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Stereoregular Copolyamides Derived from D-Xylose and L-Arabinose

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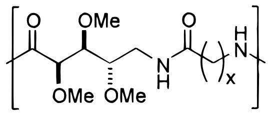
ABSTRACT: A series of carbohydrate-based stereoregular copolyamides have been prepared by the active ester polycondensation method. These new optically active polymers contain in their repeating units an aliphatic *ω*-amino acid and an *ω*-aminoaldonic acid, which is 5-amino-5-deoxy-2,3,4-tri-*O*-methyl-L-arabinonic acid in the case of copolyamides referred to as PAn, or 5-amino-5-deoxy-2,3,4-tri-*O*-methyl-D-xylonic acid for copolyamides referred to as PXn. The polymerization reactions were performed in either *N*-methyl-2-pyrrolidinone (NMP) or hexamethylphosphoramide (HMPA), and the polymers were characterized by elemental microanalysis and IR and ^{1}H and ^{13}C NMR spectroscopies. Both viscosimetry and GPC were used to estimate their molecular weights, and a preliminary exploration of the crystalline structure adopted by these copolyamides has been carried out by X-ray diffraction. Their thermal and optical properties as well as their qualitative solubilities in various solvents and water sorption have been also investigated.

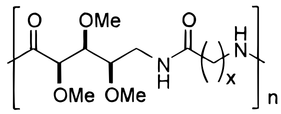
Introduction

Carbohydrates are an important natural source of building blocks for the synthesis of polymers, specially for the design of optically active polymers containing stereocenters in the repeating unit. Several reasons justify the interest in carbohydrates as polymer building blocks, namely, (a) they are easily available, even in some cases they come from agricultural wastes; (b) they are found in a very rich variety of chemical structures with a great stereochemical diversity, and, above all, (c) they constitute a renewable source thanks to solar energy. Unfortunately, polycondensation of monomers derived from sugars is not straightforward. In the first place, their multifunctionality must be reduced, making use of appropriate protecting groups to avoid side reactions leading to undesirable products. Second, to obtain regio- and stereoregular polymers, a strict control of the stereochemical course of the polymerization is required.[1] Otherwise, random orientation of the chiral unit will lead to atactic polymers.

In the past few years we have investigated the preparation of linear stereoregular polyamides from carbohydrate derivatives by applying the active ester polycondensation method. By this means, optically active polyamides containing 1,[2] 2,[3] 3,[2] and 4[4,5] chiral backbone carbon atoms in the repeating unit have been successfully prepared. These polyamides containing conveniently protected carbohydrate building blocks present high hydrophilicity, specially if they are compared with aliphatic polyamides (nylons). Even in some cases, the polyamide is water-soluble,[4] a feature which might be of interest in certain medical applications. In this paper we report on the synthesis and characterization of a series of new copolyamides containing in the repeating unit an aliphatic *ω*-amino acid and an *ω*-aminoaldonic acid, which is 5-amino-5-deoxy-2,3,4-tri-*O*-methyl-L-arabinonic acid[6] in the case of copolyamides referred to as PAn or 5-amino-5-deoxy-2,3,4-tri-*O*-methyl-D-xylonic acid[6] for copolyamides referred to as PXn. The coupling of flexible polymethylene units with the sugar units is expected to lead to optically active polyamides with intermediate properties between conventional nylons and polyamides entirely based on carbohydrate monomers. The chemical structure of these copolyamides has been confirmed by elemental microanalysis and by IR and ^{1}H and ^{13}C NMR spectroscopies, and their thermal and optical properties as well as their water sorption have been also investigated. A preliminary X-ray diffraction analysis of both PAn and PXn has been also undertaken with the aim of evaluating the influence of the sugar configuration on the crystalline structure.



PAn



PXn

Experimental Section

General Methods. Optical rotations were measured at 20 ± 5 °C with a Bellingham & Standley Inc., P20 polarimeter (5 cm cell). TLC was performed on silica gel 60 F254 (Merck) with detection by UV light, charring with sulfuric acid, and ninhydrin. Flash column chromatography was performed using Merck silica gel 60 (230−400 mesh). IR spectra (films or KBr disks) were recorded with a Michelson 100 spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded with a Bruker 200 AC-P spectrometer. Chemical shifts are reported as parts per million downfield from tetramethylsilane. The following abbreviations are used to present the ^{1}H NMR spectra results: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad. Elemental analyses were determined in the Microanalysis Laboratories at the Universidad de Sevilla and the Universidad Complutense de Madrid. Gel permeation chromatography (GPC) analyses were carried out in a Waters apparatus fitted with a Waters model 410 RI detector and a Millenium 2010 computerized data station. Three Waters styragel HR columns were placed in series, and

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the analysis was performed in chloroform–*o*-chlorophenol (95:5 v/v) at a flow rate of 1 mL/min. Molecular weight studies were determined relative to polystyrene; calibration was done using 12 polystyrene samples of narrow molecular weight distribution. Intrinsic viscosity measurements were determined in dichloroacetic acid (DCA) with a Cannon-Ubbelohde 100/L30 semi-microviscosimeter placed in a water bath with the temperature maintained at 25.0 ± 0.1 °C. Water sorptions were measured at 100% relative humidity by the method described by Mori.[7] Melting points were determined with a Gallenkamp apparatus and are uncorrected. Calorimetry measurements and thermal treatments were carried out under a nitrogen atmosphere on Perkin-Elmer DSC Pyris-1 or DSC-7 instruments calibrated with indium. Samples of about 3–5 mg weight were heated at a rate of 10 °C/min and cooled at different rates depending on the purpose. X-ray diffraction patterns were recorded on flat films in a modified Statton-type camera, using nickel-filtered Cu Kα radiation of wavelength of 0.1542 nm. Calibration was made with molybdenum sulfide.

Materials. 5-Amino-5-deoxy-2,3,4-tri-*O*-methyl-L-arabinonic acid (**1**) and 5-amino-5-deoxy-2,3,4-tri-*O*-methyl-D-xylonic acid (**2**) were prepared according to the literature.[6] However, benzyl 2,3,4-tri-*O*-methyl-D-xylonate,[6] a precursor of **2**, was prepared by a different procedure which is described below.

Synthesis of Intermediate Compounds and Monomers. Benzyl 2,3,4-Tri-*O*-methyl-D-xylonate. A solution of 2,3,4-tri-*O*-methyl-D-xylo-1,5-lactone[6] (3 g, 15.78 mmol) in water (15 mL) was stirred at room temperature for several days until total opening of the lactone ring. Then, a solution of 20% Cs_2CO_3 in water was added until pH 7. The water was eliminated under reduced pressure by codistillation twice with DMF. The residue was dissolved in DMF (40 mL), and to this solution was added benzyl bromide (2.4 mL, 19.92 mmol). After stirring at room temperature for 24 h, dichloromethane was added (30 mL); the solid formed was filtered off, and the filtrated was concentrated under reduced pressure. The syrup residue was purified by column chromatography (2:1 hexane–ethyl acetate) to give the title compound as a syrup (2.4 g, 52%). Literature[6] yield: 41%.

Pentachlorophenyl 6-(*tert*-Butoxycarbonylamino)hexanoate (3). To a solution of 6-aminohexanoic acid (5 g, 38.2 mmol) in water–acetonitrile (1:1, 40 mL) were added di-*tert*-butyl dicarbonate (8.4 g, 38.2 mmol) and triethylamine (5.33 mL, 39.1 mmol). The mixture was stirred at room temperature for 24 h and then concentrated under reduced pressure. The residue was dissolved in dry dioxane (50 mL), and to this solution were added pentachlorophenol (8.28 g, 34.4 mmol) and dicyclohexylcarbodiimide (6.68 g, 34.4 mmol). After 24 h of stirring, the solid formed was filtered out and washed with dry dioxane. The filtrated and washings were combined and concentrated; the syrup residue crystallized to give **3** (15 g, 82%), mp 80–82 °C. IR: ν_{max} 3358 (NH), 1776 (CO), 1678 (amide I), 1529 cm^{-1} (amide II). NMR data ($CDCl_3$): ^1H, δ 4.55 (bs, 1H, NH), 3.11 (q, 2H, $J_{5,6} = J_{6,NH}$ 6.3 Hz, H-6), 2.65 (t, 2H, $J_{2,3}$ 7.3 Hz, H-2), 1.78 (m, 2H, $J_{3,4}$ 7.3 Hz, H-3), 1.60–1.40 (m, 4H, H-4, 5), 1.40 (s, 9H, Me_3C). ^{13}C, δ 169.2 (C-1), 155.9 (CO, Boc), 144.1, 131.9, 131.4, 127.6 (phenyl), 79.1 (Me_3C), 40.2 (C-6), 33.4 (C-2), 29.7, 26.1, 24.3 (C-3, 4, 5), 28.4 (Me_3C). Anal. Calcd for $C_{17}H_{20}NO_4Cl_5$: C, 42.57; H, 4.20; N, 2.92. Found: C, 42.56; H, 4.15; N, 2.85.

