Synthesis and Characterization of New Carbohydrate-based Polyureas

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ABSTRACT: A batch of linear [m,n]-type sugar-based polyureas was synthesized by polyaddition reaction in solution from hexamethylene diisocyanate or 4,4′-methylene-bis(phenyl isocyanate) with the acyclic 2,3,4-tri-*O*-methyl-1,5-diamino-alditols having L-*arabino*, or *xylo* configuration or the bicyclic 1,6-diamino-1,6-dideoxy-2,4:3,5-di-*O*-methylene-D-glucitol. The polymers were obtained in good yields and fair molecular weights. All these polyureas were semicrystalline materials showing well-defined melting transition within the 86−171°C range, with T_gs being dependent on the aliphatic or aromatic nature of the diisocyanate used, and on the cyclic or acyclic chemical structure of the sugar moiety. They were found to be stable up to around 240°C, decomposing at higher temperatures through a one- or two-stage mechanism.

KEYWORDS: Polyureas, sugar-based monomers, hydrophilic polymers, thermal properties

1 INTRODUCTION

Polyureas (PURs) are thermoplastic elastomers that combine the advantages of both types of material: thermoplastics and elastomers [1]. In general, the specific properties of these materials are an end result of their morphology. Thus, urea groups are excellent functionalities to be part of thermoplastic elastomers because they are known to associate *via* bifurcated hydrogen bonds [2]. The hydrogen bond strength of urea groups exceeds that of urethanes and amides, so that many research groups make use of the strong association between urea groups to obtain gelling agents [3–7].

Despite their potential use as biomaterials [8, 9], the antecedents on sugar-derived polyurethanes and polyureas are not very numerous. The pioneering works of Kurita *et al.* described a series of polyurethanes [10, 11] and poly(urea urethane)s] [12] synthesized by the reaction of disaccharides and aminosugars, without prior protection of the hydroxyl groups, with alkyl and aryl diisocyanates. Thiem and coworkers [13–17] described a series of sugar-based polyurethanes and polyureas from the 1:4,3:6-dianhydrohexitols with D-*gluco*, L-*ido*, and D-*manno* configurations.

Among the synthetic procedures for the preparation of linear polyureas, the reaction of diamines with diisocyanate is one of greatest relevance [18, 19]. Thus, diamines are important monomers for polymer synthesis based on their reactions with electrophilic molecules, such as isocyanates, epoxides, acyl chlorides, and acrylates, and can successfully afford several classes of polymers—apart from PURs—such as polyamines, polyaminoesters, and polyamides.

The preparation of new diamines and the optimization of synthetic routes to achieve those compounds are of great interest. So far, sugar functionalized diamines have been synthesized [20, 21], and their ability to form metal complexes [22, 23] and their biological activity [24–26] have been evaluated. Therefore, the synthesis of modified carbohydrate diamine monomers and their controlled polymerization may lead to very interesting novel biopolymers.

Herein we report the preparation of three diamine sugar-based monomers having L-*arabino*, D-*gluco*, and *xylo* configurations, with the secondary hydroxyl groups protected as cyclic acetals or methyl ethers, and their use in the synthesis of new aliphatic and aromatic polyureas (PURs). Hexamethylene diisocyanate (HMDI) and 4,4′-methylene-bis(phenyl isocyanate) (MDI) were used to compare the effect of the aliphatic and aromatic constitution of the diisocyanate on the behavior of the resulting PUR (Schemes 1–4).

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2 EXPERIMENTAL

2.1 General Methods

All chemicals used were from Aldrich Chemical Co. Solvents were dried and purified when necessary, by appropriate standard procedures. Hexamethylene diisocyanate (HMDI) was vacuum distilled prior to use, and 4,4′-methylene-bis(phenylisocyanate) (MDI) was stored at 4°C until needed. Both diisocyanates were handled under inert atmosphere. Optical rotations were measured at (20 ± 5)°C on a Perkin-Elmer 341 polarimeter. Elemental analyses were determined in the Instituto de Investigaciones Químicas (CSIC) of Seville. IR spectra were recorded on a Jasco FT/IR 4200 spectrometer equipped with ATR. NMR spectra were recorded at 300 K on either a Bruker Advance AV-300 or AV-500 or a Bruker AMX-500. Chemical shifts (δ) are reported as parts per million downfield from Me_4Si. Mass spectra were obtained using a Kratos MS80RFA instrument. Intrinsic viscosity measurements were carried out in dichloroacetic acid (DCA) with Automated Microviscosimeter AMVn (Anton Paar). Gel permeation chromatography (GPC) analyses were performed using a Waters apparatus equipped with a Waters 2414 refractive index detector and two Styragel® HR columns (7.8 × 300 mm^2) linked in series, thermostatted at 60°C, and using 1-methyl-2-pyrrolidinone (NMP) as the mobile phase at a flow rate of 0.5 mL/min. Molecular weights were estimated against polystyrene standards. The thermal behavior of the polymers was examined by differential scanning calorimetry (DSC), using a TA Instruments DSC Q200 calibrated with indium. DSC data were obtained from samples of 4–6 mg at heating/cooling rates of 10°C·min^{-1} under a nitrogen flow. The glass transition temperatures (T_g) were determined at a heating rate of 20°C·min^{-1} from rapidly melt-quenched polymer samples. Thermogravimetry analyses (TGA) were performed under a nitrogen atmosphere (flow rate 100 mL·min^{-1}) with a TA Instruments SDT Q600 at a heating rate of 10°C·min^{-1}. Molecular modeling was performed using CehmBio3D Ultra from CambridgeSoft. Energy minimizations were accomplished with MM2, and molecular dynamics was carried out using a step interval of 2.0 fs, a frame interval of 10 fs, and a target temperature of 300 K with a heating rate of 1.00 Kcal/atom/ps.

