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Novel, Fully Biobased Semicrystalline Polyamides

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Supporting Information

ABSTRACT: Novel, semicrystalline polyamides and co-(polyamides) were synthesized from biobased sebacic acid (SA), 2,5-diamino-2,5-dideoxy-1,4;3,6-dianhydroiditol (diaminoisoidide, DAII) as well as from 1,4-diaminobutane (DAB), also known as putrescine in nature. Low molecular weight polyamides were obtained by melt polycondensation of the salts based on these monomers or by interfacial polycondensation. In order to increase their molecular weights the polyamide prepolymers were submitted to a solid state polymerization (SSP) process. The chemical structure of the polymers was confirmed by 2D NMR correlation



spectra (COSY), heteronuclear multiple-bond correlation spectra (HMBC) and by FT-IR spectroscopy. In the present work, FT-IR and X-ray techniques were used as a tool for the investigation of the crystal structure of the polymers after SSP. The X-ray diffractograms of the polyamides point to crystals containing both 4.10- and DAII.10-based repeat units. Because of the presence of diaminoisoidide residues the synthesized fully renewable products exhibit tunable polarities and melting points. Since most commercial polyamides have a much higher melting point than their end application requires, especially for fiber applications, this simple adaption can result in a significant reduction of energy consumption during processing.

■ INTRODUCTION

Their good physicochemical and mechanical properties as well as low cost make polyamides (PA) interesting candidates for high performance engineering thermoplastics and for fibers. Numerous studies, reporting advantages of polyamides over other thermoplastic polymers, have been published so far.^{1–5} However, it is known that many of the commonly used polyamides like polyamide 6^{6-8} and polyamide 6.6^{9-11} are based on petrochemical building blocks. Therefore, following the driving force toward the production of environmentally friendly and sustainable materials, the development of biomass-based polymers is entirely justified.

Of significant interest and extensively reported are biobased polyamides from brassylic acid,^{12–16} sebacic acid^{17–20} or 1,4-diaminobutane (see Supporting Information, Figure S1).^{4,5,19,21–26} Although succinic acid is also a renewable dicarboxylic acid, the manufacturing of these polyamides is difficult because the formation of a stable five-membered imide ring limits molecular weight and results in discoloration. Along with different synthetic approaches the morphology and crystalline transitions of these renewable polyamides have been intensively studied. The application of such monomers for the synthesis of biobased polyamides with different spacial separation between the amide groups, and thus with different hydrogen bond densities, may be a powerful method of tailoring their thermal and mechanical properties.

Currently, very promising and revealing opportunities for biobased monomers are offered by 1,4;3,6-dianhydrohexitols with *endoexo, endoendo* or *exoexo* conformation. Examples are 1,4;3,6dianhydro-D-glucidol (isosorbide), 1,4;3,6-dianhydro-D-mannitol (isomannide), 1,4;3,6-dianhydro-L-iditol (isoidide),²⁷ and their diamino derivatives (see Supporting Information, Figure S1).^{28,29} However, due to the formation of intramolecular hydrogen bonds and due to steric hindrance by one of the rings, the *endo*-oriented hydroxyl or amino groups reveal relatively low reactivity. On the other hand, the use of monomer moieties with L-ido conformation

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Scheme 1. Chemical Structure of Sebacic Acid/1,4-Diaminobutane and Sebacic Acid/Diaminoisoidide Repeat Units in the Synthesized Co- and Homopolyamides



or modified products with enhanced reactivity may provide fully biobased polymers including liquid-crystalline materials.³⁰ Thiem et al.²⁸ presented a series of polyamides synthesized by interfacial polycondensation of aromatic or aliphatic diacyl chlorides with isomannide- (DAIM), isosorbide- (DAIS), and isoidide-derived (DAII) diamines. They found that by using DAII or DAIS in combination with e.g. sebacoyl chloride polyamides with high degrees of polymerization and T_g values in the range 50–70 °C can be obtained. Recent studies of Bartolussi^{31,32} focused on interfacial polycondensation, microwave-assisted polymerization and Higashi's method as synthetic routes toward biobased polyamides. In these studies isosorbide was derivatized into the corresponding diamine or diacyl chloride and used for the preparation of optically active products. The comparative analysis performed by these authors proved that microwave-assisted polycondensation leads to the highest molecular weight of the studied polyamides (140 000 g/mol) with thermal stabilities ranging up to 400 $^{\circ}$ C.

In several papers on biodegradable polymers, poly-(ester-amides) based on 1,4;3,6-dianhydrohexitols attracted special attention.³³⁻³⁵ These biobased products were successfully obtained by the reaction of *p*-toluenesulfonic acid salts of *O*,*O'*-bis(α -aminoacyl)-1,4;3,6-dianhydro-D-glucitol with bis-(*p*-nitrophenyl) esters of dicarboxylic acids and tested for their thermal properties and enzymatic degradation. The analyses have shown a particular suitability of these polyamides as drug delivery systems. Another application for biobased poly-(ester-amides) was proposed by Philip and Sreekumar.³⁶ These authors synthesized optically active materials, having biphenolic azo chromophores and isosorbide as T_{g} -increasing building blocks, with a potential application in electro-optic devices.

