

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



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## ARTICLE INFO

### Article history:

Received 6 January 2015  
Received in revised form  
15 April 2015  
Accepted 20 April 2015  
Available online 25 April 2015

### Keywords:

Poly(L-lactic acid)  
Crystallization  
Binary phase behavior

## 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 semi-crystalline 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]

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 nucleate 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

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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 weight-averaged 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)  $\delta$ : 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 Bruker 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 × 4.0 × 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.

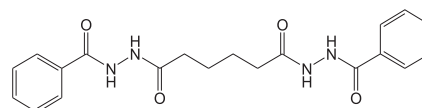


Fig. 1. Structure of N, N-Bis(benzoyl) Hexanedioic Acid Dihydrazide (BHAD).

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