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A new route to polyurethanes from ethylene carbonate, diamines and diols

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Abstract

A new method of the synthesis of aliphatic polyurethanes from diamines and diols or alternatively from α,ω-aminoalcohols using ethylene carbonate as a substitute of phosgene is presented. It has been found that the transurethanisation reaction between α,ω-bis(2-hydroxyethoxy-carbonylamino)alkanes and diols containing six or more carbon atoms in a molecule carried out in the presence of tin coordination catalysts, leads to [*n*,*m*]polyurethane, and ethylene glycol formed as a side-product. In the case of using aminoalcohols, the reaction with ethylene carbonate leads to [*n*]polyurethanes. The polymerisation products were analysed by means of ^{1}H and ^{13}C NMR spectroscopy, as well as MALDI-TOF mass spectrometry. The influence of the reaction conditions on the chemical structure of the reaction products and a plausible reaction mechanism are discussed.

Keywords: Polyurethanes; Poly(urethane–urea)s; Ethylene carbonate

1. Introduction

The chemistry of polyurethanes and poly(urea–urethane)s is extensive and well developed. A comprehensive study of the polyurethanes was made by Otto Bayer [1]. Typically, polyurethanes and polyureas are obtained in the reaction of diisocyanate with compounds having at least two reactive hydrogen atoms such as oligomers terminated with hydroxyl (polyol) or amine groups. Usually polyester, polyether, or polycarbonate are used as polyol reagents. The resulting prepolymer is reacted with chain extenders, such as low molecular diols or diamines, and polyurethane of high molecular weight is formed [2–4].

Alternatively, polyurethanes can be prepared according to non-isocyanate methods. Thus, oligomers terminated with five-membered cyclic carbonate groups are reacted with diamines. The reaction product contains, additionally, hydroxyl groups in β-position (Scheme 1) [5–11].

Another non-isocyanate synthetic method, leading to urethane species, involves the reaction of vinyl carbonates with amines. The driving force of the whole process is the transformation of the side-product—vinyl alcohol to acetic aldehyde [12].

Alternatively, aliphatic polyurethanes can be prepared according to a chain growth polymerisation method, employing ring-opening polymerisation of aliphatic cyclic urethanes [13–22]. Hall and Schneider have used NaH and *N*-acetyl-ε-caprolactam as polymerisation catalysts [23].

It was shown that other cyclic derivatives of carbonic acid (cyclic carbonates) could also be used for preparation of aliphatic polyurethanes. These polymers were obtained employing copolymerisation of tetramethylene urea with six- [24,25] or five-membered [24] cyclic carbonates. Five-membered ethylene carbonate, due to ecological and economic reasons (ethylene carbonate is easily available from ethylene oxide and carbon dioxide), seems to be a very attractive monomer and reagent. It is worth mentioning that the homopolymerisation of ethylene carbonate is impossible, due to the high positive polymerisation enthalpy (125.6 kJ/mol). However, at higher temperature (>170 °C) low molecular weight poly(ethercarbonate) is formed with lower than 50 mol% carbonate linkages retention [26].

Recently, an effective method of polyurethane preparation has been reported by Versteegen et al. [27]. High molecular weight polymers were obtained using α,ω-aminoalcohols and di-*tert*-butyltricarbonate as a source of carbonyl group for urethane linkages. Aminoalcohols containing more than three carbon atoms in a molecule lead to linear products, but not cyclic urethane.

In this paper, we report on the investigation of the synthetic aspects of obtaining polyurethanes from diamines, and diols or alternatively from α,ω-aminoalcohols, using ethylene carbonate as a substitute for phosgene. To further the study, we have performed the structural characterisation of polyurethanes by MALDI-TOF mass spectrometry. This

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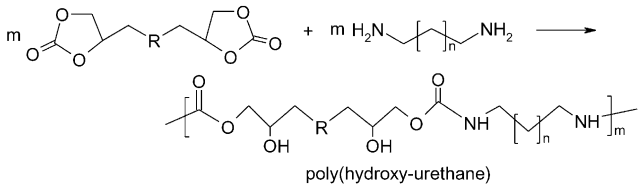


Scheme 1.

mass spectrometry is able to look at the mass of individual molecules in a mixture of homologues, and it is therefore specially suited for both structural and end-group analyses.

2. Experimental

2.1. Materials

Starting materials and reagents: ethylene carbonate (Aldrich), 1,4-butanediamine, 1,6-hexanediamine, 1,6-hexanediol, 1,10-decanediol, 3-amino-1-propanol, 4-amino-1-butanol, Bu_2SnO, $Bu_2Sn(OCH_3)_2$ were used as received. $BF_3{\cdot}OEt_2$ was purified by distillation. Solvents were dried by conventional methods and distilled under nitrogen.

2.2. Measurements

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian VXR 400 MHz spectrometer. Deuterated solvents were used and tetramethylsilane served as internal standard. IR spectra were recorded on Biorad FTIR spectrometer as KBr pellets. Polyurethanes MALDI-TOF spectra were recorded on a Kratos Kompact MALDI 4 V5.2.1 apparatus equipped with a 337 nm nitrogen laser with a 3 ns pulse duration. The measurements were carried out in the linear mode of the instrument at an acceleration voltage of +20 kV. For each sample, spectra were averaged over 200 laser shots. The samples were dissolved in DMF (5 mg/ml) and mixed with a solution of the MALDI-TOF matrix (2,5-dihydroxybenzoic acid, 0.2 M in THF). The laser power was moderated in the range 120–130 units characteristic for this apparatus, in order to avoid distortion of the mass spectrum. DSC thermograms over the temperature range −120 to 60 °C were recorded on a Perkin Elmer Pyris 1 calorimeter. The measurements were carried out at a heating rate of 20 °C/min. Sample weights were 10–25 mg.

2.3. Syntheses

2.3.1. Synthesis of 1,6-bis(hydroxyethyloxycarbonylamino)hexane (**2a**)

Ethylene carbonate (26.4 g, 0.3 mol), 1,6-hexanediamine (**1a**) (17.4 g, 0.15 mol) and 20 cm^3 of methylene chloride were stirred at room temperature up to disappearance of the absorption band at 1800 cm^{-1} in the IR spectrum of the sample. 38.4 g of **2a** were obtained (yield 94%). Mp 83.0–84.5 °C.

