Hydroxylated Nylons Based on Unprotected Esterified D-Glucaric Acid by Simple Condensation Reactions

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Abstract: Convenient procedures are described for the preparation of hydroxylated nylons (polyhydroxypolyamides) from D-glucaric acid. The procedures, which do not require protection/deprotection of carbohydrate hydroxyl groups, can be used to make a variety of polymers with a range of properties from D-glucaric acid. Simple alcohol (*e.g.* methanol or ethanol) esterification mixtures of D-glucaric acid (from oxidation of D-glucose) were reacted with bis-primary diamines in a polar solvent, typically methanol, to produce the polyamides. D-Glucaric acid esterification mixtures contain varying amounts of dialkyl D-glucarate, alkyl D-glucarate 1,4-lactone, and alkyl D-glucarate 6,3-lactone. These ester forms of D-glucaric acid are also in equilibrium under the conditions of the polymerization. Diamines employed included linear alkylenediamines, a branched alkylenediamine, arylalkylenediamines, and diamines with oxygen or nitrogen atoms in the alkylene chain. Considerable differences in polymer physical properties were observed by changing the diamine monomer. Linear aliphatic and arylalkylenediamines gave crystalline solid polyamides with high melting points. The C_2 and C_4 diamine copolymers were water soluble, whereas the C_6 and above were water insoluble. The branched diamine copolymer and those with oxygen or nitrogen in the diamine chain had lower melting points and higher alcohol solubility than the unbranched alkylenediamine copolymers.

Introduction

Typical petroleum-based polymers are prepared by polymerization of relatively simple hydrocarbon or substituted hydrocarbon monomers using standard ionic or free radical reactions. Commercially successful synthetic polymers have been developed in this century by adapting polymer reactions to an economically favorable industrial scale. In recent years, however, increased awareness of the low biodegradability characteristics of the dominant petroleum based polymers and the need for conservation of petroleum feedstocks has drawn attention to employing carbohydrates as a source of monomers in polymer chemical synthesis.

In comparison to petroleum-based polymers, envisioned commercial-scale carbohydrate-based synthetic polymers would be prepared by polymerization of small activated carbohydrate molecule monomers. Commercially attractive processes from carbohydrate source to polymer should be only a few steps, require no carbohydrate protection/deprotection, and generally avoid the need for extensive polymer purification. Furthermore, new polymerization processes based on D-glucose, from hydrolyzed starch, would be considered economically advantageous, since D-glucose is the most commercially important and least expensive simple sugar currently available. Poly(lactic acid) is a notable example of the use of D-glucose as a feedstock for a synthetic carbohydrate, biodegradable polymer.[1] L-Lactic acid, the monomer for the polymerization process, is produced from starch by a fermentation process.[2]

In concert with our studies of dicarbonyl sugars and an emerging interest in carbohydrate polymer chemistry, we have begun to employ simple carbohydrate diacids, *i.e.*, aldaric acids, as monomers for the synthesis of hydroxylated nylons, polyamides wherein the diacid monomer unit of a typical nylon copolymer, such as nylon 6,6, is replaced by a carbohydrate diacid. Carbohydrate molecules have been previously employed to make such polyamides, but the early reports required protection/deprotection steps. For example, Wolfrom and co-workers synthesized polyamides by condensation of an *O*-protected aldaroyl dichloride, tetra-*O*-acetylgalactaroyl dichloride, with ethylenediamine or piperazine to make the corresponding polymers.[3] A series of carbohydrate-based polyamides formed by Dewar and co-workers was prepared by condensation of di-*O*-alkylenehexaroyl dichlorides with diamines or of 1,6-diamino-1,6-dideoxydi-*O*-alkylenehexitols with aliphatic diacid dichlorides.[4] More recently Thiem and Bachmann carried out similar interfacial condensations between 2,5-diamino-2,5-dideoxydianhydrols and aromatic and aliphatic diacid dichlorides.[5] Polyamide polymerization processes employing unprotected activated aldaric acids were pioneered by Ogata and co-workers beginning in the 1970's.[6-12] These investigators described condensations of diethyl mucate (diethyl galactarate) and dimethyl tartarate with several diamines including hexamethylenediamine.[6-12] The condensations take place at room temperature in polar solvents such as methanol, methyl sulfoxide, and *N*-methylpyrrolidone. These workers observed that, in general, diesters having heteroatoms, such as oxygen and sulfur, bonded to the carbon α to the carbonyl carbons underwent polymerization with diamines under mild conditions.

Hoagland detailed a mechanism for the aminolysis of diethyl galactarate[13] and diethyl xylarate,[14] a mechanism requiring a two step sequence at each diester function: a fast base-catalyzed

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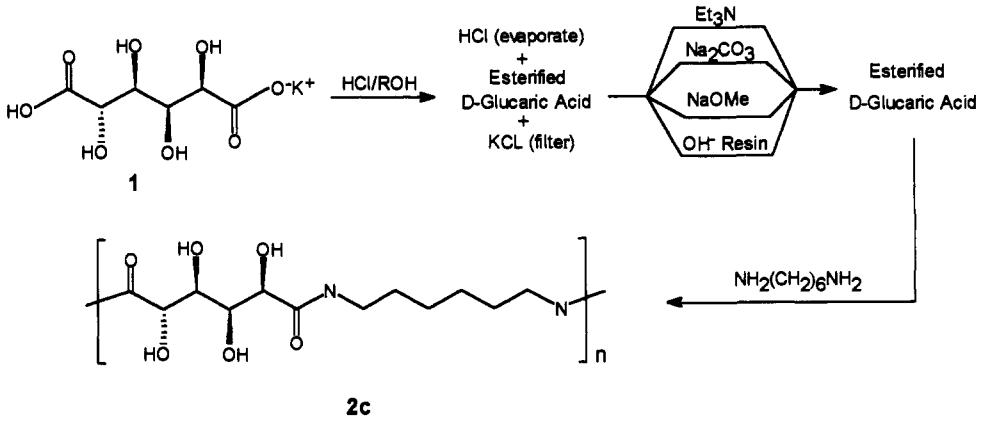
Scheme 1. Direct Method for Preparation of Poly(hexamethylene D-glucaramide) (**2c**) from Monopotassium D-Glucarate (**1**)



1

2c

five-membered lactonization step followed by a slower step, aminolysis of the lactone. It is clear from Hoagland's work that activation of five- or six-carbon aldaric acid diesters results from the facile formation and high reactivity of these five-membered aldarolactones.

Our interest in this field of study is twofold: (a) development of suitably activated D-glucaric acid ester monomers for polymerization to poly(alkylene D-glucaramides), *i.e.*, hydroxylated nylons based on commercially abundant D-glucose, and (b) preparation and characterization of the resulting polyamides.

Results and Discussion

Our efforts to prepare activated D-glucaric acid monomers began with treating a water suspension of calcium D-glucarate with a strong acid cation-exchange resin to give an aqueous solution of the free acid form.[15,16] Following removal of the water by freeze drying, the noncrystalline mixture of principally D-glucaro-1,4- and -6,3-lactones[17] was treated with methanolic HCl to give a mixture of dimethyl D-glucarate and methyl D-glucarate 1,4- and 6,3-lactones. Ogata *et al.*[6-12] employed easily isolated acyclic diester forms of L-tartaric and galactaric acids as carbohydrate monomers in their polyamide syntheses. However, since a comparable acyclic diester of D-glucaric acid was not available, the D-glucaric acid methanol esterification mixture, in methanol solution containing triethylamine, was used directly for polymerization with the diamine of choice to give the poly(alkylene D-glucaramide). The function of the added tertiary amine, triethylamine, was to insure that the important base-induced lactonization step would continue at an appreciable rate even near the end of polymerization when the concentration of diamine was very low. In order to improve the overall conversion of D-glucarate salt to polyamide method, we established two goals: (1) development of a process that avoids the use of water and subsequent need for its removal and (2) employment of easy to prepare, crystalline, activated D-glucaric acid monomers for the process. Process improvement was motivated by the practical needs to keep the process simple, employ good stoichiometric control of both monomers, and make the process as versatile as possible.

