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Novel intramolecular blocked isocyanates as stable one-component systems for poly(urea urethane)s

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Abstract

Several poly(urea urethane) oligomers **14a–e** were prepared by polycondensation of *N*-(hydroxyalkyl)-2-oxo-1,3-diazepane-1-carboxamides **11a–e** in bulk. The latter compounds were obtained under mild reaction conditions from a novel type of activated urethane/intramolecular blocked isocyanate **8** and a homologous series of amino alcohols. The influence of several catalysts (DABCO, $Sn(octoate)_2$, and Bu_2Mg) and reaction temperatures (100–150 °C) on molecular weight and microstructure of the polymers obtained was studied. The poly(urea urethane)s are semicrystalline materials and their melting points show the odd/even effect observed earlier for [*n*]-polyamides, [*n*]-polyurethanes, poly(ester amide)s, and poly(amide urethane)s. TGA analysis showed that the polymers are stable up to approximately 205–230 °C, the polymers with lower number of methylene groups in the amino alcohol decomposing at the lowest temperature.

Keywords: Activated urethanes; Blocked isocyanates; Poly(urea urethane)s

1. Introduction

Commercially manufactured polyurethanes and polyureas are prepared from di- or polyfunctional isocyanates with di- or polyfunctional hydroxy compounds, or di- or polyfunctional amines, respectively [1,2]. The synthesis of well-defined alternating poly(urea urethane)s is difficult along this route. Polymers containing different groups, e.g., urethane, urea, allophanate, biuret, isocyanurate, and uretdione groups, will be formed in a random way.

Another possibility to prepare polyurethanes or polyureas is the reaction of blocked isocyanates with hydroxy or amino compounds [3,4]. The commonly used term 'blocked isocyanate' needs further explanation (Scheme 1). Compound **1** can be considered either as a blocked isocyanate or as an activated urethane if BH is split off. At high temperatures (>150 °C) elimination of the blocking agent BH leads to the free isocyanate **2**, which then reacts with a nucleophile to form the urethane or urea **3** (i.e., elimination followed by addition). At lower temperatures (<100 °C) addition of the nucleophile to compound **1**, an activated urethane, takes place to yield a tetrahedral intermediate **4** followed by elimination of the blocking agent BH (i.e., addition followed by elimination) [3,4]. Finally, the intramolecular blocked isocyanate **5** is a latent isocyanate which thermally yields the free isocyanate **6** while the blocking group, in the presence of nucleophiles, becomes part of the product **7** [5].

Typical blocking agents are phenols, oximes, alcohols, ε-caprolactam, 3,5-dimethylpyrazole, 1,2,4-triazole, and diethyl malonate [3]. Another simple method of blocking an isocyanate represents the reversible formation of uretdiones by dimerization of isocyanates in the presence of trialkylphosphine catalysts.

Recently, Mülhaupt and Loontjens et al. reported on the use of carbonylbiscaprolactam as a new very versatile, nontoxic reagent that converts terminal as well as pendant hydroxy and amino groups of functional polymers into the corresponding caprolactam-blocked isocyanates without requiring the use of isocyanates [6,7].

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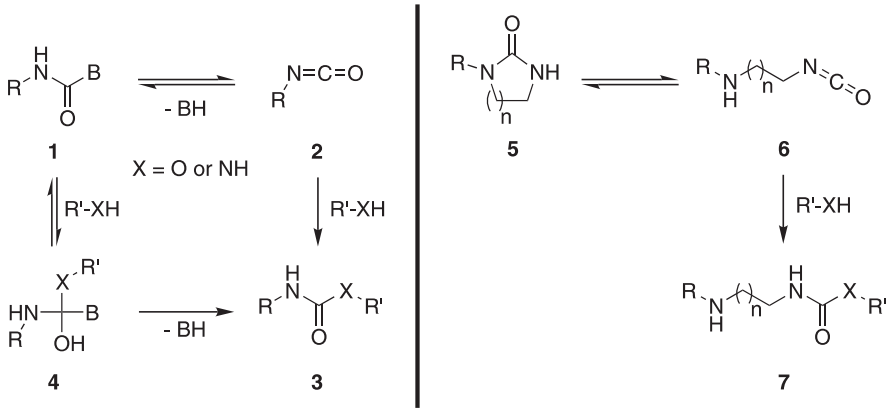


Scheme 1. Blocked isocyanates, activated urethanes, and intramolecular blocked isocyanates.

