



Synthesis, Process, Morphology and Thermal Stability of N,N'-Bis(benzoyl) Tridecanedioic Acid Dihydrazide

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(Received: 10 August 2010;

Accepted: 14 February 2011)

AJC-9624

Novel N,N'-bis(benzoyl) tridecanedioic acid dihydrazide was synthesized from benzoyl hydrazine and tridecanedioyl dichloride which was deprived from tridecanedioic acid *via* acylation and the structure of this novel bisamide compound had been characterized by FT-IR, ¹H NMR. The influence of the reaction ratio, reaction time and reaction temperature to the yield of product was further investigated, molar ratio of benzoyl hydrazine: tridecanedioyl dichloride 2:1, reaction time 6 h, reaction temperature 80 °C, the yield was 90.1 %. Scanning electron microscopy (SEM) showed the N,N'-bis(benzoyl) tridecanedioic acid dihydrazide was layered and the average size of the layered particles was 5 μm. The thermal stability of N,N'-bis(benzoyl) tridecanedioic acid dihydrazide was investigated by TGA thermal analyzer. The result showed good thermal stability of N,N'-bis(benzoyl) tridecanedioic acid dihydrazide under 165 °C and that the decomposition of N,N'-bis(benzoyl) tridecanedioic acid dihydrazide could reach 96.9 % at 500 °C.

Key Words: Benzoyl hydrazine, Tridecanedioic acid, Layered, Thermal stability.

INTRODUCTION

Amides, which are obtained by condensation reaction between carboxylic acid derivative and amines, are very important organic compounds. In recent years, amide and its derivatives have been widely used in synthesis of intermediates¹⁻⁴, materials chemistry⁵⁻⁷, drugs release⁸, polymers⁹⁻¹¹, *etc.* and obtained a lot of progress. For example, Kawamoto *et al.*¹⁰ reported that benzoylhydrazide-type compound with bisamides was found to be most effective on the enhancement of poly(L-lactic acid) crystallization. An increase in the methylene chain numbers improved the nucleation ability of benzoylhydrazide-type compound and decamethylenedicarboxylic dibenzoylhydrazide was found to provide highest crystallization temperature and enthalpy. Thus, amides had been research hot spots with field of organic chemistry, pharmaceutical industry and materials.

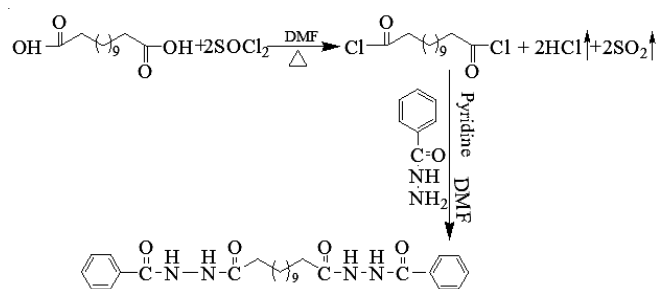
The traditional synthesis method is achieved by temperature reaction of carboxylic acids with amines. Such a reaction has limitations such as long time of reaction¹². In this paper, we use an advanced routes to synthesize amides and a novel compound named N,N'-bis(benzoyl) tridecanedioic acid dihydrazide was synthesized from benzoyl hydrazine and tridecanedioyl dichloride which was deprived from tridecanedioic acid *via* acylation, the optimum conditions of this reaction, the morphology and thermal stability of the product were further investigated.

EXPERIMENTAL

The materials used in this study were of AR grade. Benzoyl hydrazine and tridecanedioic acid were procured from Beijing Chemical Reagents Company (Beijing, Chian) and 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).

Synthesis of N,N'-bis(benzoyl) tridecanedioic acid dihydrazide: N,N'-Bis(benzoyl) tridecanedioic acid dihydrazide was prepared as shown in **Scheme-I**: Tridecanedioic acid, thionyl dichloride of 50 mL in the presence of N,N-dimethylacetamide as catalyst was mixed and the mixture was heated up to 80 °C and kept at 80 °C for 10 h with constant stirring. After cooling to room temperature and evaporation of thionyl dichloride in vacuum, the residue was tridecanedioyl dichloride.

