Synthesis of Stereoregular *Head,Tail* Hydroxylated Nylons Derived from D-Glucose

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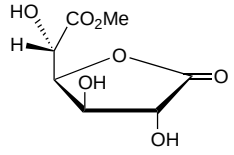
A simple procedure for the preparation of stereoregular polyhydroxypolyamides, i.e., *head,tail* hydroxylated nylons, derived from D-glucaric acid and alkylenediamines is described. Sodium D-glucarate 6,3-lactone was made in two steps from monopotassium D-glucarate by way of D-glucaro-6,3-lactone. Methanol insoluble salt of sodium 6-[*N*-(aminoalkyl)]-D-glucaramide monomer precursors were conveniently prepared by refluxing methanol solutions of even-numbered C_2 to C_{12} aliphatic diamines with insoluble sodium D-glucarate-6,3-lactone. Each of the resulting salts was esterified/lactonized at the C-1 carboxylate terminus with HCl/methanol, and the products were made basic to give the corresponding free base amino acid ester/lactone mixture. The latter spontaneously underwent self-polymerization to give the target polyamides. An important feature of this general procedure for stereoregular polyamides from chiral D-glucaric acid is that it does not require any carbohydrate hydroxyl group protection/deprotection steps.

Introduction

Hydroxylated nylons are polyamide condensation products from activated carbohydrate diacids (aldaric acids) and diamines. Ogata et al. were the first to report such polymers, notably poly(hexamethylene L-tartaramide)[1,2] and poly(hexamethylene galactaramide)[3,4] by condensation of hexamethylenediamine with dimethyl L-tartrate and diethyl galactarate, respectively, in polar solvents. Hoagland brought further understanding to this type of condensation when he established that the aminolysis of six-carbon galactaric acid diesters[5] and five-carbon xylaric acid diesters[6] occurs via five-membered lactone formation in a fast step initiated by the basic solution of the amine. Work from this laboratory extended the scope of this polymerization when esterified (activated) D-glucaric acid was condensed with a number of diamines.[7,8] Those studies were motivated by our interest in preparing potentially biodegradable, cost effective, synthetic D-glucaric acid-based polymers, starting with inexpensive and commercially available D-glucose, and employing simple procedures that do not require carbohydrate hydroxyl protection/deprotection steps. Two crystalline activated D-glucaric acid monomers, methyl D-glucarate 1,4-lactone (**1**) and ethyl D-glucarate 6,3-lactone (**2**) were prepared and polymerized with diamines that included alkylenediamines, arylalkylenediamines, and oxa- and azaalkylenediamines, to give the corresponding poly(D-glucaramides).[8] Hashimoto and co-workers also reported use of D-glucaro-1,4:6,3-dilactone (**3**) as the glucaric acid monomer in related condensation polymerizations.[9,10]

As D-glucaric [(2*R*,3*S*,4*S*,5*S*)-2,3,4,5-tetrahydroxyhexanedioic] acid is not a symmetrical diacid, condensation polymerization of its esterified forms with diamines generates polymers with randomly oriented glucaric acid units in the polymer chain. Consequently, in order to take further advantage of D-glucaric acid as an inexpensive chiral acid monomer, we undertook development of an uncomplicated synthetic procedure, which avoided carbohydrate diacid hydroxyl/protection, for preparation of stereoregular *head*(C-1),*tail*(C-6)-poly(alkylene D-glucaramides), **4**.



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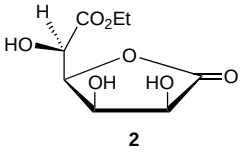

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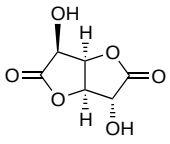

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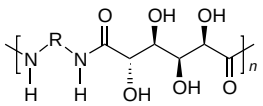

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This report describes development of such a synthetic procedure.

Ultimately, we are interested in comparing the chemical and physical properties of these stereoregular polyamides with those of their random counterparts. It is noted that synthetic polyamides derived from the *meso*-aldaric acids galactaric[3,4] and xylaric acid,[7] respectively, have random orientation, whereas those generated from L-tartaric acid (2*R*,3*R*)[11,12] and D-mannaric acid (2*S*,3*S*,4*S*,5*S*) are stereoregular.[10]

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Results and Discussion

The strategy employed to prepare stereoregularly aligned poly(alkylene D-glucaramides) was to differentiate between the reactivity of the two carboxylic acid ends of D-glucaric acid in order to make a regiospecific aminoalkylmonoamide monoester monomer which could self-condense to the desired *head*,*tail* polyamide. In our initial attempts, we treated **1** or **2** with alkylenediamines under a variety of reaction conditions in hopes of rapidly generating *in situ* such a bifunctional monomer that would self-polymerize at an appreciably slower rate than it was formed. These experiments were designed to take advantage of the high aminolysis reactivity of five-membered lactones, compared to aminolysis of esters, and to generate specific monomers, *N*-(aminoalkyl)-D-glucaramide methyl ester from **1** or *N*-(aminoalkyl)-D-glucaramide ethyl ester from **2**. However, in a basic alcohol solution of **1** or **2**, ester/lactone interconversion to a mixture of 1,4- and 6,3-lactone monoesters and diester was found to occur much faster than the regioselective aminolysis step to monoamide, and the polyamide was deduced to be a randomly connected poly(alkylene D-glucaramide).[13,14]