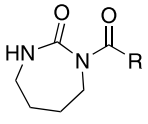
In our group activated urethanes, i.e., α-hydroxy-ω-*O*-phenyl urethanes obtained from a homologous series of amino alcohols and diphenyl carbonate were used to synthesize [*n*]-polyurethanes [8].

This paper describes the use of a novel type of 'blocked isocyanates', i.e., phenyl 2-oxo-1,3-diazepane-1-carboxylate, **8**, and ethyl 2-oxo-1,3-diazepane-1-carboxylate, **9**, in which the *O*-phenyl urethane or *O*-ethyl urethane is considered as an activated urethane and the 1,3-diazepan-2-one ring as an intramolecular blocked isocyanate (Fig. 1) [9]. In a condensation reaction of **8** with a homologous series of amino alcohols **10a–e**, new AB monomers, *N*-(hydroxyalkyl)-2-oxo-1,3-diazepane-1-carboxamides **11a–e**, were prepared (Fig. 1). The polycondensation of **11a–e** to result in alternating poly(urea urethane)s is investigated. The microstructure of the polymers obtained is determined by means of NMR spectroscopy, the molecular weight and molecular weight distribution by means of size exclusion chromatography (SEC), and the thermal properties by means of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

2. Experimental section

2.1. Materials

The synthesis of phenyl 2-oxo-1,3-diazepane-1-carboxylate, **8**, and tetramethylene urea (TeU) was described previously [9]. 2-Amino-1-ethanol (BASF), 3-amino-1-propanol (BASF), 4-amino-1-butanol (Acros Organics), 5-amino-1-pentanol (Fluka), 6-amino-1-hexanol (Fluka), formic acid (>99%, Merck), ethyl chloroformate (Acros Organics), triethylamine (Riedel de Haen), 1,4-diazabicyclo[2.2.2]octane (DABCO, Aldrich), tin(II) 2-ethylhexanoate ($Sn(octoate)_2$, Aldrich), and dibutylmagnesium (Bu_2Mg, Aldrich), 1.0 M solution in heptane, were used as received. Dichloromethane was distilled over phosphorus pentoxide before use. Where necessary, the reactions were conducted in a nitrogen atmosphere. Nitrogen (Linde) was passed over molecular sieves (4 Å) and finely distributed potassium on aluminum oxide for purification.



8: R = OPh
9: R = OEt

11a: R = $NH(CH_2)_2OH$
11b: R = $NH(CH_2)_3OH$
11c: R = $NH(CH_2)_4OH$
11d: R = $NH(CH_2)_5OH$
11e: R = $NH(CH_2)_6OH$

Fig. 1. The structures of **8**, **9**, and **11**.

2.2. Measurements

^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-300 FT-NMR spectrometer at 300 and 75 MHz, respectively. Either deuterated chloroform ($CDCl_3$) or dimethyl sulfoxide (DMSO-d_6) was used as a solvent, and tetramethylsilane (TMS) served as internal standard.

Size exclusion chromatography (SEC) analyses were carried out at 80 °C (Polymer Laboratories PL-GPC210 with a Bischoff HPLC compact pump) using a refractive index detector (Polymer Laboratories). The eluting solvent was *N*,*N*-dimethylacetamide (DMAc) with 2.44 g l^{-1} LiCl and a flow rate of 0.8 ml min^{-1}. Four columns with MZ-DVB gel were applied: length of each column, 300 mm; diameter, 8 mm; diameter of gel particles, 5 μm; nominal pore widths, 100, 100, 10^3, 10^4 Å. Calibration was achieved using polystyrene standards with a narrow molecular weight distribution.

Differential scanning calorimetric (DSC) analyses were performed on a Netzsch DSC 204 in a nitrogen atmosphere. All samples were annealed for 1 h at 170–180 °C. Heating and cooling rates of 10 K min^{-1} were applied. Calibration was achieved using indium standard samples.

Thermogravimetric analyses (TGA) were performed on a TG 209 with a TA system controller TASC 414/2 from Netzsch. The measurements were performed in a nitrogen atmosphere with a heating rate of 10 K min^{-1}.

C, H, and N elemental analysis was performed on a Heraeus CHN-O-Rapid Elementar Vario EL instrument.

Melting points were determined on a Büchi SMP 20.

