ formed SC crystal acted as nucleation sites in blends and accelerated the crystallization of PLA by decreasing the half-time ($t_{1/2}$). The nucleation efficiency of PDLA obviously increased and the crystallization induction time decreased while the content of PDLA reached up to 0.20 wt %. While the content of PDLA is 0.2 wt %, the nucleation efficiency of PDLA is up to 43.8%, and the induction time decreased from 430 to 88 s. In addition, compared with pure PLA, $t_{1/2}$ decreases from 15.1 to 3.5 min at $T_c = 127.5^\circ\text{C}$ while the amount PDLA is 1.0 wt %. The equilibrium melting temperature of PLA decreased from 187.2 to 181.2°C with the increase of PDLA content.

DOI: 10.1134/S0965545X18020165

INTRODUCTION

Poly(lactic acid) (PLA) has been attracting attention from both fundamental and practical perspectives because it is a biodegradable polymer completely derived from renewable resources and is thus environmentally and ecologically appropriate [1–3]. The improvement of thermal stability of PLA is a critical issue for realization of its widespread use as an alternative material to traditional plastic. The physical and mechanical properties of semi-crystallization polymers PLA are largely dependent on their solid-state morphology and crystallinity [4–7].

In general, addition of suitable nucleation agents can benefit the crystallization rate of polymers and enhance the nucleation density of spherulites. The added nucleation agent can reduce the free energy needed for the formation of a nucleus, resulting in the increased crystallization rate of polymers. To improve thermal stability of PLA-based materials, many kinds of nucleation agents have been widely investigated, such as talc [8], clay [9] and carbon nanotubes [10, 11]. Among these nucleation agent, the stereocomplex crystallite (SC) of PLLA and PLDA is one of the most effective and promising candidates for PLA due to the similar chemical structure with PLA and its higher melting temperature (220°C) [12–14]. It has been

reported that mixing of PDLA and PLLA in a solution or melt can lead to the formation of a stereocomplex between the two different helical polymer chains [15]. At a 50/50 blend ratio, the stereocomplex has a melting temperature of 220°C, which is 50°C higher than that of the pure PLLA or PDLA. It was also reported that the overall crystallization rate of 1 : 1 PLLA/PDLA stereocomplexes was higher than that of pure PLLA or PDLA, due to a higher radius growth rate and density (number per unit area or volume) of the stereocomplex spherulites and a shorter induction period for the formation of spherulites [16].

These properties mean that the SC crystallites will not be melted at the processing temperature of PDLA or PLLA, which indicates the SC crystallite is a potential ideal nucleating agent for PDLA or PLLA. Schmidt et al. [17] prepared PLLA/PDLA blends (0.25–15 wt % PDLA) through a solution blending method and pointed out that SC crystallites acted as heterogeneous nucleation sites for subsequent PLLA crystallization. Sawai et al. [18] also reported the effect of polylactide stereocomplex on the crystallization behavior of PLLA. They proposed that the effectiveness of h-PDLA (higher M_w) is more pronounced than that of l-PDLA (lower M_w). Yamane et al. [19] investigated the thermal property and non-isothermal crystallization behavior of PLLA blended with a small amount of PDLA (1–5 wt %). Low molecular weight

¹ The article is published in the original.

Table 1. The components of samples

Samples	PLA, wt %	PDLA, wt %
PLA	100	0
0.05%-PDLA	99.95	0.05
0.10%-PDLA	99.90	0.10
0.15%-PDLA	99.85	0.15
0.20%-PDLA	99.80	0.20
0.50%-PDLA	99.50	0.50
1.00%-PDLA	99.00	1.00

PDLA isolated in the matrix of PLLA did not form a stereocomplex crystallite with a surface area large enough to act as a nucleation site. However, high molecular weight PDLA chains formed a large stereocomplex crystallite. With increasing PDLA content, stereocomplex crystallites were more easily formed and acted as nucleation sites, which effectively increased the number of PLLA spherulites, and therefore, the overall crystallization rate.

The above mentioned report focused on the work on PDLA in pure PLLA, however, the cost of pure PLLA as a common material is too high so it is hard to be accepted as a general material. Although the commercial PLA is a random copolymer, the main constituents of commercial PLA is similar to pure PLLA and the cost of PLA is far less than that of the pure PLLA. That there are abundant relatively long poly(*L*-lactide) (PLLA) segments embedded in a PLA chain due to a very low DLA content. The PLA stereocomplex was supposed to be formed between the relatively long PLLA segments in a PLA matrix and the PDLA chains during melting blend around 200°C.

In this work, a small amount of PDLA was blended with PLA, in which the relatively long PLLA segments of the PLA and PDLA chains were proposed in-situ to form the SC crystallite during melting blending. So the primary aim of this work is to clarify whether the in-situ formed SC crystal is found in the PLA/PDLA blends, the subordinate aim of this work is to interpret how the SC crystal accelerates the crystallization of PLA. So the WAXD and DSC were employed to detect the SC crystal in a PLA matrix. Then the nucleation efficiency (*NE*) of PDLA was analyzed by the non-isothermal crystallization process. The PDLA concentration dependence of PLA crystallization was also reported. Finally, the isothermal crystallization kinetics of PLA under existence of SC crystals were reported.

EXPERIMENTAL

Material Preparation

PLA (4032D), a commercial product, was supplied by Nature Works LLC ($M_w = 2.1 \times 10^5$, and comprises about 2.1% *D*-lactic acid units). The PDLA ($M_w = 10^4$) was provided by Jinan Daigang Biomaterial Co. China.