Direct Preparation of D-Glucaric Acid Ester/Lactone Monomers. The first improvement deemed necessary was preparation of a mixture of activated D-glucaric acid esters by direct acidification/esterification of a D-glucaric acid salt in alcohol solution. This avoids use and removal of solvent water in the process, an energy-saving step if commercial preparation is to be made practical. Consequently, in a newly developed typical procedure (Scheme 1), monopotassium D-glucarate (**1**) is warmed with methanolic HCl for 3–4 h, the insoluble potassium chloride removed by filtration, the solution concentrated, and the D-glucaric acid methyl ester/lactone mixture redissolved in methanol. Small amounts of residual HCl in the solution can be conveniently neutralized with bases that include triethylamine, sodium carbonate, sodium methoxide, or hydroxide form anion-exchange resin. This neutralized solution can then be used for direct polymerization with the diamine. The procedure is illustrated using hexamethylenediamine to give poly(hexamethylene D-glucaramide), **2c**.[18] Use of ethanol in place of methanol in the acidification/esterification process works well and offers the advantage of more efficient precipitation of potassium chloride prior to polymerization.

Crystalline D-Glucaric Acid Ester/Lactone Monomers. The next targeted improvement in the process was to employ specific crystalline and weighable D-glucaric esters/lactones for purposes of obtaining good stoichiometric control of the diacid monomer in the condensation polymerization. In studying the equilibrium relationship between the components of methanol esterified D-glucaric acid, we became aware that drying the mixture under vacuum drove the equilibrium predominantly to the two five-membered lactone components, methyl D-glucarate 1,4-lactone (**3**) and methyl D-glucarate 6,3-lactone (**4**).[18a,19] Extended drying further pushed the equilibrium to the bis-lactone, D-glucaro-1,4:6,3-dilactone (**5**).[20]

Methyl D-Glucarate 1,4-Lactone (3). This ester lactone is a known crystalline D-glucaric acid derivative.[20] We found that it could be conveniently prepared directly from monopotassium D-glucarate (**1**). Stirring the potassium salt in methanol in the presence of a strong acid form cation exchange resin solubilized the salt and esterified the acid. Removing the solvent yielded crude crystalline **3** (>70%) (Scheme 2). Trituration of the product with ethanol gave **3** with a mp of 158–160 °C (lit.[20] 165 °C), overall yield 50%. Alternatively, stirring the salt with methanolic HCl, removing precipitated KCl by filtration, and concentrating the methanol solution gave crude crystalline **3** that contained about 10% residual KCl. However, salt-free, crystalline **3** could be obtained after concentration of a methanol solution of the crude product that had been treated with a limited amount of strong acid form cation-exchange resin, 58% overall yield of **3**. The residue from both preparations is a mixture of methanol esterified D-glucaric acid that can be used directly for polym-

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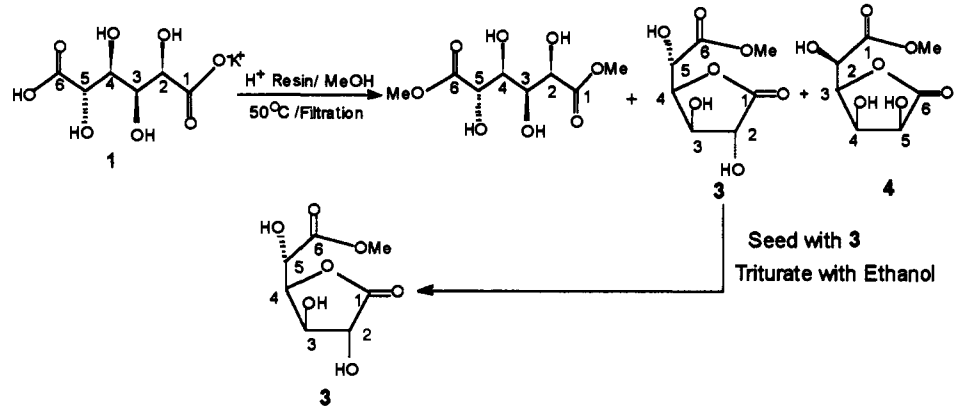
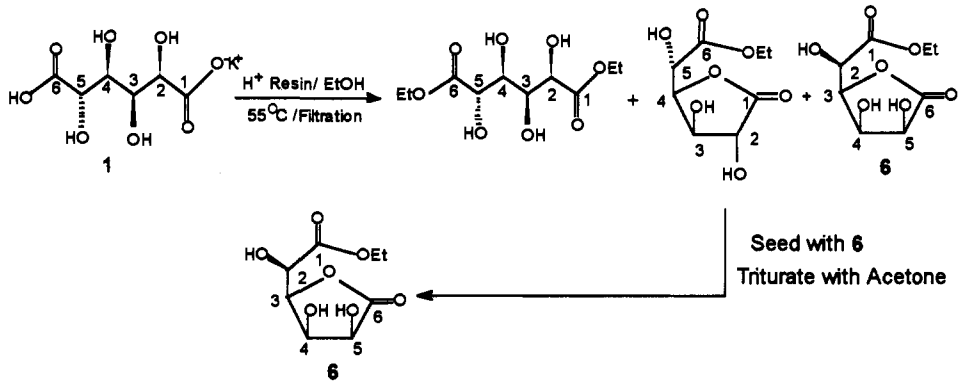
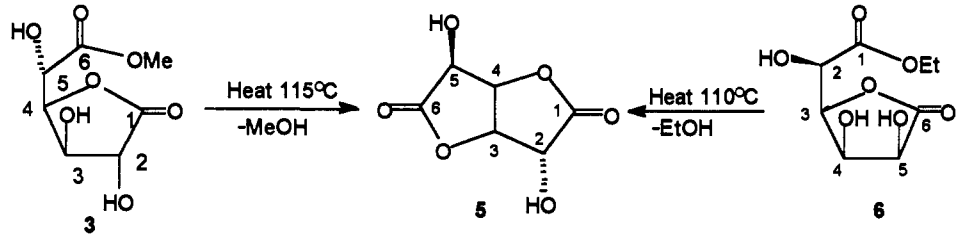
Scheme 2. Preparation of Methyl D-Glucarate 1,4-Lactone Using the H^+ Resin/Methanol Procedure



Scheme 3. Preparation of Ethyl D-Glucarate 6,3-Lactone Using the H^+ Resin/Ethanol Procedure



Scheme 4. Preparation of D-Glucaro-1,4:6,3-dilactone from D-Glucarate Ester/Lactones



erization with diamine or re-equilibrated with acid/methanol to give additional crystalline **3**.

Ethyl D-Glucarate 6,3-Lactone (6). A second previously reported crystalline D-glucarate ester/lactone, ultimately found to be well suited for polymerization, is ethyl D-glucarate 6,3-lactone (**6**).[21] This ester/lactone was prepared by stirring monopotassium D-glucarate (**1**) with a mixture of ethanol and strong acid form cation-exchange resin. Workup gave crude **6** (61%), and triturating this material with acetone gave pure product **6** (mp 121–123 °C (lit.[21] mp 122 °C)) in 58% overall yield (Scheme 3). The residue from preparation of this ethyl ester/lactone can also be used for polymerization with the diamine of choice.

