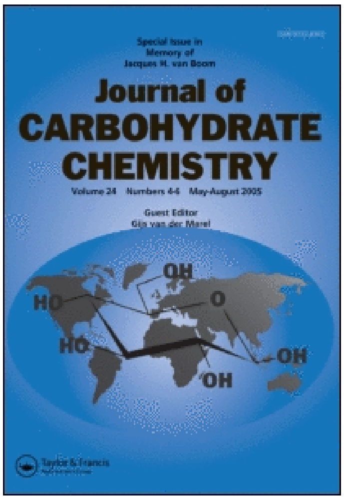

Journal of Carbohydrate Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

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To cite this Article Kiely, Donald E. , Vishwanathan, Arvind , Jarman, Bevan P. and Manley-Harris, Merilyn(2009) 'Synthesis of Poly(galactaramides) from Alkylene- and Substituted Alkylenediammonium Galactarates', Journal of Carbohydrate Chemistry, 28: 6, 348 — 368

To link to this Article: DOI: 10.1080/07328300903080749

URL: http://dx.doi.org/10.1080/07328300903080749

Journal of Carbohydrate Chemistry, 28:348–368, 2009
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ISSN: 0732-8303 print / 1532-2327 online
DOI: 10.1080/07328300903080749

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Synthesis of Poly (galactaramides) from Alkylene- and Substituted Alkylenediammonium Galactarates

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Polyhydroxypolyamides (PHPAs) represent a class of synthetic polyamides derived from aldaric acid and diamine monomer units. This paper describes the synthesis of some poly(galactaramides), a class of polyhydroxypolyamides, that employs alkylene and substituted alkylenediammonium galactarate salts, with 1:1 molar equivalency of the diacid and diamine monomer components, as precursors for the polyamides. The salts were treated with acid/alcohol and then base in order to initiate the polymerization in methanol. The polyamides, labeled as prepolyamides, precipitated from solution and were then subjected to a second polymerization (postpolymerization) in a different solvent to produce a generally larger polyamide, labeled as a postpolyamide.

Keywords Polyamides; Structure-property relationship; Polyhydroxypolyamides; Poly(galactaramides)

INTRODUCTION

Poly(alkylene galactaramides) are representatives of a class of polyhydroxypolyamides (PHPAs) generated by condensation polymerization of esterified galactaric acids with appropriate diamines. This polymerization method,

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Received December 23, 2008; accepted May 31, 2009.

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requiring no pendant hydroxyl group protection, was first described by Ogata and coworkers,[1–8] and later employed in reports from Hoagland et al.,[9,10] Hashimoto et al.,[11,12] Kiely et al.,[13,14] and Henkensmeier et al.[15]

PHPAs are of interest because of their origin in part from renewable carbohydrates and because they are readily degradable in soil,[16] with the polyamide nitrogens serving as plant nutrients.[17] Additionally, a wide structural variety of these polyamides can be made using different combinations of diamine and carbohydrate diacid (aldaric acid) monomers.

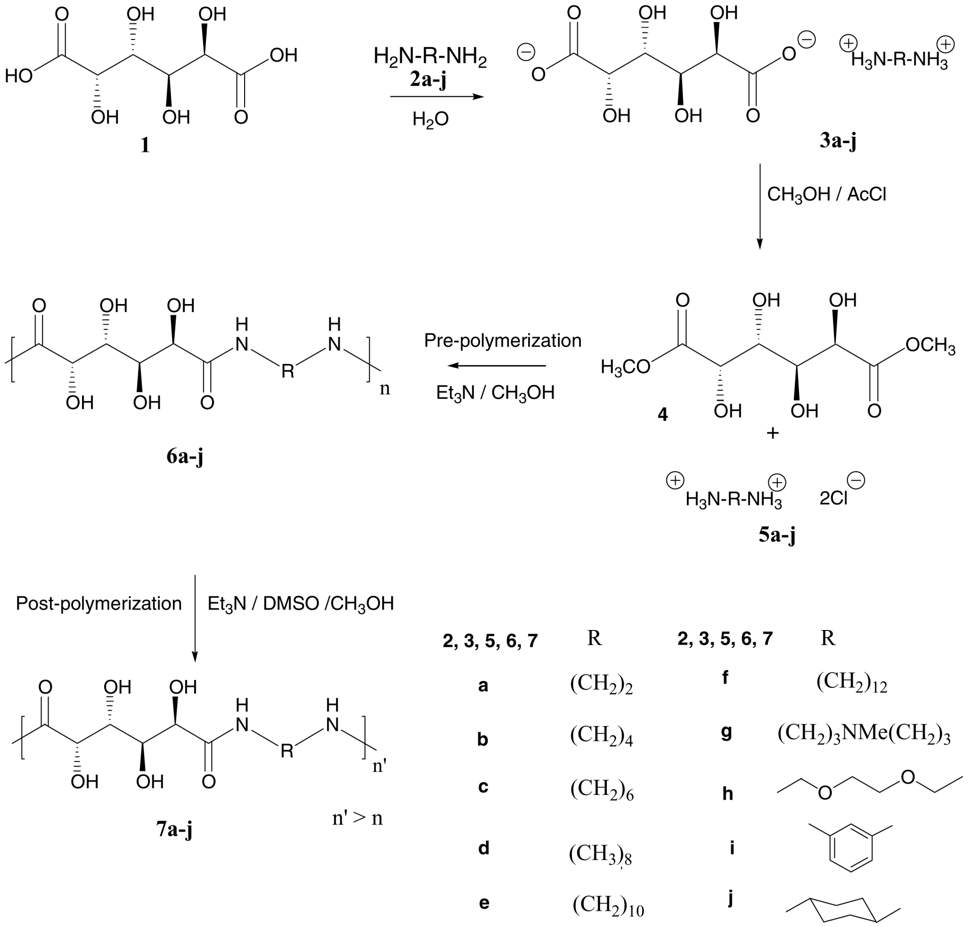
In previous studies it was determined that the physical property differences of poly(alkylene aldaramides) are in part a reflection of the conformational preferences exhibited by their different aldaric acid monomer units.[14] Whereas the *meso*-galactaryl monomer unit is dominated by an extended conformation,[14] the diastereoisomeric D-glucaryl unit tends toward an average "bent" conformation.[14,18] The differences in conformational preferences of the polymer aldaric acid units are reflected in differences in solubility, melting points, and film-forming ability of the corresponding polyamides.[14,19] For example, *meso*-galactaric acid (mucic acid)[20] and its simple ester forms have high melting points and low water solubilities, properties that are also observed with poly(alkylene galactaramides).

