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Synthesis of fully bio-based polyamides with tunable properties by employing itaconic acid

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ABSTRACT

A class of bio-based aliphatic polyamides (BDIS) was synthesized by melting copolycondensation from four biomass monomers: originated (SA), itaconic acid (IA), 1, 10-decanediamine (DD), and 1, 4-butanediamine (BD). IA was introduced into the system in order to adjust the chemical structure and the aggregation structures of the BDIS polyamide. Thus, some new polyamides with tunable properties were obtained, such as semi-crystalline polyamide with relatively low melting point, glassy polyamide with excellent toughness, and even rubbery polyamide after hydration. Some of the BDIS can be well melting spinned into fibers with comparable strength as polyamide-6. The BDIS with 100% itaconic acid can even be dissolved in ethanol, which makes it possibly be used by coating and dipping methods. In vitro cytotoxicity tests showed that these polyamides are nontoxic towards mouse fibroblasts and have great potential in biomedical applications.

1. Introduction

Nowadays, polymers, which are usually synthesized from petrochemicals, are essential in our daily life; however, with the depleting fossil resources and the related environmental issues brought by fossil feedstock utilization and consumption, it is very important and urgent for us to develop durable and high-performance materials from renewable resources. During the last few decades, many bio-based polymers emerged as alternatives for petroleum-based polymers. Approaches like biotechnology (e.g., production of microbial polyesters), chemical modification of natural polymers, and polymerization of bio-based monomers have been used to generate bio-based polymers [1].

Aliphatic polyamides are significant engineering materials that find wide industrial applications because of their outstanding properties such as high modulus, toughness, and abrasion resistance [2–7]. Among these polyamides, several all-bio-based polyamides or partly bio-based polyamides were commercialized. Polyamide-11, an all-bio-based polyamide, was synthesized from 11-aminoundecanoic acid which is derived from castor oil after a multistep chemical treatment [8]. The all-bio-based polyamide-10,10, polyamide-4, 10 and the partly bio-based polyamide-6, 10, polyamide-10, 12 with good engineering applications are synthesized by using one or two of the biobased monomers: sebacic acid (SA), 1, 10-decanediamine (DD), and 1, 4-butanediamine (BD) [9–11]. SA is the natural metabolic intermediate in the oxidation of medium- to long-chain fatty acids and can be obtained by the bacterial fermentation of castor oil [12–16]. BD and DD can be derived from bio-based succinic acid and sebacic acid.

A current trend is to utilize vegetable oils as raw materials to generate bio-based polyamides because vegetable oils contain several reactive groups that can be used for polymerization [17–19]. Pardal and Fradet [20] reported the synthesis of unsaturated polyamides from the biobased monomer z-octadec-9-enedioic acid, which can be generated by the fermentation of

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oleic acid or sunflower oil. They found the glass transition temperature and melting point of the polyamide decreased with the introduction of double bond into the molecular chains. Another series of unsaturated polyamides PA x,20 that can be obtained from plant oil derivatives were synthesized by two different metathesis steps [21]. Hablot and Averous reported dimer-acid-based thermoplastic bio-based polyamides synthesized from rapeseed-oil-based dimer-acid and 1,2-diaminoethane, 1,6-diaminohexane, or 1,8-diaminooctane [22]. Recently, Lidia reported a series of fully bio-based polyamides which were prepared from sebacic acid, 1,4-diaminobutane, and diaminoisoidide by either bulk melt polycondensation followed by solid state polymerization or by interfacial polycondensation [23–26].

It is very important and valuable to design and synthesize bio-based polyamides with new structure and new performances from the large-scaled biobased monomers. IA is a recognized large-scaled biobased monomer which can be obtained by bacterial fermentation of some plant (such as corn straw) or through the distillation of citric acid [27–30]. The trifunctional structure, large production and low cost ensured a wide application of IA in industry. The currently reported itaconate-based polymers are synthesized from IA with other monomers through radical polymerization of the alkene groups of IA or through condensation polymerization of the carboxyl group of IA [27,31–40]. Few papers focused on the synthesis of binary polyamides from IA and amine by the melting polymerization method [41,42]. Compared with the binary polymers, the copolymers with more than three co-monomers usually have more interesting and comprehensive properties. Thus, we constructed a fully bio-based polyamide with four comonomers, and IA was used to adjust the chemical structure and the aggregation structures, thus affecting the structure and properties of the final product. It was also reported that, the primary amine could react with the double bond of IA via the Michael addition, and a pyrrolidone ring formed [43]. The pyrrolidone ring could increase the molecular spacing and the chain irregularity, thus affecting the glass transition temperature and the crystal structure of the polyamides.

