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# Synthesis of novel polyurethanes from sugars and 1,6-hexamethylene diisocyanate

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**Abstract**

Synthesis of two new polyurethanes was accomplished by reaction of 1,6-hexamethylene diisocyanate with the sugars methyl 2,6-di-*O*-pivaloyl-α-D-glucopyranoside (**1**) and methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (**2**) catalysed by 1,4-diazabicyclo[2.2.2]octane. The polymers **4** and **5** obtained were characterised by physical and spectroscopic methods. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords*: Polyurethane; Sugar polymer; Synthesis

## 1. Introduction

Polyurethanes are polymers widely used in industry for the preparation of fibres, elastomers — some of them possessing biomedical applications (McMillin, 1994) — adhesives, coatings and others, according to the nature of the diisocyanate and of the diol used.

The synthesis of polymers from carbohydrate-derived building blocks may lead to novel biodegradable materials and some work has already been reported in this field. Bachmann, Reimer, Ruppenstein, & Thiem (1998) synthesised a polyurethane by catalytic polycondensation of a 2-isocyanato-L-iditol. Also a 2-azido-5-chloroformyl-iditol was used as starting material and underwent polycondensation after catalytic hydrogenation to the intermediate 2-aminocholoroformyl derivative. The preparation of polyurethanes by reaction of dianhydrohexitols with aliphatic diisocyanates has also been described (Dirlikov & Schneider, 1984).

In this work, we report the synthesis of two new polyurethanes (**4** and **5**, Scheme 1) by step-reaction polymerisation, using 1,6-hexamethylene diisocyanate, OCN–$(CH_2)_6$–NCO, and the partially protected sugars methyl 2,6-di-*O*-pivaloyl-α-D-glucopyranoside (**1**) or methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (**2**) as starting materials and 1,4-diazabicyclo[2.2.2]octane (DABCO) as catalyst.

## 2. Results and discussion

Synthesis of **1** and **2** was accomplished using the procedures reported in the literature. Regioselective pivaloylation of methyl α-D-glucopyranoside (**3**) with pivaloyl chloride in pyridine at −20°C (Klausener, Müller, Runsink, & Scharf, 1983) afforded **1** in 80% yield. Reaction of **3** with benzaldehyde in the presence of the catalyst zinc chloride, during 4 h at room temperature (Hall, 1980), gave **2** in 85% yield.

The step-reaction polymerisation was investigated using sugar/1,6-hexamethylene diisocyanate in proportion 1:1, tetrahydrofuran (THF) as solvent, at reflux temperature and under argon atmosphere. After 1 h, DABCO (2%) was added and the reaction was stopped after e.g. 60 h, giving the polyurethanes **4** and **5** in 94 and 92% conversion, respectively.

The two polymer structures were characterised by means of $^1$H, $^{13}$C NMR and IR spectroscopies. The C=O groups gave the expected IR bands at 1737 $cm^{-1}$ for **4** and 1728 $cm^{-1}$ for **5**. The bands observed at 3376 $cm^{-1}$ for **4**, and 3394 $cm^{-1}$, for **5** confirm the presence of an NH group in both polymers. In the $^1$H NMR spectrum of **4** (Table 1)

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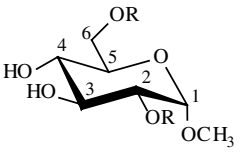
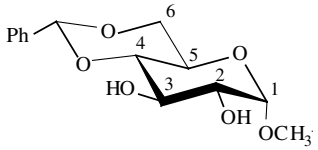
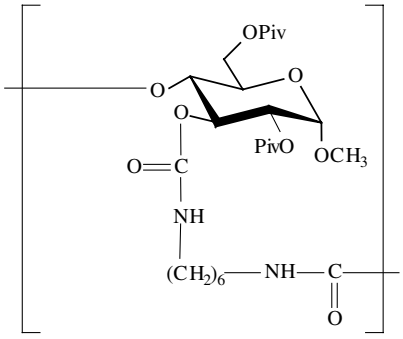


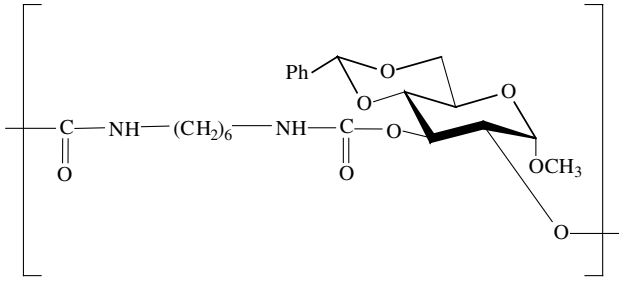
**1** R = $COC(CH_3)_3$ (Piv)
**3** R = H



