Textural properties of poly(glycidyl methacrylate)

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Synthesis and characterization of alternating poly(amide urethane)s from ε-caprolactam, amino alcohols, and diphenyl carbonate

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Abstract

Alternating poly(amide urethane)s from ε-caprolactam, amino alcohols $H_2N-(CH_2)_x-OH$ ($x = 2-6$), and diphenyl carbonate were prepared by polycondensation of α-hydroxy-ω-O-phenylurethanes **4a-e**. The degree of oligomerization was adjusted by the conversion. Oligomers with two or three O-phenylurethane end groups and predetermined molecular weight were prepared by polycondensation of the α-hydroxy-ω-O-phenylurethanes **4a-e** in the presence of comonomers with O-phenylurethane end groups in a given concentration. In order to prepare oligomers with hydroxyl and carboxyl groups at both chain ends suitable for coupling reactions, chain analogous reactions were performed with amino acids and amino alcohols. The microstructure of the polymers and the nature of end groups was determined by means of ^1H NMR spectroscopy and the molecular weights were determined by means of gel permeation chromatography. The poly(amide urethane)s **5a-e** prepared are semicrystalline materials with melting points between 150 and 200 °C.
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1. Introduction

Polyurethanes are being synthesized ubiquitously due to their unique properties. Not only polyurethanes but also urethane-containing copolymers are widely used to make foams, fibres, elastomers, adhesives, and coatings [1].

Generally these polymers and copolymers are prepared from diols and diisocyanates, the diisocyanates being obtained from diamines and phosgene. Special safety and processing precautions are required for these reactions because phosgene and isocyanates are highly toxic materials and highly sensitive towards moisture [2]. Höcker et al. explored two isocyanate free routes to synthesize polyurethanes **IV** starting with amino alcohols **I** and diphenyl carbonate. The first route is the ring-opening polymerization of suitable cyclic urethanes **II** and the second one the polycondensation of α-hydroxy-ω-O-phenylurethanes **III** (Scheme 1) [3–8].

In order to cover a wide range of properties, polymers with different functional groups were prepared, e.g. poly(ester amide)s. The properties of these polymers are determined not only by the building blocks but also by the concentration and by the distribution—random or regular—of the ester and amide groups. The polymers are biodegradable and are used as commodities as well as for medical applications. Due to the hydrogen bonds between amide groups these materials have improved mechanical and thermal properties compared with polyesters; the ester groups are mainly responsible of hydrolytical degradation [9–11]. The most prominent example of a random poly(ester amide) is BAK 1095 developed by Bayer and prepared from ε-caprolactam, butane diol, and adipic acid. BAK 1095 shows mechanical and thermal properties resembling those of polyethylene; in addition, this polymer is completely biodegradable according to DIN 54900 [12].

The aim of this work is to synthesize alternating poly(amide urethane)s by using ε-caprolactam, amino

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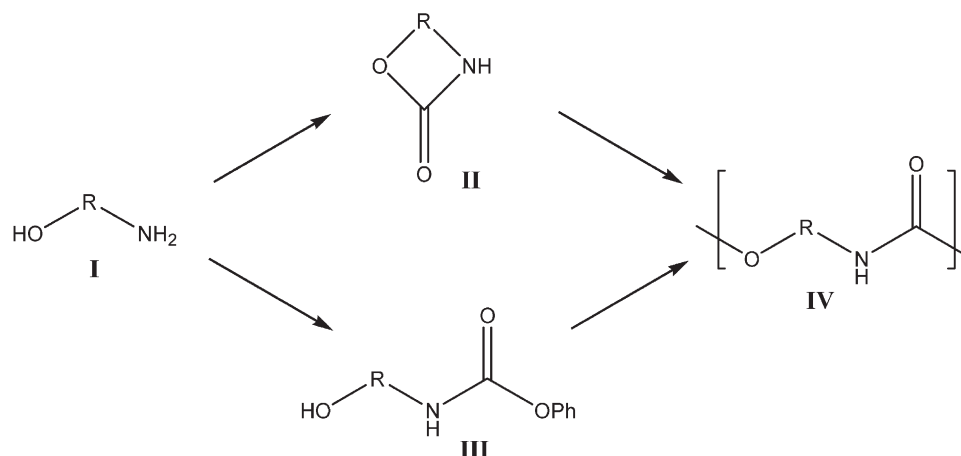
Scheme 1. General routes to polyurethanes from amino alcohols and diphenyl carbonate.

alcohols, and diphenyl carbonate as starting materials. These polymers contain amide and urethane groups thus combining the properties of two important classes of technical polymers. There are only a few scientific papers dealing with alternating poly(amide urethane)s, e.g. Mormann et al. reported the synthesis of regular poly(amide urethane)s by using diamido-diisocyanates and 1,4-butane diol as starting materials [13].

2. Experimental part

2.1. Materials

ε-Caprolactam (BASF), 1-amino-2-ethanol (Aldrich), 1-amino-3-propanol (Aldrich), 1-amino-4-butanol (Across), 1-amino-5-pentanol (Fluka), 1-amino-6-hexanol (Fluka), diphenyl carbonate (Fluka), 1,6-diaminohexane (Fluka),

tris(2-aminoethyl)amine (Aldrich), dibutyltin dimethoxide ($Bu_2Sn(OCH_3)_2$, Aldrich) were used as received. Dichloromethane, ethanol, diethyl ether and *N,N*-dimethylacetamide were distilled before use.

Polymerizations were carried out in an inert gas atmosphere. Nitrogen (Linde) was passed over molecular sieves (4 Å) and finely distributed potassium on aluminium oxide.

2.2. Measurements

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX-300 FT-NMR spectrometer at 300 and 75 MHz, respectively. Deuterated chloroform ($CDCl_3$), trifluoroacetic acid (TFA-*d*), formic acid (DCOOD), and dimethylsulfoxide (DMSO-d_6) were used as solvents, and tetramethylsilane (TMS) served as an internal standard.

Table 1
Synthesis and characteristics of α-hydroxy-ω-amino amides **3a-e**

No	Yield (%)	Mp (°C)	Characteristic ^{1}H and ^{13}C chemical shifts (δ in ppm)					
			CH_2-NH_2	CH_2-CO	CH_2-CO	CH_2-NH	CH_2-NH	CH_2-OH
3a	74	72–75	2.50[a]	2.05[a]	–	3.08[a]	7.82[a]	3.38[a]
			41.46[a]	35.33[a]	172.21[a]	41.34[a]	–	59.84[a]
			3.30[b]	2.68[b]	–	3.91[b]	n[b]	4.65[b]
			43.04[b]	36.34[b]	181.92[b]	41.74[b]	–	67.48[b]
3b	81	78–80	2.48[a]	2.03[a]	–	3.06[a]	7.79[a]	3.38[a]
			41.90[a]	35.82[a]	172.51[a]	35.93[a]	–	58.70[a]
			3.29[b]	2.75[b]	–	3.72[b]	n[b]	4.56[b]
			42.94[b]	35.78[b]	181.61[b]	40.91[b]	–	67.79[b]
3c	77	55–60	2.50[a]	2.03[a]	–	3.00[a]	7.78[a]	3.37[a]
			41.83[a]	35.85[a]	172.28[a]	38.65[a]	–	60.76[a]
3d	83	77–82	2.50[a]	2.03[a]	–	3.00[a]	7.78[a]	3.37[a]
			41.84[a]	35.84[a]	172.30[a]	38.77[a]	–	60.96[a]
3e	81	77–80	2.50[a]	2.03[a]	–	3.00[a]	7.79[a]	3.37[a]
			41.78[a]	35.82[a]	172.31[a]	38.70[a]	–	60.99[a]

n = not observed.
[a] In DMSO-d_6 as solvent.
[b] In CF_3COOD as solvent.