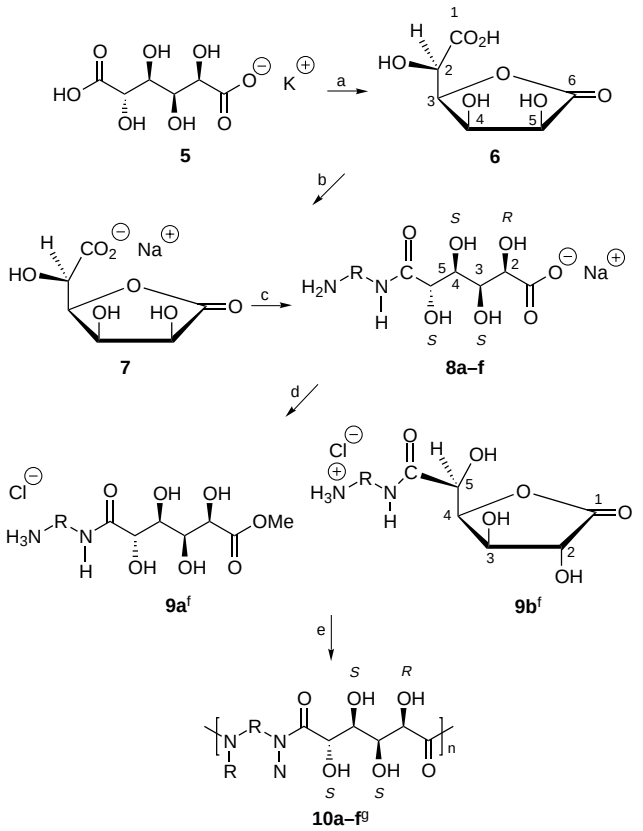
A stepwise approach to the desired stereoregular polymers was then initiated. The plan was to activate only one end carbon of glucaric acid by forming a lactone/salt and then, in a separate step, subject the salt to regiospecific aminolysis with a diamine at the activated carbon (lactone) to generate an (aminoalkyl)-D-glucaramide salt. This amino acid (salt) would then be susceptible to stereoregular self-polymerization after activation by simple esterification of the terminal carboxylic acid salt. A successful synthetic procedure for the target polymers is outlined in Scheme 1.[15,16]

On the basis of a method of Zinner and Fischer,[17] monopotassium D-glucarate (**5**) was treated with acid form resin in water, from which crystalline D-glucaro-6,3-lactone (**6**) was isolated (69%) from a mixture that also contained acyclic D-glucaric acid and D-glucaro-1,4-lactone. Methanol insoluble lactone salt, sodium D-glucarate 6,3-lactone (**7**), prepared according to Kiliani,[18] was warmed for several hours with a methanol solution of an alkylenediamine (C_2−C_{12}, even number of carbons) to give directly, a new methanol insoluble salt, sodium salt of 6-[*N*-(aminoalkyl)-D-glucaramide, compounds **8a**−**f**.

The ^{1}H NMR spectrum (300 MHz) of a representative member (**8b**) of this class of salts is shown in Figure 1. As illustrated with **8b**, the signals from the four protons on the glucaramide salt moiety of these salts are well separated in their ^{1}H NMRspectra with H-5 (δ 4.25, $J_{4,5}$ = 5.33 Hz) and H-2 (δ 4.13, $J_{2,3}$ = 3.10 Hz) each appearing as a doublet. The larger 4,5 coupling is indicative of the typically larger conformationally average dihedral angle between H-4, and H-5 as compared to that between H-2 and H-3. The H-3 (δ 4.06) and H-4 (δ 3.97) signals are upfield to H-2 and H-5 and each appears as a triplet. The internal methylene units of the alkylenediamine (**8b**, H-2′,3′, δ 1.55) are the most shielded protons in the spectra of **8a**−**f**, whereas the H-1′ protons, vicinal to the amido N−H, are the most deshielded methylene protons (**8b**, 2H, δ 3.27, t, $J_{1',2'}$ = 6.0 Hz). The remaining terminal methylene protons signal (**8b**, H-4′, 2H, δ 2.67, t, $J_{3',4''}$ = 6.7 Hz) appears between the latter two signals. The IR spectra of salts **8a**−**f** are consistent with the assigned structures, each containing characteristic N−H and O−H stretching bands, and amide I (C=O) and CO_2^- bands.

