Synthesis and Characterization of New Stereoregular AABB-Type Polyamides from Carbohydrate-based Monomers Having D-*manno* and L-*ido* Configurations

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ABSTRACT: Polycondensation of 1,6-diamino-1,6-dideoxy-2,3,4,5-tetra-*O*-methyl-D-mannitol or 1,6-diamino-1,6-dideoxy-2,3,4,5-tetra-*O*-methyl-L-iditol with aromatic and aliphatic dicarboxylic acids has been used to prepare a series of regio- and stereoregular AABB-type polyamides. We also describe the preparation of 1,6-diamino-1,6-dideoxy-3,4-*O*-isopropylidene-D-mannitol and 1,6-diamino-1,6-dideoxy-2,5-di-*O*-methyl-3,4-*O*-isopropylidene-D-mannitol and their polycondensation reactions with the same dicarboxylic acids. The obtained polyamides were gummy solids that were optically active and had a pronounced affinity for water, although most of them were not soluble in this solvent. These polyamides were characterized by viscosimetry, gel-permeation chromatography, elemental analysis, and IR and NMR spectroscopies.

Introduction

Polyamides are polymers widely recognized for their excellent mechanical properties. They are generaly very stable in aqueous medium because of the high resistance of the amide groups to hydrolysis.[1]

In recent years, sustained efforts have been devoted to rendering polyamides more hydrophilic and degradable, to extend their applications to new fields demanding materials either with lower environmental impact or displaying biodegradable and biocompatible properties.[2] The use of monomers derived from carbohydrates in the design of polyamides with enhanced hydrophilicity and biodegradability constitutes an interesting strategy that is being intensively explored.[3−5] Recently, we have reported on several types of polyamide derived from naturally occurring carbohydrates such as D-glucose, D-xylose, L-arabinose,[6] and L-tartaric acid.[7] These polyamides bear alkoxy side groups attached to the main chain, making them more hydrophilic and susceptible to water attack than are conventional nylons. In these polymers, 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.[6]

In the present paper we describe the synthesis and properties of a series of stereo- and regioregular polyamides containing monosaccharide residues, by polycondensation of 1,6-diamino-1,6-dideoxy-2,3,4,5-tetra-*O*-methyl-D-mannitol (**5**) or 1,6-diamino-1,6-dideoxy-2,3,4,5-tetra-*O*-methyl-L-iditol (**6**) with activated aromatic and aliphatic dicarboxylic acids. We also describe the preparation of 1,6-diamino-1,6-dideoxy-3,4-*O*-isopropylidene-D-mannitol (**3**) and 1,6-diamino-1,6-dideoxy-2,5-di-*O*-methyl-3,4-*O*-isopropylidene-D-mannitol (**4**) and their polycondensation reactions with the same dicarboxylic acids.

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Experimental Section

General Methods. All chemicals were used as purchased from the Aldrich Chemical Co. Solvents were dried and purified, when necessary, by appropriate standard procedures. Melting points are uncorrected. Optical rotations were measured at 20 ± 5 °C (1 cm cell). TLC was performed on Silica Gel 60 F_{254} (E. Merck) with detection by UV light or charring with H_2SO_4. Flash-column chromatography was performed using Silica Gel 60 (230−400 mesh, E. Merck). Elemental analyses were determined in the Microanalysis Laboratories of the CSIC, Isla de la Cartuja, Seville, Spain. FTIR spectra were obtained from films or KBr disks. For NMR spectra, chemical shifts are reported as parts per million downfield from Me_4Si. Intrinsic viscosity measurements were carried out in chloroform or *m*-cresol with a Cannon-Ubbelohde 100/L30 semimicroviscometer at 25.0 ± 0.1 °C. Gel-permeation chromatography (GPC) analyses were carried with two Styragel HR columns (7.8 × 300 mm) placed in series, using chloroform or chloroform-*o*-chlorophenol (95:5 v/v) as the mobile phase at a flow rate of 1 mL/min. Molecular weights were estimated against polystyrene standards.

1,6-Diamino-1,6-dideoxy-3,4-*O*-isopropylidene-D-mannitol (3). To a solution of **1**[12,13] (272 mg, 1 mmol) in MeOH (10 mL) was added 10% Pd−C (29 mg), and the mixture was treated with H_2 (40 psi) for 4 h. The catalyst was filtered off and washed with MeOH, and the filtrate was concentrated to give an oil (209 mg, 95%); $[\alpha]_D$ +22° (*c* 1, $CHCl_3$). IR: ν 3400 (NH_2), 3350 cm^{-1}(OH). ^1H NMR ($CDCl_3$, 200 MHz): δ 1.30 (s, 6 H, Me_2C), 1.60 (bs, 4 H, 2 NH_2), 3.35−3.90 (m, 6 H, H-1/6, H-1′/6′, H-2/5, H-3/4, 2 OH). ^{13}C NMR (50 MHz): δ 26.5 (Me_2C), 40.1 (C-1/6), 71.9 (C-2/5), 79.8 (C-3/4), 109.6 (CMe_2). Anal. Calcd for $C_9H_{20}O_4N_2 \cdot 0.3H_2O$: C, 47.90; H, 9.20; N, 12.41. Found: C, 48.25; H, 9.27; N, 12.12.

1,6-Diamino-1,6-dideoxy-3,4-*O*-isopropylidene-2,5-di-O-methyl-D-mannitol (4). This was prepared from **2**[8] (300 mg, 1 mmol) as described for **3**. Compound **4** was obtained as an oil (230 mg, 92%); $[\alpha]_D$ +30° (*c* 1, $CHCl_3$). IR: ν 3400 cm^{-1} (NH_2). ^1H NMR ($CDCl_3$, 200 MHz): δ 1.25 (s, 6 H, Me_2C), 1.98 (bs, 4 H, 2 NH_2), 3.10−3.40 (m, 6 H, H-1/6, H-1′/6′, H-2/5), 3.30 (s, 6 H, OMe-2/5), 3.90−4.00 (m, 2 H, H-3/4). ^{13}C NMR (50 MHz): δ 26.9 (Me_2C), 40.5 (C-1/6), 57.6 (OMe-2/5), 77.9 (C-2/5), 82.9 (C-3/4), 109.4 (CMe_2). Anal. Calcd for $C_{11}H_{24}O_4N_2 \cdot 0.2H_2O$: C, 52.44; H, 9.76; N, 11.12. Found: C, 52.11; H, 9.80; N, 10.84.

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Poly(1,6-dideoxy-2,3,4,5-tetra-*O*-methyl-D-mannitol-terephthalamide) (9). To a stirred solution of **5**[8] (236 mg, 1 mmol) and sodium carbonate (212 mg, 2 mmol) in water (10 mL), at room temperature was added a solution of terephthaloyl dichloride (**10**, 203 mg, 1 mmol) in diisopropyl ether (10 mL). After 3 h, the reaction mixture was extracted with dichloromethane, and the combined organic extracts were concentrated under diminished pressure until reaching a small volume (2 mL). The polyamide was precipitated by pouring the solution into ethyl ether, filtered, washed successively with water, methanol, acetone and ether, and finally dried under high vacuum at 40 °C for a few days. Compound **9** was obtained as a white powder (121 mg, 33%): $[\alpha]_D$ −14° (*c* 1, DMSO); M_v 1100. IR: ν 1644 (amide I), 1540 cm^{-1} (amide II). ^1H NMR ($CDCl_3$, 200 MHz): δ 3.26−3.66 (m, 20 H, OMe, H-1/6, H-1′/6′, H-2/5, H-3/4), 7.92−8.25 (m, 4H, C_6H_4), 8.64 (bs, 2H, 2 NH). ^{13}C NMR (50 MHz): δ 39.9 (C-1/6), 57.3 (OMe-2/5), 60.1 (OMe-3/4), 79.6 (C-3/4), 80.7 (C-2/5), 127.3 (C_6H_4), 136.7 (C_6H_4), 165.9 (2 CO). Anal. Calcd for $C_{18}H_{26}O_6N_2 \cdot 0.7H_2O$: C, 57.04; H, 7.29; N, 7.39. Found: C, 56.94; H, 7.01; N, 7.18.

Poly(1,6-dideoxy-2,3,4,5-tetra-*O*-methyl-D-mannitol-succinimide) (13). (a) Interfacial Polycondensation. This was prepared from **5** (236 mg, 1 mmol) and succinoyl dichloride (**11a**, 155 mg, 1 mmol) as described for **9**. Compound **13** was obtained as a white amorphous powder (254 mg, 80%): $[\alpha]_D$ −26° (*c* 1, HCOOH); M_v 260, M_w 1400, and M_w/M_n 1.34. Anal. Calcd for $C_{14}H_{26}O_6N_2 \cdot 3H_2O$: C, 45.15; H, 8.66; N, 7.52. Found: C, 44.93; H, 8.95; N, 6.98.

