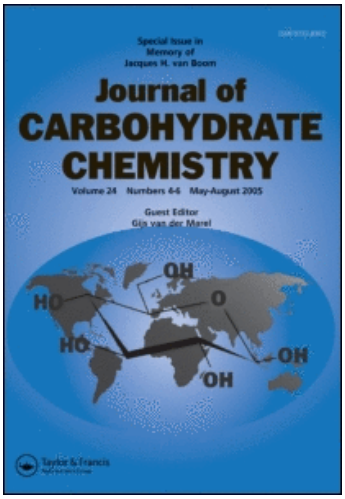

Journal of Carbohydrate Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

Alternating Stereoregular *Head*, *Tail-Tail*, *Head*-Poly(Alkylene d-Glucaramides) Derived from a Homologous Series of Symmetrical Diamido-di-d-Glucaric Acid Monomers

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Online publication date: 04 August 2003

To cite this Article Styron, Susan D. , Kiely, Donald E. and Ponder, Glenn(2003) 'Alternating Stereoregular *Head*, *Tail-Tail*, *Head*-Poly(Alkylene d-Glucaramides) Derived from a Homologous Series of Symmetrical Diamido-di-d-Glucaric Acid Monomers', Journal of Carbohydrate Chemistry, 22: 2, 123 — 142
To link to this Article: DOI: 10.1081/CAR-120020482
URL: http://dx.doi.org/10.1081/CAR-120020482

JOURNAL OF CARBOHYDRATE CHEMISTRY
Vol. 22, No. 2, pp. 123–142, 2003

Alternating Stereoregular *Head*, *Tail–Tail*, *Head*-Poly(Alkylene D-Glucaramides) Derived from a Homologous Series of Symmetrical Diamido-di-D-Glucaric Acid Monomers

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ABSTRACT

A method for the synthesis and purification of a homologous series of symmetrical diamido-diacids derived from D-glucaric acid and six alkylenediamines is described. Treating D-glucaro-6,3-lactone with an equimolar amount of lithium acetate dihydrate yielded lithium D-glucarate-6,3-lactone, which in turn was reacted with six alkylenediamines in dimethyl sulfoxide to give the target diamido-diacids. Six new alternating stereoregular polyamides, *head*, *tail–tail*, *head*-poly(alkylene D-glucaramides), were then synthesized by simple polycondensation reactions between the activated diamido-diacids [6,6′-(*N*,*N*′-alkylene)-bis(D-glucaramid-1-oic acid)s] and the alkylenediamines. Number average molecular weights for the polyamides were estimated by ^{1}H NMR end group analysis. Models for the three-dimensional shape of these alternating stereoregular polymers were produced from a combination of ^{1}H

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DOI: 10.1081/CAR-120020482
0732-8303 (Print); 1532-2327 (Online)

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NMR data, molecular modeling studies performed on D-glucaramide, and crystal structures of various acyclic D-glucaric acid derivatives.

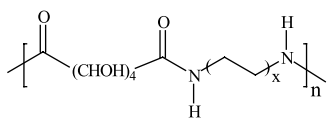
Key Words: Stereoregular; Poly(alkylene-D-glucaramides); Alternating; Diamido-diacids.

INTRODUCTION

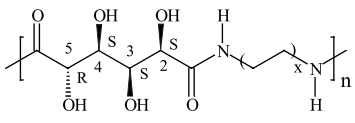
Synthesis and characterization of poly(alkylene D-aldaramides) or ''hydroxylated nylons'' have been important components of our research efforts in recent years, the focus being on polyamides derived from D-glucaric acid. The glucaramides are easily derived from D-glucose, the least expensive and most commercially available of the naturally-occurring aldohexoses. Additionally, a variety of polyamides with different properties based on the primary diamine monomer can be conveniently prepared employing a common method.[1–3] Another important feature of these polymers is the incorporation of four contiguous chiral centers for each glucaric acid moiety within a polyamide chain. This chiral glucaric acid moiety is unsymmetrical, and therefore introduces the possibility for different alignments within the polymer chain, i.e., C-1 is designated the ''*head*'' carbon of glucaric acid and C-6 the ''*tail*'' carbon. Thus, within a polyamide chain, the glucaric acid moiety may be incorporated in either a *head* to *tail* or a *tail* to *head* alignment. In a ''random'' polymerization, no effort is made to control the alignment, whereas in a stereoregular polymerization, the synthetic route requires precise control of this alignment. Both ''random''[1–3] and stereoregular repeating *head*, *tail*-poly(alkylene D-glucaramides)[4] (Figure 1) have been previously synthesized. The synthesis of a new class of stereoregular polymers, the alternating stereoregular *head*, *tail–tail*, *head*-poly(alkylene D-glucaramides)[5] (Figure 2) is presented here.

RESULTS AND DISCUSSION

A retrosynthetic analysis of the target polyamides is shown in Figure 3. It was envisioned that the polyamides could be derived from diamido-diacid [6,6′-(*N*,*N*′-alkylene)-bis(D-glucaramid-1-oic acid)] disalts **III**, by an esterification/aminolysis/polymerization sequence. Compounds **III** were seen as originating by condensation of a lactone-acid salt **I** and amido amino acid 6[*N*-(6′-aminoalkyl)-D-glucaramid-1-oic] salt **II**. Based upon previous results involving direct aminolysis of **1** (where $M^+ = Na^+$) in



"Random" poly(alkylene D-glucaramides), i.e. the stereo alignment of the repeating D-glucaryl unit is not defined.



Stereoregular repeating *head, tail*-poly(alkylene D-glucaramides)

x = 1-6

Figure 1. Random and stereoregular *head*, *tail* poly(alkylene D-glucaramide).

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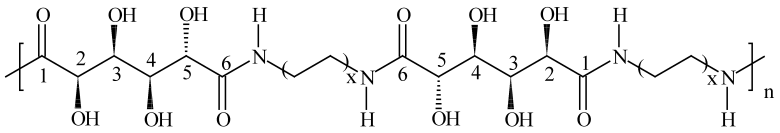

Stereoregular alternating *head, tail - tail, head* - poly(alkylene D-glucaramides)

x = 1 - 6

Figure 2. Alternating stereoregular poly(alkylene D-glucaramide).

methanol,[4] it was hoped that reaction of **1** with **2** (where $M^+ = Na^+$)[6] would produce the salts **III** (where $M^+ = Na^+$), which could then be converted to polyamide as indicated above. However, condensation of **1** with **2** (x = 3) failed, even at elevated temperatures, as both reactants had low solubility in polar methanol and dimethyl sulfoxide, the solvents of choice.[5]

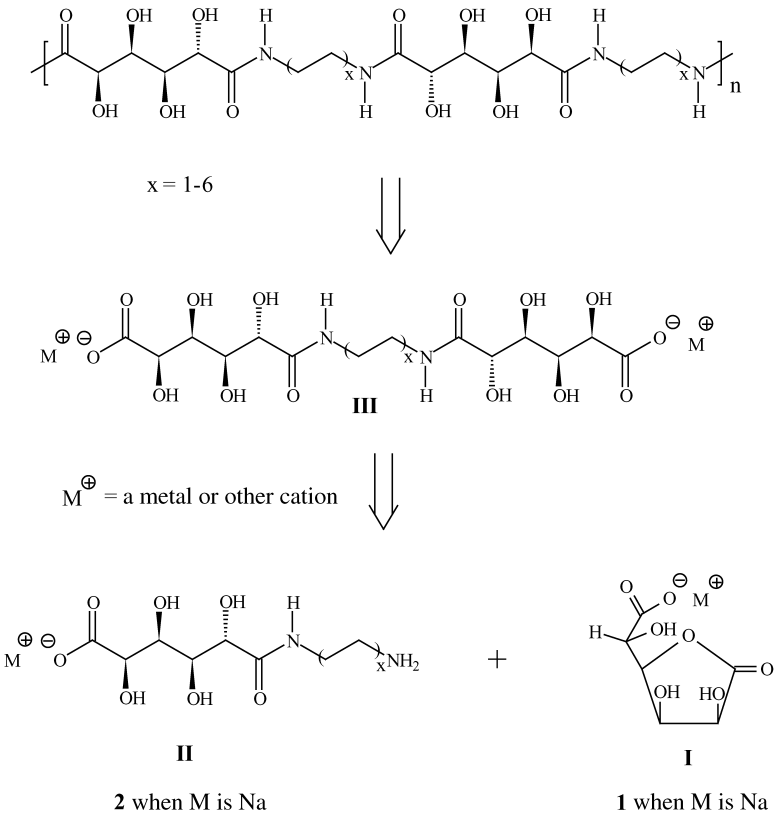

Figure 3. Retrosynthetic analysis of the target stereoregular *head*, *tail–tail*, *head* poly(alkylene-D-glucaramides).