D-Glucaro-1,4:6,3-dilactone (5). This dilactone as an activated, crystalline D-glucaric acid was condensed by Hashimoto and coworkers[22] with the arylalkyldiamine *p*-xylylenediamine to form poly(*p*-xylylene D-glucaramide). These workers prepared this dilactone by repeated lyophilization of a D-glucaric acid/lactones mixture in 1,4-dioxane and subsequent drying at 60 °C at reduced pressure. With the ester/lactones **3** and **6** on hand, we decided to try to prepare the dilactone **5** by melting the lactone/ester at reduced pressure and driving off the methanol or ethanol, respectively. Both **3** and **6** readily underwent conversion to dilactone **5** in this way, the latter being crystallized (98%) from a concentrated acetone solution after seeding (Scheme 4). This is a convenient route to **5** and gives us a third readily available activated D-glucaric acid monomer that can be used in the polymerizaton condensation with diamines.

Table 1. Characteristic IR Frequencies (cm^{-1}) from **3**, **6**, and **5**

compounds	OH	lactone (C=O)	ester (C=O)
methyl D-glucarate 1,4-lactone (**3**)	3430	1781	1728
ethyl D-glucarate 6,3-lactone (**6**)	3420	1774	1717
D-glucaro-1,3:6,3-dilactone (**5**)	3390	1790	

Spectroscopic characterization of these three monomers was carried out using IR and ^1H and ^{13}C NMR techniques (Tables 1–3). The ^1H chemical shift assignments are consistent with general observations applied to carbohydrate lactones[23] and were verified using proton–proton decoupling experiments. Assignment of D-glucaro-1,4:6,3-dilactone (**5**) protons was based upon Horton and Walaszek's earlier report.[23] The ^1H NMR spectrum of ethyl D-glucarate 6,3-lactone (**4**) was not well resolved but is similar to the previously assigned D-glucaro-6,3-lactone spectrum.[18a,19] The ^{13}C NMR chemical shift assignments for **3**, **5**, and **6** are

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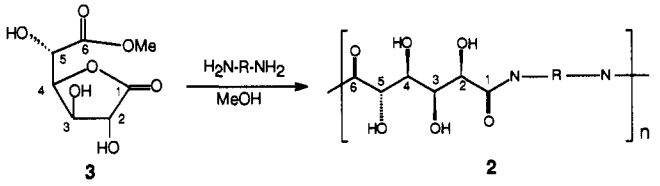
Table 2. ^{1}H NMR Chemical Shifts (ppm) and Coupling Constants (Hz) for Methyl D-Glucarate 1,4-Lactone and D-Glucaro-1,4:6,3-Dilactone

compounds	H-2	$J_{2,3}$	H-3	$J_{3,4}$	H-4	$J_{4,5}$	H-5
methyl D-glucarate 1,4-lactone (3)	4.60 (d)	8.15	4.44 (dd)	7.31	4.97 (dd)	2.36	4.49 (d)
D-glucaro-1,4:6,3-dilactone (5)	4.61 (s)		5.19 (d)	3.85	5.51 (dd)	5.37	4.98 (d)
ethyl D-glucarate 6,3-lactone (4)	spectrum not well resolved, see Experimental Section						

Table 3. ^{13}C NMR Chemical Shifts of Methyl D-Glucarate 1,4-Lactone, Ethyl D-Glucarate 6,3-Lactone and D-Glucaro-1,4:6,3-Dilactone

compounds	C-1	C-2	C-3	C-4	C-5	C-6
methyl D-glucarate 1,4-lactone (3)	172.29	71.11	81.66	71.03	71.77	177.55
ethyl D-glucarate 6,3-lactone (6)	177.35	75.54	70.79	80.49	73.68	173.19
D-glucaro-1,4:6,3-dilactone (5)	178.37	73.72	82.90	81.76	71.47	178.37

Scheme 5. Synthesis of Poly(alkylene and related D-glucaramides) (2a–2l) from Methyl D-Glucarate 1,4-Lactone (3) and Diamines



3 2

2a: R= $(CH_2)_2$ 2b: R= $(CH_2)_4$

2c: R= $(CH_2)_6$ 2d: R= $(CH_2)_8$

2e: R= $(CH_2)_{10}$ 2f: R= $(CH_2)_{12}$

2g: R= CH_2–C$_6$H$_4$–CH_2 2h: R= CH_2–C$_6$H$_4$–CH_2

2i: R= $CH_2CH_2OCH_2CH_2OCH_2CH_2$ 2j: R= $CH_2CH(CH_3)CH_2CH_2CH_2$

2k: R= $(CH_2)_3NH(CH_2)_3$ 2l: R= $(CH_2)_3N(CH_3)(CH_2)_3$

presented in the report on the equilibrium relationship of these compounds in methanol solution.[18a,19]

Poly(alkylene D-glucaramides) (2a–2l). In a typical procedure a methanol solution of an activated D-glucaric acid monomer (from **3**, **5**, or **6**, but most commonly from **3**), triethylamine, and alkylenediamine was stirred at room temperature for several hours. During this time the polymer precipitated from solution and was separated and then washed with methanol. Scheme 5 describes the preparation of twelve poly(D-glucaramides) made in this way. Table 4 contains the yield, melting point, and water and methanol solubilities of each polymer. Isolated yields of the solid products, after removal by simple filtration from the reaction mixture, ranged from 67% for poly(4′-azaheptamethylene D-glucaramide) (**2k**) to 96% for poly(*m*-xylenyl D-glucaramide) (**2h**).

Molecular Weight Determinations of Poly(hexamethylene D-glucaramide). We have begun to evaluate methods for determining molecular weights of the polymers and describe here our preliminary results. Our model polymer for evaluating these methods was poly(hexamethylene D-glucaramide) (**2c**).

^{1}H NMR Spectral Integration Method. In Figure 1 is shown the ^{1}H NMR spectrum of **2c** (in trifluoroacetic acid-*d*) prepared from a 1.05:1.00 molar ratio of hexamethylenediamine and **3** as monomers in methanol solution. The signal at 3.53 ppm is assigned to the methylene protons H-1′ and H-6′ on the carbons (diamine unit) bonded to the amide nitrogens of the polymer. The small peak at 3.30 ppm is attributed to methylene H-6′ protons adjacent to the polymer terminal NH_2 groups. When the molar ratio of diamine to activated D-glucarate used to prepare the polymer was greater than one, there was no evidence for the presence of terminal carbohydrate units (IR lactone carbonyl, ^{13}C NMR) in the polymer. Number average molecular weights (M_n) of polymer **2c** prepared using methyl D-glucarate 1,4-lactone (**3**) and hexamethylenediamine in different molar ratios, and calculated from ^{1}H NMR spectal data, are given in Table 5.

GPC Method. Samples of the poly(hexamethylene D-glucaramides) in Table 5 were subjected to per-*O*-trimethylsilylation in hexamethyldisilizane, chlorotrimethylsilane, and pyridine solution at room temperature for 7 days.[24] The trimethylsilylated polymers were then analyzed by GPC in tetrahydrofuran solution compared to polystyrene as the standard. The calculated M_n(GPC) and M_w(GPC) values for the polymers (Table 5) are for the underivatized polymers. Also presented in Table 5 are the M_w/M_n ratios derived from the GPC analyses of the polymers. Relative viscosities (η_{rel}) of the polymers versus methyl sulfoxide solvent, as obtained using an F 520 Viscometer, are also given in Table 5.

One additional polymer whose properties we have begun to examine is poly(3′,6′-dioxaoctamethylene D-glucaramide) (**2i**). Two methods were employed to make this polymer: the standard methanol solution procedure and a procedure wherein methyl D-glucarate 1,4-lactone (**3**) and 3,6-dioxaoctamethylenediamine (EDR 148, Texaco) were kept at a melt temperature of about 110 °C for 2 h. With the solution preparation method it was noted that the precipitated product was amorphous, in contrast to polymers from the alkylenediamines. DMF solutions of samples prepared by the two methods were then subjected to GPC, using polystyrene as a standard: solution polymerization method M_n = 27032, M_w = 31869, M_w/M_n = 1.18; melting polymerization method M_n = 31298, M_w = 39865, M_w/M_n = 1.27. The polydispersity ratio (M_w/M_n) values for polymer **2i** are significantly lower than those observed for poly(alkylene D-glucaramides), 2.12–2.16 (Table 5). We observed that polymer **2i** was more soluble in methanol than the alkylene polymers (**2a–2f**). This difference in solubility was also manifested by a lower isolated yield of **2i** (62.2%) compared to yields of isolated **2a–2f** (86.8–93.3%). The lower observed M_w/M_n values for **2i** may reflect a narrower molecular distribution of higher molecular weight precipitated **2i** due to preferential solubility of small molecules of **2i** in methanol. It is clear that polymer **2i** is of much higher molecular weight than polymer **2c** and that carrying out a melt polymerization to give **2i** produces an even higher molecular weight polymer.