It is well known that in order to make high-molecular-weight condensation polyamides, molar equivalency of the reactive monomers is required;[21] for example, the polyamide nylon 6,6 is generated from the 1:1 molar ratio salt of adipic acid:hexamethylenediamine at an elevated temperature of about 270°C.[22] Previous preparations of PHPAs involved direct condensation polymerization of an aldaric acid diester unit with an appropriate primary diamine, typically using methanol as the solvent.[3,4,12,13] The synthesis of PHPAs by this method does not require the high temperatures used to make nylons, temperatures that would decompose aldaric acid ester monomers. However, a shortcoming of the previously reported syntheses of PHPAs using this approach is that they do not employ an exact 1:1 molar ratio of diacid and diamine monomers, due to the difficulty in achieving this ratio by either volumetric or gravimetric methods. Consequently, in order to ultimately prepare relatively high-molecular-weight poly(galactaramides) under mild polymerization conditions, the first goal of this endeavor was to meet the requirement of equivalent diacid:diamine stoichiometry for polymerization by synthesizing 1:1 galactaric acid:diamine salts as starting monomer precursors. The second objective was to convert these salts directly into 1:1 mixtures of esterified galactaric acid and diammonium salts as precursors for polymerization in alcohol solution, preferably methanol. The final objective was to subject the initial polymer, labeled as a prepolyamide, to a second polymerization (postpolymerization) to obtain a higher-molecular-weight polymer, labeled as a postpolyamide. It was also reasoned that for successful postpolymerization to occur, a solvent was required to solubilize the prepolymer better than methanol and allow polymerization to occur at a reasonable rate. A preliminary description of the results presented here has been reported.[23]

RESULTS AND DISCUSSION

Polyamide Synthesis

The syntheses of the target poly(galactaramides), **7a–j**, are outlined in the Scheme. In the first step *meso*-galactaric acid (**1**) was treated with diamines (**2a–j**) in hot aqueous solution to generate the corresponding substituted diammonium galactarate salts, **3a–j**. Typically, within the first few minutes, complete dissolution of water-insoluble galactaric acid occurred followed



Scheme. Synthetic steps to prepare poly(alkylene galactaramides) from substituted diammonium galactarate salts.

Table 1: ^{1}H NMR chemical shifts and assignments for compounds **3a–j**

	Chemical shift, multiplicity, integration, and signal assignment[a]					
3a [b]						
3b	4.20, s, 2H H2, H5	3.90, s, 2H H3, H4	2.99, t, 4H N-C**H**$_2$	1.70, t, 4H N-CH$_2$-C**H**$_2$		
3c	4.22, s, 2H H2, H5	3.91, s, 2H H3, H4	2.95, t, 4H N-C**H**$_2$	1.63, m, 4H N-CH$_2$-C**H**$_2$	1.38, m, 4H N-CH$_2$-CH$_2$-C**H**$_2$	
3d	4.21, s, 2H H2, H5	3.90, s, 2H H3, H4	2.93, t, 4H N-C**H**$_2$	1.60, m, 4H N-CH$_2$-C**H**$_2$	1.30, bs, 8H N-CH$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$	
3e [b]						
3f [b]						
3g	4.21, s, 2H H2, H5	3.90, s, 2H H3, H4	2.97, t, 4H, N-CH$_2$	2.57, t, 4H, N-CH$_2$-C**H**$_2$-N-CH$_3$	2.29, s, 3H N-C**H**$_3$	1.85, m, 4H CH$_2$-C**H**$_2$-CH$_2$
3h	4.21, s, 2H H2, H5	3.90, s, 2H H3, H4	3.74, t, 4H N-CH$_2$-CH$_2$-O	3.70, s, 4H O-C**H**$_2$-C**H**$_2$-O	3.18, t, 4H N-C**H**$_2$-CH$_2$-O	
3i [b]						
3j	4.21, s, 2H H2, H5	3.91, s, 2H H3, H4	3.19, bs, 2H H-C-N	2.12 d, 4H H 2′, 3′, 5′, 6′ axial	1.50, m, 4H H 2′, 3′, 5′, 6′ eq.	

[a] In D$_2$O referenced to *t*-BuOH at 1.203 ppm.
[b] Insoluble in any suitable NMR solvent.

by precipitation of the white solid salt shortly thereafter. The exceptions to this were the water-soluble salts, **3g** and **3h**, which were made from diamines containing heteroatoms (**2g** and **2h**); **3g** and **3h** were isolated as solids after the aqueous solution was taken to dryness and the resultant solid resuspended in methanol. Of the salts made, all but ethylenediammonium **(3a)**, decamethylenediammonium **(3e)**, dodecamethylenediammonium **(3f),** and *m*-xylenyldiammonium **(3i)** galactarates were soluble enough in D$_2$O for ^{1}H NMR spectral determination (Table 1). These insoluble salts were also insoluble in DMSO-d_6. Crystal structure studies of salts of galactaric acid salts[24–28] and of galactaric acid itself[20] indicate that the galactarate unit is in an extended conformation with strong hydrogen bonding networks that lead to lack of solubility. These results are supported by a recent x-ray crystal study of the salts **3a**, **3b**, **3h**, **3i**, and **3j** wherein the *meso*-galactarate ion is in the fully extended conformation.[29] In all salts, dimethyl galaractate/dialkylenediammonium mixtures, and pre- and postpolyamides described in this study, the protons on C-2 and C-5 of the galactaryl moiety are equivalent in ^{1}H NMR spectra as are the protons on C-3 and C-4. The signals for these two pairs of protons appear as singlets, with the former somewhat downfield of the latter. The absence of a coupling constant indicates that, at least in solution, the dihedral angle between H-2 and H-3 and between H-4 and H-5 approaches 90° rather than the 60° expected for a fully extended conformation.

Table 2: CHN analyses of compounds **3a–j** and **4** + **5a–j**

Compound	Molecular formula	Molecular weight	Elemental analysis					
			Calculated			Found		
			C	H	N	C	H	N
3a	$C_8H_{18}N_2O_8 \cdot H_2O$	288.25	33.33	6.99	9.72	33.32	7.00	9.69
3b	$C_{10}H_{22}N_2O_8$	298.29	40.27	7.43	9.39	40.32	7.52	9.40
3c	$C_{12}H_{26}N_2O_8$	326.34	44.16	8.03	8.58	43.94	8.19	8.54
3d	$C_{14}H_{30}N_2O_8$	354.40	47.45	8.53	7.90	47.66	8.65	8.04
3e	$C_{16}H_{34}N_2O_8$	382.45	50.25	8.96	7.32	50.01	8.92	7.24
3f	$C_{18}H_{38}N_2O_8$	410.50	52.67	9.33	6.82	52.59	9.12	6.82
3g	$C_{13}H_{29}N_3O_8 \cdot H_2O$	373.40	41.82	8.37	11.25	41.96	8.21	11.17
3h	$C_{12}H_{26}N_2O_{10} \cdot 2H_2O$	394.37	36.55	7.67	7.10	36.64	7.68	7.13
3i	$C_{14}H_{22}N_2O_8 \cdot 2H_2O$	382.36	43.98	6.85	7.33	44.22	6.98	7.28
3j	$C_{12}H_{24}N_2O_8$	324.33	44.44	7.46	8.64	44.25	7.46	8.53
4 + 5a	$C_8H_{14}O_8 + C_2H_{10}Cl_2N_2$	371.21	32.36	6.52	7.55	32.10	6.41	7.53
4 + 5b	$C_8H_{14}O_8 + C_4H_{14}Cl_2N_2$	399.26	36.10	7.07	7.02	36.14	7.07	7.02
4 + 5c	$C_8H_{14}O_8 + C_6H_{18}Cl_2N_2$	427.32	39.35	7.55	6.56	39.35	7.44	6.01
4 + 5d	$C_8H_{14}O_8 + C_8H_{22}Cl_2N_2$	455.37	42.20	7.97	6.15	42.13	7.87	6.23
4 + 5e	$C_8H_{14}O_8 + C_{10}H_{26}Cl_2N_2$	483.42	44.72	8.34	5.79	44.41	8.21	5.54
4 + 5f	$C_8H_{14}O_8 + C_{12}H_{30}Cl_2N_2$	511.48	46.96	8.67	5.48	46.93	8.77	5.39
4 + 5g	$C_8H_{14}O_8 + C_7H_{22}Cl_3N_3$	492.82	36.56	7.36	8.53	36.20	7.39	7.97
4 + 5h	$C_8H_{14}O_8 + C_6H_{18}O_2Cl_2N_2 \cdot H_2O$	477.33	35.23	7.18	5.87	34.92	6.76	5.54
4 + 5i	$C_8H_{14}O_8 + C_8H_{14}Cl_2N_2$	447.31	42.96	6.31	6.26	42.93	6.34	6.42
4 + 5j	$C_8H_{14}O_8 + C_6\ H_{16}Cl_2N_2$	425.31	39.54	7.11	6.59	39.76	6.99	5.81