(b) Solution Polycondensation. To a stirred solution of **7**[8] (100 mg, 0.32 mmol) in dried CH_2Cl_2 (1 mL) at room temperature were added bis (pentachlorophenyl) succinate[14] (**12a**, 197 mg, 0.32 mmol) and *N*-ethyl-*N*,*N*-diisopropylamine (EDPA, 0.22 mL, 1.28 mmol). The solution was heated to 40 °C and left at this temperature for 6 days while stirring. The reaction mixture was added dropwise to diethyl ether (200 mL) with stirring, and the polymer formed was recovered as a syrup. It was purified by dissolving in CH_2Cl_2 and pouring the solution into ether repeatedly (62 mg, 60%): $[\alpha]_D$ −18° (*c* 0.5, $CHCl_3$); M_v 60, M_w 1200, and M_w/M_n 1.12. Anal. Calcd for $C_{14}H_{26}O_6N_2 \cdot 1.5H_2O$: C, 48.68; H, 8.46; N, 8.11. Found: C, 48.91; H, 8.19; N, 8.52.

Spectroscopic Data for Methods a and b. IR: ν 1650 (amide I), 1555 cm^{-1} (amide II). ^1H NMR ($CDCl_3$, 200 MHz): δ 2.53 (s, 4 H, 2 CH_2), 3.35−3.50 (m, 20 H, 4 OMe, H-1/6, H-1′/6′, H-2/5, H-3/4), 6.39 (bs, 2H, 2 NH). ^{13}C NMR (50 MHz): δ 31.4 (2 CH_2), 37.4 (C-1/6), 56.7 (OMe-2/5), 60.7 (OMe-3/4), 78.5 (C-3/4), 79.6 (C-2/5), 172.4 (2 CO).

Poly(1,6-dideoxy-2,3,4,5-tetra-*O*-methyl-D-mannitol-adipamide) (14). (a) Interfacial Polycondensation. This was prepared from **5** (236 mg, 1 mmol) and adipoyl dichloride (**11b**, 183 mg, 1 mmol) as described for **9**. Compound **14** was obtained as a yellow amorphous powder (270 mg, 78%): $[\alpha]_D$ −2° (*c* 1, HCOOH); M_v 260, M_w 1500, and M_w/M_n 1.67. Anal. Calcd for $C_{16}H_{30}O_6N_2 \cdot 2.5H_2O$: C, 49.09; H, 9.00; N, 7.16. Found: C, 48.96; H, 8.40; N, 6.79.

(b) Solution Polycondensation. This was prepared from **7** (100 mg, 0.32 mmol) and bis(pentachlorophenyl) adipate[14] (**12b,** 206 mg, 0.32 mmol) as described for **13**. Compound **14** was obtained as a gummy noncrystalline solid (86 mg, 77%): $[\alpha]_D$ −22° (*c* 0.5, $CHCl_3$); M_v 200, M_w 6700, and M_w/M_n 1.16. Anal. Calcd for $C_{16}H_{30}O_6N_2 \cdot 0.5H_2O$: C, 54.07; H, 8.79; N, 7.88. Found: C, 53.72; H, 9.01; N, 7.63.

Spectroscopic Data for Methods a and b. IR: ν 1646 (amide I), 1555 cm^{-1} (amide II). ^1H NMR ($CDCl_3$, 200 MHz): δ 1.64 (m, 4 H, 2 CH_2), 2.25 (m, 4 H, 2 CH_2), 3.25−3.60 (m, 20 H, 4 OMe, H-1/6, H-1′/6′, H-2/5, H-3/4), 6.26 (bs, 2H, 2 NH). ^{13}C NMR (50 MHz): δ 24.3 (2 CH_2), 35.7 (2 CH_2), 37.3 (C-1/6), 56.5 (OMe-2/5), 60.5 (OMe-3/4), 78.6 (C-3/4), 79.5 (C-2/5), 172.3 (2 CO).

Poly(1,6-dideoxy-2,3,4,5-tetra-*O*-methyl-D-mannitol-suberamide) (15). (a) Interfacial Polycondensation. This was prepared from **5** (236 mg, 1 mmol) and suberoyl dichloride (**11c**, 211 mg, 1 mmol) as described for **9**. Compound **15** was obtained as a yellow amorphous powder (280 mg, 75%): $[\alpha]_D$ −20° (*c* 1, HCOOH); M_v 320, M_w 7000, and M_w/M_n 1.69. Anal. Calcd for $C_{18}H_{34}O_6N_2 \cdot 3H_2O$: C, 50.45; H, 9.40; N, 6.53. Found: C, 50.83; H, 8.74; N, 6.61.

(b) Solution Polycondensation. This was prepared from **7** (100 mg, 0.32 mmol) and bis(pentachlorophenyl) suberate[14] (**12c**, 215 mg, 0.32 mmol) as described for **13**. Compound **15** was obtained as a gummy noncrystalline solid (85 mg, 70%): $[\alpha]_D$ −26° (*c* 1, $CHCl_3$); M_v 760, M_w 8700, and M_w/M_n 1.41. Anal. Calcd for $C_{18}H_{34}O_6N_2 \cdot 0.8H_2O$: C, 55.59; H, 9.22; N, 7.20. Found: C, 55.91; H, 8.56; N, 7.37.

Spectroscopic Data for Methods a and b. IR: ν 1646 (amide I), 1548 cm^{-1} (amide II). ^1H NMR ($CDCl_3$, 200 MHz): δ 1.27−2.17 (m, 12 H, 6 CH_2), 3.33−3.45 (m, 20 H, 4 OMe, H-1/6, H-1′/6′, H-2/5, H-3/4), 6.02 (bs, 2H, 2 NH). ^{13}C NMR (50 MHz): δ 25.4 (2 CH_2), 28.5 (2 CH_2), 36.5 (2 CH_2), 37.3 (C-1/6), 56.7 (OMe-2/5), 60.9 (OMe-3/4), 78.6 (C-3/4), 79.8 (C-2/5), 173.1 (2 CO).

Poly(1,6-dideoxy-2,3,4,5-tetra-*O*-methyl-D-mannitol-sebacamide) (16). (a) Interfacial Polycondensation. This was prepared from **5** (236 mg, 1 mmol) and sebacoyl dichloride (**11d**, 239 mg, 1 mmol) as described for **9**. Compound **16** was obtained as a yellow amorphous powder (201 mg, 50%); $[\alpha]_D$ −21° (*c* 1, HCOOH); M_v 1200, M_w 14200, and M_w/M_n 1.37. Anal. Calcd for $C_{20}H_{38}O_6N_2 \cdot H_2O$: C, 57.12; H, 9.58; N, 6.66. Found: C, 56.96; H, 9.10; N, 6.35.

(b) Solution Polycondensation. This was prepared from **7** (100 mg, 0.32 mmol) and bis(pentachlorophenyl) sebacate[14] (**12d**, 224 mg, 0.32 mmol) as described for **13**. Compound **16** was obtained as a gummy noncrystalline solid (114 mg, 88%): $[\alpha]_D$ −26° (*c* 0.5, $CHCl_3$); M_v 2200, M_w 23900, and M_w/M_n 1.44. Anal. Calcd for $C_{20}H_{38}O_6N_2 \cdot 0.7H_2O$: C, 57.86; H, 9.57; N, 6.75. Found: C, 57.66; H, 9.25; N, 6.45.

Spectroscopic Data for Methods a and b. IR: ν 1647 (amide I), 1544 cm^{-1} (amide II). ^1H NMR ($CDCl_3$, 200 MHz): δ 1.20 (m, 8 H, 4 CH_2), 1.56 (m, 4 H, 2 CH_2), 2.10 (m, 4 H, 2 CH_2), 3.20−3.90 (m, 20 H, 4 OMe, H-1/6, H-1′/6′, H-2/5, H-3/4), 6.00 (bs, 2H, 2 NH). ^{13}C NMR (50 MHz): δ 25.6 (2 CH_2), 29.0 (2 CH_2), 29.2 (2 CH_2), 36.6 (2 CH_2), 37.3 (C-1/6), 56.4 (OMe-2/5), 60.9 (OMe-3/4), 78.7 (C-3/4), 80.0 (C-2/5), 173.2 (2 CO).

Poly(1,6-dideoxy-2,3,4,5-tetra-O-methyl-D-mannitoldodecanediamide) (17). (a) Interfacial Polycondensation. This was prepared from **5** (236 mg, 1 mmol) and dodecanedioyl dichloride (**11e**, 267 mg, 1 mmol) as described for **9**. Compound **17** was obtained as a yellow amorphous powder (189 mg, 44%): $[\alpha]_D$ −34° (*c* 1, HCOOH); M_v 1300, M_w 9600, and M_w/M_n 2.01. Anal. Calcd for $C_{22}H_{42}O_6N_2 \cdot H_2O$: C, 58.90; H, 9.88; N, 6.24. Found: C, 58.55; H, 9.25; N, 5.70.

