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Note

Synthesis of D-mannitol and L-iditol derivatives as monomers for the preparation of new regioregular AABB-type polyamides

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Abstract

1,6-Diamino-1,6-dideoxy-2,3,4,5-tetra-*O*-methyl-D-mannitol (and its L-iditol analogue) suitable for their utilization as monomers in the preparation of linear polyamides are described. Regio- and stereoregular polyamides of the AABB-type have been prepared by the active ester polycondensation method from these C_2 symmetric monomers and suberic and dodecanedioic acids. The resulting polyamides were obtained in fair yields (70–60%) and were characterized by elemental analyses and infrared and ^{1}H and ^{13}C NMR spectroscopies. Their M_w and M_w/M_n were determined by GPC relative to polystyrene standards. All of them were gummy non-crystalline solids.

Keywords: Bifunctional carbohydrate-based monomers; D-Mannitol-based polyamides; L-Iditol-based polyamides; Regioregular AABB-type polyamides

Aliphatic polyamides (nylons) are an important class of functional polymers because of their excellent technical properties.[1] In order to expand their applications to new fields demanding materials either with lower environmental impact or displaying biodegradable and biocompatible properties, sustained efforts have been extensively devoted in these past years to render polyamides more hydrophilic and degradable.[2] The use of building blocks derived from carbohydrates in the design of polyamides with enhanced hydrophilicity and biodegradability constitutes an interesting strategy that is being intensively explored.[3–6]

The synthesis of regioregular poly(tartaramides), i.e., polyamides of (*n*,4)-type derived from naturally occurring L-tartaric acid, has been reported.[7] However, the response given by these polyamides, bearing only two methoxyl groups between the amide functions, to water degradation under mild conditions (pH ~7 and ~37 °C) is still too weak for many potential applications.[8]

At the same time, the regioregularity of the AABB-type polyamides relies upon the existence of a twofold axis of symmetry in the monomers, otherwise regio-isomerism may occur, affording aregic polymers.[9] Mannitol and iditol derivatives possess this C_2 symmetric character. Therefore, it was thought interesting to use them as bifunctional monomers for the preparation of linear regioregular and stereoregular AABB-type polyamides having four methoxyl groups between the amide functions to enhance their hydrophilicity.

We now describe the preparation of 1,6-diamino-1,6-dideoxy-2,3,4,5-tetra-*O*-methyl-D-mannitol dihydrochloride (**11**) and its L-iditol analogue (**12**), and their polycondensation reactions with the bis(pentachlorophenyl) esters of suberic and dodecanedioic acids.[10]

O-Methylation of 1,6-diazido-1,6-dideoxy-3,4-*O*-isopropylidene-D-mannitol (**1**,[11,12] obtained in four steps from D-mannitol) gave azide **3** (Scheme 1). Acid hydrolysis of the *O*-isopropylidene group with trifluoroacetic acid led to the glycol **5**, which was isolated as a crystalline product (77%). *O*-Methylation of **5** gave **7**, which was hydrogenated with palladium on activated carbon in methanol followed by treatment with hydrogen chloride to give the diamine dihydrochloride **11** in high yield (92%). Similarly, *O*-methylation of 1,6-diazido-1,6-dideoxy-3,4-*O*-isopropylidene-L-iditol (**2**,[12,13] obtained in five steps from D-mannitol) followed by acid hydrolysis of the *O*-isopropylidene group led to **6**. A second *O*-methylation of **6,** followed by catalytic hydrogenation of the azide functions in methanol and

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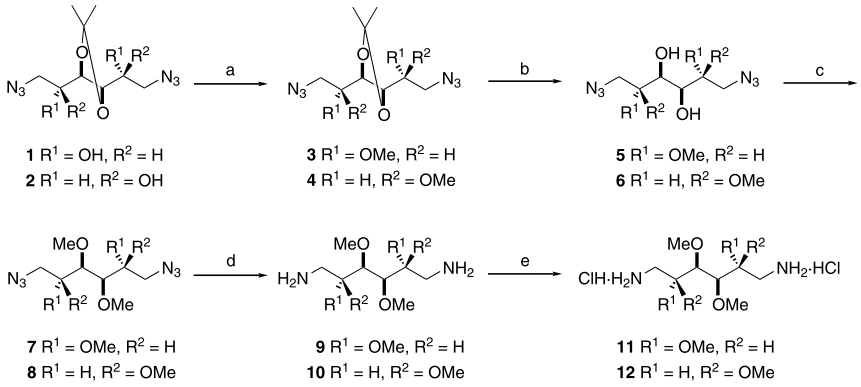