Each of the salts **8a**−**f** was then treated with methanolic HCl to convert the C-terminus to a mixture (**9a** and

Scheme 1



(a) H^+ resin/H_2O. (b) NaOAc/H_2O. (c) H_2N−R−NH_2/MeOH, R = $(CH_2)_2$ (**8a**) to $(CH_2)_{12}$ (**8f**), even number of carbons. (d) MeOH/HCl. (e) Excess Et_3N. (f) R = $(CH_2)_2$ to $(CH_2)_{12}$, even number of carbon atoms. (g) **10a**, R = $(CH_2)_2$ to **10f**, R = $(CH_2)_{12}$, even number of carbons.

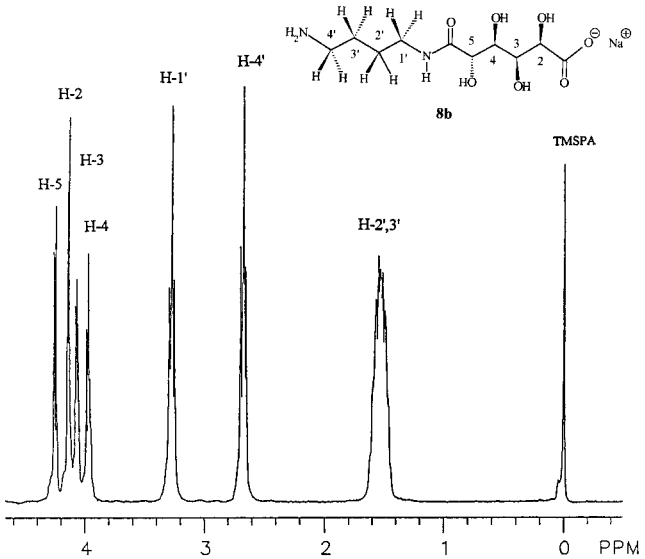


Figure 1. ^{1}H NMR spectrum (D_2O) of sodium salt of 6-[*N*-(4′-aminobutyl)]-D-glucaramide (**8b**).

Each of the salts **8a**−**f** was then treated with methanolic HCl to convert the C-terminus to a mixture (**9a** and

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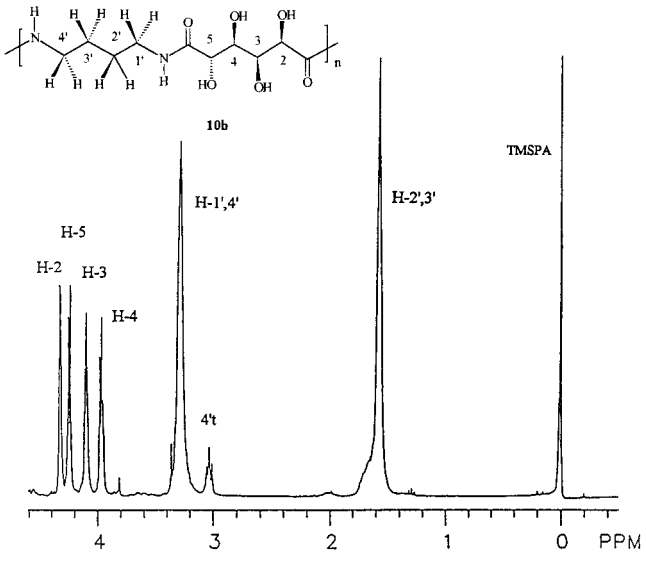

Figure 2. ^{1}H NMR spectrum of *head,tail*-poly(tetramethylene-D-glucaramide) (**10b**).

9b) of the corresponding ester/lactone (^{1}H NMR analysis), followed by basification with triethylamine. Enough triethylamine was added to neutralize any residual HCl, to convert the *N*-terminus alkylammonium function to the free amine, and to catalyze lactone formation of remaining methyl ester. Other bases, including sodium carbonate and sodium methoxide, were also used in conjunction with triethylamine with similar success.[13] As the methyl ester (**9a**)/lactone (**9b**) solutions were made basic, polymerizations began to spontaneously occur. The products, *head,tail*-poly(alkylene D-glucaramides), precipitated from methanol solution and were separated by centrifugation (**10a**) or by filtration (**10b**−**f**). Isolated yields of the polymers ranged from 82.5% (**10e**) to 91.3% (**10c**). The ^{1}H NMR spectrum of a typical stereoregular polyamide, *head,tail*-poly(tetramethylene D-glucaramide) (**10b**), is shown in Figure 2.