Pentachlorophenyl 11-(*tert*-Butoxycarbonylamino)undecanoate (4). To a solution of 11-aminoundecanoic acid (2 g, 9.93 mmol) in water–acetonitrile (1:1, 16 mL) were added di-*tert*-butyl dicarbonate (2.2 g, 9.93 mmol) and triethylamine (1.39 mL, 10.2 mmol). The mixture was stirred at room temperature for 24 h and then concentrated under reduced pressure. The residue crystallized to give 11-(*tert*-butoxycarbonylamino)undecanoic acid (1.4 g, 53%), mp 70–71 °C. IR: ν_{max} 3368 (NH, OH), 1692 (amide I), 1525 cm^{-1} (amide II). NMR data ($CDCl_3$): ^1H, δ 10.5 (bs, 1H, COOH), 4.55 (bs, 1H, NH), 3.05 (q, 2H, $J_{10,11} = J_{11,NH}$ 7.0 Hz, H-11), 2.30 (t, 2H, $J_{2,3}$ 7.4 Hz, H-2), 1.70–1.20 (m, 16H, H-3, 4, 5, 6, 7, 8, 9, 10), 1.40 (s, 9H, Me_3C). ^{13}C, δ 179.3 (C-1), 156.0 (CO, Boc), 79.1 (Me_3C), 40.6 (C-11), 34.1 (C-2), 29.9, 29.4, 29.2, 29.1, 29.0, 26.7, 24.7 (C-3, 4, 5, 6, 7, 8, 9, 10), 28.4 (Me_3C). Anal. Calcd for $C_{16}H_{31}NO_4$: C, 63.75; H, 10.36; N, 4.64. Found: C, 63.54; H, 9.97; N, 4.54.

The pentachlorophenyl ester **4** was obtained from the N-protected derivative following the procedure described above for **3**. Yield 87%, mp 76–78 °C. IR: ν_{max} 3404 (NH), 1784 (CO), 1696 (amide I), 1514 cm^{-1} (amide II). NMR data ($CDCl_3$): ^1H, δ 4.50 (bs, 1H, NH), 3.05 (q, 2H, $J_{10,11} = J_{11,NH}$ 6.4 Hz, H-11), 2.66 (t, 2H, $J_{2,3}$ 7.3 Hz, H-2), 1.76 (m, 2H, $J_{3,4}$ 7.3 Hz, H-3), 1.50–1.15 (m, 14H, H-4, 5, 6, 7, 8, 9, 10), 1.41 (s, 9H, Me_3C); ^{13}C, δ 170.0 (C-1), 155.9 (CO, Boc), 144.1, 131.9, 131.4, 127.6 (phenyl), 78.9 (Me_3C), 40.6 (C-11), 33.6 (C-2), 30.0, 29.4, 29.3, 29.2, 29.1, 28.9, 26.7, 24.6 (C-3, 4, 5, 6, 7, 8, 9, 10), 28.4 (Me_3C). Anal. Calcd for $C_{22}H_{30}NO_4Cl_5$: C, 48.06; H, 5.50; N, 2.54. Found: C, 48.06; H, 5.53; N, 2.55.

Pentachlorophenyl 12-(*tert*-Butoxycarbonylamino)dodecanoate (5). It was obtained from 12-aminododecanoic acid following the procedure described above for **4**.

12-(tert-Butoxycarbonylamino)dodecanoic Acid. Yield 57%, mp 81–83 °C. IR: ν_{max} 3365 (NH, OH), 1688 (amide I), 1522 cm^{-1} (amide II). NMR data ($CDCl_3$): ^1H, δ 10.4 (bs, 1H, COOH), 4.55 (bs, 1H, NH), 3.05 (q, 2H, $J_{11,12} = J_{12,NH}$ 7.0 Hz, H-12), 2.28 (t, 2H, $J_{2,3}$ 7.4 Hz, H-2), 1.65–1.20 (m, 18H, H-3, 4, 5, 6, 7, 8, 9, 10, 11), 1.40 (s, 9H, Me_3C); ^{13}C, δ 179.4 (C-1), 156.0 (CO, Boc), 79.0 (Me_3C), 40.6 (C-12), 34.1 (C-2), 29.9, 29.4, 29.2, 29.0, 26.7, 24.7 (C-3, 4, 5, 6, 7, 8, 9, 10, 11), 28.3 (Me_3C). Anal. Calcd for $C_{17}H_{33}NO_4$: C, 64.72; H, 10.54; N, 4.44. Found: C, 64.62; H, 10.04; N, 4.32.

Pentachlorophenyl Ester **5**. Yield 90%, mp 80–82 °C. IR: ν_{max} 3380 (NH), 1792 (CO), 1688 (amide I), 1521 cm^{-1} (amide II). NMR data ($CDCl_3$): ^1H, δ 4.50 (bs, 1H, NH), 3.07 (q, 2H, $J_{11,12} = J_{12,NH}$ 6.5 Hz, H-12), 2.64 (t, 2H, $J_{2,3}$ 7.4 Hz, H-2), 1.77 (m, 2H, $J_{3,4}$ 7.4 Hz, H-3), 1.50–1.20 (m, 16H, H-4, 5, 6, 7, 8, 9, 10, 11), 1.41 (s, 9H, Me_3C); ^{13}C, δ 169.4 (C-1), 155.9 (CO, Boc), 144.2, 131.9, 131.3, 127.6 (phenyl), 78.9 (Me_3C), 40.6 (C-12), 33.6 (C-2), 30.0, 29.4, 29.3, 29.2, 29.1, 29.0, 26.7, 24.6 (C-3, 4, 5, 6, 7, 8, 9, 10, 11), 28.4 (Me_3C). Anal. Calcd for $C_{23}H_{32}NO_4Cl_5$: C, 48.99; H, 5.72; N, 2.48. Found: C, 49.13; H, 5.81; N, 2.47.

Pentachlorophenyl 5-(6′-(*tert*-Butoxycarbonylamino)hexanamido)-5-deoxy-2,3,4-tri-*O*-methyl-L-arabinonate (12). To a stirred solution of **1** (2.7 g, 11.08 mmol) in dry DMF (34 mL) were added **3** (5,3 g, 11.08 mmol) and ethyldiisopropylamine (EDPA; 3.8 mL). After 24 h, the reaction mixture was concentrated under diminished pressure to give a residue that was redissolved in dry ethyl acetate (15 mL). To this solution were added pentachlorophenol (2.02 g, 7.65 mmol) and dicyclohexylcarbodiimide (1.58 g, 7.65 mmol). After 48 h of stirring at room temperature, the solid formed was separated and washed with ethyl acetate. The filtrate and washings were combined, concentrated, and chromatographed (2:1 hexane/ethyl acetate) to give **12** as a syrup (5.9 g, 81%), $[\alpha]_D + 4$ (*c* 1, chloroform). IR: ν_{max} 3321 (NH), 1787 and 1697 (CO), 1653 (amide I), 1541 cm^{-1} (amide II). NMR data ($CDCl_3$): ^1H, δ 5.98 (bt, 1H, NH), 4.63 (bt, 1H, NH), 4.31 (d, 1H, $J_{2,3}$ 1.9 Hz, H-2), 3.76 (dd, 1H, $J_{3,4}$ 7.7 Hz, H-3), 3.55, 3.44, 3.40 (3s, 9H, 3 OMe), 3.35–3.23 (m, 3H, H-4, 5a, 5b), 3.02 (q, 2H, $J_{5',6'} = J_{6',NH}$ 6.7 Hz, H-6′), 2.17 (t, 2H, $J_{2',3'}$ 7.5 Hz, H-2′), 1.59 (m, 2H, $J_{3',4'}$ 7.5 Hz, H-3′), 1.50–1.25 (m, 4H, H-4′, 5′), 1.35 (s, 9H, Me_3C); ^{13}C, δ 173.3, 167.9 (C-1, 1′), 156.0 (CO, Boc), 143.7, 132.1, 131.8, 127.2 (phenyl), 79.0 (Me_3C), 80.8, 79.8, 78.0 (C-2, 3, 4), 60.6, 59.8, 57.5 (3 OMe), 40.2 (C-6′), 37.5, 36.4 (C-5, 2′), 29.6, 26.2, 25.4 (C-3′, 4′, 5′), 28.3 (Me_3C). Anal. Calcd for $C_{25}H_{35}N_2O_8Cl_5$: C, 44.90; H, 5.27; N, 4.19. Found: C, 45.23; H, 5.46; N, 4.13.

Pentachlorophenyl 5-(11′-(*tert*-Butoxycarbonylamino)undecanamido)-5-deoxy-2,3,4-tri-*O*-methyl-L-arabinonate (13). It was obtained from **1** and **4** following the procedure described above for **12**. Yield 80%, $[\alpha]_D + 12$ (*c* 1.1, chloroform). IR: ν_{max} 3330 (NH), 1786 and 1690 (CO), 1643 (amide I), 1515 cm^{-1} (amide II). NMR data ($CDCl_3$): ^1H, δ 5.32 (bt, 1H, NH), 4.50 (bt, 1H, NH), 4.32 (d, 1H, $J_{2,3}$ 2.0 Hz, H-2), 3.77 (dd, 1H, $J_{3,4}$ 7.9 Hz, H-3), 3.53, 3.44, 3.40 (3s, 9H, 3 OMe), 3.70–3.30 (m, 3H, H-4,5a,5b), 3.15 (q, 2H, $J_{10',11'} = J_{11',NH}$ 6.6 Hz, H-11′), 2.15 (t, 2H, $J_{2',3'}$ 7.2 Hz, H-2′), 1.70–1.20 (m, 16H, H-3′, 4′, 5′, 6′, 7′, 8′, 9′, 10′), 1.37 (s, 9H, Me_3C); ^{13}C, δ 173.2, 168.0 (C-1, 1′), 155.5 (CO, Boc), 143.8, 132.2, 131.8, 127.2 (phenyl), 79.1 (Me_3C), 80.8, 79.8, 78.0 (C-2,3,4), 60.8, 59.8, 57.5 (3 OMe), 40.5 (C-11′), 37.3, 36.8 (C-5,2′), 30.0, 29.4, 29.3, 29.2, 29.1, 26.7, 25.7 (C-3′, 4′, 5′, 6′, 7′, 8′, 9′, 10′), 28.3 (*Me*$_3$C). Anal. Calcd for $C_{30}H_{45}N_2O_8Cl_5$: C, 48.75; H, 6.13; N, 3.79. Found: C, 48.70; H, 5.72; N, 3.65.