Table 2
Synthesis and characteristics of α-hydroxy-ω-O-phenylurethanes **4a-e**

No	Yield (%)	Mp (°C)	Characteristic ^{1}H and ^{13}C chemical shifts (δ in ppm)					
			$CH_2-NH-CO-OPh$	CH_2-CO	CH_2-CO	CH_2-NH	CH_2-NH[a]	CH_2-OH
4a	82	–	3.05[b]	2.08[b]	–	3.12[b]	7.33(ur)	3.39[b]
			40.35[b]	35.23[b]	172.17[b]	41.35[b]	7.80(am)[b]	59.93[b]
			3.43[c]	2.70[c]	–	3.88[c]	–	4.63[c]
			41.97[c]	35.75[c]	182.55[c]	43.04[c]	n[c]	67.13[c]
							–	
4b	80	–	3.05[b]	2.07[b]	–	3.11[b]	7.72–7.74[b]	3.41[b]
			40.72[b]	35.71[b]	172.50[b]	35.97[b]	–	58.78[b]
			3.40[c]	2.71[c]	–	3.67[c]	n[c]	4.50[c]
			40.94[c]	35.58[c]	181.85[c]	35.58[c]	–	67.47[c]
4c	85	67–69	3.05[b]	2.03[b]	–	3.05[b]	7.73–7.75[b]	3.38[b]
			40.78[b]	35.74[b]	172.20[b]	38.68[b]	–	60.80[b]
4d	81	58–60	3.03[b]	2.06[b]	–	3.04[b]	7.73–7.75[b]	3.38[b]
			40.76[b]	35.72[b]	172.21[b]	38.80[b]	–	61.01[b]
4e	76	73–75	3.02[b]	2.05[b]	–	3.03[b]	7.73–7.74[b]	3.37[b]
			40.67[b]	35.70[b]	172.16[b]	38.73[b]	–	61.01[b]

[a] The resonance signals of amide (am) and urethane (ur) NH are superposed for **4b-e**.
[b] In DMSO-d_6 as solvent.
[c] In CF$_3$COOD as solvent; n = not observed.

Gel permeation chromatography (GPC) analyses were carried out using a high pressure liquid chromatography pump (Bischoff HPLC pump 2200) and a refractive index detector (Waters 410). The eluting solvent was *N,N*-dimethylacetamide (DMAc) with 2.44 g L^{-1} LiCl with 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, and 10^4 Å. Calibration with polystyrene standards was used for the estimation of molecular weight and polydispersity.

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

Differential scanning calorimetric (DSC) analyses were performed on a Netzsch DSC 204 in a nitrogen atmosphere with a heating rate of 10 K min^{-1}. Calibration was achieved using indium standard samples.

2.3. Preparation of α-hydroxy-ω-amino amides **3a-e**

ε-Caprolactam (15 g, 0.13 mol), 1-amino-2-ethanol (40.77 g, 0.67 mol), and H$_2$O (18 mL) were mixed in an autoclave and heated for 24 h to 200 °C in an inert atmosphere.

Table 3
Yield and NMR data of the alternating poly(amide urethane)s **5a-e**

No	Yield (%)	Characteristic ^{1}H and ^{13}C chemical shifts (δ in ppm)						
		$CH_2-NH-CO$	$CH_2-NH-CO$	CH_2-CO	CH_2-CO	CH_2-NH	CH_2-NH	CH_2-O
5a	93	–	2.94[a]	2.04[a]	–	3.23[a]	7.10(ur)	3.90[a]
		156.86[a]	38.29[a]	36.02[a]	173.11[a]	38.93[a]	7.89(am)[a]	62.93[a]
		–	3.34[b]	2.76[b]	–	3.90[b]	–	4.47[b]
		161.14[b]	42.91[b]	35.99[b]	182.32[b]	43.60[b]	n[b]	65.27[b]
5b	79	–	2.94[a]	2.02[a]	–	3.09[a]	7.07(ur)	3.91[a]
		157.01[a]	40.78[a]	36.11[a]	172.83[a]	36.17[a]	7.80(am)[a]	62.31[a]
		–	3.30[b]	2.78[b]	–	3.71[b]	–	4.33[b]
		161.65[b]	42.77[b]	35.65[b]	181.97[b]	41.00[b]	n[b]	65.01[b]
							–	
5c	81	–	3.33[b]	2.78[b]	–	3.65[b]	n[b]	4.29[b]
		162.01[b]	44.27[b]	35.57[b]	181.62[b]	42.74[b]	–	68.09[b]
5d	79	–	3.32[b]	2.79[b]	–	3.62[b]	n[b]	4.27[b]
		162.27[b]	44.68[b]	35.45[b]	181.34[b]	42.71[b]	–	68.86[b]
5e	84	–	3.32[b]	2.79[b]	–	3.61[b]	n[b]	4.27[b]
		162.49[b]	44.91[b]	35.44[b]	181.26[b]	42.74[b]	–	69.44[b]

n = not observed.
[a] In DMSO-d_6 as solvent.
[b] In CF$_3$COOD as solvent.

Table 4
The reaction conditions and results of poly(amide urethane)s **5a-e** obtained via polycondensation of α-hydroxy-ω-*O*-phenylurethanes **4a-e** at 90 and 120 °C

Poly(amide urethane)s	Reaction time (h)	T (°C)	M_n	M_w/M_n	Yield (%)
5a	$1^n + 2^r$	90	7400	1.42	78
	$1^n + 3^r$	120	8900	1.55	93
5b	$1^n + 2^r$	90	7500	1.45	70
	$1^n + 3^r$	120	7400	1.51	79
5c	$1^n + 3^r$	90	4200	1.28	70
	$1^n + 3^r$	120	8300	1.62	81
5d	$1^n + 3^r$	90	5400	1.36	63
	$1^n + 3^r$	120	11,500	1.64	79
5e	$1^n + 3^r$	90	3300	1.16	51
	$1^n + 3^r$	120	7100	1.54	84

n = at normal pressure (1 bar), r = at reduced pressure (10^{-2} mbar). M_n and M_w/M_n were determined by GPC in DMAc with polystyrene standards.

