

## Research Article

# The Crystallization, Melting Behavior, and Thermal Stability of Poly(L-lactic acid) Induced by *N,N,N'*-Tris(benzoyl) Trimesic Acid Hydrazone as an Organic Nucleating Agent

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*N,N,N'*-Tris(benzoyl) trimesic acid hydrazone (TTAD), as a novel nucleating agent of poly(L-lactic acid) (PLLA), was synthesized and characterized by FT-IR and <sup>1</sup>H NMR. The crystallization, melting behavior, and thermal stability of PLLA induced by TTAD were investigated through DSC, TGA, depolarized-light intensity measurement, and so forth. The crystallization behavior indicated that the presence of TTAD accelerated the overall PLLA crystallization. Compared to neat PLLA, the crystallization onset temperature of PLLA/1%TTAD increased from 101.36°C to 125.26°C, the melt-crystallization peak temperature increased from 94.49°C to 117.56°C, crystallization enthalpy increased from 0.1023 J·g<sup>-1</sup> to 33.44 J·g<sup>-1</sup> at a cooling rate of 1°C/min from melt, and the crystallization half-time of PLLA/TTAD decreased from 2997.2 s to 108.9 s at 110°C. Moreover, the nonisothermal crystallization measurements also indicated that the crystallization peak became wider and shifted to a lower temperature with increasing cooling rate. With the presence of TTAD, the melting behavior of PLLA was affected significantly, and a double-melting peak occurred due to melting-recrystallization. Thermal stability research showed that there existed one degradation stage of PLLA and PLLA/TTAD samples, and the thermal degradation temperature of PLLA/TTAD decreased compared to neat PLLA.

## 1. Introduction

With reduction of oil resources and increase of environment-protecting consciousness, biomass-derived polymers have attracted more and more attention due to their renewable source [1]. Poly(L-lactic acid) (PLLA) is one of the most important biomass degradable polymers and has been widely used in more and more fields such as materials [2], medicine [3], and food packaging [4]. However, neat PLLA is very slowly crystallizing polymer, resulting in limiting its applications. Thus, it is very desirable to improve the crystallization rate of neat PLLA.

Usually, adding nucleating agent is the most viable method to increase the overall crystallization rate of polymer.

Talc was first used as a nucleating agent and can remarkably improve the crystallization rate of PLLA. Since then many additional inorganic compounds have been successfully developed to improve the overall crystallization, including montmorillonite [5], layered metal phosphonate [6], silica [1], nanocalcium carbonate [7], and carbon nanotube [8]. Although adding large amounts of inorganic compounds can accelerate the overall PLLA crystallization, the mechanical properties of PLLA modified by inorganic fillers often decrease.

Thus, more and more researchers have focused on organic nucleating agents to improve the crystallization rate of PLLA. Xu and Wu [9] reported the synthesis of a series of novel organic bisurea compounds as nucleating agents of PLLA;

the crystallization behavior indicated that the lower the CH<sub>2</sub> number of compounds exhibited is, the faster the crystallization rate was; and 1,1'-(ethane-1,2-diyl)bis(3-phenylurea) was the most effective crystallization nucleating agent. Upon the addition of 2% 1,1'-(ethane-1,2-diyl)bis(3-phenylurea), the melt-crystallization enthalpy of PLLA increased from almost 0 to 31.2 J/g, and the isothermal crystallization rate increased by 10.5 times at 140°C. Furthermore, ethylene bis-stearamide [10] and benzenetricarboxylamide derivatives [11] nucleating agents showed dramatic increases in crystallization rate of PLLA. In our previous work [12], five *N,N'*-bis(benzoyl) alkyl diacid dihydrazides with bisamides acted as powerful nucleating agent for PLLA. Among them, *N,N'*-bis(benzoyl) suberic acid dihydrazide has higher nucleating activity than the other *N,N'*-bis(benzoyl) alkyl diacid dihydrazides. Upon the addition of 0.8% *N,N'*-bis(benzoyl) suberic acid dihydrazide, the crystallization half-time of PLLA decreased from 26.5 min to 1.4 min at 115°C.

In this paper, to develop an additional organic nucleating agent with multiamide functional groups for PLLA, *N,N,N'*-tris(benzoyl) trimesic acid dihydrazide was synthesized from benzoyl hydrazine and 1,3,5-trimesic acid, and PLLA with *N,N,N'*-tris(benzoyl) trimesic acid dihydrazide materials were prepared using melting blending technology. The crystallization, melting behavior, and thermal stability of the blends were investigated in detail.

## 2. Experimental Section

**2.1. Materials.** Poly(L-lactic acid) (PLLA) was purchased from USA; 1,3,5-trimesic acid, benzoyl hydrazine, *N,N*-dimethylacetamide, thionyl dichloride, and pyridine from China were of analytical grade (AR) in this study.

