Polymer 54 (2013) 1141–1149

Contents lists available at SciVerse ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Polyamides based on the renewable monomer, 1,13-tridecane diamine II: Synthesis and characterization of nylon 13,6

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ARTICLE INFO

Article history:
Received 30 October 2012
Received in revised form
28 November 2012
Accepted 6 December 2012
Available online 19 December 2012

Keywords:
Nylon
Polyamide
Semicrystalline

ABSTRACT

Nylon 13,6 was successfully synthesized and its chemical composition, thermal properties, crystal structure, and moisture absorption characterized. Melting temperature and glass transition temperature were determined to be 206 °C and 60 °C, respectively, while the equilibrium melting temperature was determined to be 248 °C. Characterization of the crystallization kinetics showed that nylon 13,6 exhibits very fast crystallization compared to the industrially important nylons, nylon 6 and nylon 6,6. In addition, the moisture absorption of nylon 13,6 was dramatically lower than nylon 6 and nylon 6,6 which is consistent with the much lower amide content of nylon 13,6. The crystal structure was determined to be different from the expected γ-form, which possess a pseudohexagonal unit cell. Instead, the x-ray scattering pattern was more similar to the α-form. A similar result has been obtained for other odd–even nylons including nylon 5,6, nylon 5,10, nylon 9,2, nylon 11,10, and nylon 11,12.

1. Introduction

Since the pioneering work by Carothers [1,2], polyamides, commonly referred to as nylons, have become a mainstay in the plastic, film, and fiber industries [3]. While many different nylon homopolymers and copolymers have been reported and commercialized, nylon 6,6 and nylon 6 have been by far the most commercially successful. Compared to other semicrystalline, aliphatic polymers such as polyethylene, polypropylene, and polycaprolactone, aliphatic nylons exhibit relatively high melting and glass transition temperatures. The higher melting and glass transition temperatures can be attributed to hydrogen bonding between amide groups that effectively restrict molecular motions in the solid-state. The extensive hydrogen bonding associated with polyamides also provides strength, toughness, ductility, wear and abrasion resistance, and resistance to oils, greases, and other hydrocarbons. The primary drawback associated with nylon 6 and nylon 6,6 is extensive moisture absorption. At 23 °C and 100 percent relative humidity, the equilibrium moisture absorption of nylon 6,6 and nylon 6 has been determined to be 8.5 and 9.5 weight percent, respectively [4]. The high level of moisture absorption of nylon 6 and nylon 6,6 can result in poor dimensional stability of molded objects and significant changes in mechanical properties resulting from plasticization by absorbed water. Due to their lower amide content, aliphatic nylon polymers derived from longer chain diacids and diamines exhibit much lower water absorption than nylon 6,6 and nylon 6. For example, the equilibrium moisture absorption of nylon 6,12, nylon 11, and nylon 12 at 23 °C and 100 percent relative humidity has been reported to be 3.0, 1.9, and 1.6 weight percent, respectively [4].

Due to concerns over the long-term availability of chemicals derived from fossil resources, a renewed interested in the development of materials from renewable resources has occurred [5–9]. With regard to polyamides, plant oils represent an excellent source for obtaining aliphatic diacids and diamines. As illustrated in Fig. 1a, unsaturated fatty acids obtained from the hydrolysis of plant oil triglycerides can be readily utilized to produce long-chain aliphatic dicarboxylic acids through an oxidation process. Oxidation of the most common unsaturated fatty acid, i.e. oleic acid, produces the nine carbon dicarboxylic acid, azelaic acid. The ten carbon dicarboxylic acid, sebacic acid, can be obtained by alkali pyrolysis of

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http://dx.doi.org/10.1016/j.polymer.2012.12.034

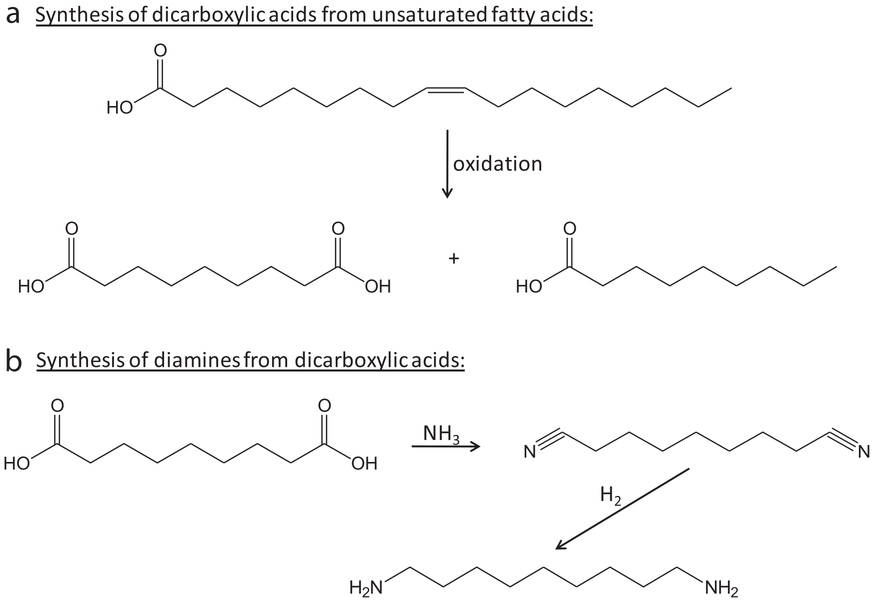

Fig. 1. Illustration of the synthesis of dicarboxylic acids and diamines from a fatty acid (oleic acid): (a) dicarboxylic acid synthesis; (b) diamine synthesis.

ricinoleic acid, which is the major fatty acid component of castor oil [10,11].