(b) Solution Polycondensation. This was prepared from **7** (100 mg, 0.32 mmol) and bis(pentachlorophenyl) dodecanedioate[14] (**12e**, 232 mg, 0.32 mmol) as described for **13**. Compound **17** was obtained as a syrup (95 mg, 68%): $[\alpha]_D$ −15° (*c* 1, $CHCl_3$); M_v 400, M_w 5000, and M_w/M_n 1.28. Anal. Calcd for $C_{22}H_{42}O_6N_2 \cdot 0.5H_2O$: C, 60.11; H, 9.86; N, 6.37. Found: C, 60.44; H, 9.41; N, 6.69.

Spectroscopic Data for Methods a and b. IR: ν 1647 (amide I), 1549 cm^{-1} (amide II). ^1H NMR ($CDCl_3$, 200 MHz): δ 1.19−2.15 (m, 20 H, 10 CH_2), 3.32−3.64 (m, 20 H, 4 OMe, H-1/6, H-1′/6′, H-2/5, H-3/4), 5.93 (bs, 2H, 2 NH). ^{13}C NMR (50 MHz): δ 25.6 (2 CH_2), 29.1 (2 CH_2), 29.2 (4 CH_2), 36.6 (2 CH_2), 37.4 (C-1/6), 55.6 (OMe-2/5), 60.9 (OMe-3/4), 78.6 (C-3/4), 79.9 (C-2/5), 173.3 (2 CO).

Poly(1,6-dideoxy-2,3,4,5-tetra-*O*-methyl-L-iditolsuccinimide) (18). To a stirred solution of **8**[8] (100 mg, 0.32 mmol) in dried $CHCl_3$ (1 mL) at room temperature were added bis-(pentachlorophenyl) succinate[14] (**12a**, 197 mg, 0.32 mmol) and *N*-ethyl-*N*,*N*-diisopropylamine (EDPA, 0.22 mL, 1.28 mmol). The solution was heated to 50 °C and left at this temperature for 7 days under stirring. The reaction mixture was added dropwise to diethyl ether (200 mL) with stirring, and the polymer formed was recovered from the reaction mixture as a syrup. It was purified by dissolving in CH_2Cl_2 and pouring the solution into ether repeatedly (54 mg, 52%): $[\alpha]_D$ −50° (*c* 0.5, $CHCl_3$); M_v 400, M_w 1000, and M_w/M_n 1.05; IR: ν 1650 (amide I), 1555 cm^{-1} (amide II). ^1H NMR ($CDCl_3$, 200 MHz): δ 2.54−2.70 (m, 4 H, 2 CH_2), 3.25−3.70 (m, 20 H, 4 OMe, H-1/6, H-1′/

6′, H-2/5, H-3/4), 6.60 (bs, 2H, 2 NH). ^{13}C NMR (50 MHz): δ 28.1 (2 CH_2), 38.6 (C-1/6), 58.1 (OMe-2/5), 60.4 (OMe-3/4), 79.0 (C-3/4), 80.4 (C-2/5), 172.8 (2 CO). Anal. Calcd for $C_{14}H_{26}O_6N_2 \cdot 2H_2O$: C, 47.45; H, 8.53; N, 7.90. Found: C, 47.79; H, 8.57; N, 8.00.

Poly(1,6-dideoxy-2,3,4,5-tetra-*O*-methyl-L-iditoladipamide) (19). This was prepared from **8** (300 mg, 0.97 mmol) and bis(pentachlorophenyl) adipate[14] (**12b**, 623 mg, 0.97 mmol) as described for **18**. Compound **19** was obtained as a syrup (190 mg, 56%): $[\alpha]_D$ −42° (*c* 0.5, $CHCl_3$); M_v 650, M_w 2800, and M_w/M_n 1.21; IR: ν 1646 (amide I), 1555 cm^{-1} (amide II). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.58−2.64 (m, 8 H, 4 CH_2), 3.33−3.43 (m, 20 H, 4 OMe, H-1/6, H-1′/6′, H-2/5, H-3/4), 6.61 (bs, 2H, 2 NH). ^{13}C NMR (50 MHz): δ 24.9 (2 CH_2), 35.8 (2 CH_2), 38.7 (C-1/6), 58.0 (OMe-2/5), 60.1 (OMe-3/4), 78.6 (C-3/4), 80.4 (C-2/5), 173.0 (2 CO). Anal. Calcd for $C_{16}H_{30}O_6N_2 \cdot H_2O$: C, 52.73; H, 8.85; N, 7.69. Found: C, 52.29; H, 8.64; N, 7.93.

Poly(1,6-dideoxy-2,3,4,5-tetra-*O*-methyl-L-iditolsuberamide) (20). This was prepared from **8** (300 mg, 0.97 mmol) and bis(pentachlorophenyl) suberate[14] (**12c**, 651 mg, 0.97 mmol) as described for **18**. Compound **20** was obtained as a syrup (210 mg, 58%): $[\alpha]_D$ −30° (*c* 1, $CHCl_3$); M_v 260, M_w 3300, and M_w/M_n 1.28; IR: ν 1637 (amide I), 1544 cm^{-1} (amide II). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.26−2.15 (m, 12 H, 6 CH_2), 3.25−3.45 (m, 20 H, 4 OMe, H-1/6, H-1′/6′, H-2/5, H-3/4), 6.27 (bs, 2H, 2 NH). ^{13}C NMR (50 MHz): δ 25.4 (2 CH_2), 28.7 (2 CH_2), 36.4 (2 CH_2), 38.8 (C-1/6), 58.1 (OMe-2/5), 60.1 (OMe-3/4), 78.5 (C-3/4), 80.6 (C-2/5), 173.4 (2 CO). Anal. Calcd for $C_{18}H_{34}O_6N_2 \cdot 2H_2O$: C, 52.66; H, 9.33; N, 6.82. Found: C, 52.98; H, 9.15; N, 6.50.

Poly(1,6-dideoxy-2,3,4,5-tetra-*O*-methyl-L-iditolsebac-amide) (21). This was prepared from **8** (100 mg, 0.32 mmol) and bis(pentachlorophenyl) sebacate[14] (**12d**, 224 mg, 0.32 mmol) as described for **18**. Compound **21** was obtained as a syrup (95 mg, 73%): $[\alpha]_D$ −24° (*c* 0.5, $CHCl_3$); M_v 960, M_w 12600, and M_w/M_n 1.85; IR: ν 1647 (amide I), 1544 cm^{-1} (amide II). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.22−2.16 (m, 16 H, 8 CH_2), 3.19−3.61 (m, 20 H, 4 OMe, H-1/6, H-1′/6′, H-2/5, H-3/4), 6.25 (bs, 2H, 2 NH). ^{13}C NMR (50 MHz): δ 25.6 (2 CH_2), 29.1 (4 CH_2), 36.5 (2 CH_2), 38.8 (C-1/6), 58.1 (OMe-2/5), 60.1 (OMe-3/4), 78.6 (C-3/4), 80.7 (C-2/5), 173.4 (2 CO). Anal. Calcd for $C_{20}H_{38}O_6N_2 \cdot 2H_2O$: C, 54.77; H, 9.65; N, 6.39. Found: C, 54.34; H, 9.82; N, 6.63.

Poly(1,6-dideoxy-2,3,4,5-tetra-*O*-methyl-L-iditoldodecanediamide) (22). (a) Interfacial Polycondensation. This was prepared from **6**[8] (480 mg, 2.03 mmol) and dodecanedioyl dichloride (**11e**, 542 mg, 2.03 mmol) as described for **9**. Compound **22** was obtained as a syrup (575 mg, 66%): $[\alpha]_D$ −38° (*c* 1, $CHCl_3$); M_v 470, M_w 5700, and M_w/M_n 1.47. Anal. Calcd for $C_{22}H_{42}O_6N_2 \cdot 1.5H_2O$: C, 57.74; H, 9.91; N, 6.12. Found: C, 57.87; H, 9.34; N, 5.95.

(b) Solution Polycondensation. This was prepared from **8** (200 mg, 0.65 mmol) and bis(pentachlorophenyl) dodecanedioate[14] (**12e**, 472 mg, 0.65 mmol) as described for **18**. Compound **22** was obtained as a syrup (170 mg, 61%): $[\alpha]_D$ −46° (*c* 1, $CHCl_3$); M_v 320, M_w 4600, and M_w/M_n 1.33. Anal. Calcd for $C_{22}H_{42}O_6N_2 \cdot H_2O$: C, 58.90; H, 9.89; N, 6.24. Found: C, 58.46; H, 9.43; N, 5.96.

Spectroscopic Data for Methods a and b. IR: ν 1637 (amide I), 1543 cm^{-1} (amide II). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.21−2.18 (m, 20 H, 10 CH_2), 3.11−3.46 (m, 20 H, 4 OMe, H-1/6, H-1′/6′, H-2/5, H-3/4), 6.27 (bs, 2H, 2 NH). ^{13}C NMR (50 MHz): δ 25.6 (2 CH_2), 29.2 (6 CH_2), 36.6 (2 CH_2), 38.9 (C-1/6), 58.1 (OMe-2/5), 60.2 (OMe-3/4), 78.6 (C-3/4), 80.8 (C-2/5), 173.6 (2 CO).