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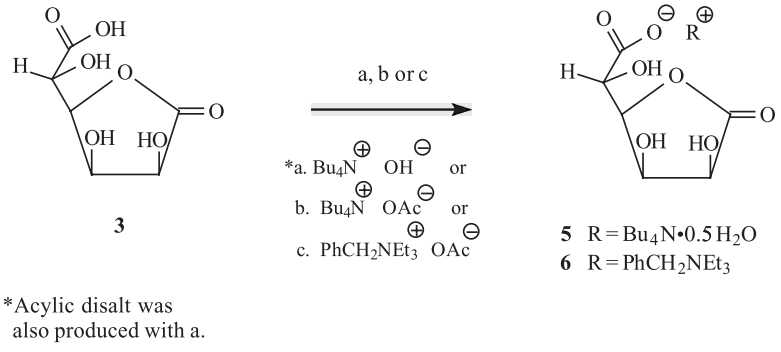
Given the insolubility of **1** and **2** in the above solvents, it was reasoned that the presence of a phase transfer catalyst, such as tetrabutylammonium acetate, in the reaction mixture might help solubilize **1** and **2** through transient exchange of Na^+ with n-Bu_4N^+ and generate soluble and thus reactive salts **I** (M^+ = n-Bu_4N^+) and **II** (M^+ = n-Bu_4N^+). However, attempts to successfully react **1** and **2** (M^+ = Na^+ and x = 3) (1:1 molar ratio) in methanol containing 10% (by mol) of a 1 M solution of tetrabutylammonium acetate gave only unreacted starting materials.[5]

Direct Formation of Quaternary Ammonium Salts of D-Glucaro-6,3-Lactone

We next focused our attention on directly preparing a quaternary ammonium salt form of the glucaric acid monomer that would have improved solubility for reactivity. Our first choice was tetrabutylammonium D-glucarate-6,3-lactone (**5**, Scheme 1), a salt we anticipated would allow us to achieve a one-pot synthesis of the bis(tetrabutylammonium) salt form of **III**. Initially, D-glucaro-6,3-lactone[6,7] (**3**) was treated with a solution of tetrabutylammonium hydroxide in methanol. Equimolar amounts were combined and stirred at room temperature for 24 h to give a syrup determined by ^1H NMR analysis to be mostly desired **5**. However, there was also some acyclic glucaric acid product present, resulting presumably from hydrolysis of the lactone by hydroxide ion under the conditions employed. Use of less basic tetrabutylammonium acetate resulted in preparation of **5** from **3** in essentially quantitative yield.

Before attempting the desired homogeneous one-pot synthesis of the diamido-diacid salts **III** (where M^+ = n-Bu_4N^+), we decided to carry out a model reaction between the new monomer **5** with an excess of hexamethylenediamine (**4c**) in methanol in order to synthesize the corresponding tetrabutylammonium monoamino monoamido salt **7** under homogeneous conditions (Scheme 2). The reaction mixture was initially a solution, but a solid began to precipitate after the solution was stirred for several hours at room temperature. The solid was collected, and from ^1H NMR analysis (D_2O) was determined to be the monoamide zwitterion (**8**), Scheme 2. Surprisingly, the tetrabutylammonium group on the C-terminus had been lost. The yield of **8** based on the starting glucarate salt was approximately 50%. The same results were obtained when



Scheme 1.

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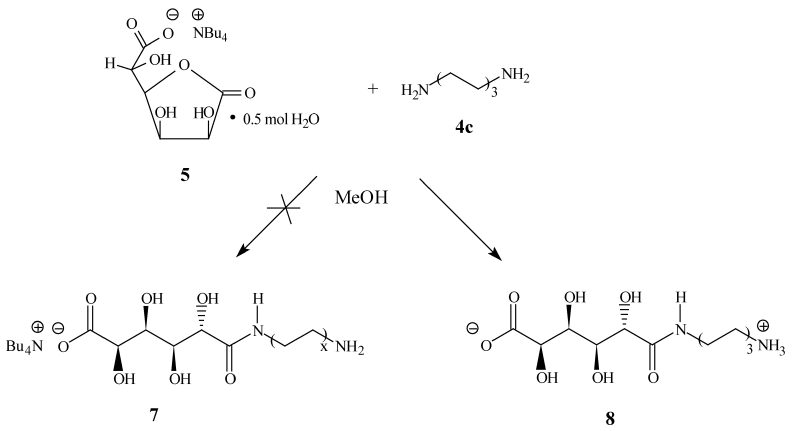
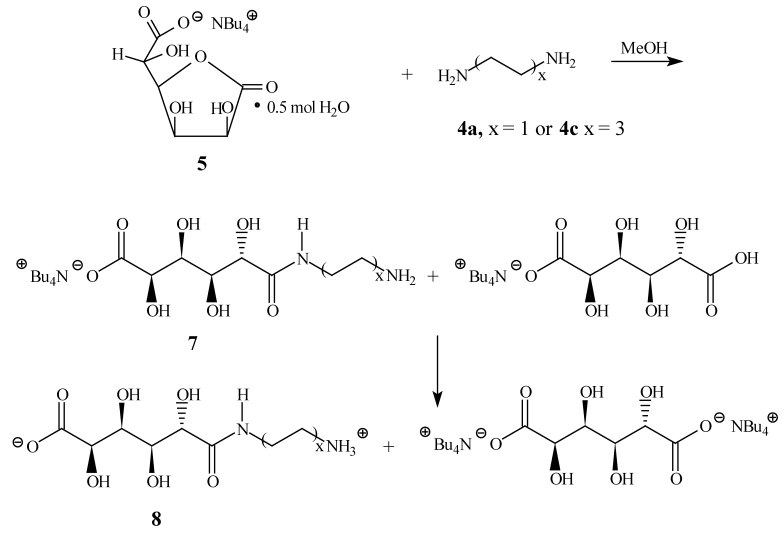


Scheme 2. The reaction of tetrabutylammonium D-glucarate-6,3-lactone (**5**) and excess hexamethylenediamine (**4c**).

higher temperatures or a larger excess of diamine were employed. In addition, a second quaternary ammonium glucaric acid salt, benzyltriethylammonium D-glucarate-6,3-lactone (**6**, Scheme 1) from **3**, was then tried but gave similar results, indicating that formation of **8** was independent of the quaternary ammonium salt employed.

In order to probe zwitterion formation further, **5** was treated with ethylenediamine (**4a**) as above, and the corresponding monoamide zwitterion precipitated, indicating that zwitterion formation was not unique to any one diamine. Examination of the filtrate (^{1}H NMR analysis) revealed that the main component was bis[tetrabutylammonium]-D-glucarate, suggesting that some of the starting lactone **5** underwent hydroly-



Scheme 3. Proposed mechanism for formation of monoamide zwitterion **8**.

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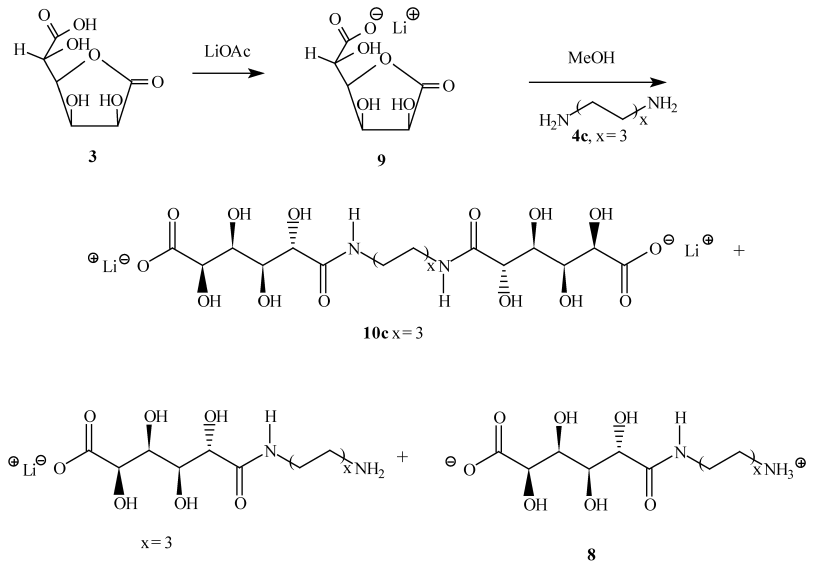
sis at some point during the reaction pathway. When elemental analysis of **5** revealed that it was hydrated (0.5 mol), we were able to formulate a possible mechanism for the formation of **8** (Scheme 3). Our proposed reaction pathway accounts for the formation of **8** in approximately 50% yield based on the amount of starting material **5**, as well as the formation of bis[tetrabutylammonium]-D-glucarate. We suggest that under the reaction conditions, 0.5 mol of **5** undergoes lactone hydrolysis leading to the tetrabutylammonium salt of glucaric acid while the remaining 0.5 mol of **5** is converted to the aminolysis product, tetrabutylammonium 6-[*N*-(6-aminoalkyl)]-D-glucaramid-1-ate (**7**). A proton exchange can then occur between these two initial products, giving **8** (ca. 50% yield based on the starting quantity of **5**), which has low solubility in methanol and precipitates, leaving bis[tetrabutylammonium]-D-glucarate in methanol solution.