**2**



**4**



**5**

Scheme 1.

the resonances corresponding to H-3 and H-4 appear at lower field than the corresponding ones of the starting material, confirming the formation of the urethane. The $NCH_2$ groups were assigned to the signals at $\delta$ 3.10 and the signals of the other four methylene groups are part of a band of multiplets containing also the methyl groups of the pivaloyl functions. The $^{13}C\{^1H\}$ NMR spectrum of **4** is in agreement with the proposed structure. The carbonyl group $^{13}C$ resonance of the urethane moiety appears at $\delta$ 155.7, and the methylene groups give signals at $\delta$ 40.8 ($NCH_2$), 29.7, and 26.2.

Assignment of the $^1H$ and $^{13}C$ NMR resonances also confirmed the proposed structure for **5**. H-2 and H-3 appear at lower field than in the starting material, and additional peaks corresponding to $NCH_2$ at $\delta$ 3.0 and to four methylene groups in the range $\delta$ 1.4–1.25 could also be detected. The peak at $\delta$ 155.7 was assigned to the carbonyl group of the urethane and the methylene groups appear at $\delta$ 40.8 ($NCH_2$), 29.4, 25.4, and 25.3.

The molecular weight distributions were measured by gel permeation chromatography (GPC), in THF, at 30°C, and are given in terms of polystyrene units (Figs. 1 and 2, Table 2). For longer reaction times (60 h, entries 1 and 4), the number-average molecular weights ($\bar{M}_n$) show values in the range of 5000 for both polymers **4** and **5** (degrees of polymerisation, $\overline{DP}_n$, ca. 10). For shorter times, under similar experimental conditions, the products obtained were, as expected, mainly oligomers. The observed increase of the molecular weight with reaction time and, consequently, the conversions seem to be similar in both polymerisation reactions (compare entries 1 and 2 with 4 and 5).

Analysis of **4** and **5** (from entries 1 and 4) by differential scanning calorimetry (DSC), using heating rates of 5 and 20°C $min^{-1}$ led to the results indicated in Fig. 3. The two

Table 1
$^1H$ NMR (300 MHz, $CDCl_3$) data for protons H-1, H-2, H-3, H-4, H-5, H-6 and H6′ of compounds **1**, **2**, **4** and **5**. Data given as: chemical shift ($\delta$), multiplicity (s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublets of doublets, m = multiplet, br = broad) and $J$ (Hz)

| Compound no. | H-1 | H-2 | H-3 | H-4 | H-5 | H-6, H-6′ |
|---|---|---|---|---|---|---|
| **1**[a] | 4.85, d $J_{1,2} = 3.7$ | 4.58, dd $J_{2,3} = 10.0$ | 3.94, ddd $J_{3,4} = 9.6$; $J_{3,OH} = 3.6$ | 3.40–3.31 (m, together with $OCH_3$) | 3.8, ddd | 4.40, dd; 4.38, dd $J_{6,6'} = 12.1$; $J_{5,6} = 5.0$; $J_{5,6'} = 1.9$ |
| **2**[b] | 4.67, d $J_{1,2} = 3.73$ | 3.56, dd $J_{2,3} = 8.9$ | 3.88, t $J_{3,4} = 9.5$ | 3.44, d $J_{4,5} = 9.10$ | 3.8, ddd | 4.33, dd; 3.73, dd $J_{6,6'} = 8.8$; $J_{5,6} = 3.4$ |
| **4** | 4.90–4.80 | 4.90–4.80 | 5.32, t $J_{2,3} = J_{3,4} = 9.3$ | 4.90–4.80 | 4.20–3.94 | 4.20–3.94 |
| **5** | 4.90, br s | 5.60–5.30 | 5.60–5.30 | 4.00–3.60 | 4.00–3.60 | 4.00–3.60 |

[a] Klausener, Müller, Rumsink & Scharf (1983).
[b] Hall (1980).