Scheme 1. (a) MeI, KOH, Me_2SO; (b) CF_3CO_2H, H_2O, 0 °C; (c) MeI, KOH, Me_2SO; (d) H_2, Pd–C, MeOH; (e) HCl, EtOAc.

further treatment with hydrogen chloride, gave the diamine dihydrochloride **12**.

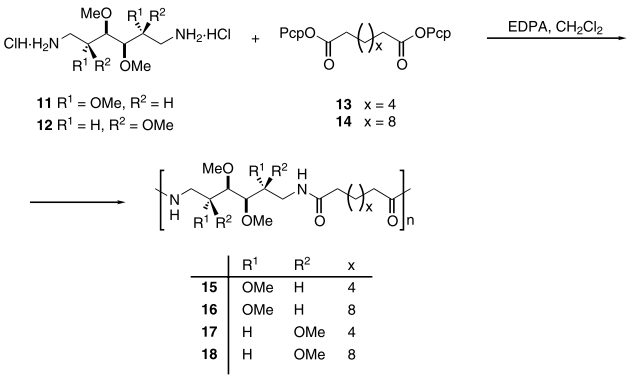
We carried out several polycondensation reactions of the dihydrochlorides **11** and **12**, or their free bases (**9**, **10**), with the pentachlorophenyl esters of the aliphatic dicarboxylic acids **13** and **14**, under different conditions, to obtain the polyamides **15**–**18** (Scheme 2). All the obtained polyamides were non-crystalline 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 1. Molecular weight determinations were conducted using gel-permeation chromatography (GPC) with $CHCl_3$ as solvent. —The values for M_w and M_w/M_n are listed in Table 1. The IR and NMR spectra, as detailed in Section 1, were consistent with the structures of the polymers. In particular, the IR spectra showed absorption peaks characteristic of the amide functions. As is 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.

In conclusion, we were able to prepare new derivatives from D-mannitol and L-iditol suitable for their utilization as monomers in the preparation of linear polyamides of the AABB-type. Despite the regio- and stereoregularity of these polyamides, they were non-crystalline and were isolated as gummy solids. They had medium molecular weights and narrow polydispersities. They were soluble in the usual organic solvents, including ethanol, chloroform, dimethyl sulfoxide, and dimethyl formamide, but insoluble in water.

1. Experimental

General methods.—Chemicals were all 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 Universidad Complutense, Madrid. FTIR spectra were obtained from films or KBr discs. For NMR spectra, chemical shifts are reported as parts per million downfield from Me_4Si. Mass spectra were recorded on a Micromass AUTOSPECQ mass spectrometer equipped with a combined EI-CI source, using methane as ionizing gas. High-resolution mass spectra (HRMS, EI 70 eV) were obtained with a resolution of 10,000. Gel-permeation chromatography (GPC) analyses were carried with two styragel® HR columns (7.8 × 300 mm) placed in series, using $CHCl_3$ as solvent at a flow rate of 1 mL/min. Molecular weight studies were determined relative to polystyrene standards.

*1,6-Diazido-1,6-dideoxy-3,4-*O*-isopropylidene-2,5-di-*O*-methyl-*D*-mannitol* (**3**).—To a stirred solution of **1** (10.0 g, 36.70 mmol) in dry Me_2SO (73.5 mL) at −5 °C, freshly powdered KOH (24.6 g, 440.4 mmol) and MeI (14.7 mL) were added. The suspension was stirred in the dark for 16 h, at rt, then poured into



	R1	R2	x
15	OMe	H	4
16	OMe	H	8
17	H	OMe	4
18	H	OMe	8

Scheme 2. EDPA, *N*-ethyl-*N*,*N*-diisopropylamine; PCP, pentachlorophenyl.

