Synthesis and Characterization of Linear Polyamides Derived from L-Arabinitol and Xylitol

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ABSTRACT: The synthesis and characterization of a new series of AABB-type polyamides based on L-arabinitol and xylitol are described. These linear polyamides were obtained by reaction of the aldaric acids or aliphatic dicarboxylic acids, with sugar-based diamine or aliphatic diamines. The pentaric diacids were activated as their pentachlorophenyl esters, and the diamino sugars were used as dihydrochlorides. Aliphatic diamines were used either as their activated trimethylsilyl derivatives or as the free bases. All the polyamides were soluble in the usual organic solvents, and those fully sugar-based were also soluble in water. All of them were very hygroscopic, especially those based on xylitol. DSC and X-ray powder diffraction studies showed that L-arabinitol-based polyamides were more crystalline than those derived from xylitol.

Introduction

The low biodegradability of petroleum-based polymers has drawn attention to natural renewing resources for the chemical synthesis of polymers. The polymers based on naturally occurring products are promising new materials with novel technical possibilities and improved properties, such as biocompatibility and biodegradability.[1] Of the different natural sources, carbohydrates stand out as highly convenient raw materials because they are inexpensive, are readily available, and provide great stereochemical diversity.[2,3]

Among synthetic sugar-based polymers, polyamides are being investigated with the aim of adding hydrophilicity and degradability to the excellent properties of the parent polymers. The advances attained in polyamides produced from carbohydrate-derived monomers have been reviewed.[4−6] More recently, we have described the preparation of a series of *O*-protected stereoregular AABB-type polyamides derived from D-mannitol,[7] L-iditol,[7] and D-mannaric acid[8] and nonstereoregular polyamides derived from tetra-*O*-methylgalactaric acid.[8] Random[9] and stereoregular[9−11] polyhydroxy AABB-type polyamides derived from galactaric, xylaric, D-glucaric, and D-mannaric acids have also been described recently by other authors.

A feature of particular interest in connection with the behavior of these polyamides is stereoregularity. In the case of AABB-type polyamides, the stereoregularity of the polymer chain entails chain regioregularity, which in turn relies upon the existence of a 2-fold axis of symmetry in the monomers. Such symmetry restriction is fulfilled only by a reduced number of sugar configurations. If the polycondensates are made from directional monomers, regioisomerism will occur, affording aregic chains. Recently, stereoregular polyhydroxy AABB-type polyamides derived from D-glucaric acid have been attained by Kiely et al. using synthetic methods able to discriminate the reactivity of each carboxyl group of the aldaric acid toward the diamine.[10,12]

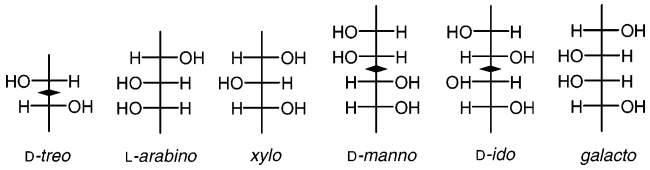

Figure 1. Symmetry properties of aldaric acids and alditols.

Within the framework of the systematic investigation that we have currently under course to explore the potential of the sugar-based polyamide family, a number of stereoregular AABB-type polyamides derived from *O*-protected carbohydrate monomers have been prepared and characterized. These are derived from optically active tartaric acid,[13] D-mannitol,[7] L-iditol,[7] and D-mannaric acid,[8] all possessing a C_2 symmetry axis (Figure 1). As could be anticipated, polytartaramides were found to be semicrystalline polymers displaying well-defined melting transitions. In contrast, polyamides built from the 1,6-diaminohexitols appeared to be noncrystalline despite having a regioregular structure. It was concluded from these results that an appropriate monomer configuration is not sufficient condition to produce semicrystalline polyamides of this type. It seems that the length of the sugar moiety could affect packing and/or crystallization kinetics, which are known to be additional factors playing a critical role in the final crystallinity attained by polyamides.

We now report on the AABB polyamides based on pentitols, specifically on L-arabinitol and xylitol. Three different types of polycondensate have been prepared: fully sugar-based polyamides (**PA-ArAr** and **PA-XyXy**), polyamides derived from aldaric acids and aliphatic diamines (**PA-*m*Ar** and **PA-*m*Xy**), and polyamides based on aliphatic dicarboxylic acids and sugar-based diamines (**PA-Ar*n*** and **PA-Xy*n***). In all these cases, aregic polymers should be expected to be formed, since both sugar configurations lack C_2 axis. In this study, our aim is to describe the synthesis and characterization

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of these new polyamides and evaluate their structure and the properties regarding their constitutions. The results obtained in this work will help to rationalize the behavior of linear sugar-containing polyamides as a function of the length and configuration of the polymethoxylated moiety that is incorporated in the chain and will contribute to systematizing the knowledge being amassed on this family of polymers.

We have previously described[14] the preparation, starting from L-arabinose and D-xylose, of the corresponding active monomers pentachlorophenyl esters of 2,3,4-tri-*O*-methyl-L-arabinaric acid (**1Ar**) and 2,3,4-tri-*O*-methylxylaric acid (**1Xy**) and the dihydrochlorides of 1,5-diamino-1,5-dideoxy-2,3,4-tri-*O*-methyl-L-arabinitol (**2Ar**) and 1,5-diamino-1,5-dideoxy-2,3,4-tri-*O*-methylxylitol (**2Xy**).

Experimental Section

General Methods. Solvents were dried and purified, when necessary, by appropriate standard procedures. Optical rotations were measured at 20 ± 5 °C (1 cm cell). Elemental analyses were determined either in the Microanalysis Laboratories at the Universidad Complutense de Madrid or in the Microanalysis Laboratories of the CSIC, Isla de la Cartuja, Seville, Spain. FTIR spectra were obtained from films or KBr disks. NMR spectra were registered at 200 MHz for ^{1}H and 50 MHz for ^{13}C. Chemical shifts (δ) are reported as parts per million downfield from Me_4Si. Gel permeation chromatography (GPC) analyses were carried out with two Styragel HR columns (7.8 × 300 mm) placed in series, using chloroform as the mobile phase at a flow rate of 1 mL/min. Molecular weights were estimated against polystyrene standards. Intrinsic viscosity measurements were carried out in dichloroacetic acid with a Cannon-Ubbelohde 100/L30 semi-microviscometer at 25.0 ± 0.1 °C. The thermal behavior of the polyamides was examined by DSC using a Perkin-Elmer DSC Pyris 1 calibrated with indium. DSC data were obtained from 4 to 6 mg samples at heating/cooling rates of 10 °C min^{-1} under a nitrogen flow of 20 mL min^{-1}. The glass-transition temperatures were determined at a heating rate of 20 °C min^{-1} from rapidly melt-quenched polymer samples. Thermogravimetric analyses (TGAs) were performed under a nitrogen atmosphere with a Perkin-Elmer TGA-6 thermobalance at a heating rate of 10 °C min^{-1}. X-ray diffraction patterns were obtained from powdered samples in a modified Statton camera using a nickel-filtered Cu Kα radiation with a wavelength of 1.5418 Å and calibrated with molybdenum sulfide (d_{002} = 6.147 Å).

