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# Nucleating effect and crystal morphology controlling based on binary phase behavior between organic nucleating agent and poly(L-lactic acid)

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#### ABSTRACT

A new kind of nucleating agent for poly(L-lactic acid) (PLLA), N,N'-bis(benzoyl) hexanedioic acid dihydrazide (BHAD), was synthesized. Differential scanning calorimetry (DSC), polarization optical microscopy (POM), wide-angle X-ray diffraction (WAXD) and rheometer were used to study the crystallization behavior and crystal morphology of PLLA nucleated by BHAD. In order to ensure the same thermal history of the samples characterized by DSC, POM and XRD, these samples were all thermally treated by DSC. In nonisothermal crystallization, BHAD showed excellent nucleating ability to PLLA. However, it was different from the traditional heterogeneous nucleation mechanism. POM observation showed that morphologies of PLLA crystals varied with the concentration of BHAD and can be classified into three types. Through the systematic investigation of DSC, POM and rheological analysis, it was clearly demonstrated that BHAD had solubility in PLLA matrix, depending on its concentration and processing temperature. Consequently, a highly schematic binary phase diagram of the PLLA/BHAD system was presented, accompanied with a reasonable mechanism of how the PLLA crystal morphologies controlled by BHAD.

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#### 1. Introduction

Poly(L-lactic acid) (PLLA) is one of the most promising biodegradable polymer materials, which is devoted to solve the problem of white pollution [1,2]. Contributing to the renewable sources, the cycle of PLLA will not produce any extra carbon dioxide into the atmosphere [3–5]. This characteristic make PLLA very attractive as alternative for petroleum-based polymers [6,7]. However, PLLA does have some inherent shortcomings, which greatly restrict its development and application. One of the main problem is its slow crystallization rate during processing, which largely affects its performance.

The additives of nucleating agent (NA) is one of the most effective way to improve the crystallization ability of semicrystalline polymer. With appropriate nucleating agent added, puzzle of slow crystallization rate can be easily conquered. Talc [8–10], montmorillonite [11,12], layered metal phosphonate [13]

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http://dx.doi.org/10.1016/j.polymer.2015.04.062 0032-3861/© 2015 Elsevier Ltd. All rights reserved. and other inorganic powders [14,15] have showed nucleating ability for PLLA. By adding small amount of Poly(D-lactide) (PDLA), a polylactide stereocomplex is formed between PLLA and PDLA. The stereocomplex is able to nucleat PLLA in cooling [16–19]. Meanwhile, organic compounds, such as benzenetricarboxylamide derivatives [20,21] and benzoylhydrazide derivatives [22,23], have also been reported as effective nucleating agents for PLLA. Generally, organic nucleating agents are preferred because of the advantages of better dispersion in polymer matrix and higher efficiency even when the addition is at low level. Moreover, it is of great interest and broad significance to study the crystal morphologies of polymers controlled by nucleating agents [24-27]. For example, Fu's group noted that, by adding a rare earth nucleating agent (WBG),  $\beta$ -form isotactic polypropylene (i-PP) can be generated into three morphologies upon different molten temperatures [24]. By controlling the crystal morphologies, the toughness of iPP can be improved, which is very important for potentially industrial applications. Later, they also reported that N,N',N"-tricyclohexyl-1,3,5-benzenetricarboxylamide (TMC-328) had noticeable effects on controlling the crystal morphologies of PLLA, such as cone-like, shish-kebab-like, and needle-like macroscopic structures [21]. The







supermolecular structure in semi-crystalline polymers is of great significance in the study of polymer crystallization and further applications. However, the underlying formation mechanism for different crystal morphologies of polymers with nucleating agents still remains unknown.

