http://www.ejchem.net

ISSN: 0973-4945; CODEN ECJHAO
E-Journal of Chemistry
2012, **9(2)**, 545-552

Synthesis and Performance of *N*-(Benzoyl) Stearic Acid Hydrazide

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Received 21 March 2011; Revised 18 August 2011; Accepted 4 September 2011

Abstract: *N*-(benzoyl) stearic acid hydrazide was synthesized from benzoyl hydrazine and stearyl chloride which was deprived from stearic acid via acylation. The structure of the compound had been characterized by FT-IR, ^{1}H NMR, at the same time, the structure of N-(benzoyl) stearic acid hydrazide was optimized by the semiempirical method PM3. The influence of the reaction ratio, reaction time and reaction temperature to the yield of *N*-(benzoyl) stearic acid hydrazide was investigated by orthogonal experiment, and the optimized reaction condition was molar ratio of benzoyl hydrazine: stearyl chloride 1:1, reaction time 6 h, reaction temperature 70 ℃, and the yield was 92.9%. The TGA thermal analysis of N-(benzoyl) stearic acid hydrazide showed that thermal stability of *N*-(benzoyl) stearic acid hydrazide was affected by heating rate, and the *N*-(benzoyl) stearic acid hydrazide enhanced the tensile strength, modulus and elongation at break of Poly(*L*-lactic acid)(PLLA).

Keywords: Stearic acid, Benzoyl hydrazine, Poly(*L*-lactic acid), Orthogonal experiment.

Introduction

With the increasing development of science and technology, amides, as a kind of very important organic compound, has a wider application fields. Besides the traditional fields of synthetic intermediates[1,2], material chemistry[3,4], amides play an active role in drug discovery[5], polymer[6-8], *etc* and obtained a lot of progress. For example, the importance of the amides in polymer has been recently highlighted by Cai and co-workers[6]. In that article, *N,N′*-bis(benzoyl) suberic acid dihydrazide as heterogeneous nucleation agent can significantly improve the crystallization of poly(*L*-lactic acid)(PLLA). *N,N′*-bis(benzoyl) suberic acid dihydrazide leads to the shift of the melt crystallization to higher temperature and becomes much sharper in the melting crystallization process of PLLA. Upon the addition of 0.8% *N,N′*-bis(benzoyl) suberic acid dihydrazide, the crystallization half-time of PLLA/ *N,N′*-bis(benzoyl) suberic acid dihydrazide decreases from 26.5 min to 1.4 min at 115 ℃.

Furthermore, Angela and co-workers[8] also reported that ethylene bis- stearamide can serve as a nucleating agent of PLLA for dramatic increasing in crystallization rate and final crystalline content as indicated by isothermal and nonisothermal crystallization measurements. Thus, amide will play more important role in industry and agriculture.

In order to further develop the more amide compounds, and adequately investigate the performance of amide compounds. In this study, *N*-(benzoyl) stearic acid hydrazide was synthesized from benzoyl hydrazine and stearyl chloride which was deprived from stearic acid via acylation. The influence of the reaction conditions to the yield and thermal stability of product was investigated by orthogonal experiment and TGA respectively. Finally, the effection of *N*-(benzoyl) stearic acid hydrazide towards PLLA's mechanical properties were further investigated.

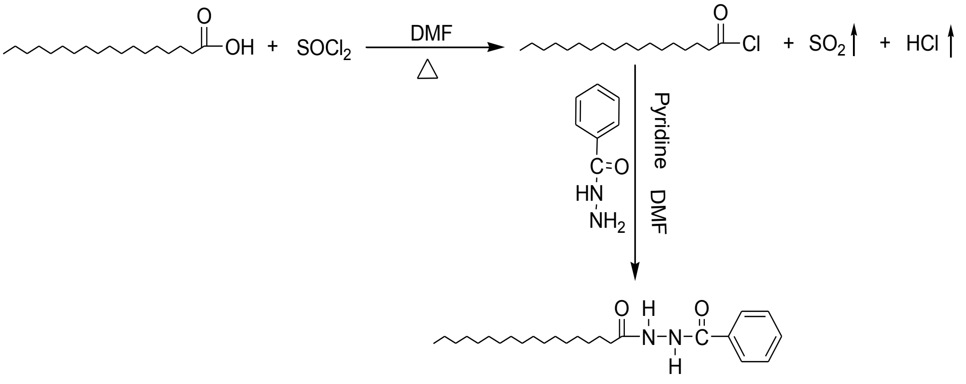
Experimental

The materials used in this study were of analytical grade (AR). Benzoyl hydrazine and stearic acid were procured from Chengdu Kelong Chemical Reagents Company respectively (Sichuan Province, China); Thionyl dichloride, N, N-dimethylacetamide and Pyridine were procured from Mianyang Rongshen Chemical Reagents Company (Sichuan Province, China). poly(*L*-lactic acid)(PLLA) was purchased from Nature Works LLC, USA.