**2.2. Synthesis of *N,N,N'*-Tris(benzoyl) trimesic Acid Dihydrazide.** *N,N,N'*-Tris(benzoyl) trimesic acid dihydrazide (TTAD) was prepared as shown in Scheme 1; the specific reaction process is similar to the other amide compounds reported in our previous works [12, 13].

**2.3. Preparation of PLLA/TTAD Samples.** PLLA was dried overnight at 50°C under vacuum to remove residual water. Blending of PLLA and dried TTAD was performed on a counter-rotating mixer with a rotation speed of 32 rpm for 5 min and then at 64 rpm for 5 min. The processing temperature was set at 185°C. The products were hot-pressed at 180°C under 20 MPa for 3 min to prepare sheets with a thickness of approximately 0.4 mm. The sheets were then cooled down to room temperature by being compressed in zero press at room temperature under 20 MPa for 10 min. All the samples for crystallization studies were cut from these films.

### 2.4. Characterization

**2.4.1. Infrared Spectra (IR).** Fourier transform infrared spectra were recorded on a Bio-Rad FTS135 spectrophotometer

from 4000 to 400 cm<sup>-1</sup>. The sample of TTAD was mixed with KBr powders and pressed into a disk suitable for IR measurement.

**2.4.2. <sup>1</sup>H Nuclear Magnetic Resonance (<sup>1</sup>H NMR).** The <sup>1</sup>H nuclear magnetic resonance of TTAD was recorded on Bruker AVANCE 300 spectrometers. The solvent was dimethyl sulphoxide (DMSO).

**2.4.3. Differential Scanning Calorimeter (DSC).** The nonisothermal crystallization behavior of PLLA was measured by DSC Q2000. The sample was heated to 190°C and maintained at that temperature for 5 min to make sure that the polymer crystals were melted completely. Then the samples were cooled from the melting state to 20°C at cooling rates of 1, 3, 5, and 10°C/min. Finally, the samples were reheated to 190°C at a heating rate of 10°C/min to observe melting behavior. The melting behavior of PLLA in other conditions was also measured by DSC.

**2.4.4. Depolarized-Light Intensity Measurement.** The isothermal crystallization of PLLA and PLLA/TTAD was investigated by GJY-III optical depolarizer in the region from 100°C to 120°C.

**2.4.5. Polarization Optical Microscopy (POM).** The spherulite of PLLA and PLLA/TTAD was observed using an XPN-203E polarization optical microscope equipped with a camera and a programmable temperature controller.

**2.4.6. Thermogravimetric Analysis (TGA).** TGA was performed using thermal analysis Q500 with a heating ramp of 10°C/min under air flow (60 mL/min) from room temperature to 500°C.

## 3. Results and Discussion

**3.1. Structure of TTAD.** The FT-IR spectrum of TTAD is shown in Figure 1. In the spectrum, the peaks at 3448.1 cm<sup>-1</sup> and 696.5 cm<sup>-1</sup> are due to the absorption of the N–H stretching vibrations and the bending vibrations; the absorption peak at 3237.7 cm<sup>-1</sup> belongs to the C–H stretching vibration of benzene; and the absorption peak at 1648.2 cm<sup>-1</sup> is due to the C=O stretching vibration of the amide group. The absorption peaks at 1576.6 cm<sup>-1</sup>, 1495.6 cm<sup>-1</sup>, and 1437.9 cm<sup>-1</sup> prove the existence of benzene. The absorption peak at 1272.2 cm<sup>-1</sup> is a mixed peak, including the C–N stretching vibrations and N–H bending vibrations absorption.

The <sup>1</sup>H NMR patterns of TTAD are depicted in Figure 2. The single peaks at δ<sub>H</sub> = 10.88 and 10.68 both are proton resonance peaks of N–H of TTAD; the multiple peaks at δ<sub>H</sub> = 7.54–7.97 are proton resonance peaks of the benzene ring of benzoyl hydrazine. However, the single peak at δ<sub>H</sub> = 8.67 belongs to the proton resonance peak of the benzene ring of trimesic acid. The FT-IR spectrum and <sup>1</sup>H NMR analysis confirm that TTAD was synthesized.