The elemental analyses of the salts (Table 2) were consistent with their molecular structures indicating also that salts **3a** and **3g** are monohydrates while **3h** and **3i** are dihydrates.

In the next step (Scheme) the salts were converted with methanolic HCl to 1:1 mixtures of dimethyl galactarate (**4**)/alkylene- or substituted alkylenediammonium dichlorides (**5a–j**). Each of these diester/disalt mixtures was obtained as a white solid in high yield and the ^{1}H NMR spectral data (Table 3) and elemental analyses results (Table 2) from each mixture were consistent with the assigned structures.

The 1:1 dimethyl galactarate (**4**)/alkylene- or substituted alkylenediammonium dichlorides (**5a–j**) mixtures were activated for polymerization (Scheme) by treating them with methanol containing an excess of triethylamine (TEA). The TEA deprotonates the diammonium salts and also catalyzes lactonization of the acylic dimethyl galactarate (**4**) in methanol, the latter step being essential for a rapid aminolysis process.[30] The use of TEA in methanol has previously been reported for the preparation of stereoregular-*head, tail*-poly(alkylene D-glucaramides).[31] While it is convenient to employ TEA as the base to deprotonate the diammonium salts and to promote lactonization of the ester functions, the monomer primary amines and TEA have comparable base strengths; therefore, a large excess of TEA is needed to adequately promote polymerization. While methanol has been shown to be an excellent solvent for polymerizations to make prepolyamides, the relatively low solubility of the poly(alkylene galactamides) in methanol limits the polymerization

Table 3: ^{1}H NMR chemical shifts and assignments for the **5a–j** moieties of compounds **4** + **5a–j**

	Chemical shift, multiplicity, integration and signal assignment[a]				
5a	8.37, s, 6H	3.08, s, 4H, $N\text{-}C\mathbf{H}_2\text{-}C\mathbf{H}_2\text{-}N$			
5b	8.07, s, 6H $N\mathbf{H}_3$	2.79, m, 4H, $N\text{-}C\mathbf{H}_2$	1.61, m, 4H, $N\text{-}CH_2\text{-}C\mathbf{H}_2$		
5c	8.06, s, 6H, $N\mathbf{H}_3$	2.75, m, 4H, $N\text{-}C\mathbf{H}_2\text{-}CH_2$	1.56, t, 4H, $N\text{-}CH_2\text{-}C\mathbf{H}_2$	1.32, m, 4H, $N\text{-}CH_2\text{-}CH_2\text{-}C\mathbf{H}_2$	
5d	8.04, s, 6H $N\mathbf{H}_3$	2.73, m, 4H, $N\text{-}C\mathbf{H}_2\text{-}CH_2$	1.55, m, 4H, $N\text{-}CH_2\text{-}C\mathbf{H}_2$	1.27,bs, 8H, $N\text{-}CH_2\text{-}CH_2\text{-}C\mathbf{H}_2\text{-}C\mathbf{H}_2$	
5e	7.99, s, 6H $N\mathbf{H}_3$	2.74, t, 4H, $N\text{-}C\mathbf{H}_2\text{-}CH_2$	1.54, m, 4H, $N\text{-}CH_2\text{-}C\mathbf{H}_2$	1.26, bs, 12H $N\text{-}CH_2\text{-}CH_2\text{-}C\mathbf{H}_2\text{-}C\mathbf{H}_2\text{-}C\mathbf{H}_2$	
5f	7.99, s, 6H $N\mathbf{H}_3$	2.74, m, 4H, $N\text{-}C\mathbf{H}_2\text{-}CH_2$	1.54, m, 4H, $N\text{-}CH_2\text{-}C\mathbf{H}_2$	1.25, bs, 16H $N\text{-}CH_2\text{-}CH_2\text{-}C\mathbf{H}_2\text{-}C\mathbf{H}_2\text{-}C\mathbf{H}_2\text{-}C\mathbf{H}_2$	
5g	8.21 s, 6H $N\mathbf{H}_3$	3.15, b, 4H, $N\text{-}C\mathbf{H}_2\text{-}CH_2$	2.91, bs, 4H, $C\mathbf{H}_2\text{-}N\text{-}CH_3$	2.71, s, 3H, $N\text{-}C\mathbf{H}_3$	2.05, m, 4H $CH_2\text{-}C\mathbf{H}_2\text{-}CH_2$
5h	8.11, s, 6H $N\mathbf{H}_3$	3.64, t, 4H, $N\text{-}CH_2\text{-}C\mathbf{H}_2\text{-}O$	3.59, s, 4H, $O\text{-}C\mathbf{H}_2\text{-}C\mathbf{H}_2\text{-}O$	2.95, m, 4H, $N\text{-}C\mathbf{H}_2\text{-}CH_2\text{-}O$	
5i	8.57 s, 6H $N\mathbf{H}_3$	7.59 – 7.48, 4H, *m*–Ar**H**	4.01, m, 4H $N\text{-}C\mathbf{H}_2$		
5j	8.06 s, 6H $N\mathbf{H}_3$	2.95 s, 2H $N\text{-}C\mathbf{H}$	1.99 bs, 4H H 2′, 3′, 5′, 6′ axial	1.39 bs, 4H H 2′, 3′, 5′, 6′ eq	

In each of these compounds singlet signals each integrating for two protons were found at approximately 4.98, 4.88, 4.32, and 3.79 ppm, which were assigned as OH-2 and OH-5, OH-3 and OH-4, H-2 and H-5, H-3 and H-4 of **4**, respectively; an additional singlet signal integrating for six protons was found at 3.64 ppm in each spectrum and assigned as $\mathbf{H}_3C\text{-}O$ of **4**.