There are complex interactions between polymer and nucleating agents, especially for organic ones. Firstly, there are several growth patterns of polymer crystals on the surface of nucleating agents, such as spherulites, transcrystalline layers and shish-kebab structures [17,28,29]. These growth patterns are related to the shape and size of nucleating agents, as well as their surface condition [28]. Secondly, nucleating agents also affect the crystal structures of polymers. By adding  $\alpha$ -nucleating agents or  $\beta$ -nucleating agents, i-PP crystals can be induced into  $\alpha$ -form or  $\beta$ -form, respectively [30–32]. Polymer with different crystal structures exhibits different morphologies. Last but not the least, some organic nucleating agents have solubility in polymer matrix. They can dissolve in polymers when heating to molten temperature, and then separate and self-organize into new crystals in subsequent cooling run [21,24]. However, the solubility of nucleating agent largely depends on the molten temperature (processing temperature) and concentration. Magnus Kristiansen et al. proposed a classical binary system of i-PP/Bis(3,4-dimethylbenzylidene)sorbitol, coming up with a schematic of four relevant composition ranges [27]. Thus, it can be concluded that the formation of different crystal morphologies of polymer is related to the interactions between polymer and nucleating agents, including the size, structure and solubility of nucleating agents.

In this paper, N,N'-bis(benzoyl) hexanedioic acid dihydrazide (BHAD), a kind of benzoylhydrazide derivative, was synthesized and studied as nucleating agent for PLLA. We presented a detailed study on the unique morphological evolution of BHAD over a concentration range, which will ultimately influence the crystallization behaviors of PLLA. Based on the analysis, a highly schematic binary phase diagram of the PLLA/BHAD system is proposed.

#### 2. Experimental section

#### 2.1. Materials

Hexanedioic acid, thionyl dichloride, triethylamine, methanol, N,N-dimethylformamide (DMF), dichloromethane (DCM) and benzoyl hydrazine were purchased from Guo Yao Chemical Reagents Company, China. PLLA (trade name 4032D) was purchased from Nature Works LLC, USA. The number-averaged and weightaveraged molecular weight of 4032D is about 120 kg/mol and 200 kg/mol, respectively.

#### 2.2. Synthesis of N,N'-bis(benzoyl) hexanedioic acid dihydrazide

0.1 mol hexanedioic acid was added into 150 mL thionyl dichloride with some drops of DMF. Then they were refluxed at 80 °C for 4 h. After reaction, rotary evaporator was used to remove the excessive thionyl dichloride to obtain hexanedioyl chloride. Residue was then dissolved in 100 mL DCM to eliminate the residual thionyl dichloride by azeotropy in rotary evaporator. DCM azeotropic operation was repeated for three times to purify the hexanedioyl chloride.

0.22 mol Benzoyl hydrazine and 0.1 mol triethylamine were dissolved in DMF. 0.1 mol hexanedioyl dichloride was slowly dropped into the mixture in ice water bath. After the addition, the mixture was heated to 80 °C for 2 h. Then the solution was poured into deionized water and stirred. The resulting precipitate was collected by suction filtration and rinsed with deionized water and hot methanol for 3 times respectively. The resultant powder was

dried at 100 °C in vacuum over night, the melting point of which was 246.6 °C (by DSC). The structure of BHAD is shown in Fig. 1.

<sup>1</sup>H NMR (DMSO, 500 MHz) δ: ppm; 10.29 (s, 2H, CONH), 9.85 (s, 2H, CONH), 7.88 (d, 4H, ArH), 7.58 (t, 2H, ArH), 7.50 (t, 4H, ArH), 2.20 (t, 4H, COCH<sub>2</sub>), 1.58–1.35 (m, 4H, CH<sub>2</sub>).

#### 2.3. Preparation of PLLA/BHAD blends

PLLA was dried for 8 h at 80 °C under vacuum before use. PLLA/ BHAD blends were prepared using an XSS-300 torque rheometer (Shanghai Ke Chuang Co., Ltd.) at 200 °C. The blends were first mixed at 32 r/min for 4 min, followed by 64 r/min for another 4 min. The concentrations of BHAD in blends were 0.1, 0.2, 0.3, 0.4, 0.5, 0.75, 1, 1.5 and 2 wt%. The samples are abbreviated as PLLA/ BHAD-x, where x is the mass fraction of BHAD in blends. PLLA/ BHAD samples were hot-pressed at 200 °C under 20 MPa for 3 min to obtain 0.4 mm thicknesses sheets, followed by cold-pressed at room temperature under 20 MPa for 10 min.