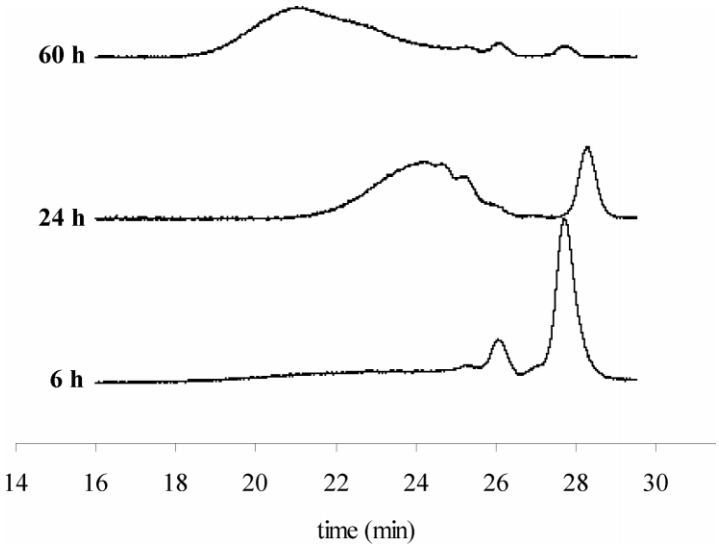



Fig. 1. GPC curves of polymer **4** obtained at reaction times of 6, 24 and 60 h.

polymers show a similar DSC pattern. At a heating rate of 5°C $min^{-1}$ an endothermic peak *a*, centred at 80°C was observed, possibly due to the evaporation of inclusions of methanol used to stop the polymerisation reaction. Peak b with an onset at 135°C for **4** and 144°C for **5** corresponds to the fusion of the polymers. This assignment was based on the microscopic examination of polymer samples, on heating at 4°C $min^{-1}$, using a melting point apparatus. Fusion was immediately followed by a series of decomposition processes. An increase of the heating rate to 20°C $min^{-1}$, shifts the positions of peaks *a* and *b* to higher temperatures but the general features of the DSC curves remain identical to those observed at 5°C $min^{-1}$. Very dark caramel-brown residues were found inside the DSC crucibles after the samples were heated to 350°C at 5°C $min^{-1}$. Heating the polymers to a temperature of 200°C, at 20°C $min^{-1}$, produced light caramel-brown residues.

## 3. Experimental part

### 3.1. General

The sugar monomers **1** and **2** were synthesised according to literature methods. (Klausener, Müller, Rumsink & Scharf, 1983; Hall, 1980). The other monomer, 1,6-hexamethylene diisocyanate (Aldrich), and the catalyst DABCO (Aldrich) were used as received. Deuteriated chloroform (Aldrich) was used as NMR solvent.

### 3.2. Polymer synthesis

In a typical polymerisation reaction, 1,6-hexamethylene diisocyanate (1 mmol) was added to the solution of the sugar monomer (1 mmol) in THF (5 ml). The mixture was stirred for 1 h under argon atmosphere, at reflux temperature, followed by addition of DABCO (2%). After refluxing

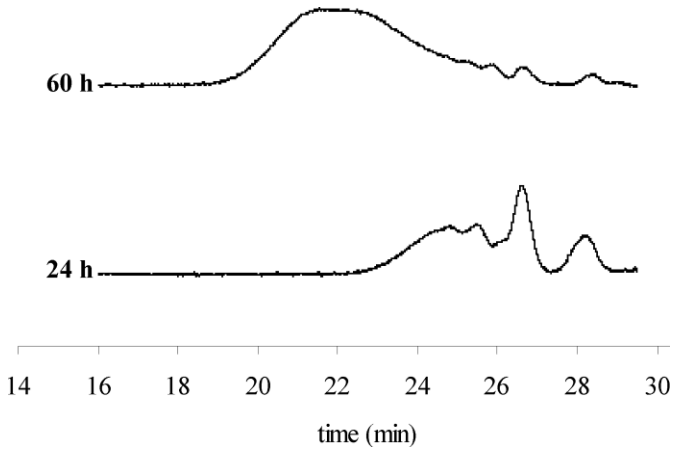



Fig. 2. GPC curves of polymer **4** obtained at reaction times of 24 and 60 h.