Poly(1,5-dideoxy-2,3,4-tri-*O*-methyl-L-arabinitol-2′,3′,4′-tri-*O*-methyl-L-arabinaramide) (PA-ArAr). To a mixture of monomers **1Ar** (375 mg, 0.52 mmol) and **2Ar** (138 mg, 0.52 mmol), under argon, dry *N*-methyl-2-pyrrolidinone (2 mL) and *N*-ethyl-*N*,*N*-diisopropylamine (0.36 mL, 4.0 mmol) were added, and the mixture was stirred at 45 °C for 4 days. The reaction mixture was diluted with acetone (6 mL) and added dropwise to diethyl ether (200 mL) under stirring. The precipitated white solid was filtered and washed with diethyl ether and dried under diminished pressure at 40 °C to obtain **PA-ArAr** (167 mg, 77%), T_d 256 °C, $[\alpha]_D$ 31° (*c* 0.52, dichloromethane), $[\eta]$ 0.31 dL/g. M_w 33 300, M_w/M_n 1.5. IR: ν_{max} 1677 (amide I), 1528 cm^{-1} (amide II). NMR data ($CDCl_3$): ^{1}H, δ 7.20−7.10 (m, 1H, NH), 6.95−6.55 (bm, 1H, NH), 3.95−3.20 [m, 28H, H-2, H-3, H-4 (diacid unit), H-1, H-1′, H-2, H-3, H-4, H-5, H-5′ (diamine unit), 6 OMe]. ^{13}C, δ 170.6, 170.4, 170.3 (CO), 82.1, 81.9, 81.7, 81.6, 81.5, 81.1, 79.3, 79.0, 77.0 (CH, main chain), 60.8, 60.7, 59.6, 59.5, 58.8, 58.7, 58.3, 58.2, 57.4 (OMe), 39.2, 37.8 (CH_2, main chain). Anal. Calcd for $C_{16}H_{30}O_8N_2 \cdot 0.5H_2O$: C, 49.60; H, 8.06; N, 7.23. Found: C, 49.47; H, 8.30; N, 7.31.

Poly(1,5-dideoxy-2,3,4-tri-*O*-methyl-xylitol-2′,3′,4′-tri-*O*-methylxylaramide) (PA-XyXy). To a mixture of monomers **1Xy** (359 mg, 0.5 mmol) and **2Xy** (132 mg, 0.5 mmol), under argon, dry chloroform (1.5 mL) and *N*-ethyl-*N*,*N*-diisopropylamine (0.34 mL, 2.0 mmol) were added, and the mixture was stirred at room temperature for 3 days. Then the reaction mixture was diluted with chloroform (3 mL) and poured into diethyl ether (200 mL) with stirring. The precipitated solid was filtered, washed with diethyl ether, and dried under diminished pressure to obtain **PA-XyXy** (150 mg, 80%), which was highly hygroscopic, T_m/T_d 200 °C, $[\eta]$ 0.2 dL/g. M_w 22 200, M_w/M_n 1.3. IR: ν_{max} 1669 (amide I), 1529 cm^{-1} (amide II). NMR data ($CDCl_3$): ^{1}H, δ 7.24−7.00 (m, 2H, 2 NH), 3.95−3.00 [m, 28H, H-2, H-3, H-4 (diacid unit), H-1, H-1′, H-2, H-3, H-4, H-5, H-5′ (diamine unit), 6 OMe]. ^{13}C, δ 170.4 (CO), 83.0, 82.8, 82.6, 82.4, 82.3, 78.2 (CH, main chain), 61.7, 60.1, 59.6, 59.5, 58.4 (OMe), 38.9, 38.7 (CH_2, main chain). Anal. Calcd for $C_{16}H_{30}O_8N_2 \cdot 1.3H_2O$: C, 47.82; H, 8.17; N, 6.97. Found: C, 47.89; H, 8.91; N, 7.54.

Synthesis of Polyamides PA-*m*Ar and PA-*m*Xy. General Procedure of Polycondensation. *Method a:* To a stirred solution of the activated ester of the aldaric acid (**1Ar** or **1Xy**, 1 mmol) in dry chloroform (1.5 mL), at 0 °C under argon, was added dropwise the corresponding freshly prepared *N*,*N*′-trimethylsilylalkanediamine (1 mmol). The mixture was allowed to reach room temperature and left to proceed for 3 days. Then the reaction mixture was diluted with chloroform, and the solution heated at 60 °C for 2 h. The polyamide was precipitated by pouring the reaction mixture onto diethyl ether and filtered and washed successively with diethyl ether, acetone, ethanol, and diethyl ether. The solid was finally dried under vacuum at 40 °C.

Poly(hexamethylene-2,3,4-tri-*O*-methyl-L-arabinaramide) (PA-6Ar). *Method a*: 68% yield, T_m 226 °C (ΔH = 50 J/g), $[\alpha]_D$ 3.6° (*c* 0.53, dimethyl sulfoxide), $[\eta]$ 0.9 dL/g. M_w 86 600, M_w/M_n 1.5. IR: ν_{max} 1654 (amide I), 1593 cm^{-1} (amide II). NMR data ($CDCl_3$): ^{1}H, δ 8.30−8.15 (m, 1H, NH), 8.00−7.85 (m, 1H, NH), 3.75−3.50 (m, 2H, H-2, H-4), 3.35−2.60 (m, 10H, H-3, 3 OMe), 1.60−1.00 (m, 12H, 6 CH_2). ^{13}C, δ 170.2, 170.1 (CO), 82.0, 81.7, 81.1 (C-2, C-3, C-4), 61.0, 59.4, 58.1 (OMe), 38.9, 29.4, 26.4 (CH_2). Anal. Calcd for $C_{14}H_{26}O_5N_2 \cdot 0.75H_2O$: C, 53.23; H, 8.77; N, 8.87. Found: C, 52.88; H, 8.43; N, 8.80.