The Preparation of PLA/PDLA

Mixtures of PLA with various contents of PDLA were prepared on a HAKEE internal mixer. The PLA was dried at 75°C for 4 h prior to blending. The temperature of the mixer is 200°C. The components of the samples are listed in Table 1.

Measurements

Wide-angle X-ray diffraction (WAXD) measurement was carried out at room temperature using a Rigaku RINT-2000 diffractometer for all samples. A monochromatized $\text{CuK}\alpha$ radiation ($\lambda = 0.154$ nm) was transmitted through the samples.

Crystallization behavior of the samples was analyzed with a differential scanning calorimetry (DSC), Perkin-Elmer Diamond DSC, which was calibrated by the melting of indium and tin. The DSC scans were carried out in a flowing-nitrogen atmosphere.

The spherulite growth in the films (thickness ca. 3 μm) was observed using an Olympus (Tokyo, Japan) polarization microscope (BX50) equipped with a heating-cooling stage and a temperature controller (Linkam LK-600PM) under a constant nitrogen gas flow. The crystallization of the films was performed as follows. The films were first heated to 200°C at 100 deg/min, and held at these temperatures for 3 min to destroy the thermal history, then cooled at 100 deg/min to an arbitrary crystallization temperature T_c in the range of 100–130°C, and then held the T_c for 60 min.

RESULTS AND DISCUSSION

Formation of SC Crystallite in PLA

The formation of SC in PLA/PDLA blends was confirmed by WAXD and DSC. WAXD can provide the quantitative information on crystalline structure, such as the lamellar thickness, time period, and lattice spacing. Figure 1a shows the WAXD patterns of pure PLA and prepared PLA/PDLA samples. Pure PLA exhibits diffraction peaks of PLLA homocrystallites at 2θ values of 16°, 18.4°, and 21.8°, corresponding to α form of PLLA crystallized in a pseudo-orthorhombic unit cell [17, 20]. With the addition of PDLA, three new diffraction peaks at 2θ values of 12.0°, 20.8°, and 24° were found, assigned to the (110) planes, (300/030) planes and (220) planes of SC crystallites