Pentachlorophenyl 5-(12′-(*tert*-Butoxycarbonylamino)dodecanamido)-5-deoxy-2,3,4-tri-*O*-methyl-L-arabinonate (14). It was obtained from **1** and **5** following the procedure described above for **12**. Yield 78%; $[\alpha]_D + 11$ (*c* 1.2, chloroform). IR: ν_{max} 3333 (NH), 1792 and 1712 (CO), 1664 (amide I), 1529 cm^{-1} (amide II). NMR data ($CDCl_3$): ^1H, δ 5.96 (bs, 1H, NH), 4.63 (bt, 1H, NH), 4.27 (d, 1H, $J_{2,3}$ 2.0 Hz, H-2), 3.73 (dd, 1H, $J_{3,4}$ 7.9 Hz, H-3), 3.50, 3.38, 3.34 (3s, 9H, 3 OMe), 3.65−3.30 (m, 3H, H-4, 5a, 5b), 2.97 (q, 2H, $J_{11',12'} = J_{12',NH}$ 6.4 Hz, H-12′), 2.10 (t, 2H, $J_{2',3'}$ 7.2 Hz, H-2′), 1.60−1.20 (m, 18H, H-3′, 4′, 5′, 6′, 7′, 8′, 9′, 10′, 11′), 1.30 (s, 9H, Me_3C); ^{13}C, δ 173.1, 167.8 (C-1, 1′), 155.8 (CO, Boc), 143.7, 131.9, 131.5, 127.1 (phenyl), 78.6 (Me_3C), 80.5, 79.6, 77.9 (C-2, 3, 4), 60.5, 59.6, 57.4 (3 OMe), 40.3 (C-12′), 37.1, 36.5 (C-5, 2′), 29.8, 29.2, 29.1, 26.5, 25.6 (C-3′, 4′, 5′, 6′, 7′, 8′, 9′, 10′, 11′), 28.2 (*Me*$_3$C). Anal. Calcd for $C_{31}H_{47}N_2O_8Cl_5$: C, 49.44; H, 6.02; N, 3.72. Found: C, 49.37; H, 5.96; N, 3.77.

Pentachlorophenyl 5-(6′-(*tert*-Butoxycarbonylamino)hexanamido)-5-deoxy-2,3,4-tri-*O*-methyl-D-xylononate (15). It was obtained from **2** and **3** following the procedure described above for **12**. Yield 84%; $[\alpha]_D + 8$ (*c* 1.1, chloroform). IR: ν_{max} 3341 (NH), 1794 and 1697 (CO), 1657 (amide I), 1526 cm^{-1} (amide II). NMR data ($CDCl_3$): ^1H, δ 6.40 (bt, 1H, NH), 4.81 (bt, 1H, NH), 4.27 (d, 1H, $J_{2,3}$ 2.6 Hz, H-2), 3.66 (dd, 1H, $J_{3,4}$ 6.0 Hz, H-3), 3.55−3.15 (m, 3H, H-4, 5a, 5b), 3.38, 3.33, 3.25 (3s, 9H, 3 OMe), 2.85 (q, 2H, $J_{5',6'} = J_{6',NH}$ 6.1 Hz, H-6′), 2.00 (t, 2H, $J_{2',3'}$ 7.2 Hz, H-2′), 1.52−1.10 (m, 6H, H-3′, 4′, 5′), 1.17 (s, 9H, Me_3C); ^{13}C, δ 172.8, 166.7 (C-1, 1′), 155.5 (CO, Boc), 143.3, 131.5, 131.2, 126.9 (phenyl), 78.1 (Me_3C), 80.7, 79.5, 78.7 (C-2, 3, 4), 59.8, 58.8, 58.0 (3 OMe), 39.8 (C-6′), 38.3, 35.8 (C-5, 2′), 29.2, 25.9, 24.8 (C-3′, 4′, 5′), 27.8 (*Me*$_3$C). Anal. Calcd for $C_{25}H_{35}N_2O_8Cl_5 \cdot 3/2H_2O$: C, 43.15; H, 5.50; N, 4.02. Found: C, 43.04; H, 5.12; N, 3.84.

Pentachlorophenyl 5-(11′-(*tert*-Butoxycarbonylamino)undecanamido)-5-deoxy-2,3,4-tri-*O*-methyl-D-xylononate (16). It was obtained from **2** and **4** following the procedure described above for **12**. Yield 82%; $[\alpha]_D + 5$ (*c* 1.1, chloroform). IR: ν_{max} 3341 (NH), 1792 and 1704 (CO), 1657 (amide I), 1537 cm^{-1} (amide II). NMR data ($CDCl_3$): ^1H, δ 6.02 (bt, 1H, NH), 4.50 (bs, 1H, NH), 4.43 (d, 1H, $J_{2,3}$ 2.6 Hz, H-2), 3.85 (dd, 1H, $J_{3,4}$ 6.1 Hz, H-3), 3.70−3.35 (m, 3H, H-4, 5a, 5b), 3.55, 3.51, 3.44 (3s, 9H, 3 OMe), 3.04 (q, 2H, $J_{10',11'} = J_{11',NH}$ 6.6 Hz, H-11′), 2.15 (t, 2H, $J_{2',3'}$ 7.1 Hz, H-2′), 1.68−1.20 (m, 16H, H-3′, 4′, 5′, 6′, 7′, 8′, 9′, 10′), 1.38 (s, 9H, Me_3C); ^{13}C, δ 173.3, 167.1 (C-1, 1′), 156.0 (CO, Boc), 143.8, 132.1, 131.8, 127.4 (phenyl), 78.5 (Me_3C), 81.4, 79.9, 78.8 (C-2, 3, 4), 60.3, 59.4, 58.5 (3 OMe), 40.5 (C-11′), 38.6, 36.7 (C-5, 2′), 30.0, 29.6, 29.4, 29.3, 29.2, 26.7, 25.7 (C-3′, 4′, 5′, 6′, 7′, 8′, 9′, 10′), 28.3 (*Me*$_3$C). Anal. Calcd for $C_{30}H_{45}N_2O_8Cl_5$: C, 48.75; H, 6.13; N, 3.79. Found: C, 48.99; H, 6.09; N, 3.74.

Pentachlorophenyl 5-(12′-(*tert*-Butoxycarbonylamino)dodecanamido)-5-deoxy-2,3,4-tri-*O*-methyl-D-xylononate (17). It was obtained from **2** and **5** following the procedure described above for **12**. Yield 78%; $[\alpha]_D + 3$ (*c* 1.1, chloroform). IR: ν_{max} 3341 (NH), 1792 and 1704 (CO), 1657 (amide I), 1529 cm^{-1} (amide II). NMR data ($CDCl_3$): ^1H, δ 5.97 (bt, 1H, NH), 4.50 (bs, 1H, NH), 4.42 (d, 1H, $J_{2,3}$ 2.6 Hz, H-2), 3.85 (dd, 1H, $J_{3,4}$ 6.1 Hz, H-3), 3.70−3.35 (m, 3H, H-4, 5a, 5b), 3.56, 3.51, 3.45 (3s, 9H, 3 OMe), 3.05 (q, 2H, $J_{11',12'} = J_{12',NH}$ 6.7 Hz, H-12′), 2.15 (t, 2H, $J_{2',3'}$ 7.5 Hz, H-2′), 1.70−1.15 (m, 18H, H-3′, 4′, 5′, 6′, 7′, 8′, 9′, 10′, 11′), 1.43 (s, 9H, Me_3C); ^{13}C, δ 173.3, 167.1 (C-1, 1′), 155.7 (CO, Boc), 143.5, 132.1, 131.8, 127.4 (phenyl), 78.3 (Me_3C), 81.4, 79.9, 78.8 (C-2, 3, 4), 60.3, 59.4, 58.5 (3 OMe), 40.6 (C-12′), 38.6, 36.7 (C-5, 2′), 30.0, 29.4, 29.3, 29.2, 29.1, 26.7, 25.7 (C-3′, 4′, 5′, 6′, 7′, 8′, 9′, 10′, 11′), 28.4 (*Me*$_3$C). Anal. Calcd for $C_{31}H_{47}N_2O_8Cl_5$: C, 49.44; H, 6.02; N, 3.72. Found: C, 49.46; H, 6.33; N, 3.57.