Poly(1,6-dideoxy-3,4-*O*-isopropylidene-D-mannitolterephthalamide) (23). This was prepared from **3** (1 g, 4.5 mmol) and terephthaloyl dichloride (**10**, 922 mg, 4.5 mmol) as described for **9**. Compound **23** was obtained as a white amorphous powder (1.38 g, 86%); M_v 260. IR: ν 1650 (amide I), 1555 cm^{-1} (amide II). ^{1}H NMR (DMSO, 200 MHz): δ 1.34 (s, 6 H, Me_2C), 3.18−4.37 (m, 8 H, H-1/6, H-1′/6′, H-2/5, H-3/4), 5.52 (bs, 2 H, 2 OH), 7.90−8.05 (m, 4H, C_6H_4), 8.66 (bs, 2H, 2 NH). ^{13}C NMR (50 MHz): δ 27.5 (Me_2C), 43.4 (C-1/6), 70.4 (C-3/4), 80.5 (C-2/5), 108.8 (*C*Me_2), 128.1 (C_6H_4), 134.5−136.6 (C_6H_4), 165.9 (2 CO). Anal. Calcd for $C_{17}H_{22}O_6N_2 \cdot 3H_2O$: C, 50.48; H, 5.48; N, 6.92. Found: C, 49.87; H, 5.20; N, 6.49.

Poly(1,6-dideoxy-3,4-*O*-isopropylidene-D-mannitolsuccinimide) (24). This was prepared from **3** (850 mg, 3.8 mmol) and succinoyl dichloride (**11a**, 598 mg, 3.8 mmol) as described for **9**. Compound **24** was obtained as a white amorphous powder (1.21 g, 98%): $[\alpha]_D$ −88° (*c* 1, HCOOH); M_v 850. IR: ν 1650 (amide I), 1560 cm^{-1} (amide II). ^{1}H NMR (DMSO, 200 MHz): δ 1.28 (s, 6 H, Me_2C), 2.24−2.38 (m, 4 H, 2 CH_2), 3.31−3.80 (m, 8 H, H-1/6, H-1′/6′, H-2/5, H-3/4), 4.30 (bs, 2 H, 2 OH), 7.93 (bs, 2H, 2 NH). ^{13}C NMR (50 MHz): δ 27.3 (Me_2C), 30.7 (2 CH_2), 42.4 (C-1/6), 70.6 (C-3/4), 80.2 (C-2/5), 108.6 (*C*Me_2), 171.8 (2 CO). Anal. Calcd for $C_{13}H_{22}O_6N_2 \cdot 0.9H_2O$: C, 49.01; H, 7.53; N, 8.79. Found: C, 48.89; H, 7.25; N, 8.47.

Poly(1,6-dideoxy-3,4-*O*-isopropylidene-D-mannitoladipamide) (25). This was prepared from **3** (1 g, 4.5 mmol) and adipoyl dichloride (**11b**, 830 mg, 4.5 mmol) as described for **9**. Compound **25** was obtained as a yellow amorphous powder (1.39 g, 93%): $[\alpha]_D$ −32° (*c* 1, HCOOH); M_v 750. IR: ν 1648 (amide I), 1560 cm^{-1} (amide II). ^{1}H NMR (DMSO, 200 MHz): δ 1.25 (s, 6 H, Me_2C), 1.50 (m, 4 H, 2 CH_2), 2.15 (m, 4 H, 2 CH_2), 3.00−3.90 (m, 8 H, H-1/6, H-1′/6′, H-2/5, H-3/4), 5.20 (bs, 2 H, 2 OH), 7.70 (bs, 2H, 2 NH). ^{13}C NMR (50 MHz): δ 24.2 (2 CH_2), 27.3 (Me_2C), 33.6 (2 CH_2), 42.4 (C-1/6), 70.6 (C-3/4), 80.1 (C-2/5), 108.6 (*C*Me_2), 172.5 (2 CO). Anal. Calcd for $C_{15}H_{26}O_6N_2 \cdot 0.8H_2O$: C, 52.25; H, 8.06; N, 8.12. Found: C, 51.96; H, 7.91; N, 8.07.

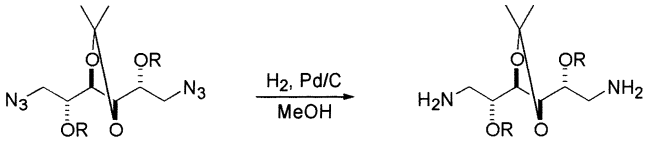
Poly(1,6-dideoxy-3,4-*O*-isopropylidene-D-mannitolsuberamide) (26). This was prepared from **3** (1.03 g, 4.6 mmol) and suberoyl dichloride (**11c**, 987 mg, 4.6 mmol) as described for **9**. Compound **26** was obtained as a yellow amorphous powder (600 mg, 36%): $[\alpha]_D$ −2° (*c* 1, HCOOH); M_v 1100. IR: ν 1644 (amide I), 1541 cm^{-1} (amide II). ^{1}H NMR (DMSO, 200 MHz): δ 1.23 (m, 4 H, 2CH_2), 1.28 (s, 6 H, Me_2C), 1.46 (m, 4 H, 2 CH_2), 2.03−2.20 (m, 4 H, 2 CH_2), 2.92−3.78 (m, 8 H, H-1/6, H-1′/6′, H-2/5, H-3/4), 5.26 (bs, 2 H, 2 OH), 7.72 (bs, 2H, 2 NH). ^{13}C NMR (50 MHz): δ 24.3 (2 CH_2), 27.3 (Me_2C), 28.2 (2 CH_2), 33.6 (2 CH_2), 42.3 (C-1/6), 70.7 (C-3/4), 80.1 (C-2/5), 108.6 (*C*Me_2), 172.7 (2 CO). Anal. Calcd for $C_{17}H_{30}O_6N_2 \cdot 0.9H_2O$: C, 54.49; H, 8.34; N, 7.47. Found: C, 54.47; H, 8.20; N, 7.39.

Poly(1,6-dideoxy-3,4-*O*-isopropylidene-D-mannitolsebacamide) (27). This was prepared from **3** (1 g, 4.5 mmol) and sebacoyl dichloride (**11d**, 1.1 g, 4.5 mmol) as described for **9**. Compound **27** was obtained as a yellow amorphous powder (1 g, 58%): $[\alpha]_D$ −4° (*c* 1, HCOOH); M_v 560. IR: ν 1644 (amide I), 1549 cm^{-1} (amide II). ^{1}H NMR (DMSO, 200 MHz): δ 1.20 (m, 8 H, 4CH_2), 1.30 (s, 6 H, Me_2C), 1.50 (m, 4 H, 2 CH_2), 2.05−2.10 (m, 4 H, 2 CH_2), 3.30−4.00 (m, 8 H, H-1/6, H-1′/6′, H-2/5, H-3/4), 5.15 (bs, 2 H, 2 OH), 7.55 (bs, 2H, 2 NH). ^{13}C NMR (50 MHz): δ 24.5 (2 CH_2), 27.3 (Me_2C), 28.6 (4 CH_2), 33.6 (2 CH_2), 42.3 (C-1/6), 70.7 (C-3/4), 80.1 (C-2/5), 108.6 (*C*Me_2), 172.7 (2 CO). Anal. Calcd for $C_{19}H_{34}O_6N_2 \cdot 0.35H_2O$: C, 58.09; H, 8.90; N, 7.13. Found: C, 58.02; H, 8.51; N, 7.10.

Poly(1,6-dideoxy-3,4-*O*-isopropylidene-D-mannitoldodecanediamide) (28). This was prepared from **3** (1 g, 4.5 mmol) and dodecanedioyl dichloride (**11e**, 1.2 g, 4.5 mmol) as described for **9**. Compound **28** was obtained as a yellow amorphous powder (1 g, 55%): $[\alpha]_D$ −26° (*c* 1, HCOOH); M_v 6500. IR: ν 1647 (amide I), 1552 cm^{-1} (amide II). ^{1}H NMR (DMSO, 200 MHz): δ 1.20 (m, 12 H, 6 CH_2), 1.30 (s, 6 H, Me_2C), 1.49 (m, 4 H, 2 CH_2), 2.05 (m, 4 H, 2 CH_2), 3.00−4.00 (m, 10 H, 2 OH, H-1/6, H-1′/6′, H-2/5, H-3/4), 7.80 (bs, 2H, 2 NH). ^{13}C NMR (50 MHz): δ 24.8 (2 CH_2), 27.3 (Me_2C), 28.8 (6 CH_2), 35.4 (2 CH_2), 42.3 (C-1/6), 69.9 (C-3/4), 80.1 (C-2/5), 108.6 (*C*Me_2), 173.2 (2 CO). Anal. Calcd for $C_{21}H_{38}O_6N_2 \cdot 1.8H_2O$: C, 56.43; H, 9.38; N, 6.26. Found: C, 56.40; H, 9.35; N, 6.19.

