

## SYNTHESIS AND CHARACTERIZATION OF NOVEL RENEWABLE, DIAMINOISOIDE-BASED POLYAMIDES

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### Introduction

The widespread application of polyamides is one of the important driving forces towards polymer technologies using raw materials, especially if the latter are biobased. Of great interest are polyamides based on sebacic or suberic acid, 1,4-diaminobutane<sup>1</sup> or furan-based dicarboxylic acid.<sup>2</sup> However, a special role in the synthesis of biobased polyamides can be played by 1,4,3,6-dianhydrohexitols with D-manno and L-ido configuration, or better their diamine derivatives.<sup>3,4</sup> In the light of the development of novel biobased polymers, we synthesized and characterized co- and polyamides based on diaminoisoidide, 1,4-diaminobutane and sebacic acid. One of the synthesis methods was based on interfacial polymerization, while another one involved bulk melt-polycondensation followed by Solid State Polymerization (SSP). The obtained products were characterized by SEC, <sup>1</sup>H NMR and FT-IR spectroscopy.

### Experimental

**Materials.** Diaminoisoidide (DAII, 2,5-diamino-2,5-dideoxy-1,4:3,6-dianhydroditol) was prepared from 1,4:3,6-dianhydro-D-mannitol.<sup>5</sup> Sebacic acid (SA, 99 %), sebacyl chloride (99 %), 1,4-diaminobutane (DAB, 99 %) and 1,4:3,6-dianhydro-D-mannitol (IM, isomannide, 95 %) were purchased from Sigma-Aldrich. Irganox 1330 was purchased from Ciba Specialty Chemicals. Trifluoroacetic acid-*d* and DMSO-*d*<sub>6</sub> (99.5 atom%D) were purchased from Cambridge Isotope Laboratories, Inc. Ethanol and dry chloroform were purchased from Biosolve. All monomers were used as received.

**Instrumentation.** Size exclusion chromatography analyses (SEC) in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) were performed using a set-up equipped with Shimadzu LC-10AD pump and a waters 2414 differential refractive index detector. <sup>1</sup>H NMR spectra were recorded using Varian Mercury V<sub>x</sub> spectrometer, with a frequency of 400 MHz. The spectra were recorded in TFA-*d* and DMSO-*d*<sub>6</sub>. Fourier Transform Infrared spectra (FT-IR) were obtained using a Varian 610-IR spectrometer equipped with an FT-IR microscope. The spectra were recorded at 30°C in a transmission mode with the resolution 2 cm<sup>-1</sup> on a zinc selenium disk.

**Synthesis of Diaminoisoidide-Sebacic Acid Salt and 1,4-Diaminobutane-Sebacic Acid Salt.** To a solution of sebacic acid (3.0g, 0.015mol) in ethanol (10mL) at 50°C a solution of diaminoisoidide (2.2g, 0.015mol) in an ethanol/water mixture (6mL, 5:1,v/v) or 1,4-diaminobutane (1.3g, 0.015mol) in ethanol (3mL) was added dropwise. During the addition a precipitate was formed. The mixture was stirred at 80°C for 1h and then at 50°C for 1h. The crude product was filtered and recrystallized from an ethanol/water mixture to afford the salt as white crystals. The products were characterized by <sup>1</sup>H NMR.

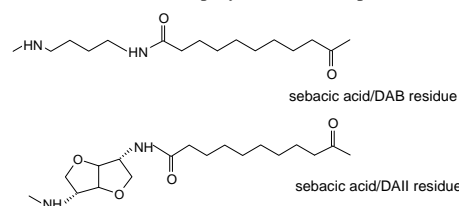
**Synthesis of Polyamides via Bulk and Solid State Polymerization.** Diaminoisoidide-sebacic acid salt (0.66g), 1,4-diaminobutane-sebacic acid salt (2.0g), 1,4-diaminobutane (0.2g), diaminoisoidide (0.066g) and Irganox 1330 (0.026g, 1wt%) were stirred in a three-necked round bottom flask equipped with a mechanical stirrer, vigreux column and a Dean-Stark type condenser. The reaction was carried out under argon atmosphere at 160°C for 0.5h. Then the temperature was raised to 190°C and the process was continued for 2h. The polyamide was ground into powder, washed with demineralized water (80°C, 12h), filtered and dried under reduced pressure at 70-80°C. In order to

increase the molecular weight of the product Solid State Polymerization (SSP) was carried out in a glass tube reactor under Ar atmosphere at 200-205°C for 27h. Similar procedures were applied for all investigated polyamides having 1,4-diaminobutane and diaminoisoidide units.