2.3. Ethyl 2-oxo-1,3-diazepane-1-carboxylate, **9**

To a solution of tetramethylene urea (4.81 g, 42.1 mmol) and triethylamine (6.39 g, 63.1 mmol) in dichloromethane (50 ml), ethyl chloroformate (6.85 g, 63.1 mmol) was added dropwise over a period of 15 min at 50 °C with stirring. The reaction mixture was refluxed for 2 h. Cooling to room temperature and evaporation of the solvent yielded a mixture of amine hydrochloride and ethyl 2-oxo-1,3-diazepane-1-carboxylate, **9**. The mixture was treated with water (65 ml), stirred for 45 min, filtered, and dried. The product was purified by column chromatography (diethyl ether/ethyl acetate = 1/1) and dried under vacuum (10^{-2} mbar) at 50 °C. Yield: 6.37 g (34.2 mmol; 81%). Colorless crystals with a mp of 128 °C were obtained (Fig. 2).

^{1}H NMR ($CDCl_3$): $\delta = 1.30$ (t, 3H, H-9, $^3J = 7.2$ Hz), 1.66 (m, 2H, H-4), 1.75 (m, 2H, H-5), 3.21 (dt, 2H, H-3, $^3J = 5.0$ Hz), 3.62 (m, 2H, H-6), 4.24 (q, 2H, H-8, $^3J = 7.2$ Hz), 6.92 (t, 1H, H-2) ppm.

^{13}C NMR ($CDCl_3$): $\delta = 14.45$ (C-9), 27.39 (C-5), 27.75 (C-4), 42.82 (C-3), 45.49 (C-6), 62.36 (C-8), 153.97 (C-7), 160.14 (C-1) ppm.

^{1}H NMR (DMSO-d_6): $\delta = 1.17$ (t, 3H, H-9, $^3J = 7.1$ Hz), 1.51 (m, 2H, H-4), 1.58 (m, 2H, H-5), 2.98 (dt, 2H, H-3, $^3J = 5.0$ Hz), 3.42 (m, 2H, H-6), 4.09 (q, 2H, H-8, $^3J = 7.1$ Hz), 7.71 (t, 1H, H-2) ppm.

^{13}C NMR (DMSO-d_6): $\delta = 14.30$ (C-9), 27.25 (C-5), 27.37 (C-4), 41.54 (C-3), 44.38 (C-6), 61.24 (C-8), 153.35 (C-7), 157.61 (C-1) ppm.

Elemental analysis: Calcd C 51.60 H 7.58 N 15.05 $C_8H_{14}N_2O_3$ (186.2). Found C 51.35 H 7.93 N 15.99.

2.4. *N*-(Hydroxyalkyl)-2-oxo-1,3-diazepane-1-carboxamides ***11a–e***

General procedure. Phenyl 2-oxo-1,3-diazepane-1-carboxylate **8** (1.56 g, 6.66 mmol) in dichloromethane (15 ml) was treated with the respective amino alcohol, e.g., 2-amino-1-ethanol (0.61 g, 9.98 mmol). After stirring for 24–48 h at room temperature, 3 ml of a strong acidic cation-exchange resin (Dowex X50; activity: 1.7 mmol ml^{-1}) was added to remove excess of amino alcohol. After filtration of the resin, the solvent was removed under vacuum. The crude product was purified by column chromatography on silicagel. First, diethyl ether was used for the removal of phenol, followed by the elution of the product with methanol. The product was dried under vacuum (10^{-2} mbar) at 50 °C. Yield: 82%. Alternatively,

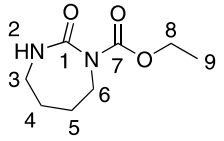
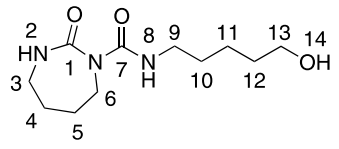


Fig. 2. Structure of ethyl 2-oxo-1,3-diazepane-1-carboxylate, **9**, with numbers for NMR assignment.



11d

Fig. 3. Structure of *N*-(hydroxypentyl)-2-oxo-1,3-diazepane-1-carboxamide, **11d**, with numbers for NMR assignment.

the crude product **11b** was isolated by precipitation into cold diethyl ether. Yield: 90%.

Colorless crystals for **11a** and **11b** with a mp of 118 and 103 °C, respectively, were obtained. Oily or waxy products were obtained for **11c–e**. The ^{1}H and ^{13}C NMR spectra of all *N*-(hydroxyalkyl)-2-oxo-1,3-diazepane-1-carboxamides were in accord with the proposed structures. The ^{1}H and ^{13}C NMR data of **11d** are given as an example (Fig. 3).

^{1}H NMR ($CDCl_3$): $\delta = 1.40$ (m, 2H, H-11), 1.57 (m, 4H, H-10, H-12), 1.79 (m, 4H, H-4, H-5), 2.51 (br s, H-14), 3.25 (m, 4H, H-3, H-9), 3.62 (t, 2H, H-13, $^3J = 6.4$ Hz), 3.80 (t, 2H, H-6), 5.49 (t, 1H, H-2), 8.33 (t, 1H, H-8, $^3J = 4.7$ Hz) ppm.