Poly(hexamethylene-2,3,4-tri-*O*-methyl-xylaramide) (PA-6Xy). *Method a*: 82% yield, T_m 98 °C (ΔH = 9 J/g), $[\eta]$ 0.25 dL/g. M_w 19 300, M_w/M_n 1.7. IR: ν_{max} 1659 (amide I), 1531 cm^{-1} (amide II). NMR data ($CDCl_3$): ^{1}H, δ 6.90−6.60 (m, 2H, 2 NH), 3.90−3.10 (m, 12H, H-2, H-3, H-4, 3 OMe), 1.75−1.15 (m, 12H, 6 CH_2); ^{13}C, δ 170.1 (CO), 83.1, 82.5 (C-2, C-3, C-4), 61.9, 59.7 (OMe), 38.9, 29.5, 26.5 (CH_2). Anal. Calcd for $C_{14}H_{26}O_5N_2 \cdot 0.45H_2O$: C, 54.16; H, 8.73; N, 9.02. Found: C, 53.95; H, 8.27; N, 9.01.

Poly(octamethylene-2,3,4-tri-*O*-methyl-L-arabinaramide) (PA-8Ar). *Method a*: 51% yield, T_m 210 °C (ΔH = 46 J/g), $[\alpha]_D$ 39.6° (*c* 0.51, dichloromethane), $[\eta]$ 0.33 dL/g. M_w 12 900, M_w/M_n 1.3. IR: ν_{max} 1660 (amide I), 1531 cm^{-1} (amide II). NMR data ($CDCl_3$): ^{1}H, δ 7.00−6.75 (m, 1H, NH), 6.60−6.35 (m, 1H, NH), 3.95−3.60 (m, 2H, H-2, H-4), 3.50−3.10 (m, 10H, H-3, 3 OMe), 1.70−1.10 (m, 16 H, 8 CH_2). ^{13}C, δ 170.2, 170.1 (CO), 82.0, 81.6, 81.0 (C-2, C-3, C-4), 61.0, 59.4, 58.1 (OMe), 39.0, 29.3, 29.0, 26.6 (CH_2). Anal. Calcd for $C_{16}H_{30}O_5N_2 \cdot 1.5H_2O$: C, 53.76; H, 9.30; N, 7.83. Found: C, 53.60; H, 8.23; N, 7.63.

Poly(octamethylene-2,3,4-tri-*O*-methyl-xylaramide) (PA-8Xy). *Method a*: 81% yield, T_m 108 °C (ΔH = 17 J/g), $[\eta]$ 0.87 dL/g. M_w 52 300, M_w/M_n 1.4. IR: ν_{max} 1654 (amide I), 1538 cm^{-1} (amide II). NMR data ($CDCl_3$): ^{1}H, δ 6.80−6.65 (m, 2H, 2 NH), 4.00−3.15 (m, 12H, H-2, H-3, H-4, 3 OMe), 1.60−0.70 (m, 16H, 8 CH_2). ^{13}C, δ 170.1 (CO), 83.0, 82.5 (C-2, C-3, C-4), 61.8, 59.6 (OMe), 39.0, 29.5, 29.1, 26.8 (CH_2). Anal. Calcd for $C_{16}H_{30}O_5N_2 \cdot H_2O$: C, 55.15; H, 9.26; N, 8.04. Found: C, 55.41; H, 9.17; N, 8.04.

Poly(dodecamethylene-2,3,4-tri-*O*-methyl-L-arabinaramide) (PA-12Ar). *Method a*: 90% yield, T_m 192 °C (ΔH = 47 J/g), $[\alpha]_D$ 37° (*c* 0.52, dichloromethane); $[\eta]$ 0.33 dL/g. M_w 16 300, M_w/M_n 1.9. IR: ν_{max} 1659 (amide I), 1532 cm^{-1} (amide II). NMR data ($CDCl_3$): ^{1}H, δ 7.00−6.75 (m, 1H, NH), 6.55−6.25 (m, 1H, NH), 3.90−3.65 (m, 2H, H-2, H-4), 3.55−3.10 (m, 10H, H-3, 3 OMe), 1.70−1.05 (m, 24H, 12 CH_2). ^{13}C, δ 170.2, 170.1 (CO), 82.0, 81.7, 81.1 (C-2, C-3, C-4), 61.0, 59.4, 58.1

Table 1. Different Conditions for the Preparation of PA-ArAr and PA-XyXy

polyamide	diamine	solvent	temp (°C)	time (days)	yield (%)	M_w[a]	M_w/M[a]
PA-ArAr	**2Ar**	NMP (EDPA)	45	4	75	33300	1.5
PA-ArAr	**2Ar**	$CHCl_3$ (EDPA)	25	2	55	11900	1.6
PA-ArAr	**2Ar**	DMF (EDPA)	25	2	70	11100	1.5
PA-ArAr	**2Ar**	HMPA (EDPA)	45	4	70	5100	1.4
PA-ArAr	**2Ar** (free base)	NMP	45	5	70	1200	1.4
PA-ArAr	**2Ar** (free base)	$CHCl_3$	25	5	30	3300	1.2
PA-XyXy	**2Xy**	NMP (EDPA)	45	4	74	6100	1.4
PA-XyXy	**2Xy**	$CHCl_3$ (EDPA)	25	4	80	22200	1.3

[a] Determined by GPC analysis with polystyrene standards using $CHCl_3$ as a mobile phase.

Table 2. Compared Molecular Weights, Polydispersities, and Yields of Polyamides

	M_w[a]	M_w/M_n[a]	yield (%)[a]	M_w[b]	M_w/M_n[b]	yield (%)[b]
PA-6Ar	86 600	1.5	68			
PA-6Xy	19 300	1.7	82	62 300	1.4	88
PA-8Ar	12 900	1.3	51	53 400	1.3	55
PA-8Xy	52 300	1.4	81	54 900	1.5	90
PA-12Ar	16 300	1.9	90	51 700	1.4	63
PA-12Xy	50 500	1.5	60	96 800	1.4	81

	M_w[c]	M_w/M_n[c]	yield (%)[c]
PA-Ar8	17 600	1.3	50
PA-Xy8	9 500	1.1	45
PA-Ar10	18 900	1.5	53
PA-Xy10	8 400	1.1	40

[a] From the trimethylsilyldiamine in chloroform, at room temperature for 3 days, then at 60 °C for 2 h. [b] From the free diamine in *N*-methyl-2-pyrrolidinone, at 45 °C for a week. [c] From the diamine dihydrochloride in *N*-methyl-2-pyrrolidinone, at 45 °C for 5 days.