Removal of NH-Protecting Group. General Procedure. A solution of **12**−**17** (1.24 mmol) in dry ethyl acetate (8 mL) was added to a cooled 14% HCl solution in ethyl acetate (12 mL). After 24 h of stirring, a stream of nitrogen was bubbled into the solution and then concentrated under diminished pressure. The residue was washed thoroughly with ether to give **18**−**23**, which were used without further purification.

Pentachlorophenyl 5-(6′-Aminohexanamido)-5-deoxy-2,3,4-tri-*O*-methyl-L-arabinonate Hydrochloride (18). Hygroscopic foam (81%); $[\alpha]_D + 4$ (*c* 1.0, chloroform). IR: ν_{max} 3365−2641 (broad, NH_3^+), 1800 (CO), 1649 (amide I), 1535 cm^{-1} (amide II). ^{13}C NMR data ($CDCl_3$): δ 174.7, 167.8 (C-1, 1′), 143.7, 132.1, 131.8, 127.2 (phenyl), 80.9, 79.8, 78.2 (C-2, 3, 4), 60.7, 59.8, 58.2 (3 OMe), 39.9, 38.9 (C-6′, 2′), 35.5 (C-5), 26.9, 26.0, 25.2 (C-3′, 4′, 5′). Anal. Calcd for $C_{20}H_{28}N_2O_6Cl_6 \cdot H_2O$: C, 38.54; H, 4.85; N, 4.49. Found: C, 38.69; H, 5.06; N, 4.52.

Pentachlorophenyl 5-(11′-Aminoundecanamido)-5-deoxy-2,3,4-tri-*O*-methyl-L-arabinonate Hydrochloride (19). Hygroscopic foam (93%); $[\alpha]_D + 5$ (*c* 1.1, chloroform). IR: ν_{max} 3349−2476 (broad, NH_3^+), 1792 (CO), 1649 (amide I), 1535 cm^{-1} (amide II). ^{13}C NMR data ($CDCl_3$): δ 176.3, 167.7 (C-1, 1′), 143.7, 132.1, 131.9, 127.2 (phenyl), 80.6, 79.8, 78.2 (C-2, 3, 4), 60.6, 59.8, 58.1 (3 OMe), 40.0, 39.5(C-11′, 2′), 35.2 (C-5), 29.1, 29.0, 28.8, 27.3, 26.4, 26.2 (C-3′, 4′, 5′, 6′, 7′, 8′, 9′, 10′). Anal. Calcd for $C_{25}H_{38}N_2O_6Cl_6 \cdot {}^1/_2H_2O$: C, 43.87; H, 5.74; N, 4.09. Found: C, 43.70; H, 5.44; N, 4.03.

Pentachlorophenyl 5-(12′-Aminododecanamido)-5-deoxy-2,3,4-tri-*O*-methyl-L-arabinonate Hydrochloride (20). Hygroscopic foam (94%); $[\alpha]_D + 9$ (*c* 1.0, chloroform). IR: ν_{max} 3333−2635 (broad, NH_3^+), 1794 (CO), 1651 (amide I), 1500 cm^{-1} (amide II). ^{13}C NMR data ($CDCl_3$): δ 173.9, 167.9 (C-1, 1′), 143.8, 132.1, 131.8, 127.2 (phenyl), 80.7, 79.8, 78.1 (C-2, 3, 4), 60.7, 59.8, 57.7 (3 OMe), 40.0, 37.9 (C-12′, 2′), 36.4 (C-5), 29.3, 29.2, 28.9, 27.5, 26.4, 25.9 (C-3′, 4′, 5′, 6′, 7′, 8′, 9′, 10′, 11′). Anal. Calcd for $C_{26}H_{40}N_2O_6Cl_6$: C, 45.30; H, 5.84; N, 4.06. Found: C, 45.56; H, 5.65; N, 4.05.

Pentachlorophenyl 5-(6′-Aminohexanamido)-5-deoxy-2,3,4-tri-*O*-methyl-D-xylononate Hydrochloride (21). Hygroscopic foam (82%); $[\alpha]_D + 4$ (*c* 1.0, chloroform). IR: ν_{max} 3603−2698 (broad, NH_3^+), 1800 (CO), 1649 (amide I), 1545 cm^{-1} (amide II). ^{13}C NMR data ($CDCl_3$): δ 173.5, 167.2 (C-1, 1′), 143.6, 132.0, 131.7, 127.2 (phenyl), 80.7, 79.5, 78.2 (C-2, 3, 4), 60.0, 59.3, 58.7 (3 OMe), 39.7, 39.1, 35.9 (C-6′, 5, 2′), 26.7, 25.8, 24.8(C-3′, 4′, 5′). Anal. Calcd for $C_{20}H_{28}N_2O_6Cl_6 \cdot 2H_2O$: C, 38.42; H, 5.15; N, 4.48. Found: C, 38.66; H, 5.37; N, 4.55.

Pentachlorophenyl 5-(11′-Aminoundecanamido)-5-deoxy-2,3,4-tri-*O*-methyl-D-xylononate Hydrochloride (22). Hygroscopic foam (73%); $[\alpha]_D + 2$ (*c* 0.9, chloroform). IR: ν_{max} 3508−2651 (broad, NH_3^+), 1800 (CO), 1633 (amide I), 1537 cm^{-1} (amide II). ^{13}C NMR data ($CDCl_3$): δ 174.2, 166.9 (C-1, 1′), 143.4, 131.8, 131.5, 127.0 (phenyl), 80.5, 79.3, 78.2 (C-2, 3, 4), 60.0, 59.1, 58.5 (3 OMe), 39.2, 36.0 (C-11′, 5), 28.9, 27.1, 26.2, 25.6 (C-2′, 3′, 4′, 5′, 6′, 7′, 8′, 9′, 10′). Anal. Calcd for $C_{25}H_{38}N_2O_6Cl_6 \cdot H_2O$: C, 43.30; H, 5.81; N, 4.04. Found: C, 43.08; H, 5.68; N, 3.96.

Pentachlorophenyl 5-(12′-Aminododecanamido)-5-deoxy-2,3,4-tri-*O*-methyl-D-xylononate Hydrochloride (23). Hygroscopic foam (86%); $[\alpha]_D + 3$ (*c* 1.0, chloroform). IR: ν_{max} 3492−2650 (broad, NH_3^+), 1792 (CO), 1647 (amide I), 1537 cm^{-1} (amide II). ^{13}C NMR data ($CDCl_3$): δ 174.4, 166.9 (C-1, 1′), 143.5, 131.8, 131.5, 127.1 (phenyl), 80.6, 79.3, 78.2 (C-2, 3, 4), 59.9, 59.1, 58.5 (3 OMe), 39.7, 39.2, 36.0 (C-12′, 5, 2′), 29.0, 28.7, 27.1, 26.2, 25.7 (C-3′, 4′, 5′, 6′, 7′, 8′, 9′, 10′, 11′). Anal. Calcd for $C_{26}H_{40}N_2O_6Cl_6 \cdot {}^3/_2H_2O$: C, 43.59; H, 6.05; N, 3.91. Found: C, 43.70; H, 5.70; N, 3.84.

Synthesis of Copolyamides. General Procedure of Polycondensation. Compounds **18**−**23** were dissolved in the chosen solvent (Table 1), and ethyldiisopropylamine was added. After 7 days at 45 °C, the solution was precipitated by pouring the solution into ether. The product was recovered by filtration on a glass filter, washed thoroughly with ether, acetone, and ethanol, and dried under vacuum at room temperature. The obtained yields, elemental analyses, and some properties of the PAn and PXn are given in Tables 1−5. We describe below their spectroscopical properties (IR and NMR).

Table 1. Compared Yields and Optical Rotations of Copolyamides PAn and PXn

copolyamide (solvent)[a]	yield (%)	repeating unit	elemental analysis (C,H,N,%) calcd			found			$[\alpha]_D{}^b$	M_D
PA6 (NMP)	90	$C_{14}H_{26}N_2O_5\cdot{}^1/_3H_2O$	54.52	8.71	9.08	54.78	9.00	8.91	+53	+160
PA6 (HMPA)	75	$C_{14}H_{26}N_2O_5\cdot{}^1/_2H_2O$	54.00	8.74	8.99	53.70	8.74	8.96	+52	+157
PA11 (NMP)	90	$C_{19}H_{36}N_2O_5$	61.26	9.74	7.52	60.82	9.76	7.28	+39	+145
PA11 (HMPA)	85	$C_{19}H_{36}N_2O_5\cdot H_2O$	58.43	9.80	7.17	58.90	9.84	7.25	+37	+138
PA12 (NMP)	95	$C_{20}H_{38}N_2O_5$	62.14	9.90	7.24	62.01	10.10	7.13	+27	+104
PA12 (HMPA)	95	$C_{20}H_{38}N_2O_5\cdot{}^1/_2H_2O$	60.73	9.93	7.08	60.93	10.09	7.06	+32	+124
PX6 (NMP)	75	$C_{14}H_{26}N_2O_5\cdot{}^1/_2H_2O$	54.00	8.74	8.99	53.72	8.38	8.73	+51	+154
PX6 (HMPA)	52	$C_{14}H_{26}N_2O_5\cdot H_2O$	52.48	8.80	8.74	52.81	8.23	8.79	+46	+139
PX11 (NMP)	90	$C_{19}H_{36}N_2O_5\cdot{}^1/_2H_2O$	59.81	9.77	7.34	59.74	9.26	7.19	+39	+145
PX11 (HMPA)	73	$C_{19}H_{36}N_2O_5\cdot{}^3/_2H_2O$	57.11	9.83	7.01	57.26	9.43	7.36	+37	+138
PX12 (NMP)	90	$C_{20}H_{38}N_2O_5\cdot{}^1/_3H_2O$	61.19	9.92	7.13	61.00	9.26	6.98	+39	+151

[a] NMP = *N*-methyl-2-pyrrolidinone; HMPA = hexamethylphosphoramide. [b] *c* 1.0, formic acid.