$C_{12}H_{24}N_2O_6$ (292.33) Calcd: C 49.30, H 8.27, N 9.58, O 32.84, found: C 49.19, H 8.32, N 9.54.

^{1}H NMR (DMSO-d_6, 25 °C): δ (ppm) = 1.21 (m, CH_2, 4H), 1.35 (m, CH_2, 4H), 2.93 (m, CH_2NH, 4H), 3.50 (t, J = 5.2 Hz, CH_2OH, 4H), 3.92 (t, J = 5.2 Hz, CH_2O, 4H), 4.67 (br, OH, 2H), 6.72 (br, NH, 0.4H), 7.05 (t, NH, 1.6H) two conformers.

^{13}C NMR (DMSO-d_6): δ (ppm) = 26.02 (CH_2), 29.45 (CH_2), 40.78 (CH_2NH), 59.57 (CH_2OH), 65.47 (CH_2O), 156.41 (C=O).

FTIR (KBr): 3330, 2950, 1687, 1535, 1464, 1340, 1269, 1221, 1139, 1056, 993, 782 cm^{-1}.

2.3.2. Synthesis of 1,4-bis(hydroxyethyloxycarbonylamino)butane (**2b**)

2b was obtained using a similar synthesis to **2a**. From 26.4 g (0.3 mol) of ethylene carbonate and 13.2 g (0.15 mol) of 1,4-butanediamine (**1b**) 33.7 g of **2b** were obtained after 6 h (yield 92%). Mp 81–82 °C.

$C_{10}H_{20}N_2O_6$ (264.28) Calcd: C 45.45, H 7.63, N 10.60, O 36.32, found: C 45.12, H 7.72, N 10.49.

^{1}H NMR (DMSO-d_6): δ (ppm) = 1.35 (m, CH_2, 4H), 2.94 (m, CH_2NH, 4H), 3.51 (t, J = 5.2 Hz, CH_2OH, 4H), 3.92 (t, J = 5.2 Hz, CH_2O, 4H), 4.66 (m, OH, 2H), 6.72 (br, NH, 0.4H), 7.08 (t, J = 5.6 Hz, NH, 1.6H).

^{13}C NMR (DMSO-d_6): δ (ppm) = 26.2 (CH_2), 29.78 (CH_2NH), 59.49 (CH_2OH), 65.42 (CH_2O), 156.34 (C=O).

FTIR (KBr): 3344, 2929, 1693, 1544, 1456, 1260, 1151, 1074, 891, 779 cm^{-1}.

2.3.3. Synthesis of [6,6]polyurethane (**4ax**)

In a 250 cm^3 three-necked flask, equipped with a mechanical stirrer, reflux condenser, thermometer and Barrett type receiver, 1,6-bis(hydroxyethyloxycarbonyloxy-amino)hexane (**2a**) (14.61 g, 0.05 mol), 1,6-hexanediol (**3x**) (5.90 g, 0.05 mol), Bu_2SnO (1.25 g, 5 mol%) and 20 cm^3 of xylene, as the azeotropic solvent, were placed. The reaction of the ethylene glycol exchange was carried out at 145–150 °C, collecting glycol as an azeotrope with xylene in a Barret receiver. After 5 h 2.6 cm^3 of glycol was collected, and the azeotropic solvent evaporated under vacuum. The product was dissolved in 15 cm^3 of hot DMF and precipitated by pouring the solution into 10 cm^3 of methanol/water (1:1). The polymer **4ax** was washed with 10 cm^3 of methanol/water and dried under vacuum at 60 °C. Yield 66%. M_n = 3500; M_w/M_n = 1.8.

^{1}H NMR (DMSO-d_6): δ (ppm) = 1.23–1.37 (m, CH_2), 1.52 (m, CH_2), 2.95, 2.93 (dt, J = 6.2 Hz each, CH_2NH), 3.37, 3.38 (dt, J = 6.2 Hz each, CH_2OH), 3.91 (t, J = 6.2 Hz, CH_2O), 4.18 (m, CH_2OH), 5.62 (m, NHC(O)NH), 6.84 (br. s, NH).

^{13}C NMR (DMSO-d_6): δ (ppm) = 24.89–25.89 (CH_2), 28.45 (NHC(O)NH*C*H$_2$), 29.19 (NH*C*H$_2$), 32.23 (HOCH$_2$*C*H$_2$),

60.48 ($HOCH_2$), 63.26 ($C(O)OCH_2$), 156.12 (C=O), 157.95 (NHC(O)NH).

FTIR (KBr): 3326, 2938, 1686, 1537, 1480, 1262, 1145, 1057, 1000, 779 cm^{-1}.

2.3.4. Synthesis of [4,10]polyurethane (*4bz*)

Polyurethane **4bz** was obtained using a similar synthesis to **4ax**. From 13.2 g (0.05 mol) of 1,4-bis(hydroxyethyloxycarbonyloxyamino)butane (**2b**) and 8.7 g (0.05 mol) of 1,10-decanediol (**3z**), 8.9 g of polyurethane (**4bz**) were obtained (yield 60%). $M_n = 1600$; $M_w/M_n = 1.9$.

^{1}H NMR (DMSO-d_6): δ (ppm) = 1.23–1.38 (m, CH_2), 1.49 (m, CH_2), 2.92 (br, CH_2NH), 3.37–3.38 (m, CH_2OH), 3.88 (m, $CH_2OC(O)$), 4.32 (m, CH_2O), 4.45 (m, CH_2O), 5.73 (m, NHC(O)NH), 6.72 (br, NH), 7.04 (br. s, NH).

^{13}C NMR (DMSO-d_6): δ (ppm) = 24.89–25.89 (CH_2), 28.45 ($NHC(O)NHCH_2$), 29.19 ($NHCH_2$), 32.23 ($HOCH_2CH_2$), 60.48 ($HOCH_2$), 63.26 ($C(O)OCH_2$), 156.12 (C=O), 157.95 (NHC(O)NH).

FTIR (KBr): 3323, 2925, 1687, 1540, 1469, 1262, 1061, 893, 779 cm^{-1}.