The results from the NMR and GPC methods for molecular weight determination give reasonably consistent results, and our efforts to expand these analyses to additional polymers is continuing. Clearly, polymer **2c** is not a high molecular weight material, but it and the other alkylenediamine polyamides are easy to prepare and isolate in pure form. In contrast, polymer **2i**, which has greater methanol solubility than **2c**, reaches higher molecular weight in solution before precipitation occurs.

Some interesting comparisons in the physical properties of the polymers are evident. Among the two-carbon to twelve-carbon (even-numbered) diamines, the ethylenediamine and tetramethylenediamine polymers are water soluble, while hexamethylenediamine and higher carbon number diamine polymers are water insoluble. All of these poly(alkylene D-glucaramides) (**2**) have a melting point in the range 185–205 °C dec. The two

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Table 4. Isolated Yields, Melting Points, and Water and Methanol Solubilities of Poly(alkylene and related D-glucaramides)

polymers	yield (%)	mp (°C)	solubility	
			water	MeOH
poly(ethylene D-glucaramide) (**2a**)[a]	93.3	185	yes	no
poly(tetramethylene D-glucaramide) (**2b**)[a]	88.3	192–195	yes	no
poly(hexamethylene D-glucaramide) (**2c**)[15,16]	89.4	192–194	no	no
poly(octamethylene D-glucaramide) (**2d**)[15,16]	86.8	195–200	no	no
poly(decamethylene D-glucaramide) (**2e**)[a]	89.8	200–205	no	no
poly(dodecamethylene D-glucaramide) (**2f**)[15,16]	93.9	200–205	no	no
poly(*p*-xylylene D-glucaramide) (**2g**)[22]	93.2	205–208	no	no
poly(*m*-xylylene D-glucaramide) (**2h**)[a]	96.6	210–215	no	no
poly(3′,6′-dioxaoctamethylene D-glucaramide (**2i**)[a]	62.2	150	yes	no
poly(2-methylpentamethylene D-glucaramide) (**2j**)[a]	73.5	115	yes	no
poly(4′-azaheptamethylene D-glucaramide) (**2k**)[a]	67.5	150	yes	yes
poly(4′-aza-4′-methylheptamethylene D-glucaramide) (**2l**)[a]	78.6	120	yes	yes

[a] New polymers.

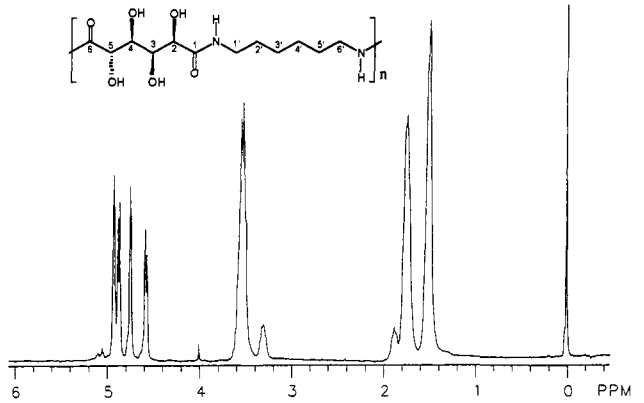

Figure 1. ^{1}H NMR spectrum (CF_3COOD) of poly(hexamethylene D-glucaramide) (**2c**).

Table 5. Molecular Weight Determinations for Poly(hexamethylene D-glucaramides)

Glu/ HMDA	yield (%)	M_n(NMR)	(η_{rel})	M_n(GPC)	M_w(GPC)	M_w/ M_n(GPC)
1.00/1.00	79.8	2116	1.226	1785	3812	2.14
1.00/1.02	80.5	2375	1.233	1813	3842	2.12
1.00/1.05	81.9	2491	1.228	1678	3549	2.12
1.00/1.10	86.2	1772	1.208	1642	3545	2.16

poly(arylalkylene D-glucaramides) (**2g** and **2h**) are both formed in very high yield and are the highest melting polymers. Introduction of a heteroatom into the diamine chain changes the properties of the polyamides significantly. When oxygen-containing 3,6-dioxaoctamethylenediamine was condensed with **3**, a white solid poly(3′,6′-dioxaoctamethylene D-glucaramide) (**2i**), with a wide melting point range (110–150 °C) was obtained. Furthermore, the polymer melted without apparent decomposition. Comparatively low melting points were also observed with two nitrogen-containing polymers: poly(4′-azaheptamethylene D-glucaramide) (**2k**), mp 135–150 °C, and poly(4′-aza-4′-methylheptamethylene D-glucaramide) (**2l**), mp 100–120 °C. The branched diamine polymer poly(2′-methylpentamethylene D-glucaramide) (**2j**), showed a lower melting point than any of the straight-chain alkylene polymers. These last four polymers were also found to be water soluble, and the polymers with nitrogen in the diamine chain were appreciably soluble in methanol.

Summary. A simple and convenient method for preparing hydroxylated nylons from D-glucaric acid is described. These polymers are poly(alkylene, arylalkyl, and heteroatom-substituted alkylene D-glucaramides). The method employs simple esterification mixtures of D-glucaric acid, crystalline D-glucaric acid lactones/esters, or a dilactone as activated D-glucaric acid monomers for condensation with primary diamines. Synthesis of the polymers does not require any carbohydrate hydroxyl protection/deprotection steps, and polymers are generally isolated by simple filtration of the polymerization reaction mixtures. As the acid monomer precursor, D-glucaric acid is available by oxidation of the most naturally abundant simple sugar, D-glucose. Differences in physical properties of the hydroxylated nylons are a consequnce of changing the diamine monomer component. The linear aliphatic and arylalkylenediamines produce better crystalline solid polyamides with high melting points. Heteroatom- or branch-containing poly(alkylene D-glucaramides) have higher water solubility, are not as crystalline as their straight-chain counterparts, and have correspondingly lower melting points and greater alcohol solubility and can form higher molecular weight polymers by the solution condensation polymerization method.

Experimental Section

General Methods. All ^{1}H and ^{13}C NMR spectra were recorded using a GE 300WB FT-NMR spectrometer at 300.13 and 75.4 MHz, respectively. Chemical shifts are reported as ppm (δ) downfield from tetramethylsilane. IR spectra were recorded with a Nicolet IR42 FT IR spectrometer as KBr pellets. All solvents used were reagent grade unless stated otherwise. Melting points were recorded with a Fisher–Johns Melting Point Apparatus and are reported uncorrected. Solvent evaporations were carried out at reduced pressure. Methanol/diamine solutions were standardized by diluting an aliquot of the solution with water and titrating with standardized hydrochloric acid. A pH meter was employed to determine the titration end points.

Poly(hexamethylene D-glucaramide)[15,16] (2c) Directly from Methanol-Esterified D-Glucaric Acid. Acetyl chloride (3.00 mL, 42 mmol, Aldrich) was added dropwise to methanol (25 mL) in a 250-mL round-bottomed flask cooled in an ice bath. Monopotassium D-glucarate (**1**, 5.00 g, 20.2 mmol) was added to the cold MeOH/HCl solution, the mixture was refluxed in an oil bath for 3–4 h and cooled to room temperature, and white solid KCl was removed by filtration and dried: yield of KCl 1.35 g (90.6%). The filtrate was concentrated at 65 °C to give a syrup which was dissolved in methanol (~15 mL) to give a clear solution of methanol-esterified D-glucaric acid suitable for each polymerization by Methods A–E.