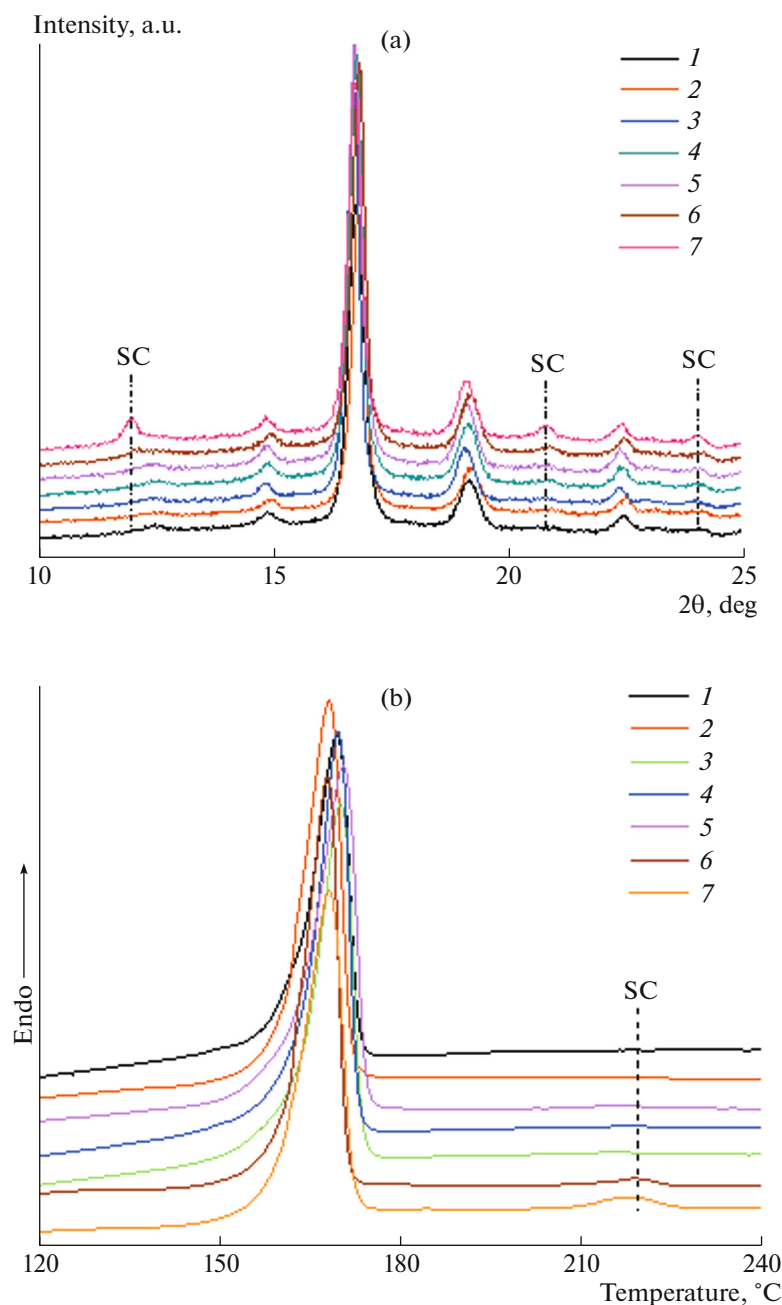


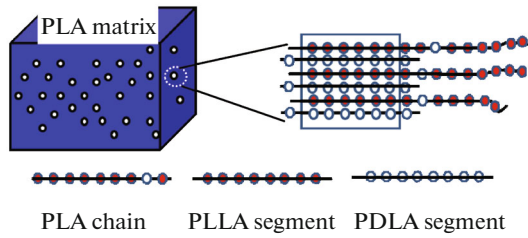
Fig. 1. (Color online) Characterization of crystallization behavior and crystalline structures of (1) pure PLA and PLLA/PDLA samples with various content PDLA: (2) 0.05, (3) 0.10, (4) 0.15, (5) 0.20, (6) 0.50, and (7) 1.00% after isothermal crystallization at 130°C for 30 min: (a) WAXD profiles; (b) DSC thermograms at a heating rate of 10 deg/min.

[12]. Furthermore, the new diffraction peaks became more obvious as the PDLA increased, indicating the amount of in-situ generated SC increase during the melting blend and shearing process.

The formation of SC in PLA/PDLA blends was further confirmed by DSC test. Figure 1b shows the DSC non-isothermal heating traces of pure PLA and PLA/PDLA blends. PLA showed an obvious endothermic melting peak around 168°C, which is attributed to the melting of PLA homocrystallites. For

PLA/PDLA blends, except the melting peak around 168°C, a new melting peak around 220°C is more obvious with increasing PDLA. Therefore, the DSC results implied the SC crystallites indeed existed in the PLA matrix although the PDLA content is less than 0.15 wt %, which is consistent with the results of WAXD.

In this work, the PLA (4032D) was provided by Nature Works, which is composed of about 98% *L*-lactide and 3% *D*-lactide. Although the PLA is a random



Scheme 1 (Color online).

copolymer, there are so many long PLLA segments in the PLA chain as illustrated in Scheme. With the effect of shear stress, the PDLA segments embedded into the PLLA segments at the matrix are arranged side by side through strong hydrogen bonding interactions, which are packed parallel in a helical conformation to form stereocomplex crystals. So the SC crystals were formed in-situ expectedly by combined the PDLA segments and the PLLA segments of PLA. Thus, partial PLA segments take a part in the formation of SC and the rest of the PLA chain plug in the matrix. So the SC crystals were mounted in the matrix just like a tree in the soil. Brizzolaro reported that SC crystallites can also be formed from the melt when PLLA and PDLA segments are in nonequimolar concentration [15]. Therefore the SC crystals in-situ were formed and symmetrically and finely dispersed in the PLA matrix, which is an essential condition as an effective nucleation agent. The in-situ formed SC crystals act as a potential nucleation site for PLA through epitaxial crystallization. Epitaxial crystallization between stereocomplex and one of the constituents has also been reported for blends of poly(α -methyl- α -ethyl β -propiolactone) (PMEPL) [21]. The concentration of nucleation sites was varied through the PDLA weight fraction. The SC crystals should be well dispersed in the PLA homogeneous melt, which is a favorable nucleating agent/polymer interaction due to the similarity of the crystal structures of the PLA homopolymer and SC crystals.

Nucleation Efficiency

In order to quantitate the efficiency of PDLA, the approach to nucleation efficiency was employed in this work. Self-nucleation is considered as an ideal situation for homopolymer crystallization due to an optimum dispersion of crystallites, ideal nuclei concentration, and the favorable interactions between polymer melt and polymer crystal fragments [6, 7]. A nucleation efficiency scale for a given polymer is determined by cooling a polymer sample from the melt. Upon cooling, the sample will crystallize at a given temperature, and an effective nucleating agent will cause the crystallization temperature of the homopolymer to increase, with a higher temperature corresponding to an increased level of nucleation [20, 21]. The nucleation efficiency (NE) of a polymer can be obtained as the following equation:

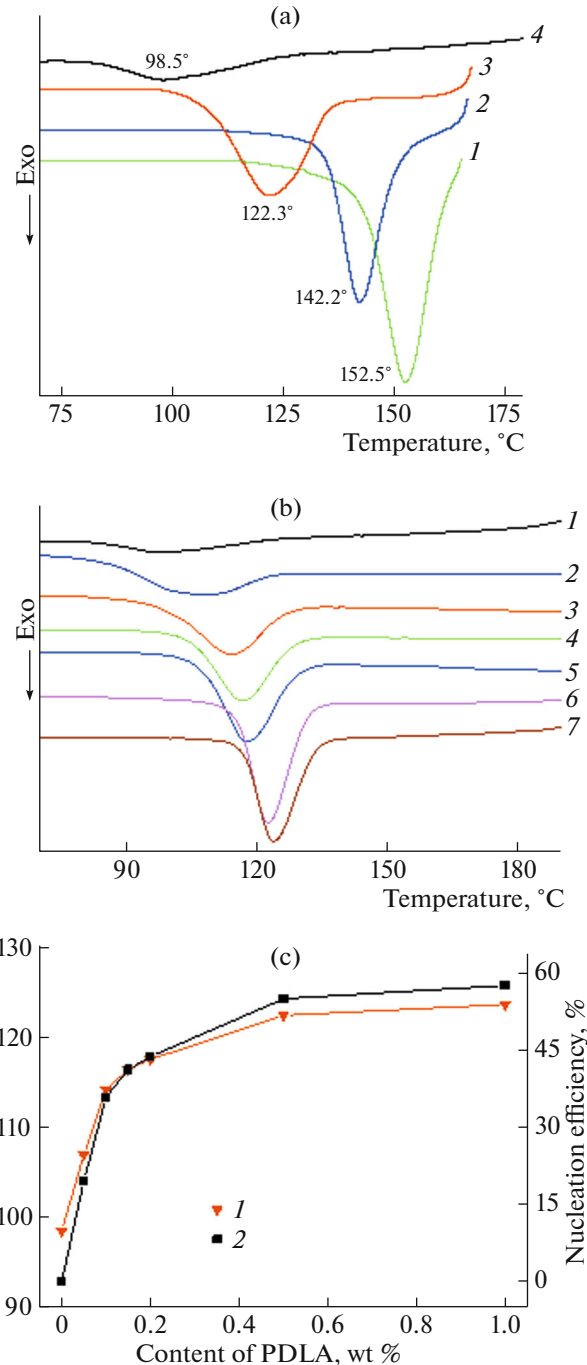


Fig. 2. (Color online) DSC cooling thermograms of (a) pure PLA after annealing at different self-nucleation temperatures: (1) 166, (2) 167, (3) 168, and (4) 200°C and (b) (1) pure PLA and PLA/PDLA blends with various content PDLA: (2) 0.05, (3) 0.10, (4) 0.15, (5) 0.20, (6) 0.50, and (7) 1.00; and (c) (1) the crystallization temperature T_{cNA} and (2) nucleation efficiency NE versus the content of PDLA.

$$NE = 100 \times \frac{T_{cNA} - T_{cmin}}{T_{cmax} - T_{cmin}}, \quad (1)$$

where T_{cmax} and T_{cmin} are the crystallization temperature at two extreme situations needed to define an effi-

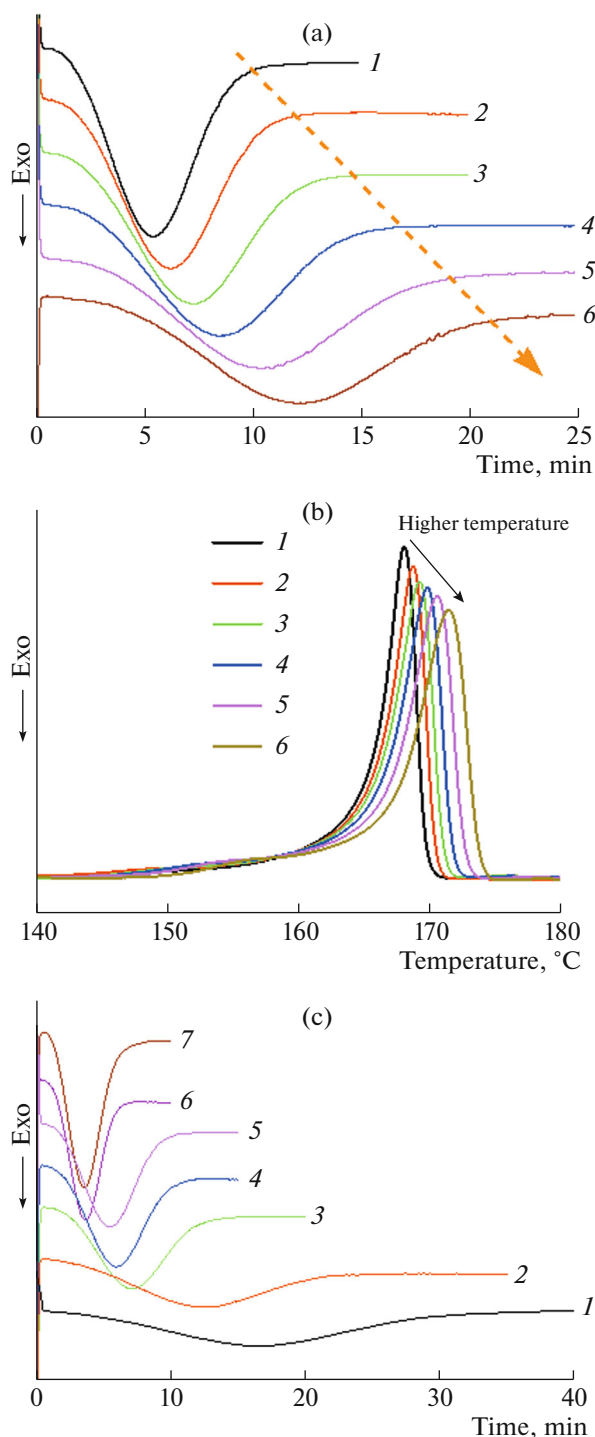


Fig. 3. (Color online) DSC traces 0.20%-PDLA (a) isothermal scans and (b) heating curves after crystallization at different crystallization temperatures: (1) 127.5, (2) 130, (3) 132.5, (4) 135, (5) 137.5, and (6) 140°C; (c) (1) pure PLA and PLA/PDLA blends with various content PDLA: (2) 0.05, (3) 0.10, (4) 0.15, (5) 0.20, (6) 0.50, and (7) 1.00% isothermal scans at $T_c = 127.5^\circ\text{C}$.

ciency scale for a given polymer. $T_{c\max}$ is the crystallization temperature of pure PLA with saturated self-nucleated and $T_{c\min}$ is the crystallization temperature