2.3.5. Synthesis of 3-(hydroxyethyloxycarbonylamino)-1-propanol (*6c*)

Ethylene carbonate (26.4 g, 0.3 mol), 3-amino-1-propanol (**5c**) (22.5 g, 0.3 mol) and 30 cm^3 of methylene chloride were added together and stirred at room temperature. The resulting powder was filtered off and washed with 30 cm^3 of cold CH_2Cl_2. 47.0 g of white crystals of **6c** were obtained (yield 96%). Mp 78–79.5 °C.

$C_6H_{13}NO_4$ (163.17) Calcd: C 44.17, H 8.03, N 8.58, O 39.22, found: C 44.12, H 8.28, N 8.49.

^{1}H NMR (DMSO-d_6): δ (ppm) = 1.52 (m, CH_2, 2H), 3.00 (dt, $J = 5.2$ Hz each, CH_2NH, 2H), 3.38 (m, CH_2OH, 2H), 3.51 (t, $J = 5.2$ Hz, CH_2OH, 2H), 3.92 (t, $J = 5.2$ Hz, $CH_2OC(O)$, 2H), 6.63 (br, NH, 0.2H), 7.01 (t, $J = 5.2$ Hz, NH, 0.8H).

^{13}C NMR (DMSO-d_6): δ (ppm) = 21.06 (CH_2), 32.77 (CH_2NH), 58.60 (CH_2OH), 59.67 (CH_2OH), 65.62 (CH_2O), 156.57 (C=O).

FTIR (KBr): 3337, 2948, 1694, 1538, 1453, 1264, 1148, 1076, 1048, 889, 777 cm^{-1}.

2.3.6. Synthesis of trimethylene urethane (tetrahydro-2H-1,3-oxazin-2-one, **7c**)

In a 100 cm^3 three-necked flask equipped with a mechanical stirrer, reflux condenser, thermometer and Barrett type receiver, 32.6 g (0.2 mol) of **6c**, 0.15 g (0.5 mmol, 0.25 mol%) of $Bu_2Sn(OCH_3)_2$ and 20 cm^3 of xylene as an azeotropic solvent were placed. The reaction was carried out at 160–170 °C, collecting ethylene glycol in a Barret receiver. After 4 h ca. 9.5 cm^3 of the glycol was collected and the azeotropic solvent evaporated under vacuum. The final product was isolated by distillation under vacuum and collecting the fraction boiling at 141 ± 1 °C/0.01 mbar. After crystallisation from butyl acetate/acetone (5:2) and sublimation 12.9 g of cyclic urethane (**7c**) were obtained (yield 64%). Mp 82–83 °C.

$C_4H_7NO_2$ (101.10) Calcd: C 47.52, H 6.98, N 13.85, O 31.65, found: C 47.36, H 7.11, N 13.62.

^{1}H NMR (DMSO-d_6): δ (ppm) = 1.79 (m, CH_2, 2H), 3.13, 3.14 (dt, $J = 2$ Hz, CH_2NH, 4H), 4.13 (t, $J = 5.6$ Hz, CH_2O, 2H), 7.11 (s, NH, 1H).

^{13}C NMR (DMSO-d_6): δ (ppm) = 21.12 (CH_2), 29.34 (CH_2NH), 66.32 (CH_2O), 153.00 (C=O).

FTIR (KBr): 3273, 2910, 1694, 1493, 1427, 1298, 1226, 1119, 1077, 949, 813, 765 cm^{-1}.

2.3.7. Synthesis of 4-(hydroxyethyloxycarbonylamino)-1-butanol (*6d*)

The synthesis of **6d** was carried out in a similar manner to that of **6c**. From 8.8 g (0.1 mol) of ethylene carbonate and 8.9 g (0.1 mol) of 4-amino-1-butanol (**5d**), 17.1 g of 4 (hydroxyethyloxycarbonylamino)-1-butanol were obtained (yield 97%).

$C_7H_{15}NO_4$ (177.20) Calcd: C 47.45, H 8.53, N 7.90, O 36.12, found: C 47.36, H 8.69, N 7.81.

^{1}H NMR (DMSO-d_6): δ (ppm) = 1.38 (m, CH_2, 2H), 2.95 (m, CH_2NH, 2H), 3.31 (m, CH_2OH, 2H), 3.51 (dt, $J = 5.2$ Hz each, CH_2OH, 2H), 3.91 (t, $J = 5.2$ Hz, $CH_2OC(O)$, 2H), 4.37 (t, $J = 5.2$ Hz, OH, 1H), 4.69 (t, $J = 5.2$ Hz, OH, 1H), 6.72 (br, NH, 0.2H), 7.10 (t, $J = 5.2$ Hz, NH, 0.8H).

^{13}C NMR (DMSO-d_6): δ (ppm) = 26.16 (CH_2), 29.79 (CH_2NH), 59.49 (CH_2OH), 60.44 (CH_2OH), 65.39 (CH_2O), 156.33 (C=O).

FTIR (KBr): 3339, 2945, 1699, 1543, 1453, 1261, 1042, 891, 644 cm^{-1}.

2.3.8. Synthesis of tetramethylene urethane (hexahydro-1,3-oxazepin-2-one, *7d*)

7d was obtained in a similar manner to that of **7c**. **7d** was obtained from 11.5 g (100 mmol) of **6d**, after distillation under vacuum and collecting the fraction boiling at 155 ± 1 °C/0.01 mbar (yield 10%). Mp 92–93 °C.

$C_5H_9NO_2$ (115.13) Calcd: C 52.16, H 7.88, N 12.17, O 27.79, found: C 51.97, H 7.92, N 11.90.

^{1}H NMR (DMSO-d_6): δ (ppm) = 1.57 (m, CH_2, 2H), 1.73 (m, CH_2, 2H), 2.94 (m, CH_2NH, 2H), 3.96 (m, CH_2O, 2H), 7.15 (br. s, NH, 1H).

^{13}C NMR (DMSO-d_6): δ (ppm) = 26.1–26.6 (CH_2), 29.7 (CH_2NH), 63.3 (CH_2O), 156.3 (C=O).

FTIR (KBr): 3344, 2943, 1699, 1475, 1314, 1279, 1232, 1123, 1048, 997, 859, 803 cm^{-1}.

2.4. Polymerisation of cyclic urethanes

2.4.1. Poly(trimethylene urethane) (*8c*)

Trimethylene urethane (**7c**) was polymerised according to the method reported by Neffgen et al. [19], using $BF_3{\cdot}OEt_2$ as a catalyst at 100 °C for 10 h. The product (**8c**) was dissolved in DMF and precipitated in methanol (yield 60%).

