

Effect of a Novel Nucleating Agent on Isothermal Crystallization of Poly(L-lactic acid)^{*}

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Abstract The effect of a novel active nucleating agent (TBC8-eb) on the isothermal crystallization of poly(L-lactic acid) (PLLA) was studied by differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR). The analysis on kinetics demonstrates that TBC8-eb can not only accelerate the crystallization rate but also transform most of the original spherulite crystals of PLLA into sheaf-like crystals. Furthermore, the free energy of folding (σ_e) of PLLA and PLLA with TBC8-eb is 0.15 and 0.06 J·m⁻², respectively, which suggests that the addition of TBC8-eb favors the regular folding of molecule chains in the crystallization of PLLA, improving its crystallization rate. The FTIR results show that TBC8-eb can accelerate the conformational ordering of PLLA in the isothermal crystallization. The conformational ordering of PLLA nucleated with TBC8-eb begins with the interchain interaction of —CH₃, and then a short helix emerges where a couple of —CH₃ groups interact.

Keywords crystallization, poly(L-lactic acid), nucleating agent

1 INTRODUCTION

Today, most plastics are derived from non-renewable crude oil and natural gas resources. While some plastics are being recycled and reused, most of them are disposed in landfills due to end-use contamination. Over the past decade, there has been a sustained research interest on biodegradable and compostable polymers derived from renewable sources as one of solutions to alleviate solid waste disposal problems and to lessen the dependence on petroleum-based plastics. Poly(L-lactic acid) (PLLA) is a disposable and biodegradable plastic, which has attracted more and more attention in the past decade [1, 2]. However, PLLA presents limitation for commercial applications, because its crystallization rate is slow compared with many other thermoplastics. As a consequence, physical nucleating agents, which act as nuclei in the crystallization process, must be added in order to improve the crystallization behavior of PLLA [3]. To date, many nucleating agents have been found, such as talc, ethylene bis-stearamide and starch [3, 4], but they need to be improved due to their low nucleation ability. Recently, metal phosphonate is found to be a type of active nucleating agent [5], but it causes polymer degradation due to the presence of metal ions [6]. As a result, developing highly active nucleating agents for PLLA has been an interesting research topic.

So far, lots of efforts focus on the influence of nucleating agent on crystallization of PLLA [3, 7, 8], while limited studies have been done on the effect of nucleating agents on the conformational change in the crystallization [9, 10]. In this paper, the effect of TBC8-eb, which is a novel powerful nucleating agent we discovered recently [11], on the isothermal crystallization of PLLA is studied.

We will study the isothermal crystallization kinetics and the conformational change of PLLA nucleated with TBC8-eb in isothermal crystallization processes.

2 EXPERIMENTAL

2.1 Materials

PLLA ($M_w = 100000$ g·mol⁻¹) was supplied by Jiu Ding Company, China. Talc (5–6 μm) was purchased from Shanghai Feida Corporation. Ethyl benzene was purchased from Shanghai Lingfeng Chemical Reagent Co. Ltd. The *p*-*tert*-butylcalix[8]arene was synthesized according to the method of Munch and Gutsche [12].

2.2 Preparation of nucleating agent

The TBC8-eb was synthesized according to our patent [11], the *p*-*tert*-butylcalix[8]arene was recrystallized from ethyl benzene, and the product was dried under vacuum at 90 °C for 12 h.

2.3 Preparation of PLLA sample

PLLA was mixed with nucleating agents in a self-designed flask, which had an inlet and an outlet for nitrogen. After removal of air with nitrogen for 10 min, the temperature was raised to 200 °C and held for 5 min to achieve equilibrium. The mixture was stirred at 200 °C for 5 min, and then collected for measurement. The neat PLLA was also subjected to the same procedure.