Elemental analysis of the second quaternary ammonium lactone **6** showed that it was not hydrated. Surprisingly, zwitterion product was still obtained from **6**, but generally less than produced from **5**. Additional studies on zwitterion formation are still required to explain absolutely the observed findings.

The assigned structure of **8** was based on its ^{1}H NMR spectral data, which also clearly showed that the product contained ca. 10–15% of structurally related impurities.

Lithium Salt of D-Glucaro-6,3-Lactone

Given that a quaternary ammonium salt of D-glucaro-6,3-lactone did not serve as an adequate precursor for the target diamido-diacid salts **III**, we decided to prepare the metal salt lithium D-glucarate-6,3-lactone (**9**), anticipating that this salt might have better methanol and/or dimethyl sulfoxide solubility than the sodium salt **2**. Compound **9** was easily prepared by the rapid reaction of D-glucaro-6,3-lactone (**3**) and lithium acetate dihydrate in a concentrated aqueous solution. A heterogeneous one-pot syn-



Scheme 4.

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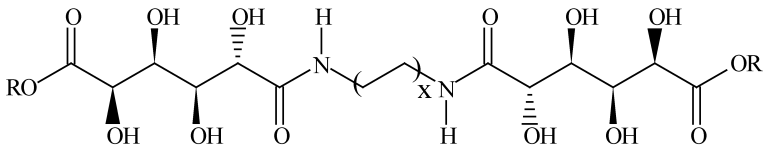
thesis of the diamide **10c** (Scheme 4) was then carried out from **9** and **4c** in methanol. ^{1}H NMR analysis of the white solid product from this reaction identified it as a mixture of the desired diamide **10c** with small amounts of the lithium salt monoamide and the zwitterion **8**.

Dimethyl sulfoxide was next evaluated as a solvent for the preceeding reaction. It was hoped that the increased solubility of **9** in DMSO over that in methanol would help to push the reaction to completion. In all cases, the use of DMSO did in fact facilitate completion of the aminolysis reactions leading to diamides **10a–f**. However, formation of the zwitterionic monoamide impurity (ca. 25%) persisted, making it necessary to purify these products chromatographically.

Chromatographic Purification of Diamido-Diacids

Isolation of the pure diamido-diacid products **11a–f** (Figure 4) was achieved via gel permeation chromatography (GPC). A slightly acidic mobile phase (0.10 M NH_4HCO_3) was needed to effect satisfactory separation using a Bio-Gel P-2 column. The impure diamido-diacids dilithium salts **10a–f** were dissolved in the minimum amount of deionized water for injection. Due to variability in water-solubility, sample loads ranged from 50 mg to 200 mg per run. The appropriate fractions containing pure diamido-diacid from several runs were combined for simultaneous work-up. Work-up involved treatment with an acid form cation exchange resin to decompose the residual NH_4HCO_3 from the eluent, followed by freeze-drying. As the purified diamido-diacid dilithium salts undergo protonation on both C-termini as a result of the chromatographic method, each of the C-termini may exist as either an acyclic carboxylic acid or as the 1,4-glucarolactone. Various proportions of lactone and acyclic carboxylic acid functionalities in the diamido-diacid products were observed by ^{1}H NMR analysis. A general trend was observed with respect to these proportions as a function of the diamine used in the preparation. The diamido-diacids comprised of the smaller diamines contained a mixture of lactonized and acyclic C-termini, whereas diamido-diacids comprised of longer chain diamines were observed to exist in the acyclic carboxylic acid form. The ^{1}H chemical shifts of the D-glucaryl protons



R = Li

10a, x = 1 **10d**, x = 4
10b, x = 2 **10e**, x = 5
10c, x = 3 **10f**, x = 6

R = H

11a, x = 1 **11d**, x = 4
11b, x = 2 **11e**, x = 5
11c, x = 3 **11f**, x = 6

Figure 4. Diamido-diacid dilithium salts **10a–f**, and purified diamido-diacids **11a–f**.

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Table 1. ^{1}H NMR chemical shifts (ppm) of purified diamido-diacids **11a–f** in D_2O.

	Purified diamido-diacids/lactones					
Proton	**11a**	**11b**	**11c**	**11d**	**11e**	**11f**
H-2 (acyclic)	4.38	4.47	4.40	4.17	4.40	4.06
H-3 (acyclic)	4.08	4.13	4.11	4.06	4.11	3.99
H-4 (acyclic)	3.92	3.98	3.98	3.96	3.98	3.89
H-5 (acyclic)	4.20	4.25	4.24	4.23	4.24	4.16
H-2 (lactone)	4.76	4.80	4.80	–	–	–
H-3 (lactone)	4.56	4.61	4.61	–	–	–
H-4 (lactone)	5.05	5.10	5.09	–	–	–
H-5 (lactone)	4.51	4.54	4.53	–	–	–

of the six purified diamido-diacids **11a–f** are given in Table 1. Table 2 indicates the relative ratios of acyclic carboxylic acid and lactone functions, as estimated from ^{1}H NMR integration, in each of the purified diamido-diacids **11a–f**.

It should be mentioned that the purification of **10f** did not proceed as smoothly as the purification of **10a–e**. It appears that **10f** was strongly absorbed by the cation exchange resin used during work-up of the fractions obtained from the HPLC separation step, resulting in a very low recovery of purified **11f**.

Synthesis of Six Alternating Polyhydroxypolyamides from D-Glucaric Acid

Six polyamides (**12a–f**, Scheme 5) were prepared by the condensation of the methanol esterified diamido-diacids 6,6′-(*N*,*N*′-alkylene)-bis(D-glucaramid-1-oic acid)s (**11a–f**) with the corresponding alkylenediamines **4a–f**. In order to activate the diamido-diacids for polymerization with a diamine, they were treated with methanolic HCl to esterify- lactonize the two terminal glucaric acid units. These activated diacids were then treated with triethylamine and a slight excess of the corresponding alkylenediamine in methanol at room temperature to promote polymerization. Each of the alternating *head*, *tail–tail*, *head*-polyamides **12a–f** precipitated from the reaction

Table 2. Approximate percentages of lactonized and acyclic C-termini of purified diamido-diacids **11a–f**.

Diamine component of diamido-diacid	Percentage of C-termini lactonized	Percentage of C-termini acyclic
ethylenediamine (**11a**)	25.4%	74.6%
tetramethylenediamine (**11b**)	39.1%	60.9%
hexamethylenediamine (**11c**)	14.8%	85.2%
octamethylenediamine (**11d**)	$\leq$ 1%	$\geq$ 99%
decamethylenediamine (**11e**)	$\leq$ 1%	$\geq$ 99%
dodecamethylenediamine (**11f**)	$\leq$ 1%	$\geq$ 99%

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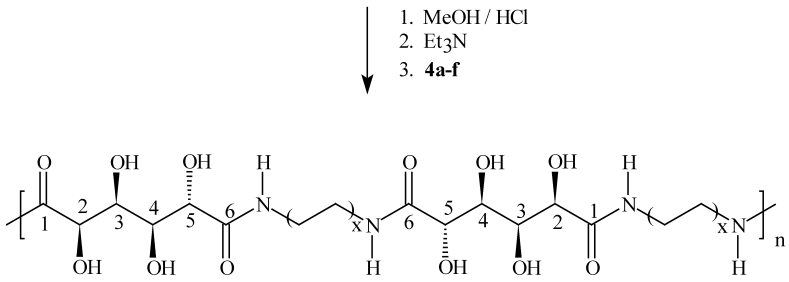
11a-f



12a, x = 1 **12d**, x = 4
12b, x = 2 **12e**, x = 5
12c, x = 3 **12f**, x = 6

Scheme 5.

mixture. The polyamides displayed ^{1}H NMR and IR spectra consistent with their structures, but as with the corresponding stereoregular *head*, *tail*-polyamides,[4] but not with the random polyamides,[2] their elemental combustion analyses all gave lower carbon values than calculated.

Molecular Weight Determinations

^{1}H NMR end group analysis[2] was performed on each of the polymers in order to obtain their respective number-average molecular weights (M_n), as listed in Table 3. As with previous studies, the ratio of methylene groups next to an amide NH within the polymer chain to methylene groups next to the terminal amine was used to calculate M_n values.

Polyamide Models

Some possible contributing conformers for both repeating and alternating stereoregular polyamides, in the solid state and/or solution state, using poly(hexamethylene D-glucaramide) as an example, are shown in Figures 5–7. Three structures are shown for each type of stereoregular polymer. In Figure 5, the polyamide structures

Table 3. Calculated molecular weights (M_n) for *head*, *tail–tail*, *head*-poly (alkylene D-glucaramides).