Then, an excess of 1-amino-2-ethanol was removed under vacuum at 60–80 °C, the residue was dissolved in ethanol (75 mL) followed by precipitation into diethyl ether. The product was isolated by filtration and dried in vacuum at 50 °C.

All α-hydroxy-ω-amino amides **3a-e** were prepared according to the same procedure (Table 1).

2.4. Preparaton of α-hydroxy-ω-O-phenylurethanes 4a-e

α-Hydroxy-ω-amino amide **3a** (5.47 g, 0.031 mol) was reacted with diphenyl carbonate (8.42 g, 0.039 mol) in methylene chloride (104 mL) at room temperature for 26 h. For purification, 60–70% of the methylene chloride was evaporated followed by precipitation into diethyl ether. The purified product was isolated by filtration and dried in vacuum at 50 °C.

All α-hydroxy-ω-*O*-phenylurethanes **4a-e** were prepared according to the same procedure (Table 2).

2.5. Polycondensation of α-hydroxy-ω-O-phenylurethane 4a-e in bulk

α-Hydroxy-ω-*O*-phenylurethane **4b** (1.00 g, 6.46 mmol) and Bu₂Sn(OCH₃)₂ (5 wt%) were heated to 90 or 120 °C in an inert gas atmosphere. The polycondensation was performed for 1 h at normal pressure and 2-3 h at reduced pressure (10^{-2} mbar). Phenol was removed by distillation. The polymer was purified by dissolution in formic acid and precipitation into diethyl ether. The product was isolated by filtration and dried in vacuum at 50 °C.

The polycondensation of all α-hydroxy-ω-*O*-phenylurethanes **4a-e** was performed according to the same procedure (Tables 3 and 4).

### 2.6. Polycondensation of α-hydroxy-ω-amino amides 3a-b with diphenyl carbonate in bulk

α-Hydroxy-ω-amino amide **3b** (5.04 g, 26.8 mmol) and diphenyl carbonate (5.737 g, 26.8 mmol) were heated to

100 °C for 1 h and subsequently Bu₂Sn(OCH₃)₂ (5 wt%) was added. The polycondensation was performed at 100 °C for 1 h at normal pressure and 4 h at reduced pressure. During this time phenol was removed by distillation from the reaction mixture. The crude product was purified by dissolution in formic acid and precipitation into diethyl ether. The purified product was isolated by filtration and dried at 50 °C under reduced pressure.

Yield: 83%, $M_n = 10,000$ and $M_w/M_n = 1.48$. The same procedure was adopted to **3a**.

2.7. Preparation of hexamethylene bis(O-phenylurethane) 7

1,6-Diaminohexane (3.61 g, 31.15 mmol) and diphenyl carbonate (20.0 g, 93.45 mmol) were dissolved in CH₂Cl₂ (50 mL and 150 mL, respectively). The solution of diaminohexane was added dropwise at room temperature to the solution of diphenyl carbonate and stirred for 3.5 h. CH₂Cl₂ was evaporated and the residue was crystallized from hexane (50 mL) and ethyl acetate (150 mL). Yield: 95%, mp 132–133 °C.
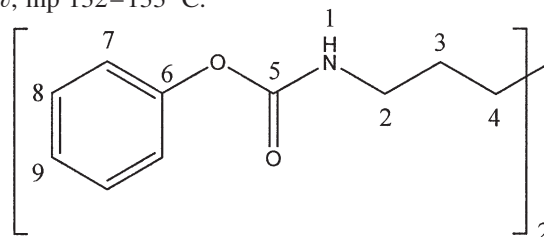
¹H NMR (DMSO-d_6): $\delta = 1.33$ (m, 4H, H-4), 1.49 (m, 4H, H-3), 3.06 (d of tr, 4H, H-2), 7.11 (d, 4H, H-7), 7.19 (tr, 2H, H-9, $^3J = 7.2$ Hz), 7.37 (tr, 4H, H-8, $^3J = 7.8$ Hz), 7.75 (tr, 2H, H-1, $^3J = 5.4$ Hz) ppm.

¹³C NMR (DMSO-d_6): $\delta = 26.31$ (C-4), 29.54 (C-3), 40.74 (C-2), 122.12 (C-7), 125.17 (C-9), 129.56 (C-8), 151.49 (C-6), 154.69 (C-5) ppm.

2.8. Preparation of tris(2-phenoxycarbonylamino-ethyl)-amine hydrochloride 9

Tris(2-aminoethyl)amine (1.0 g, 6.84 mmol) and diphenyl carbonate (7.33 g, 34.2 mmol) were dissolved in CH₂Cl₂ (40 mL and 60 mL, respectively). The solution of tris(2-amino-ethyl)amine was added dropwise to the solution of diphenyl carbonate, and the mixture was stirred for 28 h at room temperature. The resulting solution was washed with a 5% HCl solution. The organic phase was separated and all volatiles were removed by distillation under vacuum (10^{-2} mbar) at 70–80 °C. For purification, the crude product was dissolved in CH₂Cl₂ (20 mL) followed by precipitation into hexane. Yield: 88%.
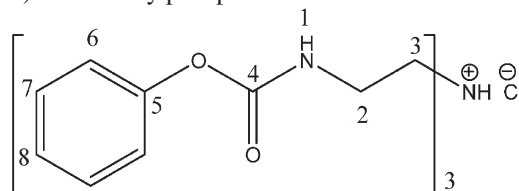
Table 5
Reaction conditions, yield, molar ratio of the reacting functional groups, molar ratio of monomers **4a** or **4b** to comonomers **7** or **9**, and molecular weight of poly(amide urethane)s

No	Reaction time (h)	Yield (%)	q	Molar ratio	M_n calcd	M_n NMR	M_n GPC	M_w/M_n GPC
8a	$2^n + 3^r$	80	1/1.30	**4a/7** = 6.75/1	1900	3700	7700	1.80
8b	$2^n + 3.5^r$	85	1/1.22	**4b/7** = 9.00/1	2500	5100	10,800	1.60
8b	$2^n + 3^r$	78	1/1.37	**4b/7** = 5.33/1	1700	2700	7300	1.40
8b	$2^n + 3^r$	69	1/1.45	**4b/7** = 4.46/1	1500	1600	5000	1.30
10a	$2^n + 3^r$	83	1/1.27	**4a/9** = 10.94/1	2300	2300	7300	1.80
10b	$2^n + 3^r$	71	1/1.26	**4b/9** = 11.52/1	2400	2900	7100	1.70

n = at normal pressure (1 bar), r = at reduced pressure (10^{-2} mbar). q = [HO–]/[PhOCONH–]. M_n calcd = theoretically calculated molecular weight. M_n NMR and M_n GPC = experimentally determined molecular weight.

^{1}H NMR (DMSO-d_6): δ = 3.44 (m, 6H, H-3), 3.57 (m, 6H, H-2), 7.15 (d, 6H, H-6), 7.20 (tr, 3H, H-8, ^3J = 7.2 Hz), 7.36 (tr, 6H, H-7, ^3J = 7.8 Hz), 8.11 (s, 3H, H-1) ppm.
^{13}C NMR (DMSO-d_6): δ = 31.05 (C-3), 51.78 (C-2), 122.18 (C-6), 125.52 (C-8), 129.60 (C-7), 151.21 (C-5), 154.88 (C-4) ppm.