2.2 Synthesis of Monomers and Polymers

2.2.1 *1,5-Diazido-1,5-dideoxy-2,3,4-tri-*O*-methylxylitol (3)*

To a solution of triphenylphosphine (3.05 g, 11.6 mmol) in dry THF (13 mL) at 0°C, a commercial 40% solution of diethyl azodicarboxylate (DEAD) in toluene (5.3 mL, 11.6 mmol) was added dropwise, and the mixture was stirred for 5 min prior to the sequential dropwise addition of diphenylphosphoryl azide (DPPA) (2.4 mL, 11.1 mmol) and a solution of 2,3,4-tri-*O*-methylxylitol [27] (**1**, 0.51 g, 2.6 mmol) in THF (13 mL). The resultant solution was stirred for 3 h and then concentrated to dryness. The residue was purified by column chromatography (*tert*-butyl methyl ether-hexane) (1:10) to give the title compound as a colorless oil (0.51 g, 80%. [27], 45%). Spectroscopic data were identical to those described in the literature [27].

2.2.2 *1,5-Diazido-1,5-dideoxy-2,3,4-tri-*O*-methyl-L-arabinitol (4)*

The reaction of 2,3,4-tri-*O*-methyl-L-arabinitol [27] (**2**, 1.0 g, 5.2 mmol) with triphenylphosphine (5.98 g, 22.7 mmol), DEAD (10.4 mL, 22.7 mmol) and DPPA (4.7 mL, 21.8 mmol) in THF (24.5 mmol) was carried out as described above for compound **2** to give the title compound as a colorless oil (1.14 g, 90%. Ref. 27, 83%). $[\alpha]_D$ –60° (*c* 0.5, dichloromethane) [Ref. 27, $[\alpha]_D$ –66° (*c* 0.6, dichloromethane)]. Spectroscopic data were identical to those described in the literature [27].

2.2.3 *1,5-Diamino-1,5-dideoxy-2,3,4-tri-*O*-methylxylitol (5)*

A solution of 1,5-diazido-1,5-dideoxy-2,3,4-tri-*O*-methylxylitol (**3**, 0.51 g, 2.1 mmol), in methanol (5 mL), was stirred with 10% Pd/C (0.1 g) for 24 h at 25°C under hydrogen atmosphere at 0.5 bar pressure. The mixture was then diluted with methanol and the catalyst was filtered off through diatomaceous earth. The resulting solution was concentrated to give the title product as a pure oil (0.4 g, quant.). IR: ν (cm^{-1}) 3379, 3300 (NH_2). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ (ppm) 1.89 (bs, 4 H, 2 NH_2), 2.80 (m, 2 H, H-1a, H-5a), 2.94 (m, 2 H, H-1b, H-5b), 3.30-3.48 (m, 3 H, H-2, H-3, H-4), 3.45 (bs, 3 H, OCH_3), 3.53 (bs, 6 H, 2 OCH_3). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ (ppm) 41.6 (C1, C-5), 58.6, 60.5 (OCH_3), 81.7 (C-3), 81.8 (C-2, C-4). HRMS (EI): Calcd for $C_8H_{21}N_2O_3$ (M + H)$^+$ 193.1552; found: 193.1541.

2.2.4 *1,5-Diamino-1,5-dideoxy-2,3,4-tri-*O*-methyl-L-arabinitol (6)*

The reaction of 1,5-diazido-1,5-dideoxy-2,3,4-tri-*O*-methyl-L-arabinitol (**4**, 0.8 g, 3.3 mmol) with hydrogen in the presence of 10% Pd/C (0.16 g) in methanol (7.8 mL) was carried out as described above for compound **5** to give the title compound as a pure oil (0.63 g, quant.). $[\alpha]_D$ –15° (*c* 1.0, methanol); IR: ν (cm^{-1}) 3378 (NH_2). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ (ppm) 1.50 (bs, 4 H, NH_2), 2.83-3.01 (m, 4 H, H-1a, H-1b, H-5a, H-5b), 3.33 (m, 2 H, H-2, H4), 3.43 (m, 1 H, H-3), 3.42, 3.49, 3.51 (3 s, 9 H, 3 OCH_3). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ (ppm) 40.6, 42.1 (C-1, C-5), 57.4, 59.1, 60.7 (3 OCH_3), 80.5 (C-3), 82.0, 82.9 (C-2, C-4). HRMS (EI): Calcd for $C_8H_{21}N_2O_3$ $(M + H)^+$ 193.1552; found: 193.1546.

2.2.5 *6-Azido-6-deoxy-2,4:3,5-di-O-methylene-D-gluconamide (8)*

To a mixture of methyl 6-azido-6-deoxy-2,4:3,5-di-*O*-methylene-D-gluconate [28, 29] (**7**, 2.63 g, 10.8 mmol) and ammonium chloride (0.23 g, 4.3 mmol), an aqueous solution of NH_3 (10.6 mL, 30% w/v) was added and the reaction mixture was stirred at 25°C for 2 h. The suspension was then cooled to 0°C and cold methanol (5 mL) was added. The title compound was isolated and purified from the media by filtration and recrystallization from methanol (2.18 g, 88%). M.p. 189–191°C. $[\alpha]_D$ +84° (*c* 0.5, dimethylsulfoxide); IR: ν (cm^{-1}) 3385, 3174 (NH_2), 2103 (N_3), 1689 (C=O); ^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) 3.41 (dd, 1 H, H6a, $J_{6a,6b} = 13.0$ Hz, $J_{6a,5} = 4.7$ Hz), 3.66 (s, 1 H, H-2), 3.93 (m, 1 H, H-5), 4.04–4.15 (m, 3 H, H-3, H-4, H-6b), 4.78 (d, 1 H O-$C\underline{H}_2$-O, $J =$ 6.5 Hz), 4.80 (d, 1 H O-$C\underline{H}_2$-O, $J = 6.8$ Hz), 4.99 (d, 1 H O-$C\underline{H}_2$-O, $J = 6.5$ Hz), 5.07 (d, 1 H O-$C\underline{H}_2$-O, $J = 6.3$ Hz), 7.10, 7.37 (2s, 2 H, NH_2). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) 46.6 (C-6), 67.2, (C-4), 70.1 (C-2), 74.5 (C-5), 76.7 (C-3), 86.3, 91.3 (2 O-$\underline{C}H_2$-O), 169.3 (C=O). HRMS (EI): Calcd for $C_8H_{11}N_4O_5$ $(M - H)^+$ 243.0729; found: 243.0727.