(A) Triethylamine Method. Triethylamine was added to a solution of the syrupy methanol-esterified D-glucaric acid in methanol (20 mL) until the solution became basic (pH paper). Additional triethylamine (1.0 mL) and then a methanol solution of 1.139 M hexamethylenediamine (17.7 mL, 20.2 mmol) were added to the above solution, and within 15 min a large amount of white solid precipitated from solution. The reaction mixture was kept stirring at room temperature for 3 h, and the white solid was removed by filtration, washed with methanol (3 × 10 mL) and acetone (3 × 10 mL), and dried at reduced pressure (0.25 Torr) and 75 °C for 6 h to yield poly(hexamethylene D-glucaramide) (**2c**; 5.475 g, 18.86 mmol, 93.6%), comparable to authentic material (^{1}H NMR and IR).

(B) Sodium Carbonate Method. Sodium carbonate (1.0 g,

9.43 mmol) was added to a solution of methanol-esterified D-glucaric acid as in method A. Carbon dioxide gas evolved immediately, and more sodium carbonate was added until gas evolution stopped and the solution was neutral (pH paper). The white, solid NaCl precipitate was removed by filtration. To the filtrate was added triethylamine (1.0 mL) and then a methanol solution of 1.14 M hexamethylenediamine (17.7 mL, 20.2 mmol). The reaction mixture was stirred at room temperature for 3 h and worked up as in method A to give poly(hexamethylene D-glucaramide) (**5c**; 5.21 g, 18.0 mmol, 89.0%).

(C) Hydroxide Form Anion-Exchange Resin Method. Hydroxide form anion-exchange resin (10 mL, 14 mmol of total OH^- exchange capacity; Dowex 1-X8, Anion-Exchange Resin, pretreated with a 1.0 N NaOH solution and methanol, Bio*Rad Laboratories) was added to a solution of methanol-esterified D-glucaric acid as in method A. The mixture was stirred at room temperature for 3 h, and the resin was removed by filtration. Triethylamine was added to the filtrate until the solution was just basic (pH paper). Additional triethylamine (1.0 mL) was added to the solution and then a methanol solution of 1.14 M hexamethylenediamine (17.7 mL, 20.2 mmol) was added. The reaction mixture was stirred at room temperature for 3 h and worked up as in method A to give poly(hexamethylene D-glucaramide) (**2c**; 3.48 g, 12.0 mmol, 59.5%).

(D) Sodium Methoxide Method. Sodium methoxide powder was added to a solution of methanol-esterified D-glucaric acid as in method A until the solution became neutral (pH paper). The insoluble, white solid (NaCl) was removed by filtration, and to the filtrate was added triethylamine (1.0 mL) and a methanol solution of 1.14 M hexamethylenediamine (17.7 mL, 20.2 mmol). The reaction mixture was stirred at room temperature for 3 h and worked up as in method A to give poly(hexamethylene D-glucaramide) (**2c**; 5.11 g, 17.6 mmol, 87.2%).

(E) Ethanol/Sodium Methoxide Method. Monopotassium D-glucarate (**1**; 5.00 g, 20.2 mmol) was treated with ethanol/HCl to give an ethanol-esterified D-glucaric acid solution following the methanol esterified D-glucaric acid preparation above. Solid KCl precipitated from the ethanol esterification reaction mixture more efficiently (96.0%) than when methanol was used for the esterification (90.6%). Concentration of the ethanol-esterified glucaric acid solution gave a syrup which was dissolved in methanol and neutralized with sodium methoxide. No insoluble NaCl was observed to form during the neutralization. Addition of triethylamine (1.0 mL) and 1.139 M hexamethylenediamine (17.7 mL, 20.2 mmol) to the solution caused precipitation of polyamide within 10 min. The mixture was stirred at room temperature for 3 h and worked up as in method A to give poly(hexamethylene D-glucaramide) (**2c**; 5.30 g, 18.3 mmol, 90.2%).

Methyl D-Glucarate 1,4-Lactone[20] (3). Method A (From Monopotassium D-glucarate). The acid form of a cation-exchange resin (REXYN 101(H), Fisher) was washed with methanol until the washings were colorless. Methanol (200 mL), the above treated resin (105 mL), and monopotassium D-glucarate (**1**) (D-saccharic acid monopotassium salt, 50.0 g, 199 mmol, 99%, Sigma) were added successively to a 1000-mL Erlenmeyer flask. The flask was sealed, placed in a shaker/water bath (Precision Scientific Co.) at a water bath temperature of 50 °C for 3 h or until the white saccharic acid salt (**1**) was completely dissolved. The resin was removed by filtration, washed with methanol (2 × 15 mL), and retained for regeneration to its acid form. The combined filtrate and washings were transferred to a 500-mL round-bottomed flask and concentrated to a thick syrup. The syrup, seeded with pure methyl D-glucarate 1,4-lactone (**3**), solidified at room temperature in 2–3 days. The solid cake was further dried at room temperature (0.25 Torr) for 36 h to give a slightly yellow solid (29.4 g, 143 mmol, 71.5%) which could be used directly for polymerization. Triturating the crude solid at room temperature with ethanol gave a white solid which was separated by filtration and dried at reduced pressure (0.25 Torr) and 65 °C for 12 h: yield of purified methyl D-glucarate 1,4-lactone (**3**) 20.89 g (101.3 mmol, 50.8%); mp 158–160 °C (lit.[20] 165 °C). Anal. Calcd for $C_7H_{10}O_7$ (206.15): C, 40.79; H, 4.89. Found: C, 40.54; H, 4.92.

Method B (From Monopotassium D-Glucarate). Monopotassium D-glucarate (**1**; 20.00 g, 80.61 mmol) was added to a 250-mL round-bottomed flask containing methanol (100 mL). To the mixture, with stirring, was added a solution of methanolic HCl prepared by careful addition of acetyl chloride (20 mL, 276 mmol, 98%, Aldrich) to methanol (25 mL) kept at ice bath temperature. The reaction mixture was refluxed for 3–4 h with an insoluble white solid being observed in the reaction vessel during the entire refluxing time. The solid was separated by filtration and dried in a vacuum oven for 12 h at 70 °C. The melting point of the solid was greater than 250 °C, and the solid gave no ^1H NMR signal (D_2O), properties consistent with KCl, the inorganic byproduct from the reaction: yield of KCl 5.386 g (72.24 mmol, 89.62%). The filtrate was concentrated at 50 °C to give a syrup which was seeded with pure methyl D-glucarate 1,4-lactone (**3**). The syrup, when kept at room temperature, solidified and was dried at reduced pressure (0.25 Torr) for 24 h to complete the crystallization: yield of crude, solid methyl D-glucarate 1,4-lactone (**3**) 16.52 g. The combined weight of solid KCl and solid methyl D-glucarate 1,4-lactone (**3**) was 21.91 g (96.80% of theoretical). The ^1H NMR and IR spectra of methyl D-glucarate 1,4-lactone (**3**) prepared by Methods A and B were identical. Elemental analysis of methyl D-glucarate 1,4-lactone (**3**) prepared by Method B indicated the presence of potassium chloride (~6% by weight) in the sample. Residual inorganic salt was removed from **1** in the following way. To solid methyl D-glucarate 1,4-lactone (**3**; 16.52 g), prepared as above and dissolved in methanol (50 mL), was added H^+ form cation-exchange resin (10 mL). The mixture was stirred at room temperature (3 h), and the resin was removed by filtration. The filtrate was concentrated to a syrup which solidified spontaneously. The solid was triturated with acetone, separated by filtration, and dried in a vacuum oven at 70 °C for 8 h to give methyl D-glucarate 1,4-lactone (**3**; 9.79 g, 47.47 mmol, 58.89%), identical (^1H NMR, IR) to that obtained from Method A. Anal. Calcd for $C_7H_{10}O_7$ (206.15): C, 40.79; H, 4.89. Found: C, 39.79; H, 4.89; K, 0.00.