2.9. Preparation of linear poly(amide urethane)s with O-phenylurethane end groups 8a-b
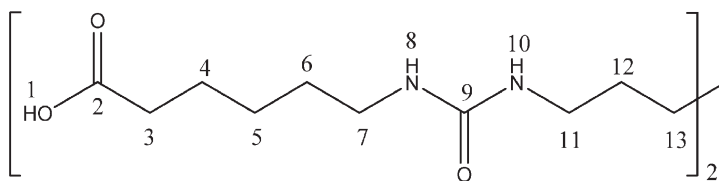
α-Hydroxy-ω-O-phenylurethane **4b** (1.70 g, 5.5 mmol) and hexamethylene bis(O-phenylurethane) **7** (0.22 g, 0.61 mmol) were reacted at 90 °C with Bu$_2$Sn(OCH$_3$)$_2$ (5 wt%) in an inert gas atmosphere. The polycondensation was performed for 2 h at normal pressure and 3.5 h at reduced pressure (10^{-2} mbar). Phenol was removed from the reaction mixture by distillation. The product was purified by dissolution in formic acid and precipitation into diethyl ether. The purified product was isolated by filtration and dried in

vacuum at 50 °C. Yield: 85%.
The same procedure was adopted to synthesize poly-(amide urethane)s **8a-b** using different molar ratios of α-hydroxy-ω-O-phenylurethanes **4a** or **4b**, and hexamethylene bis(O-phenylurethane) **7** (Table 5).

## 2.10. Synthesis of three arm star shaped poly(amide urethane)s with O-phenylurethane end groups 10a-b

α-Hydroxy-ω-O-phenylurethane **4b** (1.68 g, 5.45 mmol), tris(2-phenoxycarbonylamino-ethyl)-amine hydrochloride **9** (0.26 g, 0.47 mmol), and Bu$_2$Sn(OCH$_3$)$_2$ (5 wt%) were used for the polycondensation in bulk at 90 °C. The mixture was stirred for 2 h at normal pressure and 3 h at reduced pressure

(10^{-2} mbar), and phenol was removed from the reaction mixture by distillation. For purification, the crude product was dissolved in formic acid followed by precipitation into diethyl ether, and the purified product was isolated by filtration. Yield: 71%.
The same procedure was applied for poly(amide urethane) **10a** (Table 5).

2.11. Model reactions

Reaction of hexamethylene bis(O-phenylurethane) with sodium ε-aminocaproate. Hexamethylene bis(O-phenylurethane) (1.0 g, 2.8 mmol) and sodium ε-aminocaproate (2.15 g, 14.0 mmol) were dissolved in DMAc (5 mL). The reaction was performed at 95 °C for 2 h at normal pressure and 2 h at reduced pressure (10^{-2} mbar). During this time the phenol was removed from the reaction mixture by distillation. The residue was neutralized with a 5% aqueous HCl solution, and the product was isolated by filtration. Yield: 82%

^{1}H NMR (DMSO-d_6): δ = 1.37 (m, 16H, H-12/13/6/5), 1.54 (m, 4H, H-4), 2.19 (tr, 4H, H-3, ^3J = 7.2 Hz), 2.99 (m, 8H, H-7/11), 5.60 (s, 4H, H-8/10) ppm.
^{13}C NMR (DMSO-d_6): δ = 24.75 (C-13), 26.42 (C-12), 26.48 (C-5), 30.06 (C-4), 30.30 (C-6), 34.35 (C-3), 40.91 (C-7/11), 158.74 (C-9), 174.51 (C-2) ppm.

Reaction of hexamethylene bis(O-phenylurethane) with 1-amino-3-propanol

Hexamethylene bis(O-phenylurethane) (1.0 g, 2.80 mmol) and 1-amino-3-propanol (2.10 g, 28.0 mmol) were dissolved in DMAc (2 mL). The mixture was stirred at 90 °C for 1.5 h at normal pressure and 1 h at reduced
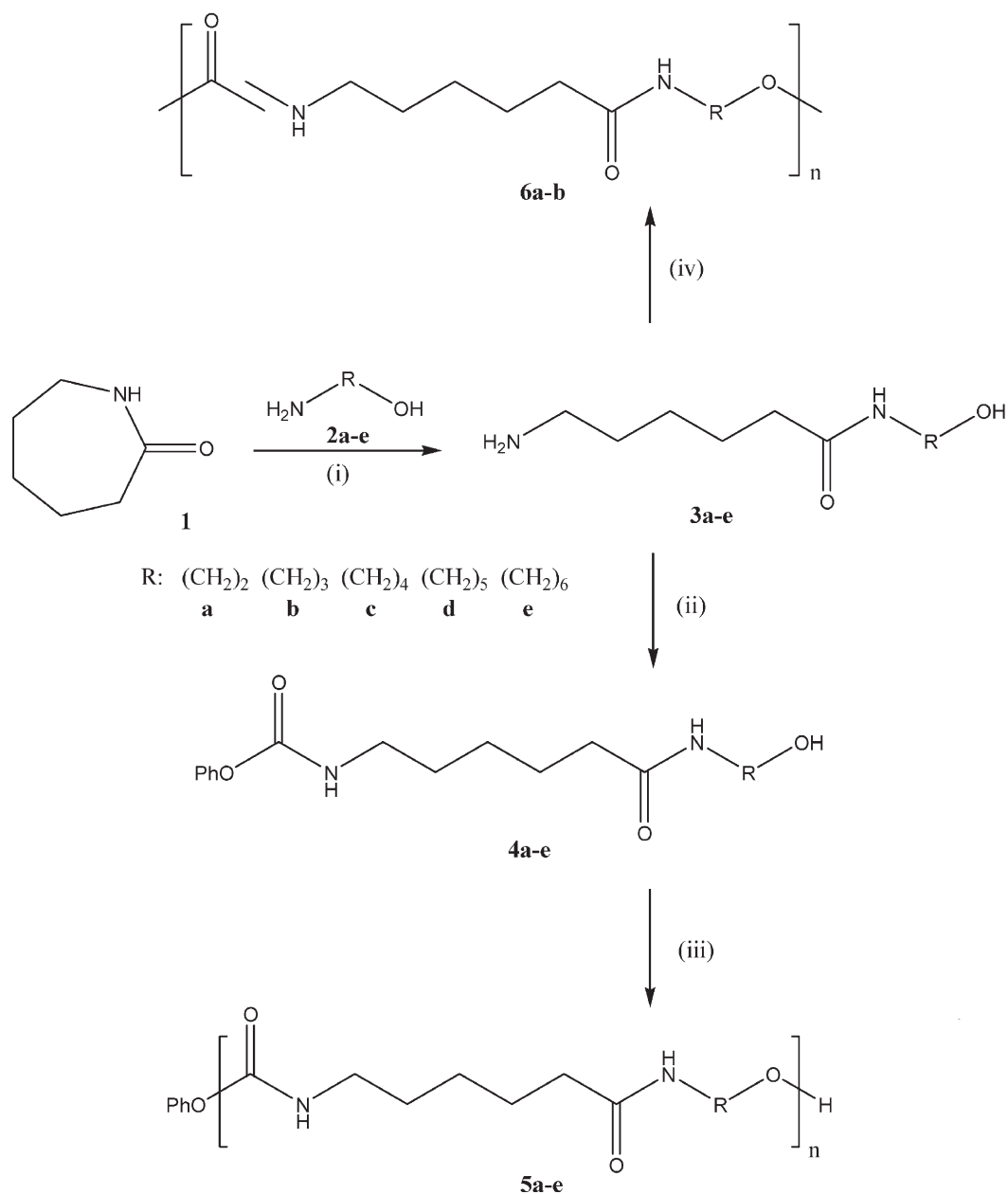
Scheme 2. Synthesis of poly(amide urethane)s from ε-caprolactam, amino alcohols, and diphenyl carbonate. (i) ε-caprolactam/**2a-e** = 1/5, H_2O, $T = 200$ °C in autoclave, $t = 24$ h; (ii) diphenyl carbonate/**3a-e** = 1/1–1.5/1, CH_2Cl_2, rt, $t = 24$ h; (iii) **4a-e** and 5 wt% $Bu_2Sn(OCH_3)_2$, $T = 90$ °C or 120 °C, $t = 1$ h at normal pressure, and $t = 2–4$ h at reduced pressure (10^{-2} mbar); (iv) diphenyl carbonate/**3a-b** = 1/1, $T = 100$ °C, $t = 1$ h at normal pressure, $t = 1$ h at normal pressure with $Bu_2Sn(OCH_3)_2$ (5 wt%), and $t = 4$ h at reduced pressure (10^{-2} mbar).