(OMe), 39.1, 29.4, 29.1, 26.8 (CH_2). Anal. Calcd for $C_{20}H_{38}O_5N_2 \cdot 0.5H_2O$: C, 58.85; H, 9.98; N, 6.86. Found: C, 58.91; H, 9.26; N, 6.73.

Poly(dodecamethylene-2,3,4-tri-*O*-methyl-xylaramide) (PA-12Xy). *Method a*. 60% yield, T_m 98 °C (ΔH = 21 J/g), [η] 0.51 dL/g. M_w 50 500, M_w/M_n 1.5. IR: ν_{max} 1654 (amide I), 1527 cm^{-1} (amide II). NMR data ($CDCl_3$): ^1H, δ 6.80−6.60 (m, 2H, 2 NH), 3.95−3.15 (m, 12H, H-2, H-3, H-4, 3 OMe), 1.60−1.10 (m, 24H, 12 CH_2). ^{13}C, δ 170.1 (CO), 82.9, 82.5(C-2, C-3, C-4), 61.8, 59.6 (OMe), 39.0, 29.5, 29.2, 26.8 (CH_2). Anal. Calcd for $C_{20}H_{38}O_5N_2 \cdot 0.7H_2O$: C, 60.18; H, 9.95; N, 7.02. Found: C, 60.49; H, 9.42; N, 7.14.

Method b: To a stirred suspension of the activated ester of the aldaric acid (**1Ar** or **1Xy**, 1 mmol) and the corresponding diamine (1 mmol) in dry *N*-methyl-2-pyrrolidinone (8 mL) was added *N*-ethyl-*N*,*N*-diisopropylamine (1.2 mL), and the mixture was stirred at 45 °C under argon for at least a week. Then the reaction mixture was diluted with chloroform, and the polyamide was precipitated by pouring the reaction mixture onto diethyl ether. The solid was filtered, washed successively with diethyl ether, acetone, ethanol, and diethyl ether, and finally dried under vacuum at 40 °C. The molecular weights, polydispersities, and yields of the polyamides thus obtained are collected in Table 2.

Synthesis of Polyamides PA-Ar*n* and PA-Xy*n*. General Procedure of Polycondensation. To a solid mixture of the dideoxydiaminoalditol dihydrochloride (**2Ar** or **2Xy**, 1 mmol) and the corresponding active diester (1 mmol) was added *N*-methyl-2-pyrrolidinone (2.5 mL) and *N*-ethyl-*N*,*N*-diisopropylamine (0.7 mL, 4.0 mmol) under argon, and the mixture was stirred at 45 °C for 5 days. Then the reaction mixture was concentrated to dryness to get a residue, which after treatment with acetone and diethyl ether afforded a solid. The polyamides obtained were filtered, washed with acetone and diethyl ether, and dried under vacuum.

Poly(1,5-dideoxy-2,3,4-tri-*O*-methyl-L-arabinitoldecanamide) (PA-Ar8). 50% yield, T_m 84 °C (ΔH = 23 J/g), $[\alpha]_D$ −3° (*c* 0.54, dichloromethane); [η] 0.46 dL/g. M_w 17 600, M_w/M_n 1.3. IR: ν_{max} 1644 (amide I), 1557 cm^{-1} (amide II). NMR data ($CDCl_3$): ^1H, δ 6.45−6.25 (m, 1H, NH), 6.15−5.95 (m, 1H, NH), 3.80−2.95 (m, 12H, H-2, H-3, H-4, 3 OMe), 2.75−2.00 (m, 4H, H-1, H-1′, H-5, H-5′), 1.70−1.45 (m, 4H, 2 CH_2), 1.35−1.10 (m, 12 H, 6 CH_2). ^{13}C, δ 173.4, 173.3 (CO), 81.9, 79.1, 78.8 (C-2, C-3, C-4), 61.8, 58.6, 57.4 (OMe), 39.5, 38.0, 36.6, 36.5, 29.1, 25.6 (CH_2). Anal. Calcd for $C_{18}H_{34}O_5N_2 \cdot 0.5H_2O$: C, 58.83; H, 9.60; N, 7.62. Found: C, 58.93; H, 9.58; N, 7.52.

Poly(1,5-dideoxy-2,3,4-tri-*O*-methyl xylitoldecanamide) (PA-Xy8). 45% yield, T_m 238 °C (ΔH = 30 J/g); [η] 0.1 dL/g; M_w 9500, M_w/M_n 1.1. IR: ν_{max} 1645 (amide I), 1557 cm^{-1} (amide II). NMR data ($CDCl_3$): ^1H, δ 6.30−6.10 (m, 2H, 2 NH), 3.70−3.10 (m, 16H, H-1, H-1′, H-2, H-3, H-4, H-5, H-5′, 3 OMe), 1.70−1.20 (m, 24H, 12 CH_2). ^{13}C, δ 173.4 (CO), 82.9, 78.2 (C-2, C-3, C-4), 60.4, 58.2 (OMe), 39.1, 36.6, 29.2, 25.6 (CH_2). Anal. Calcd for $C_{18}H_{34}O_5N_2 \cdot H_2O$: C, 57.42; H, 9.64; N, 7.44. Found: C, 57.40; H, 9.45; N, 7.69.

Poly(1,5-dideoxy-2,3,4-tri-*O*-methyl-L-arabinitoldodecanamide) (PA-Ar10). 53% yield, T_m 102 °C (ΔH = 35 J/g), $[\alpha]_D$ −6.5° (*c* 0.53, dichloromethane), [η] 0.48 dL/g. M_w 18 900, M_w/M_n 1.5. IR: ν_{max} 1644 (amide I), 1555 cm^{-1} (amide II). NMR data ($CDCl_3$): ^1H, δ 6.35−6.15 (m, 1H, NH), 6.10−5.90 (m, 1H, NH), 3.95−2.95 (m, 12H, H-2, H-3, H-4, 3 OMe), 2.30−2.00 (m, 4H, H-1, H-1′, H-5, H-5′), 1.70−1.45 (m, 4H, 2 CH_2), 1.40−1.00 (m, 16H, 8CH_2). ^{13}C, δ 173.4, 173.3 (CO), 82.0, 79.1, 78.8 (C-2, C-3, C-4), 60.8, 58.6, 57.4 (OMe), 39.5, 38.0, 36.7, 36.6, 29.3, 29.2, 25.6 (CH_2). Anal. Calcd for $C_{20}H_{38}O_5N_2 \cdot 0.5H_2O$: C, 60.73; H, 9.94; N, 7.08. Found: C, 60.50; H, 9.84; N, 7.14.

