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Synthesis and Properties of Poly(D-mannaramide)s and Poly(galactaramide)s

M. Mancera,† F. Zamora,† I. Roffé,† M. Bermúdez,‡ A. Alla,‡ S. Muñoz-Guerra,‡ and J. A. Galbis*,†

Departamento de Química Orgánica y Farmacéutica, Facultad de Farmacia, Universidad de Sevilla, 41071-Sevilla, and Departament d'Enginyeria Química, Universitat Politècnica de Catalunya, ETSEIB, 08028-Barcelona, Spain

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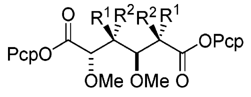
ABSTRACT: We describe a series of new *aregic* polyamides of the AABB-type by polycondensation reaction of pentachlorophenyl 2,3,4,5-tetra-*O*-methyl-D-mannarate or pentachlorophenyl 2,3,4,5-tetra-*O*-methylgalactarate with different diamines. Fully sugar-based polyamides have been prepared from the aldaric esters and the dihydrochlorides of 1,5-diamino-1,5-dideoxy-2,3,4-tri-*O*-methyl-L-arabinitol or 1,5-diamino-1,5-dideoxy-2,3,4-tri-*O*-methylxylitol. Polyamides derived from the aldaric esters and non-carbohydrate alkylenediamines are also investigated. All the polyamides were soluble in the usual organic solvents, and slightly soluble in water. All of them were very hygroscopic, especially those that were fully sugar-based. DSC and X-ray powder diffraction studies showed that most of them are crystalline and that the thermal properties and crystal structure of these carbohydrate-based polyamides depend on their constitution and on the configuration of the carbohydrate-based moiety.

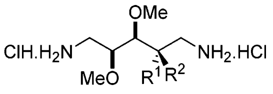
Introduction

The use of carbohydrate-derived monomers in the design of polyamides with enhanced hydrophilicity and biodegradability is an interesting strategy that is being intensively explored.[1−4] Recently, we have reported on polyamides of AABB-type derived from naturally occurring carbohydrates such as D-xylose, L-arabinose,[5,6] D-mannitol,[7−9] and L-tartaric acid.[10−12] In this type of polymer, the regioregularity of the AABB-type chains relies on the existence of a C_2 axis of symmetry in the monomers, otherwise isomerism will occur, giving rise to *aregic* polyamides.[9]

In the present work, we describe the synthesis and properties of a series of new polyamides obtained by polycondensation reaction of pentachlorophenyl 2,3,4,5-tetra-*O*-methyl-D-mannarate (**1Mn**) or pentachlorophenyl 2,3,4,5-tetra-*O*-methylgalactarate (**1Ga**) with different diamines. This method[13−15] has been extensively used by us[5−12] and other authors[16] in previous works.



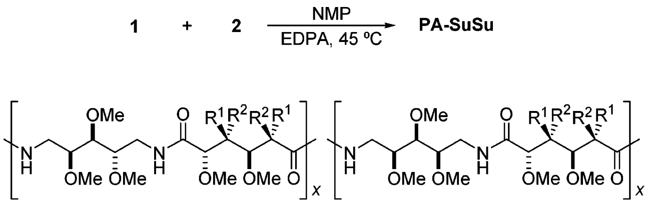
1Mn R^1 = OMe, R^2 = H
1Ga R^1 = H, R^2 = OMe
(Pcp = Pentachlorophenyl)



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

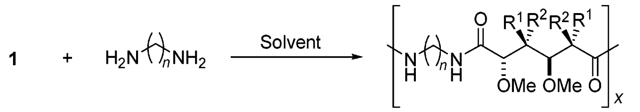
We have prepared two different types of polyamide: *a*) fully sugar-based polyamides (**PA-SuSu)** derived from the aldaric esters (**1Mn** and **1Ga**) and 1,5-diaminopentitols (**2Ar** and **2Xy**) (Scheme 1), and *b)* polyamides (**PA-*n*Su)** derived from the aldaric esters **1** and non-carbohydrate alkylenediamines (**3**) (Scheme 2).

Scheme 1



PA-ArMn R^1 = OMe, R^2 = H
PA-ArGa R^1 = H, R^2 = OMe
PA-XyMn R^1 = OMe, R^2 = H
PA-XyGa R^1 = H, R^2 = OMe

Scheme 2



3
(***n*** = 4, 6, 8, 10, 12)

PA-*n*Mn R^1 = OMe, R^2 = H
PA-*n*Ga R^1 = H, R^2 = OMe

We had previously described the preparation of the corresponding active monomers pentachlorophenyl esters (**1**),[8] 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**).[5]

Experimental Section

General Methods. Chemicals were all used as purchased from the Aldrich Chemical Co. Solvents were dried and purified, when necessary, by appropriate standard procedures. Optical rotations were measured in a Perkin-Elmer 341 polarimeter 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. IR spectra (films or KBr disks) were recorded with a JASCO FT/IR-410 spectrometer. NMR spectra were recorded at 300 K on a Bruker 200 AC-P. 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, thermostated at 35 °C, using chloroform as the mobile phase at a flow rate of 1 mL/min. Molecular weights were estimated against polystyrene standards. Intrinsic viscosity measure-

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* Corresponding author. E-mail: jgalbis@us.es.
† Universidad de Sevilla.
‡ Universitat Politècnica de Catalunya.

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ments were carried out in dichloroacetic acid with a Cannon-Ubbelohde 100/L30 semimicroviscometer at 25.0 ± 0.1 °C. The thermal behavior of the polyamides was examined by DSC using a PerkinElmer DSC Pyris 1 calibrated with indium. DSC data were obtained from samples of 4−6 mg 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 PerkinElmer 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 nickel-filtered Cu Kα radiation with a wavelength of 1.5418 Å and calibrated with molybdenum sulfide (d_{002} = 6.147 Å).