pressure. Phenol was removed by distillation under vacuum. Yield: 86%.
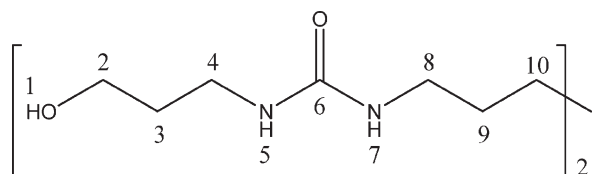
^{1}H NMR (DMSO-d_6): $\delta = 1.30$ (m, 4H, H-10), 1.39 (m, 4H, H-9), 1.55 (quin, 4H, H-3, $^3J = 6.6$ Hz), 3.01 (d of tr,

4H, H-8), 3.09 (d of tr, 4H, H-4), 3.45 (tr, 4H, H-2, $^3J = 6.3$ Hz), 4.08 (s, 2H, H-1), 5.55 (s, 4H, H-5/7) ppm.

^{13}C NMR (DMSO-d_6): $\delta = 26.48$ (C-10), 30.31 (C-9), 33.75 (C-3), 37.07 (C-8), 40.92 (C-4), 59.15 (C-2), 158.89 (C-6) ppm.

2.12. Synthesis of poly(amide urethane)s with carboxy end groups 12

Poly(amide urethane) **8b** ($M_n = 5000$) (0.90 g, 0.55 mmol) and sodium ε-aminocaproate **11** (0.91 g, 5.96 mmol) were dissolved in DMAc (2 mL) to perform
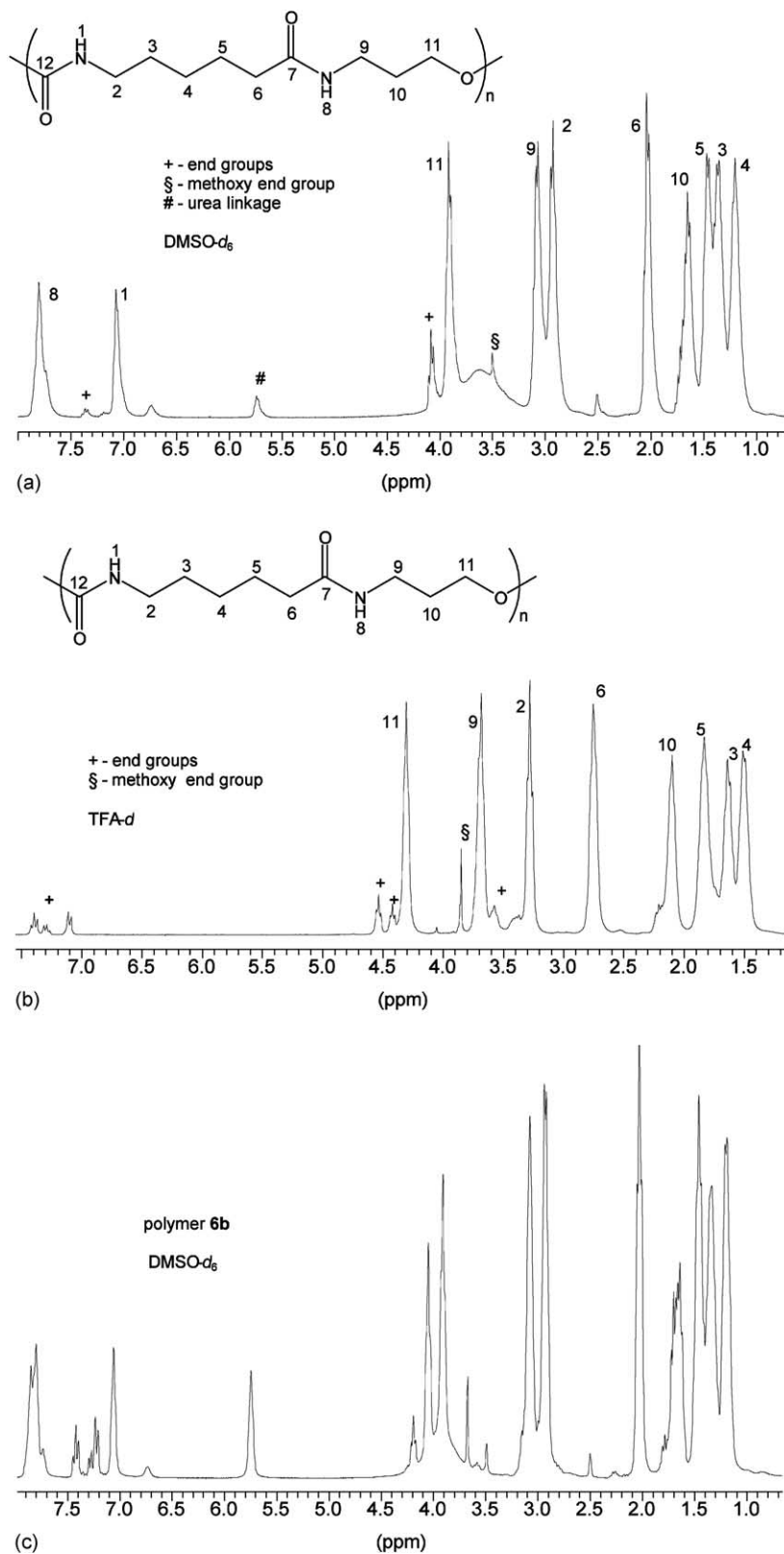
Fig. 1. ^{1}H NMR spectra of polymers. (a) **5b** in DMSO-d_6, (b) **5b** in CF$_3$COOD, (c) **6b** in DMSO-d_6.
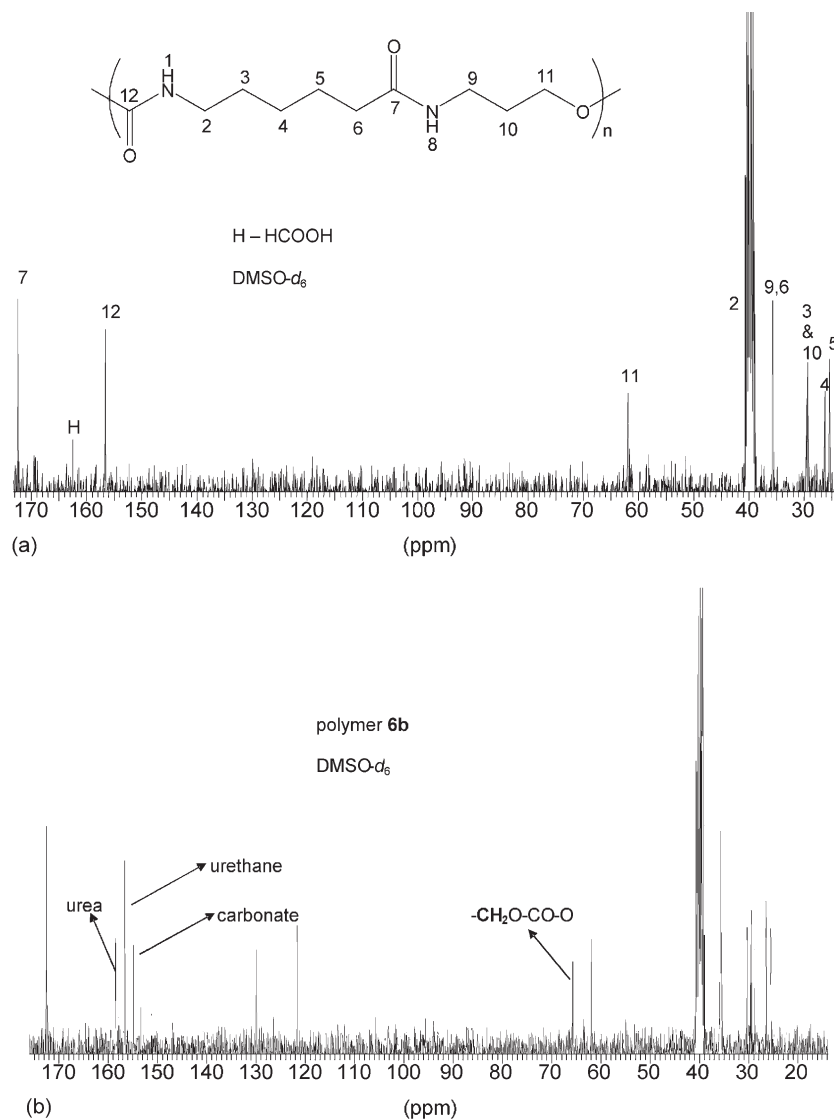
Fig. 2. ^{13}C NMR spectra of polymers in DMSO-d_6. (a) **5b**, (b) **6b**.