^{1}H NMR (DMSO-d_6): δ (ppm) = 1.65–1.66 (m, CH_2), 3.0 (m, CH_2NH), 3.37–3.38 (m, CH_2OH), 3.91 (m, CH_2O), 6.79, 7.13 (s, NH) two conformers.

^{13}C NMR (DMSO-d_6): δ (ppm) = 21 (CH_2), 29.2 (CH_2NH), 58.4 (CH_2OH), 61.5 (CH_2O), 156.3 (C=O).

FTIR (KBr): 3297, 2932, 1713, 1687, 1552, 1480, 1445, 1338, 1260, 1155, 1035, 919, 875 cm^{-1}.

2.4.2. Poly(tetramethylene urethane) (**8d**)

Tetramethylene urethane (**7d**) was polymerised in a similar manner to that of **7c** to give 5.1 g of [4] polyurethane **8d** (yield 57%).

^{1}H NMR (DMSO-d_6): δ (ppm) = 1.36–1.5 (m, CH_2), 2.92–2.96 (m, CH_2NH), 3.5 (m, CH_2OH), 3.87–3.9 (m, CH_2O), 4.4.7 (t, J = 5.2 Hz, OH), 6.76 (br, NH), 7.10 (t, J = 5.2 Hz, NH, 0.8H).

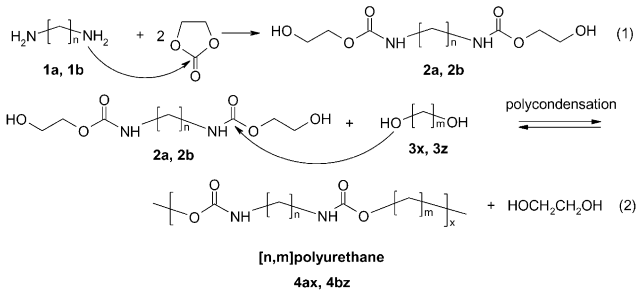
^{13}C NMR (DMSO-d_6): δ (ppm) = 26.1–26.6 (CH_2), 29.8 (CH_2NH), 60.42 (CH_2OH), 63.3 (CH_2O), 156.3 (C=O, 1C).

FTIR (KBr): 3339, 2945, 1699, 1543, 1453, 1261, 1042, 891, 644 cm^{-1}.

3. Results and discussion

3.1. Synthesis of α,ω-bis(hydroxyethyloxycarbonylamino)-alkane monomers and their polycondensation with diols

1,6-Bis(hydroxyethyloxycarbonylamino)hexane (**2a**) was obtained in a high yield (>94%) in the reaction of ethylene carbonate with 1,6-hexanediamine (**1a**) carried out at room temperature without any catalyst (Eq. (1), n = 6, Scheme 2). When the reaction was carried out in methylene chloride, the reaction product precipitated as a white powder. After 30–40 min in the IR spectrum of the liquid phase, there was



Scheme 2.

no absorption band characteristic for a carbonyl group of five-membered cyclic carbonate (1800 cm^{-1}). In the ^{1}H NMR spectrum of the reaction product, recorded at room temperature, two signals of NH groups (7.08 and 6.72 ppm, respectively) of the intensity ratio 8:2 corresponding to pseudo E and Z urethane conformers were observed, similarly to the Neffgen et al. [19]. It was shown that the monomer purity was satisfactory for subsequent polycondensation with diols (Fig. 1). According to the same method, the reactions of ethylene carbonate with other alkanediamines, e.g. 1,4-butanediamine (**1b**) (n = 4) were carried out (Eq. (1), Scheme 2).

3.2. Polycondensation

It is known that, depending on the chemical structure, urethanes decompose at different temperatures [28]. The most susceptible to thermal decomposition are aromatic urethanes (ca. 120 °C), and the least susceptible are aliphatic ones (ca. 250 °C). However, it was shown that in the presence of tin catalysts, such as $Bu_2Sn(OCH_3)_2$ or

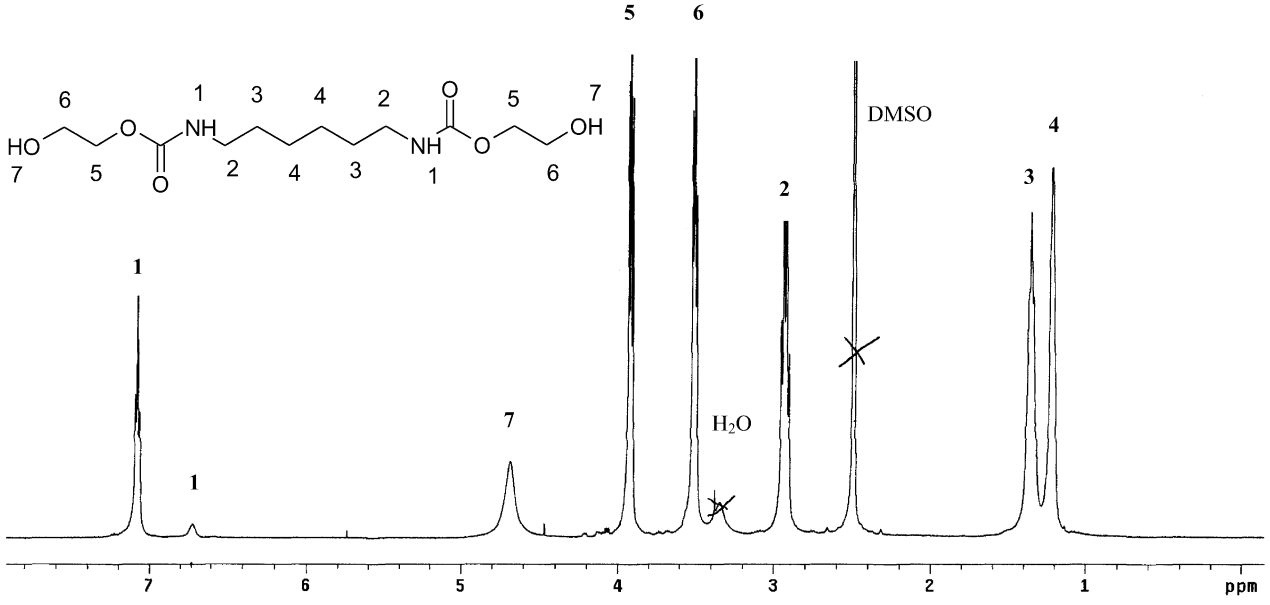


Fig. 1. ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 25 °C) of 1,6-bis(hydroxyethyloxycarbonylamino)hexane (**2a**) obtained in the reaction of 1,6-hexanediamine (**1a**) with ethylene carbonate.