#### 2.4. Characterization

#### 2.4.1. <sup>1</sup>H nuclear magnetic resonance

The <sup>1</sup>H nuclear magnetic resonance was recorded on Brucker AVANCE 500 spectrometers. Dimethyl sulfoxide-D6 (DMSO-D6) was used as solvent.

#### 2.4.2. Differential scanning calorimetry measurement (DSC)

Thermal analysis of samples was carried out by DSC Q2000 (TA Instruments-Waters LLC, USA). Temperature and enthalpy calibration had already been done with indium. Weight of all the samples varied between 4 and 6 mg. Samples were first heated to the set temperature (called "final melting temperature",  $T_f$ ) and maintained at that temperature for 5 min to establish an initial state. Then samples were cooled to 40 °C at different cooling rates (1, 5, 10 and 20 °C/min).

#### 2.4.3. Thermal treatment of PLLA/BHAD blends

In order to ensure the same thermal history of the samples characterized by DSC, POM and XRD, all these samples were thermally treated by DSC. For POM observation, samples were first hot pressed between two small glass sheets. Then, they were put into aluminum crucible, reproducing the same treatment as DSC applied. For XRD characterization,  $4.0 \times 4.0 \times 0.4$  mm samples were put into aluminum crucible, followed by DSC treatment. The process of thermal treatment is the same as DSC measurement mentioned above.

#### 2.4.4. Polarization optical microscopy (POM)

The crystal morphology of PLLA was observed on a polarized optical microscopy (Leica DM2500P, Germany) equipped with a hot stage (Linkam-THM600, U.K.). For in situ observation, samples were hot pressed between two glass sheets in the hot stage. Firstly, they were heated to 230 °C at 5 °C/min, and subsequently cooling to 40 °C at 5 °C/min. Pictures were captured in the heating and cooling process. For the samples treated by DSC, pictures were captured directly.



Fig. 1. Structure of N, N-Bis(benzoyl) Hexanedioic Acid Dihydrazide (BHAD).

#### 2.4.5. Wide-angle X-ray diffraction (WAXD)

WAXD experiments were performed on an X-ray Diffractometer (D/Max 2550, Rigaku, Japan) using Cu K<sub> $\alpha$ </sub> radiation (wavelength, 1.54 Å) in the range of 5–50° with a scanning rate of 5°/min. Samples had already been thermally treated by DSC.

#### 2.4.6. Rheological

The rheological experiments were carried out by a rotational rheometer (DHR-3, TA Instruments) with 25 mm diameter and 1 mm gap parallel plates. Each sample of disk shape was heated to 230 °C and maintained for 5 min. Then storage modulus evolutions of the samples were monitored during the cooling process at the rate of 5 °C/min. The applied strain and oscillation frequency were set at 1% and 2 rad/s, respectively. In order to minimize degradation, all rheological measurements were performed under nitrogen atmosphere.

#### 3. Results and discussion

# 3.1. Nonisothermal crystallization of PLLA/BHAD and crystal morphology

#### 3.1.1. DSC curves of PLLA/BHAD at different cooling rates

Fig. 2 shows nonisothermal crystallization curves of PLLA containing BHAD. Compared to neat PLLA, nucleated samples have higher crystallization peak temperature ( $T_c$ ), which indicates the excellent nucleating ability of BHAD to PLLA. There are two mechanisms of nucleation for polymer crystallization, homogeneous nucleation and heterogeneous nucleation. For neat polymer, homogeneous nucleation is predominant. However, in the presence of nucleating agent, heterogeneous nucleation plays a major role. Under the circumstance, polymer crystallization rate (or  $T_c$ ) increases with the concentration of nucleating agent until saturated [18,19,33,34]. However, here for BHAD, situation is quite different. At first,  $T_c$  of PLLA is elevated as the increased concentration of BHAD. When BHAD exceeds 0.4 wt%,  $T_c$  of PLLA decreases unexpectedly. This phenomenon implies that the heterogeneous nucleation mechanism of BHAD is different from traditional heterogeneous nucleating agents (i.e. layered metal phosphonate [34]).