**Synthesis of Polyamides via Interfacial Polymerization.** The reaction was carried out in a heterogeneous mixture of water/chloroform at room temperature. To an aqueous solution of diaminoisoidide (0.72g, 0.005mol) was dropwise added a solution of sebacyl chloride (1.19g, 0.005mol) in dry chloroform. The reaction was carried out for 2h in the presence of potassium carbonate (1.38g, 0.01mol). After the reaction the precipitated polyamide was filtered, washed with water, ethanol and dried under reduced pressure at 70-80°C.

### Results and Discussion

**Polyamides and co-Polyamides Based on Diaminoisoidide.** The fully biobased polyamides containing sebacic acid, 1,4-diaminobutane (Note: In nature this monomer is known as putrescine,) and diaminoisoidide residues (**Figure 1**) were synthesized in two steps involving a short melt-polycondensation and a Solid State Polymerization (PA1-5, see **Tab. 1**). This relatively mild procedure was chosen in view of the relatively low thermal stability of the diaminoisoidide/sebacic acid-based salt (maximal rate of decomposition at T<sub>max</sub>=266°C). By the incorporation of DAII into the structure of PA 4.10 significant changes in hydrogen bond density, and thus in the melting temperature of the random copolymers, were expected.



**Figure 1.** Chemical structure of sebacic acid/1,4-diaminobutane and sebacic acid/diaminoisoidide repeat units in the synthesized copolyamides.

After short-time bulk polycondensation oligomers with molecular weights around a few thousands g/mol were obtained (see **Table 1**). Simultaneously, a careful analysis of the SEC results clearly shows that the incorporation of a, compared to DAB, less reactive DAII into the structure of the copolyamides affects their molecular weight and polydispersity index.

**Table 1. Characteristics Of Co- And Polyamides From Sebacic Acid, 1,4-Diaminobutane And Diaminoisoidide.**

Symbol	Built-in composition (DAB/DAII)		Mn <sup>c)</sup> (g/mol)	PDI <sup>c)</sup>	Mn <sup>d)</sup> (g/mol)	PDI <sup>d)</sup>
	a	b				
PA1	100/0	100/0	9,560	2.3	21,900	3.0
coPA2	90/10	88/12	6,530	2.0	21,300	2.7
coPA3	80/20	83/17	5,020	1.8	18,700	2.7
coPA4	75/25	77/23	5,530	1.8	20,400	2.9
coPA5	50/50	52/48	2,510	1.7	3,900	1.9
PA6 <sup>e)</sup>	0/100	0/100	4,160	2.3	-	-

<sup>a)</sup> Determined by monomer weight <sup>b)</sup> Determined by <sup>1</sup>H NMR

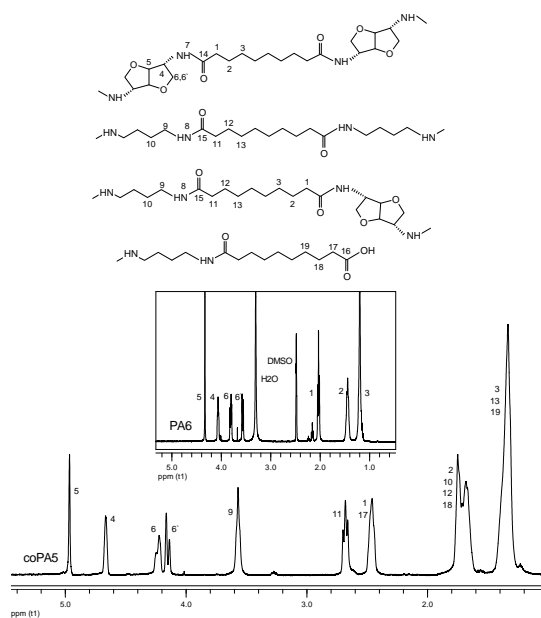
<sup>c)</sup> Determined for polyamides before and <sup>d)</sup> after Solid State Polymerization