Synthesis procedure of N-(benzoyl) stearic acid hydrazide

N-(benzoyl) stearic acid hydrazide was prepared as shown in Scheme 1: stearic acid and thionyl dichloride of 50 mL was mixed in the presence of *N,N*-dimethylacetamide as catalyst. Then the mixture was heated up to 80 ℃ and held at 80 ℃ with stirring for 7 h. After cooling to room temperature and evaporation of thionyl dichloride in vacuum, the residue was stearyl chloride.

Benzoic hydrazide and *N,N*-dimethylacetamide of 50 mL were mixed and the mixture was purged under nitrogen atmosphere. Stearyl chloride was added slowly onto the mixture, followed by adding pyridine of 0.057 mol, then the mixture was heated up to 60～ 80 ℃ and held at 60～ 80 ℃ for period of time with stirring. The reaction mixture was poured onto water of 250 mL and stirred, followed by filtrating. Obtained crude product was washed four times by water of each 250 mL at room temperature, and then washed by methanol of 200 mL at 50 ℃ to eliminate raw materials and by-products, the resulting product was dried in a vacuum at 55 ℃.



Scheme 1. Synthesis of *N*-(benzoyl) stearic acid hydrazide.

Preparation of PLLA/N-(benzoyl) stearic acid hydrazide samples

PLLA was dried overnight at 50 ℃ under vacuum to remove residual water. Blending of PLLA and dried *N*-benzoyl stearic acid hydrazide was performed on a counter-rotating mixer with a rotation speed of 32 rpm for 5min, then at 64 rpm for 5 min. The processing temperature was set at 185 ℃. Products were hot pressed at 180 ℃ 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 at room temperature under 20 MPa for 10 min.

Results and Discussion

Structure of N-(benzoyl) stearic acid hydrazide

The FT-IR spectra of *N*-(benzoyl) stearic acid hydrazide is shown in Figure 1. As showen in the spectra, the peak at 3400 cm^{-1} contributes to the absorption of N-H stretching vibration; the absorption peaks at 2917.6 cm^{-1}, 2849 cm^{-1} and 716.7 cm^{-1} contribute to CH_2 symmetrical stretching vibration, asymmetrical stretching vibration and rocking vibration respectively. Owing to conjugated effect, C=O of benzoic hydrazide moves to lower vibrational frequency. That's to say, the absorption peak at 1638.1 cm^{-1} contributes to C=O stretching vibration, and the absorption peak at 1666.7 cm^{-1} contributes to C=O of amide. Then the absorption peaks at 1602.2 cm^{-1}, 1572.7 cm^{-1}, 1500 cm^{-1}, and 1469.2 cm^{-1} prove the existence of benzene.

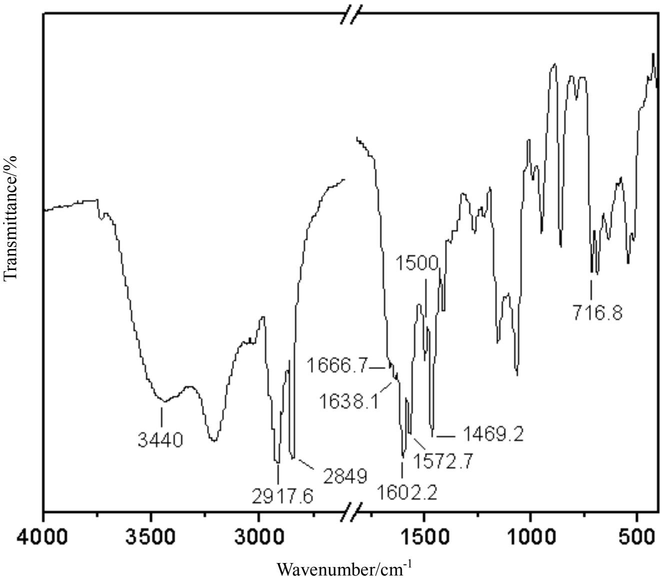


Figure 1. FT-IR spectra of *N*-(benzoyl) stearic acid hydrazide.