## 3.1.2. Crystal morphology of PLLA/BHAD after nonisothermal crystallization

With the aid of POM, the distinctly different morphologies of PLLA after nonisothermal crystallization are observed along with the concentration of BHAD. At the range of BHAD concentration, morphologies of PLLA can be classified into three types. When BHAD concentration is 0.1 wt%~0.2 wt%, PLLA crystal morphology in PLLA/BHAD is almost the same as that of neat PLLA, which can be viewed as numerous imperfect spherulites. When BHAD



Fig. 2. Nonisothermal crystallization of PLLA/BHAD at different cooling rates ( $T_f = 200 \degree C$ ): a. 1  $\degree C$ /min; b. 5  $\degree C$ /min; c. 10  $\degree C$ /min; d. 20  $\degree C$ /min.

concentration is 0.3 wt%~0.5 wt%, the morphology is changing into some pattern of branches and leaves. The crystal fibers of BHAD serve as bifurcate branches, meanwhile PLLA crystallizes on these fibers, acting as leaves. When BHAD concentration is 0.75 wt%~2 wt

%, the nucleating agent forms needle crystals, while PLLA crystallizes around them. The shift of  $T_c$  in nonisothermal crystallization may be related to the variation of PLLA crystal morphology, which is dominated by the BHAD morphology. The crystallization process of



 $\label{eq:Fig.3.} \text{FOM} \text{ images of PLLA/BHAD as BHAD concentration from 0 wt\% to 2 wt\% (T_f=200 \ ^\circ\text{C}, \text{ cooling rate}=5 \ ^\circ\text{C/min}, \text{ prepared in DSC}).$ 

PLLA depends on two factors, nucleation and crystal growth [34,35]. The addition of BHAD enhances nuclei density of PLLA. However, it can be noticed from Fig. 3 that, only when the BHAD is at an appropriate concentration can PLLA crystals have adequate place to growth on the surface of nucleating agent. It still remains a question that how BHAD changes its crystal morphology with the concentration. It will be discussed in next sections.

#### 3.2. The solubility of BHAD in PLLA and their binary phase behavior

#### 3.2.1. The influence of $T_f$ on the crystal morphologies of BHAD

It is found that  $T_f$  of sample has influence on  $T_c$  (Fig. 4), which indicates that the solubility of BHAD in PLLA matrix is related to temperature as well as BHAD concentration.  $T_c$  of the samples are summarized in Table 1, and the influences are concluded into three types, which is consistent with the crystal morphology diversity.

For the first type, the BHAD concentration is from 0.1 wt% to 0.2 wt%,  $T_c$  almost remains unchanged, which is the same as neat PLLA. This concentration range is defined as region I. In this range, BHAD completely dissolves in PLLA when temperature is above 200 °C. And in the cooling, BHAD cannot separate from PLLA. Compared to neat PLLA, T<sub>c</sub> of PLLA/BHAD-0.1 and PLLA/ BHAD-0.2 slightly depress. Under the circumstance, BHAD plays a role of solvent to PLLA and has no nucleating effect on PLLA. Similar phenomenon has been found in bis(3,4-



<sup>90 100 110 120 130 140 150 160 170 180 190 200 210 220</sup> 70 80 Temperature ( °C)

Table 1 T<sub>c</sub> of PLLA/BHAD after melting at different T<sub>f</sub>.