<sup>e)</sup> PA obtained via interfacial polymerization

For the sebacic acid/1,4-diaminobutane-based homopolymers (PA1) after the melt-polymerization an M<sub>n</sub> value was found of 9560g/mol, decreasing to 2510g/mol with an increasing content of DAII in the copolymers. However, taking into account the influence of the M<sub>n</sub> value of the polyamides on their thermal and mechanical properties, the preparation of polymers with number average molecular weight above 15,000g/mol was essential. The M<sub>n</sub> values of polyamides were successfully enhanced by using Solid State Polymerization. SSP reactions were carried out at 10-15°C below

the melting points of the oligomers, and using this route  $M_n$  values were effectively enhanced for the copolymers containing up to 25wt% of DAII. Moreover, the data obtained for the homopolyamide (PA6), synthesized via interfacial polycondensation of diaminoisouidide and sebacoyl chloride, show a  $M_n$  value slightly above 4000g/mol. This result can be explained by the relatively high solubility of DAII in water, reducing the tendency to accumulate around the interface, and possible hydrolysis of diacid chloride during the course of the reaction.

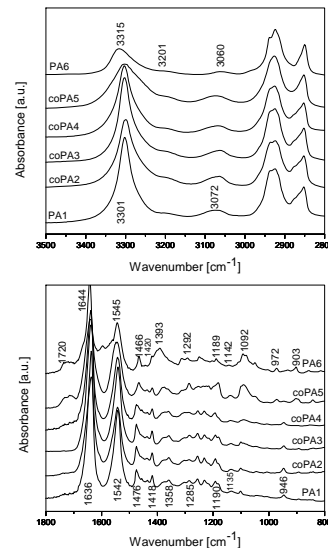
**Figure 2** shows four possible sequences of monomer residues in the synthesized polyamides and  $^1\text{H}$  NMR spectra of polyamide PA6 and copolyamide coPA5. The signals  $\text{H}^4$ ,  $\text{H}^5$ ,  $\text{H}^6$ , and  $\text{H}^6$  at 4.66ppm, 4.96ppm, 4.22ppm, and 4.16ppm were assigned to diaminoisouidide residues in the copolyamide double-side bonded to sebacic acid, while in the spectrum recorded for PA6 these signals were present at 4.06ppm, 4.33ppm, 3.80ppm, and 3.57ppm, respectively. Moreover, the signals of  $\text{H}^9$  and  $\text{H}^{10}$  at 3.57ppm and at 1.59-1.81ppm proved to correspond to a double-side linkage between 1,4-diaminobutane and diacid in the synthesized co-polyamides. Signals related to protons  $\text{H}^1$ ,  $\text{H}^2$  and  $\text{H}^3$  of sebacic acid bonded to DAII units in coPA5 or PA6 were found at 2.45ppm, 1.59-1.81ppm, 1.18-1.45ppm and 2.05ppm, 1.44ppm, 1.20ppm, respectively. Another way to analyze the sequences of sebacic acid units in the structure of the co-polyamides is to look at fragments carrying sebacic acid bonded with DAB ( $\text{H}^{11}$ ,  $\text{H}^{12}$ ,  $\text{H}^{13}$ ). These signals were found at 2.68ppm, 1.59-1.81ppm and 1.18-1.45ppm. According to our supporting analysis of the HMBC spectra, which is beyond the scope of this paper, it was possible to distinguish sebacic acid fragments as end-groups of the macromolecules. The signals, described as  $\text{H}^{17}$ ,  $\text{H}^{18}$  and  $\text{H}^{19}$  were found at 2.45ppm, 1.59-1.81ppm and 1.18-1.45ppm, respectively. Besides, NMR spectra provided detailed information regarding the possible conformational changes of DAII, which could occur during polymerization. The analysis of the signal positions proved the absence of peaks related to conformational isomers of DAII with *endo-endo* or *endo-exo* configuration.