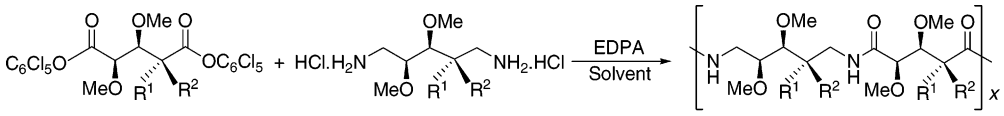
Poly(1,5-dideoxy-2,3,4-tri-*O*-methyl xylitoldodecanamide) (PA-Xy10). 40% yield, T_m/T_d 189 °C, [η] 0.26 dL/g. M_w 8400, M_w/M_n 1.1. IR: ν_{max} 1646 (amide I), 1558 cm^{-1} (amide II). NMR data ($CDCl_3$): ^1H, δ 6.20−6.00 (m, 2H, 2 NH), 3.70−3.10 (m, 16H, H-1, H-1′, H-2, H-3, H-4, H-5, H-5′, 3 OMe), 1.70−1.50 (m, 4H, 2 CH_2), 1.35−1.20 (m, 16H, 8 CH_2). ^{13}C, δ 173.5 (CO), 82.9, 78.1 (C-2, C-3, C-4), 60.4, 58.2 (OMe), 39.1, 36.7, 29.4, 29.3, 25.7 (CH_2). Anal. Calcd for $C_{20}H_{38}O_5N_2 \cdot 4.05H_2O$: C, 52.28; H, 10.11; N, 6.09. Found: C, 52.02; H, 9.91; N, 6.19.

Results and Discussion

Synthesis and Preliminary Characterization. Polyamides **PA-ArAr** and **PA-XyXy** were obtained (Scheme 1) by polycondensation reactions under different conditions (Table 1). The best results for **PA-ArAr** were attained using the diamine dihydrochloride and *N*-methyl-2-pyrrolidinone (NMP) as solvent and *N*-ethyl-*N*,*N*-diisopropylamine (EDPA) as a base at 45 °C for a few days. When the reaction took place at room temperature, the polyamide was obtained with lower molecular weight. **PA-XyXy** was better obtained from the corresponding diamine dihydrochloride in chloroform, containing EDPA, at room temperature. Under optimized conditions, both polyamides were obtained in good yields, with medium molecular weights and narrow polydispersities [33 300 (1.5) and 22 200 (1.3), respectively].

Polyamides **PA-*m*Ar** and **-*m*Xy** (***m*** = 6, 8, and 12) were obtained from the respective activated aldaric acid (**1Ar** or **1Xy**) and the corresponding aliphatic diamine

Scheme 1

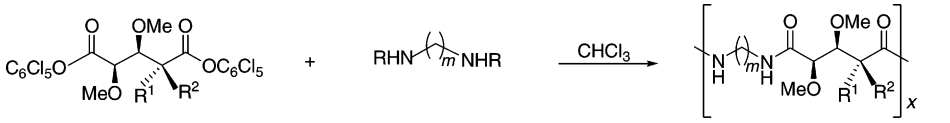


1Ar R^1 = OMe, R^2 = H
1Xy R^1 = H, R^2 = OMe

2Ar R^1 = OMe, R^2 = H
2Xy R^1 = H, R^2 = OMe

PA-ArAr R^1 = OMe, R^2 = H
PA-XyXy R^1 = H, R^2 = OMe

Scheme 2

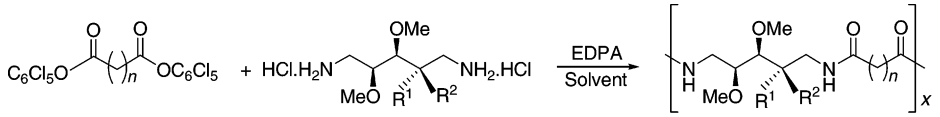


1Ar R^1 = OMe, R^2 = H
1Xy R^1 = H, R^2 = OMe

R = H
R = $SiMe_3$

	m	R^1	R^2
PA-6Ar	6	OMe	H
PA-6Xy	6	H	OMe
PA-8Ar	8	OMe	H
PA-8Xy	8	H	OMe
PA-12Ar	12	OMe	H
PA-12Xy	12	H	OMe

Scheme 3



2Ar R^1 = OMe, R^2 = H
2Xy R^1 = H, R^2 = OMe

	n	R^1	R^2
PA-Ar8	8	OMe	H
PA-Xy8	8	H	OMe
PA-Ar10	10	OMe	H
PA-Xy10	10	H	OMe

(Scheme 2). For the polycondensation reactions, we started from either the trimethylsilyldiamine derivatives or the free bases. In the former case, the reactions were conducted in homogeneous chloroform solutions at room temperature for a few days. Thus, the polyamides were obtained in high yields, the molecular weights ranging from 13 000 to 87 000 with polydispersities in the range 1.3−1.9 (Table 2). Starting from the free diamines, the initially formed suspensions of the monomers in NMP reacted slowly, and longer periods of time were required to complete the polycondensations. In general, this method gave the polyamides with higher molecular weights and yields.

Polyamides **PA-Ar*n*** and **PA-Xy*n*** (***n*** = 8 and 10) were obtained from the corresponding dihydrochlorides of 1,5-diamino-1,5-dideoxy-2,3,4-tri-*O*-methyl-L-arabinitol (**2Ar**) or 1,5-diamino-1,5-dideoxy-2,3,4-tri-*O*-methylxylitol (**2Xy**) and the pentachlorophenyl esters of deca- and dodecanedioic acids (Scheme 3). The polycondensation reactions took place in NMP in the presence of EDPA at 45 °C for a few days. Molecular weights, polydispersities, and yields are collected in Table 2.