Poly(1,6-dideoxy-3,4-*O*-isopropylidene-2,5-di-O-methyl-D-mannitolsuccinimide) (29). To a stirred solution of **4** (100 mg, 0.4 mmol) in dried $CHCl_3$ (1 mL), at room temperature was added bis (pentachlorophenyl) succinate[14] (**12a**, 246 mg, 0.4 mmol). The solution was heated to 50 °C and left at this temperature for 7 days under stirring. The reaction mixture was added dropwise to diethyl ether (200 mL) with stirring, and the polymer formed was recovered from the

Scheme 1



reaction mixture as a syrup. It was purified by dissolving in CH_2Cl_2 and pouring the solution into ether repeatedly (75 mg, 56%): $[\alpha]_D$ +14° (*c* 0.5, $CHCl_3$); M_v 150, M_w 1400, and M_w/M_n 1.03. IR: ν 1650 (amide I), 1560 cm^{-1} (amide II). ^1H NMR ($CDCl_3$, 200 MHz): δ 1.36∠2.54 (m, 10 H, 2 CH_2, Me_2C), 3.35−4.11 (m, 14 H, 2 OMe, H-1/6, H-1′/6′, H-2/5, H-3/4), 6.60 (bs, 2H, 2 NH). ^{13}C NMR (50 MHz): δ 26.9 (Me_2C), 31.4 (2 CH_2), 38.4 (C-1/6), 57.9 (OMe), 78.0 (C-3/4), 80.3 (C-2/5), 109.9 (CMe_2), 172.8 (2 CO). Anal. Calcd for $C_{15}H_{26}O_6N_2 \cdot 1.5H_2O$: C, 50.41; H, 8.18; N, 7.84. Found: C, 50.80; H, 7.89; N, 7.60.

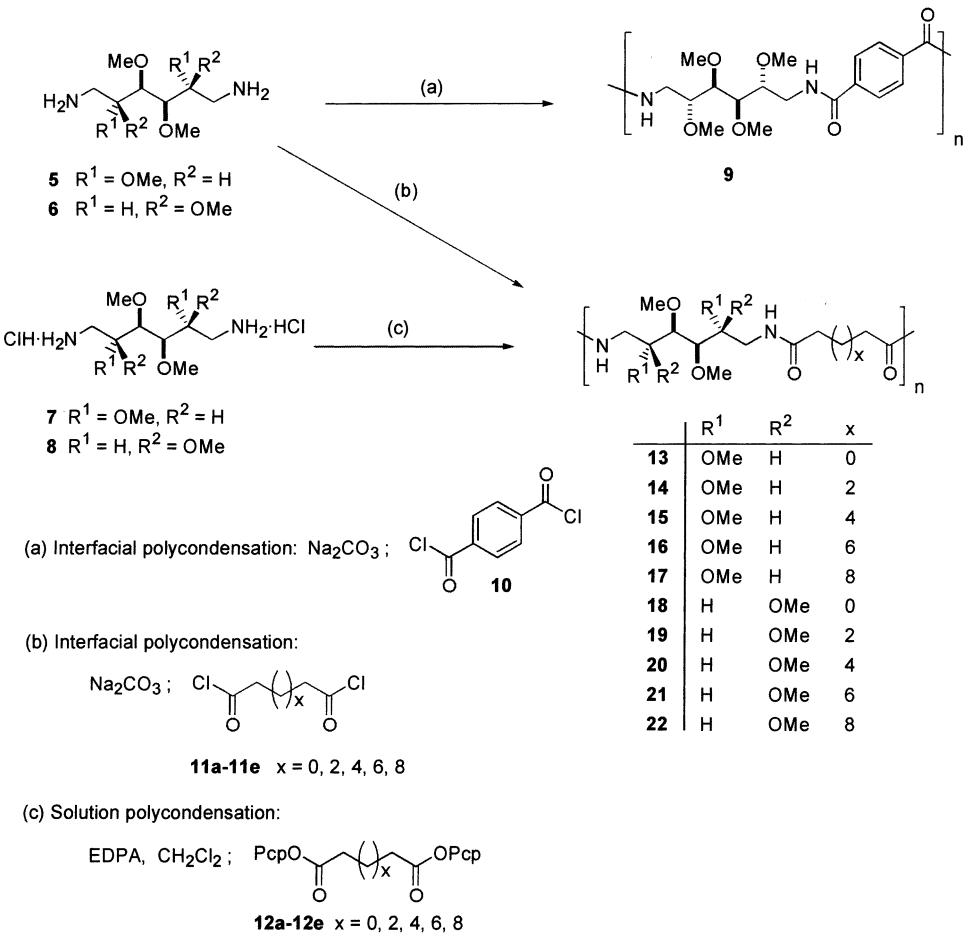
Poly(1,6-dideoxy-3,4-*O*-isopropylidene-2,5-di-O-methyl-D-mannitoladipamide) (30). This was prepared from **4** (100 mg, 0.4 mmol) and bis(pentachlorophenyl) adipate[14] (**12b**, 257 mg, 0.4 mmol) as described for **29**. Compound **30** was obtained as a syrup (89 mg, 61%): $[\alpha]_D$ +18° (*c* 0.5, $CHCl_3$); M_v 850, M_w 2600, and M_w/M_n 1.24. IR: ν 1650 (amide I), 1560 cm^{-1} (amide II). ^1H NMR ($CDCl_3$, 200 MHz): δ 1.34−2.21 (m, 14 H, 4 CH_2, Me_2C), 3.35−4.07 (m, 14 H, 2 OMe, H-1/6, H-1′/6′, H-2/5, H-3/4), 6.65 (bs, 2H, 2 NH). ^{13}C NMR (50 MHz): δ 25.1 (2 CH_2), 27.0 (Me_2C), 36.1 (2 CH_2), 38.6 (C-1/6), 58.0 (OMe), 77.9 (C-3/4), 80.1 (C-2/5), 109.9 (CMe_2), 173.2 (2 CO). Anal. Calcd for $C_{17}H_{30}O_6N_2 \cdot H_2O$: C, 54.24; H, 8.57; N, 7.44. Found: C, 54.63; H, 8.19; N, 7.31.

Poly(1,6-dideoxy-3,4-*O*-isopropylidene-2,5-di-O-methyl-D-mannitolsuberamide) (31). This was prepared from **4** (100 mg, 0.4 mmol) and bis(pentachlorophenyl) suberate[14] (**12c**, 268 mg, 0.4 mmol) as described for **29**. Compound **31** was obtained as a syrup (103 mg, 66%): $[\alpha]_D$ +20° (*c* 0.5, $CHCl_3$); M_v 470, M_w 2200, and M_w/M_n 1.06. IR: ν 1650 (amide I), 1560 cm^{-1} (amide II). ^1H NMR ($CDCl_3$, 200 MHz): δ 1.33−2.15 (m, 18 H, 6 CH_2, Me_2C), 3.39−4.03 (m, 14 H, 2 OMe, H-1/6, H-1′/6′, H-2/5, H-3/4), 6.30 (bs, 2H, 2 NH). ^{13}C NMR (50 MHz): δ 25.4 (2 CH_2), 26.9 (Me_2C), 28.7 (2 CH_2), 36.3 (2 CH_2), 38.5 (C-1/6), 57.9 (OMe), 78.1 (C-3/4), 80.0 (C-2/5), 109.8 (CMe_2), 173.4 (2 CO). Anal. Calcd for $C_{19}H_{34}O_6N_2 \cdot 2H_2O$: C, 54.01; H, 9.06; N, 6.63. Found: C, 54.53; H, 8.95; N, 6.71.

Poly(1,6-dideoxy-3,4-*O*-isopropylidene-2,5-di-O-methyl-D-mannitolsebacamide) (32). This was prepared from **4** (100 mg, 0.4 mmol) and bis(pentachlorophenyl) sebacate[14] (**12d**, 280 mg, 0.4 mmol) as described for **29**. Compound **32** was obtained as a syrup (100 mg, 60%): $[\alpha]_D$ +8° (*c* 0.5, $CHCl_3$); M_v 320, M_w 4000, and M_w/M_n 1.24. IR: ν 1650 (amide I), 1560 cm^{-1} (amide II). ^1H NMR ($CDCl_3$, 200 MHz): δ 1.25−2.19 (m, 22 H, 8 CH_2, Me_2C), 3.34−4.04 (m, 14 H, 2 OMe, H-1/6, H-1′/6′, H-2/5, H-3/4), 6.20 (bs, 2H, 2 NH). ^{13}C NMR (50 MHz): δ 25.6 (2 CH_2), 27.0 (Me_2C), 29.1 (4 CH_2), 36.6 (2 CH_2), 38.6 (C-1/6), 58.0 (OMe), 78.3 (C-3/4), 80.0 (C-2/5), 109.9 (CMe_2), 173.4 (2 CO). Anal. Calcd for $C_{21}H_{38}O_6N_2 \cdot H_2O$: C, 58.31; H, 9.32; N, 6.48. Found: C, 58.04; H, 9.15; N, 6.54.