^{13}C NMR ($CDCl_3$): $\delta = 23.10$ (C-11), 26.01 (C-4), 26.43 (C-5), 29.44 (C-10), 32.28 (C-12), 40.28 (C-9), 43.57 (C-3), 44.52 (C-6), 62.47 (C-13), 155.58 (C-7), 163.06 (C-1) ppm.

^{1}H NMR (DMSO-d_6): $\delta = 1.28$ (m, 2H, H-11), 1.42 (m, 4H, H-10, H-12), 1.60 (m, 4H, H-4, H-5), 3.04 (m, 2H, H-3), 3.09 (m, 2H, H-9), 3.38 (t, 2H, H-13, $^3J = 6.4$ Hz), 3.61 (m, 2H, H-6), 4.36 (t, 1H, H-14, $^3J = 5.1$ Hz), 7.15 (t, 1H, H-2, $^3J = 4.2$ Hz), 8.16 (t, 1H, H-8, $^3J = 5.3$ Hz) ppm.

^{13}C NMR (DMSO-d_6): $\delta = 22.89$ (C-11), 25.77 (C-4), 26.27 (C-5), 29.16 (C-10), 32.11 (C-12), 39.62 (C-9), 42.01 (C-3), 43.39 (C-6), 60.54 (C-13), 154.92 (C-7), 161.79 (C-1) ppm.

2.5. Polycondensation of *N*-(hydroxyalkyl)-2-oxo-1,3-diazepane-1-carboxamides ***11a–e***

In a dry Schlenk flask, the respective *N*-(hydroxyalkyl)-2-oxo-1,3-diazepane-1-carboxamide, e.g., **11d** (848 mg, 3.49 mmol) and catalyst, e.g., DABCO (42 mg) were heated to the desired temperature and polymerized for 24–48 h in a nitrogen atmosphere. The product was dissolved in formic acid (8 ml) and precipitated into cold diethyl ether. The product was dried under vacuum (10^{-2} mbar) at 50 °C. The ^{1}H NMR spectra of all poly(urea urethane)s were in accord with the proposed structures. The ^{1}H NMR data of **14d** are given as an example (Fig. 4).

^{1}H NMR (DMSO-d_6, 100 °C, Fig. 4): $\delta = 1.26$–1.61 (m,

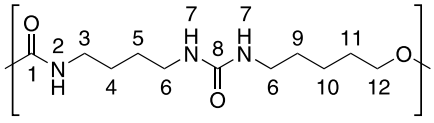
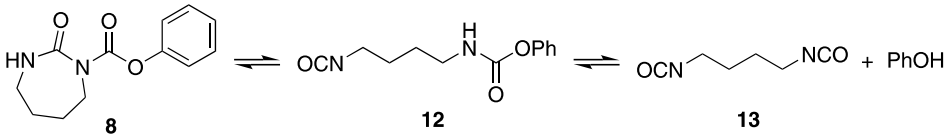


Fig. 4. Structure of poly(urea urethane) **14d** with numbers for NMR assignment.



Scheme 2. Equilibrium between activated urethane/intramolecular blocked isocyanato compound **8** and its activated urethane/isocyanato compound **12** or diisocyanato compound **13**.

H-4, H-5, H-9, H-10, H-11), 2.94 (m, H-3, H-6), 3.90 (t, H-12, $^{3}J = 6.2$ Hz), 5.76 (s, H-7), 7.07 (s, H-2) ppm.

3. Results and discussion

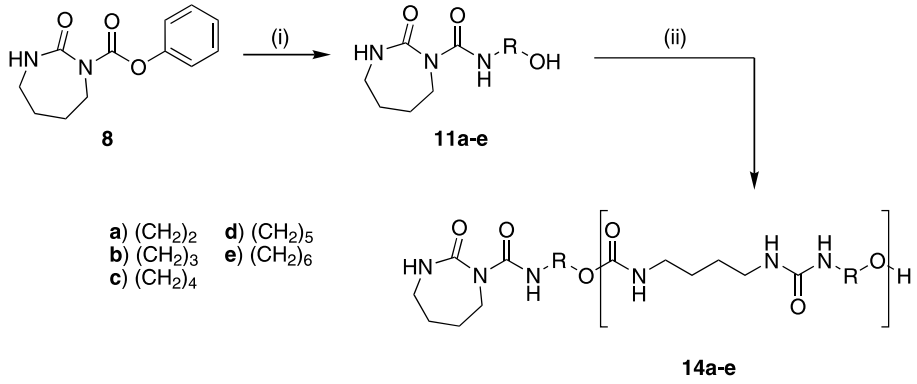
The blocking of isocyanate groups is especially useful for paint and adhesive chemistry in order to formulate stable one-component polyurethane systems [4,10]. The ideal blocking agent should become part of the polymer backbone, thereby eliminating the need for well-ventilated working areas.