In this study, a class of fully bio-based polyamides (BDIS) with tunable properties was synthesized from BD, DD, SA and IA by using melting copolycondensation method. The reaction route is shown in Scheme 1. The amount of pyrrolidone rings only depends on IA content. These new bio-based polyamides exhibit versatility in physical characteristics, mechanical properties, and hydration, thus, they could find wide applications not only in engineering materials but also in medical materials.

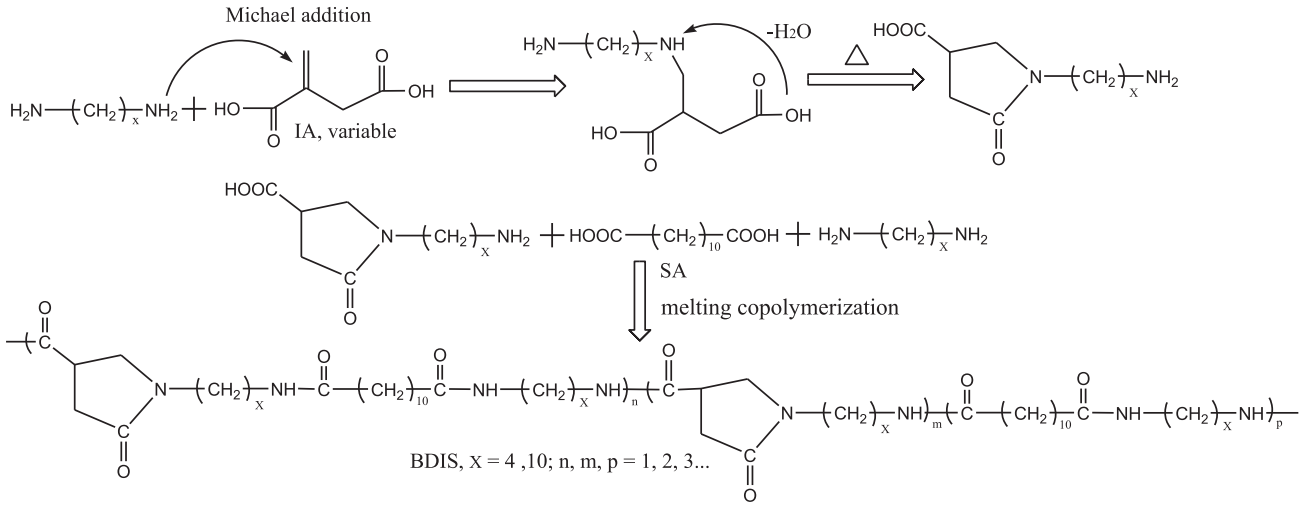
2. Experimental

2.1. Materials

Itaconic acid (≥99%) was purchased from Shandong Qingdao Langyatai Co., Ltd. (China). Sebacic acid (≥99%) and 1,4-butanediamine (≥99%) were purchased from Alfa-Aesar Chemical Inc. (USA) and used as received without further purification. 1,10-diamniodecane (≥98%) was purchased from HWRK Chemical Inc. (China) and was purified by recrystallization three times. Hydroquinone (99%) and orthophosphoric acid (99%) were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. (China). PA6 with a relative viscosity of 3.2 was purchased from Guangdong Xinhui Meida Nylon Co., Ltd. The values of PA6 are tested by ourselves under the same testing method with the polyamide BDIS.

2.2. Synthesis of BDIS polyamides

The bio-based BDIS polyamides were synthesized through a two-step process: the formation of ammonium salts and subsequent melting-polycondensation. The general procedure is described as follows: Equimolar amounts of diacids (sebacic acid and itaconic acid) and diamines (1,10-decanediamine and 1,4-butanediamine) were dissolved in absolute ethanol, and the mixture was stirred slowly for 30 min at 60 °C to allow the formation of the ammonium salt. The salt was obtained as fine white powder after elimination of the solvent and dried in a vacuum oven at 40 °C for 12 h before use. The bio-based aliphatic polyamides were synthesized by allowing the salts to react with each other. Reagents were charged in a three-necked flask equipped with a nitrogen inlet, a central mechanical stirrer, a distillation head connected to a condenser, and a receiver flask. The inhibitors hydroquinone and orthophosphoric acid at 0.05 wt% and 0.01 wt% of the total mass of monomers, respectively, were also added into the flask. The flask was placed in an oil bath at 180 °C for 1 h. The temperature was increased first to 200 °C and kept constant for 2 h. It was then further increased to the final temperature of 210 °C and kept constant for another 3 h, with a pressure reduction to 300 Pa. The final products were obtained and characterized after cooling to room temperature. The BDIS polyamides with different monomer



Scheme 1. Synthesis scheme of BDIS polyamides.