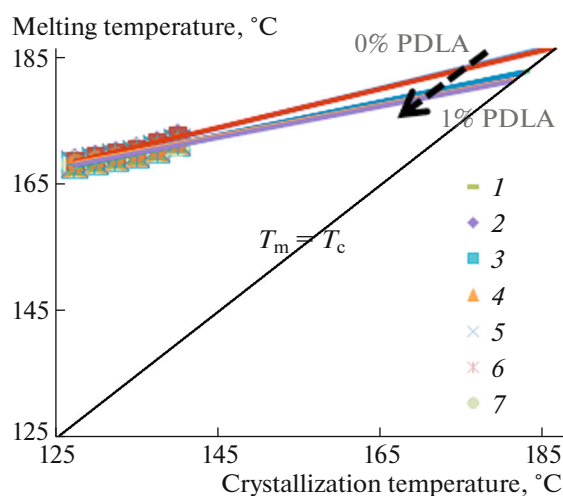


Fig. 4. (Color online) Hoffman–Weeks plots for (1) pure PLA and PLA/PDLA blends with various content PDLA: (2) 0.05, (3) 0.10, (4) 0.15, (5) 0.20, (6) 0.50, and (7) 1.00%.

without any self-nucleated polymer. Therefore correspondence to the 100% NE, $T_{c\max}$ can be obtained. $T_{c\text{NA}}$ is the crystallization temperature of PLA with PDLA.

Figure 2a shows the DSC cooling traces of pure PLA after annealing at different self-nucleation temperatures at a cooling rate of 5 deg/min, as is shown, at a self-nucleation temperature T_s of 200°C, $T_{c\min} = 98.5^\circ\text{C}$. Because of the self-nucleation seeds created by melting in the partial melting zone, the crystallization peak temperature increases sharply with the decrease of T_s . $T_{c\max}$ should occur at the lowest T_s of the partial melting zone which is defined as the temperature at which stable crystal fragments reach a state of saturation and insufficient melting occurs at temperatures lower than it. As the shown in Fig. 2a, there is no obvious plateau heat flow while the T_s is 167°C. However, a plateau was observed if the T_s was increased to 167°C, in this case, the crystallization temperature is 142.2°C. So the $T_{c\max}$ of PLA is equal to 142.2°C.

In order to investigate the effect of PDLA content on the NE of PLA/PDLA. The DSC cooling traces of PLA/PDLA were tested (Fig. 2b). The samples were cooled from 200°C at a cooling rate of 5 deg/min, and the PLA was completely melted, but this temperature was lower than the T_m of SC crystals so the SC crystallites were left intact to promote the crystallization of PLA as a nucleating agent. The $T_{c\text{NA}}$ was recorded from the cooling traces. It was found that the $T_{c\text{NA}}$ of blends shifted to higher temperatures with increasing PDLA content, which can be attributed to the blends containing more SC crystal, meaning more nucleation sites. On the other hand, higher PDLA content would

Table 2. Isothermal crystallization parameters of pure PLA and PLA/PDLA blends

Samples	T_c , °C	$t_{1/2}$, min	T_m , °C	T_m^0 , °C	X_c , %
Pure PLA	127.5	15.1	168.2	187.2	37.8
	130.0	18.8	168.8	"	39.1
	132.5	19.4	169.5	"	40.4
	135.0	23.2	170.2	"	41.5
	137.5	30.2	171.1	"	42.9
	140.0	47.1	172.3	"	44.2
0.05%-PDLA	127.5	12.0	168.6	186.2	39.1
	130.0	14.1	169.2	"	40.4
	132.5	16.5	169.7	"	41.4
	135.0	19.5	170.4	"	43.3
	137.5	24.3	171.3	"	45.0
	140.0	31.0	172.5	"	45.9
0.10%-PDLA	127.5	7.2	167.7	182.6	37.5
	130.0	10.2	168.3	"	39.1
	132.5	12.5	168.8	"	40.5
	135.0	15.5	169.4	"	41.9
	137.5	19.1	170.1	"	42.9
	140.0	25.1	171.2	"	44.4
0.15%-PDLA	127.5	6.0	168.0	182.3	41.0
	130.0	6.8	168.7	"	42.2
	132.5	7.9	169.1	"	43.7
	135.0	9.3	169.7	"	45.2
	137.5	11.5	170.4	"	46.6
	140.0	14.9	171.5	"	48.0
0.20%-PDLA	127.5	5.5	168.0	182.3	40.8
	130.0	6.3	168.6	"	42.5
	132.5	7.3	169.1	"	43.8
	135.0	8.6	169.7	"	45.0
	137.5	10.6	170.5	"	47.0
	140.0	12.2	171.3	"	48.0
0.50%-PDLA	127.5	3.7	168.0	181.3	31.1
	130.0	4.2	168.5	"	32.1
	132.5	4.8	169.1	"	33.3
	135.0	5.6	169.5	"	34.3
	137.5	6.8	170.3	"	35.7
	140.0	8.8	171.4	"	36.5
1.00%-PDLA	127.5	3.5	168.0	181.2	35.5
	130.0	3.9	168.5	"	36.6
	132.5	4.6	169.2	"	38.3
	135.0	5.4	169.7	"	39.0
	137.5	6.5	170.3	"	40.2
	140.0	8.3	171.1	"	41.5

result in a larger SC crystalline size and favor nucleation of PLA.