Ulrich et al. published in 1978 the use of cyclic ureas (five- to eight-membered ring ureas) as intramolecular blocked isocyanates [5]. Therefore, he synthesized *N*-benzoylureas from the corresponding cyclic ureas and benzoyl chloride and found that the five- and six-membered ring ureas do not appreciably undergo ring opening upon heating in an inert high-boiling solvent, while the seven- and eight-membered ring ureas undergo ring opening on refluxing in *o*-dichlorobenzene.

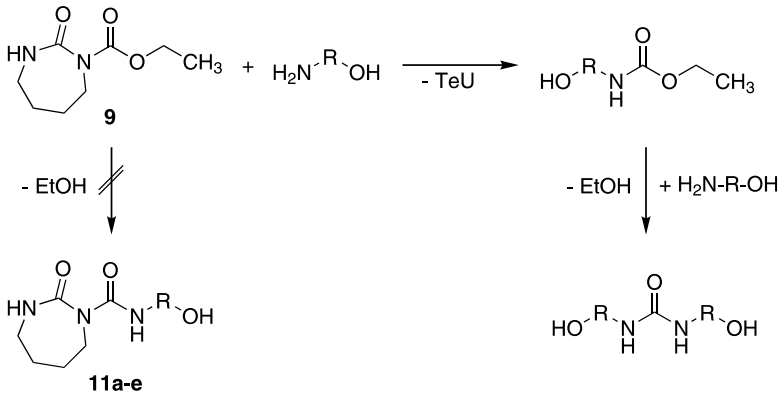
Recently, we showed that it is possible to copolymerize the seven-membered cyclic urea (tetramethylene urea, TeU) with ethylene carbonate, 1,2-propylene carbonate, or γ-butyrolactone to obtain polyurethanes or poly(amide urethane)s [9,11,12]. A novel type of activated urethane/intramolecular blocked isocyanate, i.e., phenyl 2-oxo-1,3-diazepane-1-carboxylate, **8**, from TeU and phenyl chloroformate, was synthesized in 90% yield and investigations on the equilibrium between compound **8** and (4-isocyanatobutyl)-carbamic acid phenyl ester, **12**, or 1,4-diisocyanatobutane, **13**, was used to clarify the reaction mechanism of the copolymerization of TeU with the aforementioned non-homopolymerizable monomers (Scheme 2). It was shown by means of ^{1}H NMR spectroscopy that this equilibrium is completely shifted to the left side at 100 °C [9]. This means that at room temperature the *O*-phenyl urethane is considered as an activated urethane and the 1,3-diazepan-2-one ring as an intramolecular blocked isocyanate.

This led us to the idea to synthesize new AB monomers from **8** in a facile condensation reaction with a homologous series of amino alcohols. *N*-(Hydroxyalkyl)-2-oxo-1,3-diazepane-1-carboxamides **11a–e**, with a nucleophilic chain end (the hydroxy group) on the one hand and an electrophilic chain end (the intramolecular blocked isocyanate) on the other, were synthesized under mild conditions from **8** with an excess of amino alcohols **10a–e** (Scheme 3). It should be mentioned that, under the reaction conditions applied, the nucleophilic amino group of the amino alcohol reacts selectively with the electrophilic carbonyl carbon of the *O*-phenyl urethane; the urea ring remains intact. Excess of amino alcohol is removed from the reaction medium by extraction with a strong acidic cation-exchange resin. The AB monomers were isolated by precipitation or column chromatography in yields higher than 79%.

In addition, from TeU and ethyl chloroformate ethyl 2-oxo-1,3-diazepane-1-carboxylate, **9**, was synthesized which has the advantage of a nontoxic leaving group, i.e., ethanol. Several attempts were made to synthesize *N*- (hydroxyalkyl)-2-oxo-1,3-diazepane-1-carboxamides **11a–e** from **9** and amino alcohols (e.g., 3-amino-1-propanol or 6-amino-1-hexanol) in dichloromethane or chloroform solution at room temperature, 50 °C, and reflux. Furthermore, attempts were made to synthesize **11a–e** from **9** in excess of amino alcohol (5–10 equiv.) at room temperature, 50, and 80 °C.