Poly(1,6-dideoxy-3,4-*O*-isopropylidene-2,5-di-O-methyl-D-mannitoldodecanediamide) (33). This was prepared from **4** (100 mg, 0.4 mmol) and bis(pentachlorophenyl) dodecanedioate[14] (**12e**, 291 mg, 0.4 mmol) as described for **29**.

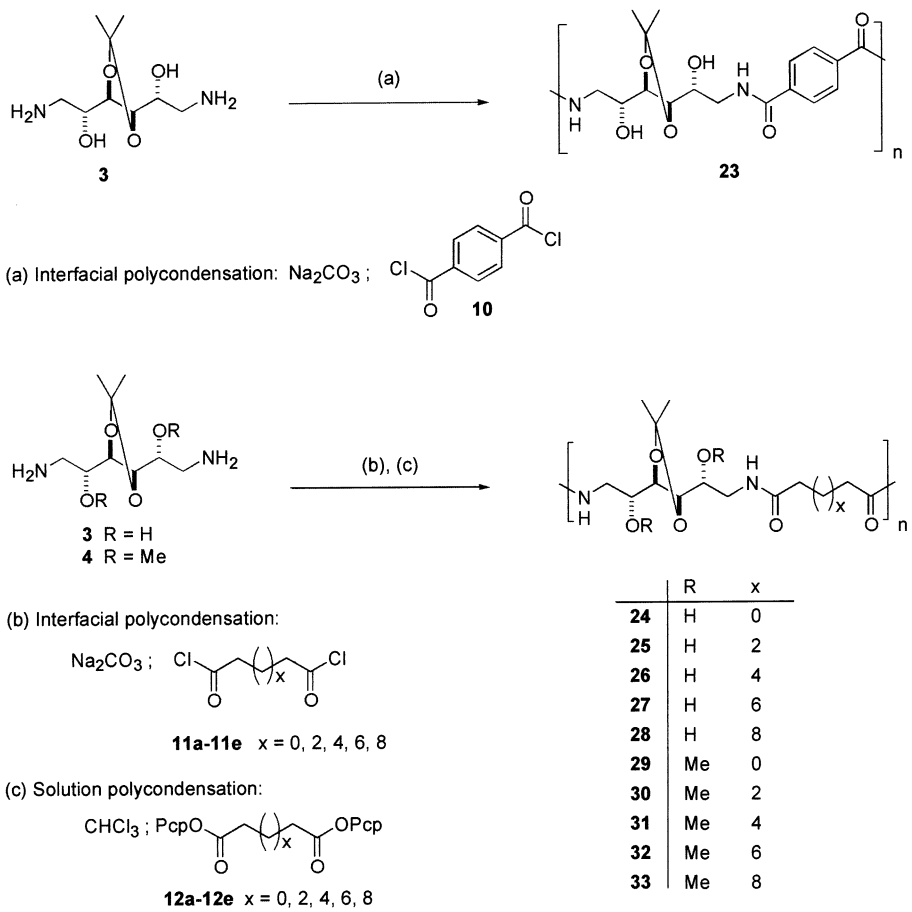
Scheme 2



	R^1	R^2	x
13	OMe	H	0
14	OMe	H	2
15	OMe	H	4
16	OMe	H	6
17	OMe	H	8
18	H	OMe	0
19	H	OMe	2
20	H	OMe	4
21	H	OMe	6
22	H	OMe	8

EDPA: *N*-ethyl-*N*,*N*-diisopropylamine; Pcp: pentachlorophenyl

Scheme 3



Pcp: pentachlorophenyl

Compound **33** was obtained as a syrup (120 mg, 67%): $[\alpha]_D$ +22° (*c* 0.5, $CHCl_3$); M_v 1200, M_w 6400, and M_w/M_n 1.37. IR: *ν* 1650 (amide I), 1560 cm^{-1} (amide II). ^1H NMR ($CDCl_3$, 200 MHz): *δ* 1.22−2.19 (m, 26 H, 10 CH_2, Me_2C), 3.34−4.05 (m, 14 H, 2 OMe, H-1/6, H-1′/6′, H-2/5, H-3/4), 6.24 (bs, 2H, 2 NH). ^{13}C NMR (50 MHz): *δ* 25.6 (2 CH_2), 27.0 (Me_2C), 29.2 (2 CH_2), 29.3 (2 CH_2), 29.4 (2 CH_2), 36.6 (2 CH_2), 38.6 (C-1/6), 58.0 (OMe), 78.3 (C-3/4), 80.0 (C-2/5), 109.9 (CMe_2), 173.5 (2 CO). Anal. Calcd for $C_{23}H_{42}O_6N_2 \cdot H_2O$: C, 59.97; H, 9.63; N, 6.08. Found: C, 60.14; H, 9.67; N, 5.84.

Results and Discussion

The synthesis of diamines **5** and **6** and their dihydrochlorides (**7**, **8**) from D-mannitol, was described in full detail in a preceding paper.[8] The diamino compounds **3** and **4** were obtained from the corresponding diazido derivatives **1** and **2** by catalytic hydrogenation in methanol (Scheme 1). We carried out the formation of polyamides from the diaminocarbohydrate derivatives **3**, **5,** and **6** with aromatic as well as aliphatic dicarboxylic acid dichlorides (**10** and **11a**−**e**) by interfacial polycondensation in emulsion made up from different organic solvents and aqueous sodium carbonate. Alternatively, polycondensation of the dihydrochlorides **7** and **8**, or their free bases (**5**, **6**) and the diamine **4**, with the pentachlorophenyl esters of the aliphatic dicarboxylic acids (**12a**−**e**) was processed in solution under different conditions (Schemes 2 and 3).

Initially, compounds **5** and **6** were reacted by interfacial polycondensation to yield the amorphous solid polyamides **9**, **13**−**17**, and **22**, respectively. As usual, elemental analyses differed slightly from the calculated ones, probably due to the difficulty of washing and drying these polymers, particularly when they were precipitated in a rubbery form. All the synthesized polyamides were optically active. Specific rotatory powers were measured in formic acid, dimethyl sulfoxide, or chloroform (see Experimental Section). However, it should be taken into account that the hygroscopic character of these polyamides may introduce some error into their rotatory values. All polyamides may be easily dissolved at room temperature in hydrogen-bond-breaking solvents such as formic acid, but they do not dissolve in oxygenated solvents such as ethyl ether. The obtained polyamides were also soluble in ethanol as well as in polar aprotic solvents such as dimethyl sulfoxide, *N*,*N*-dimethylformamide, or *N*-methylpyrrolidinone. The solubility in chloroform is remarkable, because while such behavior is unusual in conventional polyamides, it is quite common in stereoregular polyamides containing stereocenters in the main chain.[9] This is currently interpreted as being a consequence of the occurrence of ordered helical conformations stabilized by intramolecular hydrogen bonds.[10] The solubility of aromatic polyamide (**9**) is greater than that of polyamides from aliphatic diacids. The appreciable solubility in water displayed by the lower members of the series ($x = 0, 2$) is also worth mentioning. They all display a noticeable hydrophilicity due to the presence in the chain of the hydrophilic methoxyl groups. Intrinsic viscosities were determined for these polymers, and from them, rough

Table 1. Results of the Preparation of Polyamides 9, 13−17, and 22−28 by Interfacial Polycondensation

polymer	diamine	solvent	temp (°C)	time (h)	yield (%)
9	**5**	$H_2O/(Me_2CH)_2O$	rt	3	33
13	**5**	Cl_4C	rt	3	80
14	**5**	Cl_4C	rt	3	78
15	**5**	Cl_4C	rt	3	75
16	**5**	Cl_4C	rt	3	50
17	**5**	Cl_4C	rt	3	44
22	**6**	Cl_4C	rt	3	66
23	**3**	$H_2O/(Me_2CH)_2O$	rt	3	86
24	**3**	Cl_4C	rt	3	98
25	**3**	Cl_4C	rt	3	93
26	**3**	Cl_4C	rt	3	36
27	**3**	Cl_4C	rt	3	58
28	**3**	Cl_4C	rt	3	55