Ethyl D-Glucarate 6,3-Lactone[21] (6). Acid form cation-exchange resin (110 mL, REXYN 101(H), Fisher) was washed with ethanol until the washings were colorless. Ethanol-washed resin, monopotassium D-glucarate (**1**; 50.00 g, 201.5 mmol, Sigma), and ethanol (200 mL) were added to a 1000-mL Erlenmeyer flask. The flask containing the insoluble salt was sealed and put in a shaker/water bath at 55 °C for 4 h or until the white solid (**1**) was dissolved. The resin was removed by filtration and washed with ethanol (3 × 10 mL), and the combined filtrate and washings were concentrated to give a thick syrup. The syrup was seeded with ethyl D-glucarate 6,3-lactone (**6**) and kept for 2–3 days at room temperature, by which time most of the syrup had solidified. The sticky cake was then kept under vacuum (0.25 Torr) for 3 days at room temperature to yield solid and slightly yellow crude ethyl D-glucarate 6,3-lactone (**6**) (26.81 g, 121.8 mmol, 61.13%). Trituration of this solid with acetone followed by filtration gave a white solid product. The acetone filtrate was concentrated and the resulting solid triturated and separated as above. The combined white solids were dried in a vacuum oven at 55 °C for 6 h to give ethyl D-glucarate 6,3-lactone (**6**; 25.83 g, 117.3 mmol, 58.9%): mp 121–123 °C (lit.[20] 122 °C); IR (KBr) 1774 cm^{-1} (C=O stretch, five-membered lactone) and 1717 cm^{-1} (C=O stretch, ester); ^1H NMR (D_2O) δ 1.10 (t, 3H, O–CH_2CH_3), 4.10 (q, 2H, O–CH_2CH_3), 4.45–4.60 (m, 4H, H-2, H-3, H-4, H-5); the unresolved portion of the spectrum (H-2, H-3, H-4, H-5) was very similar to that from the

corresponding acid, D-glucaro-6,3-lactone; ^{13}C NMR (D_2O) δ 178.8 (lactone C=O), 172.8 (ester C=O), 81.6 (C-3), 71.6 (C-5), 71.3 (C-2) and 70.2 (C-4), 64.3 (O-CH_2CH_3), 14.4 (O-CH_2CH_3). Anal. Calcd for $C_8H_{12}O_7 \cdot (H_2O)_{0.5}$ (229.19): C, 41.93; H, 5.72. Found: C, 42.01; H, 5.10.

D-Glucaro-1,4:6,3-dilactone[22] **(5).** A 100-mL round-bottomed flask containing solid methyl D-glucarate 1,4-lactone (**3**; 1.00 g, 4.85 mmol) was held under vacuum (0.25 Torr). The flask was immersed in an oil bath which was gradually heated to 110 °C, by which temperature the methyl D-glucarate 1,4-lactone (**3**) had melted and the melt was bubbling. After the bubbling ceased (about 12 h), the contents were returned to atmospheric pressure and dry acetone (5 mL) was added to dissolve the glassy solid on the walls of the flask. The acetone solution was concentrated and seeded with crystalline D-glucaro-1,4:6,3-dilactone (**5**), resulting in the crystallization of the syrup in 5 h. The crystalline solid was dried under vacuum to give D-glucaro-1,4:6,3-dilactone (**5**; 0.826 g, 4.75 mmol, 98.0%): mp 130 °C (lit.[20] 132 °C). When ethyl D-glucarate 6,3-lactone (**6**) was used with similar success as the starting material for **5**, melting and bubbling of the melt occurred at an oil bath temperature of 105 °C.

Poly(ethylene D-glucaramide) (2a). Triethylamine (0.5 mL) and then a methanol solution of 0.476 M ethylenediamine (20.4 mL, 9.70 mmol, 1:1 molar ratio of diamine to lactone, Eastman Kodak) were added to a methanol solution of methyl D-glucarate 1,4-lactone (**3**; 40 mL, 2.00 g, 9.70 mmol). Addition of the diamine solution to the solution of **3** immediately produced a clear light-yellow solution which upon stirring at room temperature for 30 min became cloudy. The polymerization mixture was stirred at room temperature for 48 h, and the solid was removed by filtration. Methanol (40 mL), containing the suspended solid, was refluxed for 4 h, and the solid was removed by filtration and dried at 60 °C at reduced pressure (0.25 Torr) to give water-soluble poly(ethylene D-glucaramide) (**2a**; 2.12 g, 9.05 mmol, 93.3%): mp 185 °C; IR (KBr) 3346 (O—H, stretch), 2935 (C—H stretch), 1646 (amide I C=O stretch), 1546 cm^{-1} (amide II, N—H); ^1H NMR (D_2O) δ 4.351 (d, 1H, H-2, $J_{2,3}$ = 1.38 Hz), 4.113 (t, 1H, H-3, $J_{3,4}$ = 4.36 Hz), 3.976 (t, 1H, H-4, $J_{4,5}$ = 5.08 Hz), 4.263 (d, 1H, H-5), 3.44 (s, 4H, H-1′ and H-2′). Anal. Calcd for $C_8H_{14}N_2O_6$ (234.21): C, 41.03; H, 6.02; N, 11.96. Found: C, 40.97; H, 6.36; N, 11.53.

Poly(tetramethylene D-glucaramide) (2b). Triethylamine (0.5 mL) and a methanol solution of 1.893 M tetramethylenediamine (2.69 mL, 5.09 mmol, 1.05:1 molar ratio of diamine to lactone, Aldrich) were added to a methanol solution of methyl D-glucarate 1,4-lactone (**3**; 40 mL, 1.000 g, 4.851 mmol). The colorless solution was stirred at room temperature, and within 20 min a precipitate began to form. The initial precipitate had an oily consistency and stuck to the walls of the reaction flask, but over time with stirring, the oil solidified and could be easily scraped from the walls of the reaction flask. Because the precipitation process was slow, stirring was normally allowed to continue for 48 h before the solid was removed. The white solid product was dried at reduced pressure (0.25 Torr) and 75 °C for 36 h to give poly(tetramethylene D-glucaramide) (**2b**; 1.12 g, 4.28 mmol, 88.36%). Poly(tetramethylene D-glucaramide) (**2b**) was readily soluble in water and had a mp of 192–195 °C dec: IR (KBr) 3314 (O—H, stretch), 2938 (C—H, stretch), 1638 (amide I, C=O stretch), 1543 cm^{-1} (amide II, N—H bending); ^1H NMR (D_2O) δ 4.32 (d, 1H, H-2, $J_{2,3}$ = 1.77 Hz), 4.09 (dd, 1H, H-3, $J_{3,4}$ = 4.47 Hz), 3.96 (t, 1H, H-4, $J_{4,5}$ ≈ 5.94 Hz), 4.24 (d, 1H, H-5), 3.28 (s, 4H, H-1′ and H-4′), 1.58 (s, 4H, H-2′ and H-3′). Anal. Calcd for $C_{10}H_{18}N_2O_6$ (262.26): C, 45.80; H, 6.92; N, 10.68. Found: C, 45.54; H, 7.05; N, 10.60.