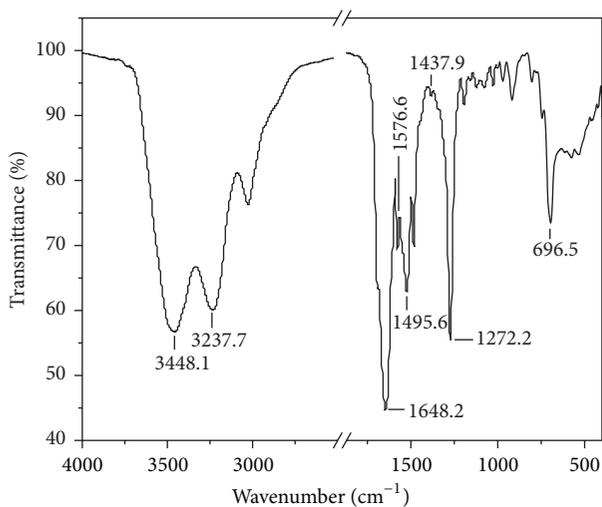
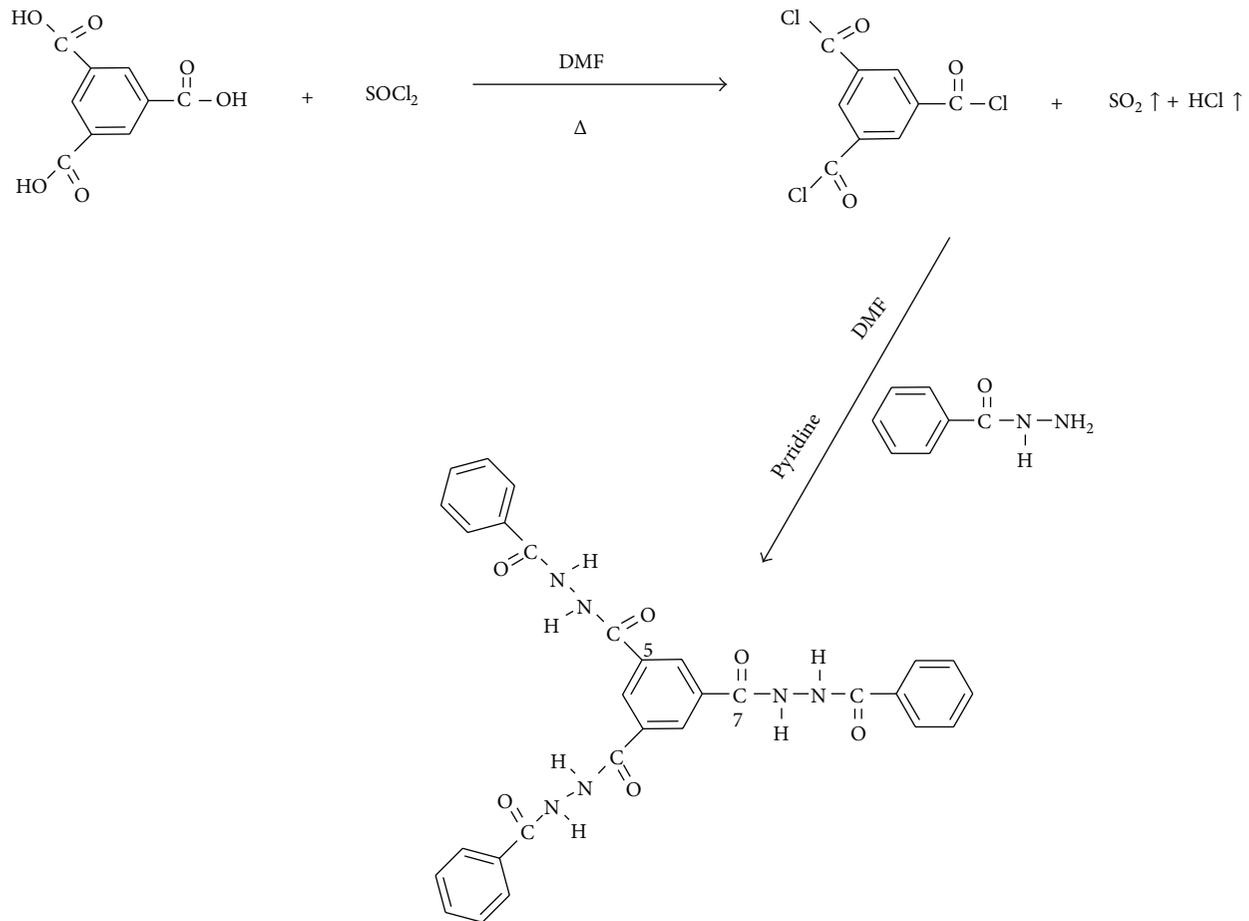


FIGURE 1: FT-IR spectrum of TTAD.

3.2. *Crystallization Behavior of PLLA/TTAD.* The crystallization behavior of neat PLLA is very important. To confirm the nucleating effect of TTAD, thus, we first investigated

TABLE 1: DSC data of neat PLLA crystallized from the melt at different cooling rates.