Since both L-arabinitol- and xylitol-based monomers **1Ar**, **2Ar** and **1Xy**, **2Xy** are molecules without C_2 axis of symmetry, their polycondensation was expected to lead to aregic polyamides due to the nonregioselective addition of the monomers. In fact, the ^{13}C NMR spectra of polyamide **PA-ArAr** showed three signals (one of them double) for the carbonyl groups, corresponding to the four stereochemical possibilities for the triads centered on the arabinaric unit (Figure 2). Similarly, the achiral xylitol-based monomers (**1Xy** and **2Xy**) afforded an aregic polyamide, but in this case the ^{13}C

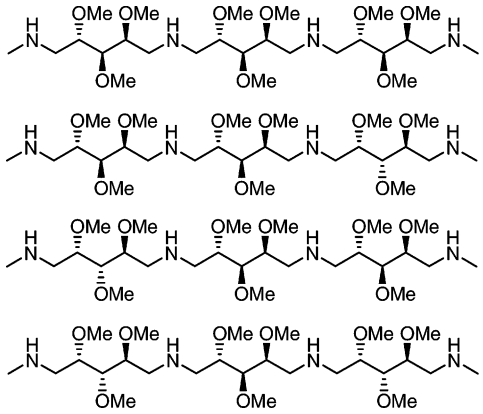


Figure 2. Stereochemical possibilities for the triads centered on the arabinaric unit.

NMR spectra presented fewer signals. For instance, only one signal for the two equivalent carbonyl group at δ 170.4 ppm was detected. As could be anticipated from the chirality of their respective monomers, **PA-ArAr** displayed a considerable optical rotation, while **PA-XyXy** was found to be optically inactive.

All the polyamides were soluble in the usual organic solvents, and those fully sugar-based (**PA-ArAr** and **PA-XyXy**) were also very soluble in water (Table 3). Figure 3 shows the moisture sorption determined at room temperature and under a relative humidity of 100%. All the polyamides were found to be very hygroscopic as a consequence of the high number of methoxyl groups present in the repeating unit of these polymers, especially **PA-ArAr**, **PA-XyXy**, **PA-Ar*n***, and **PA-Xy*n*** (Figure 3b). In general, it was noticed that polyamides

Table 3. Compared Qualitative Solubilities of Polyamides[a]

	PA-ArAr	PA-XyXy	PA-6Ar	PA-6Xy	PA-8Ar	PA-8Xy	PA-12Ar	PA-12Xy	PA-Ar8	PA-Xy8	PA-Ar10	PA-Xy10
water	++	++	-	−	−	−	−	−	−	−	−	−
Et_2O	−	−	-	−	−	−	-	−	+	−	−	−
EtOH	++	+	-	++	−	−	−	+	-	++	−	−
Cl_3CH	++	++	+	++	++	++	++	+	++	+	+	++
acetone	++	++	−	−	−	−	−	−	−	−	−	+
DMSO	++	++	+	++	+	+	+	++	++	+	+	+
DMF	++	+	+	++	-	+	−	++	++	+	+	++
DCA	++	+	+	+	++	+	++	+	+	+	+	+
HFP	++	++	++	++	++	++	++	++	++	++	++	++
TFE	++	++	++	++	++	++	++	++	++	++	++	++

[a] (−) Insoluble; (+) soluble; (++) very soluble at room temperature; DMSO: dimethyl sulfoxide; DMF: *N*,*N*-dimethylformamide; DCA: dichloroacetic acid; HFP: hexafluoro-2-propanol; TFE: 2,2,2-trifluorethanol.

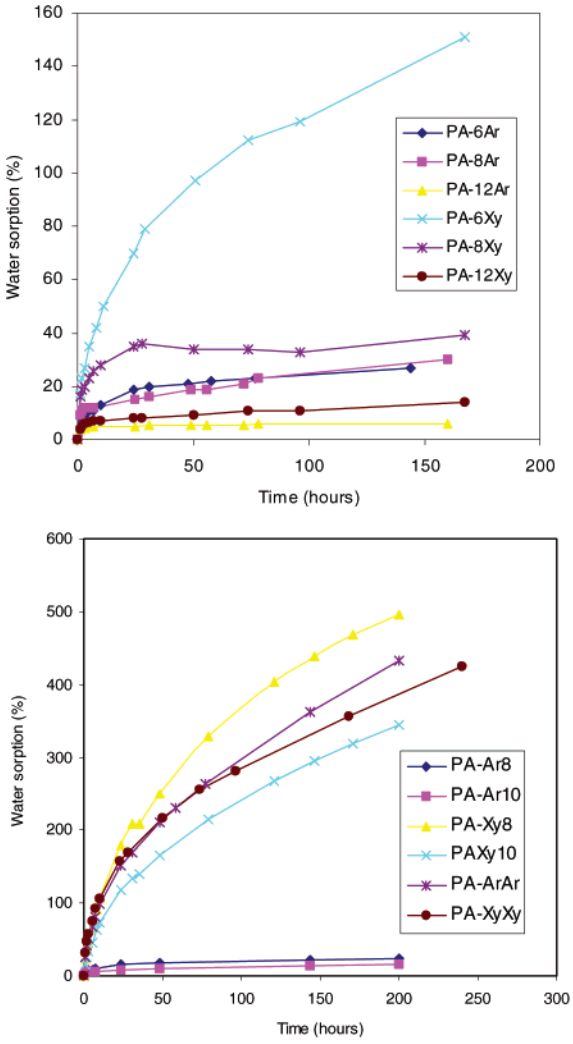


Figure 3. Moisture sorption of polyamides as a function of time at room temperature and under 100% relative humidity.

derived from xylitol were more hygroscopic and less crystalline than those derived from L-arabinitol. This difference is clearly evidenced in Figure 3, where the water sorption for xylitol- and arabinitol-based polyamides is compared. Such difference becomes less, however, with the increment of the methylene number in the polymethylene segment of the non-carbohydrate (Figure 2). Stereochemical possibilities for the triads centered on the arabinaric unit.