Table 1
Results obtained in the preparation of polyamides **15**–**18**

Polymer	Diamine	Solvent	Temperature (°C)	Time (days)	Yield (%)	M_w [a]	M_w/M_n
15	**11**	CH_2Cl_2 (EDPA) [b]	40	6	70	8727	1.41
16	**11**	CH_2Cl_2 (EDPA) [b]	40	6	68	5015	1.28
15	**9**	$CHCl_3$	40	6	75	8684	1.91
16	**9**	$CHCl_3$	40	6	74	4564	1.45
17	**12**	CH_2Cl_2 (EDPA) [b]	60	5	58	3286	1.28
18	**12**	CH_2Cl_2 (EDPA) [b]	50	4	61	4627	1.33
17	**10**	TCE [c]	120	4	63	3243	1.45
18	**10**	TCE [c]	120	5	63	4038	1.48

[a] Determined by GPC analysis with polystyrene standards using $CHCl_3$ as mobile phase.
[b] *N*-Ethyl-*N*,*N*-diisopropylamine.
[c] 1,1,2,2-Tetrachloroethane.

water and extracted with CH_2Cl_2. The combined organic extracts were dried (anhyd $MgSO_4$) and concentrated to a syrup (9.9 g, 90%). An analytical sample was obtained after column chromatography (silica gel; 7:1 CH_2Cl_2–Et_2O); $[\alpha]_D$ +7° (*c* 1, CH_2Cl_2); IR: *v* 2050 cm^{-1} (N_3). ^1H NMR ($CDCl_3$, 200 MHz): δ 1.35 (s, 6 H, Me_2C), 3.35–3.70 (m, 6 H, H-1/6, H-1′/6′, H-2/5), 3.50 (s, 6 H, OMe-2/5), 4.05 (m, 2 H, H-3/4); ^{13}C NMR (50 MHz): δ 26.8 (*Me*$_2$C), 50.1 (C-1/6), 58.0 (OMe-2/5), 77.7 (C-2/5), 81.3 (C-3/4), 109.8 (*C*Me_2). Anal. Calcd for $C_{11}H_{20}N_6O_4$: C, 43.99; H, 6.71; N, 27.98. Found: C, 44.28; H, 6.60; N, 27.88.

1,6-Diazido-1,6-dideoxy-2,5-di-O-*methyl*-D-*mannitol* (**5**).—Compound **3** (3.0 g, 10 mmol) was dissolved in trifluoroacetic acid (75 mL) and water (7.5 mL), and the resulting solution was stirred for 15 h at 0 °C, then poured into water (50 mL) and extracted with CH_2Cl_2 (3 × 200 mL). The combined organic extracts were washed with a 3% aqueous solution of sodium hydrogen carbonate (150 mL) and saturated solution of sodium chloride (150 mL), dried (anhyd $MgSO_4$) and evaporated to give crystalline **5** (2.0 g, 77%): mp 94–96 °C (from MeOH); $[\alpha]_D$ −33° (*c* 1, $CHCl_3$); IR: *v* 2052 cm^{-1} (N_3). ^1H NMR ($CDCl_3$, 200 MHz): δ 2.90 (bs, 2 H, OH-3/4), 3.35–3.50 (m, 4 H, H-1/6, H-1′/6′), 3.45 (s, 6 H, OMe-2/5), 3.58 (m, 2 H, H-2/5), 3.77 (m, 2 H, H-3/4); ^{13}C NMR (50 MHz): δ 50.2 (C-1/6), 58.5 (OMe-2/5), 69.0 (C-3/4), 81.2 (C-2/5). Anal. Calcd for $C_8H_{16}N_6O_4$: C, 36.92; H, 6.19; N, 32.29. Found: C, 37.27; H, 5.86; N, 32.20.