2.2.6 *1,6-Diamino-1,6-dideoxy-2,4:3,5-di-O-methylene-D-glucitol (9)*

To a suspension of 6-azido-6-deoxy-2,4:3,5-di-*O*-methylene-D-gluconamide (**8**, 0.45 g, 1.8 mmol), in dry THF (10.5 mL) at 0°C, a 1 M solution of $LiAlH_4$ in THF (11.5 mL) was added and the mixture was allowed to warm up to 25°C. The reaction mixture was then stirred for 24 h. Once the reaction had taken place, a saturated aqueous solution of sodium sulfate was added to the reaction mixture and the suspended aluminum salts were filtered off through diatomaceous earth. The salts were washed with THF (70 mL), and the combined organic solutions concentrated to dryness to give the title compound as a pure oil (0.26 g, 70%). $[\alpha]_D$ +11° (*c* 0.6, chloroform); IR: ν (cm^{-1}) 3363, 3304 (NH_2); ^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) 1.74 (bs, 4 H, NH_2), 2.73–2.82 (m, 2 H, H-1a, H-6a), 2.97-3.17 (m, 2 H, H-1b, H6b), 3.44–3.88 (m, 4 H, H-2, H-3, H-4, H-5), 4.70–5.13 (m, 4 H, 2 O-$C\underline{H}_2$-O). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) 39.4, 42.0 (C-1, C-6), 67.8, 72.4 (C3, C-4), 77.8, 79.5 (C-2, C-5), 87.4, 93.0 (2 O-$\underline{C}H_2$-O). HRMS (EI): Calcd for $C_8H_{17}N_2O_4$ $(M + H)^+$ 205.1188; found: 205.1185.

2.2.7 *PUR(XMe-HMDI) (10)*

In a typical procedure, 1,5-diamino-1,5-dideoxy-2,3,4-tri-*O*-methylxylitol (**5**, 205 mg, 1.06 mmol) was charged in a round-bottom flask provided with an inlet of Ar/vacuum; *N,N*-dimethyl acetamide (DMAc) (1 mL) was added under stirring, and the mixture was stirred to homogenization at room temperature. HMDI (0.16 mL, 1.06 mmol) was added and the mixture was stirred for 24 h, at 25°C, under inert atmosphere. Once the polymerization had taken place, methylamine (0.5 mL) was added, and the mixture stirred for 30 min. The solution was dropped into cold *tert*-butyl methyl ether (100 mL) and the polymer precipitated. The polyurea was purified by several washes with the same solvent. The pure polymer (white solid) was dried under vacuum for 2 days and stored in a desiccator (340 mg, 89%). IR: ν (cm^{-1}) 3330 (NH), 1622 (C=O), 1582 (NH δ, urea). ^{1}H-NMR (DMSO-d_6, 500 MHz): δ (ppm) 1.21 (bs, 4 H, $C\underline{H}_2$-c), 1.31 (bs, 4 H, $C\underline{H}_2$-b), 2.85 (bs, 4 H, $C\underline{H}_2$-a), 2.75-3.10 (m, 3 H, H-2, H-3, H-4), 3.20-3.50 (m, 4 H, H-1a, H-5a, H1b, H-5b), 3.33 (s, 3 H, OCH_3), 3.36 (bs, 6 H, 2 OCH_3), 5.62-5.94 (m, 4 H, NH). ^{13}CNMR (DMSO-d_6, 125 MHz): δ (ppm) 26.1 ($\underline{C}H_2$-c), 26.3 ($\underline{C}H_2$-b), 38.9 (C-1, C-5), 39.0 ($\underline{C}H_2$-a), 57.7, 59.4 (3 OCH_3), 79.7 (C-3), 80.8 (C-2, C-4), 158.1 (C=O). Anal. Calcd. for $C_{23}H_{26}N_4O_6$: C, 60.78; H, 5.77; N, 12.33. Found: C, 60.74; H, 5.87; N, 12.29.

2.2.8 *PUR(ArMe-HMDI) (11)*

This polymer was prepared from 1,5-diamino-1,5-dideoxy-2,3,4-tri-*O*-methyl-L-arabinitol (**6**, 140 mg, 0.72 mmol) and HMDI (0.11 mL, 0.72 mmol) in DMAc (1 mL), at 25°C, to give the title compound as a white solid (260 mg, 98%). $[\alpha]_D$ +19° (*c* 1, trifluoroacetic acid). IR: ν (cm^{-1}) 3328 (NH), 1622 (C=O), 1567 (NH δ, urea). ^{1}H-NMR (DMSO-d_6 , 500 MHz): δ (ppm) 1.22 (bs, 4 H, $C\underline{H}_2$c), 1.32 (bs, 4 H, $C\underline{H}_2$-b), 2.95 (bs, 4 H, $C\underline{H}_2$-a), 3.05–3.85 (m, 7 H, H-1a, H-1b, H-2, H-3, H-4, H-5a, H-5b), 3.24, 3.26, 3.31 (3 s, 9 H, 3 OCH_3), 5.72-5.91 (m, 4 H, NH). ^{13}C-NMR (DMSO-d_6, 125 MHz): δ (ppm) 26.0 ($\underline{C}H_2$-c), 29.9 ($\underline{C}H_2$b), 38.7, 41.3 (C-1, C-5), 39.0 ($\underline{C}H_2$-a), 57.1, 57.8, 59.7 (3 OCH_3), 79.8 (C-3), 82.6, (C-2, C-4), 157.9 (C=O). Anal. Calcd. for $C_{16}H_{32}N_4O_5$: C, 53.31; H, 8.95; N, 15.54. Found: C, 53.26; H, 8.68; N, 15.77.