The ^1H NMR patterns of *N*-(benzoyl) stearic acid hydrazide is depicted in Figure 2. The single peak at δ_H=10.27 and 9.82 are proton resonance peak of N-H of *N*-(benzoyl) stearic acid hydrazide, the multiple peaks at δ_H=7.47-7.88 are proton resonance peaks of benzene, the triplet peaks at δ_H=2.15-2.18 are CH_2 which is near amide proton resonance peak. As for the multiple peaks at δ_H=1.24-1.56, they belong to other CH_2 proton resonance peaks, the triplet peaks at δ_H=0.84-0.86 are CH_3 proton resonance peaks. NMR analysis further confirms that N-(benzoyl) stearic acid hydrazide was synthesized.

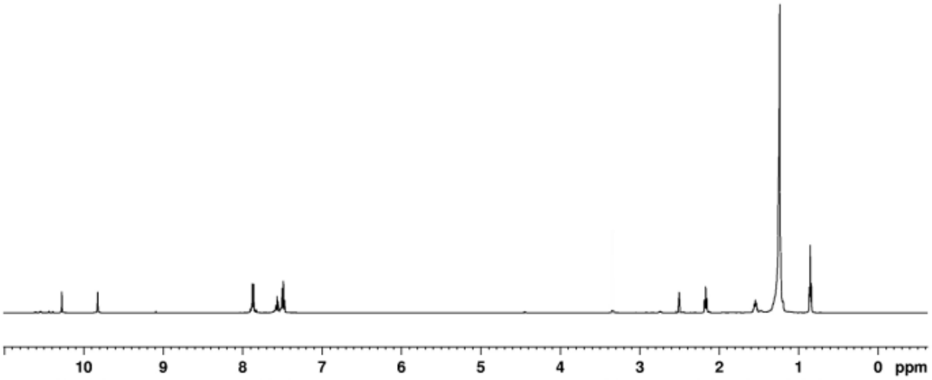


Figure 2. ^{1}H NMR spectra of *N*-(benzoyl) stearic acid hydrazide.

In order to further investigate the structure of N-(benzoyl) stearic acid hydrazide, the optimized geometric structure of N-(benzoyl) stearic acid hydrazide was carried out by the theoretical calculation which were performed by the program VAMP using the semiempirical method PM3. The optimized geometry structure of *N*-(benzoyl) stearic acid hydrazide is shown in Figure 3 and the HOMO and LUMO of phthalimide is -9.852 eV and -0.309 eV, respectively.

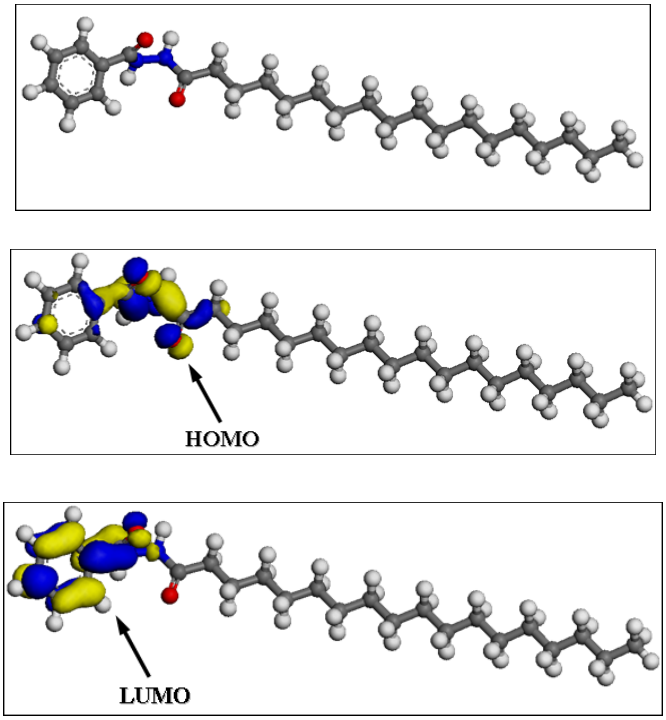


Figure 3. Optimized geometric structure, HOMO and LUMO of *N*-(benzoyl) stearic acid hydrazide.