[a] In DMSO-*d*6 referenced to TMS at 0.00 ppm.

to preparation of low-molecular-weight materials. By employing a 1:1 molar ratio of galactaric acid:diamine to prepare the prepolymers in methanol, it was anticipated that on average, the number of C-terminal ester and N-terminal amine groups would be the same and allow for further polymerization of the polymers in solution using an appropriate solvent. Several solvents were evaluated for potential use as a general postpolymerization solvent, using prepolymer poly(hexamethylene galactaramide), **6c**, as a model for postpolymerization. Alcohols as solvents have proven critical for polymerization at reasonable rates, but do not solubilize the growing polymers very effectively. In contrast, polar, aprotic dimethyl sulfoxide is a good solvent for PHPAs, but rates of polymerization are significantly reduced in this solvent.[30]

The solvents evaluated as postpolymerization solvents were ethylene glycol and the solvent pairs ethylene glycol/dimethyl sulfoxide and methanol/dimethyl sulfoxide. Ultimately, the prepolymer was first swelled in dimethyl sulfoxide, then diluted with methanol and the reaction mixture heated for a period of time.

Polyamide Analysis

The ^{1}H NMR chemical shift data for prepolyamides **6a–j** are reported in Table 4, the data from the postpolyamides being essentially the same. The number average molecular weight (M_n) and the degree of polymerization (DP) of each polyamide, both prepolyamide and postpolyamide (Table 5), were determined by end-group analysis from ^{1}H NMR spectra by calculating the ratio of the integrals for methylene protons adjacent to terminal amine groups with those for methylene protons adjacent to internal amide nitrogens and applying the formula DP = (Ratio + 1)/2. This formula was derived by plotting a graph of the theoretical ratio of internal to terminal methylene protons versus DP for degrees of polymerization 1–20.[32] A convenient gel permeation chromatography method to obtain molecular weights and molecular weight distributions of these polymers that does not use expensive hexafluroisopropanol as eluent has not yet been established, but work is in progress toward developing such a method.

The prepolymerizations were carried out in methanol under reflux conditions and, in keeping with previous results, solid was present throughout the reaction.[14] Dimethyl galactarate has low solubility in the methanol/TEA medium but gradually dissolves and then rapidly reacts to form polyamide, which quickly precipitates.

Low polyamide solubility was suspected to be the limiting factor for polymer growth; however, stoichiometric imbalances in previous studies could have played a role. This study focuses on the effects that stoichiometric equivalency of starting galactaric acid and diamine might offer in producing larger polyamides than previously prepared where stoichiometric equivalency of monomers was not employed. As a means to investigate the role of solubility, a postpolymerization step to make yet larger poly(galactaramides) was investigated. The results from both the pre- and postpolymerizations are presented in Table 5.

Inexplicitly, the prepolymerization procedure starting from ethylenediamine was found not to work because the prepolyamide product **6a** has a DP value of only 1, a value that does not change in the postpolymerization process. The tetramethylenediamine prepolyamide **6b**, with a DP = 6.0, is larger than **6a** but also suffers from low methanol solubility. However, with the exception of **6a** and **6d**, increases in DP of 25% to 50% were obtained as compared to previously reported values.[14]

In the preparation of **6** and **7 g–i**, clear solutions or gels were obtained during both polymerization processes, and therefore greater degrees of polymerization were expected for these polyamides. Indeed, the prepolymer **6g**

Table 4: ^1H NMR chemical shifts and assignments for compounds **6a–j**

	Chemical shift[a] and signal assignment							
6a	4.98 H2 H5	4.57 H3 H4	3.94 $CONC\mathbf{H}_2$	3.62 $H_2NC\mathbf{H}_2$				
6b	5.08 H2 H5	4.67 H3 H4	3.61 $CONC\mathbf{H}_2$	3.40 $H_2NC\mathbf{H}_2$	1.84 $CONCH_2C\mathbf{H}_2$			
6c	5.15 H2 H5	4.70 H3 H4	3.61 $CONC\mathbf{H}_2$	3.35 $H_2NC\mathbf{H}_2$	1.81 $CONCH_2C\mathbf{H}_2$	1.57 $CON(CH_2)_2C\mathbf{H}_2$		
6d	5.09 H2 H5	4.64 H3 H4	3.54 $CONC\mathbf{H}_2$	3.27 $H_2NC\mathbf{H}_2$	1.73 $CONCH_2C\mathbf{H}_2$	1.45 $CON(CH_2)_2(C\mathbf{H}_2)_2$		
6e	5.12 H2 H5	4.66 H3 H4	3.55 $CONC\mathbf{H}_2$	3.30 $H_2NC\mathbf{H}_2$	1.74 $CONCH_2C\mathbf{H}_2$	1.42 $CON(CH_2)_2(C\mathbf{H}_2)_3$		
6f	5.07 H2 H5	4.60 H3 H4	3.50 $CONC\mathbf{H}_2$	3.25 $H_2NC\mathbf{H}_2$	1.68 $CONCH_2C\mathbf{H}_2$	1.36 $CON(CH_2)_2(C\mathbf{H}_2)_4$		
6g[b]	4.37 H2 H5	3.98 H3 H4	3.3[c] $CONC\mathbf{H}_2$	2.8[c] $H_2NC\mathbf{H}_2$	2.42 $CH_2C\mathbf{H}_2NCH_3$	2.20[d] $NC\mathbf{H}_3$	1.69 $CH_2C\mathbf{H}_2CH_2$	
6h[b]	4.40 H2 H5	4.00 H3 H4	3.66 $OC\mathbf{H}_2C\mathbf{H}_2O$	3.63 $CONCH_2C\mathbf{H}_2O$	3.45 $CONC\mathbf{H}_2CH_2O$	3.14 $H_2NC\mathbf{H}_2CH_2O$		
6i[e]	8.08 $CH_2N\mathbf{H}$	7.15 – 7.24 *m*-Ar**H**	5.36 OH-2,OH-5	4.37 OH-3,OH-4	4.33 $C\mathbf{H}_2NHCO$	4.24 H2, H5	3.88 H3,H4	3.36 $C\mathbf{H}_2NH_2$
6j	5.10 H2 H5	4.60 H3 H4	4.01 CON-C**H**	3.48 HN-C**H**	2.20 H 2′, 3′,5′,6′ ax	1.68 H 2′, 3′,5′, 6′ eq		

[a] In TFA-*d* referenced to residual TFA at 11.50 ppm unless otherwise indicated.

[b] In D_2O referenced to *t*-BuOH at 1.203 ppm.

[c] Very broad multiplet.

[d] Split in D_2O but becomes a singlet on addition of base.

[e] In DMSO-*d6* referenced to TMS at 0.00 ppm.