Polymer	**12a**	**12b**	**12c**	**12d**	**12e**	**12f**
M_n	1600	3500	4600	7300	5500	4900

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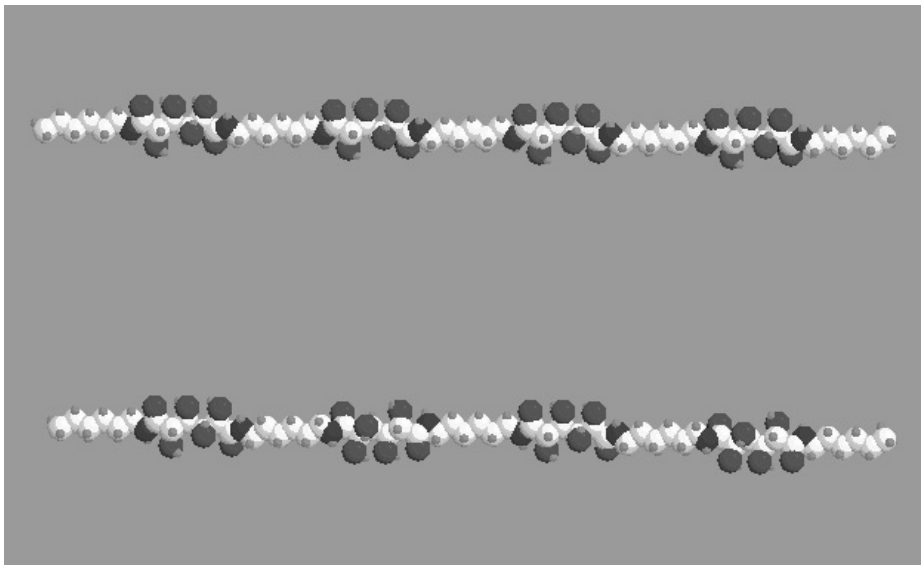

Figure 5. Molecular models of *repeating* (top) and *alternating* (bottom) extended conformations of polymer poly(hexamethylene D-glucaramide).

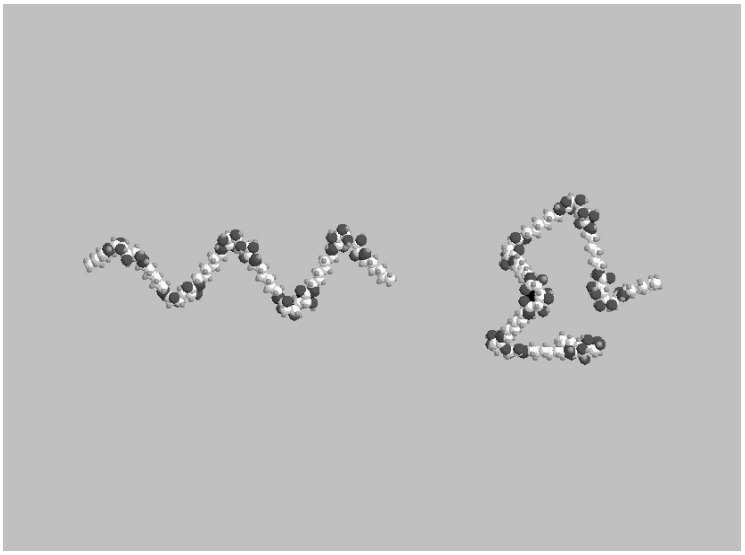

Figure 6. Molecular models of *repeating* (left) and *alternating* (right) conformations of polymer poly(hexamethylene D-glucaramide) based on average glucaryl unit vicinal ^{1}H NMR coupling constants.

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correspond to the *repeating* (top) and *alternating* (bottom) stereoregular polymers, respectively, with the glucaryl unit depicted in an extended (''zig-zag'') conformation throughout the polymer chain based on both calculated low-energy conformations from the molecular modeling of D-glucaramide as well the crystal structure of *N*,*N*′-dimethyl D-glucaramide.[8] In Figure 6, the D-glucaryl units in the conformations for the *repeating* (left) and *alternating* (right) polyamides are shown as very different bent conformations derived from matching the observed average D-glucaramide vicinal couplings with calculated vicinal couplings and corresponding dihedral angles along the carbon chain.[8] The structures in Figure 7 correspond to the same polymers but with each glucaryl unit as a coiled conformation based on the calculated global minimum from the molecular modeling of D-glucaramide,[8] as well as the crystal structure of sodium potassium D-glucarate.[8] The *repeating* and *alternating* structures are left then right, respectively. Figures 5 and 7 represent two extreme conformations of the the polymers, extended and coiled, with the structures in Figure 6 representing conformations somewhere in between the extreme conformations.

For both stereoregular polyamides, when the glucaric acid moiety is incorporated in an extended conformation, the polymers differ only slightly. On the top side of the *repeating* polymer, three out of the four glucaryl unit hydroxyl groups in each glucaryl unit are oriented consistently to one side of the chain, making that surface of the chain slightly more hydrophilic than that of the *alternating* polymer. In the *alternating* polyamide, chain alignment of the glucaryl unit results in an approximately even distribution of hydroxyl groups oriented to each side of the polymer chain. With

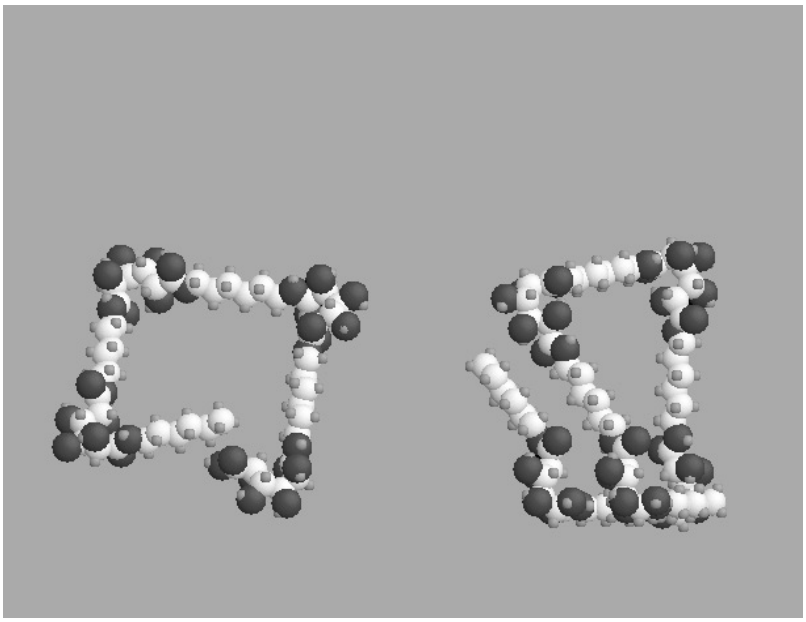

Figure 7. Molecular models of *repeating* (left) and *alternating* (right) conformations of polymer poly(hexamethylene D-glucaramide) based on calculated global minimum from the molecular modeling of D-glucaramide.

smaller repeating alkylene units such as tetramethylene or ethylene in the polymers and the glucaryl units closer together, the difference in the hydrophilic/hydrophobic character of the polymer surface should be magnified, suggesting at least subtle property differences between corresponding *repeating* and *alternating* polyamides.

The conformational views of the polymers employing the molecular modeling global minimum conformation for the glucaryl unit depicted in Figure 7 are similar; both form a somewhat planar square cavity, with the glucaryl units occupying the four corners. The inside of both cavities appears to be relatively hydrophobic, as the hydroxyl groups of the corner carbohydrate units are oriented to the exterior. Clearly, these conformations are very different from the linear structures based on an extended glucaryl unit.

The conformations of the two polyamides constructed based on ^{1}H NMR vicinal coupling data (Figure 6) from the glucaryl unit, differ considerably from each other and from the linear structures (Figure 5). Whereas the *repeating* polymer is seen as having a wormlike structure, the *alternating* polymer is somewhat coiled but not nearly as compacted as the polymer conformations based on a global minimum structure for the glucaryl unit (Figure 7).

The three-dimensional shapes of the polyamides constructed with the extended and bent conformations of the glucaric acid component probably represent two extremes. It may be that those constructed with the NMR model may best approximate the actual three-dimensional shapes of these two types of polymers in solution, not fully extended nor in a tightly coiled structure, given that the ^{1}H NMR coupling constants upon which the structures were derived represent average dihedral angles resulting from a conformational distribution. Whatever that conformational distribution of the glucaryl units and the actual polymers might be, the models shown at least provide some initial insight into the possible three-dimensional characteristics of the polymers. They are presented as a starting point to further explore and evaluate the three dimensional structures of these polymers, both in the solid state and in solution.