Dicarboxylic acids can be readily used as a substrate to produce diamines. Fig. 1b shows the synthetic scheme commonly used to produce diamines from dicarboxylic acids on an industrial scale. The nine carbon diamine, 1,9-nonane diamine, has recently been used for the production of a semi-aromatic nylon commercialized by Kuraray under the tradename, Genestar™.

The authors have been interested in nylons derived, at least in part, from erucic acid, which is a major component of crambe and rapeseed oil [12]. Crambe oil and industrial rapeseed oil contain 55–60 weight percent and 40–55 weight percent erucic acid, respectively [13]. Oxidation of erucic acid yields the thirteen carbon dicarboxylic acid, brassylic acid, which can be subsequently used to produce the thirteen carbon diamine, 1,13-tridecane diamine (TDA). Most of the published research involving euric acid as a renewable source for the production of nylons appears to have been done within laboratories at the United States Department of Agriculture (USDA) and Southern Research Institute (SRI) [12–18]. These researchers focused their efforts on the study of nylon 13 [17], nylon 13,13 [16,18], and nylon 6,13 [14]. The physical properties of these three nylons were fully evaluated and compared to nylon 11 and nylon 6,10. The most significant difference between the three nylons derived from brassylic acid and nylon 11 or nylon 6,10 was the lower water absorption for the brassylic acid-based nylons. Of these three brassylic acid-based nylons, nylon 13,13 appears to have been investigated to the greatest extent as suggested by scale-up efforts directed toward this polymer [16]. In addition to scale-up, a detailed cost analyses for the production of nylon 13,13 was published [15]. The physical properties of the nylon 13,13 produced at the multi-pound scale were thoroughly evaluated and compared to two commercially available long-chain nylons, nylon 11 and nylon 12. It was found that the physical and mechanical properties of nylon 13,13 were similar to nylon 11 and nylon 12. The primary differences were lower melting point, slightly lower density, and lower moisture absorption for nylon 13,13.

In addition to researchers at the USDA and SRI laboratories, a few other groups have investigated nylon 13,13 or other nylons based brassylic acid. Wang and coworkers [19] characterized the thermal properties, crystal structure, and mechanical properties of nylon 13,13 samples that were uniaxially drawn by solid-state extrusion. The glass transition temperature (Tg) and melting temperature (Tm) were determined to be 56 °C and 174 °C, respectively. The crystal structure for nylons have been classified, according to Kinoshita [20], into two basic forms, namely, the α and γ forms. It was determined that the crystal structure for nylon 13,13 was of the γ form with a monoclinic unit cell. The crystal structure and Tm observed by Wang et al. [19] was also observed by Prieto and coworkers [21]. Gidanian and Howard synthesized the brassylic acid-based polyamides, nylon 6,13 and nylon 10,13, and compared the physical properties to the commercial polyamide, nylon 6,12. The Tm and Tg of nylon 6,13 was determined to be 205 °C and 47 °C, respectively, while the Tm and Tg of nylon 10,13 was determined to be 187 °C and 43 °C, respectively. Kim and Yu [22] prepared a series of homopolyamides and copolyamides based on brassylic acid and characterized various properties. The hompolyamides prepared were nylon 12,13, nylon 10,13, nylon 8,13, and nylon 6,13. The Tms of these polymers ranged from 175 °C to 208 °C with Tm increasing with a decrease in the number of carbon atoms of the diamine component, while the Tgs increased from 42 °C to 51 °C with decreasing diamine chain length. All of these long-chain, brassylic acid-based polyamides exhibited moisture absorption in the range of 1.0–1.6 weight percent. Copolyamides were produced from hexamethylene diamine and mixtures of brassylic acid with adipic, terephthalic, or isophthalic acid. All copolymer systems exhibited eutectic behavior with respect to the influence of copolymer composition on Tm. Cui and coworkers [23] synthesized seven different polyamides based on brassylic acid with the length of the diamine component ranging from 3 carbons to 11 carbons. For this series of brassylic acid-based nylons, Tg ranged between 29 °C and 36 °C while Tm ranged between 176 °C and 191 °C. Analysis of the crystal structure of these polymers revealed that all of the nylons except nylon 6,13 exhibited the γ form with a monoclinic unit cell. The wide-angle X-ray diffraction pattern for nylon 6,13 exhibited two distinct diffractions at 0.44 nm and 0.38 nm. This diffraction pattern is similar to that expected for the α-structure; however, as pointed out by Puiggali and coworkers