Benzoic hydrazide and N,N-dimethylacetamide (50 mL each) were mixed and the mixture was purged under nitrogen atmosphere. Tridecanedioyl dichloride was added slowly onto the mixture, followed by adding pyridine (0.057 mol) and the mixture was heated up to 60-80 °C and kept at 60-80 °C for 8 h with constant stirring. Reaction mixture was poured onto water of 300 mL and stirred, followed by filtration. The crude product was washed 4 times by water of each 300 mL at room



Scheme-1: Synthesis of *N,N'*-bis(benzoyl) tridecanedioic acid dihydrazide

temperature and then washed by methanol of 300 mL at 50 °C to eliminate raw materials and by-products. The resulting product was dried in a vacuum at 65 °C. IR (KBr, ν_{\max} , cm^{-1}): 3439, 3221.3, 2920.9, 2850, 1642.9, 1604.8, 1574.3, 1503.2, 1468.4, 1407.8, 1382.9, 1358.1, 1266.9, 1158.7, 1072.5, 997, 951.2, 861.4, 711.1, 691.6, 636.4, 548.3, 522.9, 449.8; ^1H NMR (DMSO, 500 MHz) δ : ppm; 10.28 (s, 1H, NH), 9.83 (s, 1H, NH), 7.48-7.88 (m, 5H, Ar), 2.16-2.19 (t, 2H, CH_2), 1.54-1.55 (d, 2H, CH_2), 1.21-1.27 (d, 2H, CH_2).

RESULTS AND DISCUSSION

Synthesis conditions of product: The reaction of tridecanedioyl dichloride and benzoic hydrazide can fully occur due to the high reactivity of tridecanedioyl dichloride. Thus, in order to decrease by-products of reaction, the molar ratio of benzoyl hydrazine and tridecanedioyl dichloride is 2:1.

The molar ratio of benzoyl hydrazine:tridecanedioyl dichloride 2:1, reaction temperature 80 °C, the influence of the reaction time to the yield of product is further investigated. The result is indicated in Table-1, the yield of *N,N'*-bis(benzoyl) tridecanedioic acid dihydrazide increases with increasing of reaction time, the yield reach the maximum value 90.1 % when the reaction time is 6 h and the yield decreases with further increasing of reaction time. Therefore, the optimum reaction time is 6 h.

TABLE-1
EFFECT OF REACTION TIME ON YIELD OF PRODUCT

Reaction time (h)	1	2	4	6	8
Yield (%)	67.3	79.9	85.7	90.1	87.5

Upon reaction time 6 h, the influence of the reaction temperature to the yield of product is also discussed. As seen in Table-2, it is clear that the influence of the reaction temperature to yield has same trend with that of reaction time. When the reaction temperature is 80 °C, the yield appear maximum value 90.1 %, then the yield decrease, the reason is that the activation energy of the reaction is low and side effects increase with further increasing of reaction temperature.

TABLE-2
EFFECT OF REACTION TEMPERATURE
ON YIELD OF PRODUCT

Reaction temperature (°C)	65	70	75	80	85
Yield (%)	73.3	78.3	84.8	90.1	86.5

Morphology of product: Fig. 1 is SEM images of the obtained *N,N'*-bis(benzoyl) tridecanedioic acid dihydrazide

particles (B is the partly amplificatory images of A, respectively). The SEM images show that the particles of *N,N'*-bis(benzoyl) tridecanedioic acid dihydrazide are not completely regular and there exist large particles and a little small particles, resulting from uneven mixing during reaction and purification or van der Waals and coulombic forces between the particles. However, as seen in Fig. 1, the morphology of most *N,N'*-bis(benzoyl) tridecanedioic acid dihydrazide is layered and the average size of the layered particles is 5 μm . From Fig. 1, the thickness of each layer of the layered particles is thin, thus, the aspect ratio of *N,N'*-bis(benzoyl) tridecanedioic acid dihydrazide is large. This result show that *N,N'*-bis(benzoyl) tridecanedioic acid dihydrazide with large aspect ratio may serve as crystallization nucleating agent of poly(L-lactic acid)¹³.