Poly(hexamethylene D-glucaramide)[15,16] **(2c). Method A (From Methyl D-Glucarate 1,4-Lactone.** Triethylamine (0.5 mL) and a methanol solution of 1.139 M hexamethylenediamine (4.47 mL, 5.09 mmol, 1.05:1 molar ratio of diamine to lactone, Aldrich) were added to a methanol solution of methyl D-glucarate 1,4-lactone (**3**; 40 mL, 1.000 g, 4.851 mmol). The colorless solution was stirred at room temperature, and within the first 5–10 min a considerable amount of white precipitate was observed. The mixture was stirred at room temperature for 48 h, the solid was removed by filtration, washed with methanol (2 × 15 mL) and acetone (2 × 15 mL), and dried at reduced pressure (0.25 Torr) and 75 °C for 36 h to give poly(hexamethylene D-glucaramide) (**2c**; 1.259 g, 4.33 mmol, 89.39%): mp 192–194 °C dec (lit.[15] 190–205 °C); IR (KBr) 3306 (O—H, stretch), 2931 (C—H, stretch), 1641 (amide I C=O stretch), 1545 cm^{-1} (amide II N—H); ^1H NMR (CF_3COOD) δ 4.92 (d, 1H, H-2, J_{2-3} = 2.77 Hz), 4.74 (broad s, 1H, H-3), 4.57 (t, 1H, H-4, $J_{4,5}$ = 6.17 Hz), 4.87 (d, 1H, H-5), 3.53 (d, 4H, H-1′ and H-6′), 1.78 (s, 4H, H-2′ and H-5′), 1.50 (s, 4H, H-3′ and H-4′). Anal. Calcd for $C_{12}H_{22}N_2O_6$ (290.31): C, 49.65; H, 7.64; N, 9.65. Found: C, 49.42; H, 7.82; N, 9.51.

Poly(hexamethylene D-glucaramide) (2c). Method B (From Ethyl D-Glucarate 6,3-Lactone (6). Triethylamine (0.5 mL) and a methanol solution of 1.139 M hexamethylenediamine (3.73 mL, 4.25 mmol, 1.05:1 molar ratio of diamine to lactone, Aldrich) were added to a methanol solution of ethyl D-glucarate 6,3-lactone (**6**; 40 mL, 1.00 g, 4.05 mmol). Polymerization proceeded as with Method A to give poly(hexamethylene D-glucaramide) (**2c**; 1.01 g, 3.49 mmol, 86.2%).

Poly(octamethylene D-glucaramide)[15,16] **(2d).** Triethylamine (0.5 mL) and a methanol solution of octamethylenediamine (0.735 g, 5.09 mmol, 1.05:1 molar ratio of diamine to lactone, Aldrich) were added to a methanol solution of methyl D-glucarate 1,4-lactone (**3**; 40 mL, 1.000 g, 4.851 mmol). Polymerization occurred as in Method A of **2c** to give poly(octamethylene D-glucaramide) (**2d**; 1.341 g, 4.21 mmol, 86.8%): mp 195–200 °C (dec) (lit.[15] mp 190–200 °C); IR (KBr) 3306 (O—H, stretch), 2926 (C—H, stretch), 1641 (amide I C=O stretch), 1543 cm^{-1} (amide II N—H); ^1H NMR (CF_3COOD) δ 4.93 (d, 1H, H-2), 4.75 (broad s, 1H, H-3), 4.59 (d, 1H, H-4), 4.87 (d, 1H, H-5), 3.56 (d, 4H, H-1′ and H-8′), 1.72 (s, 4H, H-2′ and H-7′), 1.44 (s, 8H, H-3′, H-4′, H-5′ and H-6′). Anal. Calcd for $C_{14}H_{26}N_2O_6$ (318.36): C, 52.82; H, 8.23; N, 8.80. Found: C, 52.19; H, 8.35; N, 8.67.

Poly(decamethylene D-glucaramide) (2e). Triethylamine (0.5 mL) and a methanol solution of decamethylenediamine (0.878 g, 5.09 mmol, 1.05:1 molar ratio of diamine to lactone, Aldrich) were added to a methanol solution of methyl D-glucarate 1,4-lactone (**3**; 40 mL, 1.000 g, 4.851 mmol). Polymerization occurred as in Method A of **2c** to give poly(decamethylene D-glucaramide) (**2e**; 1.51 g, 4.36 mmol, 89.8%): mp 200–205 °C dec; IR (KBr) 3313 (O—H, stretch), 2923 (C—H, stretch), 1642 (amide I C=O stretch), 1546 cm^{-1} (amide II N—H); ^1H NMR (CF_3COOD) δ 4.96 (d, 1H, H-2, $J_{2,3}$ = 2.89 Hz), 4.77 (broad s, 1H, H-3), 4.61 (d, 1H, H-4, $J_{4,5}$ = 6.23), 4.87 (d, 1H, H-5), 3.59 (d, 4H, H-1′ and H-10′), 1.78 (d, 4H, H-2′ and H-9′), 1.43 (s, 12H, H-3′, H-4′, H-5′, H-6′, H-7′, and H-8′). Anal. Calcd for $C_{16}H_{30}N_2O_6$ (346.43): C, 55.47; H, 8.73; N, 8.09. Found: C, 54.90; H, 8.85; N, 8.00.

Poly(dodecamethylene D-glucaramide)[15,16] **(2f).** Triethylamine (0.5 mL) and a methanol solution of dodecamethylenediamine (1.02 g, 5.09 mmol, 1.05:1 molar ratio of diamine to lactone, Aldrich) were added to a methanol solution of methyl D-glucarate 1,4-lactone (**3**; 40 mL, 1.000 g, 4.851 mmol). Polymerization occurred as in Method A of **2c** to give poly(dodecamethylene D-glucaramide) (**2f**; 1.71 g, 4.55 mmol, 93.9%): mp 200–205 °C dec (lit.[15] mp 205 °C); IR (KBr) 3296 (O—H, stretch), 2921 (C—H, stretch), 1641 (amide I C=O stretch), 1547 cm^{-1} (amide II N—H); ^1H NMR (CF_3COOD) δ 4.93 (d, 1H, H-2, $J_{2,3}$ = 2.36 Hz), 4.75 (broad s, 1H, H-3), 4.58 (d, 1H, H-4, $J_{4,5}$ = 6.38 Hz), 4.88 (d, 1H, H-5), 3.52 (m, 4H, H1′ and H-12′), 1.78 (d, 4H, H-2′ and H-11′), 1.40 (s, 16H, H-3′, H-4′, H-5′, H-6′, H-7′, H-8′, H-9′, and H-10′). Anal. Calcd for $C_{18}H_{34}N_2O_6$ (374.48):

C, 57.33; H, 9.15; N, 7.48. Found: C, 56.96; H, 9.25; N, 7.50.

Poly(*p*-xylylene D-glucaramide)[22] (2g). Triethylamine (0.5 mL) and a methanol solution of *p*-xylylenediamine (0.351 g, 2.55 mmol, 1.05:1 molar ratio of diamine to lactone, Aldrich) were added to a methanol solution of methyl D-glucarate 1,4-lactone (**3**; 30 mL, 0.500 g, 2.43 mmol). Polymerization occurred as in Method A of **2c** to give poly(*p*-xylylene D-glucaramide) (**2g**; 0.701 g, 2.26 mmol, 93.2%): mp 200–208 °C (dec) (lit.[22] mp 217–232 °C); IR (KBr) 3351 (O—H stretch), 2928 (C—H stretch), 1643 (amide I C=O stretch), 1537 cm^{-1} (amide II and phenyl); ^1H NMR (CF_3COOD) δ 4.92 (d, 1H, H-2), 4.81 (broad s, 1H, H-3), 4.60 (d, 1H, H-4, $J_{4,5}$ = 5.70 Hz), 4.86 (d, 1H, H-5), 7.49 (s, terminal phenyl), 7.37 (s, 4H, phenyl), 4.65 (m, 4H, N–CH_2–Ph–). Anal. Calcd for $C_{14}H_{18}N_2O_6$ (310.3): C, 54.19; H, 5.85; N, 9.03. Found: C, 53.73; H, 6.15; N, 8.83.