Molecular Weight Determinations of Polymers 10a−f. Proton signal integration data from the ^{1}H NMR spectra of the stereoregular polymers (**10a**−**f**) were used to calculate polymer number average molecular weights (M_n). The number average molecular weights (M_n) of the polymers were calculated using an end-group analysis method in which the ^{1}H NMR spectra integral values from the methylene protons on the carbon bonded to the the amido nitrogens (e.g., H-1′ and H-4′ for **10b**, Figure 2) were compared to those of the methylene protons (4′t for **10b**) on the carbon bonded to the terminal amine nitrogen. The calculated M_n values are 1200 (**10a**), 2100 (**10b**), 2440 (**10c**), 1600 (**10d**), 4400 (**10e**), and 3800 (**10f**), respectively. Of the six polymers only **10a** and **10d** were lower than expected, while the value (2400) for sterereoregular *head,tail*-poly(hexamethylene D-glucaramide), **10c**, was comparable to that calculated for the corresponding random polymer.[8] However, it should be noted that the M_n values calculated using NMR end-group analysis are considerably lower than those calculated by a procedure utilizing molecular weight sensitive online light scattering and viscometric detectors following size exclusion chromatographic separation of underivatized polymers.[19] For example, the NMR method gave a M_n of ∼2400 for random poly(hexamethylene-D-glucaramide)[8] but a M_n of 4800 for the same polymer using the molecular weight sensitive method.[19] While methanol was a convenient solvent for the polymerizations described here, other solvents and/or modified experimental procedures may prove to be better for generating higher molecular weight distributions.

Random vs Stereoregular Polymer Properties. Some properties of the polymers investigated thus far are clearly very similar to those of the corresponding random polymers,[8] including high melting points (185−200 °C) and comparable solubilities. The IR and NMR spectra of the stereoregular polymers are consistent with their assigned structures and are very similar to those from the previously described random polymers.[8] However, although all of the solid stereoregular polymers were carefully washed and dried prior to elemental analyses, only the elemental analyses (C,H,N) data for **10b** met the normal standards for analytically pure samples. While the source of this discrepancy has not yet been estalished, there is a possibility that under the reaction conditions employed a small fraction of the N-terminal amino groups in the polymers end up as hydrochloride salts due to HCl interchange with dissolved triethylammonium chloride. In preparation of the random polymers,[8] there is no possibility for terminal amine hydrochloride formation and the elemental analyses are as expected. Further comparisons of the properties of the randon and corresponding stereoregular polymers are under investigation.

Polyamide Conformations. In order to probe the conformational possibilites of the stereoregular polyamides in solution, some preliminary molecular modeling studies (MM2)[20] have been conducted. ^{1}H NMR spectra of the polyamides, e.g., poly(hexamethylene D-glucaramide), and the corresponding diamides, e.g., dihexyl-D-glucaramide, were compared and found to have comparable carbohydrate proton chemical shifts and coupling constants, suggesting comparable carbohydrate conformations in solution (DMSO-d_6 or CF_3CO_2D). A low-energy sickle conformation of the glucaramide monomer unit coupled with an extended conformation of the diamine monomer unit were then used to generate computer-derived drawings of the polymers (e.g., **10c**, Figure 3).[21] These drawings suggest a square-like cavity in the somewhat helical conformation of the polymers, the hole becoming smaller as the alkylenediamine monomer unit becomes shorter. Interestingly, when the alkylenediamine monomer unit has an odd number of carbons in the chain, the computer-derived conformations show a significantly different and triangular shaped cavity in the polymer.[21] Additional molecular modeling studies are planned for the purpose of evaluating in more detail the structures of both the stereoregular and corresponding random polymers.

Summary

Six examples of a new type of stereoregularly aligned carbohydrate-based polyamide, *head,tail*-poly(alkylene-D-glucaramide), have been prepared from monopotassium D-glucarate and aliphatic diamines as starting materials by a process that does not require carbohydrate hydroxyl protection/deprotection.

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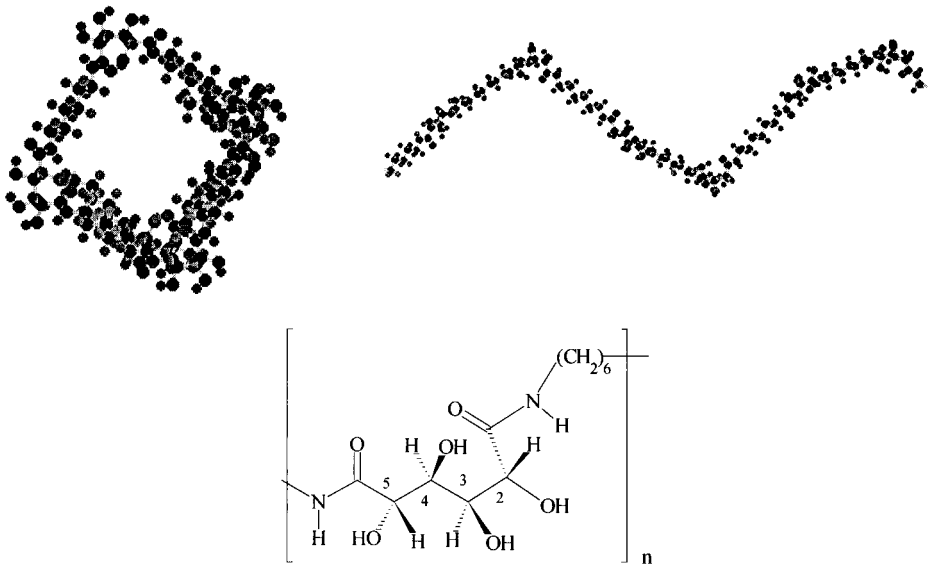

Figure 3. End-on and side view of *head,tail*-poly(hexamethylene D-glucaramide)[a] (**10c**) based on MM2 calculations.[20] (Reproduced in part with permission from ref 21. Copyright 1993 American Chemical Society.)