$T_{f} / C$			200	210	220	230
$T_{q}/^{\circ}C$		neat PLLA	98.4	98.7	98.5	99.7
	Ι	PLLA/BHAD-0.1	95.9	95.8	95.8	95.1
		PLLA/BHAD-0.2	98.9	94.3	94.8	95.7
	II	PLLA/BHAD-0.3	106.8	101.6	96.4	93.2
		PLLA/BHAD-0.4	131.4	122.7	102.1	96.0
		PLLA/BHAD-0.5	125.2	132.6	133.4	110.7
	III	PLLA/BHAD-0.75	126	125.4	134.9	132.8
		PLLA/BHAD-1	127	125.4	132.9	135.5
		PLLA/BHAD-1.5	128.3	127.4	130.5	135.3
		PLLA/BHAD-2	127.4	127.5	125.7	134.1

dimethylbenzylidene)sorbitol/iPP system. Kristiansen et al. [27] suggested that very low content additive would be inactive due to "complete solubility" in the polymers. So the crystal morphologies of PLLA/BHAD-0.1 and PLLA/BHAD-0.2 are similar to that of neat PLLA (Fig. 3).

For the second type, the BHAD concentration is from 0.3 wt% to 0.5 wt%,  $T_c$  is in inverse proportion to  $T_f$ . This concentration range is defined as region II. In this range, BHAD is partially dissolved in PLLA matrix. When  $T_f$  is low, BHAD concentration will slightly exceed its saturated solubility. Those undissolved BHAD crystals become nuclei for the dissolved BHAD and for PLLA in cooling. However, if *T<sub>f</sub>* rises, the solubility of BHAD will increase. The more





70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 60 Temperature ( °C)

Fig. 4. Nonisothermal crystallization of PLLA/BHAD at 5 °C/min from different T<sub>f</sub>: a. 200 °C; b. 210 °C; c. 220 °C; d. 230 °C.

BHAD will tend to dissolve in PLLA, the fewer BHAD nuclei will be left in the melt. In this way,  $T_c$  of PLLA will drop when  $T_f$  increases.

For the third type, the BHAD concentration is from 0.75 wt% to 2 wt%,  $T_c$  is in direct proportion to  $T_f$ , which is opposite to region **II**. This concentration range is defined as region III. In order to investigate the difference, optical microscope with hot stage was used for in situ observation (Fig. 5). In the heating process, a lot of needle-like BHAD crystals can be seen at 200 °C, which means the BHAD concentration at this temperature is far beyond its saturated solubility. As the temperature rises, the amount of needle-like BHAD will decrease. Also, liquid phase separation can be seen when temperature is over 220 °C. At 230 °C, almost all the BHAD needle-like crystals disappear. In the cooling process, BHAD begins to crystallize. Interestingly, the crystal morphology of BHAD is changing into dendritic structures. The increasing of  $T_c$  is related to the BHAD morphological change, although the deep mechanism needs further study. A similar dissolution and recrystallization process of nucleating agent was found in WBG/i-PP [24]. Needlelike WBG dissolved and then self-organized into flower-like structure with i-PP  $\beta$ -crystallites growing on its surface.

The solubility of BHAD in PLLA is strongly influenced by temperature. This means there is a complex binary phase behavior between PLLA and BHAD. It needs to be emphasized that PLLA/ BHAD-0.2 locates at the boundary between region **I** and region **II**, meanwhile PLLA/BHAD-0.5 is between region **II** and region **III**.