the chain analogous reaction at 100 °C for 2 h at normal pressure and 2 h at reduced pressure (10^{-2} mbar). During this time, phenol was removed from the reaction mixture by distillation. The crude product was purified by dissolution in formic acid and precipitation into diethyl ether. Yield: 84%.

2.14. Synthesis of poly(amide urethane)s with hydroxy end groups 13b

Poly(amide urethane) **8b** ($M_n = 5000$) (0.90 g, 0.55 mmol) and 1-amino-3-propanol (0.39 g, 5.21 mmol) were dissolved in DMAc (1.5 mL). This reaction was heated at 90 °C for 2 h at normal pressure and 3 h at reduced pressure (10^{-2} mbar), and phenol was removed by distillation. The crude product was purified by dissolution in formic acid and precipitation into diethyl ether. The purified product was isolated by decantation of solvents and dried at 50 °C under reduced pressure. Yield: 86%.

3. Results and discussion

Alternating poly(amide urethane)s were obtained from ε-caprolactam (**1**), a homologous series of amino alcohols **2a-e** and diphenyl carbonate in three steps. First the amino alcohols react with ε-caprolactam inducing ring-opening in a selective manner giving the α-hydroxy-ω-amino amides **3a-e**. These react with diphenyl carbonate again selectively to result in the corresponding α-hydroxy-ω-O-phenylurethanes **4a-e** which finally are converted to the corresponding poly(amide urethane)s **5a-e** by polycondensation in bulk (Scheme 2). The α-hydroxy-ω-amino amides **3a-e** were obtained by aminolysis of ε-caprolactam with an excess of the amino alcohol to circumvent the formation of higher oligomers. A temperature of 200 °C and the presence of water are necessary for a high conversion of ε-caprolactam. For the preparation of α-hydroxy-ω-O-phenylurethanes **4a-e**, the α-hydroxy-ω-amino amides **3a-e** were treated with
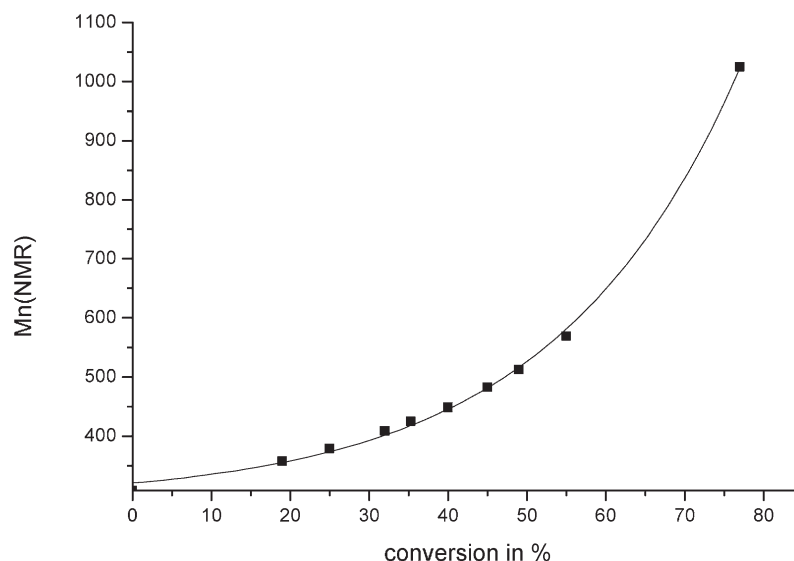
Fig. 3. Polycondensation of α-hydroxy-ω-O-phenylurethane **4b** at 90 °C: M_n versus conversion (determined by NMR).

diphenyl carbonate in methylene chloride at room temperature. Only the amino group reacts with diphenyl carbonate under these conditions, not the hydroxyl group.