1,6-Diazido-1,6-dideoxy-2,3,4,5-tetra-O-*methyl*-D-*mannitol* (**7**).—A cooled solution of **5** (3.3 g, 12.69 mmol) in dry Me_2SO was treated with MeI and KOH as described above for **5**. The oily residue was purified by flash-column chromatography (1:5 ether–hexane) to give **7** as an oil (2.9 g, 79%); $[\alpha]_D$ +24.1° (*c* 1.7, CH_2Cl_2); IR: *v* 2050 cm^{-1} (N_3). ^1H NMR ($CDCl_3$, 200 MHz): δ 2.80–3.20 (m, 4 H, H-1/6, H-1′/6′), 3.40–3.80 (m, 4 H, H-2/5, H-3/4), 3.40 (s, 6 H, 2 OMe), 3.50 (s, 6 H, 2 OMe); ^{13}C NMR (50 MHz): δ 48.4 (C-1/6), 56.2 (OMe-2/5), 59.9 (OMe-3/4), 79.0 (C-3/4), 80.0 (C-2/5). Anal. Calcd for $C_{10}H_{20}N_6O_4$: C, 41.66; H, 6.99; N, 29.15. Found: C, 41.94; H, 6.68; N, 28.98.

1,6-Diamino-1,6-dideoxy-2,3,4,5-tetra-O-*methyl*-D-*mannitol* (**9**).—To a solution of **7** (288 mg, 1 mmol) in MeOH (10 mL) was added 10% Pd–C (29 mg) and the mixture was treated with H_2 (276 kPa) for 4 h. The catalyst was filtered off and washed with MeOH, and the filtrate was concentrated to give an oil (217 mg, 97%); $[\alpha]_D$ +20° (*c* 1, $CHCl_3$); IR: *v* 3400 cm^{-1} (NH_2). ^1H NMR ($CDCl_3$, 200 MHz): δ 1.60 (bs, 4 H, 2 NH_2), 2.73 (dd, 2 H, $J_{1,2}$ 4.1, $J_{1,1'}$ 13.7 Hz, H-1/6), 2.95 (dd, 2 H, $J_{1',2}$ 3.6 Hz, H-1′/6′), 3.16 (ddd, 2 H, $J_{2,3}$ 7.0 Hz, H-2/5), 3.25 (s, 6 H, 2 OMe), 3.35 (s, 6 H, 2 OMe), 3.37 (d, 2 H, H-3/4); ^{13}C NMR (50 MHz): δ 38.4 (C-1/6), 55.4 (OMe-2/5), 59.2 (OMe-3/4), 78.0 (C-3/4), 80.0 (C-2/5). Anal. Calcd for $C_{10}H_{24}N_2O_4 \cdot 0.4\,H_2O$: C, 49.32; H, 9.93; N, 11.50. Found: C, 49.53; H, 9.68; N 11.22.

1,6-Diamino-1,6-dideoxy-2,3,4,5-tetra-O-*methyl*-D-*mannitol dihydrochloride* (**11**).—The diamine **9** (0.5 g, 2.12 mmol) was treated with a 10% solution of HCl in EtOAc (15 mL), and the hydrochloride **11** was obtained as an amorphous solid, which was filtered and washed with EtOAc (0.57 g, 95%); $[\alpha]_D$ −13° (*c* 1, pyridine); ^{13}C NMR (Me_2SO-d_6, 50 MHz): δ 38.6 (C-1/6), 57.2 (OMe-2/5), 60.1 (OMe-3/4), 78.4 (C-3/4), 79.3 (C-2/5). Anal. Calcd for $C_{10}H_{26}Cl_2N_2O_4$: C, 38.84; H, 8.47; N, 9.05. Found: C, 38.91; H, 8.29; N, 8.82.

1,6-Diazido-1,6-dideoxy-3,4-O-*isopropylidene-2,5-di*-O-*methyl*-L-*iditol* (**4**).—This was prepared from **2** (4 g, 14.69 mmol) as described for **3**. Flash-column chromatography (CH_2Cl_2) of the syrup gave **4** as a yellowish syrup (2.7 g, 61%); $[\alpha]_D$ +33° (*c* 1, $CHCl_3$). ^1H NMR ($CDCl_3$, 200 MHz): δ 1.35 (s, 6 H Me_2C), 3.39 (m, 6 H, H-2/5, H-1/6, H-1′/6′), 3.49 (m, 6 H, 2 OMe), 4.06 (m, 2 H, H-3/4); ^{13}C NMR (50 MHz): δ 26.7 (*Me*$_2$C), 50.8 (C-1/6), 59.2 (2 OMe), 75.8 (C-2/5), 79.2 (C-3/4), 109.3 (*C*Me_2); CIHRMS Calcd for $C_{11}H_{21}N_6O_4$: 301.1624. Found: 301.1632.