Table 5: Degrees of polymerization for pre- and postpolymers and number average molecular weights (M_n) of postpolymers

Compound	DP prepolymer[a]	Post polymer	DP Postpolymer	% Increase in DP upon postpolymerization	M_n postpolymer
6a	1.0	**7a**	1.0	0	234
6b	6.0	**7b**	6.4	6.7	1677
6c	11.0	**7c**	11.3	2.7	3277
6d	12.0	**7d**	12.0	0	3816
6e	11.4	**7e**	13.5	18.4	4671
6f	10.5	**7f**	10.5	0	3927
6g[b]	[c]	**7g**	[c]		[c]
6h[b]	10.4	**7h**	14.0	51.9	5088
6i[d]	9.1	**7i**	10.7	17.6	3317
6j	3.3	**7j**	3.9	18.2	1132

[a] Determined by NMR in TFA-*d*.
[b] Determined by NMR in D_2O.
[c] Too great to be determined by this method.
[d] Determined by NMR in DMSO-*d*6.

appeared too large for DP determination by the NMR method. A lesser DP of 26 has been reported for this compound prepared by direct reaction of the diamine with dimethyl galactarate.[33] In addition, prepolymer **6h** underwent an approximately 50% increase in DP in the postpolymerization process. Prepolyamide (**6i**), derived from the single arylalkylenediamine employed in this study, had a DP of 9.1, with the postpolyamide **7i** showing a small increase in DP to a value of 10.7. The DP values for polyamides **6i** and **7i** were comparable to those observed with the hexamethylenediamine polyamide **6c** (DP 11.0) and **7c** (DP 11.3). Prepolyamide **6i**, although soluble in TFA-*d*, did not yield a spectrum amenable to integration because of overlap of the relevant signals with the signals for the galactaryl moiety. However, those signals were resolved when DMSO-d_6 was used as the NMR solvent. The location of the terminal methylene protons was verified after preparation in ethanol of a small DP prepolyamide with a large sharp $C\mathbf{H}_2$-NH_2 singlet at 3.39 ppm. Both pre- and postpolyamides **6j** and **7j**, respectively, were poorly soluble in the pre- and postpolymerization solvents, and consequently had small DP values (3.3 and 3.9).

SUMMARY AND CONCLUSIONS

An experimental protocol for the preparation of poly(galactaramides) from precursor polyalkylenediammonium galactarates has been developed. The method begins with preparation of a 1:1 galactaric acid/diamine salt, to ensure stoichiometric equivalence of the monomer components for subsequent polymerization. The salt is subjected to Fischer esterification in methanolic HCl, producing a 1:1 mixture of dimethyl galactarate and the substituted diammonium dichloride. This mixture is then warmed in methanol in the presence of triethylamine wherein polymerization occurs and the polyamide typically precipitates. The poly(galactaramide) formed, labeled as a prepolyamide, is then subjected to a second polymerization in a mixed solvent that allows for greater polymer solubility than methanol, resulting in a larger poly(galactaramide), labeled a postpolyamide. The latter polyamides are larger than those produced by previous methods where stoichiometric control of monomers was not established. Among the alkylenediamines employed, reasonable-size polyamides (Table 5) were prepared starting with the hexamethylenediamine polyamide **6c** and continuing with the $(CH_2)_8$, $(CH_2)_{10}$, and $(CH_2)_{12}$ polyamides **6d**, **6e**, and **6f**, respectively. A similar DP polyamide formed was poly(*m*–xylenenyl galactaramide), **6i**. It is clear that the nonpolar diamine monomer units and the poorly soluble galactaryl unit work together to limit the solubility of these polyamides. In contrast, poly(4-aza-4-methylheptamethylene galactaramide), **6g**, has a nitrogen atom and a branching methyl substituent in the alkylene chain, both of which make the growing polyamide more methanol soluble and allow polymerization to occur to a greater extent than with the less methanol-soluble polymers. Postpolymerizations generally resulted in larger polymers, but again low solubilities of the polymers limited their growth. The two-stage polymerization strategy was employed because it was determined that a single polymerization in a typical postpolymerization solvent such as methanol/dimethylsulfoxide did not yield polyamide that was as large or as pure as that generated by the method employed here. Overall, the approach applied to prepare polyamides of this type was effective even with the low solubility poly(alkylene galactaramides), but has been found to work much better with more organic solvent-soluble polyamides of this class, as described in a preliminary report describing the preparation of a number of poly(D-glucaramides).[34]

EXPERIMENTAL

General Methods

Reagent-grade chemicals were purchased from commercial vendors and used without further purification. Deionized water was generated by a Millipore Simplicity 185 system. Solutions were concentrated under reduced pressure. ^1H NMR spectra were recording using a 400 Varian Unity *Plus* spectrometer in DMSO-d_6 referenced to tetramethylsilane (0.00 ppm), in TFA-*d* referenced to residual TFA, or in D_2O referenced to *t*-butyl alcohol (1.203 ppm). Data were processed using ACD/SpecManager software version 9.13, 2006.

*Ethylenediammonium galactarate (**3a**)*

To a mixture of galactaric acid (**1**, 97% from Aldrich, 10.00 g, 47.6 mmol) and deionized water (100 mL) in a round bottom flask was added ethylenediamine (**2a**, 3.2 mL, 2.88 g, 47.8 mmol) and the solution stirred (75°C, 20 h). The solution was allowed to cool to rt and diluted with methanol (100 mL). The solid that formed was removed by filtration, washed with methanol (2 × 50 mL), and dried under reduced pressure at rt (16 h) to give ethylenediammonium galactarate (**3a**, 11.10 g, 81.0%).

*Tetramethylenediammonium galactarate (**3b**)*

The procedure for **3a** was adapted as follows: galactaric acid (**1**, 11.9 g, 56.6 mol), deionized water (50 mL), tetramethylenediamine (**2b**, 5.8 mL, 5.09 g, 57.7 mmol), and stirring at 75°C for 18 h. The solution was allowed to cool to rt and diluted with methanol (100 mL). The solid product, tetramethylenediammonium galactarate (**3b**, 15.41 g, 91.2%), was isolated as described for **3a**.

*Hexamethylenediammonium galactarate (**3c**)*

The procedure for **3a** was adapted as follows: galactaric acid (**1**, 10.00 g, 47.6 mmol), deionized water (50 mL); hexamethylenediamine (**2c**, 5.54 g, 47.6 mmol) dissolved in deionized water (50 mL) was added to the stirred water/galactaric acid mixture, and the reaction mixture stirred at 70°C (1 h) and then at rt (20 h). The reaction mixture was diluted with methanol (100 mL) and the solid product, hexamethylenediammonium galactarate (**3c**, 14.09 g, 90.8%), isolated as described for **3a**.

*Octamethylenediammonium galactarate (**3d**)*

The procedure for **3a** was adapted as follows: galactaric acid (**1**, 10.00 g, 47.6 mmol), deionized water (100 mL), octamethylenediamine (**2d**, 6.90 g, 47.8 mmol), and stirring at 70°C (1 h) and then at rt (20 h). The reaction mixture was diluted with methanol (100 mL) and the solid product, octamethylenediammonium galactarate (3d, 15.78 g, 93.5%), isolated as described for **3a**.

*Decamethylenediammonium galactarate (**3e**)*

The procedure for **3a** was adapted as follows: galactaric acid (**1**, 10.00 g, 47.6 mmol), deionized water (100 mL), decamethylenediamine (**2e**, 8.6 g, 49.9 mmol), and stirring at 70°C (1 h) and then at rt (20 h). The reaction mixture was diluted with methanol (100 mL) and the solid product, decamethylenediammonium galactarate (**3e**, 16.78 g, 92.2%), isolated as described for **3a**.