Experimental Section

General Methods. All ^{1}H and ^{13}C NMR spectra were recorded at 300.13 and 75.4 MHz, respectively. Chemical shifts are reported as ppm (δ) downfield from tetramethylsilane (TMS) or 3-(trimethysilyl)propionic-2,2,3,3-d_4 acid, sodium salt, (TMSPA). IR spectra were recorded as KBr pellets. All solvents used were reagent grade unless stated otherwise. Melting points are reported uncorrected. Solvent evaporations were carried out at reduced pressure.

D-Glucaro-6,3-lactone (6).[17] To a mixture of monopotassium D-glucarate (10.0 g, 39.89 mmol) (**5**) and water (100 mL) was added acid form cation exchange resin [20 mL, 40 mequiv of total exchange capacity, Rexyn 100(H)] that had been prewashed with deionized water. The potassium salt dissolved within 10 min, the mixture was stirred for 3 h, and the resin was removed by filtration and washed with deionized water (3 × 10 mL). The resin was left aside for regeneration to its acid form, and the filtrate was concentrated to a syrup at 60 °C. The syrup was seeded with pure D-glucaro-3,6-lactone (**7**) and solidified as a cake in 2−3 days. The cake was triturated with acetone (15 mL), and the white solid was removed by filtration and air-dried to yield D-glucaro-6,3-lactone (**6**, 4.85 g, 62.7%). When this experiment was scaled up to 50.0 g of monopotassium D-glucarate (**5**), D-glucaro-6,3-lactone was obtained in 69.1% yield (26.49 g, 137.9 mmol): mp 130−135 °C (lit.[17] mp 133−135 °C); IR (KBr), 2913, 1780, and 1725 cm^{-1}; ^{1}H NMR (CD_3OD) δ 4.59 (dd, 1H, J = 6.73 Hz, J = 2.12), 4.53 (m, 2H), 4.51 (m, 1H); proton decoupled ^{13}C NMR (D_2O) δ 178.8, 174.5, 81.61, 71.65, 71.31, and 69.89. Anal. Calcd for $C_6H_8O_7$ (192.1): C, 37.51; H, 4.20. Found: C, 37.18; H, 4.16.

Sodium D-glucarate 6,3-Lactone (7).[18] To a solution of D-glucaro-6,3-lactone (**6**, 3.00 g, 15.6 mmol) in deionized water (10 mL) was added sodium acetate (2.125 g, 15.62 mmol, $CH_3COONa\cdot 3H_2O$, FW 136.08) which readily dissolved. The solution was set aside without stirring at room temperature for 6 h with white crystals beginning to form within 20 min after scratching the walls of the reaction glass. The crystalline product was removed by filtration and washed with acetone (3 × 5 mL). Additional product crystallized from the aqueous acetone over 2 h and was combined with the first crop of crystals. The acetone washings, crystallization, and filtration process was repeated once more, and the combined white solids were dried at reduced pressure (0.25 Torr) and 50 °C to give sodium D-glucarate 6,3-lactone (**7**, 2.60 g, 12.1 mmol, 77.6%): mp 180 °C dec; IR (KBr) 3292, 2860, 1782, and 1597 cm^{-1}; proton decoupled ^{13}C NMR (D_2O) δ 177.34, 175.50, 81.61, 70.50, 69.53; ^{1}H NMR (D_2O) δ 4.765 (d, 1H, J = 5.1 Hz), 4.626 (m, 2H), and 4.392 (m, 1H). Anal. Calcd for $C_6H_7O_7Na$ (214.11): C, 33.67; H, 3.30; Na, 10.74. Found: C, 33.42; H, 3.35; Na, 10.61.