1,6-Diazido-1,6-dideoxy-2,5-di-O-*methyl*-L-*iditol* (**6**). —This was prepared from **4** (0.6 g, 2 mmol) as described for **5**. Compound **6** was obtained as a syrup (0.48 g, 92%); $[\alpha]_D$ +12° (*c* 0.5, $CHCl_3$). ^1H NMR ($CDCl_3$, 200 MHz): δ 2.50 (bs, 2 H, OH-3/4), 3.35–3.60 (m, 6 H, H-1/6, H-1′/6′, H-2/5), 3.50 (s, 6 H, OMe-2/5), 3.75 (m, 2 H, H-3/4); ^{13}C NMR (50 MHz): δ 49.9 (C-1/6), 58.6 (OMe-2/5), 69.9 (C-3/4), 81.5 (C-2/5); CIHRMS Calcd for $C_8H_{17}N_6O_4$: 261.1311. Found: 261.1305.

1,6-Diazido-1,6-dideoxy-2,3,4,5-tetra-O-*methyl*-L-*iditol* (**8**). —This was prepared from **6** (4 g, 15.37 mmol) as described for **7**. Compound **8** was obtained as a syrup after flash-column chromatography (silica gel; 1:100 EtOAc–CH_2Cl_2) (3.4 g, 77%); $[\alpha]_D$ +28° (*c* 1, $CHCl_3$). ^1H NMR ($CDCl_3$, 200 MHz): δ 3.25–3.55 (m, 8 H, H-1/6, H-1′/6′, H-2/5, H-3/4), 3.40 (s, 12 H, 4 OMe); ^{13}C NMR (50 MHz): δ 50.8 (C-1/6), 58.3 (OMe-2/5), 59.4 (OMe-3/4), 78.2 (C-3/4), 79.5 (C-2/5); CIHRMS Calcd for $C_{10}H_{21}N_6O_4$: 289.1624. Found: 289.1642.

1,6-Diamino-1,6-dideoxy-2,3,4,5-tetra-O-*methyl*-L-*iditol* (**10**). —This was prepared from **8** (2.2 g, 7.63 mmol) as described for **9**. Compound **10** was obtained as a syrup (1.6 g, 89%); $[\alpha]_D$ −25° (*c* 1, $CHCl_3$). ^1H NMR ($CDCl_3$, 200 MHz): δ 2.26 (bs, 4 H, 2 NH_2), 2.61 (dd, 2 H, $J_{1,2}$ 6.5, $J_{1,1'}$ 13.3 Hz, H-1/6), 2.82 (dd, 2 H, $J_{1',2}$ 4.0 Hz, H-1′/6′), 3.22–3.44 (m, 4 H, H-2/5, H-3/4), 3.31 (s, 6 H, 2 OMe), 3.33 (s, 6 H, 2 OMe); ^{13}C NMR (50 MHz): δ 41.7 (C-1/6), 58.3 (OMe-2/5), 59.8 (OMe-3/4), 79.4 (C-3/4), 82.4 (C-2/5); CIHRMS Calcd for $C_{10}H_{25}N_2O_4$: 237.1814. Found: 237.1812.

1,6-Diamino-1,6-dideoxy-2,3,4,5-tetra-O-*methyl*-L-*iditol dihydrochloride* (**12**). —The diamine compound **10** (2 g, 8.46 mmol) was treated with a 10% solution of HCl in EtOAc (120 mL), and the hydrochloride **12** was obtained as a very hygroscopic syrup which was co-evaporated several times with ether (2.5 g, 95%); $[\alpha]_D$ −9° (*c* 1, pyridine). ^1H NMR (Me_2SO-d_6, 200 MHz): δ 2.77 (m, 2 H, H-1/6), 3.02 (m, 2 H, H-1′/6′), 3.35 (s, 6 H, 2 OMe), 3.38 (s, 6 H, 2 OMe), 3.43–3.78 (m, 4 H, H-2/5, H-3/4), 8.15 (bs, 6 H, 2 NH_3^+); ^{13}C NMR (50 MHz), δ 39.5 (C-1/6), 58.2 (OMe-2/5), 58.3 (OMe-3/4), 76.1 (C-3/4), 76.5 (C-2/5).