Poly(*m*-xylylene D-glucaramide) (2h). Triethylamine (0.5 mL) and a methanol solution of 2.473 M *m*-xylylenediamine (2.06 mL, 5.09 mmol, 1.05:1 molar ratio of diamine to lactone, Aldrich) were added to a methanol solution of methyl D-glucarate (**3**; 40 mL, 1.000 g, 4.85 mmol). Polymerization occurred as in Method A of **2c** to give poly(*m*-xylylene D-glucaramide) (**2g**; 1.454 g, 4.69 mmol, 96.6%): mp 210–215 °C dec; IR (KBr) 3336 (O—H stretch), 2930 (C—H stretch), 1646 (amide I C=O stretch), 1535 cm^{-1} (amide II and phenyl); ^1H NMR (CF_3COOD) δ 4.90 (d, 1H, H-2), 4.79 (broad s, 1H, H-3), 4.60 (d, 1H, H-4), 4.84 (d, 1H, H-5), 7.50 (s, 1H, Ar), 7.32 (s, 3H, phenyl, Ar), 4.66 (s, 4H, CH_2–Ar). Anal. Calcd for $C_{14}H_{18}N_2O_6$ (310.3): C, 54.19; H, 5.85; N, 9.03. Found: C, 54.04; H, 5.94; N, 8.76.

Poly(3′,6′-dioxaoctamethylene D-glucaramide) (2i). Triethylamine (0.5 mL) and a methanol solution of 1.631 M 3′,6′-dioxaoctamethylenediamine (EDR 148, 6.24 mL, 10.2 mmol, 1.05:1 molar ratio of diamine to lactone, Texaco) were added to a methanol solution of methyl D-glucarate 1,4-lactone (**3**; 40 mL, 2.000 g, 9.70 mmol). The colorless solution was stirred at room temperature, and within 30 min, a precipitate began to form. The initial precipitate had an oily consistency and stuck to the walls of the reaction flask, but over time with stirring, the oil solidified and could be easily scraped from the walls of the reaction flask. Because the precipitation process was slow, stirring was normally allowed to continue for 48 h before the solid was removed and washed with acetone. The white solid product was dried at reduced pressure (0.25 Torr) and 75 °C for 36 h to give poly(3′,6′-dioxaoctamethylene D-glucaramide) (**2i**; 1.944 g, 6.03 mmol, 62.2%): mp softened at 110 °C and completely liquified by 150 °C; IR (KBr) 3309 (O—H stretch), 2876 (C—H stretch), 1645 (amide I C=O stretch), 1542 cm^{-1} (amide II N—H stretch); ^1H NMR (D_2O) δ 4.351 (d, 1H, H-2, $J_{2,3}$ = 2.31 Hz), 4.116 (t, 1H, H-3, $J_{3,4}$ = 4.55 Hz), 3.979 (t, 1H, H-4, $J_{4,5}$ = 5.16 Hz), 4.274 (d, 1H, H-5), 3.702 (s, 4H, –O–CH_2–CH_2–O–), 3.669 (t, 4H, N–C–CH_2–O–), 3.474 (broad s, 4H, –NH–CH_2–), 2.915 (t, CH_2-NH_2). Anal. Calcd for $C_{12}H_{22}O_8N_2$ (322.31): C, 44.72; H, 6.88; N, 8.69. Found: C, 44.05; H, 6.98; N, 8.28.

Poly(2-methylpentamethylene D-glucaramide)[15,16] (2j). Triethylamine (0.5 mL) and a methanol solution of 1.50 M 2-methylpentamethylenediamine (3.23 mL, 4.85 mmol, 1.05:1 molar ratio of diamine to lactone, DuPont) were added to a methanol solution of methyl D-glucarate 1,4-lactone (**3**; 40 mL, 1.000 g, 4.85 mmol). The colorless solution was stirred at room temperature, but within 20 min the reaction mixture became cloudy and a thick and slightly yellow syrup formed on the bottom of the flask. The mixture was stirred at room temperature for 24 h and concentrated at 50 °C to give a syrup. The syrup was stirred with methanol (20 mL) for 4 h, the clear methanol layer was decanted, and the insoluble syrup was dried at reduced pressure (0.25 Torr) and an oil bath temperature of 75 °C for 6 h to give amorphous poly(2-methylpentamethylene D-glucaramide) (**2j**; 1.04 g, 3.57 mmol, 73.5%): mp softened at 95 °C and completely liquified by 115 °C; IR (KBr) 3364 (O—H stretch), 2936 (C—H stretch), 1647 (amide I C=O stretch), 1541 cm^{-1} (amide II N—H stretch); ^1H NMR (D_2O) δ 4.31 (s, 1H, H-2), 4.24 (d, 1H, H-5), 4.10 (s, 1H, H-3), 3.97 (t, 1H, H-4), 3.24 (s, 2H, H-5′), 3.13 (m, 2H, H-2′), 1.70, 1.57 and 1.38 (three peaks overlapping, 4H, H-4′ and H-5′), 1.17 (broad s, 1H, H-2′), 0.89 (d, 3H, CH_3). Anal. Calcd for $C_{12}H_{22}N_2O_6$ (290.31): C, 49.65; H, 7.64; N, 9.65. Found: C, 49.23; H, 7.92; N, 9.52.

Poly(4′-azaheptamethylene D-glucaramide) (2k). Triethylamine (0.5 mL) and a methanol solution of 1.52 M 4-azaheptamethylenediamine (*i.e.*, 3,3-iminobispropylamine, 3.20 mL, 4.85 mmol) were added to a methanol solution of methyl D-glucarate 1,4-lactone (**3**; 40 mL, 1.00 g, 4.85 mmol). Polymerization occurred as with **2j** to give amorphous poly(4′-azaheptamethylene D-glucaramide) (**2k**; 1.00 g, 3.27 mmol, 67.5%): mp softened at 135 °C and completely liquified by 150 °C; IR (KBr) 3368 (O—H stretch), 2936 (C—H stretch), 1653 (amide I C=O stretch), 1558 cm^{-1} (amide II N—H bend); ^1H NMR (D_2O) δ 4.32 (s, 1H, H-2), 4.24 (d, 1H, H-5), 4.10 (s, 1H, H-3), 3.97 (t, 1H, H-4), 3.30 (s, 4H, H-1′ and H-7′), 2.62 (t, 4H, H-3′ and H-5′), 1.73 (t, 4H, H-2′ and H-6′). Anal. Calcd for $C_{12}H_{23}O_6N_3$ (305.33): C, 47.20; H, 7.59; N, 13.76. Found: C, 46.42; H, 7.79; N, 12.77.

Poly(4′-aza-*N*-methylheptamethylene D-glucaramide) (2l). Triethylamine (0.5 mL) and a methanol solution of 1.53 M 4-aza-*N*-methylheptamethylenediamine (*i.e.*, 3,3-diamino-*N*-methyldipropylamine, 6.34 mL, 9.70 mmol) were added to a methanol solution of methyl D-glucarate 1,4-lactone (**3**; 60 mL, 2.00 g, 9.70 mmol). Polymerization occurred as with **2j** to give amorphous poly(4′-aza-*N*-methylheptamethylene D-glucaramide) (**2l**; 2.43 g, 7.63 mmol, 78.6%): mp softened at 100 °C and completely liquified by 120 °C; IR (KBr) 3422 (O—H stretch), 2945 (C—H stretch), 1646 (amide I C=O stretch), 1541 cm^{-1} (amide II N—H bend); ^1H NMR (D_2O) δ 4.32 (s, 1H, H-2), 4.23 (d, 1H, H-5), 4.10 (s, 1H, H-3), 3.97 (t, 1H, H-4), 3.27 (s, 4H, H-1′ and H-7′), 2.47 (s, 4H, H-3′ and H-5′), 2.24 (s, 3H, -CH_3), 1.74 (s, 4H, H-2′ and H-6′). Anal. Calcd for $C_{13}H_{25}O_6N_3$ (319.36): C, 48.89; H, 7.89; N, 13.16. Found: C, 48.62; H, 7.97; N, 10.60.

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