In this paper, we present synthetic routes, the structural characterization, the thermal properties and some XRD analysis of the semicrystalline polyamides and co(polyamides) from the renewable monomers diaminoisoidide (DAII, prepared from isomannide), 1,4-diaminobutane (DAB, in nature known as putrescine) and the castor oil-derived sebacic acid (see Scheme 1). The monomer combination was chosen in view of their natural origin and possibility to obtain relatively high molecular weight polymers, while by using the more readily available succinic acid the growth of the polyamide chain can be limited by the formation of fivemembered imide rings, acting as a chain stopper. One of the two synthetic methods is based on interfacial polycondensation of the diacyl chloride derivative of sebacic acid with DAII, while the second method involves solvent-free bulk polycondensation accomplished by solid state polymerization (SSP) after a prepolymerization in the melt. SSP provided the ability to achieve biobased polyamides with number-average molecular weights above 18 000 g/mol. The chemical structure of the synthesized polymers was confirmed using 2D NMR and FT-IR spectroscopy. To investigate the influence of diaminoisoidide on the crystal structure and melting points of the polyamides wide-angle X-ray diffraction, FT-IR, and DSC techniques were applied. To the best of our knowledge, these fully biomass-based co(polyamides) have not yet been described in the literature.

EXPERIMENTAL SECTION

Materials. 2,5-Diamino-2,5-dideoxy-1,4;3,6-dianhydroiditol (diaminoisoidide, DAII) was prepared by the published method from 1,4:3,6dianhydro-D-mannitol.²⁹ Sebacic acid (99%), sebacoyl chloride (99%), 1,4-diaminobutane (99%), 1,4:3,6-dianhydro-D-mannitol (isomannide, 95%), *p*-toluenesulfonyl chloride (\geq 99%), potassium phthalimide (\geq 99%), dimethyl sulfoxide (\geq 99.9%), hydrochloric acid (reagent grade 37%), ethanolic HCl solution (1.25 N), Amberlyst A26-OH, potassium carbonate (\geq 99%), chloroform-*d* (99.8 atom %D), and benzene-*d*₆ (99 atom %D) were purchased from Sigma-Aldrich. Irganox 1330 was available from Ciba Specialty Chemicals. Magnesium sulfate (99%) was purchased from Acros Organics. Acetic acid (glacial, 99-100%), pyridine (99.5%), and D₂O (99.8 atom %D) were purchased from Merck. Trifluoroacetic acid-d (99.5 atom %D) was purchased from Cambridge Isotope Laboratories, Inc. Activated carbon was purchased from Norit. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP), diethyl ether, methanol, ethanol and dry chloroform were purchased from Biosolve. All the chemicals were used as received, unless denoted otherwise.

1,4;3,6-Dianhydro-2,5-di-O-*p***-tosyl-D-mannitol.²⁹** To a solution of isomannide (50.0 g, 0.34 mol) in pyridine (150 mL) at 0 °C was added a solution of *p*-toluenesulfonyl chloride (130.5 g, 0.68 mol) in pyridine (350 mL) dropwise. The mixture was stirred under Ar atmosphere for 3 h and subsequently stored for 24 h at 0–3 °C. The reaction product was poured into 2.5 L of an ice/water mixture, stirred and allowed to warm up to room temperature. The resulting precipitate was filtered and the product was recrystallized from ethanol to afford isomannidebistosylate as white crystals (142.9 g, 92%). ¹H NMR (CDCl₃): δ = 7.75 (d, 4H), 7.30 (d, 4H), 4.80 (m, 2H), 4.43 (m, 2H), 3.86 (dd, 2H), 3.66 (dd, 2H), 2.41 (s, 6H). ¹³C NMR (CDCl₃): δ = 145.33, 132.85, 129.94, 127.91, 79.94, 77.96, 70.05, 21.65.

2,5-Diphthalimido-2,5-dideoxy-1,4;3,6-dianhydroiditol.²⁹ Isomannidebistosylate (50 g, 0.11 mol) and potassium phthalimide (45.4 g, 0.25 mol) in DMSO (500 mL) were stirred at 130 °C for 24 h under Ar atmosphere. The solution was then cooled to room temperature and water (1 L) was added. The mixture was extracted with chloroform (3 × 500 mL) and the combined organic extracts were washed with water (4 × 400 mL), dried over MgSO₄, decolorized with activated carbon and concentrated under reduced pressure to give 2,5-diphthalimido-2,5-dideoxy-1,4;3,6-dianhydroiditol as a yellow solid (36.4 g, 82%). ¹H NMR (CDCl₃): δ = 7.84 (m, 4H), 7.72 (m, 4H), 5.36 (s, 2H), 4.89 (m, 2H), 4.34 (m, 2H), 3.97 (m, 2H). ¹³C NMR (CDCl₃): δ = 167.52, 134.26, 131.63, 123.40, 88.07, 71.06, 55.71.

2,5-Diamino-2,5-dideoxy-1,4;3,6-dianhydroiditol Dihydrochloride.²⁹ 2,5-Diphthalimido-2,5-dideoxy-1,4;3,6-dianhydroiditol (20.2 g, 0.05 mol) and 6 N HCl/AcOH (125 mL, 4:1, v/v) were stirred at 135 °C for 24 h. The solution was allowed to cool and crystallized phthalic acid was filtered off. The filtrate was washed with diethyl ether (3 × 150 mL) and evaporated to dryness. The crude product was dissolved in methanol (25 mL) at 50 °C and then ethanol (25 mL) was added. Subsequently, methanol was distilled and ethanolic HCl solution (50 mL) was added dropwise to precipitate 2,5-diamino-2,5-dideoxy-1,4;3,6-dianhydroiditol dihydrochloride as a brownish/white solid (7.3 g, 67%). ¹H NMR (D₂O): δ = 5.15 (s, 2H), 4.34 (m, 2H), 4.20 (m, 2H), 4.17 (m, 2H). ¹³C NMR (D₂O): δ = 84.49, 70.46, 56.20.