Thermal Properties. The thermogravimetric analysis revealed that those polyamides containing a polymethylene moiety, either in the diacid or in the diamine counterpart, are stable well above 300 °C. Illustrative

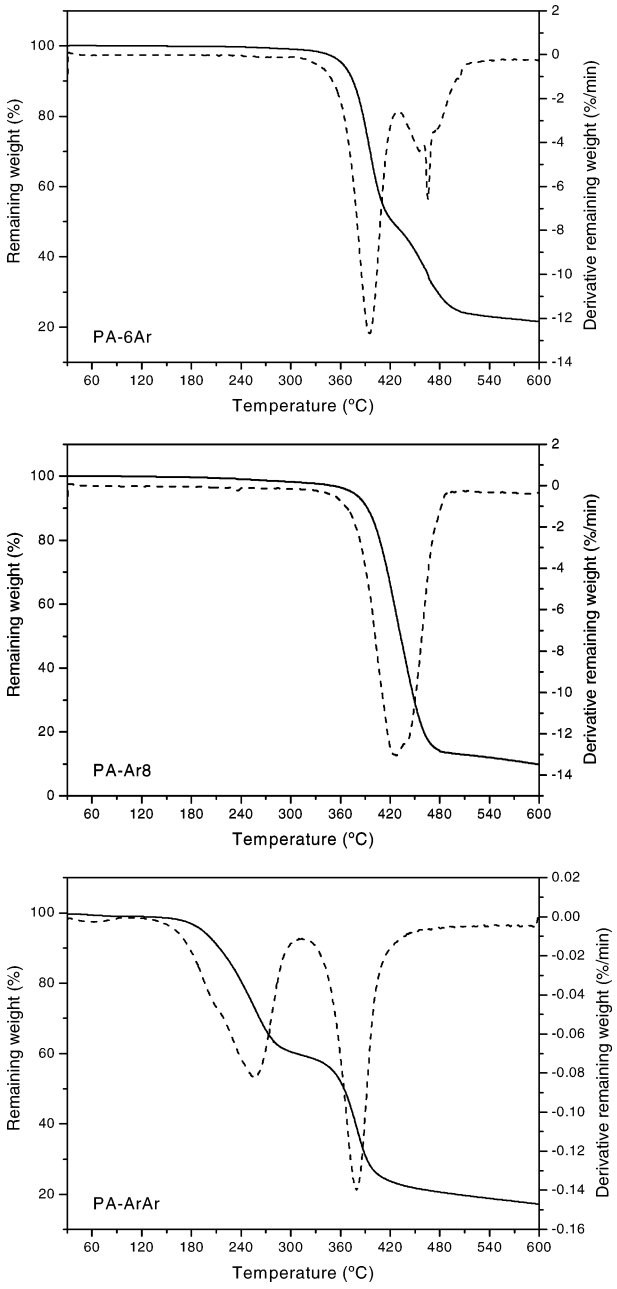


Figure 4. TGA traces (solid lines) and their derivative curves (dashed lines) of the indicated polyamides.

TGA traces are shown in Figure 4. Most of them show decomposition in two steps, which appear clearly separated in the case of polyamides deriving from aldaric acids but which merge into a single shouldered peak in the case of polyamides **PA-Ar*n***. Polyamides **PA-ArAr**

Table 4. Thermal Properties and X-ray Diffraction Spacings of Polyamides

	DSC			TGA		X-ray spacings,[c] *d* (Å)						
	T_m (°C)	ΔH (J/g)	T_g (°C)	T_d[a] (°C)	ΔW[b] (%)							
PA-6Ar	226	50	94	**395**/460	48/22	10.7 w	8.4 s	6.7 m	5.5 w	4.8 s	4.4 w	3.9 w
PA-8Ar	210	46	80	**395**/463	53/18	12.9 m	8.0 s	7.1 w	6.0 w	4.8 s	4.5 w	3.8 w
PA-12Ar	192	47	70	398/**474**	55/13	16.2 s	8.4 s	7.5 m	5.7 w	4.7 s	4.3 s	3.7 w
PA-6Xy	98	9	70	**386**/463	50/23	11.1 m		7.1 m		4.4−4.8 s		
PA-8Xy	108	17	57	**391**/467		14.1 s		7.5 m		4.4−4.8 s		
PA-12Xy	98	21		396/**470**	58/11	17.2 vs		7.5 m		4.4−4.8 s		
PA-Ar8	84	23	39	**424**/450	−/10	15.5 w	11.5 m		6.5 m		4.5 s	
PA-Ar10	102	35	32	**435**/450	−/11	18.2 w	12.4 w		6.6 m		4.5 s	
PA-Xy8			42	**425**	7		11.9 s(df)				4.3 vs (df)	
PA-Xy10			26	225/**439**	53/6	20.6 m	12.4 m	7.5 w (df)			4.2 s (df)	
PA-ArAr			71	256/**378**	60/17				6.8 s (df)			4.0 (df)
PA-XyXy			77	**265**/372	53/30							

[a] Decomposition temperatures measured at the peaks of the derivative curves; major peak in bold. [b] Remaining weight at the respective decomposition step. [c] Intensities visually estimated and denoted as vs = very strong, s = strong, m = medium, and w = weak (very weak reflections not reported).

and **PA-XyXy** appear to be much less stable, showing significant weight loss above 150 °C, and also decomposing in two steps, at temperatures around 260 and 380 °C, respectively. The decomposition temperatures, as well as the sample weight remaining at the end of each decomposition stage, are given in Table 4.

A detailed DSC study was carried out to measure the characteristic thermal parameters and to evaluate the crystallinity and "crystallizability" of these polyamides. Thermal parameters are collected in Table 4, and representative DSC traces are shown in Figure 5. The T_g could be estimated in most cases from the heating traces recorded from samples that were quenched from the melt. T_g values ranged between 26 and 94 °C, depending on the polyamide constitution. **PA-Ar*n*** and **PA-Xy*n***, deriving from aliphatic diacids, had considerably lower T_g, indicative of a more flexible chain. All the polyamides except **PA-ArAr**, **PA-XyXy**, and **PA-Xy*n*** showed melting at the first heating, but both melting temperature and enthalpy were much higher for polyamides **PA-*m*A**r. In fact, exceptionally low melting temperatures were observed for both **PA-*m*Xy** and **PA-Ar*n***, some of the former also showing very low melting enthalpies. Since this peak is quite near the T_g in **PA-*m*Xy**, it might be interpreted as arising from a relaxation process taking place just above T_g. Such rationale is unlikely, since annealing of **PA-12Xi** at 90 °C induced both a shift of the peak to higher temperature and an increase of the peak area. Fully sugar-based polyamides **PA-ArAr** and **PA-XyXy** showed no heat exchange attributable to melting, as was also observed for the polyamides **PA-Xy*n***, derived from 1,5-diamino-1,5-dideoxy-2,3,4-tri-*O*-methylxylitol. On the other hand, crystallization at cooling, with subsequent second-heat melting, could be observed only for **PA-*m*Ar**, despite the fact that these polyamides were those showing the highest T_g and which should therefore be expected to have lesser chain mobility.