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2.4 Measurement

Differential scanning calorimetry (DSC, Diamond, Perkin-Elmer) was carried out to study the crystallization peak temperature and analyze the isothermal crystallization kinetics in a nitrogen atmosphere. Before the measurements, the temperature was calibrated using indium as a standard medium. All DSC operations were carried out under a nitrogen environment. The mass of samples were in the range of 3 to 4 mg, and all samples were heated to 200 °C and held in their molten state for 5 min to eliminate the thermal history. The crystallization peak temperatures were determined from the crystallization curves. The samples were heated from 50 °C to 200 °C at a heating rate of 20 °C·min⁻¹, held at 200 °C for 5 min, and then cooled from 200 °C to 50 °C at a cooling rate of 5 °C·min⁻¹. Data of crystallization temperature were recorded in the process, and from this DSC curve we obtained crystallization peak temperatures. In isothermal crystallization experiments, the sample melts was subsequently cooled rapidly to the crystallization temperature, and kept at that temperature until the DSC trace returned to the calorimeter baseline. The fractional crystallinity X_t , which developed at time t , was

$$X_t = \frac{\int_0^t \left(\frac{dH_c}{dt} \right) dt}{\int_0^\infty \left(\frac{dH_c}{dt} \right) dt}$$

where dH_c/dt is the heat flow rate, and $\int_0^\infty (dH_c/dt) dt$ is the total area under the crystallization exotherm at the crystallization temperature.

Optical micrographs were obtained with an Olympus BX51 (Japan) polarized optical microscope (POM) attached with a DP70 digital camera and a THMS600 hot-stage. The PLLA samples were placed between two microscopy slides, melted and pressed at 200 °C for 5 min to erase any trace of crystal, and then rapidly cooled to a predetermined crystallization temperature.

The crystal morphology of the PLLA sample was also investigated by scanning electron microscopy (SEM, JEOL JSM-6360LV, Japan). The 1 : 2 water-methanol mixture containing 0.025 mol·L⁻¹ of sodium hydroxide was used for etching experiment. PLLA blended with 1% (mass) TBC8-eb was melt on a glass plate, followed by isothermal crystallization at 140 °C for 1 min. The crystallized sample was then subjected to etching in the mixed solution of sodium hydroxide at 25 °C for 12 h.

The Fourier transform infrared spectroscopy (FTIR) measurements were performed on a Nicolet 5700 FTIR spectrometer. The samples were prepared by casting melt PLLA samples on the potassium bromide pellets. The potassium bromide plates with the cast film were placed in a heating chamber, and each sample was kept at 200 °C for 5 min, then it was cooled to 140 °C in less than 1 min.

3 RESULTS AND DISCUSSION

3.1 Nucleating ability of TBC8-eb

In general, the nucleating ability of a nucleating agent is characterized by the crystallization peak temperature (T_{cp}). Higher T_{cp} indicates stronger nucleating ability and faster crystallization rate. Herein, the mass content of nucleating agents was select as 1%, which is the amount commonly used in PLLA nucleation [7, 8]. The DSC curves of the PLLA samples are presented in Fig. 1. The T_{cp} value of PLLA, which is 108.5 °C in the pure state, shifts to higher temperature with the addition of talc and TBC8-eb, indicating their nucleation effects on the crystallization of PLLA. Furthermore, for the conventional nucleating agent, -talc, the T_{cp} is only 119.3 °C, while T_{cp} of PLLA nucleated with TBC8-eb (PLLA/TBC8-eb) is 134.3 °C, which is 15 °C higher. Therefore, TBC8-eb, is a high performance nucleating agent for PLLA and, is more powerful than the conventional nucleating agent -talc.

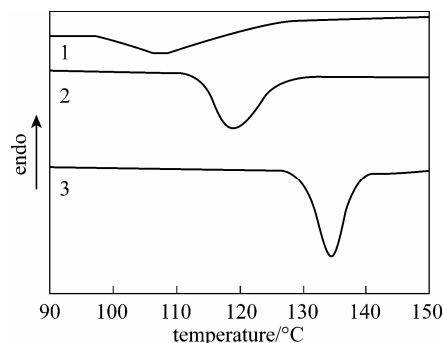


Figure 1 DSC cooling curves of PLLA samples with 1% (by mass) of nucleating agent
1—PLLA; 2—PLLA/talc; 3—PLLA/TBC8-eb

3.2 Isothermal crystallization kinetics

A kinetic analysis was employed to disclose further the effect of nucleating agents on the crystallization behavior of PLLA. The heat flow evolution of the samples was obtained (Fig. 2) by cooling the molten polymer to the crystallization temperature.