Cooling rate/ $^{\circ}\text{C}/\text{min}$	$T_o/^{\circ}\text{C}$	$T_m/^{\circ}\text{C}$	$\Delta H_c/\text{J}\cdot\text{g}^{-1}$	$\Delta H_m/\text{J}\cdot\text{g}^{-1}$
0.3	106.61	97.58	5.528	6.022
0.5	105.31	97.41	1.877	1.909
0.7	104.89	95.22	0.4008	0.797
1.0	101.36	94.49	0.1023	0.1321
3.0	—	—	—	0.01026
5.0	—	—	—	—
10.0	—	—	—	—

the nonisothermal crystallization behavior of neat PLLA. Figure 3 shows the DSC curves of nonisothermal crystallization of neat PLLA from the melt at various cooling rates. Above the cooling rate of  $1^{\circ}\text{C}/\text{min}$ , the crystallization peak (P) of PLLA could not be detected, which indicates that the crystallizability of neat PLLA is very weak. The DSC data of neat PLLA crystallized from melt at different cooling rates are listed in Table 1; the crystallization onset temperature ( $T_o$ ), melt-crystallization peak temperature ( $T_m$ ), crystallization enthalpy ( $\Delta H_c$ ), and melting enthalpy ( $\Delta H_m$ )

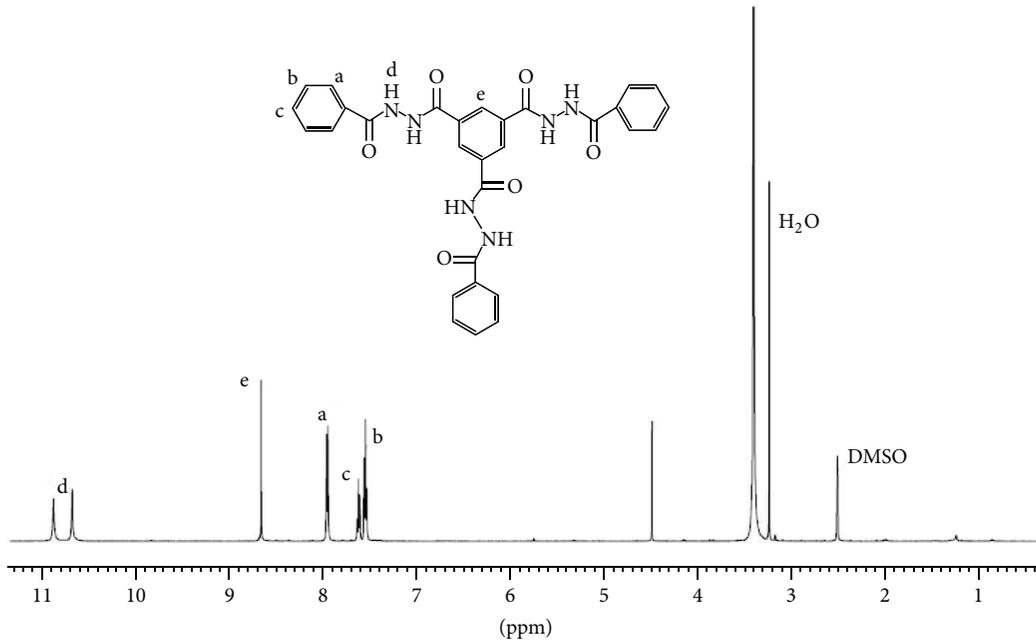
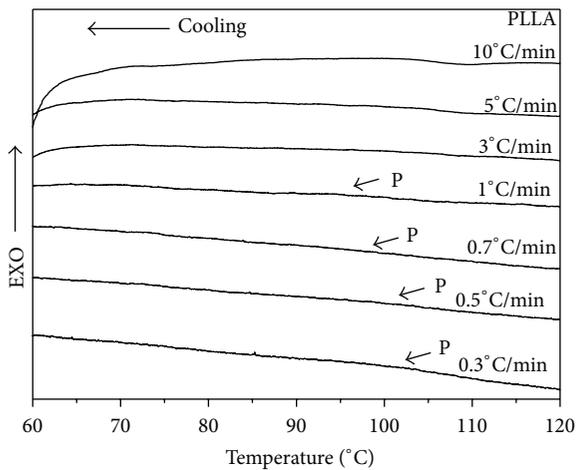
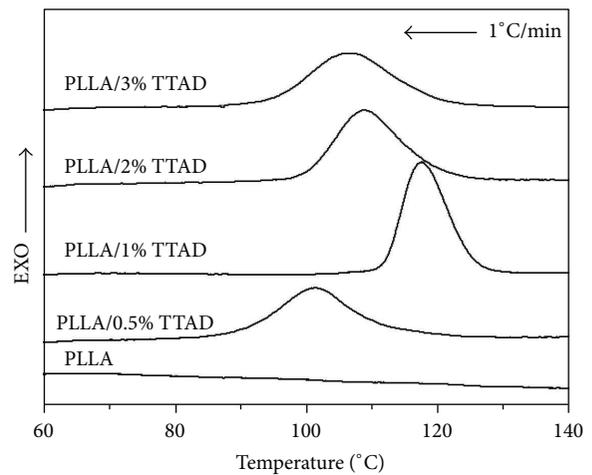
FIGURE 2:  $^1\text{H}$  NMR spectrum of TTAD.