2.2.9 *PUR(XMe-MDI) (12)*

This polymer was prepared from 1,5-diamino-1,5-dideoxy-2,3,4-tri-*O*-methylxylitol (**5**, 108 mg, 0.56 mmol) and MDI (141 mg, 0.56 mmol) in DMAc (1 mL) at 25°C to give the title compound as a white solid (235 mg, 95%). IR: ν (cm^{-1}) 3316 (NH), 1653 (C=O), 1543 (NH δ, urea). ^{1}H-NMR (DMSO-d_6, 500 MHz) : δ (ppm) 3.32 (s, 3 H, OCH_3), 3.34 (s, 6 H, 2 OCH_3), 3.23-3.50 (m, 7 H, H-1a, H-1b, H-5a, H-5b, H-2, H-3, H-4), 3.73-3.75 (m, 2 H, Ph-$C\underline{H}_2$-Ph), 6.10 (bs, 2 H, N$\underline{H}$-sugar), 7.01 (d, 2 H, H-b arom., $J = 8.2$ Hz), 7.09 (d, 2 H, H-b′ arom., $J = 8.2$ Hz), 7.26 (d, 2 H, H-a arom., $J = 8.3$ Hz), 7.33 (d, 2 H, H-a′

arom., *J* = 8.2 Hz), 8.47-8.54 (m, 2 H, N$\underline{H}$-Ph). ^{13}C-NMR (DMSO-d_6, 125 MHz): δ (ppm) 39.2 (Ph-$\underline{C}H_2$-Ph), 57.7, 59.5 (3 OCH_3), 39.9 (C-1, C-5), 79.2 (C-3), 80.7 (C-2, C-4), 117.7, 118.3, 128.7, 128.9 134.2, 134.9, 137.6, 138.4 (Ph), 152.5, 155.2 (C=O). Anal. Calcd. for $C_{23}H_{30}N_4O_5$: C, 62.43; H, 6.83; N, 12.66. Found: C, 62.51; H, 6.61; N, 12.76.

2.2.10 *PUR(ArMe-MDI) (13)*

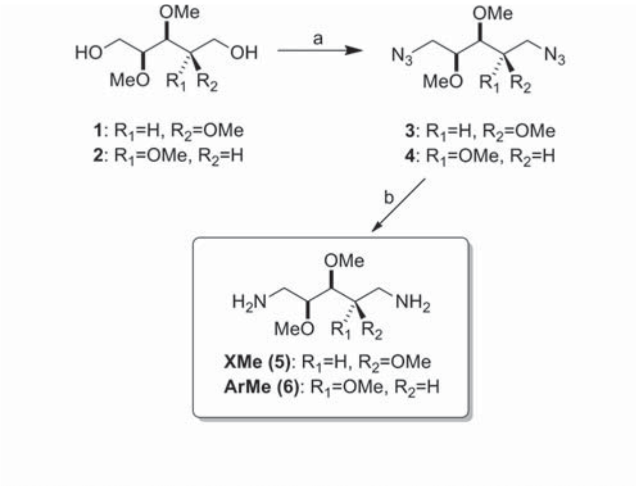
This polymer was prepared from 1,5-diamino-1,5-dideoxy-2,3,4-tri-*O*-methyl-L-arabinitol (**6**, 200 mg, 1.03 mmol) and MDI (260 mg, 1.03 mmol) in DMAc (1 mL) at 25°C to give the title compound as a white solid (414 mg, 91%). $[\alpha]_D$ +29° (*c* 1, trifluoroacetic acid). IR: ν (cm^{-1}) 3327 (NH), 1653 (C=O), 1540 (NH δ, urea). ^{1}H-NMR (DMSO-d_6, 500 MHz): δ (ppm) 3.25, 3.36, 3.37 (3 s, 9 H, 3 OCH_3), 3.25-3.56 (m, 7 H, H-1a, H-1b, H-2, H-3, H-4, H-5a, H-5b), 3.66-3.78 (m, 2 H, Ph-C$\underline{H}_2$-Ph), 6.05-6.16 (m, 2 H, N$\underline{H}$-sugar), 7.01 (bs, 2 H, H-b arom.), 7.08 (d, 2 H, H-b′ arom., *J* = 7.5 Hz), 7.26 (d, 2 H, H-a arom., *J* = 7.6 Hz), 7.32 (d, 2 H, H-a′ arom., *J* = 8.0 Hz), 8.43-8.53 (m, 2 H, N$\underline{H}$-Ph). ^{13}CNMR (DMSO-d_6, 125 MHz): δ (ppm) 38.9, 39.4 (C-1, C-5), 39.3 (Ph-$\underline{C}H_2$-Ph), 56.5, 57.8, 59.8 (3 OCH_3), 78.9, (C-3), 82.3, (C-2, C-4), 117.3, 118.0, 128.6, 128.7, 134.0, 134.7, 137.4, 138.1 (Ph), 152.3, 155.0 (C=O). Anal. Calcd. for $C_{23}H_{30}N_4O_5$: C, 62.43; H, 6.83; N, 12.66. Found: C, 62.43; H, 6.73; N, 12.61.