Poly[*N*,*N*′-(1′,5′-dideoxy-2′,3′,4′-tri-*O*-methyl-L-arabinitol-1′,5′-ylidene)-2,3,4,5-tetra-*O*-methyl-D-mannaramide] (PA-ArMn). To a mixture of monomers **1Mn** (359 mg, 0.47 mmol) and **2Ar** (125 mg, 0.47 mmol), under N_2, were added dry *N*-methylpyrrolidinone (0.85 mL) and *N*-ethyl-*N*,*N*-diisopropylamine (0.12 mL, 1.33 mmol), and the mixture was stirred at 45 °C for 13 days. Then the reaction mixture was diluted with acetone (5 mL) and added dropwise to diethyl ether (200 mL) with stirring. The precipitate was filtered, washed with ether, and dried under diminished pressure at 40 °C, to obtain **PA-ArMn** (145 mg, 73%): $[\alpha]_D$ −12 ° (*c* 1, chloroform); M_w 24 500, M_w/M_n 1.35. IR: ν_{max} 1674 (amide I), 1531 (amide II) cm^{-1}. NMR data ($CDCl_3$): ^1H (200 MHz), δ 3.35 (s, 6 H, 2 OMe), 3.42 (s, 6 H, 2 OMe), 3.45 (s, 9 H, 3 OMe), 3.20−3.60 (m, 7 H, H-1′-5′), 3.67 (s, 2 H, H-3/4), 4.10 (s, 2 H, H-2/5), 7.00 (t, 1 H, 1 NH); 7.15 (t, 1 H, 1 NH); ^{13}C (50 MHz), δ 36.8 (C-1′/5′), 57.2 (OMe), 58.0 (OMe), 58.7 (OMe), 60.8 (OMe), 61.3 (OMe), 78.5 (C-3/4), 81.4 (C-3′), 82.1 (C-2′, C-4′), 82.4 (C-2/5), 170.4 (C-1/6). Anal. Calcd for $C_{18}H_{34}N_2O_9\cdot H_2O$: C, 49.08; H, 8.24; N, 6.36. Found: C, 49.06; H, 8.82; N, 7.38.

Poly[*N*,*N*′-(1′,5′-dideoxy-2′,3′,4′-tri-*O*-methyl-xylitol-1′,5′-ylidene)-2,3,4,5-tetra-*O*-methyl-D-mannaramide] (PA-XyMn). To a mixture of monomers **1Mn** (359 mg, 0.47 mmol) and **2Xy** (125 mg, 0.47 mmol) under N_2, dry *N*-methylpyrrolidinone (0.85 mL) and *N*-ethyl-*N*,*N*-diisopropylamine (0.12 mL, 1.33 mmol) were added and the mixture was stirred at 45 °C. After 19 days, the reaction mixture was diluted with acetone (5 mL) and added dropwise to diethyl ether (200 mL) with stirring. The precipitate was filtered, washed with ether, and dried under diminished pressure at 40 °C, to obtain **PA-XyMn** (160 mg, 80%): $[\alpha]_D$ −12 ° (*c* 1, chloroform); M_w 31 300, M_w/M_n 1.43. IR: ν_{max} 1674 (amide I), 1538 (amide II) cm^{-1}. NMR data ($CDCl_3$): ^1H (200 MHz), δ 3.40 (s, 6 H, 2 OMe), 3.47 (s, 6 H, 2 OMe), 3.51 (s, 9 H, 3 OMe), 3.20−3.70 (m, 7 H, H-1′-5′), 3.75 (s, 2 H, H-3/4), 4.10 (s, 2 H, H-2/5), 7.10 (bs, 2 H, 2 NH); ^{13}C (50 MHz), δ 38.1 (C-1′/5′), 57.4 (OMe), 57.6 (OMe), 59.7 (OMe), 60.7 (OMe), 61.3 (OMe), 76.4 (C-3/4), 77.0 (C-3′), 81.8 (C-2′, C-4′), 82.1 (C-2/5), 169.7 (C-1/6). Anal. Calcd for $C_{18}H_{34}N_2O_9\cdot 2H_2O$: C, 47.15; H, 8.35; N, 6.11. Found: C, 47.90; H, 9.69; N, 6.43.

Poly[*N*,*N*′-(1′,5′-dideoxy-2′,3′,4′-tri-*O*-methyl-L-arabinitol-1′,5′-ylidene)-2,3,4,5-tetra-*O*-methylgalactaramide] (PA-ArGa). This compound was prepared from **1Ga** (132 mg, 0.17 mmol) and **2Ar** (45 mg, 0.17 mmol) as described above for **PA-ArMn**. The title compound was obtained as a solid (60 mg, 84%): $[\alpha]_D$ −10 ° (*c* 1, chloroform); M_w 20 100, M_w/M_n 1.55. IR: ν_{max} 1668 (amide I), 1526 (amide II) cm^{-1}. NMR data ($CDCl_3$): ^1H (200 MHz), δ 3.30 (s, 6 H, 2 OMe), 3.35 (s, 6 H, 2 OMe), 3.40 (s, 9 H, 3 OMe), 3.10−3.60 (m, 7 H, H-1′-5′), 3.70 (s, 2 H, H-3/4), 3.80 (s, 2 H, H-2/5), 7.10 (bs, 2 H, 2 NH); ^{13}C (50 MHz), δ 38.3 (C-1′/5′), 57.6 (OMe), 58.6 (OMe), 59.3 (OMe), 60.3 (OMe), 60.8 (OMe), 76.4 (C-2′), 77.0 (C-3′), 79.6 (C-4′), 81.1 (C-3/4), 81.2 (C-2/5), 171.2 (C-1/6). Anal. Calcd for $C_{18}H_{34}N_2O_9\cdot H_2O$: C, 49.08; H, 8.24; N, 6.36. Found: C, 48.52; H, 8.50; N, 7.20.