The α-hydroxy-ω-O-phenylurethanes **4a-e** obtained in high purity were used as starting material for the polycondensation performed in bulk at 90 or 120 °C in the presence of $Bu_2Sn(OCH_3)_2$ as a catalyst. The ^1H NMR spectra of the purified products **5a-e** show that the obtained poly(amide urethane)s have a regular microstructure comprising alternating amide and urethane linkages; approximatively 5% urea groups indicate the existence of a side reaction which will be discussed in a subsequent paper. The ^1H NMR spectra of the poly(amide urethane)s in DMSO-d_6 (Fig. 1(a)) clearly show distinct resonance lines for each methylene group, two distinct resonance lines for the proton of the urethane and amide groups of equal intensity between 7.00–7.10 and 7.70–7.90 ppm, respectively, and a signal of small intensity for the protons of the urea group. In CF_3COOD the NH protons of the amide and urethane groups can not be observed due to a fast H–D exchange (Fig. 1(b)). The characteristic chemical shifts of the methylene groups adjacent to the amide and urethane groups are given in Section 2. The reaction conditions, number average molecular weights, polydispersities, and yields of poly(amide urethane)s **5a-e** are given in Table 4. At 90 °C, the molecular weight and the yield of the polymers are relatively low for the higher amino alcohol homologues. At 120 °C, polymer yields and molar masses obtained after the same time are higher than at 90 °C as is to be expected.

An attempt was made to prepare poly(amide urethane)s directly from the amino alcohols **3a-b** and an equimolar amount of diphenyl carbonate. The reaction was performed at 100 °C with $Bu_2Sn(OCH_3)_2$ as a catalyst (Scheme 2, step iv). A comparison of the ^1H NMR (Fig. 1(a) and (c)) and ^{13}C NMR spectra of polymer **5b** and **6b** (Fig. 2) revealed clear

differences in the microstructure of these polymers. (a) The ratio of urethane/urea units ($\delta = 7.10$ ppm for NH urethane and $\delta = 5.75$ ppm for NH urea) as determined from ^1H NMR spectroscopy in DMSO-d_6 is 19:1 for polymer **5b** and 2.3:1 for **6b**. (b) The carbonyl region of polymer **6b** shows urea, urethane, and carbonate carbonyls in a ratio of 1:2:1 while in **5b** the signals for urea and carbonate are absent. The polymers prepared directly from the amino alcohols **3a-b** and an equimolar amount of diphenyl carbonate are not considered in this paper.

3.1. Synthesis of poly(amide urethane)s with predetermined molecular weight and functional end groups

There has been recent interest in using end functionalized low molecular weight polymers as building blocks for block, star, and graft copolymers; particularly the synthesis of low molecular weight poly(amide urethane)s with well defined end groups as precursors for powder coatings is of interest.

In order to prepare oligomers by step-growth reactions two variables can be considered: the conversion (p) and the initial molar ratio of reacting functional groups (q). The degree of polymerization ($\bar{P}_n$) in a polycondensation reaction is determined by the Carothers equation:

$$\bar{P}_n = (1 + q)/(1 + q - 2pq)$$

$$\text{for } q = 1, \quad \bar{P}_n = 1/(1 - p) \tag{1}$$

$$\text{for } p = 1, \quad \bar{P}_n = (1 + q)/(1 - q).$$

The α-hydroxy-ω-O-phenylurethanes **4a-e** are A–B monomers (with $q = 1$) and under these conditions the degree of polymerization is only a function of conversion. We have determined the dependence of $\bar{M}_n$ on conversion for the first stage of the polycondensation in which the condensate
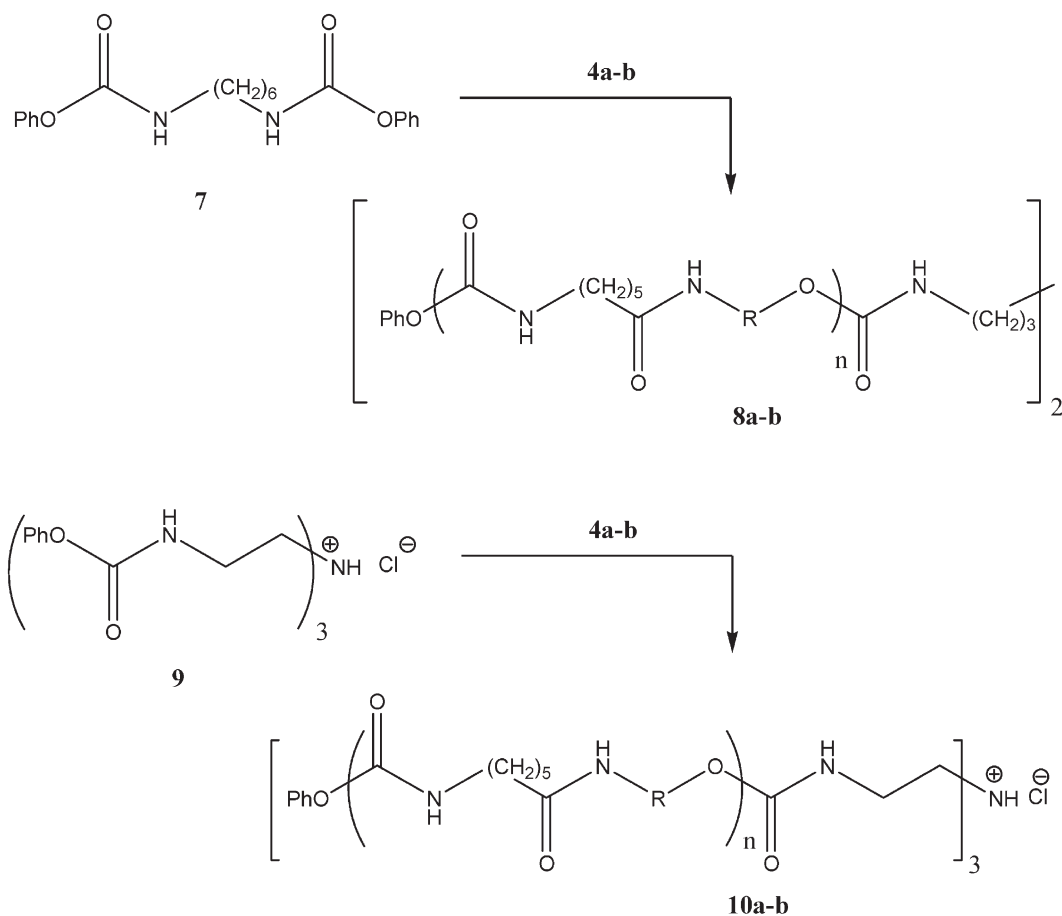
Scheme 3. Preparation of linear and star shaped poly(amide urethane)s with *O*-phenylurethane end groups.