2.2.11 *PUR(MedGlu-HMDI) (14)*

This polymer was prepared from 1,6-diamino-1,6-dideoxy-2,4:3,5-di-*O*-methylene-D-glucitol (**9**, 44 mg, 0.22 mmol) and HMDI (0.35 mL, 0.22 mmol) in DMAc (0.5 mL) at 40°C to give the title compound as a white solid (81 mg, quant.). $[\alpha]_D$ +30° (*c* 0.5, trifluoroacetic acid). IR: ν (cm^{-1}) 3329 (NH), 1622 (C=O), 1572 (NH δ, urea). ^{1}H-NMR (DMSO-d_6, 500 MHz): δ (ppm) 1.24 (bs, 4 H, C$\underline{H}_2$-c), 1.33 (bs, 4 H, C$\underline{H}_2$-b), 2.94 (m, 4 H, C$\underline{H}_2$-a), 3.20-4.30 (m, 8 H, H-1a, H-1b, H-2, H-3, H-4, H-5, H-6a, H-6b), 4.60-5.20 (m, 4 H, 2 O-C$\underline{H}_2$-O), 5.71–5.97 (m, 4 H, NH). ^{13}C-NMR (DMSO-d_6, 125 MHz): δ (ppm) 26.4 ($\underline{C}H_2$-c), 30.0 ($\underline{C}H_2$-b), 37.1 (C-1, C-6), 39.5 ($\underline{C}H_2$-a), 67.2, 70.6 (C-3, C-4), 74.9, 77.1 (C-2, C-5), 86.6, 91.5 (2 O-C$\underline{H}_2$-O), 158.3 (C=O). Anal. Calcd. for $C_{16}H_{28}N_4O_6$: C, 51.60; H, 7.58; N, 15.04. Found: C, 51.62; H, 7.64; N, 15.04.

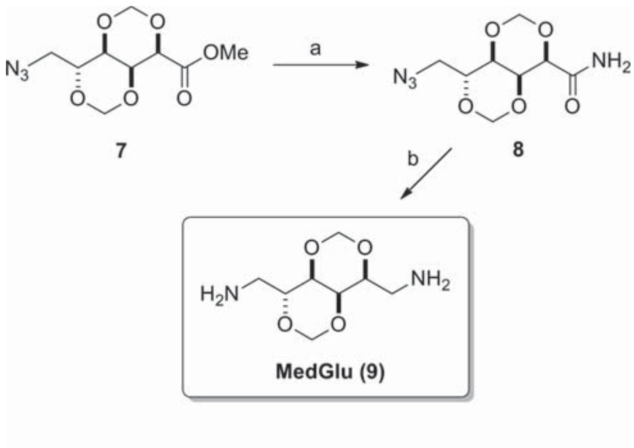
2.2.12 *PUR(MedGlu-MDI) (15)*

This polymer was prepared from 1,6-diamino-1,6-dideoxy-2,4:3,5-di-*O*-methylene-D-glucitol (**9**, 24 mg, 0.12 mmol) and MDI (29 mg, 0.12 mmol) in DMAc (0.5 mL) at 40°C to give the title compound as a white solid (52 mg, quant.). $[\alpha]_D$ +30° (*c* 0.5, trifluoroacetic acid). IR: ν (cm^{-1}) 3330 (NH), 1660 (C=O), 1538 (NH δ, urea). ^{1}H-NMR (DMSO-d_6, 500 MHz): δ (ppm) 3.25–4.12 (m, 8 H, H-1a, H-1b, H-2, H-3, H-4, H-5, H-6a, H6b), 3.77-3.85 (m, 2 H, Ph-C$\underline{H}_2$-Ph), 4.72-5.08 (m, 4 H, 2 O-C$\underline{H}_2$-O), 6.20 (bs, 2 H, N$\underline{H}$-sugar), 7.05 (bs, 2 H, H-b arom. *J* = 8.1 Hz), 7.11 (d, 2 H, H-b′ arom., *J* = 8.1 Hz), 7.29 (d, 2 H, H-a arom., *J* = 8.1 Hz), 7.35 (d, 2 H, H-a′ arom., *J* = 8.3 Hz), 8.43-8.55 (m, 2 H, N$\underline{H}$-Ph). ^{13}C-NMR (DMSO-d_6, 125 MHz): δ (ppm) 39.9 (Ph-$\underline{C}H_2$-Ph), 40.3 (C-1, C6), 67.5, 70.9, 75.1, 76.3 (C-2, C-3, C-4, C-5), 87.0, 92.4 (2 O-$\underline{C}H_2$-O), 118.8, 129.9, 134.8, 135.4, 138.1, 138.7 (Ph), 153.0, 155.8 (C=O). Anal. calcd for $C_{23}H_{26}N_4O_6$: C, 60.78; H, 5.77; N, 12.33. Found: C, 60.74; H, 5.87; N, 12.29.