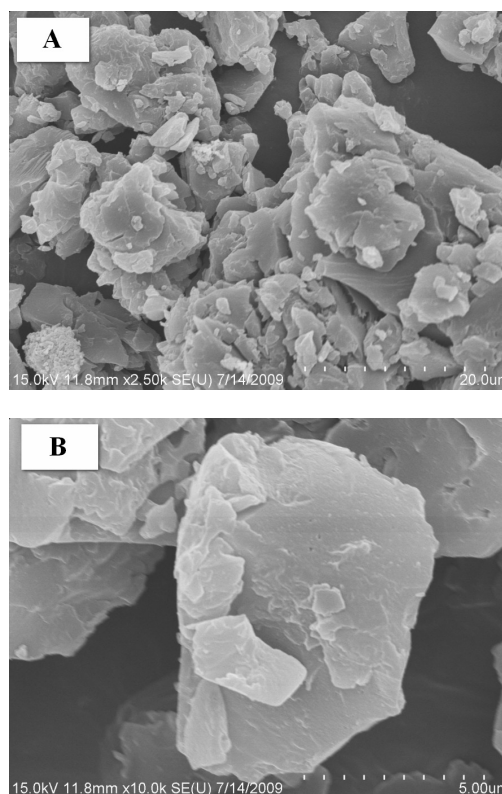


Fig. 1. SEM of *N,N'*-bis(benzoyl) tridecanedioic acid dihydrazide

Thermal stability of product: Thermal stability of amides is very important for its application. Especially, amides are required to be good thermal stability during blending of amides and polymer. Thus, we try to investigate the thermal stability of *N,N'*-bis(benzoyl) tridecanedioic acid dihydrazide. Fig. 6 shows the TGA curves of present amide with a heating ramp of 2.5, 5, 10, 15, 20, 30 °C/min under nitrogen flow from room temperature to 500 °C. As seen in Fig. 2, *N,N'*-bis(benzoyl) tridecanedioic acid dihydrazide begin to decomposition above 165 °C, which can suggest that *N,N'*-bis(benzoyl) tridecanedioic acid dihydrazide has good thermal stability. During the initial stages of decomposition, the decomposition rate is slow and degree of decomposition reached 24.4 %. During the latter stages of decomposition, the decomposition rate significantly becomes fast and degree of decomposition also increases to 72.5 %. What is more, with the increasing of

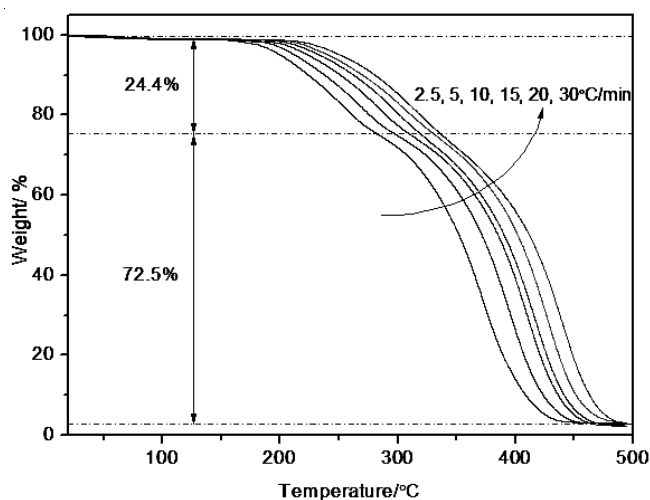


Fig. 2. TGA curves of *N,N'*-bis(benzoyl) *p*-phthalic acid dihydrazide

heating rate, the decomposition temperature increases, the reason is that rapid heating rate make decomposition of *N,N'*-bis(benzoyl) tridecanedioic acid dihydrazide 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.

Conclusion

In this paper, novel *N,N'*-bis(benzoyl) tridecanedioic acid dihydrazide was successfully synthesized from benzoyl hydrazine and tridecanedioyl dichloride which was deprived

from tridecanedioic acid *via* acylation. We investigated influence of the molar ratio, reaction temperature and reaction time to the yields of product, SEM showed the *N,N'*-bis(benzoyl) tridecanedioic acid dihydrazide was layered and the average size of the layered particles is 5 μm . TGA result indicated good thermal stability of *N,N'*-bis(benzoyl) tridecanedioic acid dihydrazide.

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