To a solution of sebacic acid (3.0g, 0.015mol) in ethanol (10mL) at 50 oC a solution of diaminoisoidide (2.2g, 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 160oC for 0.5h. Then the temperature was raised to 190 oC and the process was continued for 2h. After 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_{max}=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.

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

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Built-in composition (DAB/DAII)</th>
<th>Mn&lt;sup&gt;a&lt;/sup&gt; (g/mol)</th>
<th>PDI&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Mn&lt;sup&gt;c&lt;/sup&gt; (g/mol)</th>
<th>PDI&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA1</td>
<td>100/0</td>
<td>9,560</td>
<td>2.3</td>
<td>21,900</td>
<td>3.0</td>
</tr>
<tr>
<td>coPA2</td>
<td>90/10</td>
<td>6,530</td>
<td>2.0</td>
<td>21,300</td>
<td>2.7</td>
</tr>
<tr>
<td>coPA3</td>
<td>80/20</td>
<td>5,020</td>
<td>1.8</td>
<td>18,700</td>
<td>2.7</td>
</tr>
<tr>
<td>coPA4</td>
<td>75/25</td>
<td>5,530</td>
<td>1.8</td>
<td>20,400</td>
<td>2.9</td>
</tr>
<tr>
<td>coPA5</td>
<td>50/50</td>
<td>2,510</td>
<td>1.7</td>
<td>3,900</td>
<td>1.9</td>
</tr>
<tr>
<td>PA6&lt;sup&gt;e&lt;/sup&gt;</td>
<td>0/100</td>
<td>4,160</td>
<td>2.3</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

<sup>a</sup> Determined by monomer weight  
<sup>b</sup> Determined by H NMR  
<sup>c</sup> Determined for polyamides before and after Solid State Polymerization  
<sup>d</sup> PA obtained via interfacial polymerization  
<sup>e</sup> For the sebacic acid/1,4-diaminobutane and sebacic acid/diaminoisoidide repeat units in the synthesized copolyamides.

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, Mₙ values were effectively enhanced for the copolymers containing up to 25 wt% of DAII. Moreover, the data obtained for the homopolyamide (PA6), synthesized via interfacial polycondensation of diaminoisoidide and sebacoyl chloride, show a Mₙ 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 ¹H NMR spectra of polyamide PA6 and copolyamide coPA5. The signals H₁, H₂, H₃, and H₄ at 4.66 ppm, 4.96 ppm, 4.22 ppm, and 4.16 ppm were assigned to diaminoisoidide residues in the copolyamide double-side bonded to sebacic acid, while in the spectrum recorded for PA6 these signals were present at 4.06 ppm, 4.33 ppm, 3.80 ppm, and 3.57 ppm, respectively. Moreover, the signals of H₅ and H₆ at 3.57 ppm and at 1.59–1.81 ppm proved to correspond to a double-side linkage between 1,4-diaminobutane and diacid in the synthesized co-polyamides. Signals related to protons H₁, H₂ and H₃ of sebacic acid bonded to DAII units in coPA5 or PA6 were found at 2.45 ppm, 1.59–1.81 ppm, 1.18–1.45 ppm, and 1.20 ppm, 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 (H⁴, H⁵, H⁶). These signals were found at 2.68 ppm, 1.59–1.81 ppm, and 1.18–1.45 ppm. 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 H₁⁷, H₁₈, and H₁₉ were found at 2.68 ppm, 1.59–1.81 ppm, and 1.18–1.45 ppm, 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.

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 methane bands at 2800–3000 cm⁻¹. The infrared bands at 3301–3315 cm⁻¹, 3201 cm⁻¹ and 3060–3072 cm⁻¹ were attributed to NH stretch vibrations and NH stretch vibrations with Amide I (CO stretch, 1636–1644 cm⁻¹), Amide II (in-plane NH deformation with CO and CN stretches, 1542–1545 cm⁻¹), Amide III (1358 cm⁻¹, 1285–1292 cm⁻¹, 1189–1190 cm⁻¹) and the “crystallinity band” (C-CO stretch, 946 cm⁻¹). Interesting information provided the presence of bands at 1476 cm⁻¹, 1466 cm⁻¹ and 1418–1420 cm⁻¹, which were assigned to CH₂ scissoring next to NH groups with trans conformation, CH₂ scissoring not adjacent to the amide group and CH₂ scissoring next to CO group with trans conformation, respectively. Furthermore, the weak bands at 1135–1142 cm⁻¹ were recognized and assigned to skeletal C-C stretch, gauche conformation. In the analyzed spectral region also bands related to CH₃ rocking vibration at 972 cm⁻¹ and amide stretch vibrations in the crystalline phase at 903 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 2. The possible sequences of monomer residues and ¹H NMR spectra of coPA5 and PA6 recorded in TFA-d and DMSO-d₆, 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 methane bands at 2800–3000 cm⁻¹. The infrared bands at 3301–3315 cm⁻¹, 3201 cm⁻¹ and 3060–3072 cm⁻¹ were attributed to NH stretch vibrations and NH stretch vibrations with Amide I (CO stretch, 1636–1644 cm⁻¹), Amide II (in-plane NH deformation with CO and CN stretches, 1542–1545 cm⁻¹), Amide III (1358 cm⁻¹, 1285–1292 cm⁻¹, 1189–1190 cm⁻¹) and the “crystallinity band” (C-CO stretch, 946 cm⁻¹). Interesting information provided the presence of bands at 1476 cm⁻¹, 1466 cm⁻¹ and 1418–1420 cm⁻¹, which were assigned to CH₂ scissoring next to NH groups with trans conformation, CH₂ scissoring not adjacent to the amide group and CH₂ scissoring next to CO group with trans conformation, respectively. Furthermore, the weak bands at 1135–1142 cm⁻¹ were recognized and assigned to skeletal C-C stretch, gauche conformation. In the analyzed spectral region also bands related to CH₃ rocking vibration at 972 cm⁻¹ and amide stretch vibrations in the crystalline phase at 903 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 cm⁻¹ and from 1800 to 800 cm⁻¹.

Conclusions

Fully biobased co- and polyamides from sebacic acid, 1,4-diaminobutane and diaminoisoidide were successfully synthesized. The polymers were characterized by SEC, ¹H NMR and FT-IR techniques. Using bulk polycondensation followed by Solid State Polymerization products with molecular weights above 18,000 g/mol and polydispersity index below 3.0 were obtained. However, using the interfacial polymerization route the molecular weight of the sebacic acid and diaminoisoidide 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 ¹H NMR spectra proved the presence of diaminoisoidide, 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.

Acknowledgements

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References