Scheme 3. Synthesis of poly(urea urethane)s **14a–e** by polycondensation of *N*-(hydroxyalkyl)-2-oxo-1,3-diazepane-1-carboxamides **11a–e**: (i) amino alcohol **10a–e**, CH_2Cl_2, rt; (ii) DABCO/150 °C/48 h, $Sn(octoate)_2$/150 °C/24 h, or Bu_2Mg/100–125 °C/24 h.



Scheme 4. Reaction of ethyl 2-oxo-1,3-diazepane-1-carboxylate, **9**, with amino alcohols.

However, either no conversion, or a urea and a urethane with elimination of TeU and ethanol were obtained (Scheme 4). Obviously, the cyclic urea is the preferred leaving group upon nucleophilic attack at the exocyclic carbonyl group (in analogy to ε-caprolactam as blocking agent).

The *N*-(hydroxyalkyl)-2-oxo-1,3-diazepane-1-carboxamides **11a–e** were subjected to polycondensation. Several reaction conditions, including different types of catalysts, which all are well-known in the polyurethane chemistry [1,3], were investigated (Table 1).

With DABCO (5 wt%) as a catalyst, the *N*-(hydroxyalkyl)-2-oxo-1,3- diazepane-1-carboxamides **11a–e** were polymerized in bulk for 48 h at 150 °C.

Only low molecular weight material is formed at lower temperatures than 150 °C ($\bar{M}_n = 2100$ at $T = 125$ °C). Small amounts of crystals (2–7 mol%) sublimed at the mouth of the flask and were identified by means of NMR spectroscopy as TeU and DABCO. This indicates that a nucleophilic attack takes place at the exocyclic carbonyl moiety as well. According to SEC analysis of the purified products, poly(urea urethane)s with moderate molecular weights ($5400 < \bar{M}_n < 13,500$; $7000 < \bar{M}_w < 26,200$) were obtained. All poly(urea urethane)s show unimodal elution curves ($1.29 < \bar{M}_w/\bar{M}_n < 1.95$). It should be mentioned that the low yield of polymer **14e** is due to the removal of low molecular weight material upon fractionation ($\bar{M}_w/\bar{M}_n = 1.29$) (Table 1).

Alternatively, the *N*-(hydroxyalkyl)-2-oxo-1,3-diazepane-1-carboxamides **11a–e** were polymerized in bulk for 24 h at 150 °C with $Sn(octoate)_2$ (5 wt%) as a catalyst. However, according to SEC analysis of the purified products only oligomers ($3500 < \bar{M}_n < 6000$; $3700 < \bar{M}_w < 9400$) with low yield-due to the removal of low molecular weight material upon fractionation ($1.08 < \bar{M}_w/\bar{M}_n < 1.59$)-were obtained.

Finally, the *N*-(hydroxyalkyl)-2-oxo-1,3-diazepane-1-carboxamides **11a–e** were polymerized in bulk for 24 h with Bu_2Mg as a catalyst, i.e., **11a** (mp 118 °C) and **11b** (mp 103 °C) at 125 and 115 °C and **11c–e** at 100 as well as at 125 °C. SEC analysis of the purified products **14c–e** shows

Table 1
Yield, molecular weight, and polydispersity of the poly(urea urethane)s obtained

Polymer	Catalyst	T (°C)	t (h)	Yield (%)	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
14a	DABCO	150	48	96	7700	12,700	1.65
14b	DABCO	150	48	90	8600	14,400	1.68
14c	DABCO	150	48	93	10,000	16,100	1.61
14d	DABCO	150	48	98	13,500	26,200	1.95
14e	DABCO	150	48	60	5400	7000	1.29
14d	DABCO	125	72	–	2100	2400	1.14
14a	$Sn(octoate)_2$	150	24	65	4400	5100	1.17
14b	$Sn(octoate)_2$	150	24	45	4200	4900	1.16
14c	$Sn(octoate)_2$	150	24	30	4800	6300	1.31
14d	$Sn(octoate)_2$	150	24	17	3500	3700	1.08
14e	$Sn(octoate)_2$	150	24	22	6000	9400	1.59
14a	Bu_2Mg	125	24	93	9000	14,900	1.67
14b	Bu_2Mg	115	24	90	13,300	26,600	1.99
14c	Bu_2Mg	100	24	95	3200	7,600	2.36
14d	Bu_2Mg	100	24	98	7900	35,300	4.48
14e	Bu_2Mg	100	24	70	6600	18,400	2.79
14c	Bu_2Mg	125	24	93	13,300	52,700	3.97
14d	Bu_2Mg	125	24	96	13,600	30,700	2.26
14e	Bu_2Mg	125	24	75	12,800	37,300	2.92