Table 2. Intrinsic Viscosities and Molecular Weights of Copolyamides

copolyamide (solvent)	$[\eta]^a$ (dL/g)	$M_v{}^b$	$M_n{}^c$	$M_w{}^c$	M_w/M_n
PA6 (NMP)	0.42	5700	6400	16900	2.6
PA6 (HMPA)	0.16	1000	3200	5300	1.6
PA11 (NMP)	0.50	7900	8200	30200	3.7
PA11 (HMPA)	0.16	1000	3200	5400	1.7
PA12 (NMP)	0.61	11400	10000	38200	3.8
PA12 (HMPA)	0.24	2000	4600	9900	2.2
PX6 (NMP)	0.50	7900	7600	18200	2.4
PX6 (HMPA)	0.30	3100	6800	10700	1.6
PX11 (NMP)	0.92	24100	12700	65600	5.1
PX11 (HMPA)	0.41	5500	7800	20100	2.6
PX12 (NMP)	0.64	12400	14200	62600	4.4

[a] Intrinsic viscosities measured in dichloroacetic acid at 25 °C. [b] Calculated by applying the viscosimetric equation reported for nylon 6,6.[8] [c] Determined by GPC analysis with polystyrene standards. Mobile phase: (95:5) chloroform–*o*-chlorophenol.

Table 3. Qualitative Solubilities[a] and Water Sorption[b] of Copolyamides

solvent	PA12	PA11	PA6	PX12	PX11	PX6
water	−	−	++	−	−	++
ether	−	−	−	−	−	−
ethanol	−	−	−	−	−	−
chloroform	++	++	++	++	++	++
DMSO	±	±	+	+	+	+
DMF	±	+	+	+	+	+
acetone	−	−	−	−	−	−
ethyl acetate	−	−	−	−	−	−
formic acid	++	++	++	++	++	++
water sorption (%)	10	10	44	9	7	43

[a] Estimated according to the method of Braun:[9] (−) insoluble, (±) slightly swollen, (+) soluble on warming at 100 °C, (++) soluble at room temperature. [b] Estimated according to the method of Mori.[7]

Table 4. Thermal Properties of Copolyamides PAn and PXn

copolyamide	$T_m{}^a$ (°C)	$T_m{}^b$ (°C)	ΔH (J/g)	T_g (°C)	T_g/T_m
PA6	176, 185	182	47	76	0.77
PA11	182	190	44	60	0.72
PA12	176, 194	195	43	58	0.71
PX6	184, 194	180	39	68	0.75
PX11	173	174	51	51	0.72
PX12	148	149	35	48	0.76

[a] First heating. [b] After annealing.

PA6. IR: ν_{max} 3340 (NH), 1654 (amide I), 1534 cm^{-1} (amide II). NMR data (CDCl$_3$): ^{1}H, δ 6.77 (bt, 1H, NH), 5.87 (bt, 1H, NH), 3.76 (s, 1H, H-2), 3.70−3.06 (m, 6H, H-3, 4, 5a, 5b, 6′), 3.33, 3.25, 3.22 (3s, 9H, 3 OMe), 2.12 (t, 2H, $J_{2',3'}$ 7.0 Hz, H-2′), 1.85−1.10 (m, 6H, H-3′, 4′, 5′); ^{13}C, δ 172.7, 170.8 (C-1, 1′), 81.0, 80.4, 77.6 (C-2, 3, 4), 60.8, 59.7, 56.9 (3 OMe), 38.8, 36.6, 36.2 (C-6′, 5, 2′), 29.1, 26.3, 25.0 (C-3′, 4′, 5′).

PA11. IR: ν_{max} 3317 (NH), 1657 (amide I), 1537 cm^{-1} (amide II). NMR data (CDCl$_3$): ^{1}H, δ 6.70 (t, 1H, NH), 5.80 (bt, 1H, NH), 3.80 (s, 1H, H-2), 3.80−3.10 (m, 6H, H-3, 4, 5a, 5b, 11′), 3.43, 3.31, 3.27 (3s, 9H, 3 OMe), 2.13 (t, 2H, $J_{2',3'}$ 7.0 Hz, H-2′), 1.75−1.05 (m, 16H, H-3′, 4′, 5′, 6′, 7′, 8′, 9′, 10′); ^{13}C, δ 173.2, 170.7 (C-1, 1′), 81.1, 80.5, 77.8 (C-2, 3, 4), 60.9, 59.7, 56.9 (3 OMe), 39.0, 36.6 (C-11′, 5, 2′), 29.1, 26.7, 25.6 (C-3′, 4′, 5′, 6′, 7′, 8′, 9′, 10′).

PA12. IR: ν_{max} 3317 (NH), 1664 (amide I), 1529 cm^{-1} (amide II). NMR data (CDCl$_3$): ^{1}H, δ 6.70 (t, 1H, NH), 5.80 (bt, 1H, NH), 3.82 (s, 1H, H-2), 3.80−3.20 (m, 6H, H-3, 4, 5a, 5b, 12′), 3.39, 3.32, 3.27 (3s, 9H, 3 OMe), 2.15 (t, 2H, $J_{2',3'}$ 7.0 Hz, H-2′), 1.85−1.00 (m, 18H, H-3′, 4′, 5′, 6′, 7′, 8′, 9′, 10′, 11′); ^{13}C, δ 173.2, 170.7 (C-1, 1′), 81.1, 80.5, 77.6 (C-2, 3, 4), 60.9, 59.6, 56.8 (3 OMe), 39.0, 36.6 (C-12′, 5, 2′), 29.2, 29.1, 26.7, 25.6 (C-3′, 4′, 5′, 6′, 7′, 8′, 9′, 10′, 11′).

PX6. IR: ν_{max} 3325 (NH), 1657 (amide I), 1545 cm^{-1} (amide II). NMR data (CDCl$_3$): ^{1}H, δ 6.65 (t, 1H, NH), 6.00 (bt, 1H, NH), 3.75 (d, 1H, $J_{2,3}$ 2.0 Hz, H-2), 3.70−3.20 (m, 6H, H-3, 4, 5a, 5b, 6′), 3.44, 3.42, 3.41 (3s, 9H, 3 OMe), 2.17 (t, 2H, $J_{2',3'}$ 6.8 Hz, H-2′), 1.75−1.30 (m, 6H, H-3′, 4′, 5′); ^{13}C, δ 172.7, 170.2 (C-1, 1′), 82.1, 81.5, 79.7 (C-2, 3, 4), 60.7, 59.4, 58.9 (3 OMe), 39.1, 38.8, 36.2 (C-6′, 5, 2′), 29.2, 26.3, 25.0 (C-3′, 4′, 5′).

PX11. IR: ν_{max} 3317 (NH), 1647 (amide I), 1537 cm^{-1} (amide II). NMR data (CDCl$_3$): ^{1}H, δ 6.60 (bt, 1H, NH), 5.90 (bt, 1H, NH), 3.75 (d, 1H, $J_{2,3}$ 1.9 Hz, H-2), 3.70−3.10 (m, 6H, H-3, 4, 5a, 5b, 11′), 3.43, 3.41, 3.40 (3s, 9H, 3 OMe), 2.16 (t, 2H, $J_{2',3'}$ 7.2 Hz, H-2′), 1.75−1.05 (m, 16H, H-3′, 4′, 5′, 6′, 7′, 8′, 9′, 10′); ^{13}C, δ 173.1, 170.1 (C-1, 1′), 82.2, 81.4, 79.7 (C-2, 3, 4), 60.7, 59.4, 59.0 (3 OMe), 39.2, 39.0, 36.6 (C-11′, 5, 2′), 29.1, 26.7, 25.5 (C-3′, 4′, 5′, 6′, 7′, 8′, 9′, 10′).

PX12. IR: ν_{max} 3317 (NH), 1664 (amide I), 1545 cm^{-1} (amide II). NMR data (CDCl$_3$): ^{1}H, δ 6.60 (bt, 1H, NH), 5.90 (bt, 1H, NH), 3.76 (d, 1H, $J_{2,3}$ 2.1 Hz, H-2), 3.65−3.15 (m, 6H, H-3, 4, 5a, 5b, 12′), 3.44, 3.42, 3.41 (3s, 9H, 3 OMe), 2.15 (t, 2H, $J_{2',3'}$ 7.6 Hz, H-2′), 1.75−1.20 (m, 18H, H-3′, 4′, 5′, 6′, 7′, 8′, 9′, 10′, 11′); ^{13}C, δ 173.2, 170.2 (C-1, 1′), 82.3, 81.5, 79.8 (C-2, 3, 4), 60.8, 59.4, 59.0 (3 OMe), 39.3, 39.1, 36.7 (C-12′, 5, 2′), 29.4, 29.2, 26.7, 25.6 (C-3′, 4′, 5′, 6′, 7′, 8′, 9′, 10′, 11′).