Sodium Salt of 6-[*N*-(2′-Aminoethyl)]-D-glucaramide (8a). A mixture of finely ground sodium D-glucarate 6,3-lactone (**7**, 0.600 g, 2.80 mmol), methanol (12 mL), and ethylenediamine (6 mL, 89.7 mmol) in a 100 mL round-bottomed flask was refluxed for 3 h at an oil bath temperature of 95 °C. During reflux, the amount of insoluble white solid in the reaction mixture appeared to increase. The mixture was cooled to room temperature, and the white solid was removed by filtration, washed with methanol (2 × 10 mL), acetone (2 × 10 mL), and dried at reduced pressure (0.25 torr) and 60 °C for 6 h to give sodium salt of 6-[*N*-(2′-aminoethyl)]-D-glucaramide (**8a**, 0.704 g, 2.57 mmol, 91.7%): mp 195−299 °C dec; IR (KBr) 3412, 3170, 1664, 1620, and 1517 cm^{-1}; ^{1}H NMR (D_2O) δ 4.15 (d, 1H, J = 3.14 Hz), 4.07 (dd, 1H) 3.69 (dd, 1H, J = 5.35 Hz), 4.27 (d, 1H), 3.34 (t, 2H, J = 6.0 Hz), 2.77 (t, 2H). Anal. Calcd for $C_8H_{15}O_7N_2Na$: C, 35.04; H, 5.52; N, 10.21; Na, 8.38. Found: C, 35.01; H, 5.51; N, 10.12; Na, 8.29.

Sodium salt of 6-[*N*-(4′-aminobutyl)]-D-glucaramide (8b) was prepared according to the method for **8a**: salt **7** (2.00 g, 9.34 mmol), methanol (50 mL), tetramethylenediamine (5.0 mL, 49.7 mmol), reflux 3 h, oil bath temperature 95 °C. Sodium salt of 6-[*N*-(4′-aminobutyl)]-D-glucaramide (**8b**, 2.68 g, 8.86 mmol, 94.9%): mp 205−208 °C dec; IR (KBr) 3396, 3343, 3169, 1659, 1613, and 1522 cm^{-1}; ^{1}H NMR (D_2O) δ 4.13 (d, 1H, J = 3.10 Hz), 4.06 (t, 1H), 3.97 (t, 1H, J = 5.33 Hz), 4.25 (d, 1H), 3.27 (t, 2H, J = 6.0 Hz), 1.55 (m, 4H), 2.67 (t, 2H, J = 6.7 Hz). Anal. Calcd for $C_{10}H_{19}O_7N_2Na$: C, 39.73; H, 6.34; N, 9.27; Na, 7.62. Found: C, 39.69; H, 6.38; N, 9.24; Na, 7.54.

Sodium salt of 6-[*N*-(6′-aminohexyl)]-D-glucaramide (8c) was prepared according to the method for **8a**: salt **7** (0.50 g, 2.34 mmol), methanol (30 mL), hexamethylenediamine (5.0 mL, 42.03 mmol), reflux 3 h, oil bath temperature 95 °C. Sodium 6-[*N*-(6′-aminohexyl)]-D-glucaramide (**8c**, 0.701 g, 2.12 mmol, 90.9%): mp 209−212 °C dec; IR (KBr) 3393, 3341, 3167, 1655, 1625, and 1519 cm^{-1}; ^{1}H NMR (D_2O) δ 3.93 (d, 1H, J = 2.63 Hz), 3.86 (t, 1H), 3.77 (t, 1H, J = 4.89 Hz), 4.04 (d, 1H), 3.05 (t, 2H, J = 6.6 Hz), 2.44 (t, 2H, J = 6.9 Hz), 1.35 (m, 2H), 1.26 (m, 2H), 1.14 (s, 4H). Anal. Calcd for $C_{12}H_{23}O_7N_2Na$: C, 43.63; H, 7.03; N, 8.48; Na, 6.96. Found: C, 43.61; H, 7.06; N, 8.37; Na, 6.94.

Sodium salt of 6-[*N*-(8′-aminooctyl)]-D-glucaramide (8d) was prepared according to the method for **8a**: salt **7** (1.00 g, 4.67 mmol), methanol (30 mL), octamethylenediamine (3.37 mL, 23.4 mmol), reflux 3 h, oil bath temperature 95 °C. Sodium salt of 6-[*N*-(8′-aminooctyl)]-D-glucaramide (**8d**, 1.57 g, 4.38 mmol, 93.8%): mp 205−208 °C; IR (KBr) 3392, 3165,1654, 1627, and 1517 cm^{-1}; ^{1}H NMR (D_2O) δ 4.13 (d, 1H, J = 3.01 Hz), 4.06 (t, 1H, J = 4.44 Hz), 3.97 (dd, 1H, J = 5.03

Hz), 4.24 (d, 1H), 3.25 (t, 2H, $J = 6.6$ Hz), 2.68 (t, 2H, $J = 7.2$ Hz), 1.48 (m, 4H), 1.32 (s, 8H). Anal. Calcd for $C_{14}H_{27}O_7N_2$-Na (358.4): C, 46.92; H, 7.60; N, 7.82; Na, 6.41. Found: C, 46.70; H, 7.55; N, 7.78; Na, 6.46.

