

# Synthesis, Geometry Structure and Properties of *N, N'*-Carbonic Bis(Piperonylic Acid) Dihydrazide

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**Abstract.** In this study, *N, N'*-carbonic bis(piperonylic acid) dihydrazide (BPACH) was synthesized to broaden the category of piperonylic acid derivative and evaluate its influences on the thermal properties of poly(L-lactic acid) (PLLA). The geometry optimization of BPACH showed that the highest occupied molecular orbital mainly focused on the formed amide group and carbonic dihydrazide, whereas the lowest unoccupied molecular orbital mainly focused on the piperonylic acid, and the orbital energy gap was 0.10418 eV. The differences in melt-crystallization processes of the neat PLLA and PLLA/BPACH samples indicated that the BPACH could provide the effective nucleation site to accelerate the crystallization of PLLA, but the crystallization accelerating effect was still further improved compared to some reported nucleating agents. The melting behaviors of PLLA/BPACH samples after crystallization depended on the crystallization temperatures and heating rates; additionally, the melting processes could also effectively reflect the previous crystallization behaviors.

## 1. Introduction

Piperonylic acid is an important natural carboxylic acid with methylenedioxy, exhibiting the excellent antioxidant and antibacterial activities [1], tyrosinase inhibition [2], etc. Thus, more and more piperonylic acid derivatives were synthesized to evaluate their bioactivity [3, 4]. However, it is pity that the studies on the piperonylic acid derivative focused on their bioactivity, the reports that the piperonylic acid derivative was introduced into the polymers to improve their performances are very few.

Poly(L-lactic acid) (PLLA) as a typical biodegradable polymer material has obtained increasing attentions due to its biodegradability, excellent compatibility and transparency, which promotes its applications to be developed to the biomaterials [5], food packaging [6], agriculture [7], etc. But the inherent defect of the slow crystallization speed seriously exhibits an inhibition for application of wide application. To overcome this slow crystallization speed, the nucleating agent was added into the PLLA resin to improve the nucleation density, because the crystallization of the semi-crystalline polymer firstly need to nucleate during the crystallization process. Therefore, in this study, a piperonylic acid derivative of *N, N'*-carbonic bis(piperonylic acid) dihydrazide (BPACH) was firstly synthesized, and its geometrical structure was optimized via DMol3 density functional theory. And then the BPACH was blended with the PLLA to obtain the modified PLLA materials containing the different

BPACH contents, finally, the effects of BPACH on the melt-crystallization and melting process of PLLA were further studied by differential scanning calorimetry (DSC).

## 2. Experimental section

### 2.1. Reagents and materials

The BPACH was synthesized in our lab, and the main reagents including piperonylic acid, carbonic dihydrazide, sulfoxide chloride were analytical purity. And the PLLA used in this work was produced by Nature Works LLC, USA, and the trade names was 4032D.

### 2.2. Preparation of BPACH and PLLA/BPACH

The synthetic route of BPACH was shown in Fig.1. As seen in Fig.1, two step reactions, including acylation of piperonylic acid and amination of carbonic dihydrazide with piperonylic acid chloride, were performed to obtain the BPACH, the detailed operation process was similar with the other amide derivatives reported by our lab [8]. Fourier Transform Infrared Spectrometer (FT-IR)  $\nu$ : 3412.9, 2900.7, 1707.8, 1664.8, 1643.4, 1608.3, 1535.7, 1504.7, 1491.8, 1445.8, 1384.0, 1350.3, 1290.2, 1261.5, 1194.3, 1167.1, 1105.9, 1064.6, 1036.6, 923.2, 877.7, 852.8, 813.5, 752.9, 719.5  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$ : ppm;

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10.04 (s, 1H, NH), 8.46 (s, 1H, NH), 7.00~7.51 (m, 3H, Ar), 6.10 (s, 2H, CH<sub>2</sub>).

A torque rheometer was used to perform the blend of PLLA with different BPACH content (1 wt%, 2 wt% and 3 wt%), and the blending temperature was set at 190 °C, and the rotation rate was set at 32 rpm for 5 min and 64 rpm for 5 min.