Table 2
Number- and weight-average molecular weights, polydispersity and number-average degree of polymerisation of polymers **4** and **5** (in polystyrene units)

| Entry | Reaction time (h) | Polymers | $\bar{M}_n$ | $\bar{M}_w$ | $\bar{M}_w/\bar{M}_n$ | $\overline{DP}_n$ |
|---|---|---|---|---|---|---|
| 1 | 60 | **4** | 5250 | 16000 | 3.0 | 9.9 |
| 2 | 24 | **4** | 1550 | 3600 | 2.3 | 2.9 |
| 3 | 6 | **4** | 950 | 4100 | 4.3 | 1.8 |
| 4 | 60 | **5** | 4650 | 10900 | 2.3 | 10.3 |
| 5 | 24 | **5** | 1350 | 2150 | 1.6 | 3.0 |

for 60 h under argon atmosphere, methanol (2 ml) was added and the reaction mixture was concentrated. The reactions were followed by thin layer chromatography (TLC) with silica gel foils $GF_{254}$ (Merck) and methanol–dichloromethane (1:9) as eluent. Detection was accomplished by UV radiation absorption and/or spraying with sulphuric acid/vanillin (2%) and subsequent heating at 120°C. Chromatographic separations were performed by column chromatography at 2 bar with silica gel 60 (230–400 mesh, Merck) with the above-mentioned system as eluent or with Sephadex LH20 using methanol–dichloromethane (1:1) as solvent. After chromatographic separation, the yields obtained were 94% for **4** and 92% for **5**.

Physical data for **4**: m.p. 135°C; $[\alpha]_D^{20}$ +51° (*c* 1.0, $CH_2Cl_2$); IR 1737 $cm^{-1}$ (C=O), 3376 $cm^{-1}$ (NH); $^1H$ NMR ($CDCl_3$): $\delta$ 5.32 (t, 1H, H-3, $J_{2,3} = J_{3,4} =$ 9.3 Hz), 4.90–4.80 (m, 3H, H-1, H-2, H-4), 4.20–3.94 (m, 3H, H-5, H-6, H-6′), 3.39 (s, 3H, $OCH_3$), 3.10 (br s, 4H, $NCH_2$), 1.44–1.17 (m, 26H, $4CH_2$, $6CH_3$ of pivaloyl); $^{13}C$ {$^1H$} NMR ($CDCl_3$): $\delta$ 178.9, 178.3 (*C*=O, pivaloyl), 155.7, 155.2 (*C*(=O)NH), 96.5 (C-1), 70.8, 70.3, 69.3, 67.7 (C-2, C-3, C-4, C-5), 62.7 (C-6), 55.0 ($OCH_3$), 40.8 ($NCH_2$), 38.8 ($C(CH_3)_3$ of pivaloyl), 29.7, 26.2 (chain $CH_2$), 26.8, 26.5 ($C(CH_3)_3$ of pivaloyl).

Physical data for **5**: m.p. 144°C; $[\alpha]_D^{20}$ +44° (*c* 1.0, $CH_2Cl_2$); IR 1728 $cm^{-1}$ (C=O), 3394 $cm^{-1}$ (NH); 1620 $cm^{-1}$ (phenyl); $^1H$ NMR ($CDCl_3$): $\delta$ 7.60–7.30 (m, 5H, Ph), 5.60–5.30 (m, 3H, H-2, H-3, C*H* of benzylidene), 4.90 (br s, 1H, H-1), 4.00–3.60 (m, 4H, H-4, H-5, H-6, H-6′), 3.40 (s, 3H, $OCH_3$), 3.00 (br s, 4H, $NCH_2$), 1.40–1.25 (m, 8H, 4 groups $CH_2$); $^{13}C$ {$^1H$} NMR ($CDCl_3$): $\delta$ 155.7 (*C*=O), 137.4 ($C_{ipso}$, Ph), 129.3, 128.1, 126.3 (*o*-, *m*- and *p*-carbons of Ph), 101.5 (C*H* of benzylidene), 98.4 (C-1), 79.3, 71.4, 69.4(C-2, C-3, C-4), 67.4 (C-6), 62.4 (C-5), 55.3 ($OCH_3$), 40.8 ($NCH_2$), 29.4, 25.4, 25.3 (chain $CH_2$).