Poly[*N*,*N*′-(1′,5′-dideoxy-2′,3′,4′-tri-*O*-methylxylitol-1′,5′-ylidene)-2,3,4,5-tetra-*O*-methylgalactaramide] (PA-XyGa). This compound was prepared from **1Ga** (132 mg, 0.17 mmol) and **2Xy** (45 mg, 0.17 mmol) as described above for **PA-XyMn**. The title compound was obtained as a solid (62 mg, 87%): M_w 24 200, M_w/M_n 1.31. IR: ν_{max} 1667 (amide I), 1524 (amide II) cm^{-1}. NMR data ($CDCl_3$): ^1H (200 MHz), δ 3.32 (s, 6 H, 2 OMe), 3.35 (s, 6 H, 2 OMe), 3.40 (s, 9 H, 3 OMe), 3.20−3.70 (m, 7 H, H-1′-5′), 3.75 (s, 2 H, H-3/4), 3.80 (s, 2 H, H-2/5), 7.17 (bs, 2 H, 2 NH); ^{13}C (50 MHz): δ 38.5 (C-1′/5′), 58.3 (OMe), 58.5 (OMe), 59.1 (OMe), 59.2 (OMe), 60.1 (OMe), 77.6 (C-2′), 78.0 (C-3′), 80.0 (C-4′), 81.1 (C-3/4), 81.7 (C-2/5), 171.1 (C-1/6). Anal. Calcd for $C_{18}H_{34}N_2O_9\cdot 1.5H_2O$: C, 48.10; H, 8.30; N, 6.23. Found: C, 48.22; H, 8.77; N, 6.62.

Poly[*N*,*N*′-(1′,4′-butylidene)-2,3,4,5-tetra-*O*-methyl-D-mannaramide] (PA-4Mn). To a mixture of **1Mn** (382 mg, 0.5 mmol) and tetramethylenediamine (44 mg, 0.5 mmol), under N_2, was added dry chloroform (4 mL), and the mixture was stirred at room temperature for 7 days. The reaction mixture was then heated at 60 °C for 1 h, diluted with dichloromethane (5 mL) and added dropwise to diethyl ether (200 mL) with stirring. The white precipitate was filtered, washed with diethyl ether, and dried under diminished pressure, to obtain **PA-4Mn** (120 mg, 75%): $[\alpha]_D$ +40° (*c* 0.5, chloroform): M_w 8000, M_w/M_n 1.22. IR: ν_{max} 1652 (amide I), 1540 (amide II) cm^{-1}. NMR data ($CDCl_3$): ^1H (200 MHz), δ 1.56 [s, 4 H, 2 CH_2 (2′)], 3.44−3.28 [m, 4 H, 2 CH_2 (1′)], 3.46 (s, 6 H, 2 OMe), 3.49 (s, 6 H, 2 OMe), 3.76 (s, 2 H, H-3/4), 4.09 (s, 2 H, H-2/5), 6.72 (t, 2 H, 2 NH); ^{13}C (50 MHz), δ 26.8 (C-2′), 38.4 (C-1′), 57.9 (OMe- $^2/_5$), 61.4 (OMe-3/4), 81.9 (C-3/4), 82.3 (C-2/5), 170.2 (C-1/6). Anal. Calcd for $C_{14}H_{26}N_2O_6\cdot 0.75H_2O$: C, 50.67; H, 8.35; N, 8.44. Found: C, 50.70; H, 8.00; N, 8.32.

Poly[*N*,*N*′-(1′,6′-hexylidene)-2,3,4,5-tetra-*O*-methyl-D-mannaramide] (PA-6Mn). This compound was prepared from **1Mn** (382 mg, 0.5 mmol) and hexamethylenediamine (58 mg, 0.5 mmol) as described above for **PA-4Mn**. The title compound was obtained as a white solid (135 mg, 78%): $[\alpha]_D$ +48° (*c* 0.5, chloroform); M_w 42 300, M_w/M_n 1.37. IR: ν_{max} 1654 (amide I), 1542 (amide II) cm^{-1}. NMR data ($CDCl_3$): ^1H (200 MHz), δ 1.33 [t, 4 H, 2 CH_2 (3′)], 1.50 [t, 4 H, 2 CH_2 (2′)], 3.18−3.38 [m, 4 H, 2 CH_2 (1′)], 3.46 (s, 6 H, 2 OMe), 3.49 (s, 6 H, 2 OMe), 3.76 (s, 2 H, H-3/4), 4.09 (s, 2 H, H-2/5), 6.64 (t, 2 H, 2 NH); ^{13}C (50 MHz), δ 26.5 (C-3′), 29.5 (C-2′), 38.7 (C-1′), 58.0 (OMe- $^2/_5$), 61.4 (OMe-3/4), 82.0 (C-3/4), 82.3 (C-2/5), 170.0 (C-1/6). Anal. Calcd for $C_{16}H_{30}N_2O_6\cdot 0.3H_2O$: C, 54.62; H, 8.77; N, 7.96. Found: C, 54.57; H, 8.49; N, 7.97.