In this study, Avrami equation [13, 14] is used to analyze the crystallization rate and morphology of PLLA samples:

$$1 - X_t = \exp(-Kt^n) \quad (1)$$

where X_t is the relative degree of crystallization at time t , the exponent n is a mechanism constant depending on the type of nucleation and the growth dimension, and K is the overall rate constant associated with both nucleation and growth contributions. Eq. (1) can be written as

$$\ln[-\ln(1 - X_t)] = n \ln t + \ln K \quad (2)$$

Avrami theory is a useful tool to study the crystal morphology, and the typical Avrami plots obtained at

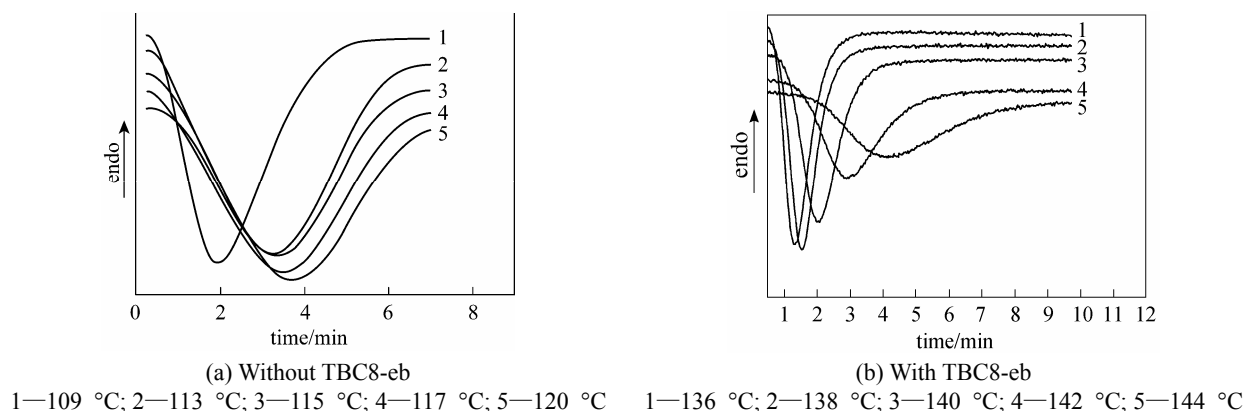


Figure 2 DSC curves of crystallization for PLLA without and with TBC8-eb

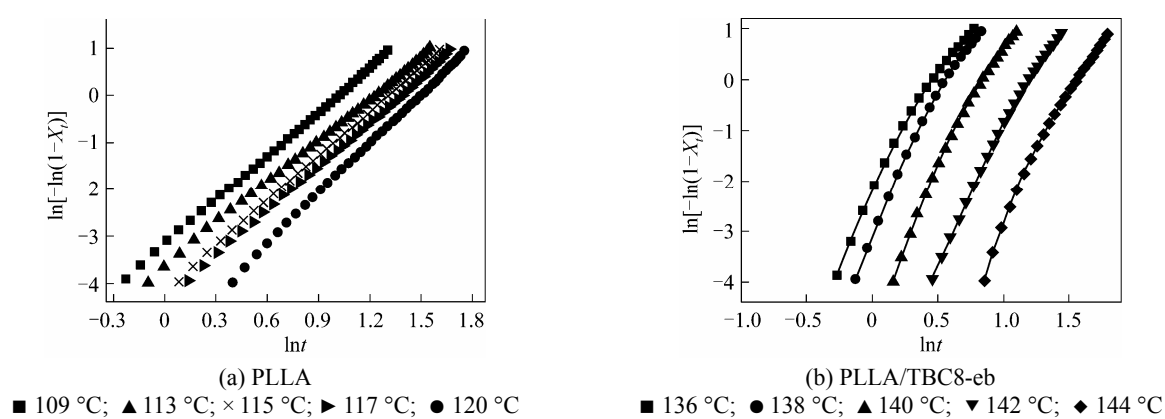


Figure 3 Avrami plots of PLLA, and PLLA/TBC8-eb for isothermal crystallization

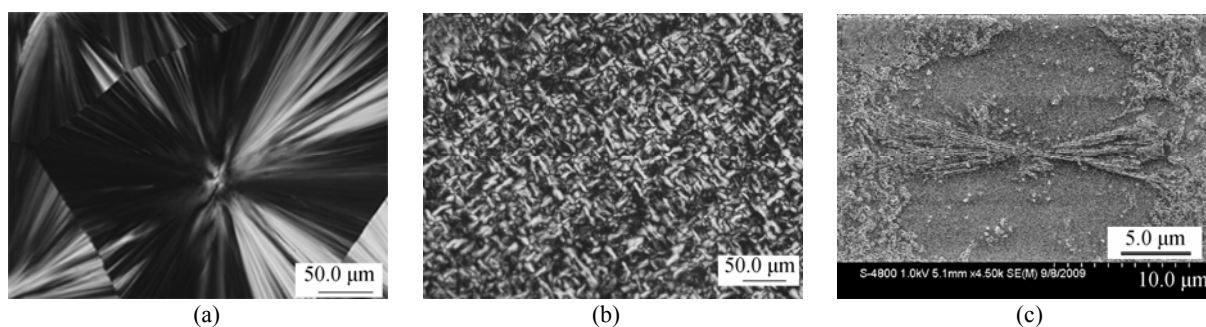


Figure 4 Isothermal crystallization process of PLLA(a), and PLLA/TBC8-eb (b) isothermally crystallized at 140 °C, and SEM image of PLLA/TBC8-eb (c) etched by mixed solution of sodium hydroxide after crystallization at 140 °C for 1 min