*Dodecamethylenediammonium galactarate (**3f**)*

The procedure for **3a** was adapted as follows: galactaric acid (**1**, 10.00 g, 47.6 mmol), deionized water (100 mL), dodecamethylenediamine (**2f**, 9.90 g, 49.5 mmol), and stirring at 70°C (2 h) then at rt (20 h). The reaction mixture was diluted with methanol (100 mL) and the solid product, dodecamethylenediammonium galactarate (**3f**, 17.41 g, 89.1%), isolated as described for **3a**.

*4′-aza-N-methylheptamethylenediammonium galactarate (**3g**)*

The procedure for **3a** was adapted as follows: galactaric acid (**1**, 10.00 g, 47.6 mmol), deionized water (100 mL), and 4′-aza-*N*-methylheptamethylenediamine (**2g**, 7.74 mL, 6.97 g, 48.0 mmol) were mixed together at rt and the resulting solution stirred at 75°C (2 h) and then at rt (22 h) with no precipitation occurring. The resulting dark brown solution was concentrated to an orange-colored syrup and dried under vacuum overnight to give a pale pink solid. Methanol (100 mL) was added to the solid and the mixture ground to a slurry with a mortar and pestle. The solid product, 4′-aza-*N*-methylheptamethylenediammonium galactarate (**3g**, 15.80 g, 88.9%), was isolated as described for **3a**.

*3′,6′-dioxaoctamethylenediammonium galactarate (**3h**)*

The procedure for **3a** was adapted as follows: galactaric acid (**1**, 10.00 g, 47.6 mmol), deionized water (100 mL), and 3′,6′-dioxaoctamethylenediamine (**2h**, 7.01 mL, 7.11 g, 47.98 mmol) were stirred together. Upon addition of the diamine, the galactaric acid immediately dissolved with no precipitation occurring over the course of the reaction. The solution was stirred at rt (18 h) and then concentrated to give a cream-colored solid. Methanol (125 mL) was added to the flask and the solid broken up to form a suspension, which was stirred (40°C, 1 h). The solid product, 3′,6′-dioxaoctamethylenediammonium galactarate (**3h**, 16.95 g, 99.3%), was isolated as described for **3a**.

*m-Xylylenediammonium galactarate (**3i**)*

The procedure for **3a** was adapted as follows: galactaric acid (**1**, 10.00 g, 47.6 mmol), deionized water (100 mL), and *m*-xylylenediamine (**2i**, 6.30 mL, 6.50 g, 47.8 mmol) were stirred together at rt for 16 h. Solid remained in the solution throughout the course of the reaction. The reaction mixture was diluted with methanol (100 mL) and the solid product, *m*-xylylenediammonium galactarate (**3i**, 15.48 g, 85.1%), isolated as described for **3a**.

*trans-1,4-Cyclohexanediammonium galactarate (**3j**)*

The procedure for **3a** was adapted as follows: galactaric acid (**1**, 5.017 g, 23.9 mmol), deionized water (50 mL), and *trans*-1,4-cyclohexyldiamine (**2j**, 2.833 g, 24.8 mmol) were stirred together (75°C, 16 h). Solid remained in the solution throughout the course of the reaction. The reaction mixture was cooled and methanol (100 mL) added. The solid product, *trans*-1,4-cyclohexanediammonium galactarate (**3j**, 7.18 g, 92.7%), was isolated as described for **3a**.

Dimethyl Galactarate/Alkylenediammonium Dichloride Salts

*1:1 Dimethyl galactarate/ethylenediammonium dichloride (**4** + **5a**)*

Acetyl chloride (3.0 mL) was added drop-wise to a stirred solution of methanol (100 mL) in an ice bath. Ethylenediammonium galactarate (**3a**, 4.00 g, 13.88 mmol) was added to the solution and the reaction mixture heated at reflux with stirring (4 h) and then concentrated to a white powder, which was dried under vacuum at rt (16 h) to give solid 1:1 dimethyl galactarate/ethylenediammonium dichloride (**4** + **5a**, 4.91 g, 95.3%).

*1:1 Dimethyl galactarate/tetramethylenediammonium dichloride (**4** + **5b**)*

The procedure for **4** + **5a** was adapted as follows: methanol (200 mL), acetyl chloride (6.0 mL), and tetramethylenediammonium galactarate (**3b**, 4.00 g, 13.41 mmol) were stirred at reflux (4 h). The solid product, 1:1 dimethyl galactarate/tetramethylenediammonium dichloride (**4** + **5b**, 4.79 g, 89.5%), was isolated as described for **4** + **5a**.

*1:1 Dimethyl galactarate/hexamethylenediammonium dichloride (**4** + **5c**)*

The procedure for **4** + **5a** was adapted as follows: methanol (100 mL), acetyl chloride (3.0 mL), and hexamethylenediammonium galactarate (**3c**, 4.00 g, 12.27 mmol) were stirred at reflux (4 h). The solid product, 1:1 dimethyl galactarate/hexamethylenediammonium dichloride (**4** + **5c**, 4.90 g, 93.2%), was isolated as described for **4** + **5a**.

*1:1 Dimethyl galactarate/octamethylenediammonium dichloride (**4** + **5d**)*

The procedure for **4** + **5a** was adapted as follows: methanol (100 mL), acetyl chloride (3.0 mL), and octamethylenediammonium galactarate (**3d**, 4.00 g, 11.29 mmol) were stirred at reflux (4 h). The solid product, 1:1 dimethyl galactarate/octamethylenediammonium dichloride (**4** + **5d**, 4.93 g, 95.9%), was isolated as described for **4** + **5a**.

*1:1 Dimethyl galactarate/decamethylenediammonium dichloride (**4** + **5e**)*

The procedure for **4** + **5a** was adapted as follows: methanol (100 mL), acetyl chloride (3.0 mL), and decamethylenediammonium galactarate (**3e**, 4.00 g, 10.46 mmol) were stirred at reflux (4 h). The solid product, 1:1 dimethyl galactarate/decamethylenediammonium dichloride (**4** + **5e**, 4.81 g, 95.0%), was isolated as described for **4** + **5a**.

*1:1 Dimethyl galactarate / dodecamethylenediammonium dichloride (**4** + **5f**)*

The procedure for **4** + **5a** was adapted as follows: methanol (100 mL), acetyl chloride (3.0 mL), and dodecamethylenediammonium galactarate (**3f**, 4.00 g, 9.74 mmol) were stirred at reflux (4 h). The solid product, 1:1 dimethyl galactarate/dodecamethylenediammonium dichloride (**4** + **5f**, 4.57 g, 91.6%), was isolated as described for **4** + **5a**.

*1:1 Dimethyl galactarate / 4′-aza- N-methylheptamethylenetriammonium trichloride (**4** + **5g**)*

The procedure for **4** + **5a** was adapted as follows: methanol (100 mL), acetyl chloride (8.0 mL), and 4′-aza-*N*-methylheptamethylenediammonium galactarate (**3g**, 4.00 g, 10.71 mmol) were stirred at reflux (4 h). The solid product, 1:1 dimethyl galactarate/4′-aza-*N*-methylheptamethylenetriammonium trichloride (**4** + **5g**, 4.58 g, 86.7%), was isolated as described for **4** + **5a**.