FIGURE 3: The DSC curves of nonisothermal crystallization from melt at different cooling rates.

FIGURE 4: DSC curves of nonisothermal crystallization of PLLA/TTAD at a cooling rate of  $1^\circ\text{C}/\text{min}$ .

of PLLA decrease with increasing cooling rate. These results also indicate that the cooling rate significantly affects the crystallization of the PLLA.

Figure 4 shows the DSC curves of the nonisothermal crystallization of PLLA/TTAD samples from the melt at a cooling rate of  $1^\circ\text{C}/\text{min}$ . With a cooling rate of  $1^\circ\text{C}/\text{min}$ , the crystallization peak of neat PLLA could not be detected. With addition of TTAD, a crystallization peak appears in the DSC cooling curves. Compared to neat PLLA, TTAD causes the melt-crystallization peak to shift to higher temperature and become much sharper in the cooling process; the results show that TTAD can increase the overall crystallization rate of neat PLLA. In addition, we also observe that the crystallization

peak shifts to higher temperature with increasing of TTAD content up to 1% TTAD and then decreases and broadens; thus the best effect on the crystallization is at 1% TTAD. With the addition of 1% TTAD, as listed in Table 2,  $T_o$  increases from  $101.36^\circ\text{C}$  to  $125.26^\circ\text{C}$ ,  $T_m$  increases from  $94.49^\circ\text{C}$  to  $117.56^\circ\text{C}$ , and the  $\Delta H_c$  increases from  $0.1023\text{ J}\cdot\text{g}^{-1}$  to  $33.44\text{ J}\cdot\text{g}^{-1}$  at a cooling rate of  $1^\circ\text{C}/\text{min}$  from melt.

The nonisothermal crystallization exotherms of PLLA/TTAD samples with different TTAD contents from the melt at different cooling rates are shown in Figure 5. With increasing cooling rate, the crystallization peak becomes wider and shifts to a lower temperature. The possible reason is that increasing the cooling rate causes the crystals of