various temperatures for PLLA samples are illustrated in Fig. 3. The values of n and K obtained are listed in Table 1. The Avrami exponent (n) for PLLA is about 3, suggesting three-dimensional spherical growth of crystals [15, 16]. The values of n are similar to those reported for pure PLLA [17, 18]. The POM images also provide an evidence for this point. As shown in Fig. 4 (a), the geometry of pure PLLA crystal is from three-dimensional spherical growth. In other words, the predicted crystal morphology of pure PLLA by the value of n is in agreement with the POM images [Fig. 4 (a)].

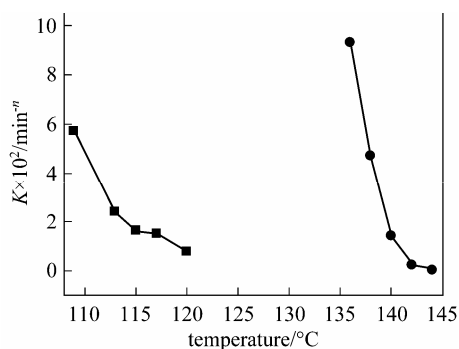
The crystals of PLLA show spherulitic growth. However, the increase of n for PLLA/TBC8-eb indi-

cates that the growth mechanism is changed, and n is between 4 and 5. Based on the previous report [19, 20], the value of n within this range corresponds to that the growth geometry of PLLA is mainly sheaf-like structure in isothermal crystallization. Therefore, most of original spherulite crystal of PLLA are transformed into sheaf-like crystal by adding TBC8-eb. The images of POM [Fig. 4 (b)] and SEM [Fig. 4 (c)] provide evidences to this point. The crystallization morphology of the PLLA is spherulite, while it is difficult to observe spherulite crystals for PLLA/TBC8-eb, in which most of the original spherulite crystals of PLLA are transformed into sheaf-like crystal.