that at 125 °C higher molecular weights were obtained than at 100 °C. However, partially cross-linked material is formed from **11c–e** but not from **11a** at 125 °C, which became evident from the partial insolubility of the material in formic acid. It is likely that cross-linking occurs involving the NH of a urethane or urea group of the polymer, a feature which was used by Li et al. to synthesize soluble cross-linked polyurethane macromolecules [13,14]. SEC analysis of the purified products in hot DMAc and, if necessary, filtration of parts of insoluble material, shows bimodal elution curves for **14c–e** ($2.26 < \bar{M}_w/\bar{M}_n < 3.97$), indicating that branched polymers are formed, and a unimodal elution curve for **14a** ($\bar{M}_w/\bar{M}_n = 1.67$). For the materials obtained at 100 (**14c–e**) and 115 °C (**14b**), no cross-linking was observed, however, SEC analysis shows bimodal elution curves ($1.99 < \bar{M}_w/\bar{M}_n < 4.48$). It should be mentioned that in all cases a precipitate is immediately formed after the addition of Bu_2Mg.

Fig. 5 shows as an example the ^{1}H NMR spectrum of the purified poly(urea urethane) **14c** obtained with DABCO as a catalyst. Therefore, the polymer was dissolved in hot DMSO-d_6 ($\sim$15 mg ml^{-1}) and a long-time NMR experiment was done at 100 °C. The urethane and urea signals are found at 6.53 and 5.55 ppm, respectively. The signals of the methylene protons adjacent to the nitrogen atom of the urea or urethane group are observed at 3.02 ppm and are partly covered by the residual water signal of DMSO-d_6. The signals of the methylene protons adjacent to the oxygen atom of the urethane group are found at 3.97 ppm. Because of the work-up, a formate end-group is observed at 4.14 and 8.18 ppm. All other methylene protons are found at high field between 1.3 and 1.7 ppm.

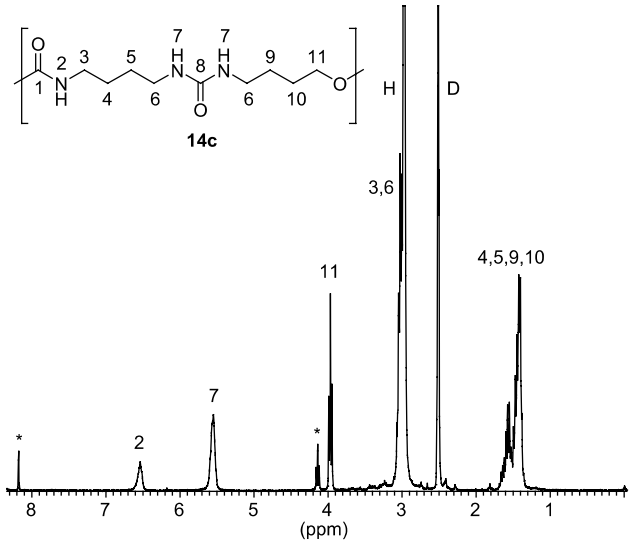


Fig. 5. ^{1}H NMR spectrum in DMSO-d_6 at 100 °C of poly(urea urethane) **14c** obtained by polycondensation of **11c** with DABCO as a catalyst (D = DMSO; H = water; * = formate end-group).

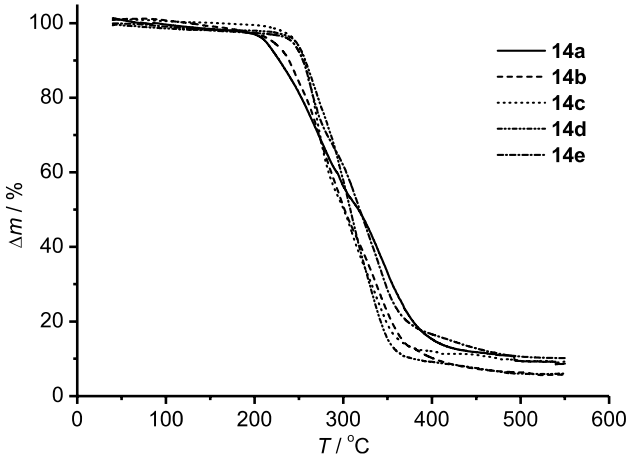


Fig. 6. TGA of poly(urea urethane)s **14a–e**.