CONCLUSIONS

Six new diamido-diacid monomers targeted for polymerization with diamines have been synthesized, purified, and characterized. The synthetic route to these monomers evolved initially as a result of solubility limitations, and later developed around the surprising phenomenon of zwitterion formation which occurred when solubilized reactants were finally obtained. It was determined that methanol or DMSO soluble salts of D-glucaro-6,3-lactone would be needed to allow the desired aminolysis reaction to occur, but that this necessary solubility would also limit the purity of the diamido-diamide obtained due to zwitterionic side-product formation. The quaternary ammonium salts of D-glucaro-6,3-lactone afford the highest solubility in methanol or DMSO, but also yield mainly the zwitterionic monoamide under the aminolysis reaction conditions. However, the lithium salt provides intermediate solubility in methanol and DMSO, and thus allows the formation of the desired diamido-diamide contaminated with a small proportion of monoamide zwitterion which can be removed by chromatography. Other salts of D-glucaro-6,3-lactone or alternative reaction pathways may eventually be discovered which conveniently produce the desired pure diamido-diacids.

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Six examples of a new class of stereoregular polymers, *head*, *tail–tail*, *head*-poly(alkylene D-glucaramides), were made by simple condensation polymerization. These new polymers have melting points and solubilities comparable to both their random and repeating *head*, *tail* counterparts. Molecular weights as calculated from ^{1}H NMR end group analysis were reported, and representative conformations for the polyamides were produced using relevant ^{1}H NMR, crystal structure, and molecular modeling data from various acyclic D-glucaric acid derivatives. The overall shapes for the alternating *head*, *tail–tail*, *head*-polyamide conformers were compared with those of their repeating *head*, *tail*-counterparts.

EXPERIMENTAL

General methods. NMR spectra were obtained on Bruker DRX-400 and ARX-300 spectrometers. All ^{1}H NMR spectra were recorded at either 300.14 or 400.13 MHz. Chemical shifts measured in D_2O are reported as ppm (δ)downfield from 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid, sodium salt (TSP). Chemical shifts measured in dimethyl sulfoxide-d_6 are referenced to the solvent. IR spectra were recorded on a Beckman Acculab II as KBr pellets. Dimethyl sulfoxide was Certified A.C.S. grade. All other solvents used were reagent grade unless stated otherwise. Hexamethylenediamine was recrystallized from hexanes prior to use. Melting points for non-hygroscopic compounds were obtained on a Fisher–Johns melting point apparatus and are reported uncorrected. Melting points for hygroscopic diamido-diacids **11a–c** were obtained in sealed capillaries using a Mel-Temp II apparatus and are also reported uncorrected. Solvent evaporations were carried out at reduced pressure. Elemental analyses were performed by Atlantic Microlab, Norcross, Georgia. Mass spectral data were obtained on a Micromass Platform LCZ Electrospray equipped with a quadrupole mass analyzer coupled to a Hewlett-Packard HP1100 HPLC. Diamido-diacid samples were dissolved in water and 20 μL aliquots were used for loop injection into the mass spectrometer. The HPLC mobile phase was 50/50 acetonitrile/water with 0.5% formic acid.

Tetrabutylammonium D-Glucarate-6,3-lactone (5). Finely ground D-glucaro-6,3-lactone[6,7] (**3**, 1.35 g, 7.00 mmol) and a 1 M solution of tetrabutylammonium acetate in water (70 mL, 7.00 mmol) were combined in a round bottom flask. Deionized water (2.5 mL) was added to aid in the dissolution of the lactone. The flask was stoppered, and the homogeneous reaction mixture was stirred overnight. The following morning the odor of the acetic acid by-product was easily detectable in the reaction mixture. The solution was then concentrated in an air stream and stored in the refrigerator overnight, during which time small needle crystals began to form. The syrupy mixture was dried at reduced pressure for 24 h, yielding tetrabutylammonium D-glucarate-6,3-lactone (**5**, 3.35 g, 110% yield due to residual acetic acid). In a later reaction, the acetic acid was removed by repeated evaporation with 1:1 methanol–toluene, yielding **5** as an off-white hydrated solid; mp 116–118°C; IR 3415 cm^{-1} (OH stretch), 2940 cm^{-1} (C-H, stretch), 1785 cm^{-1} (C = O stretch, five-membered lactone), 1625 cm^{-1} (C = O stretch, carboxylate); ^{1}H NMR (D_2O) δ 4.73 (d, 1H, H-2, $J_{2,3}$ = 4.50 Hz), 4.60 (m, 2H, H-3 and H-5), 4.37 (m, 1H, H-4), 3.18 (t, 9H, H-1′, $J_{1',2'}$ = 8.40 Hz), 1.64 (m, 9H, H-2′), 1.33 (m, 9H, H-3′), 0.94 (t, 12H, H-4′, $J_{4',3'}$ = 7.35 Hz).

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Anal. Calcd for $C_{22}H_{43}NO_7 \cdot 0.5\ H_2O$ (442.59): C, 59.70; H, 10.02; N, 3.16. Found: C, 59.43; H, 9.70; N, 3.17.

6[*N*-(6′-Ammoniumhexyl)]-D-Glucaramid-1-ate (8). Tetrabutylammonium D-glucarate-6,3-lactone (**5**, 0.55 g, 1.3 mmol) was added to a 100 mL round bottom flask containing hexamethylenediamine (**4c**, 0.2 g, 1.7 mmol) dissolved in a small amount of distilled methanol, and the total volume of the reaction mixture was adjusted to 10 mL with the addition of more distilled methanol. The flask was warmed gently with a heat gun to aid in dissolution of the lactone. The reaction flask was then stoppered, and the reaction mixture stirred at room temperature overnight, after which time a white solid was suspended in the reaction mixture. The solid was removed by filtration, washed with methanol (5 mL) and dried at reduced pressure to give **8** (0.2 g, 50% yield); mp 89–90°C; ^{1}H NMR (D_2O) δ 4.15 (d, 1H, H-2, $J_{2,3}$ = 3.30 Hz), 4.09 (t, 1H, H-3), 4.01 (t, 1H, H-4, $J_{4,5}$ = 5.10 Hz), 4.29 (d, 1H, H-5), 3.28 (m, 2H, H-1′, $J_{1',2'}$ = 6.75 Hz), 1.70 (m, 2H, H-2′), 1.41 (m, 4H, H-3′ and H-4′), 1.59 (m, 2H, H-5′), 3.03 (t, 2H, H-6′).

Benzyl Triethylammonium D-Glucarate-6,3-lactone (6). Hydroxide-form anion exchange resin (Amberlite IRA-400, 11 mL, 16.5 meq) was slurried in deionized water and poured into a small chromatography column. The resin was washed with additional deionized water until the washings were clear, then washed with five column volumes of methanol. A 1M solution of acetic acid in methanol (35 mL) was passed slowly through the resin column to convert the Resin-OH into Resin-OAc. The column was then washed with 10 column volumes of methanol to insure removal of any residual acetic acid. A solution of benzyl triethylammonium chloride[9] (1.8 g, 7.9 mmol) dissolved in the minimum volume of methanol was slowly applied to the resin column to effect the conversion to benzyl triethylammonium acetate. Fractions were collected and the compound was detected by UV light in fractions 2-11. The fractions were combined and the solution concentrated at reduced pressure for 24 h. The syrup was stored in the refrigerator for several days, and needle crystals began to form. The syrupy crystals were analyzed by ^{1}H NMR to confirm the product identity as benzyl triethylammonium acetate (1.8 g, 7.1 mmol, 90% yield). This material was used without purification in the following reaction. The quaternary ammonium lactone **6** was obtained by dissolving D-glucaro-6,3-lactone (**5**, 0.50 g, 2.6 mmol) in the minimum volume of distilled methanol to which a solution of benzyl triethylammonium acetate (0.55 g, 2.6 mmol, dissolved in 4 mL of distilled methanol) was added. The reaction mixture was stirred overnight, then concentrated at reduced pressure. Residual acetic acid by-product was removed by repeated evaporation with 1:1 methanol/toluene to give **6** (0.95 g, 2.5 mmol, 95% yield): mp 138–139°C (dec); IR (KBr) 3395 cm^{-1} (broad, OH stretch), 2998 cm^{-1} (C-H, stretch), 1792 cm^{-1} (C = O stretch, five-membered lactone), 1620 cm^{-1} (C = O stretch, carboxylate), 1132 cm^{-1} (C-N, stretch); ^{1}H NMR (D_2O) δ 4.74 (d, 1H, H-2, $J_{2,3}$ = 3.90 Hz), 4.62 (m, 2H, H-3 and H-5), 4.43 (m, 3H, H-4 and H-3′ overlapping), 3.24 (q, 6H, H-1′, $J_{1',2'}$ = 7.20 Hz), 1.41 (t, 9H, H-2′), 7.53 (s, 5H, aromatic).

Anal. Calcd for $C_{19}H_{29}NO_7$ (383.44): C, 59.52; H, 7.62; N, 3.65. Found: C, 59.33; H, 7.55; N, 3.54.