2,5-Diamino-2,5-dideoxy-1,4;3,6-dianhydroiditol (Diaminoi-soidide).²⁹ 2,5-Diamino-2,5-dideoxy-1,4;3,6-dianhydroiditol dihydrochloride (7.0 g, 0.032 mol) was dissolved in demineralized water (100 mL) and stirred with activated carbon (50 mg) at 35 °C for 30 min. The mixture was filtered and sonificated with washed Amberlyst A-26-OH (28.0 g, 0.035 mol) in an ultrasonic bath at room temperature for 1 h. The aqueous solution was filtered and evaporated to dryness to afford 2,5-diamino-2,5-dideoxy-1,4;3,6-dianhydroiditol as a white solid (4.3 g, 93%). ¹H NMR (D₂O): δ = 4.67 (s, 2H), 3.94 (dd, 2H), 3.77 (dd, 2H), 3.67 (m, 2H). ¹³C NMR (D₂O): δ = 85.69, 71.55, 55.96.

Diaminoisoidide—**Sebacic Acid Salt.** To a solution of sebacic acid (3.0 g, 0.015 mol) in ethanol (10 mL) at 50 °C a solution of diaminoisoidide (2.2 g, 0.015 mol) in an ethanol/water mixture (6 mL, 5:1, v/v) was added dropwise. During the addition, a precipitate was formed. The mixture was stirred at 80 °C for 1 h and then at 50 °C for 1 h. The crude product was filtered and recrystallized from ethanol/water mixture (8:1, v/v) to afford the salt as white crystals (4.7 g, 86%). ¹H NMR (D₂O): δ = 4.84 (s, 2H), 4.05 (dd, 2H), 3.89 (d, 2H), 3.86 (m, 2H), 2.12 (m, 4H), 1.42 (m, 4H), 1.17 (m, 6H).

1,4-Diaminobutane—**Sebacic Acid Salt.** To a solution of sebacic acid (3.0 g, 0.015 mol) in ethanol (10 mL) at 50 °C a solution of 1,4-diaminobutane (1.3 g, 0.015 mol) in ethanol (3 mL) was added dropwise. During the addition, a precipitate was formed. The mixture was stirred at 80 °C for 1 h and then at 50 °C for 1 h. The crude product was filtered and recrystallized from ethanol/water mixture (10:1, v/v) to afford the salt as white crystals (4.1 g, 95%). ¹H NMR (D₂O): δ = 2.86 (m, 4H), 1.97 (m, 4H), 1.58 (m, 4H), 1.36 (m, 4H), 1.13 (m, 6H).

Polymerization of Salt Monomers. This example is representative for all conducted co(polymerizations). A mixture of diaminoisoidide-sebacic acid salt (0.66 g) and 1,4-diaminobutane-sebacic acid salt (2.0 g), 1,4-diaminobutane (0.2 g, 2.3 mmol), diaminoisoidide (0.066 g, 0.45 mmol) was stirred in a three-necked round-bottom flask equipped with a mechanical stirrer, vigreux column and a Dean-Stark type condenser. The reaction mixture was heated at 160 °C for 0.5 h and then the temperature was raised to 190 °C. The polycondensation process was conducted in the presence of Irganox 1330 (0.026 g) as an antioxidant. The reaction was carried out for 2 h under argon atmosphere. The low molecular weight polyamide was ground into powder, washed with demineralized water at 80 °C for 12 h, filtered, and dried under reduced pressure at 80 °C. In order to increase the molecular weight of the polyamide prepolymer solid state polymerization (SSP) was applied. SSP of the polyamide powder was carried out in a glass tube reactor (2.5 cm diameter) equipped with a sintered glass plate at the bottom on which the polyamide prepolymer powder was deposited. Below this glass plate the SSP reactor contained an inert gas inlet through which the heated gas was introduced. During the reaction course the temperature was raised gradually from 200 to 205 °C for 27 h and maintained 10-15 °C below the melting point of the polyamide prepolymer. The reactor was heated using a salt mixture of KNO₃ (53 wt %), NaNO₂ (40 wt %), NaNO₃ (7 wt %).³⁷ SSP was carried out in Ar atmosphere at a gas flow rate of 2.5 L/min.

Interfacial Polycondensation. To a solution of diaminoisoidide (0.72 g, 0.005 mol) and potassium carbonate (1.38 g, 0.01 mol) in water (35 mL) a solution of sebacoyl chloride (1.19 g, 0.005 mol) in dry chloroform (5 mL) was added dropwise. The heterogeneous mixture was stirred at room temperature for 2 h under Ar atmosphere. The obtained polyamide was filtered, washed with water, ethanol, and dried under reduced pressure at 80 °C (1.42 g, 92%).

Measurements. Size exclusion chromatography analyses (SEC) in 1,1,1,3,3,3-hexafluoro-2-propanol were performed using a setup equipped with a Shimadzu LC-10AD pump and a waters 2414 differential refractive index detector. PSS (2 × PFG-lin-XL, 7 μ m, 8 × 300 mm) columns were used. The eluent flow rate was 1.0 mL/min. Calibration of the measurements was carried out with PMMA standards.

The data acquisitions were performed using Viscotek OmniSec 4.0 and Waters Empower 2.0 software.