3.1. Thermal properties

The TGA thermograms of poly(urea urethane)s **14a–e** (Fig. 6) show a dependence of the degradation temperature on the microstructure. Polymers **14a–b** start to decompose at around 205 and 210 °C, respectively, which is about 20–30 °C lower than the starting temperature of decomposition of polymers **14c–e**. However, the degradation temperature does not increase with increasing number of methylene groups in **14c–e** as was previously observed for, e.g., poly(amide urethane)s [15]. Table 2 shows the temperature of the poly(urea urethane)s **14a–e** at 5, 10, 50, and 80% weight loss. According to Table 2, the temperature at 50% weight loss is 300–319 °C.

The DSC data were obtained after annealing each sample for 1 h at around 170–180 °C and are listed in Table 2. DSC analysis indicated that all poly(urea urethane)s are semi-crystalline materials. The poly(urea urethane)s with an even number of carbon atoms in the amino alcohol units have a higher melting point than those with an odd number of carbon atoms (Fig. 7). A pronounced odd–even effect was

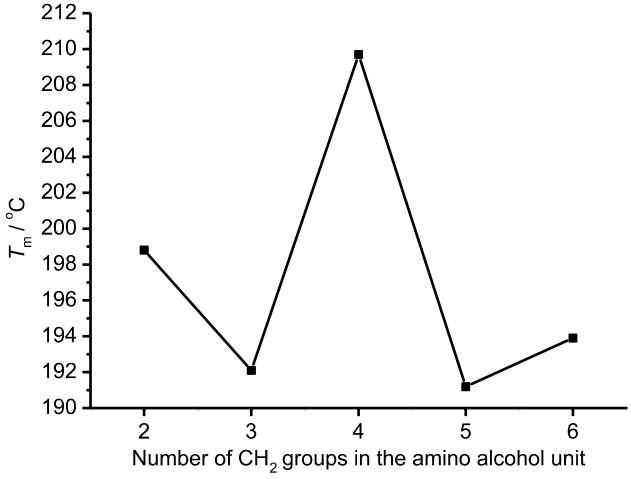


Fig. 7. Melting points of poly(urea urethane)s **14a–e** after annealing.

Table 2
TGA and DSC results of the polymers **14a–e** (DSC results obtained after annealing)

Polymer	T at 5% weight loss (°C)	T at 10% weight loss (°C)	T at 50% weight loss (°C)	T at 80% weight loss (°C)	T_g (°C)	T_m (°C)	ΔH_m (J g^{-1})
14a	212.9	228.0	317.2	378.8	23.0	198.8	33.7
14b	221.0	239.6	301.5	354.7	37.0	192.1	37.5
14c	247.2	256.6	300.7	348.2	31.3	209.7	38.3
14d	246.6	257.3	308.0	342.2	27.7	191.2	47.5
14e	242.5	254.5	318.6	372.5	32.0	193.9	56.5

observed earlier for [*n*]-polyamides [16], [*n*]-polyurethanes [8,17], poly(ester amide)s [18], and poly(amide urethane)s [15]. The glass transition temperatures were found to lie between 23–37 °C (Table 2).

4. Conclusions

Under mild reaction conditions, AB monomers, i.e., *N*-(hydroxyalkyl)-2-oxo-1,3-diazepane-1-carboxamides **11a–e**, with an intramolecular blocked isocyanate and a hydroxy group, were synthesized from a novel type of activated urethane/intramolecular blocked isocyanate (phenyl 2-oxo-1,3-diazepane-1-carboxylate, **8**) and a homologous series of amino alcohols. Several catalysts for the polycondensation of **11a–e**, leading to polymeric building blocks with urea and urethane groups without the release of a blocking agent, were investigated. With Sn(octoate)$_2$ as a catalyst at 150 °C, only oligomers are formed. Polycondensation of **11a** and **11c–e** with Bu_2Mg as a catalyst at 125 °C leads for **11c–e**, but not for **11a**, to partially cross-linked material. Branched polymers are obtained with Bu_2Mg as a catalyst at 115 °C for **11b** and at 100 °C for **11c–e**. Poly(urea urethane)s with moderate molecular weights ($5400 < \bar{M}_n < 13,500$; $7000 < \bar{M}_w < 26,200$) and unimodal elution curves ($1.29 < \bar{M}_w/\bar{M}_n < 1.95$) were obtained with DABCO as a catalyst at 150 °C. However, to a small extent nucleophilic attack of the hydroxy group takes place at the exocyclic carbonyl moiety as well.

Acknowledgements

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