Sodium salt of 6-[*N*-(10′-Aminodecyl)]-D-glucaramide (8e) was prepared according to the method for **8a**: salt **7** (1.00 g, 4.67 mmol), methanol (30 mL), decamethylenediamine (5.00 g, 29.0 mmol), reflux 3 h, oil bath temperature 95 °C. Sodium salt of 6-[*N*-(10′-aminodecyl)]-D-glucaramide (**8e**, 1.63 g, 4.22 mmol, 90.3%): mp 195−198 °C; IR (KBr) 3391, 3165,1653, 1628, and 1518 cm^{-1}; ^1H NMR (D_2O) δ 4.14 (d, 1H, $J = 3.18$ Hz), 4.06 (t, 1H), 3.97 (t, 1H, $J = 5.36$ Hz), 4.24 (d, 1H), 3.24 (t, 2H, $J = 6.77$ Hz), 2.69 (t, 2H, $J = 7.10$ Hz), 1.50 (m, 4H), 1.30 (s, 12H). Anal. Calcd for $C_{16}H_{31}O_7N_2Na$ (386.46): C, 49.73; H, 8.10; N, 7.25; Na, 5.95. Found: C, 49.45; H, 7.96; N, 7.23; Na, 5.99.

Sodium salt of 6-[*N*-(12′-aminododecyl)]-D-glucaramide (8f) was prepared according to the method for **8a**: salt **7** (1.00 g, 4.67 mmol), methanol (30 mL), dodecamethylenediamine (5.0 g, 25.0 mmol), reflux 3 h, oil bath temperature 95 °C. Sodium salt 6-[*N*-(12′-aminododecyl)]-D-glucaramide (**8f**, 1.77 g, 4.27 mmol, 91.5%): mp 198−200 °C; IR (KBr) 3390, 3338, 3163, 1653, 1630, and 1520 cm^{-1}; ^1H NMR (acetic acid-d_6) δ 4.52 (d, 1H, $J = 2.40$ Hz), 4.32 (dd, 1H, $J = 3.12$ Hz), 4.15 (dd, 1H, $J = 5.90$ Hz), 4.35 (d, 1H), 3.30 (t, 2H), 3.04 (t, 2H), 1.69 (m, 2H), 1.55 (m, 2H), 1.32 (s, 16H). Anal. Calcd for $C_{18}H_{35}O_7N_2Na$ (414.5): C, 52.15; H, 8.52; N, 6.76; Na, 5.55. Found: C, 52.20; H, 8.50; N, 6.72; Na, 5.55.

***head,tail*-Poly(ethylene D-glucaramide) (10a).** A mixture of sodium salt of 6-[*N*-(2′-aminoethyl)]-D-glucaramide (**8a**, 1.00 g, 3.65 mmol) and methanol (10 mL) in a 100 mL round-bottomed flask was cooled in an ice bath, and to the mixture was added acetyl chloride (1.5 mL, 20 mmol) with stirring to dissolve the monoamide salt. The solution was stirred at room temperature for 3 h and then concentrated to a syrup. The ^1H NMR (D_2O) spectral data from the syrup was consistent with a mixture the of the C-1 methyl ester salt (**9a**) and 1,4-lactone salt (**9b**): for **9b**, δ 5.13 (dd, 1H, $J = 3.69$ Hz), 4.82 (d, 1H, $J = 8.94$ Hz), 4.73 (d, 1H, $J = 3.69$), 4.63 (dd, 1H, $J = 7.91$ Hz, $J = 8.94$); for **9a**, 4.55 (d, 1H, $J = 3.02$ Hz), 4.31 (d, 1H, $J = 4.88$ Hz), 4.14 (dd, 1H, $J = 5.26$ Hz, $J = 3.02$ Hz), 3.96 (dd, 1H, $J = 5.26$ Hz, $J = 4.88$ Hz), 3.82 (s, 3H), 3.18 (q, 2H). The molar ratio of **9b** to **9a** was estimated to be 1.6:1.0. The syrup was dissolved in methanol (15 mL) and made just basic by careful addition of triethylamine (pH paper). Additional triethylamine (0.5 mL) was added to the solution which was then stirred at room temperature for 30 min. The insoluble solid product was removed by centrifugation, washed with methanol (2 × 5 mL) and acetone (2 × 5 mL), and dried at reduced pressure and at an oil bath temperature of 70 °C. *head,tail*-Poly(ethylene-D-glucaramide) (**4a**, 0.753 g, 3.22 mmol, 88.2%): mp 185 °C dec; IR (KBr) 3343, 2950, 1651, and 1545 cm^{-1}; ^1H NMR (D_2O) δ 4.34 (d, 1H, $J = 2.3$ Hz), 4.10 (s, 1H), 3.96 (m, 1H, $J = 5.77$ Hz), 4.26 (d, 1H), and 3.43 (s, 4H). Anal. Calcd for $C_8H_{14}O_6N_2$ (234.21): C, 41.03; H 6.02; N, 11.96. Found: C, 37.94; H, 5.83; N, 10.84.