The NE values were then calculated using Eq. (1). The nucleation efficiency of SC dependence of PDLA content was calculated as shown in Fig. 2c. It is clear

that the NE rapidly increases with the increase of PDLA content while the content is lower than 0.20 wt %, and the NE is about 43.8% for 0.20%-PDLA. After that, the NE slowly increased to 57.7% with 1.00 wt % PDLA content. If the cost of PDLA was taken into account, the recommended PDLA content is 0.20 wt %.

The Isothermal Crystallization of PLA with PDLA

The isothermal crystallization behavior of pure PLA and PLA/PDLA blends were investigated by DSC. The results in the form of thermograms for 0.20%-PDLA at 6 different crystallization temperatures (127.5, 130, 132.5, 135, 137.5, and 140°C) and then heated after crystallization at different crystallization temperatures, and all samples isothermally crystallized at $T_c = 127.5^\circ\text{C}$ are presented in Figs. 3a, 3b, 3c, respectively. The thermograms for the other crystallization conditions showed very similar trends and, hence, are not presented, but all the corresponding enthalpy values are listed in Table 2. From Fig. 3a, the isothermal crystallization time of 0.20%-PLA increased with T_c , which agrees with the general polymer physical theory. For example, the $t_{1/2}$ decreased from 12.2 to 5.5 min while the crystallization temperature decreased from 140 to 127.5°C. This trend is consistent with the traditional polymer physical theory about polymer crystallization. Samples were isothermally crystallized for enough time and then the melting temperatures T_m were determined (Fig. 3b). All the corresponding data are listed in Table 2, although the thermograms are not presented for the sake of brevity. As expected, the PDLA content strongly influenced the crystallization behavior of PLA. Generally, two major factors, nucleation and mobility of chain segments, control the crystallization behavior. Figure 3c shows the DSC traces of PLA/PDLA with various PDLA content at 127.5°C isothermal crystallization. With the increasing of PDLA, the $t_{1/2}$ significantly decreased. Compared with pure PLA, $t_{1/2}$ decreases from 15.1 to 3.5 min at $T_c = 127.5^\circ\text{C}$ while the amount PDLA is 1.00 wt %. The decreased crystallization time of PLA/PDLA indicates that the homocrystallization of PLA is accelerated by the increase of stereocomplex crystallites.

Usually, the T_m is proportional to T_c , as shown in Fig. 4, which is the Hoffman-Weeks plot. The equilibrium melting temperatures T_m^0 were determined by extrapolated the fitline. The T_m^0 was defined to be the melting temperature with ideal crystal that has infinite crystal size. It is clear from Fig. 4 that the T_m^0 of PLA decreased with the content of PDLA. The T_m^0 of PLA/PDLA are 187.2, 186.2, 182.6, 182.3, 182.3, 181.3, and 181.2°C, respectively. The explicit trend is listed in Table 2. The decreased T_m^0 with PDLA con-