Poly[*N*,*N*′-(1′,8′-octylidene)-2,3,4,5-tetra-*O*-methyl-D-mannaramide] (PA-8Mn). This compound was prepared from **1Mn** (382 mg, 0.5 mmol) and octamethylenediamine (72 mg, 0.5 mmol) as described above for **PA-4Mn**. The title compound was obtained as a white solid (150 mg, 80%): $[\alpha]_D$ +40° (*c* 0.5, chloroform); M_w 78 400, M_w/M_n 1.37. IR: ν_{max} 1656 (amide I), 1541 (amide II) cm^{-1}. NMR data ($CDCl_3$): ^1H (200 MHz), δ 1.28 [bs, 8 H, 2 CH_2 (3′), 2 CH_2 (4′)], 1.49 [t, 4 H, 2 CH_2 (2′)], 3.18−3.35 [m, 4 H, 2 CH_2 (1′)], 3.46 (s, 6 H, 2 OMe), 3.50 (s, 6 H, 2 OMe), 3.77 (s, 2 H, H-3/4), 4.09 (s, 2 H, H-2/5), 6.63 (t, 2 H, 2 NH); ^{13}C (50 MHz), δ 26.8 (C-3′), 29.2 (C-4′), 29.5 (C-2′), 38.8 (C-1′), 58.0 (OMe-2/5), 61.4 (OMe-3/4), 82.0 (C-3/4), 82.3 (C-2/5), 170.1 (C-1/6). Anal. Calcd for $C_{18}H_{34}N_2O_6\cdot H_2O$: C, 55.08; H, 9.25; N, 7.14. Found: C, 55.40; H, 8.91; N, 6.98.

Poly[*N*,*N*′-(1′,10′-decylidene)-2,3,4,5-tetra-*O*-methyl-D-mannaramide] (PA-10Mn). This compound was prepared from **1Mn** (382 mg, 0.5 mmol) and decamethylenediamine (86 mg, 0.5 mmol) as described above for **PA-4Mn**. The title compound was obtained as a white solid (161 mg, 80%): $[\alpha]_D$ +56° (*c* 0.5, chloroform); M_w 71,000, M_w/M_n 1.55. IR: ν_{max} 1656 (amide I), 1542 (amide II) cm^{-1}. NMR data ($CDCl_3$): ^1H (200 MHz), δ 1.25 [bs, 12 H, 2 CH_2 (3′), 2 CH_2 (4′), 2 CH_2 (5′)], 1.59 [s, 4 H, 2 CH_2 (2′)], 3.19−3.36 [m, 4 H, 2 CH_2 (1′)], 3.48 (s, 6 H, 2 OMe), 3.51 (s, 6 H, 2 OMe), 3.79 (s, 2 H, H-3/4), 4.11 (s, 2 H, H-2/5), 6.64 (t, 2 H, 2 NH); ^{13}C (50 MHz), δ 26.8 (C-3′), 29.2 (C-4′), 29.4 (C-5′), 29.5 (C-2′), 38.9 (C-1′), 58.0 (OMe- $^2/_5$), 61.4 (OMe-3/4), 82.1 (C-3/4), 82.3 (C-2/5), 170.1 (C-1/6). Anal. Calcd for $C_{20}H_{38}N_2O_6\cdot 0.5H_2O$: C, 58.37; H, 9.55; N, 6.81. Found: C, 58.27; H, 9.24; N, 6.91.

Poly[*N*,*N*′-(1′,12′-dodecylidene)-2,3,4,5-tetra-*O*-methyl-D-mannaramide] (PA-12Mn). This compound was prepared from **1Mn** (382 mg, 0.5 mmol) and dodecamethylenediamine (100 mg, 0.50 mmol) as described above for **PA-4Mn**. The title

Table 1. Preparation[a] and Some Properties of Polyamides PA-SuSu

polymer	active ester	diamine	time (days)	yield (%)	M_w[b]	M_w/M_n	$[\alpha]_D$[c]	T_g (°C)	T_d (°C)
PA-ArMn	1Mn	2Ar	13	73	24 500	1.35	−12	49	214
PA-XyMn	1Mn	2Xy	19	80	31 300	1.43	−12	49	161
PA-ArGa	1Ga	2Ar	13	84	20 100	1.55	−10	62	200
PA-XyGa	1Ga	2Xy	19	87	24 200	1.31	0	73	190

[a] In NMP and EDPA at 45 °C. [b] Determined by GPC with polystyrene standards and $CHCl_3$ as mobile phase. [c] *c* 1, in $CHCl_3$.

compound was obtained as a white solid (160 mg, 74%): $[\alpha]_D$ +32° (*c* 0.5, chloroform); M_w 158,100, M_w/M_n 1.27. IR: ν_{max} 1655 (amide I), 1542 (amide II) cm^{-1}. NMR data ($CDCl_3$): ^1H (200 MHz), δ 1.22 [bs, 16 H, 2 CH_2 (3′), 2 CH_2 (4′), 2 CH_2 (5′), 2 CH_2 (6′)], 1.46 [t, 4 H, 2 CH_2 (2′)], 3.21−3.31 [m, 4 H, 2 CH_2 (1′)], 3.46 (s, 6 H, 2 OMe), 3.50 (s, 6 H, 2 OMe), 3.78 (s, 2 H, H-3/4), 4.10 (s, 2 H, H-2/5), 6.63 (t, 2 H, 2 NH); ^{13}C (50 MHz), δ 26.8 (C-3′), 29.3 [(C-4′), (C-5′), (C-6′)], 29.6 (C-2′), 38.9 (C-1′), 58.0 (OMe-2/5), 61.4 (OMe-3/4), 82.1 (C-3/4), 82.4 (C-2/5), 170.1 (C-1/6). Anal. Calcd for $C_{22}H_{42}N_2O_6{\cdot}0.5H_2O$: C, 60.11; H, 9.86; N, 6.37. Found: C, 59.95; H, 9.79; N, 6.48.