#### 3.2.2. Rheological analysis

The solubility of BHAD in PLLA and binary phase behavior can also be demonstrated by rheology (Fig. 6). Phase separation and crystallization of BHAD is reflected by evolution of the storage modulus. For PLLA/BHAD-0.1 and PLLA/BHAD-0.2, the curves are similar with the neat PLLA. No transition is found in the curves, which means BHAD are totally dissolved in PLLA and cannot separate from the matrix. This is in accordance with the crystal morphology and  $T_f$  influence discussed before. For BHAD concentration in range of 0.3 wt%-0.5 wt%, only one storage modulus transition can be seen in the curves. The transition temperature is



Fig. 6. Rheology measurement of PLLA/BHAD.

below the melting temperature of PLLA. Therefore, the transition is mainly attributed to the crystallization of PLLA. In this range, the dissolved BHAD separates from the PLLA matrix and turns into nucleating agent for PLLA. Then, PLLA crystallizes almost simultaneously with the separated BHAD. For BHAD concentration in range of 0.75 wt%~2 wt%, two transitions are found in the curves. The high temperature transition is attributed to the phase separation of BHAD, and the low temperature transition belongs to the subsequent crystallization of PLLA. Similar observations have been also reported previously, which indicates that the high temperature transition is related to the network formed by nucleating agents [21,27,36].

#### 3.2.3. Binary phase behavior scheme

Base on the data from DSC, POM and rheology, a schematic binary phase behavior of PLLA and BHAD is proposed in Fig. 7. For region *I*, in which BHAD concentration is below 0.2 wt%, BHAD is



Fig. 5. The morphology evolution of PLLA/BHAD-1 as temperature increasing from 200 °C to 230 °C, and then cooling to 140 °C, both at 5 °C/min (Bright field image).



Fig. 7. Binary phase behavior scheme of PLLA/BHAD.

completely dissolved in PLLA and unable to separate from the matrix. In this region, BHAD is not effective to nucleate PLLA. For region **II**, in which BHAD concentration is between 0.2 wt% and 0.5 wt%, BHAD will dissolve in the PLLA when temperature is elevated. In the cooling, BHAD is able to separate from the matrix, and at the same time, PLLA crystallizes on the surface of the embryo BHAD. For region **III**, in which BHAD concentration is above 0.5 wt%,

most of the BHAD is undissolved in PLLA. When the temperature increases, some BHAD will dissolve in PLLA matrix, leaving the rest changing into liquid, followed by the liquid phase separation between PLLA and BHAD. In the cooling, BHAD separates and crystallizes long before the crystallization of PLLA.

#### 3.3. Crystal morphology evolution of PLLA/BHAD

#### 3.3.1. The different BHAD crystals formed in PLLA

It still remains a question that the relationship between different morphologies of BHAD crystals is unknown. Three typical morphologies of needle-like, furcated-fiber-like, and dendrite-like patterns can be observed. As is discussed above, crystal morphology of BHAD is associated with its additive concentration and  $T_{f}$ . It is supposed that, these two variables can determine the residual BHAD crystals persisted in the PLLA melt, which subsequently influence the BHAD morphologies. It implies that, for the same sample, different types of morphologies of BHAD can be acquired by changing T<sub>f</sub> from higher to lower. Take PLLA/BHAD-1 as an example, when  $T_f$  is 200 °C, most of the BHAD is undissolved in PLLA. A dynamic balance between dissolved and undissolved BHAD is achieved. In this case, imperfect crystals dissolve and crystallize on the undissolved crystals. Finally, crystal sizes become uniform, as shown in Fig. 8a'. For the reason of high nuclei density, BHAD crystals will not grow large, but form needle-like crystals. When  $T_f$ is up to 220 °C, most of the BHAD dissolve or turn into liquid phase.



**Fig. 8.** Three types of BHAD crystal morphologies of PLLA/BHAD-1 (prepared in DSC) crystallized from different T<sub>f</sub>: a, T<sub>f</sub> = 200 °C; b, T<sub>f</sub> = 220 °C; c, T<sub>f</sub> = 230 °C. Picture (a, b, c) are polarized images and picture (a', b', c') are their bright field images.



Fig. 9. PLLA crystals grow perpendicularly on BHAD (prepared in POM). Picture (a) is polarized image, and picture (a') is bright field image. Picture (b) and (b') are the magnified images of (a) and (a').