*1:1 Dimethyl galactarate / 3′,6′-dioxaoctamethylenediammonium dichloride (**4** + **5h**)*

The procedure for **4** + **5a** was adapted as follows: methanol (100 mL), acetyl chloride (3.0 mL), and 3′,6′-dioxaoctamethylenediammonium galactarate (**3h**, 4.00 g, 11.16 mmol) were stirred at reflux (4 h). The solid product, 1:1 dimethyl galactarate/3′ ,6′-dioxaoctamethylenediammonium dichloride (**4** + **5h**, 4.38 g, 82.1%), was isolated as described for **4** + **5a**.

1:1 Dimethyl galactarate / m*-xylylenediammonium dichloride (**4** + **5i**)*

The procedure for **4** + **5a** was adapted as follows: methanol (100 mL), acetyl chloride (3.0 mL), and *m*-xylylenediammonium galactarate (**3i**, 4.00 g, 10.47 mmol) were stirred at reflux (4 h). The solid product, 1:1 dimethyl galactarate/*m*-xylylenediammonium dichloride (**4** + **5i**, 4.36 g, 93.2%), was isolated as described for **4** + **5a**.

*1:1 Dimethyl galactarate / trans-1,4-cyclohexanediammonium dichloride (**4** + **5j**)*

The procedure for **4** + **5a** was adapted as follows: methanol (100 mL), acetyl chloride (3.0 mL), and *trans*-1,4-cyclohexyldiammonium galactarate (**3j**, 4.00 g, 12.32 mmol) were stirred at reflux (4 h). The solid product, 1:1 dimethyl galactarate/*trans*-1,4-cyclohexyldiammonium dichloride (**4** + **5j**, 4.76 g, 90.9%), was isolated as described for **4** + **5a**. ^{1}H NMR (D_2O) 4.56, s, 2H (H_2,H_5), 4.06, s, 2H (H_3, H_4), 3.77, s, 6H (O-CH_3), 3.20, bs, 2H (H1′, H4′), 2.13, d, 4H (H2′, H3′, H5′, H6′ axial), 1.51, m, 4H (H2′, H3′, H5′, H6′ equatorial).

Poly(alkylene galactaramide) Prepolymers

*Prepolymer Poly(ethylene galactaramide) (**6a**)*

1:1 Dimethyl galactarate (**4**)/ethylenediammonium dichloride (**5a**, 2.50 g, 6.73 mmol) was added to methanol (100 mL) with stirring. Triethylamine (20 mL) was added and the stirred mixture was heated (70°C, 16 h). The reaction mixture was cooled to rt and diluted with methanol (100 mL). The solid product was removed by filtration, washed with methanol (2 × 50 mL), and dried under vacuum at rt (16 h) to give prepolymer poly(ethylene galactaramide) (**6a**, 1.39 g, 88.5%). NMR in TFA-*d* showed that the degree of polymerization was 1 and that only the dimer had formed.

*Prepolymer poly(tetramethylene galactaramide) (**6b**)*

The procedure for **6a** was adapted as follows: dimethyl galactarate (**4**)/tetramethylenediammonium dichloride (**5b**), 2.50 g, 6.26 mmol), methanol (80 mL), and triethylamine (20 mL) were stirred (70°C, 16 h). The reaction mixture was cooled to rt and diluted with methanol (100 mL) and the solid product was isolated as described for **6a** to give prepolymer poly(tetramethylene galactaramide) (**6b**, 1.41 g, 69.5%). NMR in TFA-*d* showed that the degree of polymerization was 6.0.

*Prepolymer poly(hexamethylene galactaramide) (**6c**)*

The procedure for 6a was adapted as follows: 1:1 dimethyl galactarate (**4**)/hexamethylenediammonium dichloride (5c) (2.00 g, 4.68 mmol), methanol (80 mL), and triethylamine (13.2 mL) were stirred (70°C, 16 h). The reaction mixture was cooled to rt and diluted with methanol (100 mL) and the solid product was isolated as described for **6a** to give prepolymer poly(hexamethylene galactaramide) (**6c**, 1.06 g, 78.1%). NMR in TFA-*d* showed that the degree of polymerization was 11.0.

*Prepolymer poly(octamethylene galactaramide) (**6d**)*

The procedure for **6a** was adapted as follows: 1:1 dimethyl galactarate (**4**)/octamethylenediammonium dichloride (**5d**) (2.50 g, 5.49 mmol), methanol (100 mL), and triethylamine (13.2 mL) were stirred (70°C, 16 h). The reaction mixture was cooled to rt and diluted with methanol (100 mL) and the solid product was isolated as described for **6a** to give prepolymer poly(octamethylene galactaramide) (**6d**, 1.108 g, 63.5%). NMR in TFA-*d* showed that the degree of polymerization was 12.0.

*Prepolymer poly(decamethylene galactaramide) (**6e**)*

The procedure for **6a** was adapted as follows: 1:1 dimethyl galactarate (**4**)/decamethylenediammonium dichloride (**5e**) (2.50 g, 5.17 mmol), methanol

(100 mL), and triethylamine (15 mL) were stirred (70°C, 16 h). The reaction mixture was cooled to rt and diluted with methanol (100 mL) and the solid product was isolated as described for **6a** to give prepolymer poly(decamethylene galactaramide) (**6e**, 1.17 g, 65.3%). NMR in TFA-*d* showed that the degree of polymerization was 11.4.

*Prepolymer poly(dodecamethylene galactaramide) (**6f**)*

The procedure for **6a** was adapted as follows: 1:1 dimethyl galactarate (**4**)/dodecamethylenediammonium dichloride (**5f**) (2.54 g, 4.97 mmol), methanol (120 mL), and triethylamine (14 mL) were stirred (70°C, 16 h). The reaction mixture was cooled to rt and diluted with methanol (100 mL) and the solid product was isolated as described for **6a** to give prepolymer poly(dodecamethylene galactaramide) (**6f**, 1.37 g, 74.0%). NMR in TFA-*d* showed that the degree of polymerization was 10.5.

*Prepolymer poly(4′-aza-N-methylheptamethylene galactaramide) (**6g**)*

The procedure for **6a** was adapted as follows: 1:1 dimethyl galactarate (**4**)/4′-aza-*N*-methylheptamethylenetriammonium trichloride (**5g**) (2.50 g, 5.07 mmol), methanol (90 mL), and and triethylamine (15.5 mL) were stirred (70°C, 16 h). The reaction mixture was cooled to rt and diluted with methanol (100 mL) and the solid product was isolated as described for **6a** to give prepolymer poly(4′-aza-*N*-methylheptamethylene galactaramide) (**6g**, 1.08 g, 66.8%). NMR in D_2O showed that the degree of polymerization was too great to measure by this method.