Poly[*N*,*N*′-(1′,4′-butylidene)-2,3,4,5-tetra-*O*-methyl-galactaramide] (PA-4Ga). To a mixture of **1Ga** (191 mg, 0.25 mmol) and tetramethylenediamine (22 mg, 0.25 mmol), under N_2, dry *N*-methylpyrrolidinone (2 mL) was added and the mixture was stirred at 45 °C for 7 days. The reaction mixture was diluted with dichloromethane (5 mL) and added dropwise to diethyl ether (200 mL) with stirring. The white precipitate was filtered, washed with diethyl ether, and dried under diminished pressure, to obtain **PA-4Ga** (55 mg, 76%): M_w 3600, M_w/M_n 1.41. IR: ν_{max} 1662 (amide I), 1534 (amide II) cm^{-1}. NMR data ($CDCl_3$): ^1H (200 MHz), δ 1.46 [s, 4H, 2 CH_2 (2′)], 3.20 [bs, 4 H, 2 CH_2 (1′)], 3.29 (s, 6 H, 2 OMe), 3.34 (s, 6 H, 2 OMe), 3.49 (s, 2 H, H-3/4), 3.55 (s, 2 H, H-2/5), 8.00 (t, 2 H, 2 NH); ^{13}C (50 MHz), δ 26.8 (C-2′), 38.4 (C-1′), 57.9 (OMe-2/5), 61.4 (OMe-3/4), 81.9 (C-3/4), 82.3 (C-2/5), 170.7 (C-1/6). Anal. Calcd for $C_{14}H_{26}N_2O_6{\cdot}H_2O$: C, 49.99; H, 8.39; N, 8.33. Found: C, 50.12; H, 8.48; N, 8.23.

Poly[*N*,*N*′-(1′,6′-hexylidene)-2,3,4,5-tetra-*O*-methyl-galactaramide] (PA-6Ga). This compound was prepared from **1Ga** (191 mg, 0.25 mmol) and hexamethylenediamine (29 mg, 0.25 mmol) as described above for **PA-4Ga**. The title compound was obtained as a white solid (74 mg, 85%): M_w 25 100, M_w/M_n 1.60. IR: ν_{max} 1655 (amide I), 1535 (amide II) cm^{-1}. NMR data ($CDCl_3$): ^1H (200 MHz), δ 1.29 [t, 4 H, 2 CH_2 (3′)], 1.47 [t, 4 H, 2 CH_2 (2′)], 3.20 [bs, 4 H, 2 CH_2 (1′)], 3.23 (s, 6 H, 2 OMe), 3.34 (s, 6 H 2 OMe), 3.63 (s, 2 H, H-3/4), 3.71 (s, 2 H, H-2/5), 6.75 (t, 2 H, 2 NH); ^{13}C (50 MHz), δ 26.5 (C-3′), 29.5 (C-2′), 38.7 (C-1′), 58.0 (OMe-2/5), 61.4 (OMe-3/4), 82.0 (C-3/4), 82.3 (C-2/5), 170.0 (C-1/6). Anal. Calcd for $C_{16}H_{30}N_2O_6{\cdot}0.6H_2O$: C, 53.80; H, 8.80; N, 7.84. Found: C, 53.58; H, 8.89; N, 8.10.

Poly[*N*,*N*′-(1′,8′-octylidene)-2,3,4,5-tetra-*O*-methyl-galactaramide] (PA-8Ga). This compound was prepared from **1Ga** (191 mg, 0.25 mmol) and octamethylenediamine (36 mg, 0.25 mmol) as described above for **PA-4Ga**. The title compound was obtained as a white solid (90 mg, 96%): M_w 55 300, M_w/M_n 1.45. IR: ν_{max} 1653 (amide I), 1536 (amide II) cm^{-1}. NMR data ($CDCl_3$): ^1H (200 MHz), δ 1.30−1.53 (m, 16 H, 8 CH_2), 3.31 (s, 6 H, 2 OMe), 3.41 (s, 6 H, 2 OMe), 3.71 (s, 2 H, H-3/4), 3.79 (s, 2 H, H-2/5), 6.72 (t, 2 H, 2 NH); ^{13}C (50 MHz), δ 26.8 (2 CH_2), 29.0−39.1 (6 CH_2), 39.1 (2 CH_2), 59.1 (OMe-2/5), 60.4 (OMe-3/4), 80.2 (C-3/4), 81.1 (C-2/5), 170.7 (C-1/6). Anal. Calcd for $C_{18}H_{34}N_2O_6{\cdot}0.33H_2O$: C, 56.83; H, 9.18; N, 7.36. Found: C, 56.78; H, 9.14; N, 7.66.

Poly[*N*,*N*′-(1′,10′-decylidene)-2,3,4,5-tetra-*O*-methyl-galactaramide] (PA-10Ga). This compound was prepared from **1Ga** (191 mg, 0.25 mmol) and decamethylenediamine (43 mg, 0.25 mmol) as described above for **PA-4Ga**. The title compound was obtained as a white solid (96 mg, 95%): M_w 72 150, M_w/M_n 1.36. IR: ν_{max} 1655 (amide I), 1534 (amide II) cm^{-1}. NMR data ($CDCl_3$): ^1H (200 MHz), δ 1.26−1.53 (m, 20 H, 10 CH_2), 3.32 (s, 6 H, 2 OMe), 3.41 (s, 6 H, 2 OMe), 3.71 (s, 2 H, H-3/4), 3.80 (s, 2 H, H-2/5), 6.72 (t, 2 H, 2 NH); ^{13}C (50 MHz), δ 26.9 (2 CH_2), 29.1−29.4 (6 CH_2), 39.2 (2 CH_2), 59.1 (OMe-2/5), 60.4 (OMe-3/4), 80.2 (C-3/4), 81.1 (C-2/5), 170.7 (C-1/6). Anal. Calcd for $C_{20}H_{38}N_2O_6{\cdot}0.75H_2O$: C, 57.74; H, 9.57; N, 6.73. Found: C, 57.79; H, 8.95; N, 7.37.