2D NMR spectra were recorded on a Varian Unity 500 plus spectrometer at room temperature. Chemical shifts were referenced to residual signals of C₆D₆. Correlation spectra (COSY) were acquired using standard programs provided by a Varian spectrometer library with the following parameters: spectral width SW1 = SW2 = 6075.3 Hz, acquisition time 0.221 s, relaxation delay 1.4 s, and number of scans 8 imes 300 increments. Heteronuclear multiple-bond correlation spectra (HMBC) were recorded with pulse field gradients. The spectral windows for ¹H and ¹³C axes were 6075.3 and 21367.4 Hz, respectively. The data were collected in a 2560 \times 210 matrix and processed in a 1K \times 1K matrix. The spectra were recorded with the acquisition time 0.211 s, relaxation delay 1.4 s and number of scans equal to 144×210 increments. ¹H NMR and ¹³C NMR spectra were recorded using a Varian Mercury V_x spectrometer with the frequency of 400 MHz. For ¹H NMR experiments the spectral width was 6402.0 Hz, acquisition time 1.998 s, and the number of recorded scans equal to 64. ¹³C NMR spectra were recorded with the spectral width 24154.6 Hz, acquisition time 1.300 s, and the number of recorded scans equal to 256.

Thermogravimetric analyses (TGA) were performed on a TA Instruments Q500 TGA in a nitrogen atmosphere. Samples were heated from 50 to 600 $^{\circ}$ C with a heating rate of 10 $^{\circ}$ C/min.

DSC measurements were performed using a DSC Q100 from TA Instruments. The measurements were carried out in a nitrogen atmosphere with a heating rate of 10 $^{\circ}$ C/min. The transitions were deduced from the second heating and cooling curves.

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 transmission mode with a resolution of 2 cm⁻¹. PA films obtained from HFIP were analyzed on a zinc selenium disk and heated using a Linkam TMS94 hotstage and controller. Varian Resolution Pro software version 4.0.5.009 was used for the analysis of the spectra.

X-ray diffraction patterns were obtained employing a Bruker AXS HI-STAR area detector installed on a P4 diffractometer, using graphitemonochromated Cu K α radiation (λ = 1.5418 Å) and a 0.5 mm collimator. The data were collected at room temperature on SSP-synthesized powder contained in glass capillaries. The 2D data were subsequently backgroundcorrected and transformed into 1D profiles via integration.

RESULTS AND DISCUSSION

Synthesis and Molecular Characterization of the (Co)polyamides. Co(polyamides) (co-PAs) were prepared via melt and solid state bulk polycondensation of the salts obtained from sebacic acid, diaminoisoidide and 1,4-diaminobutane, as described in the Experimental Section. This method was also used for the synthesis of the homopolyamide PA1 based on sebacic acid and 1,4-diaminobutane (DAB), polyamide 4.10. The purity of the salts was confirmed by ¹H NMR spectroscopy while their thermal transitions and stability were determined using DSC and TGA, respectively. These parameters are highly important in view of selecting the time/temperature conditions of the polycondensation. The melting points of the sebacic acid/DAII and sebacic acid/DAB salts were 133 and 130 °C, respectively. Despite the relatively low melting points of both salts and the high thermal stability of the sebacic acid/DAB salt (maximum rate of decomposition at T_{max} = 468 °C) the low thermal stability of the synthesized sebacic acid/DAII salt (maximum rate of decomposition at $T_{\text{max}} = 266 \text{ °C}$) restricted the temperature of the polycondensation reaction of the salt mixtures in the melt. An extensive duration of the polymerization above 200 °C should be



Figure 1. 500 MHz heteronuclear multiple-bond correlation spectrum (HMBC) of co(polyamide) coPA5.

Table 1. Characteristics of Co- and Homopolyamides from Sebacic Acid, 1,4-Diaminobutane, and Diaminoisoidide (DAB = 1,4-Diaminobutane, DAII = Diaminoisoidide)

symbol	monomer feed, mol ratio $(DAB/DAII)^a$	built-in composition $(DAB/DAII)^b$	$M_{\rm n}^{\ c}$ (g/mol) prepolymer	PDI^{c}	$M_{\rm n}^{\ d}$ (g/mol) after SSP	PDI^d
PA1	1.0/0	1.0/0	9600	2.3	21 900	3.0
coPA2	0.91/0.09	0.89/0.11	6500	2.0	21 300	2.7
coPA3	0.83/0.17	0.86/0.14	5000	1.8	18 700	2.7
coPA4	0.78/0.22	0.80/0.20	5500	1.8	20 400	2.9
coPA5	0.55/0.45	0.57/0.43	2500	1.7	3900	1.9
PA6 ^e	0/1.0	0/1.0	4200	2.3	-	-

^{*a*} Determined by weighed-in monomers. ^{*b*} Determined by NMR. ^{*c*} Determined for polyamides before solid state polymerization using the SEC method with PMMA standards in HFIP solvent. ^{*d*} Determined for polyamides after solid state polymerization using SEC method with PMMA standards in HFIP solvent. ^{*c*} PA obtained via interfacial polymerization, PA1 = PA 4.10, coPA2 = PA 4.10/DAII.10–2, coPA3 = PA 4.10/DAII.10–3, coPA4 = PA 4.10/DAII.10–4, coPA5 = PA 4.10/DAII.10–5, PA6 = PA DAII.10.

avoided and so a two-step method for the synthesis of co-PAs leading to white products with M_n above 18 000 g/mol was applied. In a first step (bulk melt-polycondensation for 2 h at 190 °C) low molecular weight, semicrystalline prepolymers with variable molar ratios DAB/DAII were obtained, which were subsequently subjected to solid state polymerization (see Table 1), 10–15 °C below their melting points.