Table 1
Results and conditions of the polycondensation of **2a** and **2b** with diols (**3x** and **3z**) using xylene as azeotropic solvent for the glycol removing from the reaction system (reaction temperature 145–150 °C)

No.	2	3	Catalyst[a] (mol%)	Time (h)	MALDI-TOF		Yield (%)
					M_n	M_w/M_n	
1	**a**	**x**	5	5	3500	1.8	66
2	**a**	**x**	5	5	2800	1.8	62
3	**b**	**z**	5	6	1600	1.9	59
4	**b**	**z**	5[b]	6	1580	1.9	57.5

[a] Bu_2SnO was used as a catalyst.
[b] $Bu_2Sn(OCH_3)_2$ was used as a catalyst.

Bu_2SnO, the glycol exchange reaction can be carried out at relatively low temperature (ca. 150 °C).

Taking into account that the equilibrium constant of the transurethanisation is rather small, an effective method of removing small amounts of ethylene glycol is a decisive parameter of the polyurethane formation.

It was found that the polycondensation of α,ω-bis(hydroxyethyloxycarbonylamine) alkane with α,ω-diols containing six or more carbon atoms in a molecule ($m \geq 6$) led to [*n*,*m*]polyurethane (Eq. (2), Scheme 2) (Table 1). The reaction was carried out using azeotropic solvent (xylene) that enabled continuous removal of ethylene glycol, formed as a by-product, from the reaction system.

The chemical structure of the polyurethanes obtained by the transurethanisation method was confirmed by spectroscopic (^1H, ^{13}C NMR, FTIR) as well as MALDI-TOF mass spectrometric analyses. Thus, in the MALDI-TOF mass spectrum (Fig. 2) of [6,6]polyurethane (**3ax**), obtained from ethylene carbonate, 1,6-hexanediamine (**1a**) and 1,6-hexanediol (**3x**), in the presence of Bu_2SnO as a catalyst, the series of peaks (a) ($M_n = 1750$ Da) are assigned to the adducts of sodium ion with polyurethane molecules. There is the counterpart series corresponding to the H^+ adducts (a′). The mass increment between these two series of peaks is 22 Da.

These series of peaks characterised by mass increment of 286 Da from one peak to the next is equal to the mass of the repeating unit (U) in the [6,6]polyurethane. The above-mentioned series of peaks corresponds to polyurethane molecules terminated with 1,6-hexanediol (residual mass: 118 Da) (a and a′). The series b and b′ correspond to [6,6]polyurethane molecules containing, additionally, one urea unit (M) in a molecule (residual mass: 260 Da). The presence of the urea unit in some of the polyurethane macromolecules was additionally confirmed by ^1H and ^{13}C NMR spectroscopic analyses. In the ^1H NMR spectrum, besides the signal of the NH urethane group (6.84 ppm), there is the signal of much lower intensity corresponding to the NH urea group (5.62 ppm) (Fig. 3). In the ^{13}C NMR spectrum, two signals corresponding to the carbon atoms of urethane C=O group (156.2 ppm) and urea C=O group (157.9 ppm) can also be seen.

These urea units can be formed in the back-biting reaction of the hydroxyl group of a hydroxyethyloxycarbonylamine

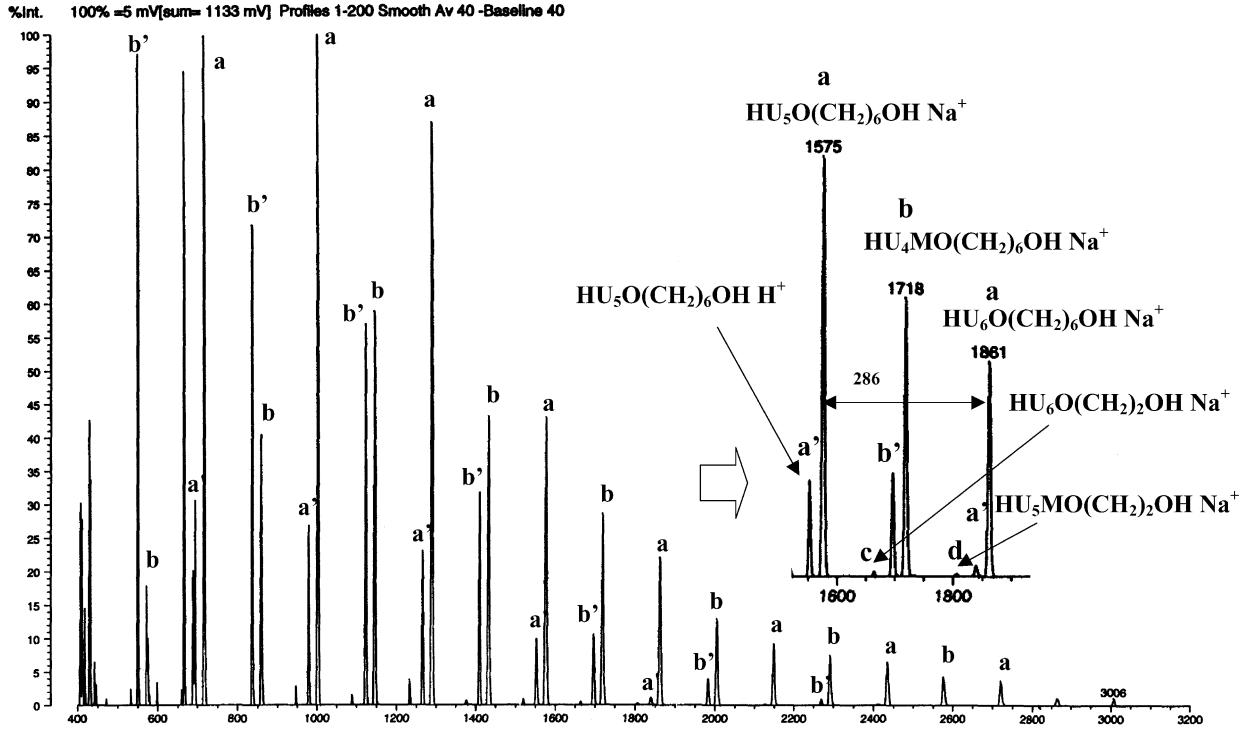


Fig. 2. MALDI-TOF mass spectrum of [6,6]polyurethane (**4ax**), obtained from ethylene carbonate, 1,6-hexanediamine (**1a**) and 1,6-hexanediol (**3x**) in the presence of Bu_2SnO, using xylene as azeotropic solvent. U = $O(CH_2)_6OC(O)NH(CH_2)_6NHC(O)$. M = $O(CH_2)_6OC(O)NH(CH_2)_6NHC(O)NH(CH_2)_6NHC(O)$.