Poly[*N*,*N*′-(1′,12′-dodecylidene)-2,3,4,5-tetra-*O*-methyl-galactaramide] (PA-12Ga). This compound was prepared from **1Ga** (191 mg, 0.25 mmol) and dodecamethylenediamine (50 mg, 0.25 mmol) as described above for **PA-4Ga**. The title compound was obtained as a white solid (92 mg, 85%): M_w 107 700, M_w/M_n 1.42. IR: ν_{max} 1656 (amide I), 1529 (amide II) cm^{-1}. NMR data ($CDCl_3$): ^1H (200 MHz), δ 1.23−1.53 (m, 24 H, 12 CH_2), 3.32 (s, 6 H, 2 OMe), 3.41 (s, 6 H, 2 OMe), 3.72 (s, 2 H, H-3/4), 3.80 (s, 2 H, H-2/5), 6.72 (t, 2 H, 2 NH); ^{13}C (50 MHz), δ 26.9 (2 CH_2), 29.2−29.4 (8 CH_2), 39.2 (2 CH_2), 59.1 (OMe-2/5), 60.4 (OMe-3/4), 80.2 (C-3/4), 81.1 (C-2/5), 170.7 (C-1/6). Anal. Calcd for $C_{22}H_{42}O_6N_2 \cdot 0.5\ H_2O$: C, 60.11; H, 9.86; N, 6.37. Found: C, 60.21; H, 9.67; N, 6.20.

Results and Discussion

Synthesis and Preliminary Characterization. Fully sugar-based polyamides (**PA-SuSu**) were obtained by polycondensation from the aldaric esters (**1Mn** and **1Ga**) and the 1,5-diaminopentitols (**2Ar** and **2Xy**). The best results were attained using the diamine dihydrochloride, *N*-methylpyrrolidinone (NMP) as solvent, and *N*-ethyl-*N*,*N*-diisopropylamine (EDPA) as a base, at 45 °C, for a few days (Scheme 1 and Table 1). These polyamides (**PA-SuSu**) were obtained as solid compounds which were purified by repeated pouring of an acetone solution of the polymer into diethyl ether and filtration of the precipitate. They were amorphous materials, or at least unable to crystallize under the crystallization conditions used. This was also recently observed for other fully sugar-based polyamides derived from L-arabinaric and xylaric acids.[6]

The presence of seven methoxyl groups in the repeating unit makes these polyamides markedly hygroscopic, an effect that is known to increase with the number of such groups attached to the polymer chain. The synthesized polyamides were optically active, except **PA-XyGa**, and they were soluble in ethanol, acetone, dimethyl sulfoxide, *N*,*N*-dimethylformamide, *N*-methylpyrrolidinone, and chloroform but only slightly soluble in water. Both IR and NMR spectroscopies (see Experimental Section) confirmed the structure of these polymers.

Polyamides **PA-*n*Su** (Scheme 2) were obtained by polycondensation reaction of the aldaric esters (**1Mn** and **1Ga**) with common non-carbohydrate alkylenediamines (**3**, n = 4, 6, 8, 10, 12), under different conditions (see Table 2). The solubility and water sorption of these polyamides were in accordance with those expected. All of them were soluble in the usual organic solvents, including chloroform, and only slightly soluble in water, although they displayed a high hygroscopicity due to the presence of the hydrophilic methoxyl groups. The molecular weight of these polyamides increased with the length of the diamine. Anomalously low molecular weights were obtained for **PA-4Su**, without apparent explanation. IR and NMR spectroscopies (see Experimental Section) confirmed the structure of these polymers.

Table 2. Results of the Preparation of Polyamides PA-*n*Su

polymer	solvent	temp (°C)	time^a	yield (%)	M_w^{b}	M_w/M_n	$[\alpha]_D$^{c}
PA-4Mn	Cl_3CH	60	1 h	75	8 000	1.22	+40
PA-6Mn	Cl_3CH	60	1 h	78	42 300	1.37	+48
PA-8Mn	Cl_3CH	60	1 h	80	78 400	1.37	+40
PA-10Mn	Cl_3CH	60	1 h	80	71 000	1.55	+56
PA-12Mn	Cl_3CH	60	1 h	74	158 100	1.27	+32
PA-4Ga	NMP	45	7 days	76	3 600	1.41	
PA-6GA	NMP	45	7 days	85	25 100	1.60	
PA-8GA	NMP	45	7 days	96	55 300	1.45	
PA-10Ga	NMP	45	7 days	95	72 150	1.36	
PA-12Ga	NMP	45	7 days	85	107 700	1.42	

[a] After 7 days at room temperature. [b] Determined by GPC with polystyrene standards using $CHCl_3$ as mobile phase. [c] *c* 0.5, in $CHCl_3$.

Table 3. Thermal Properties of PA-*n*Mn and PA-*n*Ga

	T_g (°C)	T_m^{1} (°C)	T_m^{2} (°C)^a	ΔH^1 (J/g)	ΔH^2 (J/g)	T_d (°C)^b	% W^c
PA-4Mn	135	248	222	74	26	247/285/**386**	16
PA-6Mn	88	194	188	38	34	**397**/460	18
PA-8Mn	78	180	173	41	26	454/**400**	15
PA-10Mn	71	169	165	16	13	**400**/474	9
PA-12Mn	71	157	156	36	18	**403**/472	12
PA-4Ga	113	220		15		**280**/318	0
PA-6Ga	106	222	205	32	30	**391**/454	21
PA-8Ga	83	213	213	63	32	**396**/453	16
PA-10Ga	79	201	197	51	24	**398**/471	13
PA-12Ga	84	204	203	47	23	394/**465**	10

[a] Endotherm peaks observed on the heating traces: (1) first heating; (2) second heating after crystallization. [b] Decomposition temperatures measured as the peaks of the derivative curves; main peak in bold. [c] Weight remaining after heating at 600 °C, as determined by TGA.