Results and Discussion

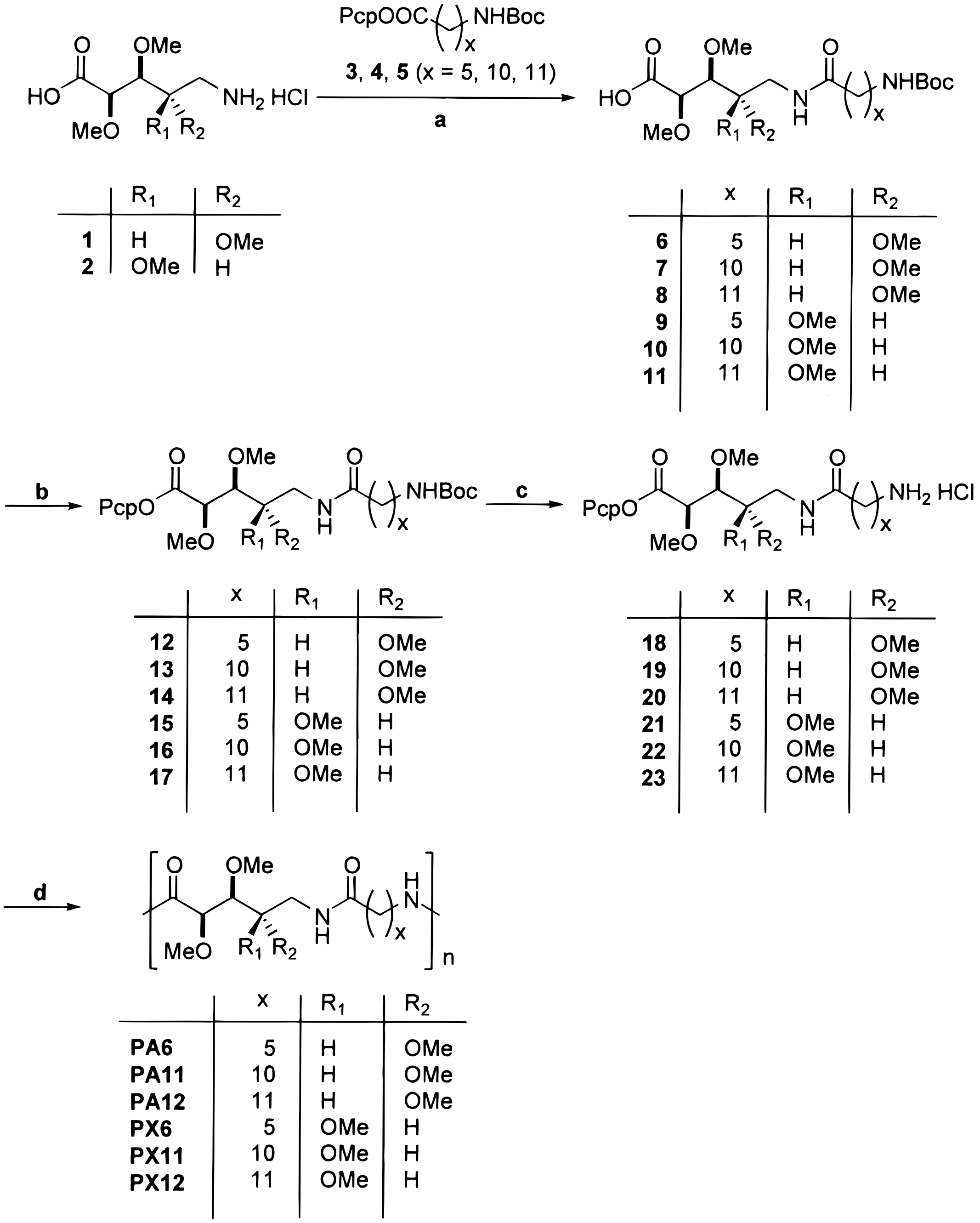
The synthesis of copolyamides PAn and PXn was carried out by applying the ester active polycondensation method which we had successfully applied in the preparation of other carbohydrate-based polyamides.[2] It was accomplished in four reaction steps: (1) condensation of the ω-aminoaldonic acid with the N-protected aliphatic ω-amino acid activated as pentachlorophenyl ester; (2) activation of the carboxyl group as pentachlorophenyl ester; (3) removal of the N-protecting group, and (4) polycondensation reaction (Scheme 1). Compounds **3**−**5** were prepared by reaction of the commercial ω-amino acids with di-*tert*-butyl dicarbonate and subsequent reaction of the *N-tert*-butoxycarbonyl derivatives with pentachlorophenol and dicyclohexylcar-

Table 5. Powder X-ray Spacings (nm) of Copolyamides PAn and PXn[a]

PA6	PX6	PA11	PX11	PA12	PX12
1.1 (m)	1.3 (w, dif)	1.5 (s)	1.5 (ms)	1.8 (ms)	1.8 (ms)
0.61 (vs)	0.65 (s)	0.69 (s)	0.71 (vs)	0.62 (s)	0.62 (m, dif)
0.51 (w)	0.58 (m)	0.55 (m)	0.58 (w)		
0.45 (vs)	0.46 (vs)	0.44 (vs)	0.45 (vs, dif)	0.45 (vs)	0.46 (vs, dif)
0.39 (m)	0.40 (m, dif)			0.38 (m, dif)	0.40 (m, dif)
0.35 (m)	0.36 (m)				

[a] Intensities visually estimated and denoted as vs = very strong, s = strong, m = medium, w = weak, and d = diffuse.

Scheme 1[a]



	R1	R2
1	H	OMe
2	OMe	H

	x	R1	R2
6	5	H	OMe
7	10	H	OMe
8	11	H	OMe
9	5	OMe	H
10	10	OMe	H
11	11	OMe	H

	x	R1	R2
12	5	H	OMe
13	10	H	OMe
14	11	H	OMe
15	5	OMe	H
16	10	OMe	H
17	11	OMe	H

	x	R1	R2
18	5	H	OMe
19	10	H	OMe
20	11	H	OMe
21	5	OMe	H
22	10	OMe	H
23	11	OMe	H

	x	R1	R2
PA6	5	H	OMe
PA11	10	H	OMe
PA12	11	H	OMe
PX6	5	OMe	H
PX11	10	OMe	H
PX12	11	OMe	H

[a] Reagents: (a) EDPA, DMF; (b) PcpOH/DCC, EtAcO; (c) HCl (g), EtAcO; (d) EDPA, NMP or HMPA.

bodiimide (DCC). Compounds **1** and **2** had been previously synthesized in our laboratory,[6] from L-arabinose and D-xylose, respectively. The condensation reaction of the ω-aminoaldonic acids (**1**, **2**) with compounds **3**−**5** was carried out in dimethylformamide using ethyldiisopropylamine (EDPA) as an acid acceptor. Subsequent esterification with pentachlorophenol and DCC gave the active esters **12**−**17**, which were isolated by column chromatography in good yield (~80%). Removal of the N-protecting group was easily accomplished with a solution of hydrogen chloride in anhydrous ethyl acetate to give the hydrochloride derivatives **18**−**23**. These are suitable compounds for the polycondensation reaction, as the carboxyl group is activated and the terminal amino group can be readily liberated under basic conditions; furthermore, the distance separating the reacting groups is longer enough to avoid intramolecular reaction.[4,5] Polycondensations were conducted at 45 °C in *N*-methyl-2-pyrrolidinone (NMP) or hexamethylphosphoramide (HMPA). Ethyldiisopropylamine (EDPA) was always added to the condensation medium as an acid acceptor. All the polyamides were purified by pouring a chloroformic solution of the polymer into ether, and the precipitated polymer was washed several times with acetone and ethanol. Results obtained in these polymerization reactions are displayed in Table 1.

The elemental analyses of the resulting polymers were consistent with their expected chemical constitutions provided that they contain a small amount of absorbed water. This is according to expectations given the hygroscopic character of these copolyamides. All the synthesized copolyamides are optically active. Specific rotatory powers measured in formic acid (Table 1) have similar values for isomeric copolyamides independent of the configuration of the sugar. On the other hand, a decrease of the value of the specific rotatory power is generally observed as the number of methylenes in the repeating unit increases. A less pronounced trend is observed, as can be expected, for the molar rotations (M_D). However, it should be taken into account that the hygroscopic character of these copolyamides may introduce some error in the determination of their rotatory powers. The fact that copolyamides obtained in HMPA systematically show lower [α] values than those obtained in NMP may be interpreted to be due to the higher content in absorbed water of the formers according to what is inferred from elemental analysis data (Table 1).

As is observed in Tables 1 and 2, *N*-methyl-2-pyrrolidinone appears to be a better solvent than hexamethylphosphoramide for carrying out these polycondensation reactions since higher yields and molecular weights were obtained in such solvent. The molecular weight distributions of these copolyamides were studied by gel permeation chromatography (GPC) using styragel columns and chloroform−*o*-chlorophenol (95:5 v/v) as the mobile phase. The obtained values for M_n and M_w are listed in Table 2. A steady increase in these parameters is observed with the number of methylenes in the repeating unit. Polydispersities appear to be unusually high for polymers prepared by the polycondensation method. This is due to the fact that most of the chromatograms presents long tails in the low molecular weight region. Nevertheless, a good correspondence is observed between GPC data and intrinsic viscosities. M_v values roughly estimated by using the Mark−Houwink parameters reported for nylon 6,6.[8] However, it must be said that the application of this viscosimetric equation in estimating the size of these copolyamides may be rather inadequate.