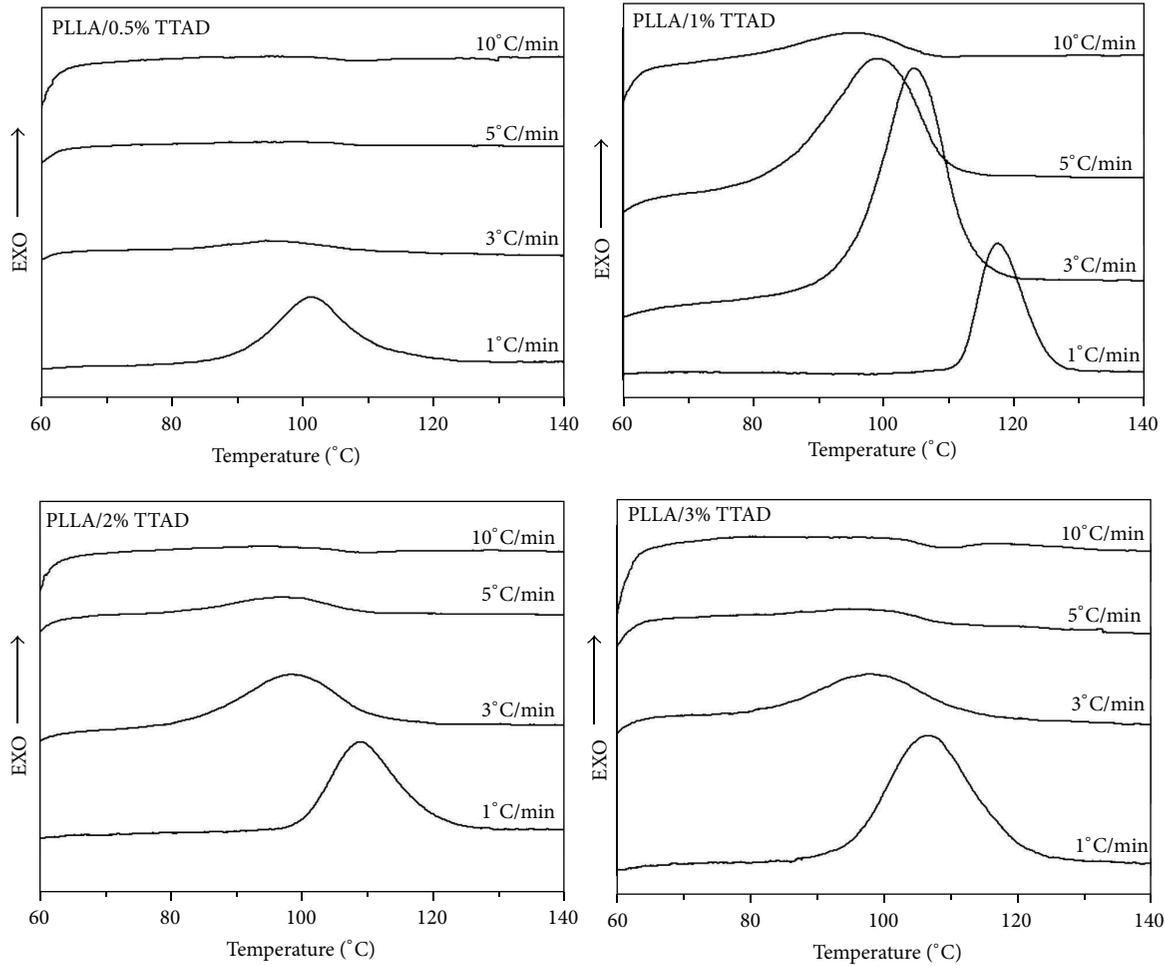


FIGURE 5: DSC curves of PLLA/TTAD with varying amounts of TTAD in the crystallization process at various cooling rates.

TABLE 2: DSC data of PLLA and PLLA/TTAD crystallized from the melt at cooling rate of 1°C/min.

Sample	$T_o/^\circ\text{C}$	$T_{m0}/^\circ\text{C}$	$\Delta H_c/\text{J}\cdot\text{g}^{-1}$	$\Delta H_m/\text{J}\cdot\text{g}^{-1}$
PLLA	101.36	94.49	0.1023	0.1321
PLLA/0.5% TTAD	112.12	101.44	26.84	27.58
PLLA/1% TTAD	125.26	117.56	33.44	33.93
PLLA/2% TTAD	119.99	108.71	32.02	31.57
PLLA/3% TTAD	119.57	106.37	30.45	30.69

PLLA to become more imperfect, and the crystallization process lags decreasing of crystallization temperature. At the same time, it is also observed that increasing the TTAD content makes the crystallization peak become more obvious. However, the crystallization peak becomes lower when TTAD content is larger than 1%, which also confirms that the best effect on the crystallization is at 1% TTAD. In addition, the nonisothermal crystallization peaks of all PLLA/TTAD samples become very weak at cooling rate of 10°C/min; this further indicates the importance of cooling rate on the crystallization of PLLA.

Meantime, isothermal crystallization behavior of PLLA/TTAD has also been investigated to confirm the role of TTAD in crystallization process of PLLA matrix. Figure 6 is the effect of the TTAD content and the crystallization temperature against the half-time of overall PLLA crystallization  $t_{1/2}$ ; it is clear that TTAD and crystallization temperature remarkably affect the crystallization of PLLA, and there exist similar trends of influence of crystallization temperature and TTAD content on the  $t_{1/2}$  of PLLA. The  $t_{1/2}$  firstly decreases and then increases with increasing crystallization temperature and TTAD content. Compared to neat PLLA, 1% TTAD makes the  $t_{1/2}$  have minimum value in 110°C, and the  $t_{1/2}$  decreases from 2997.2 s to 108.9 s.

Besides, the spherulite morphology of PLLA with TTAD during isothermal crystallization process was observed by POM. Figure 7 shows the POM of PLLA and PLLA/1% TTAD during isothermal crystallization process at 105°C. It is observed from Figure 7 that PLLA has typical spherulite structure, but the spherulite density is small during the initial stages of crystallization. However, the PLLA/1% TTAD displays higher nucleation speed and more spherulite during the initial stages of crystallization, and the number of spherulites of PLLA/1% TTAD increases faster than that of neat PLLA;