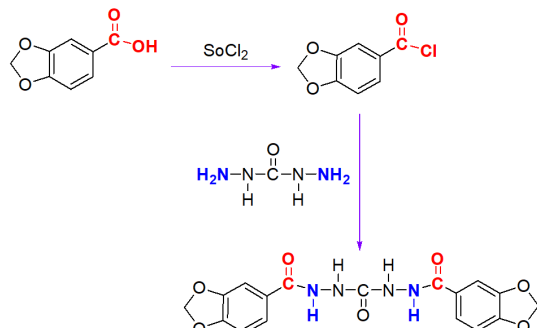


Fig.1. Synthetic route of BPACH

### 2.3.Characterization and test

The characterization of BPACH's molecular structure was determined by 1H NMR and FT-IR. The melt-crystallization and melting processes of the pure PLLA and PLLA/BPACH were tested by DSC with 50 mL/min nitrogen.

## 3.Results and discussion

### 3.1.Geometrical structure of BPACH

The geometrical structure of BPACH was optimized by DMol3, the calculation task was geometry optimization, the quality was medium, the calculation used symmetry. Figure.2 is the optimized geometrical structure of BPACH, and the frontier orbital energy was also obtained. It is observed from Fig.2 that the highest occupied molecular orbital (HOMO) mainly focuses on the formed amide group and carbonic dihydrazide, and the HOMO is -0.187727 eV; the lowest unoccupied molecular orbital (LUMO) mainly focuses on the piperonylic acid, and the LUMO is -0.083547 eV. The LUMO-HOMO energy gap is 0.10418 eV.

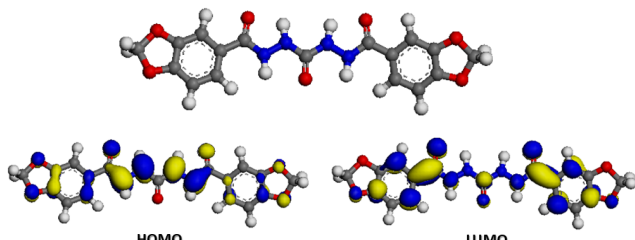


Fig.2. Frontier orbitals of BPACH

### 3.2.Melt-crystallization of PLLA/BPACH

Figure.3 is the melt-crystallization DSC curves of the neat PLLA and PLLA/BPACH from the melt for 3 min. Upon cooling of 1 °C/min, the neat PLLA does almost not have the crystallization peak in DSC curve, whereas

the PLLA/BPACH samples have the obvious crystallization peak, meaning that the presence of BPACH promotes the PLLA to form the crystals in cooling, and the BPACH is thought to be effective nucleation site for accelerating the crystallization. Additionally, with the increasing of BPACH content, the melt-crystallization peak firstly shifts toward the high-temperature side, and then moves toward the low-temperature side, and the PLLA/2%BPACH has the highest crystallization peak temperature of 124.4 °C. For the melt-crystallization enthalpy, the melt-crystallization enthalpy exhibits a consecutive increases from 48.3 J/g to 53.4 J/g. Through analysis of peak shape and crystallization peak temperature, it is found that the crystallization accelerating effect of BPACH is relatively weaker than the other adjuvants such as BAS [9], AHA [10], BAAD [11], TBOD [12], etc.

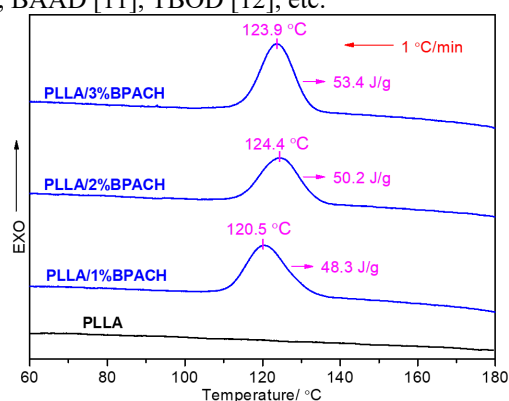
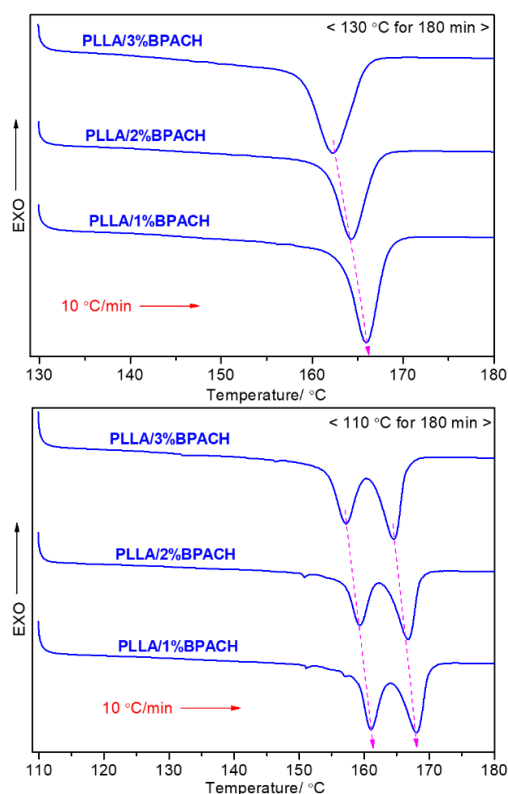