*Prepolymer poly[3′,6′-dioxaoctamethylene galactaramide] (**6h**)*

The procedure for 6a was adapted as follows: 1:1 dimethyl galactarate (**4**)/3′,6′-dioxaoctamethylenediammonium dichloride (5h), (2.50 g, 5.24 mmol), methanol (100 mL), and triethylamine (16 mL) were stirred (70°C, 16 h). The reaction mixture was cooled to rt and diluted with methanol (100 mL) and the solid product was isolated as described for 6a to give prepolymer poly(3′,6′-dioxaoctamethylene galactaramide) (**6h**, 0.659 g, 39.0%). NMR in D_2O showed that the degree of polymerization was 10.4.

*Prepolymer poly(*m*-xylylene galactaramide) (**6i**)*

The procedure for **6a** was adapted as follows: 1:1 dimethyl galactarate (**4**)/*m*-xylylenediammonium dichloride (**5i**) (3.00 g, 6.71 mmol), methanol (120 mL), and triethylamine (19.0 mL) were stirred (70°C, 16 h). The reaction mixture was cooled to rt and diluted with methanol (100 mL) and the solid product was isolated as described for **6a** to give prepolymer poly(*m*-xylylene galactaramide) (**6i**, 1.77 g, 85.1%). NMR in DMSO-*d*6 showed that the degree of polymerization was 9.1.

*Prepolymer poly(trans-1,4-cyclohexane galactaramide) (**6j**)*

The procedure for **6a** was adapted as follows: 1:1 dimethyl galactarate (**4**)/*trans*-1,4-cyclohexanediammonium dichloride (**5j**) (2.00 g, 4.70 mmol), methanol (100 mL), and triethylamine (15.0 mL) were stirred (70°C, 24 h). The reaction mixture was cooled to rt and diluted with methanol (100 mL) and the solid product was isolated as described for **6a** to give prepolymer poly(*trans*-1,4-cyclohexane galactaramide) (**6j**, 0.582 g 42.9%). NMR in TFA-*d* showed that the degree of polymerization was 3.3.

*Procedures evaluated for optimization of postpolymerization of prepolymers using prepolymer **6c***

Procedure (a) 1:2 DMSO:Ethylene Glycol: **6c** (28.0 mg) in DMSO (280 μL), ethylene glycol (560 μL), and triethylamine (75 μL) was heated with stirring (60°C, 2 h). Excess methanol was added to precipitate the polymer, which was separated by vacuum filtration, washed with methanol, and dried under vacuum. Yield 19.5 mg, 69.6%; DP 8.0.

Procedure (b) 1:2 DMSO:Methanol: as for procedure (a) above but using **6c** (26.8 mg), DMSO (268 μL), methanol (536 μL), and triethylamine (72 μL). Yield 17.6 mg, 65.7%; DP 8.0.

Procedure (c) 2:1 DMSO:Ethylene Glycol: as for procedure (a) above but using **6c** (34.1 mg), DMSO (682 μL), ethylene glycol (341 μL), and triethylamine (91 μL). Yield 21.76 mg, 63.6%; DP 9.7.

Procedure (d) 2:1 DMSO:Methanol: as for procedure (a) above but using **6c** (26.4 mg), DMSO (528 μL), methanol (264 μL), and triethylamine (71 μL). Yield 13.9 mg, 52.6%; DP 8.0.

Procedure (e) 1:1 DMSO:Methanol with preswelling: **6c** (100 mg) was preswelled (50°C, 2 h) in DMSO (2 mL); methanol (2 mL) and triethylamine (100 μL) were added and the mixture was heated with stirring (60°C, 24 h). The mixture was cooled, methanol (4 mL) was added, and the resultant mixture stirred at rt (2 h). The solid product was collected by vacuum filtration and resuspended in methanol (5 mL) with stirring (15 min). The solid product was again collected by vacuum filtration and dried in a vacuum oven (25°C, 24 h). Yield 74.0 mg, 74%; DP 11.2.

Procedure (f) 1:2 DMSO: Methanol with preswelling: Exactly as for procedure (e) above except that DMSO (1 mL) was used for the preswelling step. Yield 77.6 mg, 77.6%; DP 11.3.

General Method for Preparation of Postpolymers

Prepolymer (100.0 mg) was preswelled in DMSO (1.00 mL) with stirring (120 min, 50°C), methanol (2.00 mL) and triethylamine (100 mL) were added, and the resultant mixture was stirred (25 h, 60°C). After cooling, methanol (4.00 mL) was added and the mixture stirred (120 min, 25°C). The solid product was collected by vacuum filtration and resuspended in methanol (5 mL) with stirring (15 min). The solid product was again collected by vacuum filtration and dried in a vacuum oven (25°C, 24 h).

*Postpolymer poly(ethylene galactaramide) (**7a**)*

Upon swelling, the prepolymer formed a suspension. Recovery was 73.3%. NMR in TFA-*d* showed that the DP was 1 and the prepolymer was unchanged from the postpolymer.

*Postpolymer poly(tetramethylene galactaramide) (**7b**)*

Upon swelling, the prepolymer formed a stiff gel, which required breaking up to mix with the methanol. Recovery was 78.2%. NMR in TFA-*d* showed that the DP was 6.4.

*Postpolymer poly(hexamethylene galactaramide) (**7c**)*

Upon swelling the prepolymer formed a suspension. Recovery was 77.6%. NMR in TFA-*d* showed that the DP was 11.3.

*Postpolymer poly(octamethylene galactaramide) (**7d**)*

Upon swelling the prepolymer formed a suspension. Recovery was 92.0.6%. NMR in TFA-*d* showed that the DP was 12.0.

*Postpolymer poly(decamethylene galactaramide) (**7e**)*

Upon swelling the prepolymer formed a suspension. Recovery was 83.4%. NMR in TFA-*d* showed that the DP was 13.5.

*Postpolymer poly(dodecamethylene galactaramide) (**7f**)*

Upon swelling the prepolymer formed a suspension. Recovery was 87.9%. NMR in TFA-d showed that the DP was unchanged at 10.5.

*Postpolymer poly(4′-aza-N-methylheptamethylene galactaramide) (**7g**)*

Upon swelling the prepolymer formed a clear gel that became cloudy upon addition of methanol. Recovery was 42.1%. NMR in D_2O showed that the degree of polymerization was too large to be measured by this method.

*Postpolymer poly(3′,6′-dioxaoctamethylene galactaramide) (**7h**)*

Upon swelling the prepolymer formed a clear solution that became cloudy some time after addition of methanol. Recovery was 57.7%. NMR in D_2O showed that the DP was 14.

*Postpolymer poly(*m*-xylylene galactaramide) (**7i**)*

Upon swelling the prepolymer formed a clear solution that became cloudy upon addition of methanol. Recovery was 62.1%. NMR in DMSO-*d*6 showed that the DP was 10.7.

*Postpolymer poly(trans-1,4-cyclohexane galactaramide) (**7j**)*

Upon swelling the prepolymer formed a clear solution that became cloudy upon addition of methanol. Recovery was 70.3%. NMR in TFA-*d* showed that the DP was 3.9.

ACKNOWLEDGMENTS

Significant financial support for this research was from the U.S. Department of Agriculture (USDA-CREES Grant Nos. 2004-364463, 2005-34463-11561, and 2006-34463-16886) and is gratefully acknowledged.

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