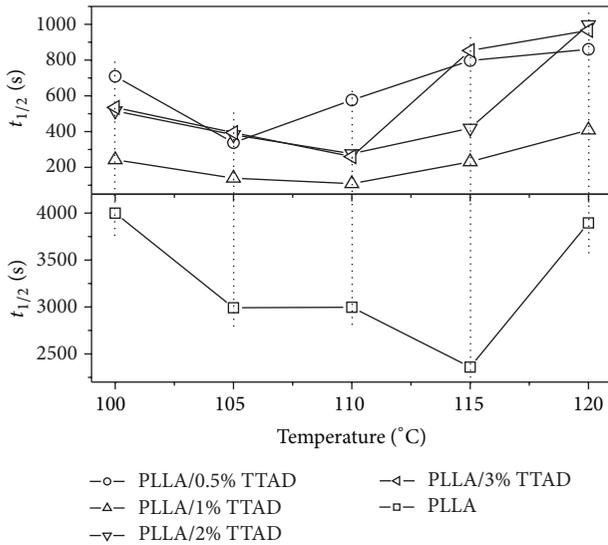


FIGURE 6: The half-time of overall crystallization of PLLA and PLLA/TTAD with the crystallization temperature and TTAD content.

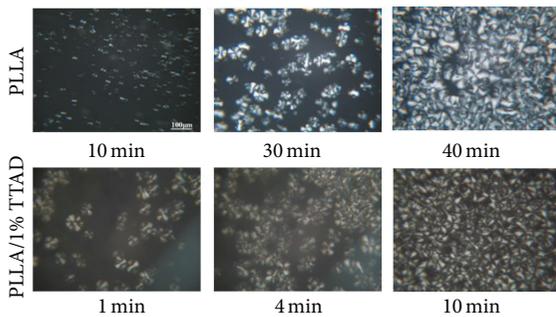


FIGURE 7: POM images of PLLA and PLLA/1% TTAD during isothermal crystallization process at 105°C.

it also indicates that TTAD as a powerful nucleating agent can improve the crystallization performance of PLLA again. From Figure 7 we can see that the total crystallization rate of PLLA/1% TTAD is much higher than that of neat PLLA.

**3.3. Melting Behavior of PLLA/TTAD.** Melting behavior of PLLA can also reflect the nucleating effect of TTAD. Figure 8 shows the melting behavior of neat PLLA at heating rate of 10°C/min after nonisothermal crystallization at different cooling rates. The melting peak is very weak at nonisothermal crystallization cooling rates higher than 1°C/min. In contrast, there exists obvious melting peak for cooling rates lower than 1°C/min. These results indicate that cooling rate affects the melting behavior of PLLA and that low cooling rate can improve the crystallization of neat PLLA. The results emphasize the weak crystallization ability of neat PLLA. It is also seen in Figure 6 that there exists double-melting behavior after nonisothermal crystallization at different cooling rates. The double-melting behavior of PLLA has been reported in the literature [14]; the low-temperature peak is attributed to

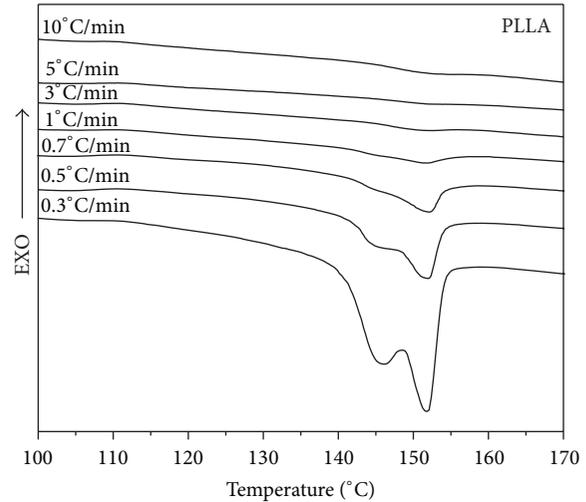


FIGURE 8: Melting behavior of PLLA at heating rate of 10°C/min after nonisothermal crystallization with different cooling rates.

the melting of the primary crystallites formed at crystallization temperature, and the high-temperature melting peak reflects the stacks of relatively perfect thicker lamella resulting from recrystallization during the heating scan.

Figure 9 shows the melting behavior of neat PLLA and PLLA/TTAD samples at a heating rate of 10°C/min after nonisothermal crystallization at a cooling rate of 1°C/min. The melting peak of neat PLLA is very weak and could almost not be detected. However, obvious melting peak of PLLA appears after addition of TTAD, resulting from TTAD improving the crystallization ability of PLLA. What is more, upon addition of 1% TTAD, there exists only one sharp melting peak in the melting process; this result indicates that 1% TTAD makes the crystallization of PLLA complete as soon as possible at cooling rate of 1°C/min, and there exists hardly new crystal during second heating, meaning that the crystals of PLLA are very perfect. Moreover, with increasing of TTAD content, the ratio of the areas between the low-temperature melting peak and the high-temperature melting peak first increases and then decreases. This result is consistent with the aforementioned nonisothermal crystallization measurement results.