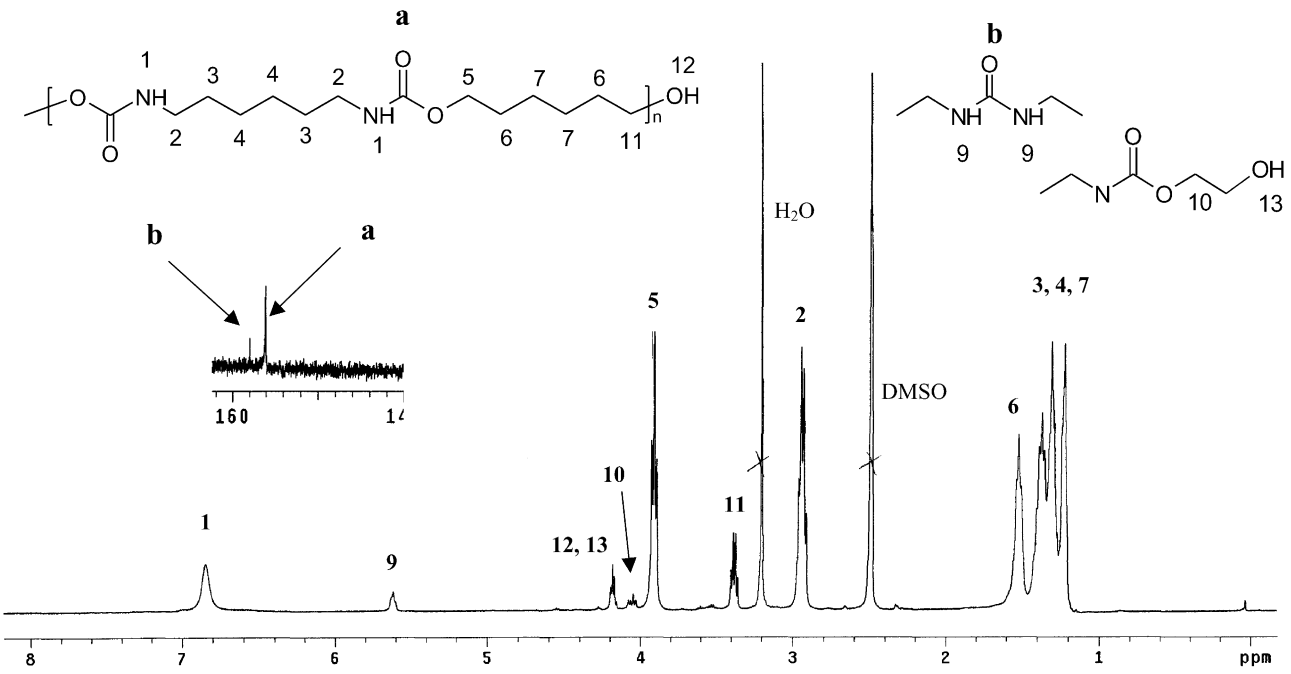


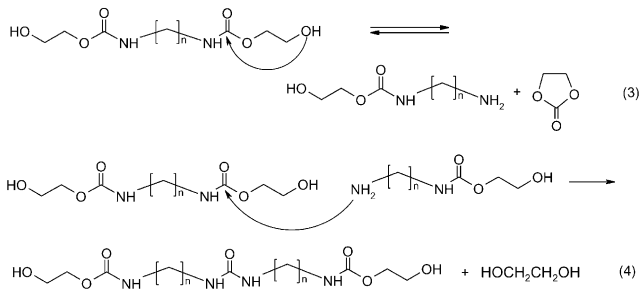
Fig. 3. ^{1}H NMR spectrum and fragment ^{13}C NMR spectrum (400 MHz, DMSO-d_6, 25 °C) of [6,6]polyurethane (**4ax**), obtained from ethylene carbonate, 1,6-hexanediamine (**1a**) and 1,6-hexanediol (**3x**) in the presence of Bu_2SnO, using xylene as azeotropic solvent.

moiety, with the nearest urethane linkage leading to ethylene carbonate and amine end group (Eq. (3), Scheme 3). The resultant amine can react with another hydroxyethyloxycarbonylamine moiety to yield urea linkages and ethylene glycol (Eq. (4), Scheme 3).

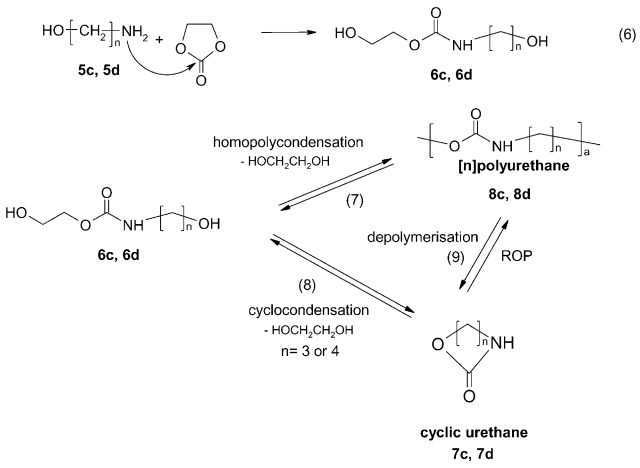
In the MALDI-TOF mass spectrum, the series of the signals (c and d) of minor intensity are also present (residual mass: 206 and 62 Da, respectively). These signals can be assigned to macromolecules terminated with unreacted hydroxyethyloxycarbonylamine groups (Fig. 2).