(**a**) Ph_3P, DEAD, DPPA, THF, 25 °C; (**b**) H_2, 20 psi, 10% C/Pd, MeOH, 25 °C

Scheme 1 Reaction scheme for the synthesis of diamines **5** and **6.**



(**a**) NH_3 (aq), NH_4Cl, 25 °C; (**b**) $LiAlH_4$, THF, 25 °C

Scheme 2 Reaction scheme for the synthesis of diamine **9.**

3 RESULTS AND DISCUSSION

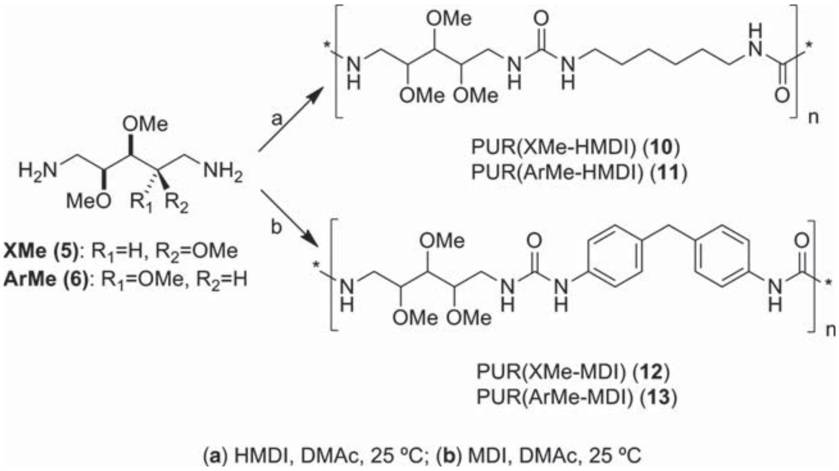
Three sugar-based diamino-monomers, 1,5-diamino-1,5-dideoxy-2,3,4-tri-*O*-methylxylitol (**5**), 1,5-diamino-1,5-dideoxy-2,3,4-tri-*O*-methyl-L-arabinitol (**6**), and 1,6-diamino-1,6-dideoxy-2,4:3,5-di-*O*-methylene-D-glucitol (**9**), were prepared with success following the synthetic Schemes 1 and 2.

The starting diol compounds 2,3,4-tri-*O*-methylxylitol (**1**) and 2,3,4-tri-*O*-methyl-L-arabinitol (**2**), used for the synthesis of the diamines **5** and **6**, respectively, were prepared as previously described from the commercially available xylitol and L-arabinitol [27]. The synthesis of the diamines **5** and **6** as dihydrochlorides was first described in earlier works of our group [27]. The procedure involved the synthesis of dimesyl derivatives and subsequent displacement with azide to achieve the corresponding diazide-compounds which eventually led to the target compounds. However, the substitution of the mesyl groups was accompanied by the formation of cyclic tetrahydrofuranoid derivative byproducts with a decrease in the overall yields of the diazides. To overcome this drawback, a new approach—previously used for the synthesis of other sugar-based diamine monomers [19]—was successfully explored. Thus, the transformation of diols **1** and **2** into the diazido compounds **3** and **4**, respectively, was achieved in a one-pot reaction by using triphenylphosphine, diethylazodicarboxylate (DEAD), and diphenylphosphoryl azide (DPPA) in THF, at 25°C (Scheme 1). This new approach is less time-consuming, and rendered enhanced yields compared with the published method (from 45% to 80% for xylitol- and from 83 to 93%, for L-arabinitol-derivatives). The reduction of the azide groups for the synthesis of the diamines **5** and **6** was carried out by hydrogenolysis (H_2, 0.5 bar, 10% Pd/C), with quantitative yields.

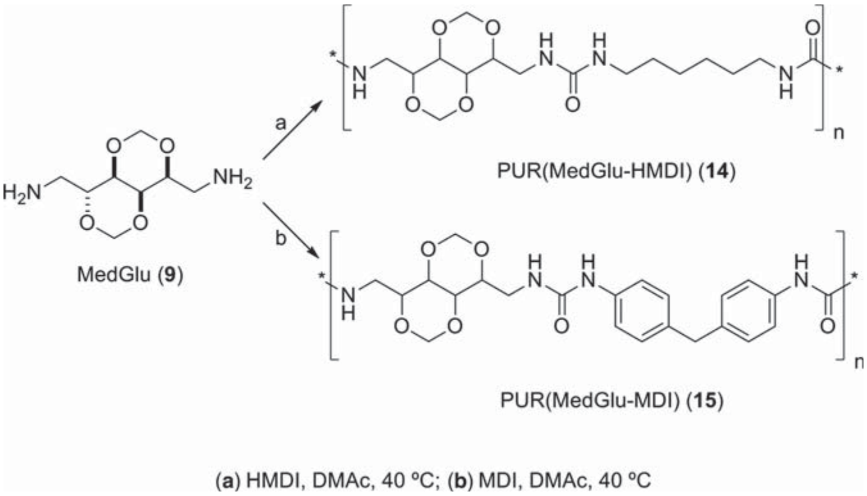
Methyl 6-azido-6-deoxy-2,4:3,5-di-*O*-methylene-D-gluconate (**7**) [28, 29] was the starting material for the synthesis of the diamine **9** (Scheme 2). Compound **7** was treated with an aqueous solution of NH_3/NH_4Cl to render the gluconamide **8** in good yields, and this was further reduced by $LiAlH_4$ in THF to give the 1,6-diamino-1,6-dideoxy-2,4:3,5-di-*O*-methylene-D-glucitol (**9**) as a pure oil (70% yield).

The synthesis of polyureas was carried out by polyaddition reaction in *N,N*-dimethylacetamide (DMAc) of 1,5-diamino-1,5-dideoxy-2,3,4-tri-*O*-methylxylitol (**XMe**, **5**), 1,5-diamino-1,5-dideoxy-2,3,4-tri-*O*-methyl-L-arabinitol (**ArMe**, **6**), or 1,6-diamino-1,6-dideoxy-2,4:3,5-di-*O*-methylene-D-glucitol (**MedGlu**, **9**) with the diisocyanates hexamethylene diisocyanate (HMDI) and 4,4′-methylene bis(phenyl isocyanate) (MDI) (Schemes 3 and 4) in absence of catalyst. The polymerizations proceeded at room temperature for the diamino monomers **5** and **6**, whereas the reaction mixtures were warmed up to 40°C when the highly rigid bicyclic diamino monomer **9** was used. At the end of the polymerizations, the reactive terminal isocyanate groups were deactivated by addition of methylamine to prevent undesirable crosslinking reactions [30–32].