***head,tail*-Poly(tetramethylene D-glucaramide) (10b)** was prepared according to the method for **4a**: salt **8b** (1.00 g, 3.31 mmol), methanol (10 mL), cooled (ice bath), acetyl chloride (1.5 mL, 20 mmol), room temperature 3 h, workup. *head,tail*-Poly(tetramethylene-D-glucaramide) (**11b**, 0.749 g, 2.85 mmol, 86.3%): mp 185−188 °C dec; IR (KBr) 3312, 2940, 1635, and1543 cm^{-1}; ^1H NMR (D_2O) δ 4.32 (d, 1H, $J = 2.87$ Hz), 4.09 (dd, 1H, $J = 4.53$ Hz), 3.96 (dd, 1H, $J = 5.23$ Hz), 3.30 (s, 4H) and 1.59 (s, 4H). Anal. Calcd for $C_{10}H_{18}O_6N_2$ (262.26): C, 45.80; H, 6.92; N, 10.68. Found: C, 45.72; H, 6.94; N, 10.42.

***head,tail*-Poly(hexamethylene D-glucaramide) (10c)** was prepared according to the method for **4a**: salt **8c** (1.00 g, 3.03 mmol), methanol (10 mL), cooled (ice bath), acetyl chloride (1.5 mL, 20 mmol), room temperature 3 h, workup. *head,tail*-Poly(hexamethylene-D-glucaramide) (**4c**, 0.802 g, 2.76 mmol, 91.3%): mp 187−190 °C dec; IR (KBr) 3313, 2931, 1637, and 1544 cm^{-1}; ^1H NMR (CF_3COOD). δ 4.95 (s, 1H), 4.75 (s, 1H), 4.60 (d, 1H, 4.90 (d, 1H), 3.58 (s, 4H), 1.78 (s, 4H), 1.50 (s, 4H). Anal. Calcd for $C_{12}H_{22}O_6N_2$ (290.31): C, 49.65; H, 7.64; N, 9.65. Found: C, 48.71; H, 7.41; N, 9.56.

***head,tail*-Poly(octamethylene D-glucaramide) (10d)** was prepared according to the method for **4a**: salt **8d** (1.00 g, 3.03 mmol), methanol (10 mL), cooled (ice bath), acetyl chloride (1.5 mL, 20 mmol), room temperature 3 h, workup. *head,tail*-Poly(octamethylene-D-glucaramide) (**4d**, 0.761 g, 2.39 mmol, 85.7%): mp 185−190 °C dec; IR (KBr) 3304, 2926, 1639, and 1544 cm^{-1}; ^1H NMR (CF_3COOD) δ 4.97 (s, 1H), 4.77 (s, 1H), 4.60 (d, 1H, $J = 5.7$ Hz), 4.91 (d, 1H), 3.58 (s, 4H), 1.78 (s, 4H), 1.50 (s, 8H). Anal. Calcd for $C_{14}H_{26}O_6N_2$ (318.36): C, 52.82; H, 8.23; N, 8.80. Found: C, 49.14; H, 7.95; N, 8.65.

***head,tail*-Poly(decamethylene D-glucaramide) (10e)** was prepared according to the method for **4a**: salt **8e** (0.50 g, 1.29 mmol), methanol (10 mL), cooled (ice bath), acetyl chloride (1.5 mL, 20 mmol), room temperature 3 h, workup. *head,tail*-Poly(decamethylene-D-glucaramide) (**4e**, 0.370, 1.07 mmol, 82.5%): mp 193−196 °C dec; IR (KBr) 3305, 2923, 1640, and 1546 cm^{-1}; ^1H NMR (CF_3COOD) δ 4.93 (s, 1H), 4.75 (s, 1H), 4.58 (d, 1H, $J = 5.7$ Hz), 4.88 (d, 1H), 3.58 (s, 4H), 1.71 (s, 4H), 1.41 (s, 12H). Anal. Calcd for $C_{16}H_{30}O_6N_2$ (346.43): C, 55.47; H, 8.73; N, 7.48. Found: C, 56.43; H, 8.94; N, 7.28.

***head,tail*-Poly(dodecamethylene D-glucaramide) (10f)** was prepared according to the method for **4a**: salt **8f** (0.50g, 1.21 mmol), methanol (10 mL), cooled (ice bath), acetyl chloride (1.5 mL, 20 mmol), room temperature 3 h, workup. *head,tail*-Poly(dodecamethylene-D-glucaramide) (**4f**, 0.386, 1.03 mmol, 85.5%): mp 193−196 °C dec; IR (KBr) 3300 cm^{-1} (O−H, stretch), 2921, 1641, and 1547 cm^{-1}; ^1H NMR (CF_3COOD) δ 4.94 (s, 1H), 4.75 (s, 1H), 4.58 (d, 1H, $J = 6.0$ Hz), 4.90 (d, 1H), 3.58 (s, 4H), 1.71 (s, 4H), 1.45 (s, 16 H). Anal. Calcd for $C_{18}H_{34}O_6N_2$ (374.48): C, 57.33; H, 9.15; N, 7.48. Found: C, 56.88; H, 9.16; N, 7.46.

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