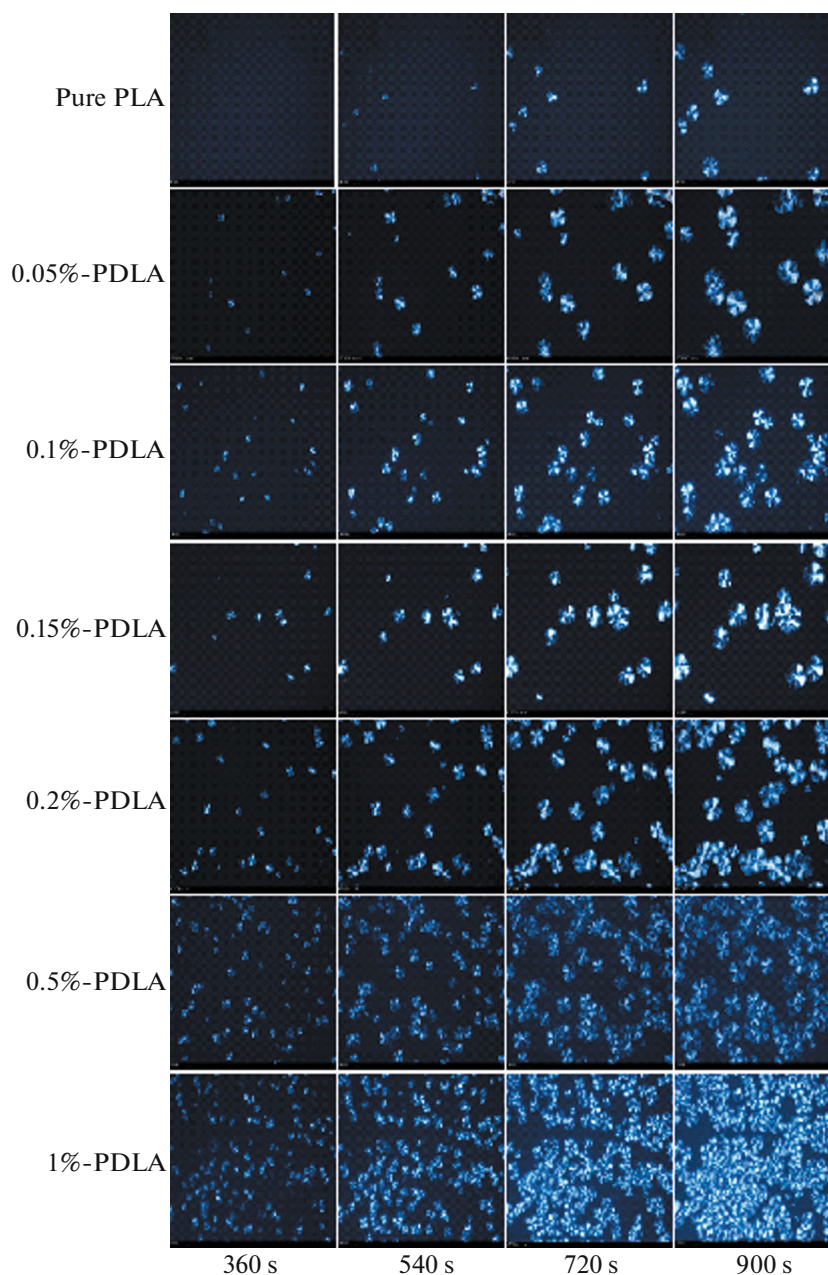


Fig. 5. (Color online) A series of POM photos of pure PLA and PLA/PDLA in a consecutive time sequence at 135°C.

tent expressed thinner lamellar crystals with the PDLA content. One can conclude that the lamellar crystal of PLA was reconfigured by PDLA. A possible reason is that the relatively long PLLA segments in PLA take part in the SC crystallites with PDLA chain as the as elucidated in Scheme and then the mobility of the PLA chain was hindered by those SC crystallites due to the tethering effect. As the proposed idea in Scheme 1, those PLA segments preceded SC crystallites are more resistant to be folded into a compact crystalline form due to the steric effect, and subsequently resulting in a defect at the crystal growth front.

So the lamellar crystal of the PLA is not perfect as those without SC tethering. As a sequence, the melting temperature decreased with PDLA. Therefore, the T_m^0 variations with PDLA content also proved that the PDLA chain participated in the crystallization of PLA and bound the PLA chain to form perfect spherulites.

The Crystallization Morphology of PLA with PDLA

The polarizing optical microscope (POM) is one of the most effective ways to observe the morphology of spherulites during crystallization, and the spherulites

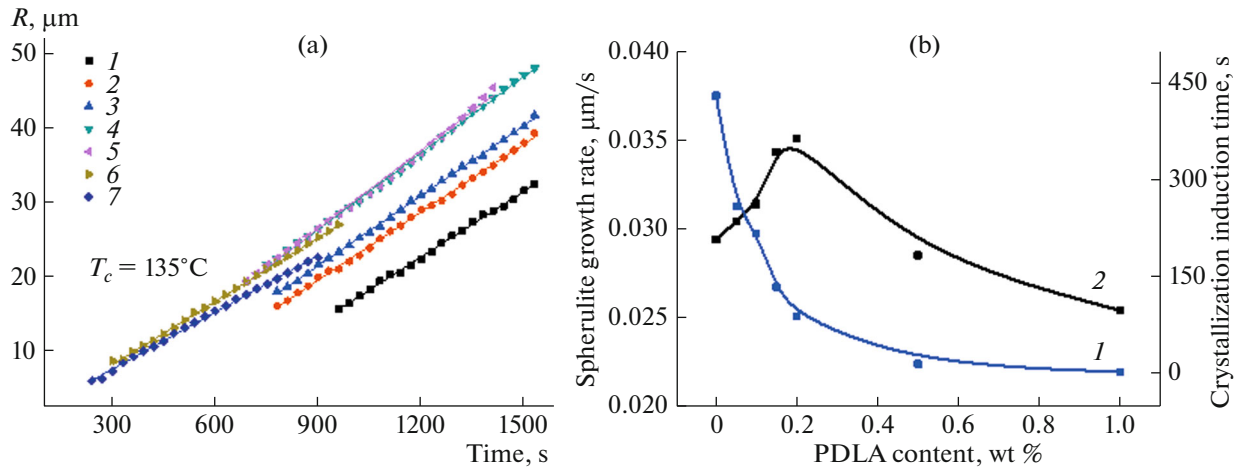


Fig. 6. (Color online) (a) The spherulites radius of (1) pure PLA and PLA/PDLA blends with various content PDLA: (2) 0.05, (3) 0.10, (4) 0.15, (5) 0.20, (6) 0.50, and (7) 1.00%, and (b) (1) induction time and (2) spherulites growth rate versus the content of PDLA.

growth rate can be calculated by this way. In this work, the spherulites density and the spherulites radius of PLA with PDLA at different temperatures were traced by POM with a hot stage. Figure 5 shows the spherulites morphology of pure PLA and PLA/PDLA blends at 135°C for different times. The selected crystallization time in this work is 360, 540, 720 and 900 s, respectively. While the crystallization time is less than 360 s, a number of petal like or point like small spherulites were observed. It was found that spherulite radius systematically increased with increasing crystallization time. After 900 s, the spherulite radius became bigger and most of spherulites became well-defined. All spherulites exhibited negative birefringence and high ordered spherulitic texture.

Spherulite growth rates, defined by $G = dr/dt$, is the growth rate of spherulites in polymer matrix. Figures 6a and 6b show the effect of PDLA content on the spherulite radius, and the effect of PDLA content on the spherulite growth rate and induction time, respectively. It is clear that the G of PLA/PDLA increased when the content of PDLA was less 0.20 wt % at T_c of 135°C . It is generally accepted that polymer spherulites developed from a single lamella through unidirectional growth, and the spherical shape is attained through continuous splaying apart and occasional branching of lamellae. Therefore, the spherulites growth rate is determined by the chain mobility and lamellae growth. Although the chain mobility is the same in all samples at the same temperature, higher PDLA content in PLA matrix means more single lamellae, which favors spherulites growth. However, the G of PLA/PDLA with more PDLA decreased. It is clear that the nucleation density increased when the content of PDLA increased, however, the spherulite growth rate of the blend decreased while the PDLA content is over 0.20 wt %. The possible reason is more

PDLA resulted in higher density of SC crystal, resulting in much more nucleation sites, in consequence the smaller spherulites and slower spherulite growth rate.