Table 1 Isothermal crystallization kinetic parameters of PLLA samples

Sample	Crystallization temperature/°C	<i>n</i>	<i>K</i> ×10 ² /min ^{-<i>n</i>}
PLLA	109	3.11	5.70
	113	2.93	2.37
	115	3.16	1.60
	117	3.11	1.53
	120	3.52	0.74
PLLA/TBC8-eb	136	4.36	9.32
	138	4.87	4.70
	140	4.74	1.43
	142	4.85	0.25
	144	4.78	0.05

In addition to T_{cp} , the kinetic constant K is also an important indicator of the crystallization rate. The constant K shows strong dependence on the crystallization temperature (Fig. 5). As crystallization temperature increases, the value of K decreases. Moreover, compared with that of pure PLLA, the K values of PLLA and PLLA/TBC8-eb shift to higher temperature regions, confirming that the crystallization rate of PLLA is increased by the addition of TBC8-eb, which is in accordance with the above T_{cp} results.

**Figure 5** Plots of K versus crystallization temperature for PLLA samples

■ PLLA; ● PLLA/TBC8-eb

In order to get deep insight into the crystallization of PLLA, the Lauritzen and Hoffman (LH) model [21, 22] is employed here to calculate the free energy of folding (σ_e). The value of σ_e indicates the energy needed to fold the polymer chains in crystallization of polymer.

The crystallization growth rate, G , can be described by the following equation [23]

$$G = G_0 \exp\left(-\frac{\Delta F}{kT_c}\right) \exp\left(-\frac{\Delta \phi}{kT_c}\right) \quad (3)$$

where ΔF is the free energy of activation for a chain crossing the barrier to the crystal, $\Delta \phi$ is the free energy of formation of a surface nucleus of critical size, T_c is the crystallization temperature, and k is the Boltzmann constant.

The values of ΔF and $\Delta \phi$ can be described by the following equations [23]:

$$\Delta F = \frac{C_1 T_c}{C_2 + T_c - T_g} \quad (4)$$

$$\Delta \phi = \frac{2b_0 \sigma \sigma_e T_m^0}{\Delta H_m^0 \cdot \Delta T} \quad (5)$$

where $C_1 = 4120$, $C_2 = 51.6$, T_m^0 is the equilibrium melting temperature, σ is the lateral surface free energy, σ_e is the free energy of folding, and ΔH_m^0 is the enthalpy of fusion. $\Delta T = T_m^0 - T_c$, f is expressed as $2T_c/(T_m^0 + T_c)$, and $\Delta \phi/(kT_c)$ can be replaced by $K_g/(\Delta T \cdot T_c)$, where K_g is the nucleation constant. As a result, Eq. (3) can be written as

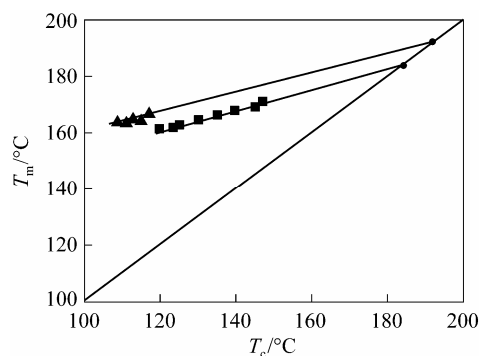
$$G = G_0 \exp\left(\frac{-\Delta F}{kT_c}\right) \exp\left(\frac{-K_g}{\Delta T \cdot T_c}\right) \quad (6)$$

where
$$K_g = \frac{2b_0 \sigma \sigma_e T_m}{\Delta H_m^0 \cdot k} \quad (7)$$

The value of G can be given by $1/t_{1/2}$, where $t_{1/2}$ is the half-time of crystallization, and $1/t_{1/2}$ can be expressed as a function of temperature with the following relationship [21, 22]

$$\left(\frac{1}{t_{1/2}}\right) = \left(\frac{1}{t_{1/2}}\right)_0 \exp\left[-\frac{U^*}{R(T_c - T_\infty)}\right] \exp\left[-\frac{K_g}{T_c \Delta T f}\right] \quad (8)$$