As far as concerns other diamines and diols used in the reaction with ethylene carbonate, similar results were obtained (Table 1). In the MALDI-TOF mass spectrum of the [4,10]polyurethane (**4bz**) obtained from 1,4-butanediamine (**1b**) and 1,10-decanediol (**3z**), besides the series of peaks (a and a′) corresponding to [4,10]polyurethane molecules and those containing an urea unit (b and b′), there were series of peaks corresponding to the molecules containing hydroxyethyloxycarbonylamine terminal groups (c, c′, d and d′) (Fig. 4). In the ^{1}H NMR spectrum of the reaction product, there are signals corresponding to CH_2 groups originated from ethylene glycol (4.06 ppm) neighbouring to urethane linkages. The higher intensity of the signals was due to the lower molecular weight of the polymer in which not all ethylene glycol residues were exchanged for 1,10-decanediol.

The glass transition temperatures and melting points of aliphatic polyurethanes were in the same range as those prepared using α,ω-aminoalcohols and di-*tert*-butyltricarbonate [27]. The polyurethane (**4ax**) obtained from **1a** and **3x** exhibits the glass transition temperature (T_g) 18.5 °C and melting point (T_m) 141.5 °C.



Scheme 3.



Scheme 4.

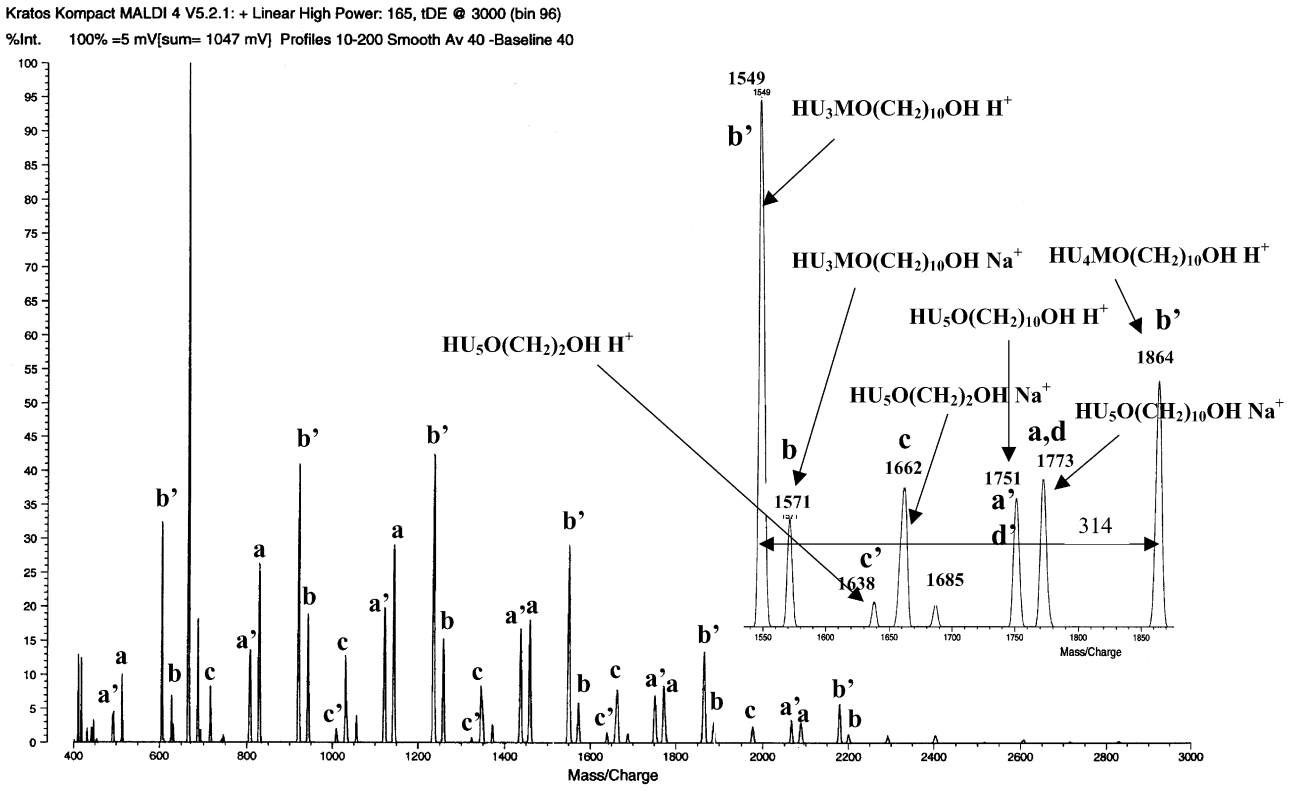


Fig. 4. MALDI-TOF mass spectrum of [4,10]polyurethane (**4bz**), obtained from ethylene carbonate, 1,4-butanediamine (**1b**) and 1,10-decanediol (**3z**) in the presence of Bu_2SnO, using xylene as azeotropic solvent. U = $O(CH_2)_{10}OC(O)NH(CH_2)_4NHC(O)$. M = $O(CH_2)_{10}OC(O)NH(CH_2)_4NHC(O)NH(CH_2)_4NHC(O)$.

3.3. Syntheses of cyclic urethane monomers and their polymerisation

Ethylene carbonate can also be used for the preparation of six- and seven-membered cyclic urethanes. These cyclic urethanes were obtained in the reaction of ethylene carbonate with appropriate α,ω-aminoalcohols. Thus, in the first step 3-(hydroxyethyloxycarbonylamino)-1-propanol (**6c**) was prepared from 3-amino-1-propanol (**5c**) and ethylene carbonate (Eq. (6), Scheme 4).

The synthesis of cyclic monomers **7c** and **7d** was carried out using an azeotropic solvent (xylene) that enables removal of ethylene glycol from the reaction system as a by-product formed in the intramolecular and intermolecular transurethanisation reactions (Eqs. (8) and (7), Scheme 4). The condensation was carried out in the presence of tin catalyst [$Bu_2Sn(OCH_3)_2$, Bu_2SnO] at relatively low temperature (140–150 °C), to reduce the possibility of side reactions. Additionally, the dilution of the reaction system with xylene favoured the cyclic urethane formation.