As expected, the presence of diaminoisoidide in the polymer backbone of the synthesized copolymers significantly affected their properties, including molecular weight and polydispersity index. The melt prepolymerizations yielded products with M_n ranging between 2500 and 9600 g/mol (Table 1). The homopolymer PA1 based on DAB and sebacic acid exhibits an M_n value around 9600 g/mol, decreasing to approximately 2500 g/mol with increasing DAII monomer residue concentration. These results clearly reflect the lower reactivity of the secondary amine; diaminoisoidide, in comparison to 1,4-diaminobutane. It is wellknown, that mechanical and thermal properties of polyamides are directly related to their molecular weight. Higher molecular weights promote higher melting points and better mechanical properties (toughness, tensile strength, elongation at break etc.), at least as long as the molecular weight is below a critical value.¹⁸ Therefore, the M_n values of the prepolymers needed to be enhanced to values above this critical value, which for aliphatic polyamides is ca. 12 000–15 000 g/mol. Taking into account the low thermal stability and high weight loss above 260 °C of both DAII and the sebacic acid/DAII salt, the use of SSP for obtaining the targeted polymers with number-average molecular weights above 15000 g/mol turned out to be a suitable method (Table 1). Because of the low melting temperature of the coPA5 prepolymer (see below) and hence the need for carrying out the SSP of this specific prepolymer at 150 °C, which is not sufficient for proper polycondensation, for coPA5 the SSP treatment only resulted in a very modest enhancement of the $M_{\rm n}$.

2D NMR spectra of the synthesized co(polyamides) provided detailed information regarding the chemical structure, purity and possible changes of the stereochemistry of DAII, which could occur during the synthesis of the PAs. The analysis of the *COSY correlation spectra* (see Supporting Information, Figure S2) and heteronuclear multiple-bond correlation spectra (HMBC) (Figure 1) confirmed the incorporation of DAII into the structure of the co(polyamides). Because of the absence of separated signals related to the amine end-groups of PAs, although these should be present from the statistical point of view, the calculation of their molecular weights from NMR spectra was impossible. However, given the structure of the synthesized polyamides and the possible sequence of the different monomer residues (Scheme 2), 2D NMR spectra should clearly display the signals related to the repeat units of diaminoisoidide, 1,4-diaminobutane and sebacic acid residues of which both functional groups had been transferred into amides.

The analysis of the signals originating form DAII residues was successfully accomplished by the study of ${}^{1}H-{}^{1}H$ COSY and ¹H-¹³C HMBC spectra. The cross-peaks H⁷/H⁴, H⁴/H⁶, H⁴/ $H^{6'}$, $H^{6}/H^{6'}$, and \hat{H}^{5}/H^{4} found in the COSY spectrum at 7.78, 4.46, 4.02, 3.96, and 4.80 ppm prove the presence of protons H^{\prime} , H^4 , H^6 , H^6 , and H^5 , respectively. Moreover, two- and three-bond correlations between these protons and carbons were verified by HMBC spectra. The HMBC signals at 4.80/57.8, 4.80/71.5, 4.80/86.2, and 4.46/86.2 are assigned to the correlations H⁵/ C^4 , H^5/C^6 , H^5/C^5 , and H^4/C^5 , while H^6/C^4 , $H^{6'}/C^4$, H^6/C^5 , and $H^{6'}/C^5$ signals are found at 4.02/57.8 ppm, 3.96/57.8 ppm, 4.02/86.2 ppm, and 3.96/86.2 ppm. Further assignments of the signals at 4.46/180.5 ppm, 7.78/180.5 ppm, 7.78/57.8 ppm, and 7.78/71.5 ppm for $\hat{H^4/C^{14}}$, H^7/C^{14} , $\hat{H^7/C^4}$, and $H^7/\hat{C^6}$ correspond to the linkage between diaminoisoidide and sebacic acid units. On the basis of the NMR results, it should be noted that in view of the presence of the singlet at 4.67 ppm of diaminoisoidide monomer and the signal at 4.80 ppm of DAII-based polyamides the bicyclic building blocks have L-ido conformation and epimerization of the initial L-ido into the D-manno conformation of the diamine during synthesis can be excluded. Nonetheless, even after the purification procedure of the polyamides, a set of weak signals at around 3.9, 2.1, and 1.4 ppm in the ¹H NMR spectra can be seen. These signals can be associated with the presence of trace amounts of the polyamide salts, which were used in the synthesis of the polymers (see also Supporting Information, Figure S3).

The sequence of 1,4-diaminobutane bonded with sebacic acid units (Scheme 2) is confirmed by the presence of the cross-peaks Scheme 2. Possible Sequences of Monomer Residues of Sebacic Acid, Diaminoisoidide, and 1,4-Diaminobutane in the Co- and Homopolyamides



 $\rm H^9/H^{10}$ and $\rm H^9/H^8$ at 3.38 ppm in the corresponding *COSY* spectrum (see Supporting Information, Figure S2). Additional evidence for the presence of this structural fragment in the co(polyamides) are the signals at 3.38/25.0 ppm, 3.38/180.5 ppm, 1.57/42.0 ppm, and 8.43/180.5 ppm assigned to $\rm H^9/C^{10}$, $\rm H^9/C^{15}$, $\rm H^{10}/C^9$, and $\rm H^8/C^{15}$ in the *HMBC* spectrum, as shown in Figure 1.