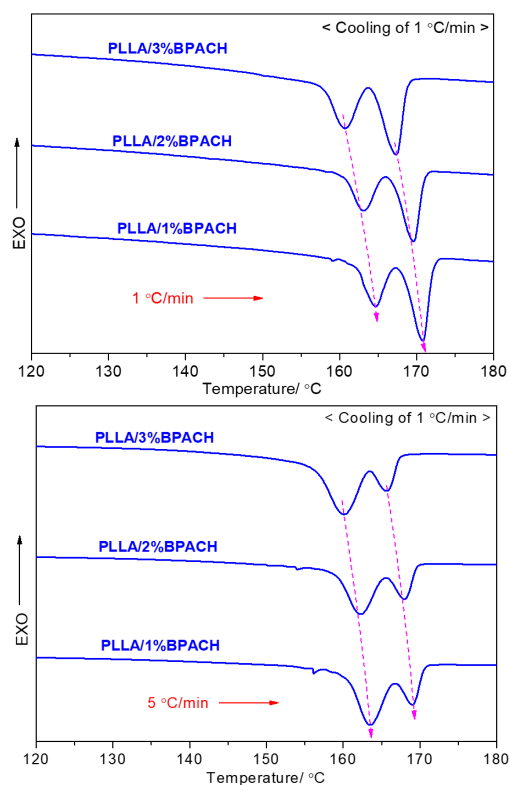
Fig.3. Melt-crystallization of the neat PLLA and PLLA/BPACH

### 3.3.Melting process of PLLA/BPACH

The melting processes of PLLA/BPACH samples after crystallization were further investigated. Figure.4 is the melting behavior of PLLA/BPACH samples at a heating rate of 10 °C/min after crystallization at 110 °C or 130 °C for 180 min. It is clear that there exists only single melting peak after crystallization at 130 °C for 180 min, moreover, the melting peak moves toward the lower temperature with increasing of BPACH content. However, after crystallization at 110 °C for 180 min, all DSC curves exhibit the double melting peaks, and this double melting peaks are often assigned to the melt-recrystallization [13]. The low-temperature melting peak is attributed to the primary crystals, and the high-temperature melting peak results from the new crystals formed during the second heating scan.



**Fig.4.** Melting of PLLA/BPACH after crystallization at different crystallization temperatures for 180 min



**Fig.5.** Melting processes of PLLA/BPACH samples after non-isothermal crystallization at 1 °C/min

Figure.5 is the melting processes of PLLA/BPACH samples at different heating rates after melt-crystallization at a cooling rate of 1 °C/min. It is found that the double melting peaks appear in all DSC curves, indicating that the crystallization cannot be completed in cooling, which further confirms the moderate crystallization promoting ability of BPACH for PLLA. With increasing of heating rate, the high-temperature melting peak gradually becomes smaller comparing with the low-temperature, the reason is that there is not enough time to form crystal during the faster heating rate. In addition, the double melting peaks shift toward the low temperature with increasing of heating rate.

## 4. Conclusions

BPACH was synthesized via two step reactions of acylation and amination, and its molecular structure was characterized by FT-IR and <sup>1</sup>H NMR. The density functional theory method obtained the optimized geometry structure and frontier orbital energy of BPACH, the calculation results showed that the HOMO of BPACH focused on the formed amide group and carbonic dihydrazide, and the LUMO focused on the piperonylic acid. The addition of BPACH could promote the crystallization of PLLA in cooling, and the PLLA/2%BPACH sample had the highest melt-crystallization peak temperature of 124.4 °C, whereas the PLLA/3%BPACH sample had the largest melt-crystallization enthalpy of 53.4 J/g. Both the crystallization temperature and heating rate significantly affected the melting processes of PLLA/BPACH in this study, and the melting processes could also reflect the crystallization before the melt.

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