X-ray Diffraction Studies. X-ray diffraction results were in full agreement with DSC observations. Representative powder diffraction patterns are depicted in Figure 6, and the most characteristic spacings measured for each polymer are compared in Table 4. Well-defined patterns, consisting of nearly a dozen discrete rings, were obtained from polyamides **PA-*m*Ar**, indicating that they are well crystallized. In contrast, genuine **PA-*m*Xy** produced diffuse patterns that could be slightly sharpened by subjecting the sample to annealing, although the reflections continued to be scarce and poorly defined. Nevertheless, it can be conjectured from comparison of spacings and intensities that the molecular conformation and crystal structure of polyamides

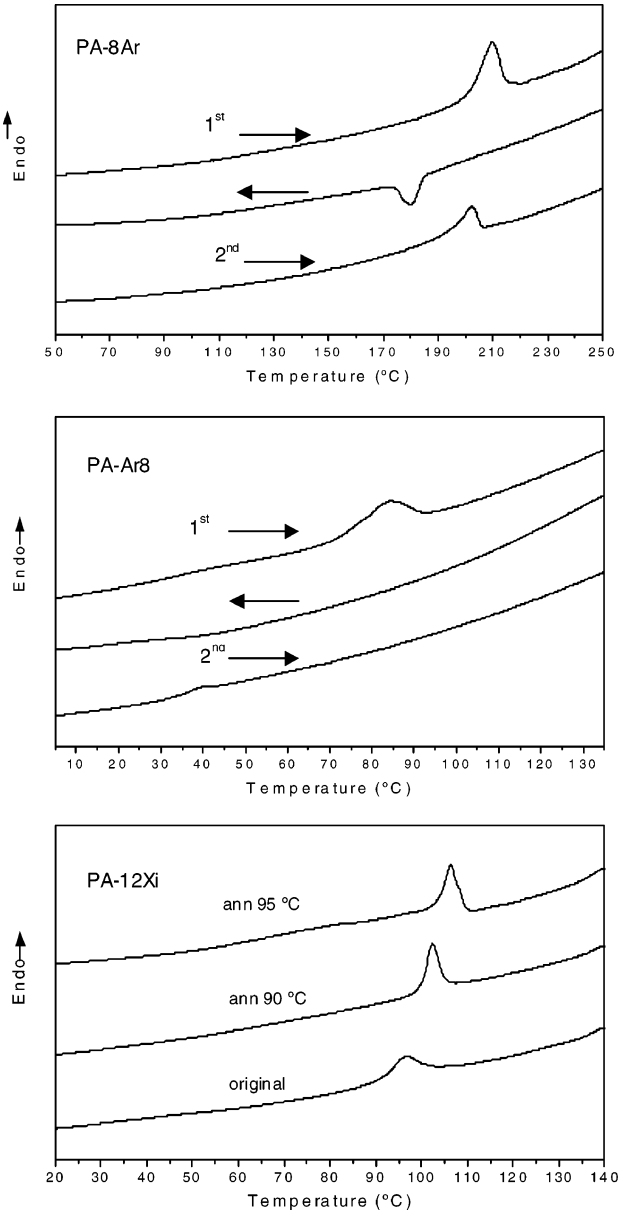


Figure 5. Heating and cooling DSC scans of polyamides **PA-8Ar** (top) and **PA-Ar8** (middle). At bottom, DSC traces of original and annealed **PA-12Xy** samples.

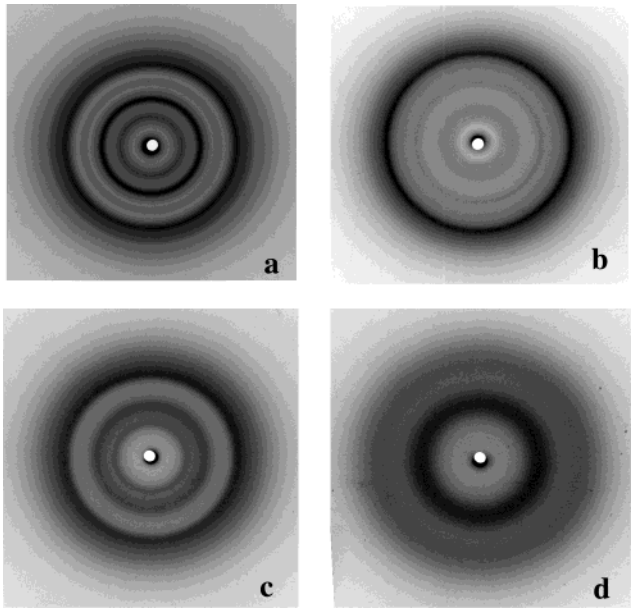


Figure 6. Powder X-ray diffraction patterns of polyamides (a) **PA-8Ar**, (b) **PA-Ar8**, (c) **PA-6Xy** annealed at 95 °C for 1 h, and (d) **PA-ArAr**.

PA-*m*Ar and **PA-*m*Xy** may be quite close. Polyamides **PA-Ar*n*** gave sharp diffraction patterns, though containing far fewer rings than those coming from **PA-*m*Ar**, which is in agreement with the lower crystallinity measured for these polyamides by DSC. Finally, polyamides **PA-ArAr** and **PA-XyXy** invariably produced a largely diffuse pattern characteristic of amorphous material, as could be anticipated from DSC results.

Concluding Remarks. The preparation of aregic polyamides of the AABB-type using monomers derived from naturally occurring aldopentoses L-arabinose and D-xylose is feasible by polycondensation.

The properties and crystal structures of these carbohydrate-based polyamides depend on their constitution and on the configuration of the carbohydrate-based moiety. All the polyamides were soluble in the usual organic solvents, and those fully sugar-based were also very soluble in water. All of them were very hygroscopic, especially those based on xylitol.

DSC and X-ray powder diffraction studies showed that L-arabinitol-based polyamides were more crystalline, especially those synthesized from L-arabinaric acid and aliphatic diamines. Fully sugar-based polyamides **PA-ArAr** and **PA-XyXy** were amorphous materials or at least unable to crystallize under the crystallization conditions used in this study. The evaluation of the biodegradability of these new polymers is currently under way.

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