European Polymer Journal 66 (2015) 57–66

Contents lists available at ScienceDirect

European Polymer Journal

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

Bio-based, amorphous polyamides with tunable thermal properties

Juliën L.J. van Velthoven [a], Linda Gootjes [b], Bart A.J. Noordover [a], Jan Meuldijk [c,*]

[a] *Laboratory of Polymer Materials, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*
[b] *Wageningen UR Food & Biobased Research, P.O. Box 17, 6708 WG Wageningen, The Netherlands*
[c] *Laboratory of Polymer Reaction Engineering/Chemical Reactor Engineering, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*

ARTICLE INFO

Article history:
Received 5 December 2014
Received in revised form 27 January 2015
Accepted 28 January 2015
Available online 7 February 2015

Keywords:
Renewable resources
Polyamides
Resins
Amorphous materials
Copolymerization

ABSTRACT

The aim of this work is to synthesize amorphous polyamides from renewable monomers derived from vegetable oils and sugars. By making use of the odd–even effect to hamper intermolecular hydrogen bonding, combined with either the incorporation of dimerized fatty acid monomers or isoidide diamine (IIDA) produced from fructose, the crystallization of the polyamides was suppressed considerably. Polyamides based on the dimerized fatty acid showed T_g values below 10 °C. The introduction of the isoidide-based diamine enhanced the rigidity of the polymer backbone, which enabled the synthesis of amorphous polyamides with T_g values up to 100 °C. For both series incomplete reaction has been observed as both end groups, i.e. amine and carboxylic acid, were detected in ^{1}H NMR. This results in M_n values from ^{1}H NMR for the fatty acid-based series in the range of 4700–21,000 g mol^{-1}. The M_n values measured by SEC for the IIDA-based were in the range of 3000–10,700 g mol^{-1}. The broad range of T_g values found for these materials in combination with their relatively low molecular weights and the corresponding large amount of reactive end-groups make them suitable for application in coatings, composites, or soft-touch surfaces.

1. Introduction

In recent years, the interest for bio-based polymers increased noticeably. Estimates on remaining fossil resources vary considerably, yet it cannot be denied that this feedstock is finite. Furthermore, crude oil is predominantly used as fuel while the global energy consumption is growing. This will lead to a continuously increase of feedstock prices, making exploration and exploitation of renewable resources to produce energy and chemicals, including monomers, a necessity. In some instances, these renewable monomers can be drop-in replacements such as ethylene produced from bioethanol [1]. However, such conversions are not necessarily atom efficient and do not take advantage of the range of functionalities Nature has to offer. Introducing these functionalities starting from conventional petrochemicals is not trivial and requires a number of synthetic steps, resulting in a lower atom efficiency and lower yields compared to renewable monomers. Therefore, natural compounds should be used with only minor or preferably no alteration to provide monomers which may give rise to novel polymers with differentiated properties.

Amorphous polyamides are uncommon but they may have applications in coatings, composites, or soft-touch materials. However, the preparation of bio-based, amorphous polyamides is a challenge. Some examples of

---

[*] Corresponding author. Tel.: +31 40 247 2328.
E-mail address: j.meuldijk@tue.nl (J. Meuldijk).

http://dx.doi.org/10.1016/j.eurpolymj.2015.01.040
0014-3057/© 2015 Elsevier Ltd. All rights reserved.

biobased, amorphous polyesters are known, including isosorbide- and furandicarboxylic acid-based polymers [2–5]. Suppression of crystallinity in polyamides is mostly accomplished by combining appropriate monomers, e.g. non-linear bicyclic diamines with longer chain diacids or by enforcing kinks in the polymer chains [6,7]. Polyamides obtain their good solvent resistance, hydrolytic stability, and mechanical strength from the amide linkage. It displays hydrogen bonding as each amide linkage contains a H-bond donor as well as an acceptor, and its pseudo-double bond character provides rigidity to the polymer main chain. However, due to the fact that linear polyamides easily form hydrogen bonds, it is hard to prepare materials having a low degree of crystallinity and reduced melting temperatures (T_m) to obtain a good flow behavior in the melt at acceptable processing temperatures.