Table 2. Results of the Preparation of Polyamides 13−22 and 29−33 by Polycondensation in Homogeneous Solution

polymer	diamine	solvent	temp (°C)	time (days)	yield (%)
13	**7**	CH_2Cl_2 (EDPA)[a]	40	6	60
	5	CH_2Cl_2			61
14	**7**	CH_2Cl_2 (EDPA)[a]	40	6	77
	5	CH_2Cl_2			66
15	**7**	CH_2Cl_2 (EDPA)[a]	40	6	70
	5	CH_2Cl_2			75
16	**7**	CH_2Cl_2 (EDPA)[a]	40	6	88
	5	CH_2Cl_2			78
17	**7**	CH_2Cl_2 (EDPA)[a]	40	6	68
	5	CH_2Cl_2			74
18	**8**	$CHCl_3$ (EDPA)[a]	50	7	52
	6	TCE[b]	120	7	59
19	**8**	$CHCl_3$ (EDPA)[a]	50	7	56
	6	TCE[b]	120	7	61
20	**8**	$CHCl_3$ (EDPA)[a]	60	5	58
	6	TCE[b]	120	7	63
21	**8**	$CHCl_3$ (EDPA)[a]	50	4	73
	6	TCE[b]	102	4	76
22	**8**	$CHCl_3$ (EDPA)[a]	60	5	61
	6	TCE[b]	120	7	63
29	**4**	$CHCl_3$	50	7	56
30	**4**	$CHCl_3$	50	7	61
31	**4**	$CHCl_3$	50	4	66
32	**4**	$CHCl_3$	50	4	60
33	**4**	$CHCl_3$	50	4	67

[a] *N*-Ethyl-*N*,*N*-diisopropylamine. [b] 1,1,2,2-Tetrachloroethane.

M_v values were estimated, using for calculations the Mark−Houwink[11] parameters reported for nylon 66, notwithstanding that this viscosimetric equation may be somewhat inappropriate for estimating the size of these polyamides. A high viscosity was not obtained, owing to the rapid hydrolysis of these dicarboxylic acid dichlorides in the carbon tetrachloride-aqueous sodium carbonate systems. The molecular weight distributions of polyamides were studied by gel permeation chromatography (GPC) using Styragel columns and chloroform or chloroform-*o*-chlorophenol (95:5 v/v) as the mobile phase. The values for M_w and M_w/M_n are listed in Table 3. No good correspondence could be observed between GPC data and M_v values. Weight-average values obtained ranged between 1400 (**13**) and 14200 (**16**) with polydispersity ratio (M_w/M_n) values between 1.34 and 1.37. The [η] and M_w values of the D-*manno* polyamide **17** were higher than those found for polyamide **22** obtained by polycondensation of L-*ido* diamine **6** with the same aliphatic dicarboxylic acid dichloride (**11e**).

Both IR and NMR spectroscopies, as detailed in the Experimental Section, confirmed the structures of these polymers. The IR spectra showed the characteristic absorptions for the N−H stretching and the amide I (C−O stretching) and amide II bands. In the ^{1}H NMR spectra, the signals at higher field were due to the methylene protons from the acid dichloride unit. The signals arising from an ABX system integrated by the methine and methylene protons of the diamine unit appeared partly overlapped with the central protons, H-3/H-4, and the two singlet signals of the four methoxyl groups. The amide protons appeared as broadened singlets. The aromatic proton of polyamide **9** gave a multiplet between 7.92 and 8.25 ppm. The signal at higher field in the ^{13}C NMR spectra of these polyamides (Figures 1 and 2) was due to the methylene carbon of the diacid unit, and appeared with inverse phase in the DEPT experiment. The methylene carbon bonded to the amide nitrogens gave a signal at about 37.0 ppm. The four methoxyl carbons gave two signals: at about 56.0 and 60.0 ppm. The methynic carbons gave two signals: at about 78.0 (C-3/C-4) and 80.0 (C-2/C-5) ppm. The signal at lower field was assigned to the carbonyl group of the amide functions. All the carbons gave single signals in agreement with the expected regio- and stereoregularity of these polymers.

The dihydrochlorides **7** and **8**, or their free bases (**5**, **6**), were additionally reacted with pentachlorophenyl esters of the aliphatic dicarboxylic acids (**12a**−**e**) in a

Table 3. Intrinsic Viscosities and Molecular Weights of Polyamides 9 and 13−33

polymer	diamine	[η][a] (dL/g)	M_v[b]	M_w[c]	M_w/M_n
9	**5** (interfacial)	0.17	1100		
13	**5** (interfacial)	0.08	260	1400	1.34
13	**5** (solution)	0.07	200	1100	2.07
13	**7** (solution)	0.04	60	1200	1.12
14	**5** (interfacial)	0.08	260	1500	1.67
14	**5** (solution)	0.09	320	7900	1.33
14	**7** (solution)	0.07	200	6700	1.16
15	**5** (interfacial)	0.09	320	7000	1.69
15	**5** (solution)	0.12	560	8700	1.91
15	**7** (solution)	0.14	750	8700	1.41
16	**5** (interfacial)	0.18	1200	14 200	1.37
16	**5** (solution)	0.22	1700	21 400	1.44
16	**7** (solution)	0.25	2200	23 900	1.44
17	**5** (interfacial)	0.19	1300	9600	2.01
17	**5** (solution)	0.08	260	4600	1.45
17	**7** (solution)	0.10	400	5000	1.28
18	**6** (solution)	0.08	260	1200	1.04
18	**8** (solution)	0.10	400	1000	1.05
19	**6** (solution)	0.11	470	1700	1.09
19	**8** (solution)	0.13	650	2800	1.21
20	**6** (solution)	0.11	470	3200	1.45
20	**8** (solution)	0.08	260	3300	1.28
21	**6** (solution)	0.17	1100	10 100	2.34
21	**8** (solution)	0.16	960	12 600	1.85
22	**6** (interfacial)	0.11	470	5700	1.47
22	**6** (solution)	0.11	470	4000	1.48
22	**8** (solution)	0.09	320	4600	1.33
23	**3** (interfacial)	0.08	260		
24	**3** (interfacial)	0.15	850		
25	**3** (interfacial)	0.14	750		
26	**3** (interfacial)	0.17	1100		
27	**3** (interfacial)	0.12	560		
28	**3** (interfacial)	0.45	6500		
29	**4** (solution)	0.06	150	1400	1.03
30	**4** (solution)	0.15	850	2600	1.24
31	**4** (solution)	0.11	470	2200	1.06
32	**4** (solution)	0.09	320	4000	1.24
33	**4** (solution)	0.18	1200	6400	1.37

[a] Intrinsic viscosities measured in dichloroacetic acid at 25 °C. [b] Calculated by applying the viscosimetric equation reported for nylon 6.6.[11] [c] Determined by GPC analysis with polystyrene standards using $CHCl_3$ as mobile phase.