It is easy to find the induction time decreased with the content of PDLA, which is due to the chain mobility decreases with increasing PDLA content. With the PDLA content increase, the crystal size of SC becomes larger and the density of formed SC increases, which results in reducing the mobility of PLA chains for the tethering effect. No doubt it is favor of accelerating orderly arrangement of PLA chains and promoting crystallization of PLA, and shortening the crystallization induction time in sequence. In addition, the larger SC crystals are also conducive to promoting PLA chains epitaxial growth on the SC crystal surface and shortening the crystallization induction time. So the addition of PDLA accelerates the crystallization processing.

CONCLUSIONS

To overcome the slow crystallization rate of the biodegradable PLA material, in this work we considered to enhance the crystallization of PLA by blending PLA with a small amount of PDLA as a perfect candidate for pairing with PLA, and the in-suit formed SC crystal with higher melting point during processing will accelerate the crystallization of PLA. We prepared PLA/PDLA blends and investigated the nucleation and spherulitic growth rates of PLA by using DSC and polarized optical microscope. Our results clearly indicate that the SC crystal forms in PLA/PDLA blends and significantly accelerates the spherulitic growth rates of PLA. The nucleation efficiency of PLA matrix obviously increased and the crystallization induction time decreased while the content of PDLA reached up to 0.20 wt %. In addition, compared with pure PLA,

$t_{1/2}$ decreases from 15.1 to 3.5 min at $T_c = 127.5^\circ\text{C}$ while the amount of PDLA is 1.00 wt %. The equilibrium melting temperature of PLA decreased from 187.2 to 181.2 $^\circ\text{C}$ with the increase of PDLA content.

ACKNOWLEDGMENTS

Authors acknowledges the financial support from the Natural Science Foundation of Jiangsu Province with grant no. BK20130255 and Natural Science Foundation of Jiangsu Province Universities Program projects funded (15KJB150001).

REFERENCES

1. R. T. Bartus, M. A. Tracy, D. F. Emerich, and S. E. Zale, *Science* **281**, 1161 (1998).
2. T. Miyata and T. Masuko, *Polymer* **39**, 5515 (1998).
3. R. E. Drumright, P. R. Gruber, and D. E. Henton, *Adv. Mater.* **12**, 1841 (2000).
4. G. Liu, X. Zhang, and D. Wang, *Adv. Mater.* **26**, 6905 (2014).
5. S. Saeidlou, M. A. Huneault, H. B. Li, and C. B. Park, *Prog. Polym. Sci.* **37**, 1657 (2012).
6. H. Fang, Y. Zhang, J. Bai, and Z. Wang, *Macromolecules* **46**, 6555 (2013).
7. J. M. Zhang, Y. X. Duan, H. Sato, H. Tsuji, I. Noda, S. Yan, and Y. Ozaki, *Macromolecules* **38**, 8012(2005).
8. A. Shakoor and N. L. Thomas, *Polym. Eng. Sci.* **54**, 64 (2014).
9. J. J. Kolstad, *J. Appl. Polym. Sci.* **62**, 1079 (1996).
10. Z. Xu, Y. Niu, Z. Wang, H. Li, L. Yang, J. Qiu, and H. Wang, *ACS Appl. Mater. Interfaces* **3**, 3744 (2011).
11. Y. Zhong, Y. Zhang, J. Yang, W. Li, Z. Wang, D. Xu, S. Chen, and Y. Ding, *Sci. China: Chem.* **56**, 181 (2013).
12. Y. Ikada, K. Jamshidi, H. Tsuji, and S. H. Hyon, *Macromolecules* **20**(4), 904 (1987).
13. H. Tsuji, Y. Ikada, S. H. Hyon, Y. Kimura, and T. Kitao, *J. Appl. Polym. Sci.* **51**, 337 (1994).
14. J. Shao, S. Xiang, X. Bian, J. Sun, G. Li, and X. Chen, *Ind. Eng. Chem. Res.* **54**, 2246 (2015).
15. D. Brizzolara, H. J. Cantow, K. Diederichs, E. Keller, and J. Domb, *Macromolecules* **29**, 191 (1996).
16. H. Tsuji and Y. Tezuka, *Biomacromolecules* **5**, 1181 (2004).
17. S. C. Schmidt and M. A. Hillmyer, *J. Polym. Sci., Part B: Polym. Phys.* **39**, 300 (2001).
18. D. Sawai, Y. Tsugane, M. Tamada, T. Kanamoto, M. Sungil, and S. H. Hyon, *J. Polym. Sci., Part B: Polym. Phys.* **45**, 2632 (2007).
19. H. Yamane and K. Sasai, *Polymer* **44**, 2569 (2003).
20. N. Rahman, T. Kawai, G. Matsuba, K. Nishida, T. Kanaya, H. Watanabe, H. Okamoto, M. Kato, A. Usuki, M. Matsuda, K. Nakajima, and N. Honma, *Macromolecules* **42**, 4739 (2009).
21. D. Grenier and R. E. Prud'homme, *J. Polym. Sci., Polym. Phys. Ed.* **22**, 577 (1984).