Residual concentration of BHAD crystals is quite low. However, they still retain the needle-like morphology. In cooling, oversaturated BHAD will separate and crystallize along the length direction on these residual crystals. With the increase of the length, BHAD crystals begin to furcate (Fig. 8b'). When  $T_f$  is 230 °C, all the BHAD crystals dissolve or turn into liquid phase, which means no BHAD crystals exist in the PLLA melt. Upon the cooling process, BHAD homogeneously nucleates and grows in the form of furcated branch. Finally, several dendrite-like BHAD crystals can be clearly seen in the image (Fig. 8c'). Thus, three morphologies of BHAD crystals are obtained from PLLA/BHAD-1, and they are determined by the residual concentration of BHAD crystals at the highest temperature in the heating process.

#### 3.3.2. The PLLA crystals grow on the BHAD

Based on the analysis of Fig. 8, we concludes that when BHAD concentration exceeds 0.2 wt%, the nucleating agent will form needle-like, furcated-fiber-like, or dendrite-like crystal frameworks in PLLA matrix. It is interesting to investigate the crystal growth pattern of PLLA on BHAD. Fig. 9 shows the polarized and bright field images of PLLA/BHAD-1 at the beginning stage of nonisothermal crystallization. It is clear to see that PLLA is no longer spherulite morphology. They grow perpendicularly on BHAD frameworks. which become the transcrystalline regions [37–39]. This unique combination creates a supermolecular structure of PLLA and BHAD, which will probably provide different properties compared with PLLA spherulite [24,40]. However, the detailed differences, such as mechanical properties, is out of our concern in this paper, and will be studied later. From XRD data in Fig. 10, it is clearly seen that PLLA keeps  $\alpha$  structure in all samples [23]. Although the morphology of PLLA is totally changed, the crystal structures are kept same.

Hongwei Bai found that an organic nucleating agent, N,N',N"tricyclohexyl-1,3,5- benzenetricarboxylamide (TMC-328), formed shish-kebab structure with PLLA [21]. Eric D. Laird noted that, by inducing foreign fibers, polymer would form shish-kebab or transcrystalline layer with them, which was decided by the fiber diameter [28]. With large fiber diameter, transcrystalline layer is preferred. And when fiber diameter is quite small, shish-kebab will be dominated. It is supposed that, the high nucleating efficiency of the dendrite-like BHAD may be related to the shishkebab structure between PLLA and BHAD. There are many fine fiber structures at the end of the highly branched BHAD. These fibers tend to form the shish structure and later nucleate PLLA to form the kebab, which is clearly illustrated in Fig. 11. However, this is still a speculation, which needs to be further studied in future.

#### 4. Conclusions

In summary, N,N'-bis(benzoyl) hexanedioic acid dihydrazide was synthesized as nucleating agent for PLLA, which showed excellent nucleating effect as well as the ability to control the crystal morphology of PLLA. By changing BHAD concentration or



Fig. 10. XRD of PLLA/BHAD samples.



Fig. 11. Supermolecular structure of PLLA/BHAD.

 $T_{f}$ , different morphologies of PLLA crystal can be obtained. It is found that BHAD has solubility in PLLA. The blend of PLLA/BHAD can be viewed as a binary phase system, which is related to BHAD concentration and the processing temperature. Three regions have been found in this binary phase system at the BHAD concentration less than 2 wt%. Mechanism for PLLA morphology controlling by BHAD is given at viewpoint of binary phase behavior. It has been demonstrated that, PLLA crystal morphology is determined by the residual concentration of BHAD crystals at the highest temperature in the heating process. In cooling, dissolved BHAD gradually separates from PLLA and accumulates on those undissolved BHAD crystals. Then they form needle-like, furcated-fiber-like, or dendrite-like crystal frameworks. PLLA crystals grow perpendicularly on these frameworks, which will become the transcrystalline regions. This unique combination creates a supermolecular structure of PLLA and BHAD, which is of great value to be further studied later.

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