Synthesis conditions of N-(benzoyl) stearic acid hydrazide

The influence of the reaction ratio, reaction time and reaction temperature to the yield of product was investigated by orthogonal experiment. Factors and levels of orthogonal experiment are listed in Table 1 and the results are listed in Table 2. As seen in Table 2. It is clear that reaction time is more important to yield than other factors. The reason is that the high reactivity of stearyl chloride can result in shorter reaction time, which lower the side effects greatly. And the optimized reaction condition are as follows: molar ratio of benzoyl hydrazine: stearyl chloride 1:1, reaction time 6 h, reaction temperature 70 ℃, and the yield is 92.9 %.

Table 1. Factors and levels of orthogonal experiment.

Level	**Factor**		
	Reaction time (A)	Reaction ratio[(a)](B)	Reaction temperature(C)
1	4 h	1:1	60 ℃
2	6 h	2:3	70 ℃
3	8 h	1:2	80 ℃

(a) Benzoic hydrazide: stearyl chloride.

Table 2. Results of orthogonal experiment.

Run	A	B	C	Scheme	Yield/%
1	1	1	1	$A_1B_1C_1$	77
2	1	2	2	$A_1B_2C_2$	80.4
3	1	3	3	$A_1B_3C_3$	81.7
4	2	2	3	$A_2B_2C_3$	72.1
5	2	3	1	$A_2B_3C_1$	82.2
6	2	1	2	$A_2B_1C_2$	92.9
7	3	3	2	$A_3B_3C_2$	70.4
8	3	1	3	$A_3B_1C_3$	73.4
9	3	2	1	$A_3B_2C_1$	61.8
K_1	2.09	2.13	1.91		
K_2	2.17	1.84	2.14		
K_3	1.76	2.04	1.98		
Extreme difference	0.41	0.29	0.23		
Important factor			A B C		
Optimized scheme			A_2 B_1 C_2		

Thermal decomposition of N-(benzoyl) stearic acid hydrazide

Thermal stability is very important for application of *N*-(benzoyl) stearic acid hydrazide, thus, the thermal stability of *N*-(benzoyl) stearic acid hydrazide was investigated by TGA. Figure 4 shows the TGA curves of N-(benzoyl) stearic acid hydrazide with a heating ramp of 2.5, 5, 10, 20, 30 ℃/min from room temperature to 500 ℃ under nitrogen flow. As seen in Figure 4, N-(benzoyl) stearic acid hydrazide begins to decomposition above 185 ℃, which suggests that *N*-(benzoyl) stearic acid hydrazide has good thermal stability in daily application. After that, *N*-(benzoyl) stearic acid hydrazide decomposes fast and completely in one stage above 200 ℃ at all heating rates. Furthermore, with the increasing of heating rate, the decomposition temperature increases and heating decomposition degree decreases. Rapid heating rate makes the decomposition of *N*-(benzoyl) stearic acid hydrazide not achieve at set temperature, at the same time, the temperature has get into the following set temperature, resulting in decomposition achieving at higher temperature.

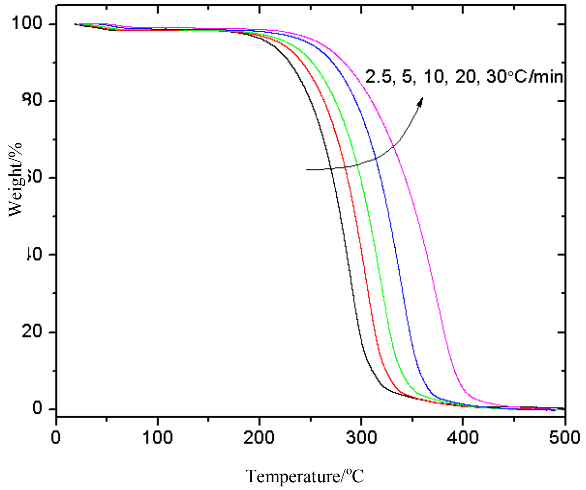


Figure 4. TGA curves of N-(benzoyl) stearic acid hydrazide.