Lithium D-Glucarate-6,3-lactone (9). To a solution of D-glucaro-6,3-lactone (**3**, 3.013 g, 15.68 mmol) in deionized water (5.5 mL) was added solid lithium acetate

dihydrate (1.599 g, 15.68 mmol) with stirring. A white precipitate formed almost immediately. After the mixture was stirred for 5 min, the white precipitate was removed by filtration and washed with methanol. The filtrate and washings were combined and stirred for an additional five min, producing a second crop of white precipitate which was removed by filtration and washed with methanol. Two more crops of white solid were isolated in this manner, however, the fourth crop contained approximately 10% acyclic glucaric acid products (^{1}H NMR) and so it was discarded. The three crops of white precipitate were combined to give **9** (2.590 g, 13.08 mmol, 83.4% yield): mp 169°C (onset of decomposition); IR (KBr) 3200 cm^{-1} (broad, OH), 2880 cm^{-1} (C-H, stretch), 1802 cm^{-1} (C = O stretch, five membered lactone), 1635 cm^{-1} (C = O stretch, carboxylate); ^{1}H NMR (D_2O) δ 4.75 (d, 1H, H-2, $J_{2,3}$ = 4.5 Hz), 4.60 (m, 2H, H-3 and H-5), 4.38 (m, 1H, H-4).

Anal. Calcd for $C_6H_7O_7Li$ (198.06): C, 36.38; H, 3.56; Li, 3.50. Found: C, 36.29; H, 3.61; Li, 3.46.

6,6′-(*N,N′*-ethylene)-bis(D-glucaramid-1-oic acid) (11a). A syringe was used to deliver 1,2-diaminoethane (4**a**, 77 μL, 0.069 g, 1.15 mmol) into a 100 mL round bottom flask. Dimethyl sulfoxide (6 mL) was added, followed by the addition of finely ground lithium D-glucarate-6,3-lactone (**9**, 0.500 g, 2.52 mmol). A magnetic stir bar was added, and the flask was fitted with a drying tube ($CaCl_2$). The reaction mixture was placed in a 45°C oil bath for 44–48 h, becoming homogeneous after approximately 3 h. After removing the flask from the oil bath, the crude diamide-disalt (**10a**) was precipitated by the addition of methanol (10 mL) with stirring at room temperature and collected by centrifugation. The solid was then dried at reduced pressure and 70°C for several h, during which time the solid was transformed into a thick yellow syrup. The syrup was then triturated with acetone (resulting again in a white solid), centrifuged, and the trituration/centrifugation process repeated twice more. The extremely hygroscopic white solid was then dried at reduced pressure and stored in a dessicator prior to chromatography. The chromatographic procedure involved dissolution of impure **10a** in the minimum volume of deionized water. Several injections were made into a Bio-Gel P-2 column (90 × 2.6 cm i.d.; bead size < 45 μm) at a mobile phase (0.10 M NH_4HCO_3) flow rate of 1.0 mL/min. Fractions collected over several injections were combined and treated with excess Amberlite IR-120 (H^+) resin to decompose the NH_4HCO_3. The resin was removed by filtration, and the filtrate freeze-dried to give purified **11a** (60–70% recovery): mp 107–110°C (dec.); IR 3350 cm^{-1} (broad, O-H, stretch), 2930 cm^{-1} (C-H, stretch), 1730 cm^{-1} (C = O, carboxylic acid), 1640 cm^{-1} (Amide I, C = O), 1540 (Amide II, N-H); ^{1}H NMR (D_2O) δ 4.38 (d, 1H, H-2 in acyclic form, $J_{2,3}$ = 3.0 Hz), 4.08 (m, 1H, H-3 acyclic, $J_{3,4}$ = 5.0 Hz), 3.92 (t, 1H, H-4 acyclic, $J_{4,5}$ = 5.0 Hz), 4.20 (d, 1H, H-5 acyclic), 4.76 (dd, 1H, H-2 in lactonized form, $J_{2,3}$ = 9.2 Hz), 4.56 (t, 1H, H-3 lactonized, $J_{3,4}$ = 8.0 Hz), 5.05 (dd, 1H, H-4 lactonized, $J_{4,5}$ = 2.4 Hz), 4.51 (d, 1H, H-5 lactonized), 3.36 (m, 4H, H-1′ and H-2′, $J_{1',2'}$ = 6.4 Hz). MS: m/z 445.4 [M + 1], 427.4 [M-H_2O (one end lactonized) + 1], 409.4 [M-2H_2O (both ends lactonized) + 1], 444.3 [M-1], 425.3 [M-H_2O (one end lactonized)-1], 407.3 [M-2H_2O (both ends lactonized)-1].

6,6′-(*N,N′*-tetramethylene)-bis(D-glucaramid-1-oic acid) (11b). Diamide diacid **11b** was prepared according to the method for **11a**: 1,4-diaminobutane (**4b**, 110 μL,

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0.096 g, 1.09 mmol), dimethyl sulfoxide (5 mL), and finely ground **9** (0.477 g, 2.41 mmol). The hygroscopic white solid was then dried at reduced pressure and stored in a desiccator prior to chromatography. The chromatographic procedure utilized was identical to the method used for **11a**, resulting in purified **11b** (60–65% recovery): mp 113–118°C (dec); IR 3350 cm^{-1} (broad, O-H, stretch), 2945 cm^{-1} (C-H, stretch), 1745 cm^{-1} (C = O, carboxylic acid), 1635 cm^{-1} (Amide I, C = O), 1545 cm^{-1} (Amide II, N-H); ^{1}H NMR (D_2O) δ 4.80 (d, 1H, H-2 of 1,4-lactone form, $J_{2,3}$ = 8.8 Hz), 4.61 (t, 1H, H-3 lactonized, $J_{3,4}$ = 8.0 Hz), 5.10 (dd, 1H, H-4 lactonized, $J_{4,5}$ = 2.3 Hz), 4.54 (d, 1H, H-5 lactonized), 4.47 (d, 1H, H-2 of acyclic form, $J_{2,3}$ = 3.2 Hz), 4.13 (t, 1H, H-3 acyclic, $J_{3,4}$ = 4.1 Hz), 3.98 (t, 1H, H-4 acyclic), 4.25 (d, 1H, H-5 acyclic, $J_{4,5}$ = 4.8 Hz), 3.25 (m, 4H, H-1′ and H-4′), 1.54 (s, 4H, H-2′ and H-3′). MS: *m/z* 473.4 [M + 1], 455.4 [M-H_2O (one end lactonized) + 1], 437.4 [M-$2H_2O$ (both ends lactonized) + 1], 471.4 [M-1], 453.4 [M-H_2O (one end lactonized)-1], 435.4 [M-$2H_2O$ (both ends lactonized)-1].

6,6′-(*N,N′*-hexamethylene)-bis(D-glucaramid-1-oic acid) (11c). Finely ground **9** (0.625 g, 3.16 mmol) and 1,6-diaminohexane (**4c**, 0.167 g, 1.44 mmol) were combined in a 100 mL round bottom flask. Dimethyl sulfoxide (8 mL) was added, along with a magnetic stir bar. The flask was fitted with a drying tube and placed in a 45°C oil bath for 44–48 h. After approximately 3 h, all starting materials had dissolved. However, near the end of the reaction a small amount of white precipitate began to form. Additional white solid was precipitated by the addition of methanol (12–15 mL) with stirring. The solid was collected by centrifugation and dried at reduced pressure and 70°C for 8 h. Chromatography was performed by the method used for **11a**, yielding purified **11c** (60–65% recovery): mp 118–122°C (dec); IR 3370 cm^{-1} (broad, O-H, stretch), 2955 cm^{-1} (C-H, stretch), 1725 cm^{-1} (C = O, carboxylic acid), 1635 cm^{-1} (Amide I, C = O), 1545 cm^{-1} (Amide II, N-H);. ^{1}H NMR (D_2O) δ 4.80 (d, 1H, H-2 in 1,4-lactone form, $J_{2,3}$ = 8.7 Hz), 4.61 (t, 1H, H-3 lactonized, $J_{3,4}$ = 8.0 Hz), 5.09 (dd, 1H, H-4 lactonized, $J_{4,5}$ = 2.6 Hz), 4.53 (d, 1H, H-5 lactonized), 4.40 (d, 1H, H-2 in acyclic form, $J_{2,3}$ = 3.2 Hz), 4.11 (q, 1H, H-3 acyclic, $J_{3,4}$ = 5.2 Hz), 3.98 (t, 1H, H-4 acyclic, $J_{4,5}$ = 4.8 Hz), 4.24 (d, 1H, H-5 acyclic), 3.23 (t, 4H, H-1′ and H-6′, $J_{1',2'}$ = $J_{5',6'}$ = 6.8 Hz), 1.52 (m, 4H, H-2′ and H-5′), 1.33 (s, 4H, H-3′ and H-4′). MS: *m/z* 501.4 [M + 1], 483.4 [M-H_2O (one end lactonized) + 1], 465.4 [M-$2H_2O$ (both ends lactonized) + 1], 499.4 [M-1], 481.4 [M-H_2O (one end lactonized)-1], 463.4 [M-$2H_2O$ (both ends lactonized)-1].