The ^{1}H and ^{13}C NMR data detailed in the Experimental Section were consistent with the chemical constitution anticipated for these polyamides. Figure 1 shows the NMR spectra of PX6 as a representative example. The infrared spectra also showed the characteristic absorption frequencies of the amide functions.

Qualitative solubilities[9] of copolyamides in various solvents are listed in Table 3. All copolyamides, irrespective of their constitution, may be easily dissolved at room temperature in hydrogen-bond-breaking solvents such as formic acid. No solubility at all was observed in nonaggressive oxygenated solvents such as acetone, ethyl acetate, or ether. The solubility in chloroform is worth mentioning since chiral polyamides adopting regular folded conformations stabilized by intramolecular hydrogen bonding are known to be readily soluble in this solvent.[10] All the copolyamides, except those derived from 6-aminohexanoic acid (PA6 and PX6), are not soluble in water. Nevertheless, they all still display a noticeable hydrophilicity due to the presence in the chain of the hydrophilic methoxyl groups. Table 3 also shows the moisture sorption of these copolyamides determined[7] at room temperature under a relative humidity of 100%.

The thermal behavior of copolyamides PAn and PXn was studied by differential scanning calorimetry. The thermal parameters measured in this study for the two sets of copolyamides are given in Table 4. In all cases, broad endotherms associated with melting appeared during the first heating cycle. In some cases two peaks were observed in these traces which is a common phenomenon in polyamides usually interpreted as due to the fusion of two populations of crystallites differing in size.[11] In general, exotherm peaks due to cold crystallization were found to precede the melting peaks. This indicates that copolyamides were not well crystallized upon precipitation. The cooling traces obtained after melting at slow cooling rates showed crystallization peaks for the whole PAn series but only for PX11 in the PXn series. When copolyamides were annealed at 10−20 °C below their respective melting points for a few hours, all of them produced traces consisting of a single peak at a temperature usually higher than those observed in the heating traces of the untreated samples. These traces are shown in Figure 2. The melting points (T_m) of copolyamides were taken as the maxima of the peaks appearing at the highest temperature regardless the thermal history of the sample. The occurrence of such rather well-defined melting peaks indicates the capability of both PAn and PXn to form well-formed crystallites in agreement with the stereorregular microstructure anticipated for these copolyamides.

Second-order thermal transitions (T_g) were observed for all the copolyamides in the heating traces obtained from samples that were quenched from the melt. The T_g values displayed by these polymers are found to be significantly higher than in conventional polyamides with a similar density of amide groups, indicating that the aminoaldonic moiety must restrict the mobility of the polymer chain. The T_g/T_m (K/K) values resulting for all of them lie within the 0.70−0.77 range, not very far from the 0.66 value defined by the Boyer−Beaman rule.

T_m and T_g of PAn and PXn are graphically compared in Figure 3. Although the number of examined systems in each series is too small to draw a definite conclusion from the plots, the comparison of the collected data provides insights worth mentioning. The trend displayed by T_g in both series is according to expectations with values steadily going down as *n* increases. The extremely good correlation found for T_g in both series gives confidence to the observed tendency. Obviously, the flexibility of the polyamide chain increases with the length of the polymethylene segment. The fact that T_g's are higher for the PAn series reveals a slightly greater flexibility for the polyamides with the xylo configuration. On the other hand, the trend observed for T_m is more complex and not easy to explain. The sudden fall observed for PX12 is really surprising as is also the fact

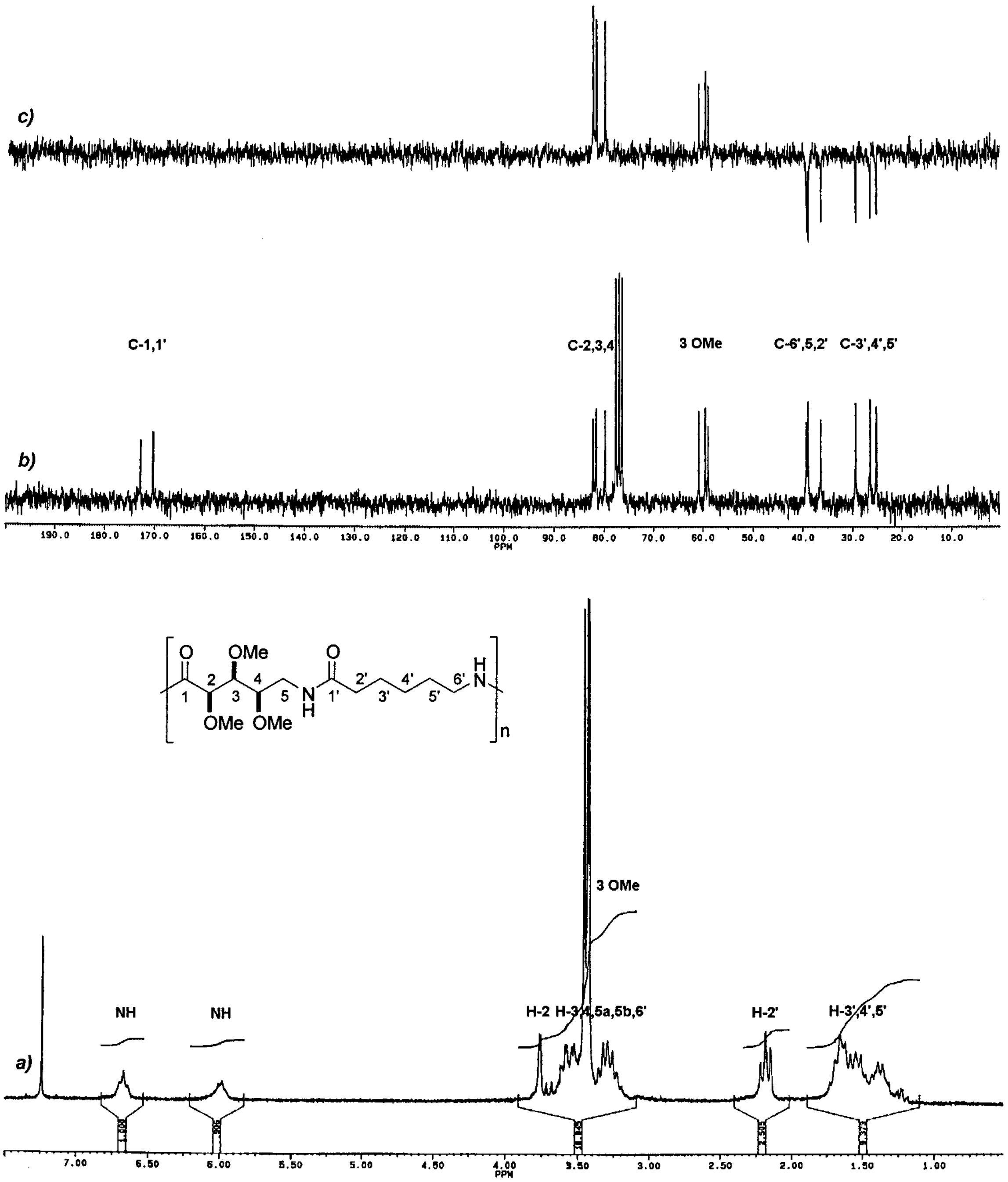


Figure 1. NMR spectra of PX6 ($CDCl_3$): (a) ^1H (200 MHz); (b) ^{13}C (50.3 MHz), BB; (c) ^{13}C (50.3 MHz), DEPT.

that the trend displayed by the PXn series is opposite to that observed for PAn's. As we will see below, such unexpected behavior does not seem to be due to structural reasons. It is clear in this case that further data for both higher and lower homologues within each series should be added to validate the observed trend and to help in the interpretation.

A preliminary exploration of the crystalline structure adopted by these copolyamides has been carried out by X-ray diffraction. Powdered samples coming directly from synthesis appeared to be crystalline giving well-outlined Debye–Sherrer diffraction patterns as that shown in Figure 4a for the representative case of PA12. It should be noted that rings in a larger number and displaying sharper definition were systematically observed for arabinonic acid deriving copolyamides, indicating that better crystallites may be formed when the sugar is in the arabino configuration. This is in agreement with the higher T_m displayed by the PAn copolyamides with respect to their PXn isomers. The most characteristic spacings observed in the powder patterns of the six examined copolyamides are listed in Table 5. It can be seen that the large spacing appearing between 1 and 2 nm, which is associated with the axial repeat of the structure, steadily increases with *n* as it should be expected from the chemical structure of the copolyamide. On the other hand, spacings around 0.6–0.7 and 0.44–0.46 nm, which are related to the side-by-side packing of the chains, appear to be largely independent of *n*.