Poly(1,6-dideoxy-2,3,4,5-tetra-O-*methyl*-D-*mannitol-suberamide)* (**15**). —To a stirred solution of **11** (100 mg, 0.32 mmol) in dried CH_2Cl_2 (1 mL) at rt, bis(pentachlorophenyl) suberate[10] (**13**, 214 mg, 0.32 mmol) and *N*-ethyl-*N*,*N*-diisopropylamine (0.22 mL, 1.28 mmol) were added. The solution was heated to 40 °C and left stirring at this temperature for 6 days. Then, the reaction mixture was added dropwise to Et_2O (200 mL) while stirring. The formed polymer was recovered from the reaction mixture as a syrup and purified by dissolving in CH_2Cl_2 and pouring the solution into ether repeatedly (85 mg, 70%); $[\alpha]_D$ −26° (*c* 1, $CHCl_3$); M_w 8727, M_w/M_n 1.41; 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, 2 H, 2 NH); ^{13}C NMR (50 MHz): δ 25.4 (2 CH_2), 28.5 (2 CH_2), 36.5 (2 CH_2), 37.34 (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). Anal. Calcd for $C_{18}H_{34}N_2O_6 \cdot 0.8\ H_2O$: C, 55.59; H, 8.81; N, 7.20. Found: C, 55.91; H, 8.56; N, 7.37.

Poly(1,6-dideoxy-2,3,4,5-tetra-O-*methyl*-D-*mannitol-dodecanediamide)* (**16**). —This was prepared from **11** (100 mg, 0.32 mmol) and bis(pentachlorophenyl) dodecanedioate[10] (**14**, 232 mg, 0.32 mmol) as described for **15**. Compound **16** was obtained as a syrup (95 mg, 68%); $[\alpha]_D$ −15° (*c* 1, $CHCl_3$); M_w 5015, M_w/M_n 1.28; 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, 2 H, 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). Anal. Calcd for $C_{22}H_{42}N_2O_6 \cdot 0.5\ H_2O$: C, 60.11; H, 9.63; N, 6.51. Found: C, 60.44; H, 9.41; N, 6.69.

Poly(1,6-dideoxy-2,3,4,5-tetra-O-*methyl*-L-*iditol-suberamide)* (**17**). —To a stirred solution of **12** (300 mg, 0.97 mmol) in dried CH_2Cl_2 (4 mL) at rt were added bis(pentachlorophenyl) suberate[10] (**13**, 651 mg, 0.97 mmol) and *N*-ethyl-*N*,*N*-diisopropylamine (EDPA, 0.67 mL, 3.88 mmol). The solution was heated to 60 °C and left stirring at this temperature for 5 days. The reaction mixture was added dropwise to Et_2O (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 (210 mg, 58%); $[\alpha]_D$ −30° (*c* 1, $CHCl_3$); M_w 3286, M_w/M_n 1.28; IR: ν 1637 (amide I), 1544 cm^{-1} (amide II); ^1H 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, 2 H, 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 $C_{18}H_{34}N_2O_6 \cdot 2\ H_2O$: 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-*iditol-dodecanediamide)* (**18**). —This was prepared from **12** (200 mg, 0.65 mmol) and bis(pentachlorophenyl) dodecanedioate[10] (**14**, 472 mg, 0.65 mmol) in CH_2Cl_2 (2.5 mL) as described for **17**. Compound **18** was obtained as a syrup (170 mg, 61%); $[\alpha]_D$ −46° (*c* 1, $CHCl_3$); M_w 4627, M_w/M_n 1.33; IR: ν 1637 (amide I), 1543 cm^{-1} (amide II); ^1H 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, 2 H, 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). Anal. Calcd for $C_{22}H_{42}N_2O_6 \cdot H_2O$: C, 58.90; H, 9.89; N, 6.24. Found: C, 58.46; H, 9.43; N, 5.96.

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