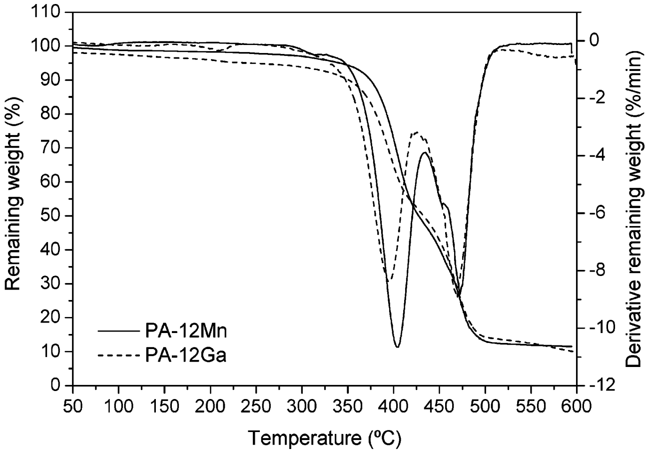

Figure 1. TGA curves of the indicated polyamides.

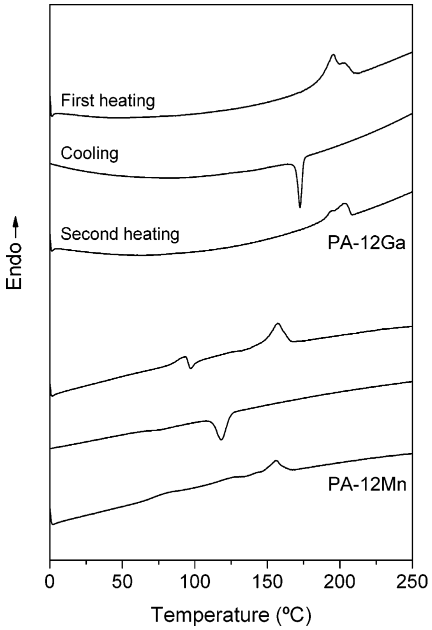

Figure 2. DSC traces of the indicated polyamides.

Thermal Properties. The thermogravimetric analysis revealed that polyamides **PA-*n*Su**, except **PA-4Mn** and **PA-4Ga,** are stable well above 300 °C, which allows an easy process of the melt. They all show decomposition in two steps, with maximum rate at about 400−450 °C.

The decomposition temperatures are practically independent of the constitution and configuration of the polyamides **PA-*n*Su**. However, polyamides **PA-SuSu** present lower T_d (Table 1) than **PA-*n*Su** whose T_d as well as the sample weight remaining after the decomposition are given in Table 3. The weights remaining are between 10% and 20% and decrease in each series with the length of the polymethylenic unit. It can be assumed that the aldaric acid unit contributes mainly to the final residue.

A detailed DSC study was carried out in order to characterize the thermal properties of these polyamides. Thermal parameters are collected in Table 3. All of the polyamides, except the fully sugar-based ones (**PA-SuSu**), are crystalline, with T_g values showing a good correlation with the chain flexibility in both series. Polyamides **PA-*n*Mn** have lower T_g than **PA-*n*Ga**, indicative of a more flexible chain. The same can be inferred from comparison of their respective T_m's. The T_m/T_g (K/K) values are in the range of 1.25−1.28 for the **PA-*n*Mn** and 1.28−1.34 for the **PA-*n*Ga**, which are lower than the universal range (1.4−2.0). The high molecular symmetry may be responsible for the relatively high T_g values found for these polyamides. All the polyamides showed melting in the first heating cycle, the melting temperature being higher for polyamides **PA-*n*Ga**. In both series, T_m decreased with the length of the polymethylene segment of the diamine unit. The annealing treatment did not produce any significant effect on either T_m or crystallinity. All of them, except **PA-4Ga**, crystallized from the melt with crystallinities about 50% of that present in the samples coming directly from synthesis. The TGA and DSC curves of selected polyamides are shown in Figures 1 and 2, respectively.

Crystal Structure. X-ray diffraction results were in full agreement with DSC observations. Representative powder diffraction patterns are depicted in Figure 3, and the most-characteristic spacings measured for each polymer are compared in Table 4. Well-defined patterns were obtained for **PA-*n*Su** polyamides, indicating that they are well-crystallized, but better definitions were obtained for **PA-*n*Ga**, which is in agreement with the higher crystallinity measured for these polyamides by DSC. Nevertheless, it can be conjectured from comparison of spacings and intensities that the crystal structures of polyamides **PA-*n*Mn** and **PA-*n*Ga** may follow the same model in all the cases. The high spacings, at values above 11 Å, systematically increase with the length of the repeating unit, indicating that they are related with the periodicity of the chain. The spacings observed at about 8 Å, with medium-strong intensities, are common for all the polyamides, and may be inter-

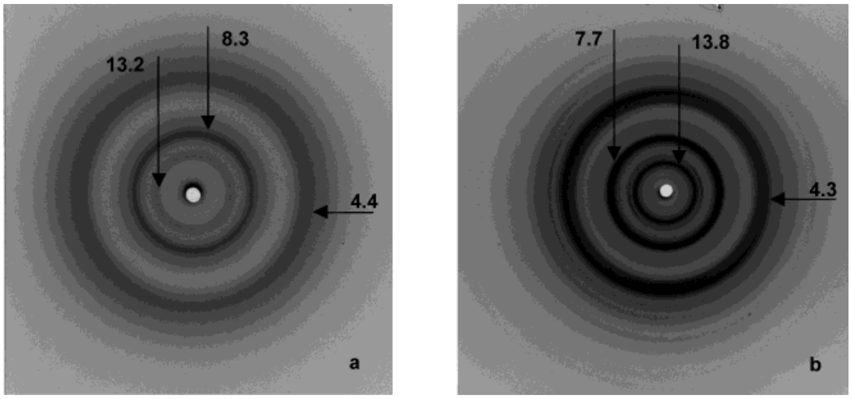

Figure 3. X-ray diffraction paterns: (a) **PA-8Mn**; (b) **PA-10Ga**.