To fully accomplish the proton and carbon peak assignment the analysis of sebacic acid units in PA was performed. In the COSY spectrum the cross-peaks at 2.32 ppm, 1.52 ppm, 1.21 ppm are described as H^1/H^2 , H^2/H^3 and H^3/H^2 signals and are related to sebacic acid residues bonded to diaminoisoidide. This unit sequence was also confirmed by the HMBC spectrum by the presence of the signals at 2.32/26.0 ppm, 2.32/28.5 ppm, 1.52/ 35.2 ppm, 1.52/28.5 ppm, 1.21/26.0 ppm, 1.21/35.2 ppm from H^{1}/C^{2} , H^{1}/C^{3} , H^{2}/C^{1} , H^{2}/C^{3} , H^{3}/C^{2} , and H^{3}/C^{1} correlations. Two- and three-bond correlations between H^1/C^{14} and H^2/C^{14} are found at 2.32/180.5 ppm and 1.52/180.5 ppm (Figure 1). Similarly, the presence of sebacic acid units bonded to 1,4diaminobutane is evidenced by the cross-peaks at 1.21, 1.58, and 2.50 ppm, depicted as H¹³, H¹², H¹¹ (Scheme 2 and Figure S2, Supporting Information). A careful examination of the HMBC spectrum allows to indentify these signals as H/C correlations at 1.21/36.0 ppm, 1.21/34.0 ppm, 1.58/34.0 ppm, 2.50/26.0 ppm, 2.50/28.5 ppm. Additional evidence of sebacic acid units bonded to 1,4-diaminobutane were the signals at 2.50/ 180.5 ppm and 1.58/180.5 ppm from H¹¹/C¹⁵ and H¹²/C¹⁵ respectively. Finally, due to the presence of the signals at 2.30/ 184.0 ppm and 1.52/184.0 ppm and originating from two- and three-bond correlations of H^{17}/C^{16} and H^{18}/C^{16} , it was possible to prove the existence of sebacic acid units as end groups of the PA (Figure 1).

Polyamide based exclusively on sebacic acid and diaminoisoidide (entry 6 in Tables 1, 2, and 3) was obtained via interfacial polycondensation of diaminoisoidide and sebacoyl chloride in a water/chloroform emulsion. The reaction was carried out in the presence of potassium carbonate. As reported by Thiem and Bachmann²⁸ the formation of polyamides during interfacial polycondensation takes place in the organic solvent near the aqueous phase. Simultaneously, the results presented by these authors clearly indicate that the molecular weight of polyamides based on DAII is dependent on many factors such as temperature, type of organic solvent or molar ratio of the used monomers. SEC data show that the molecular weight of the polyamide based on diaminoisoidide and sebacic acid is slightly above 4000 g/mol (Table 1). This low molecular weight might be explained by the high solubility of diaminoisoidide in water, reducing the tendency to accumulate around the interface, and possible hydrolysis of diacid chloride resulting in a change of the molar ratio of the reactive compounds.¹⁸ The ¹H NMR spectrum presented in Figure 2 provides information regarding the chemical structure of the PA based on sebacic acid and diaminoisoidide (entry 6 in Table 1, see also Scheme 2 for the labeling of the protons). The signals at 8.05 ppm are related to H^7 protons from the amide group. The peaks at δ = 4.33, 4.07, 3.80, and 3.58 ppm are assigned to DAII protons H^5 , H^4 , H^6 , and $H^{6'}$. They do not suggest any conformational change of the DAII structure during the synthesis. As expected, the signals related to sebacic acid units H¹, H², and H³ are observed at 2.05, 1.44, and 1.20 ppm, respectively.

Figures 3 and S4 (in the Supporting Information) show FT-IR spectra of the synthesized polyamides and co(polyamides) recorded at 30 °C. The spectra were normalized according to the area under the symmetric and asymmetric methylene bands in the interval 2800-3000 cm⁻¹. In Figure S4 (Supporting Information) the spectral range from 2800 to 3500 cm⁻¹ is presented. It shows several significant differences between the synthesized materials with different DAII contents. The signals at 3301-3315, 3201, and 3060-3072 cm⁻¹ are assigned to the NH stretch, NH stretch and amide (I + II overtone), and NH stretch with amide II overtone vibrations, respectively. $^{38-41}$ It is interesting, however, that for the polyamides with increasing content of DAII (coPA2-PA6), these bands appear broader and weaker, which suggests a decrease of the crystalline order and a reduction of the hydrogen bond density. This phenomenon is consistent with the appearance and growth of the intensity of the bands around 1720 cm⁻¹ associated with "free" nonhydrogen-bonded carbonyl groups (Figure 3).42 The infrared spectra in the region 1800-800 cm⁻¹ show signals related to amide I (CO stretch, 1636-1642 cm⁻¹), amide II (in-plane NH deformation with CO and CN stretches, 1542-1543 cm⁻¹), amide III coupled with hydrocarbon skeleton (1358, 1291, 1189-1190 cm⁻¹), and the amide IV "crystallinity band" (C–CO stretch, 946 cm⁻¹).^{40,41,43} Interesting information is also provided by the presence of bands at 1476, 1466, and 1418 cm⁻¹, which are assigned to CH₂ scissoring next to NH groups with trans conformation and visible exclusively for PA 4.10 and copolymers having 1,4-diaminobutane residues, CH2 scissoring not adjacent to the amide group, and CH₂ scissoring next to the CO group with trans conformation, respectively.^{39,41} Furthermore, the weak bands at 1135–1142 cm⁻ were identified and are assigned to skeletal C-C stretch, gauche conformation.⁴⁴ In the analyzed spectral region also bands related to C-O stretching vibrations at 1080-1100 cm⁻¹, CH₂ wagging/ twist vibrations at 1392 and 1314 cm⁻¹, skeletal C-C stretch vibrations at 1255 and 1231 cm⁻¹, CH₂ rocking vibrations at 971 cm⁻¹ and amide stretching vibrations in the "crystalline phase" at 903 cm⁻¹ are observed.^{44–46} The "crystalline" signals at 903 cm⁻¹ are visible for the polymers containing DAII units and give strong evidence for the presence of DAII residues in the crystalline phase of these polyamides.