6,6′-(*N,N′*-octamethylene)-bis(D-glucaramid-1-oic acid) (11d). Finely ground **9** (0.704 g, 3.56 mmol) and 1,8-diaminooctane (**4d**, 0.233 g, 1.62 mmol) were combined in a 100 mL round bottom flask. Dimethyl sulfoxide (8 mL) was added, along with a magnetic stir bar. The flask was fitted with a drying tube and placed in a 50°C oil bath for 24 h. The reaction mixture contained a small amount of suspended white solid at the end of the reaction, and additional solid was obtained by precipitation with 50:50 ethyl acetate/methanol solution (12 mL). The solid was collected by centrifugation and dried at reduced pressure and 70°C for 8 h, then purified chromatographically by the method used for **11a** to give purified **11d** (60–65% recovery): mp 133–136°C (dec); IR 3480 cm^{-1} (N-H, stretch), 3345 cm^{-1} (broad, O-H, stretch), 2940 cm^{-1} (C-H, stretch),

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1735 cm^{-1} (C = O, carboxylic acid), 1650 cm^{-1} (Amide I, C = O), 1545 cm^{-1} (Amide II, N-H);. ^1H NMR (D_2O) δ 4.17 (d, 2H, H-2, $J_{2,3}$ = 3.2 Hz), 4.06 (t, 2H, H-3), 3.96 (t, 2H, H-4, $J_{4,5}$ = 5.4 Hz), 4.23 (d, 2H, H-5), 3.23 (t, 4H, H-1′ and H-8′, $J_{1',2'} = J_{7',8'}$ = 6.8 Hz), 1.53 (t, 4H, H-2′ and H-7′), 1.31 (s, 8H, H-3′, H-4′, H-5′, and H-6′). MS: *m/z* 529.4 [M + 1], 511.4 [M-H_2O (one end lactonized) + 1], 493.4 [M-$2H_2O$ (both ends lactonized) + 1], 527.4 [M-1], 509.4 [M-H_2O (one end lactonized)-1].

6,6′-(*N,N′*-decamethylene)-bis(D-glucaramid-1-oic acid) (11e). Finely ground **9** (0.634 g, 3.20 mmol) and 1,10-diaminodecane (**4e**, 0.251 g, 1.46 mmol) were combined in a 100 mL round bottom flask. Dimethyl sulfoxide (9 mL) was added, along with a magnetic stir bar. The flask was fitted with a drying tube and placed in a 50°C oil bath for 18 h. At the end of the reaction a white solid was suspended in the reaction mixture. Additional solid was precipitated upon addition of methanol (12 mL) and collected by centrifugation, then dried at reduced pressure and 70°C for 8 h, followed by chromatographic purification by the method used for **11a** to give purified **11e** (60–65% recovery): mp 153–155°C; IR 3480 cm^{-1} (N-H, stretch), 3350 cm^{-1} (broad, O-H, stretch), 2940 cm^{-1} (C-H, stretch), 1735 cm^{-1} (C = O, carboxylic acid), 1655 cm^{-1} (Amide I, C = O), 1540 cm^{-1} (Amide II, N-H); ^1H NMR (D_2O) δ 4.40 (d, 2H, H-2, $J_{2,3}$ = 3.2 Hz), 4.11 (dd, 2H, H-3), 3.98 (t, 2H, H-4), 4.24 (d, 2H, H-5, $J_{4,5}$ = 4.8 Hz), 3.23 (t, 4H, H-1′ and H-10′, $J_{1',2'} = J_{9',10'}$ = 6.8 Hz), 1.52 (t, 4H, H-2′ and H-9′), 1.28 (s, 12H, H-3′, H-4′, H-5′, H-6′, H-7′, H-8′). MS: *m/z* 557.6 [M + 1], 539.6 [M-H_2O (one end lactonized) + 1], 521.6 [M-$2H_2O$ (both ends lactonized) + 1], 555.6 [M-1], 537.6 [M-H_2O (one end lactonized)-1].

6,6′-(*N,N′*-dodecamethylene)-bis(D-glucaramid-1-oic acid) (11f). Finely ground **9** (0.642 g, 3.24 mmol) and 1,12-diaminododecane (**4f**, 0.295 g, 1.47 mmol) were combined in a 100 mL round bottom flask. Dimethyl sulfoxide (6 mL) was added, along with a magnetic stir bar. The flask was fitted with a drying tube and placed in a 100°C oil bath for 2 h. At the end of the reaction, a white solid was suspended in the reaction mixture. Additional solid was precipitated upon addition of methanol (30 mL) and collected by centrifugation, then dried at reduced pressure and 70°C for 8 h. Chromatographic purification was achieved by the method used for **11a**, yielding purified **11f** (10–15% recovery): mp 137–141°C (dec); IR 3300 cm^{-1} (broad, O-H, stretch), 2920 cm^{-1} (C-H, stretch), 1740 cm^{-1} (C = O, carboxylic acid), 1660 cm^{-1} (Amide I, C = O), 1540 cm^{-1} (Amide II, N-H); ^1H NMR (D_2O) δ 4.06 (d, 2H, H-2, $J_{2,3}$ = 3.2 Hz), 3.99 (t, 2H, H-3), 3.89 (t, 2H, H-4, $J_{4,5}$ = 5.4 Hz), 4.16 (d, 2H, H-5), 3.18 (m, 4H, H-1′ and H-12′, $J_{1',2'} = J_{11',12'}$ = 6.8 Hz), 1.46 (t, 4H, H-2′ and H-11′), 1.22 (2, 16H, H-3′, H-4′, H-5′, H-6′, H-7′, H-8′, H-9′, and H-10′). MS: *m/z* 585.6 [M + 1], 567.6 [M-H_2O (one end lactonized) + 1], 583.7 [M-1], 565.8 [M-H_2O (one end lactonized)-1].

***Head, tail–tail, head*-poly(ethylene D-glucaramide) (12a).** 6,6′-(*N,N′*-ethylene)-bis(D-glucaramid-1-oic acid)[5] (**11a**, 61.1 mg, 0.138 mmol) was suspended in distilled methanol (2 mL) in a small round bottom flask equipped with a pressure-equalizing addition funnel and a drying tube. The suspension was stirred in an ice bath for 10 min. Acetyl chloride (7 drops) was added to the cooled suspension dropwise via the addition funnel with stirring. The reaction mixture remained in the ice bath throughout the

addition with stirring, and for approximately 5 min after addition was complete. It was then removed from the ice bath and stirred at room temperature for 3 h, with the reaction mixture becoming homogeneous. This activated diamido-diacid solution was then concentrated on a rotary evaporator at 35°C. The resulting residue was redissolved in 1.5 mL of distilled methanol and stirred at room temperature while triethylamine was added. The reaction flask was purged with dry nitrogen during the addition of triethylamine. Enough triethylamine was added to basify the reaction mixture (pH 8–9), and then a solution of 0.15 M ethylenediamine in methanol (1.0 mL, 0.15 mmol) was added. The reaction mixture was stirred for 48 h at room temperature. Precipitation of *head*, *tail–tail*, *head*-poly(ethylene D-glucaramide) (**12a**) commenced within 0.5 h of addition of the diamine solution. The precipitate was collected by centrifugation, then dried at reduced pressure and 70°C for 24 h to give **12a** (56.1 mg, 0.120 mmol, 86.8%): mp 179–183°C (dec); IR 3340 cm^{-1} (O-H, stretch), 2960 cm^{-1} (C-H, stretch), 1655 cm^{-1} (Amide I, C = O), 1545 cm^{-1} (Amide II, N-H bend); ^1H NMR (D_2O) δ 4.34 (s, 2H, H-2), 4.26 (d, 2H, H-5, $J_{4,5}$ = 4.6 Hz), 4.12 (s, 2H, H-3), 3.97 (t, 2H, H-4), 3.44 (s, 8H, H-1′ and H-2′).

Anal. Calcd for $C_{16}H_{28}N_4O_{12}$ (468.42): C, 41.03; H, 6.02; N, 11.96. Found: C, 39.23; H, 6.16; N, 12.06.

***Head, tail–tail, head*-poly(tetramethylene D-glucaramide) (12b).** Polymer **12b** was prepared according to the method for **12a**: 6,6′-(*N*,*N*′-tetramethylene)-bis(D-glucaramid-1-oic acid)[5] (**11b**, 64.5 mg, 0.136 mmol), distilled methanol (2 mL), acetyl chloride (7 drops, ice bath), room temperature 3 h, and concentrated. The residue was redissolved in methanol (1.5 mL), basified with triethylamine, and then reacted with 0.10 M tetramethylenediamine in methanol (1.5 mL, 0.15 mmol). The resulting precipitate was filtered and dried at reduced pressure and 70°C to give **12b** (52.7 mg, 0.100 mmol, 73.6%): mp 188–190°C (dec); IR 3340 cm^{-1} (O-H, stretch), 2955 cm^{-1} (C-H, stretch), 1640 cm^{-1} (Amide I, C = O), 1545 cm^{-1} (Amide II, N-H bend); ^1H NMR (D_2O) δ 4.31 (d, 2H, H-2, $J_{2,3}$ = 2.8 Hz), 4.09 (t, 2H, H-3, $J_{3,4}$ = 4.4 Hz), 3.96 (t, 2H, H-4), 4.27 (d, 2H, H-5, $J_{4,5}$ = 5.2 Hz)), 3.28 (s, 8H, H-1′ and H-4′), 1.57 (s, 8H, H-2′ and H-3′).