The polymers were isolated from the reaction mixture by precipitation on *tert*-butyl methyl ether and later by filtration under vacuum; the isolated PURs were then washed with *tert*-butyl methyl ether and subsequently dried under vacuum for at least 2 days. In some cases, the resulting polymers precipitated from the reaction media, which prevented high molecular weights being reached. High yields were attained in every case (89%-quant.). The synthesized new materials exhibited reduced solubility in organic solvents, being only slightly soluble in *N*-methylpyrrolidinone and dimethylsulfoxide.



Scheme 3 Reaction scheme for the synthesis of PURs with *L-arabino* and *xylo* configurations.



Scheme 4 Reaction scheme for the synthesis of PURs with *D-gluco* configuration.

The structures proposed for the monomers and polyureas were validated by FTIR and NMR spectroscopies; these data are fully detailed in the experimental section. Both ^{1}H-NMR and ^{13}C-NMR spectra were elucidated with the aid of other NMR experiments, such as COSY, DEPT, and heteronuclear correlation.

Characteristic IR absorption bands of the urea groups and the sugar moieties were observed in the expected ranges of wavenumber and intensity. Related to the urea groups, the NH stretching bands appeared at about 3330 cm^{-1} in every polyurea. However, there were some significant differences between aromatic and aliphatic products in the C=O stretching bands. Thus, the carbonyl stretching bands appearing at about 1620 cm^{-1} in aliphatic polyureas moved up about 30 cm^{-1} in the MDI-based PURs. In contrast, the bending vibration bands of N-H bonds came out at lower wavenumber for aromatic PURs (~ 1540 cm^{-1}) than those for the HMDI-based materials (~ 1575 cm^{-1}).

Likewise, ^{1}H- and ^{13}C-NMR spectra were in full agreement with the proposed chemical structures. In the ^{13}C-NMR spectra, the peaks encountered between 86 ppm and 92 ppm proved the existence of the acetal groups in PURs **14** and **15**. Peaks attributable to the methyl ether groups in polymers **10–13** were located in the range of 56.5–59.8 ppm. In addition, the ^{13}C-NMR spectra displayed the peaks corresponding to the carbonyl groups at about 158 ppm in the aliphatic polymers, whereas in MDI-based PURs, two signals due to the carbons from the carbonyl groups were found at higher fields (~152 and 155 ppm). The presence of these signals suggests the existence of different surroundings for the two carbonyl groups joined to the diphenyl methylene moiety in the two preferential conformations that this system can present (Figure 1), as was demonstrated by MM2 calculations. This hypothesis is also supported by the ^{1}H-NMR spectra of MDI-based polyureas in which four doublets due to the aromatic protons are displayed.

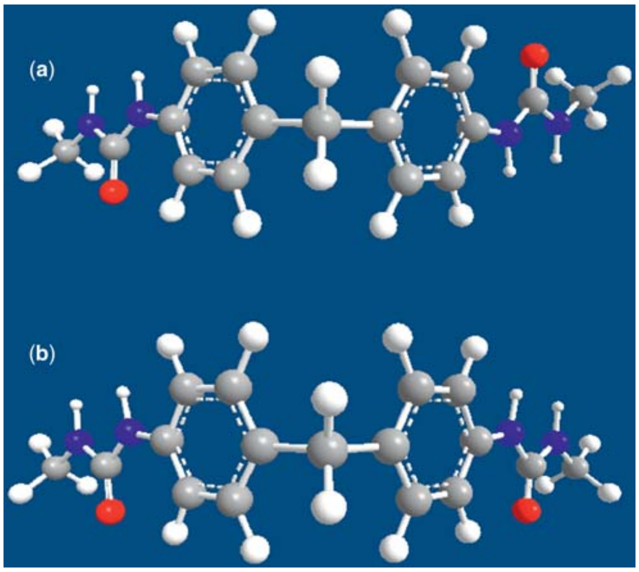


Figure 1 The two most-stable conformations for the 4,4′-methylene-bis(phenyl urea) moiety. (**a**) Antiparallel carbonyl groups. (**b**) Parallel carbonyl groups.

The PURs presented an average molecular weight (M_W) ranging between 4500 Da and 35100 Da and polydispersities in the range of 1.5–2.5. The viscosimetric average molecular weight (M_v) of PUR(MedGlu-HMDI) **14** was calculated by viscosimetry using the Mark-Houwink parameters, modified for polyureas, obtaining a value of 50900 Da. The intrinsic viscosities in dichloroacetic acid (DCA) were found to be in the range of 0.16–0.81 dL·g^{1}. Molecular weights, polydispersities, and intrinsic viscosities of the obtained polymers are collected in Table 1.

Table 1 Intrinsic viscosity and molecular weights of polyureas.

PUR	η^a (dL.g^{-1})	M_v^b	M_w^c	M_w/M_n^c
PUR(XMe-HMDI) (**10**)	0.16	–	13800	1.5
PUR(ArMe-HMDI) (**11**)	–	–	4500	2.0
PUR(XMe-MDI) (**12**)	0.18	–	19200	1.7
PUR(ArMe-MDI) (**13**)	0.21	–	35100	2.5
PUR(MedGlu-HMDI) (**14**)	0.81	50900	–	–
PUR(MedGlu-MDI) (**15**)	0.27	–	21000	2.0

[a] Intrinsic viscosity in dL/g determined in dichloroacetic acid at 25°C. [b] Estimated by viscosimetry using the Mark-Houwink parameters $100[\eta] = 0.5 + 0.338 \cdot M^{0.505}$. [c] Determined by GPC analysis against polystyrene standards using NMP as mobile phase.