Fiber patterns of similar characteristics were obtained from both PA12 and PX12, indicating no substantially structural differences between these two copolyamides. For illustration the pattern recorded from a fiber of

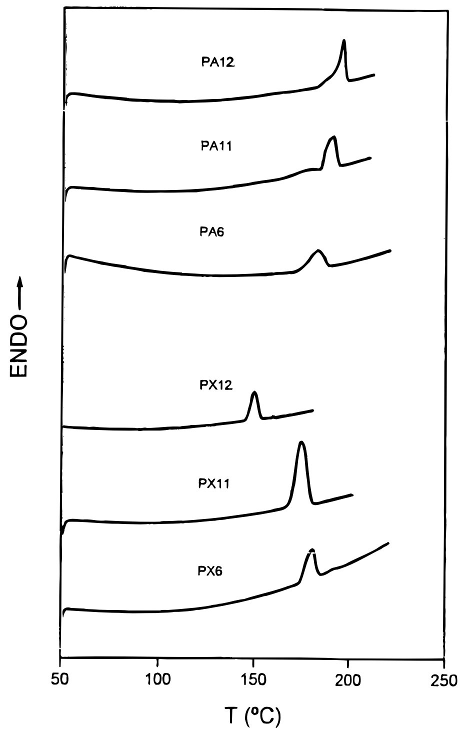


Figure 2. DSC traces of annealed PAn and PXn.

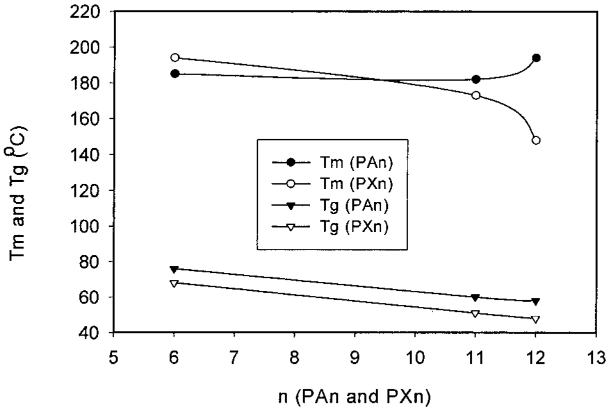


Figure 3. T_m and T_g of PAn and PXn as a function of *n*.

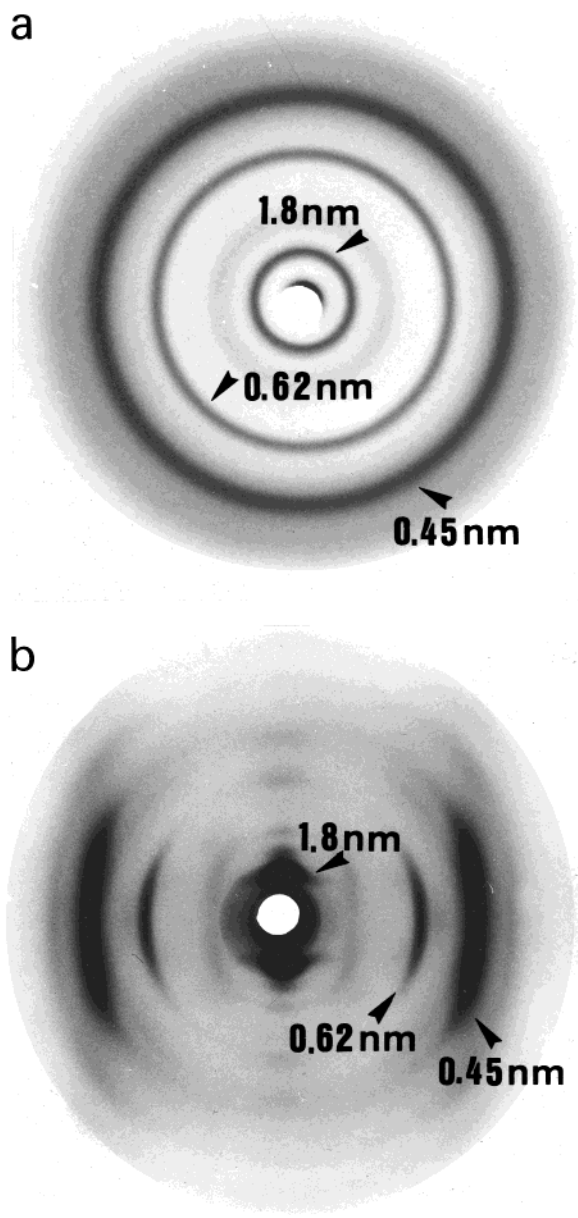


Figure 4. X-ray diffraction patterns of copolyamide PA12: (a) powder pattern; (b) fiber pattern (stretching direction is vertical).

PA12 prepared by stretching from the melt and then annealed at 130 °C overnight is shown in Figure 4b. The features displayed by this pattern are consistent with a structure in which the chains are in a folded conformation with the chemical repeating unit contracted about 0.5 nm with respect to its length in a fully extended conformation. Such a contraction turns to be considerably higher than the 0.2 nm observed in polyamides *n*,4 derived from tartaric acid.[13] In that case the distortion in the trajectory of the chain provoked by the tartaric $(CHOMe)_2$ moiety is apparently much less severe than in the present cases where three neighboring CHOMe units are in close interaction. By analogy with the 12-copolyamides, a shortening of the chain around 0.7 nm would result for the odd−odd pair PA11−PX11 revealing certain structural dissimilarities with the odd−even pair. Since no significant differences are noticed however between the two isomeric copolyamides in either of these two pairs, it can be provisionally concluded that the influence of the configuration of the sugar moiety on the crystalline structure is not relevant. It is not the case indeed of the pair PA6−PX6 in which differences in spacings between the two components are noticeable. It seems that large flexible polymethylene segments dilute the effect that the configuration of the sugar may exert on the conformation of the polyamide. This point deserves further investigation, which is currently under way.

Concluding Remarks

A series of alternating copolyamides based on δ-amino pentonic acids and ω-amino aliphatic acids of varying length have been synthesized for the first time. The active ester polycondensation method carried out in solution has been proved to be effective for the preparation of these compounds with acceptable molecular weights provided that the convenient solvent was used. These copolyamides distinguish in bearing three neighboring methoxy side groups in either the D-xilo or L-arabino configuration in every repeating unit of the polymer. This hydrophilic group alternates with a hydrophobic polymethylene segment of varying length according to the ω-amino acid of choice. Such a peculiar structure confers to these copolyamides a hygroscopicity considerably greater than that displayed by unsubstituted conventional polyamides without rendering them soluble in water as is known to be the case of polyamides entirely based on carbohydrate deriving monomers. These copolyamides being stereoregular polymers, they display optical activity in solution and readily crystallize in the solid state. They melt in the 150−190 °C range without apparent decomposition, a feature that makes them of interest for their potential ability to be processed by conventional techniques. The influence of the sugar moiety on the crystalline structure of these copolyamides is such that a folded conformation is adopted by all copolyamides. However, specifically structural differences arising from differences in the configuration of the sugar unit become only perceivable when the length of the polymethylene chain separating the sugar moieties along the polymer chain is not excessively large.

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References and Notes

(1) Orgueira, H. A.; Varela, O. *Tetrahedron: Asymmetry* **1997**, *8*, 1383.

(2) Bueno, M.; Zamora, F.; Molina, I.; Orgueira, H. A.; Varela, O.; Galbis, J. A. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 3645.

(3) Bou, J. J.; Rodríguez-Galán, A.; Muñoz-Guerra, S. *The Polymeric Materials Encyclopedia*; Salamone, E., Ed.; CRC Press: Boca Raton, FL, 1996; Vol. 1, p 561.

(4) Bueno, M.; Galbis, J. A.; García-Martín, M. G.; de Paz, M. V.; Zamora, F.; Muñoz-Guerra, S. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 299.

(5) Orgueira, H. A.; Bueno, M.; Funes, J. L.; Galbis, J. A.; Varela, O. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 2741.

(6) Zamora, F.; Bueno, M.; Molina, I.; Orgueira, H. A.; Varela, O.; Galbis, J. A. *Tetrahedron: Asymmetry* **1996**, *7*, 1811.

(7) Mori, T.; Tanaka, R.; Tanaka, T. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 1633.

(8) Bandrup, J.; Immergut, H. *Polymer Handbook;* Wiley: New York, 1989; Vol. VII, p 25.

(9) Braun, D.; Chedron, H.; Kern, W. *Praktikum der Makromolecularen Organischen Chemie*; Alfred Huthig Verlag: Heidelberg, Germany, 1966.

(10) Bou, J. J.; Rodríguez-Galán, A.; Muñoz-Guerra, S. *Macromolecules* **1993**, *26*, 5664.

(11) Bell, J. P.; Slade, D. E.; Dumblenton, J. H. *J. Polym. Sci., Polym. Phys. Ed.* **1968**, *6*, 1773.

(12) Van Krevelen, D. W. *Properties of Polymers*; Elsevier: Amsterdam, The Netherlands, 1990; p 166.

(13) Iribarren, I.; Alemán, C.; Bou, J. J.; Muñoz-Guerra, S. *Macromolecules* **1996**, *29*, 4397. Bou, J. J.; Rodríguez-Galán, A.; Muñoz-Guerra, S. *The Polymeric Materials Encyclopedia*; Salamone, E., Ed.; CRC Press: Boca Raton, FL, 1996; Vol. 1, p 561.

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