Equation (8) is the Lauritzen and Hoffman equation, which is widely used for studying the kinetics of polymer crystallization [24–27]. Fig. 6 shows the relationship between crystallization and melting peak temperatures (T_m). T_m versus T_c is extrapolated to the line $T_m = T_c$ to get T_m^0 , the values of which for PLLA and PLLA/TBC8-eb are 191.3, and 182.1 °C, respectively (Fig. 6). U^* is the activation energy for transport of segments to the site of crystallization, R is the gas constant, T_∞ is the hypothetical temperature at which all the motions associated with viscous flow ceases. $T_\infty = T_g - 30$ K, and $U^* = 6276$ J·mol⁻¹ is utilized, as done in previous studies on PLLA [24]. $(1/t_{1/2})$ is the front factor.

**Figure 6** Melting point T_m of PLLA and PLLA/TBC8-eb as a function of crystallization temperature T_c

■ PLLA/TBC8-eb; ▲ PLLA

The plot of $\ln(1/t_{1/2}) + U^*/[R(T_c - T_\infty)]$ as a function of $1/(T_c \Delta T f)$ is presented in Fig. 7, and K_g values of PLLA and PLLA/TBC8-eb are 7.3×10^5 and 2.9×10^5 , respectively, which are employed to calculate the free energy of folding according to Eq. (7).

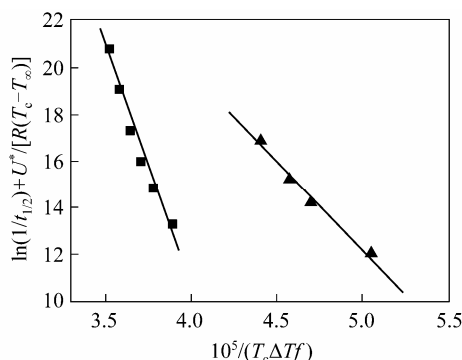


Figure 7 Hoffman-Lauritzen analysis of crystal growth data of PLLA samples

■ PLLA; ▲ PLLA/TBC8-eb

In order to determine the lateral surface free energy, the following empirical relation [21] is used

$$\sigma = \alpha \Delta H_m^0 (a_0 b_0)^{1/2} \quad (9)$$

where a_0 is the width of the stem added on the substrate, and $\alpha = 0.25$, appropriate to high melting polyesters [23]. Using the literature values of $\Delta H_m^0 = 1.11 \times 10^8 \text{ J} \cdot \text{m}^{-3}$ [26], $a_0 = 5.97 \text{ nm}$ and $b_0 = 5.17 \text{ nm}$ [27], the calculated values of σ_e for PLLA and PLLA/TBC8-eb are 0.15 and $0.06 \text{ J} \cdot \text{m}^{-2}$, respectively. This indicates that the addition of TBC8-eb favors the regular folding of molecule chains improving the crystallization of PLLA.

3.3 Conformational change in the isothermal crystallization progress

In order to get deep insight into the crystallization behavior of PLLA, FTIR was used to study its crystallization. The peaks at 1456 and 1210 cm^{-1} , which reveal the interchain interaction, are used to probe the conformational changes in the backbone [9, 10], while the band at 921 cm^{-1} is recognized as PLLA crystals in the α form with a distorted 10_3 helix conformation [9, 10], and the appearance of the 921 cm^{-1} band indicates the 10_3 helix formation. The period before the crystal of PLLA emerges is generally defined as the induction period. As a result, the induction periods for crystallization of PLLA and PLLA/TBC8-eb are 1380 and 208 s, respectively (Fig. 8). In other words, the induction period is shortened apparently in the presence of TBC8-eb. To disclose the reason why the induction period of PLLA/TBC8-eb is much shorter than that of PLLA, the normalized intensities of the bands at 1456, 1210 and 921 cm^{-1} as function of time are usually used to probe the interchain and intrachain interactions of PLLA [9, 10]. The interchain and intrachain interactions during melt crystallization of