Mechanical properties of PLLA/N-(benzoyl) stearic acid hydrazide samples

Dumbbell-shaped tensile test specimens with effective dimensions of 25 mm×6 mm×1.0 mm were prepared by pneumatic-controlled impact shaping machine. Tensile tests were conducted on a D&G DX-10000 electronic tensile tester at the speed of 50 mm/min at room temperature. The tensile strength, elastic modulus and elongation at break were obtained by averaging over five specimens. The tensile strength, tensile modulus and elongation at break of PLLA with different *N*-(benzoyl) stearic acid hydrazide contents are presented in Figure 5(a), Figure 5(b) and Figure 5(c), respectively. The figure shows that *N*-(benzoyl) stearic acid hydrazide can improve the tensile strength, tensile modulus and elongation at break of PLLA and the tensile strength, tensile modulus and elongation at break increase with the increase of *N*-(benzoyl) stearic acid hydrazide contents and possesses a maximum value for the critical *N*-(benzoyl) stearic acid hydrazide loading 0.5%, 0.8% and 0.3%, respectively. Upon addition of optimized content of *N*-(benzoyl) stearic acid hydrazide, comparing with the neat PLLA, the tensile strength, tensile modulus and elongations at break of PLLA/ *N*-(benzoyl) stearic acid hydrazide increase from 74.4 MPa, 3592.8 MPa, 2.72% to 81.3 Mpa, 4328.7 Mpa and 3.3%, respectively. Low N-(benzoyl) stearic acid hydrazide contents in PLLA maybe existe a good dispersion and compatibility.

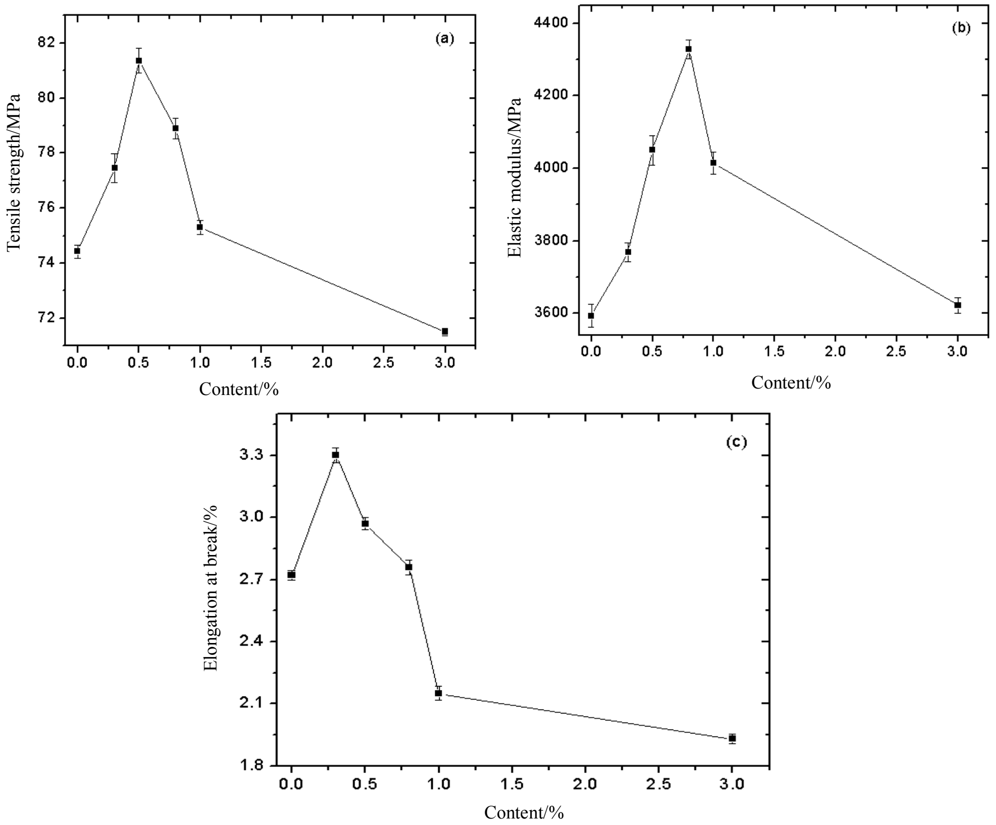


Figure 5. The mechanical properties of PLLA with different N-(benzoyl) stearic acid hydrazide contents.

Conclusion

N-(benzoyl) stearic acid hydrazide was synthesized from benzoyl hydrazine and stearyl chloride which was deprived from stearic acid via acylation. The optimum reaction conditions were determined by orthogonal experiment as follows: molar ratio of benzoyl hydrazine to stearyl chloride 1:1, reaction time 6 h, reaction temperature 70 ℃ and the yield was 92.9 %. TGA results indicated good thermal stability of *N*-(benzoyl) stearic acid hydrazide, and thermal stability was affected by heating rate. Besides, the *N*-(benzoyl) stearic acid hydrazide enhanced tensile strength, modulus and elongation at break of PLLA.

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