3.1 Thermal Properties

The thermal behavior of the new PURs was studied by DSC and TGA. Characteristic parameters resulting from the experiments are given in Table 2. The diamino sugar-based monomers **5**, **6**, and **9** used in the present study lack a C2 symmetry axis, which produces non-stereoregular polymers (Scheme 3 and 4). However, all of them are semicrystalline materials showing an endothermic peak indicative of melting. Apparently, the micro-structural heterogeneity of these materials did not impede a partial packing of the polymer chains into microcrystalline domains. Furthermore, the low volume of the side methoxy and methylene acetal groups did not completely prevent that packaging despite side substituents being known to distort it, lowering their crystallinity [33]. For each sugar monomer, the polyurea based on MDI exhibited the highest T_m.

Glass transitions took place at well-defined temperatures, with values that were highly dependent on the polymer constitution. The glass transition temperatures (T_g) were measured in quenched samples with the same thermal history, and are displayed in Table 2. For L-*arabino*- and *xylo*-based PURs, a great increase in T_g was observed when the aliphatic diisocyanate unit was replaced by MDI. This is a largely expected result attributable to the chain stiffness caused by the presence of the diphenyl-methylene unit. On the other hand, the higher T_m and ΔH_m observed for the L-*arabino*-based PURs than for the *xylo*-based PURs are in full agreement with our previous results on pentose-based polyamides [34, 35], poly(esteramide)s [36], and polycarbonates [37] which always showed a higher crystallinity for those polymers with sugar units having an L-*arabino* configuration than for those having *xylo* configuration. Such a difference was explained [37] in terms of the conformational preferences exhibited by these two configurations [38–40].

However, in the case of polyureas **14** and **15** there was no marked influence of the diisocyanate monomer on their T_g values. The stiffness of the bicyclic acetalized sugar moiety dramatically reduced the movement of the polymer chain, being the main factor that apparently controlled the final stiffness of those materials. Thus, the insertion of the rigid 2,4:3,5-di-*O*-methylene-D-glucitol residue in the PUR chains caused an increase in their T_g values (83°C and 84°C), exceeding those of the other PURs described [41], based on more-flexible 1,6-diaminohexitols.

The thermal stability of the polyureas was evaluated by thermogravimetry under an inert atmosphere. Detailed temperature and weight-loss data for all the studied materials are given in Table 2. The TGA curves of the described polyureas showed that all of them were thermally stable under inert atmosphere over a wide temperature range (°Td values between 237°C and 283°C). The thermal degradation of PURs **11**, **12**, and **13** took place through a one-stage process (${}^{max}T_d$ from 333°C to 355°C), with associated weight loss ranging from 88% to 96%. With regard to the L-*arabino*- and *xylo*-based PURs, the highest final residues were found for MDI-based polymers. In contrast, the decomposition of the *xylo*-derivative polymer **10** and polyureas synthesized from 1,6-diamino-1,6-dideoxy-2,4:3,5-di-*O*-methylene-D-glucitol (**9**) occurred through a two-stage process, suggesting that a modified decomposition mechanism must be operating in such stages. Polymers **14** and **15** were found to have the highest final residues (18% and 25%, respectively).

Table 2 Thermal properties of polyureas.

	DSC[a]			**TGA**[b]		
	T_g **(°C)**	T_m **(°C)**	**ΔH_m (J/g)**	**$^{\circ}T_d$ (°C)**	**$^{max}T_d$ (°C)**	**–ΔW (%)**
PUR(XMe-HMDI) (**10**)	21	86	2	237	254/**349**	21/**71**
PUR(ArMe-HMDI) (**11**)	61	146	35	283	355	96
PUR(XMe-MDI) (**12**)	82	146	9	277	333	89
PUR(ArMe-MDI) (**13**)	81	170	11	270	333	88
PUR(MedGlu-HMDI) (**14**)	84	166	7	256	**363**/441	**62**/20
PUR(MedGlu-MDI) (**15**)	83	171	10	251	**340**/441	**64**/11

[a] Glass transition temperature (T_g), melting temperature (T_m), and enthalpy (ΔH_m) measured by DSC. [b] Onset decomposition temperature corresponding to 10% of weight loss ($^{\circ}T_d$), maximum rate decomposition temperatures ($^{max}T_d$) and weight lost at the respective decomposition step [–ΔW(%)] determined by TGA.

4 CONCLUSIONS

The preparation of three diamine sugar-based monomers—having L-*arabino*, D-*gluco* and *xylo* configuration—with the secondary hydroxyl groups protected as cyclic acetals or methyl ether groups, was successfully achieved. Their use in the synthesis of new linear sugar-based polyureas was accomplished by polymerization in solution using aliphatic (HMDI) and aromatic (MDI) diisocyanates as comonomers. In these systems, the activation of the polyaddition reaction by a catalyst is avoided because of the intrinsic nucleophilicity of the amino groups, leading to the formation of linear polymers in high yields and fair molecular weights. These polyureas behaved as semicrystalline materials despite their non-stereoregularity, and all of them presented endothermic melting transitions; this behavior contrasts with that of the structurally related polyurethanes. As can be inferred from their T_g values, for the polyureas based on acyclic-sugar monomers, the aromatic diisocyanate (MDI) produced stiffer polyureas than those synthesized from the aliphatic diisocyanate (HMDI). However, in the case of the polyureas based on the bicyclic-sugar monomer there was no marked influence of the diisocyanate monomer on their T_g values; the stiffness of the bicyclic acetalized sugar moiety is the main factor that apparently controlled the final stiffness of these materials. These sugar-based polyureas showed a thermal stability comparable to that of structurally similar polyurethanes and polyureas made from non-sugar-based linear aliphatic diols.

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