**3.4. Thermal Stability of PLLA/TTAD.** The thermal stability of polymers is very important for many of their applications. Therefore, the thermal stability of PLLA/TTAD samples was investigated. Figure 10 shows the TGA curves of thermal degradation for PLLA and PLLA/TTAD samples at a heating rate of 10°C/min from 40°C to 500°C. The thermal degradation temperature of TTAD is lower than that of PLLA and PLLA/TTAD samples, and the thermal degradation temperatures of TTAD and PLLA are 309.6°C and 346°C, respectively. Furthermore, there is only one degradation stage of the PLLA and PLLA/TTAD samples, which indicates little effect of a small amount of TTAD on thermal degradation of PLLA. However, the thermal degradation temperature of the PLLA/TTAD samples decreases with increasing of

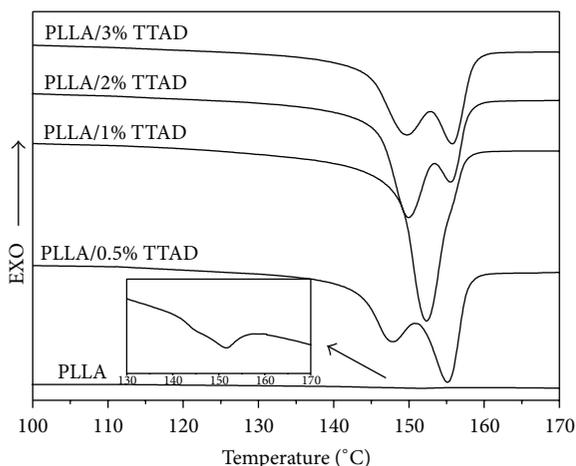


FIGURE 9: Melting behavior of neat PLLA and PLLA/TTAD at a heating rate of  $10^{\circ}\text{C}/\text{min}$  after nonisothermal crystallization at a cooling rate of  $1^{\circ}\text{C}/\text{min}$ .

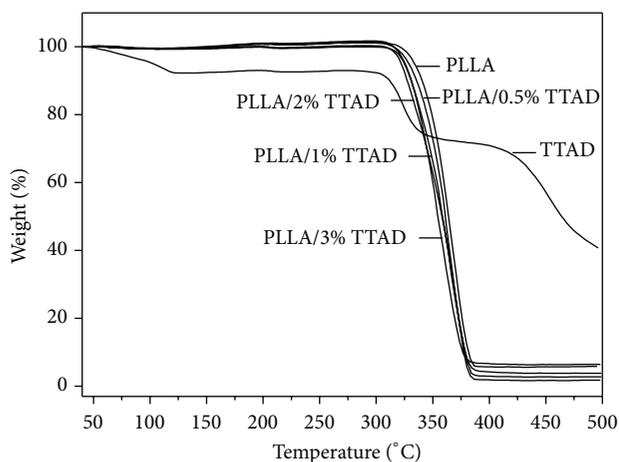


FIGURE 10: TGA curves of thermal degradation for PLLA and PLLA/TTAD samples.

TTAD content. This phenomenon's possible reason is that increasing PLLA makes dispersity of TTAD increase, and coating effect of PLLA makes thermal degradation of TTAD increase. Thus, the thermal degradation of TTAD occurred at higher temperature.

#### 4. Conclusions

The thermal properties including crystallization, melting behavior, and thermal stability of PLLA/TTAD with different contents of TTAD were investigated. Crystallization process and POM analysis of PLLA/TTAD samples showed that the presence of TTAD accelerated the overall PLLA crystallization. Compared to neat PLLA, the  $T_o$  of PLLA/1% TTAD increased from  $101.36^{\circ}\text{C}$  to  $125.26^{\circ}\text{C}$ , the  $T_m$  increased from  $94.49^{\circ}\text{C}$  to  $117.56^{\circ}\text{C}$ ,  $\Delta H_c$  increased from  $0.1023\text{ J}\cdot\text{g}^{-1}$  to  $33.44\text{ J}\cdot\text{g}^{-1}$  at a cooling rate of  $1^{\circ}\text{C}/\text{min}$  from melt, and the  $t_{1/2}$  of PLLA/TTAD decreased from  $2997.2\text{ s}$  to  $108.9\text{ s}$  at  $110^{\circ}\text{C}$ .

The melting behavior of PLLA was affected significantly by TTAD, and a double-melting peak occurred due to melting-recrystallization. Thermal stability research indicated that the thermal degradation temperature of PLLA/TTAD decreased compared to neat PLLA.

#### Conflict of Interests

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

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