**Figure 2.** The possible sequences of monomer residues and  $^1\text{H}$  NMR spectra of coPA5 and PA6 recorded in TFA-*d* and DMSO-*d*<sub>6</sub>, respectively.

The FT-IR spectra of co- and polyamides, recorded at 30°C, are presented in **Figure 3**. The spectra were normalized according to the area under the symmetric and asymmetric stretch methylene bands at 2800-3000 $\text{cm}^{-1}$ . The infrared bands at 3301-3315 $\text{cm}^{-1}$ , 3201 $\text{cm}^{-1}$  and 3060-3072 $\text{cm}^{-1}$  were attributed to NH stretch vibrations and NH stretch vibrations with Amide (I+II) overtone, respectively. It is interesting, however, that for the polymers with increasing content of DAII (coPA2-PA6) these bands appear broader and weaker, which in turn suggests formation of more disordered crystalline structures and reduction in the hydrogen bonds density of the PAs. The

infrared spectra in the region 1800-800 $\text{cm}^{-1}$  show signals related to Amide I (CO stretch, 1636-1644 $\text{cm}^{-1}$ ), Amide II (in-plane NH deformation with CO and CN stretches, 1542-1545 $\text{cm}^{-1}$ ), Amide III (1358 $\text{cm}^{-1}$ , 1285-1292 $\text{cm}^{-1}$ , 1189-1190 $\text{cm}^{-1}$ ) and the "crystallinity band" (C-CO stretch, 946 $\text{cm}^{-1}$ ). Interesting information provided the presence of bands at 1476 $\text{cm}^{-1}$ , 1466 $\text{cm}^{-1}$  and 1418-1420 $\text{cm}^{-1}$ , which were assigned to  $\text{CH}_2$  scissoring next to NH groups with trans conformation,  $\text{CH}_2$  scissoring not adjacent to the amide group and  $\text{CH}_2$  scissoring next to CO group with trans conformation, respectively. Furthermore, the weak bands at 1135-1142 $\text{cm}^{-1}$  were recognized and assigned to skeletal C-C stretch, gauche conformation. In the analyzed spectral region also bands related to  $\text{CH}_2$  rocking vibration at 972 $\text{cm}^{-1}$  and amide stretch vibrations in the crystalline phase at 903 $\text{cm}^{-1}$  were found. However, these signals are more pronounced for the co- and polymers having DAII units and the latter one is a strong evidence for the presence of DAII in the crystalline phase of the polyamides.



**Figure 3.** FT-IR spectra of co- and polyamides. In the spectra are shown frequency ranges from 3500 to 2800 $\text{cm}^{-1}$  and from 1800 to 800 $\text{cm}^{-1}$ .

## Conclusions

Fully biobased co- and polyamides from sebacic acid, 1,4-diaminobutane and diaminoisouidide were successfully synthesized. The polymers were characterized by SEC,  $^1\text{H}$  NMR and FT-IR techniques. Using bulk polycondensation followed by Solid State Polymerization products with molecular weights above 18,000g/mol and polydispersity index below 3.0 were obtained. However, using the interfacial polymerization route the molecular weight of the sebacic acid and diaminoisouidide based polymers was significantly lower, which may have been caused by possible hydrolysis of diacid chloride during the course of the reaction. The analysis of  $^1\text{H}$  NMR spectra proved the presence of diaminoisouidide, 1,4-diaminobutane and sebacic acid units as chain fragments, while sebacic acid residues were also found as end-groups of the macromolecules. The FT-IR spectra demonstrated that the presence of DAII significantly affects hydrogen bond density in the polyamides. Close inspection of the infrared bands allowed to distinguish signals related to DAII residues incorporated into crystalline phase.

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