Anal. Calcd for $C_{20}H_{36}N_4O_{16}$ (524.52): C, 45.80; H, 6.92, N, 10.68. Found: C, 44.93; H, 6.90; N, 10.51.

***Head, tail–tail, head*-poly(hexamethylene D-glucaramide) (12c).** Polymer **12c** was prepared according to the method for **12a**: 6,6′-(*N*,*N*′-hexamethylene)-bis(D-glucaramid-1-oic acid)[5] (**11c**, 60.6 mg, 0.121 mmol), distilled methanol (2 mL), acetyl chloride (6 drops, ice bath), room temperature 3 h, and concentrated. The residue was redissolved in methanol (1.5 mL), basified with triethylamine, and then reacted with 0.09 M hexamethylenediamine in methanol (1.5 mL, 0.14 mmol). The resulting precipitate was filtered and dried at reduced pressure and 70°C to give **12c** (40.1 mg, 0.072 mmol, 57.0%): mp 188–190°C (dec); IR 3340 cm^{-1} (O-H, stretch), 2940 cm^{-1} (C-H, stretch), 1645 cm^{-1} (Amide I, C = O), 1540 cm^{-1} (Amide II, N-H bend); ^1H NMR (DMSO-d_6) δ 7.82 (t, 2H, NH-6, J = 5.6 Hz), 7.58 (t, 2H, NH-1, J = 5.2 Hz), 3.98 (d, 2H, H-2, $J_{2,3}$ = 3.2), 3.86 (s, 2H, H-3), 3.68 (s, 2H, H-4), 3.91 (d, 2H, H-5, $J_{4,5}$ = 6.0 Hz), 5.34 (s, 2H, OH-2), 4.58 (d, 2H, OH-3, J = 5.6 Hz), 4.73 (s, 2H, OH-4), 5.49 (s, 2H, OH-5), 3.07 (t, 8H, H-1′ and H-6′, $J_{1',2'}$ = $J_{5',6'}$ = 6.4 Hz), 1.49 (s, 8H, H-2′ and H-5′), 1.24 (s, 8H, H-3′ and H-4′).

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Anal Calcd for $C_{24}H_{44}N_4O_{12}$ (580.63): C, 49.65; H, 7.64; N, 9.65. Found: C, 48.40; H, 7.50; N, 9.25.

***Head, tail–tail, head*-poly(octamethylene D-glucaramide) (12d).** Polymer **12d** was prepared according to the method for **12a**: 6,6′-(*N*,*N*′-octamethylene)-bis(D-glucaramid-1-oic acid)[5] (**11d**, 64.1 mg, 0.121 mmol), distilled methanol (2 mL), acetyl chloride (7 drops, ice bath), room temperature 3 h, and concentrated. The residue was redissolved in methanol (1.5 mL), basified with triethylamine, and then reacted with 0.13 M octamethylenediamine in methanol (1.0 mL, 0.13 mmol). The resulting precipitate was filtered and dried at reduced pressure and 70°C to give **12d** (60.2 mg, 0.094 mmol, 78.0%): mp 191–194°C (dec); IR 3340 cm^{-1} (O-H, stretch), 2940 cm^{-1} (C-H, stretch), 1640 cm^{-1} (Amide I, C = O), 1545 cm^{-1} (Amide II, N-H bend); ^1H NMR (DMSO-d_6) δ 7.81 (t, 2H, NH-6, J = 5.2 Hz), 7.56 (t, 2H, NH-1, J = 5.6 Hz), 3.97 (s, 2H, H-2), 3.90 (s, 2H, H-5), 3.86 (s, 2H, H-3), 3.63 (s, 2H, H-4), 5.33 (s, 2H, OH-2), 4.58 (d, 2H, OH-3, J = 6.0 Hz), 4.73 (s, 2H, OH-4), 5.48 (s, 2H, OH-5), 3.06 (m, 8H, H-1′ and H-8′, $J_{1',2'} = J_{7',8'}$ = 6.4 Hz), 1.40 (s, 8H, H-2′ and H-7), 1.24 (s, 16H, H-3′, H-4′, H-5′, and H-6′).

Anal Calcd for $C_{28}H_{52}N_4O_{12}$ (636.74): C, 52.82; H, 8.23; N, 8.80. Found: C, 51.60; H, 8.21; N, 8.54.

***Head, tail–tail, head*-poly(decamethylene D-glucaramide) (12e).** Polymer **12e** was prepared according to the method for **12a**: 6,6′-(*N*,*N*′-decamethylene)-bis(D-glucaramid-1-oic acid)[5] (**11e**, 62.3 mg, 0.118 mmol), distilled methanol (2 mL), acetyl chloride (7 drops, ice bath), room temperature 3 h, and concentrated. The residue was redissolved in methanol (1.5 mL), basified with triethylamine, and then reacted with 0.12 M decamethylenediamine in methanol (1.0 mL, 0.12 mmol). The resulting precipitate was filtered and dried at reduced pressure and 70°C to give **12e** (70.4 mg, 0.102 mmol, 82.5%): mp 192–194°C (dec); IR 3320 cm^{-1} (O-H, stretch), 2935 cm^{-1} (C-H, stretch), 1635 cm^{-1} (Amide I, C = O), 1535 (Amide II, N-H bend); ^1H NMR (DMSO-d_6) δ 7.81 (t, 2H, NH-6, J = 5.6 Hz), 7.56 (t, 2H, NH-1, J = 5.6 Hz), 3.97 (d, 2H, H-2, $J_{2,3}$ = 3.2 Hz), 3.86 (s, 2H, H-3), 3.64 (s, 2H, H-4), 3.91 (d, 2H, H-5, $J_{4,5}$ = 6.0 Hz), 5.32 (s, 2H, OH-2), 4.58 (s, 2H, OH-3), 4.74 (s, 2H, OH-4), 5.48 (s, 2H, OH-5), 3.06 (m, 8H, H-1′ and H-10′, $J_{1',2'} = J_{9',10'}$ = 6.8 Hz), 1.40 (s, 8H, H-2′ and H-9′), 1.24 (s, 24H, H-3′, H-4′, H-5′, H-6′, H-7′, and H-8′).

Anal. Calcd for $C_{32}H_{60}N_4O_{12}$ (692.84): C, 55.47; H, 8.73; N, 8.09. Found: C, 54.39; H, 8.65; N, 7.87.

***Head, tail–tail, head*-poly(dodecamethylene D-glucaramide) (12f).** Polymer **12f** was prepared according to the method for **12a**: 6,6′-(*N*,*N*′-dodecamethylene)-bis(D-glucaramid-1-oic acid)[5] (**11f**, 62.3 mg, 0.11 mmol), distilled methanol (2 mL), acetyl chloride (7 drops, ice bath), room temperature 3 h, and concentrated. The residue was redissolved in methanol (1.5 mL), basified with triethylamine, and then reacted with 0.12 M dodecamethylenediamine in methanol (1.0 mL, 0.12 mmol). The resulting precipitate was filtered and dried at reduced pressure and 70°C to give **12f** (61.8 mg, 0.08 mmol, 77.2%): mp 188–190°C (dec); IR 3310 cm^{-1} (O-H, stretch), 2950 cm^{-1} (C-H, stretch), 1640 cm^{-1} (Amide I, C = O), 1545 (Amide II, N-H bend); ^1H NMR (DMSO-d_6) δ 7.81 (s, 2H, NH-6), 7.56 (s, 2H, NH-1), 3.97 (d, 2H, H-2, J2,3 = 3.5 Hz),

3.86 (s, 2H, H-3), 3.68 (m, 2H, H-4), 3.91 (d, 2H, H-5, $J_{4,5}$ = 6.0 Hz), 5.46 (s, 4H, OH-2 and OH-5), 4.73 (s, 4H, OH-3 and OH-4), 3.06 (m, 8H, H-1′ and H-12′, $J_{1',2'} = J_{9',10'}$ = 6.2 Hz), 1.40 (s, 8H, H-2′ and H-11′), 1.24 (s, 32H, H-3′, H-4′, H-5′, H-6′, H-7′, H-8′, H-9′, and H-10′).

Anal Calcd for $C_{36}H_{68}N_4O_{12}$ (748.95): C, 57.73; H, 9.15; N, 7.48. Found: C, 56.37; H, 9.08; N, 7.37.

ACKNOWLEDGMENT

This work was supported partially by a Graduate Assistance in Areas of National Need (GAANN) fellowship to S. Styron and a USDA CRESS grant to the University of Montana.

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Received July 21, 2002
Accepted September 14, 2002