In this paper, we describe the synthesis of two series of renewable amorphous polyamides, one from fatty acid- and one from sugar-based monomers. The selected approach to achieve amorphous polymers is based on the hampering of the regular organization of the polymer chains. To prevent H-bonds from forming, it is necessary to perturb the alignment of the amide bonds in adjacent polyamide chains. This can be achieved by the odd–even effect, causing the misalignment of the repeating units by simultaneously using monomers of different lengths [8–10]. Because of the molecular structure of the monomers used, we expect to target a broad range of T_g values for these polyamides. Dimerized fatty acid (Pripol™ 1009, Scheme 1) has been previously reported to yield polyamides with reduced crystallinity [11]. The presence of non-functional side chains or bulky, asymmetric chain elements in the fatty acid monomer prevents the alignment of chains. In the work reported in this paper, the steric effects of the monomer will be combined with the introduction of the odd–even effect in the polyamide backbone. The second series is based on isoidide diamine (see Scheme 2 for its structure) [12,13]. Previous studies indicated that the cocrystallization of polyamide chains containing isoidide diamine (IIDA) with chains containing butane-1,4-diamine (BDA), which has the same number of carbon atoms in the main chain, is limited [14,15]. Similar to the other series, the odd–even effect is introduced by using an odd-numbered dicarboxylic acid in an attempt to prepare fully amorphous polyamides based on isoidide diamine. The use of the more rigid isoidide diamine is likely to increase the T_g of the polymer significantly compared to the fatty acid series [16]. Besides using renewable monomers, synthesis in the melt was selected as it is an industrially relevant technology and limits the use of solvents and harmful chemicals, as would be required in e.g. biphasic acid chloride-based synthesis.

In summary, the aim of this work is to design amorphous polyamides with tunable T_g values, to establish appropriate synthetic routes to prepare these materials and to study their thermal and morphological properties.

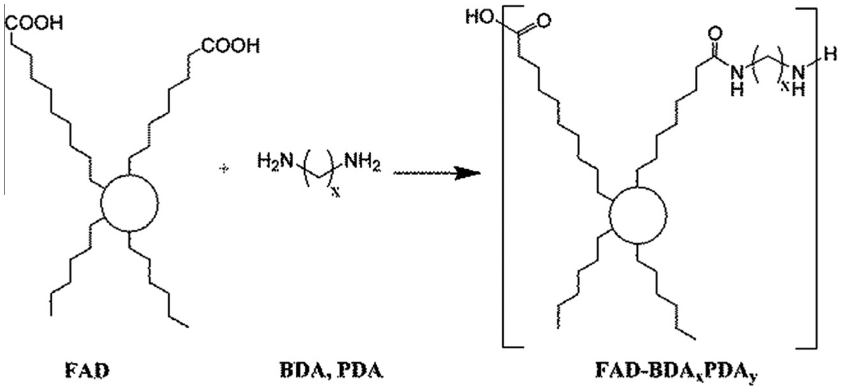
2. Materials and methods

2.1. Materials

The reactants pimelic acid (PA, 98%), butane-1,4-diamine (BDA, 99%) and pentane-1,5-diamine (PDA, ⩾97%) were purchased from Sigma–Aldrich. Pripol™ 1009 (FAD, 98.7% dicarboxylic acid, 1% tricarboxylic acid) was kindly supplied by Croda. 2,5-diamino-2,5-dideoxy-1,4-3,6-dianhydroiditol (isoidide diamine, IIDA, ⩾95%) was synthesized by Wageningen UR Food and Biobased Research [17,18]. Solvents were obtained from Biosolve in AR grade. Deuterated solvents for NMR spectroscopy were purchased from Cambridge Isotope Laboratories, Inc. All chemicals were used as received without further purification.

2.2. General methods

^{1}H NMR spectroscopy measurements were performed on an Agilent 400-MR NMR system in DMSO-d_6. Data was acquired using VnmrJ3 software. Chemical shifts are reported in ppm relative to tetramethylsilane (TMS). Thermogravimetric analysis (TGA) was performed on a TA Q500 instrument (TA Instruments). Samples with a typical mass of 5–10 mg were heated at a rate of 10 °C/min to 600 °C in an N_2 atmosphere. Differential Scanning Calorimetry (DSC) was performed on a TA Q100 DSC. Approximately 5 mg of



Scheme 1. Synthesis of (co)polyamides **FAD-BDA$_x$PDA$_y$** based on fatty acid dimer (circles indicate structural uncertainty, as FAD consists of a mixture of several different but structurally comparable compounds, of which most contain 36 carbon atoms; note that at least 98.7% of the compound is dicarboxylic acid-functional, butane-1,4-diamine (**BDA**, $x = 4$) and pentane-1,5-diamine (**PDA**, $x = 5$)).