Thermal Properties of the Polyamides. From the thermogravimetric and DSC analysis data, presented in Table 2, it is clear that the thermal stability of the novel renewable polyamides is



Figure 2. 400 MHz ¹H NMR spectrum of the homopolyamide based on diaminoisoidide and sebacic acid.



Figure 3. FT-IR spectra of homopolymers PA1 and PA6 and copolymers coPA2, coPA3, coPA4, and coPA5, recorded at 30 °C. The spectra show frequency ranges $1750-800 \text{ cm}^{-1}$.

directly related to the content of diaminoisoidide residues in the polymers. With increasing DAII content in the polyamides a reduction in their thermal stability was observed. Upon heating of PA1 (PA 4.10) a 5 wt % weight loss was observed around 420 °C. The temperature at 5% weight loss decreases to 300 °C (entry 6 in Table 2) with increasing DAII content. However, for the compositions with a DAB/DAII mol ratio of 0.80/0.20 the differences in thermal stability, compared to PA 4.10, were less pronounced (5% weight loss $T_{5\%} = 377$ °C). The explanation of this phenomenon might be oxidation at the carbon atom in the α -position of the ether oxygens in the diaminoisoidide residues, resulting in a lower thermal stability of the materials containing DAII units. This decrease in the thermal stability of the co- and homopolyamides containing diaminoisoidide units in comparison to the commercially available PA 4.10, PA 6, or PA 6.6 can restrict their melt processing and further applications at high temperature working conditions. Nevertheless, the thermal stabilities in combination with the corresponding melting points should enable melt processing of all co(polyamides) synthesized in this work. Moreover, TGA measurements carried out for the co(polyamides) with a DAII content lower than 43 mol % show that these materials can be still valuable for many demanding applications, similar to those found for PA 4.10 (see Table 2).

 Table 2. Thermal Stability, Melting and Crystallization

 Temperatures, and Enthalpy of the Transitions Analyzed from

 the Second DSC Heating and Cooling Runs^a

symbol	$T_{5\%} \left(^{\circ} \mathrm{C} \right)$	T_{max} (°C)	T_m (°C)	$\Delta H_m \left({\rm J}/{\rm g} \right)$	T_c (°C)	$\Delta H_c (J/g)$
PA1	424	483	246	67.3	221	75.4
coPA2	388	457	242	57.3	209	56.0
coPA3	379	460	236	50.6	201	47.8
coPA4	377	456	232	40.9	198	45.3
coPA5	321	455	179, 198	32.8	156	39.3
PA6	300	437	152	15.1	96	11.4

^{*a*} $T_{5\%}$ = temperature of 5% mass loss, T_{max} = temperature of maximal rate of decomposition, T_m = melting point, T_c = crystallization temperature, ΔH = enthalpy of the transition.



Figure 4. DSC traces of the second heating cycle of the co- and homopolyamides with different contents of diaminoisoidide.

To investigate the melting and crystallization of the polyamides, DSC analyses were performed. From the data presented in Table 2, taken from the second heating and cooling scans, it follows that a partial replacement of DAB units by diaminoisoidide in the structure of polyamide 4.10 influences the melting point. The co(polyamides) containing diaminoisoidide have lower melting and crystallization temperatures in comparison to the homopolymer based on sebacic acid and 1,4-diaminobutane. The synthesized, fully renewable co(polyamides) exhibit tunable polarities and melting points. As mentioned, lower melting points, and therewith lower processing temperatures of the obtained DAII-containing co(polyamides), can facilitate processing of these materials. The presence of DAII in the structure of the PAs influences ΔH of the observed transitions. With increasing DAII content in the polymers the enthalpy of the transitions is strongly reduced compared to entry PA1 in Table 2. These changes can be understood in terms of a reduction of the hydrogen bond density in the co(polyamides), as was found by FT-IR spectroscopy discussed above, less perfect chain packing of DAIIcontaining polymers and a reduction of the lamellar crystal thickness.⁴³ Moreover, the widely reported effect related to structural rearrangement and the resulting two-peak melting⁴⁷ was especially visible for the copolymer containing around 43 mol % of DAII (see Figure 4). This phenomenon can be explained by melting of imperfect crystals (low temperature peak), recrystallization upon heating and remelting of the more perfectly formed crystals (high temperature peak).



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Figure 5. X-ray powder diffraction patterns of as-prepared co- and homopolyamides with different contents of diaminoisoidide measured at room temperature. The indices correspond to the packing mode of the α -phase and the β -phase of common polyamides.