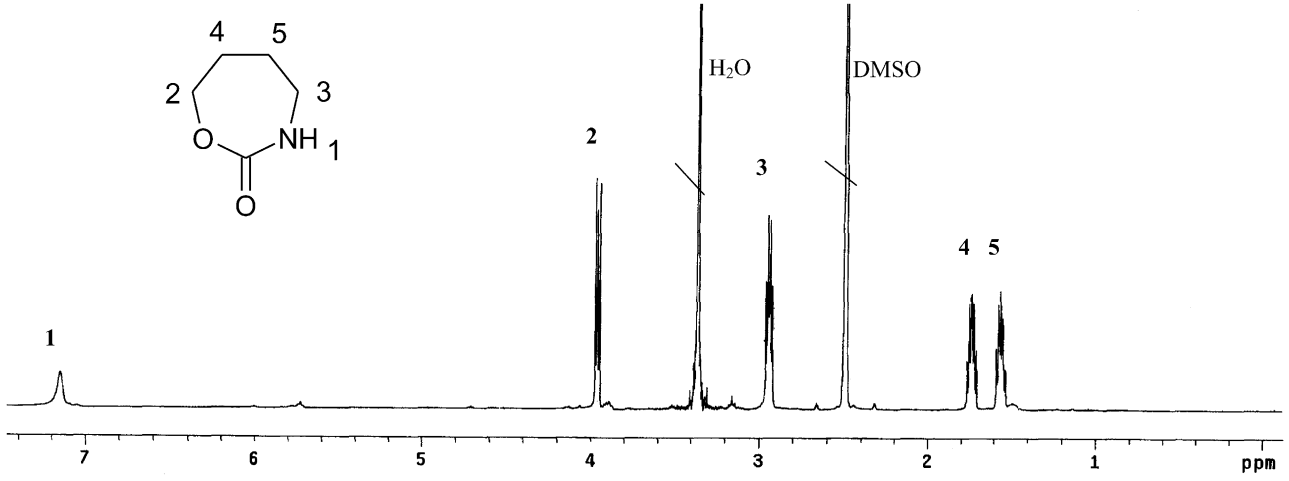


Fig. 5. ^1H NMR spectrum (400 MHz, DMSO-d_6, 25 °C) of tetramethylene urethane (**7d**) obtained from ethylene carbonate and 4-aminobutanol-1 (**5d**).

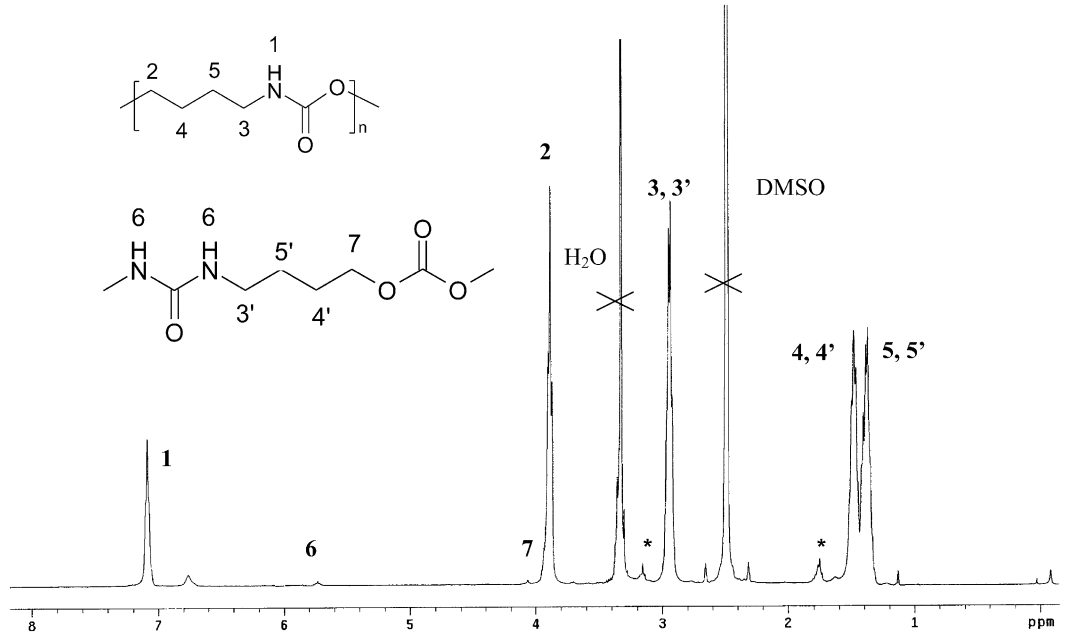


Fig. 6. ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 45 °C) of the tetramethylene urethane polymerisation product (**8d**). (*) resonance of N-substituted pyrrolidyne end groups.

Thus in the next step, a lower amount of oligourethanes was needed to be depolymerised towards cyclic urethane (Eq. (9), Scheme 4). The depolymerisation process was carried out at 160 °C, under reduced pressure. In contrast to six-membered cyclic urethane, the yield of the seven-membered cyclic urethane (hexahydro-1,3-oxazepin-2-one, **7d**), due to lower stabilisation of the seven-membered ring, was rather low (ca. 10%). In the case of using aminoalcohol with five and more carbon atoms in a molecule, only linear products were formed (Eq. (7), Scheme 4).

The cyclic structure of **7d** was confirmed by spectroscopic analysis. In the ^{1}H NMR spectrum, there is only one signal corresponding to NH group (one conformer) (Fig. 5).

Polymerisation of cyclic urethanes **7c** and **7d**, carried out in the presence of $BF_3{\cdot}OEt_2$, led to the polyurethanes of the chemical structures similar to those obtained earlier by the Höcker group [19,22]. However, in the ^{1}H NMR spectrum of the polymerisation product, besides urethane-NH signals, there are signals assigned to the urea groups, which indicate that head-to-head connected repeating units are present in the polymer chains (Fig. 6).

4. Conclusions

Ethylene carbonate, easily available from ethylene oxide and CO_2, can be used for polyurethane production excluding hazardous monomers such as phosgene and isocyanates. The transurethanisation reaction of α,ω-bis(hydroxyethyloxycarbonylamine)alkanes with longer chain diols leads to [*n*,*m*]polyurethanes, whereas the ring-opening-polymerisation of six- or seven-membered cyclic urethane leads to [*n*]polyurethanes.

Acknowledgements

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