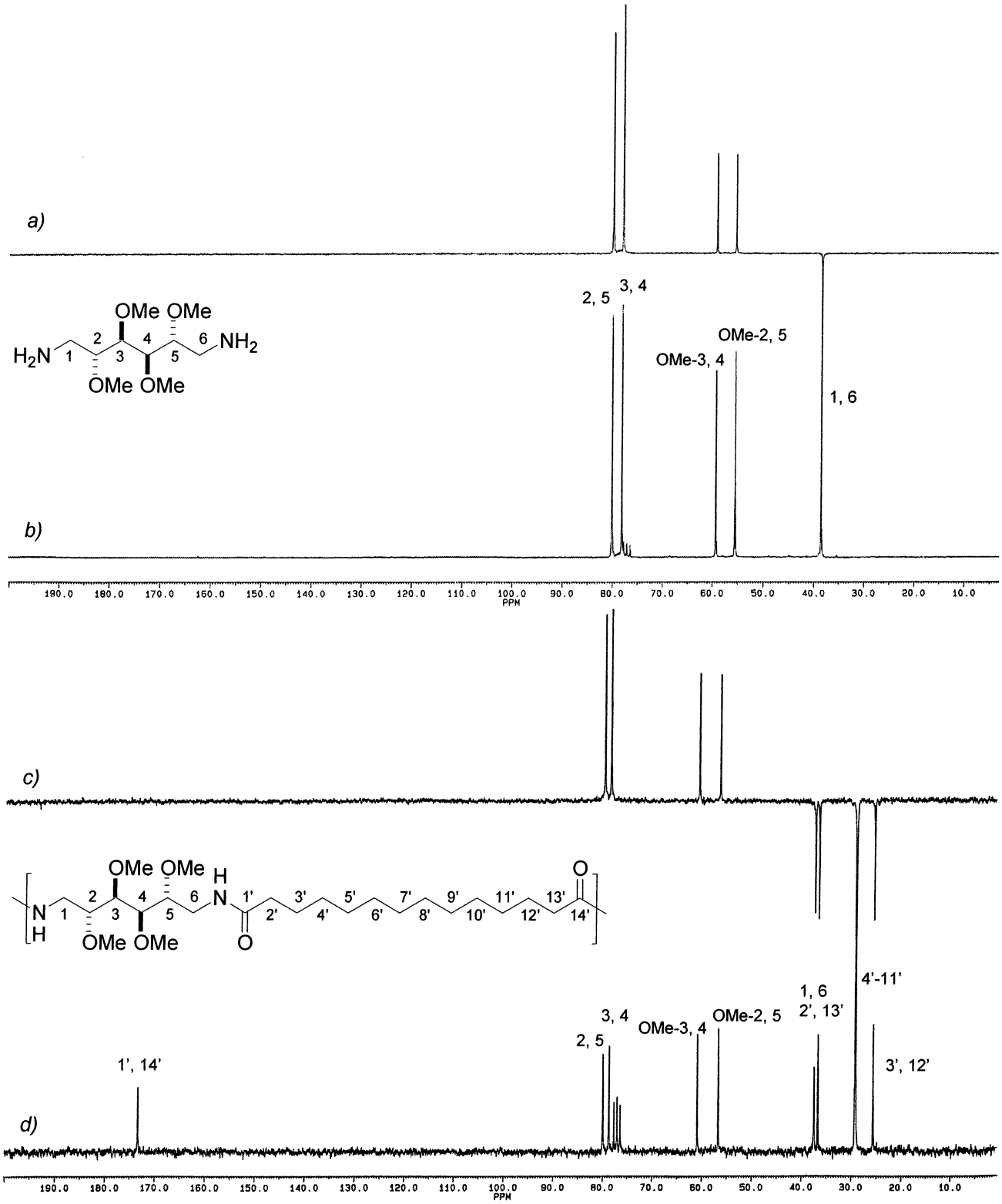


Figure 1. ^{13}C NMR spectra recorded in $CDCl_3$: (a) DEPT-135 and (b) BB of the diamine **5**; (c) DEPT-135 and (d) BB of the polyamide **17** (sugar configuration: D-*manno*).

homogeneous solution polycondensation reaction (Scheme 2). Solvents such as dichloromethane, chloroform, 1,1,2,2-tetrachloroethane, and acid receptors (*N*-ethyl-*N*,*N*-diisopropylamine) were tested (Table 2). All the obtained polyamides were noncrystalline and were purified by repeatedly pouring a dichloromethane solution of the polymer into ether and decantation of the gummy precipitate. A selection of results obtained in these reactions is displayed in Table 2. The intrinsic viscosities and M_w values of polyamides obtained from the free base **5** were slightly higher than those found for polyamides synthesized by heterogeneous interfacial polycondensation (**13**−**17**) but comparable to those of polyamides obtained from its dihydrochloride (**7**, Table 3). Two anomalies observed were the very low M_w of polyamide **13** and the significantly higher than average M_w of polyamide **16**. No obvious dependence of molecular weight on the parameters reaction temperature,

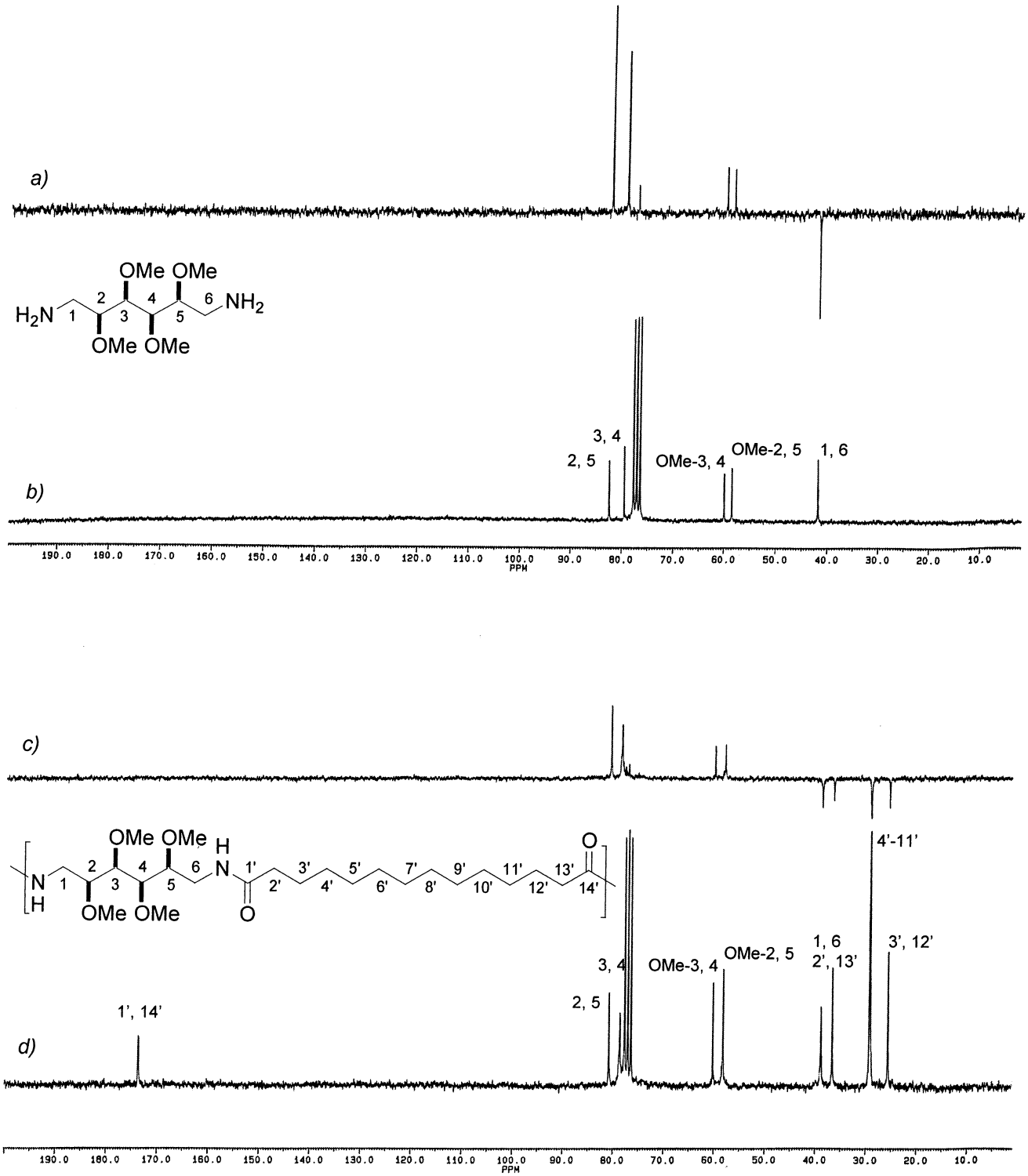


Figure 2. ^{13}C NMR spectra recorded in $CDCl_3$: (a) DEPT-135 and (b) BB of the diamine **6**; (c) DEPT-135 and (d) BB of the polyamide **22** (sugar configuration: L-*ido*).

catalyst concentration, conversion, or polydispersity, could be detected. The M_w of the polyamides of L-*ido* configuration were also slightly lower than those of D-*manno*. This fact may be due to the different conformation that these sugar units can adopt in solution. Polyamides with the D-*manno* configuration can adopt an extended planar conformation of the diamine monomer unit, with no 1,3-paralel interaction between the methoxyl substituents, while polyamides with the L-*ido* configuration must adopt a sickle conformation of the diamine unit to avoid the 1,3-paralel interaction between the methoxyl substituents on C-2/4 and C-3/5. This sickle conformations may favor the formation of cycles during the polymerization process yielding polymers with lower M_w values. The IR and NMR spectra, as detailed in Experimental, were consistent with the structures of the polymers.

Similarly, diamines **3** and **4** were polycondensated by interfacial and solution polycondensation to give polyamides **23**−**33** (Scheme 3). Aliphatic polyamides synthesized by interfacial polycondensation (**24**−**28**) were soluble in ethanol and dimethyl sulfoxide, slightly

soluble in acetone and ether, and insoluble in chloroform and water. The aromatic polyamide **23** was insoluble in chloroform, dimethyl sulfoxide and formic acid, so its specific rotatory power determination was not possible. The [η] and M_v values were slightly higher than those found for the polyamides **13**−**17** obtained by interfacial polymerization, but comparable to those of polyamides obtained by the active ester polycondensation method (**29**−**33**). Characteristic data of the polyamides are compared in Tables 1 and 3. The IR and NMR spectra, as detailed in the Experimental Section, were also consistent with the structures of the polymers.

In conclusion, we were able to prepare a series of stereo- and regioregular polyamides of the AABB-type from 1,6-diamino derivatives of D-mannitol and L-iditol and aliphatic and aromatic dicarboxylic acids. Despite the stereo- and regioregular structures of these polyamides, they were noncrystalline and were isolated as gummy solids. The polyamides derived from aliphatic diacids and the methoxylated 1,6-diaminoalditols were soluble in chloroform. Their molecular weights were low-medium, with a tendency to be higher as the number of methylene groups of the diacid units increased. Usually, the polyamides having D-*manno* configuration gave M_w values slightly higher than their homologues with the L-*ido* configuration. As could be expected, all of them were optically active.

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