### 3.3. Polymer characterisation

$^1H$ and $^{13}C$ NMR spectra were recorded on a Brüker MSL 300 P spectrometer operating at 300.13 and 75.47 MHz, for

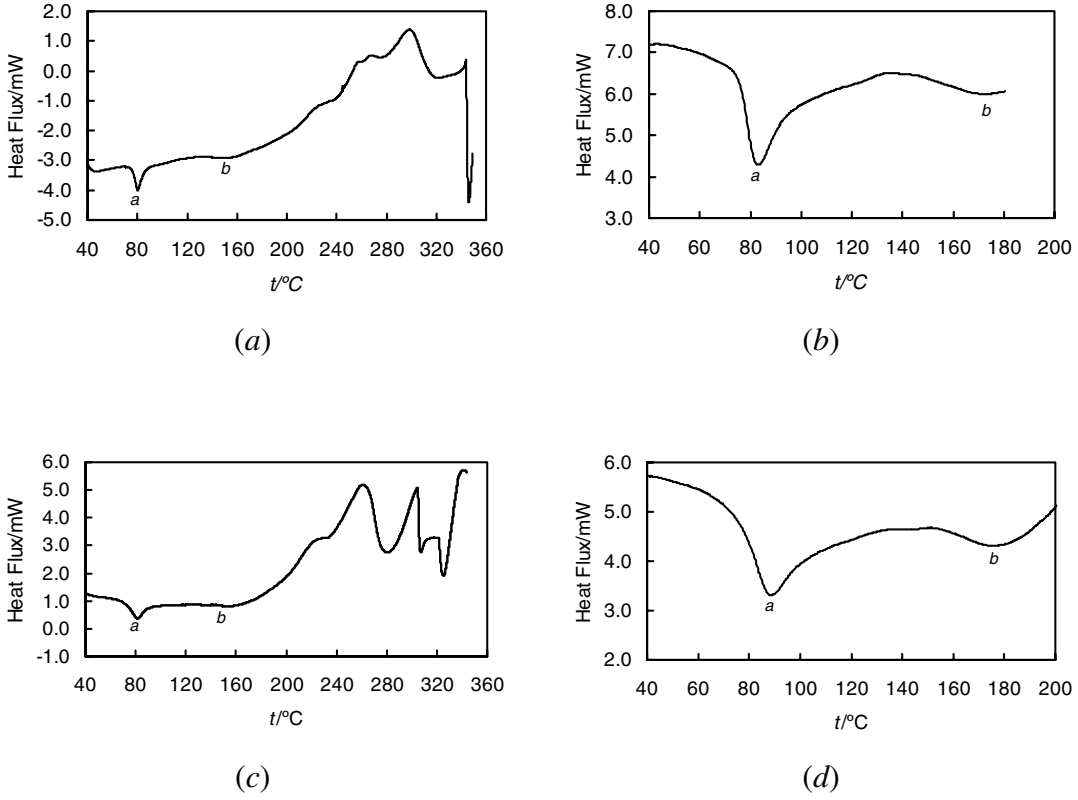



Fig. 3. Differential scanning calorimetry analysis of **4** and **5**. (a) **4**: $m = 7.25$ mg; heating rate = 5°C $min^{-1}$; $t_a = 80$°C; $t_b = 150$°C (onset of the transition at 135°C). (b) **4**: $m = 8.67$ mg; heating rate = 20°C $min^{-1}$; $t_a = 83$°C; $t_b = 167$°C (onset of the transition at 147°C). (c) **5**: $m = 8.31$ mg; heating rate = 5°C $min^{-1}$; $t_a = 81$°C; $t_b = 154$°C (onset of the transition at 140°C). (d) **5**: $m = 7.14$ mg; heating rate = 20°C $min^{-1}$; $t_a = 89$°C; $t_b = 176$°C (onset of the transition at 155°C).

$^{1}H$ and $^{13}C$ observation, respectively. Tetramethylsilane was used as internal standard for the chemical shift reference. In order to facilitate the assignment of the signals, $^{1}H$-2D-COSY and $^{13}C$-DEPT were run. IR spectra were recorded on an FT-IR Hitachi 270-50 and optical rotations were determined with a polarimeter Perkin Elmer 343.

Molecular weight measurements of **4** and **5** were determined by GPC on a Waters 150 CV chromatograph, at 30°C. A series of three columns Waters Ultrastyragel HR-1, HR-3 and HR-4 (10 μm; $30 \times 0.8$ cm) were used, and the eluent was THF at a flow rate of $1\ cm^3\ min^{-1}$. The calibration was made using polystyrene standards (TSK Tosoh Co.).

The DSC analysis of the samples of **4** and **5** (60 h) were made with a DSC 121 from Setaram. The samples with masses of ca. 7–9 mg, were sealed in aluminium crucibles and studied at heating rates of 5 or $20°C\ min^{-1}$. Argon was used as the purging gas. A Leica Galen III melting point apparatus was used to observe the physical changes occurring in the polymers as a function of the temperature; a heating rate of $4°C\ min^{-1}$ was selected in this case.

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