20 [deg]

Wide-Angle X-ray Diffraction. The synthesized polyamides are semicrystalline in the entire studied range of copolymer compositions (see Figure 5). The X-ray diffraction profiles of all copolymers present strong analogueies with the X-ray diffraction patterns of the corresponding homopolymers. In particular the patterns of samples with a DAII content lower than 43 mol % are similar to that of the sebacic acid/DAB homopolymer, displaying the typical four polyamide reflections in the 2θ ranges $3-7^\circ$, $10-12^\circ$, and $18-25^\circ$, indexed as 001, 002, 100, and 010/110 (Table 3). Therefore, it can be concluded that coPAs with DAII

 Table 3. X-ray Diffraction Spacings for Co- and Homopolyamides with Different Contents of Diaminoisoidide

	X-ray diffraction (nm)				2θ (deg)			
symbol	001	002	100	010/110	001	002	100	010/110
PA1	1.561	0.776	0.442	0.379	5.66	11.38	20.00	23.46
coPA2	1.555	0.771	0.442	0.380	5.68	11.46	20.00	23.44
coPA3	1.555	0.771	0.442	0.380	5.68	11.46	20.00	23.44
coPA4	1.555	0.775	0.442	0.380	5.68	11.40	20.00	23.44
coPA5	1.686	-	0.442	-	5.24	-	20.00	-
PA6	1.624	-	0.442	-	5.44	-	20.00	-

contents lower than 43 mol % have a crystal structure similar to that of the polyamide 4.10 based on 1,4-diaminobutane and sebacic acid. This structure consists of stacked hydrogen-bonded sheets, in which the polymer chains are arranged side-by-side.^{24,48} The 100 peak corresponds to the interchain distance and the 010/110 peak to the intersheet distance. With increasing DAII content the 010/110 reflection decreases in intensity, but it does not show any shift in position. This suggests that the intersheet distance is not affected by increasing the DAII content for coPAs with a DAII content lower than 43 mol %.

The XRD pattern of the co(polyamide) with a DAII content of 43 mol % shows close resemblance to that of the sebacic acid/ DAII homopolymer, i.e. it gives only two strong reflections in the 2θ range $3-7^{\circ}$ and $15-25^{\circ}$ (see Figure 5). The latter single peak in the 2θ range of $15-25^{\circ}$ indicates that the material has crystallized into a close to hexagonal packing of polymer chains. In the XRD patterns of the coPA5 and SA/DAII-based homopolyamide the reflection indexed as 001 shifts to lower 2θ values compared to the same reflection of the other polyamides. This shift reveals an increase of the *c*-axis dimension of coPA5 due to cocrystallization of the two comonomers in the same crystal lattice.⁴⁹

Further and more detailed information will be described in a following publication concerning crystallographic studies of the new biobased co(polyamides). It will be also shown that for the copolymers having up to 20 mol % of DAII the comonomer units are included in the crystalline PA 4.10 phase, even though visible changes of the unit cell dimensions do not occur.

CONCLUSIONS

Fully biobased polyamides from sebacic acid, 1,4-diaminobutane, and diaminoisoidide (prepared from isomannide) were successfully synthesized by either bulk melt polycondensation followed by solid state polymerization (SSP) or by interfacial polycondensation. The molecular weight and chemical structure of the polymers were characterized by SEC, FT-IR, and 2D NMR, viz. by recording COSY correlation spectra and heteronuclear multiple-bond correlation spectra (HMBC). After a short melt polycondensation followed by SSP white products with number-average molecular weights above 18 000 g/mol and polydispersity indexes below 3.0 were obtained. However, the interfacial polymerization route led to a polymer with a significantly lower molecular weight, most probably caused by hydrolysis of diacid chloride during the course of the reaction. The analysis of 2D 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. More characterization details were provided by FT-IR spectroscopy which showed that the presence of DAII influenced the hydrogen bond density in the co(polyamides). Moreover, FT-IR analysis also allowed to distinguish bands at around 903 cm⁻¹ related to DAII residues incorporated into the crystal structure also XRD analysis showed that the new biobased co(polyamides) are semicrystalline. The XRD data indicate that with increasing DAII content the typical polyamide structure with different interchain and intersheet distances is preserved for samples with DAII content lower than 43 mol %. At higher DAII contents the structure changes into a structure with a close to hexagonal packing of polymer chains. As expected, with the introduction of DAII into the main chain of the polyamides the melting temperature decreased. Significant differences between the melting points of the homopolymers based on sebacic acid/1,4-diaminobutane ($T_{\rm m} = 246 \,^{\circ}{\rm C}$) and sebacic acid/diaminoisoidide ($T_{\rm m}$ = 152 °C) provide many opportunities for the synthesis of co(polyamides) with tunable melting temperatures. These properties can be further modified by the incorporation of biobased dicarboxylic acids having different chain length like suberic acid, azelaic acid or brassylic acid. For example for fiber applications lower melting points are required than for engineering plastics applications. The lower melting enthalpies together with the lower melting points imply lower energy consumption during processing. In view of the expected higher moisture absorption, due to the presence of the hydrophilic DAII residues, fibers based on the co(polyamides) are expected to result in a higher wearing comfort of clothes based thereon.

ASSOCIATED CONTENT

Supporting Information. Figures showing the chemical structure of the biobased monomers, 500 MHz COSY correlation

spectrum of co(polyamide) coPA5, ¹H NMR spectrum of the DAII/sebacic acid salt and FT-IR spectra of the polyamides recorded at 30 $^{\circ}$ C in the frequency range 3500–2800 cm⁻¹. This material is available free of charge via the Internet at http://pubs.acs.org.

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