Table 4. X-ray Spacings of PA-*n*Mn and PA-*n*Ga, (*d*, Å)[a]

PA-4Mn	12.9 m		8.3 m	7.0 s	4.5 s	3.5−3.3 m
PA-6Mn	14.4 m	10.9 w	8.1 m	6.5 m	4.6 w	3.4 w
PA-8Mn	13.2 m		8.3 s	6.6 m	4.4 s	3.7 m
PA-10Mn	14.4 s		8.1 s	6.6 w	4.4 s	3.9 w
PA-12Mn	16.0 dif		8.1 m	6.6 vw	4.5 m	
PA-4Ga	14.5 w		7.9 m	6.9 m	5.0−4.1 m	
PA-6Ga	11.1 w				4.0−4.5 s	
PA-8Ga	12.7 s	10.5 vw	7.9 s	6.1 m	4.8 s, 4.3 s	3.5 m, 3.4 w, 3.1 m
PA-10Ga	13.8 s	11.3 m	7.7 vs	6.0 m	4.7 s, 4.3 s	3.5 m, 3.4 d, 3.1 m
PA-12Ga	14.4 s		7.9 m		4.4 m, 4.0 s	

[a] Intensities were visually estimated and denoted as follows: vs, very strong; s, strong; m, medium; w, weak; vw, very weak, dif, diffuse.

preted as the apparent diameters of a nonextended regular conformation.

Concluding Remarks. We describe the preparation of AABB-type polyamides using monomers derived from the naturally occurring alditols D-mannitol and galactitol and the aldopentoses L-arabinose and D-xylose, by polycondensation reaction in solution. The fully sugar-based polyamides (**PA-SuSu**) have medium values of M_w. In the series **PA-*n*Su**, the M_w of the polyamides increases with the length of the polymethylenic segment. All the polyamides were soluble in the usual organic solvents, including chloroform, and slightly soluble in water. All of them were very hygroscopic, especially those fully sugar-based.

The thermal properties and crystal structure of these carbohydrate-based polyamides depend on their constitution and on the configuration of the carbohydrate-based moiety. DSC and X-ray powder diffraction studies showed that all the **PA-*n*Su** polyamides are crystalline, with T_g values well-correlated with the chain flexibility in both series. Polyamides **PA-*n*Mn** have lower T_g than **PA-*n*Ga**, indicative of a more flexible chain. **PA-*n*Ga** polyamides were more crystalline than **PA-*n*Mn**; however, comparison of spacings and intensities indicates that the crystal structures of polyamides **PA-*n*Mn** and **PA-*n*Ga** may follow the same model in all the cases, which may be interpreted as a nonextended regular conformation. No evidence of crystallinity were found for the fully sugar-based polyamides (**PA-SuSu**).

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References and Notes

(1) Thiem, J.; Bachmann, F. *Trends Polym. Sci.* **1994**, *2*, 425−432.
(2) Varela, O.; Orgueira, H. A. *Adv. Carbohydr. Chem. Biochem.* **1999**, *55*, 137−174.
(3) Kiely, D. E.; Chen, L.; Lin, T.-H. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 594−603.
(4) Gonsalves, K. E.; Mungara, P. M. *Trends Polym. Sci.* **1996**, *4*, 25−31.
(5) García-Martín, M. G.; Ruiz Pérez, R.; Benito Hernández, E.; Galbis, J. A. *Carbohydr. Res.* **2001**, *333*, 95−103.
(6) García-Martín, M. G.; Benito Hernández, E.; Ruiz Pérez, R.; Alla, A.; Muñoz-Guerra, S.; Galbis, J. A. *Macromolecules*, submitted.
(7) Mancera, M.; Roffé, I.; Rivas, M.; Silva, C.; Galbis, J. A. *Carbohydr. Res.* **2002**, *337*, 607−611.
(8) Mancera, M.; Roffé, I.; Rivas, M.; Galbis, J. A. *Carbohydr. Res.* **2003**, *338*, 1115−1119.
(9) Mancera, M.; Roffé, I.; Al-Kass, S. S. J.; Rivas, M.; Galbis, J. A. *Macromolecules* **2003**, *36*, 1089−1097.
(10) Bou, J. J.; Rodríguez-Galán, A.; Muñoz-Guerra, S. In *Polymeric Materials Encyclopedia*; Salomone, J. C., Ed.; CRC: Boca Raton, FL, 1996; Vol. 1 (A−B), pp 561−569.
(11) Regaño, C.; Martínez de Ilarduya, A.; Iribarren, I.; Rodríguez-Galán, A.; Galbis, J. A.; Muñoz-Guerra, S. *Macromolecules* **1996**, *29*, 8404−8412.
(12) Bou, J.; Iribarren, I.; Martínez de Ilarduya, A.; Muñoz-Guerra, S. *J. Polym. Sc., Polym. Chem.* **1999**, *37*, 983−993.
(13) Katsarava, R. D.; Kharadze, D. P.; Bendiashvili, T. M.; Urman, Ya. G.; Slonim, I. Ya.; Alekseeva, S. G.; Cefelin, P.; Janout, V. *Acta Polym.* **1988**, *39*, 523−533.
(14) Katsarava, R. D.; Kharadze, D. P.; Avalishvili, L. M. *Makromol. Chem.* **1986**, *187*, 2053−2062.
(15) Katsarava, R. D.; Kharadze, D. P.; Avalishvili, L. M.; Zaalishvili, M. M. *Makromol. Chem., Rapid Commun.* **1984**, *5*, 585−591.
(16) Pascual, S.; Gachard, I.; Coutin, B.; Sekiguchi, H. *Macromol. Chem. Phys.* **2001**, *202*, 873−881.

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