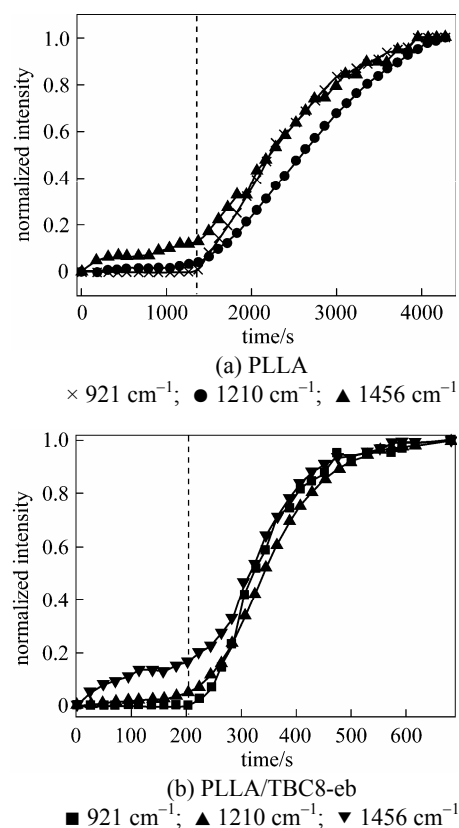


Figure 8 Normalized peak intensities at 921, 1210, and 1456 cm^{-1} as a function of crystallization time for PLLA and PLLA/TBC8-eb

PLLA have been widely studied by FTIR [9, 10, 28]. The order of intensity changes for the three bands of PLLA in induction period is as follows: $1456 \text{ cm}^{-1} > 1210 \text{ cm}^{-1} > 921 \text{ cm}^{-1}$, indicating that the interchain interaction of $-\text{CH}_3$ (1456 cm^{-1}) precedes the intrachain helix format (921 cm^{-1}). As shown in Fig. 8, the order of intensity changes for the bands of PLLA/TBC8-eb is the same with those of PLLA, namely, the conformational ordering begins with the interchain interaction of $-\text{CH}_3$, then a short helix emerges where a couple of $-\text{CH}_3$ groups interact. Therefore, TBC8-eb does not alert the sequence of conformational change. Since TBC8-eb decreases the induction period of crystallization, the function of TBC8-eb is just to accelerate the conformational ordering of PLLA in its isothermal crystallization.

4 CONCLUSIONS

The influence of a novel nucleating agent on crystallization of PLLA was studied. TBC8-eb turns out to be a high performance nucleating agent, whose T_{cp} of PLLA nucleated with TBC8-eb is 15°C higher than that of the PLLA with conventional nucleating agent -talc. Isothermal crystallization kinetics shows that the addition of TBC8-eb accelerates the crystallization rate. TBC8-eb also transforms most of the original

spherulite crystals of PLLA into sheaf-like crystals. The σ_e values of PLLA and PLLA/TBC8-eb are 0.15 and 0.06 J·m⁻², respectively, indicating that the addition of TBC8-eb favors the regular folding of molecule chains in the crystallization of PLLA. The FTIR results show that in the isothermal crystallization process, the conformational ordering of PLLA nucleated with TBC8-eb begins with the interchain interaction of —CH₃, then a short helix emerges where a couple of —CH₃ groups interact. This sequence of conformational change is the same with neat PLLA, and TBC8-eb accelerates the conformational ordering of PLLA rather than alters the sequence of conformational change.

NOMENCLATURE

a_0	width of the stem added on the substrate
ΔH_m^0	enthalpy of fusion
K	overall rate constant
k	Boltzman constant
n	mechanism constant
T_c	crystallization peak temperature
T_m	melting peak temperatures
T_m^0	equilibrium melting temperature
$t_{1/2}$	half-time of crystallization
X_t	relative degree of crystallization
σ	lateral surface free energy
σ_e	free energy of folding

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