(phenol) is not removed from the reaction mixture (Fig. 3). In addition, the last point in the diagram shows the $\bar{M}_n$ value obtained after removal of phenol in vacuo. The conversion and the number average molecular weight were determined by integration of the ^{1}H NMR resonance lines for the CH_2OH end groups and CH_2O groups in the repeating unit. It should be mentioned that the oligomers obtained under these conditions have the same functional end groups as the monomers from which they were prepared.

The preparation of oligomers from A–B monomers using the second approach-the inequivalence of functional groups-needs the addition of a second monomer with suitable functional end groups. In this case not only the molecular weight but also the nature of the end groups is
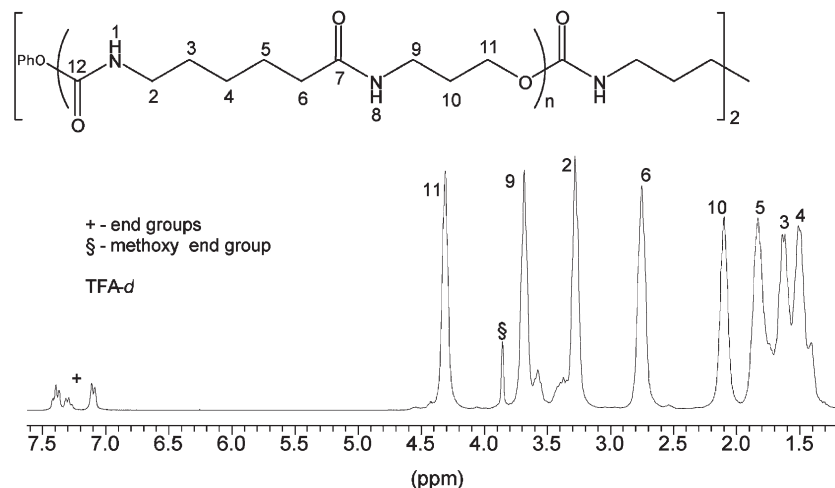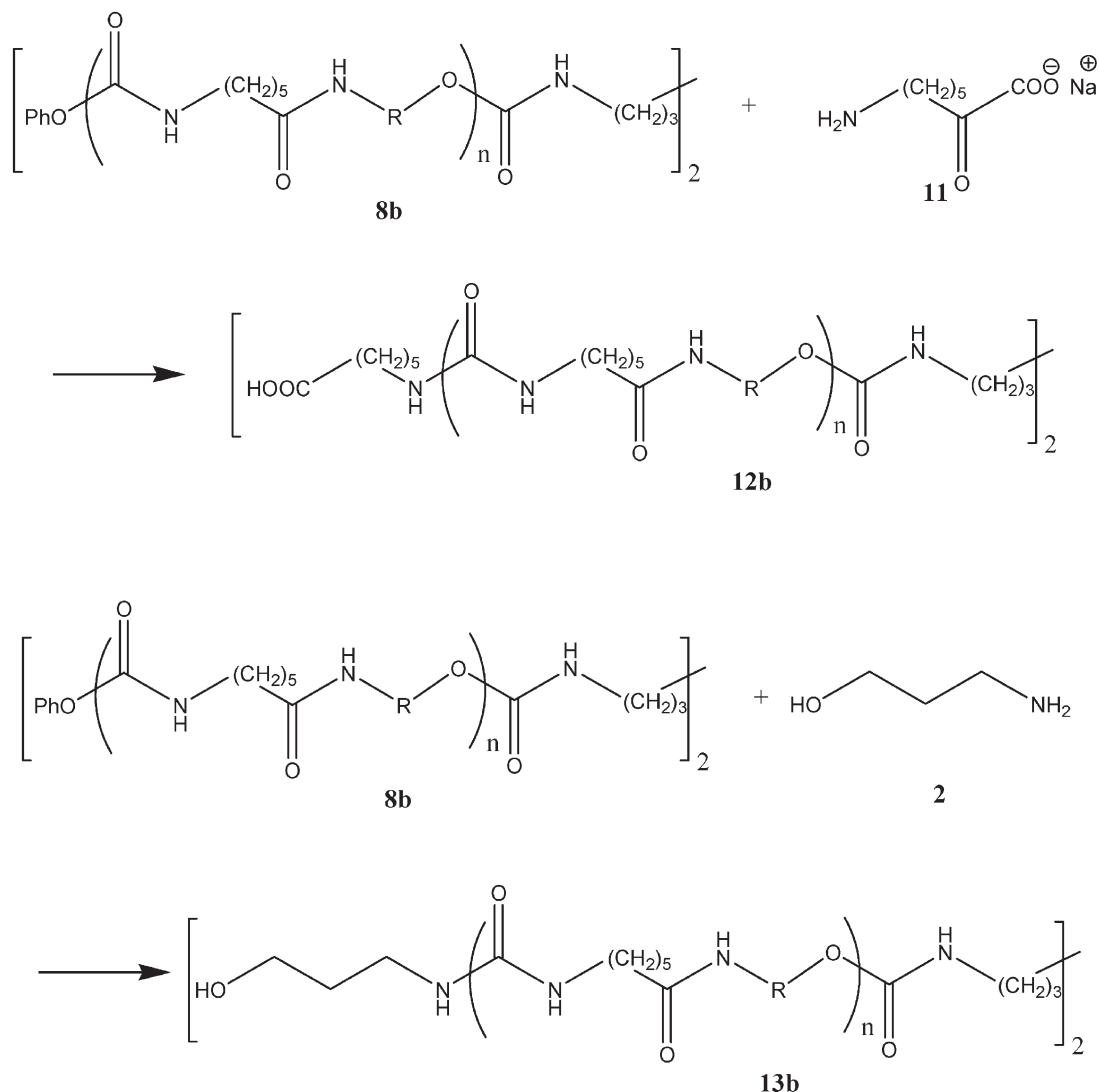

Fig. 4. ^{1}H NMR spectrum of poly(amide urethane) **8b** in CF$_3$COOD obtained via polycondensation of α-hydroxy-ω-*O*-phenylurethane **4b** and hexamethylene bis(*O*-phenylurethane) **7** at 90 °C.

Scheme 4. Preparation of linear poly(amide urethane)s with hydroxy and carboxy end groups.

adjusted. By addition of certain amounts of the di- or tri-O-phenylurethane comonomer **7** or **9**, the degree of polymerization for a complete conversion of the functional groups is determined by Eq. (1). By this procedure also the architecture of the polymers can be adjusted: linear or star shaped molecules are obtained (Scheme 3). Analysis of the ^{1}H NMR spectrum of a sample prepared according to

Table 6
Reaction conditions, number average molecular weight, polydispersity, and yield of poly(amide urethane)s with different functional end groups

No	Functional end groups	T (°C)	Reaction time (h)	M_n	M_w/M_n	Yield
8b	PhOCONH–	90	$2^n + 3^r$	5000	1.29	70
12b	HOOC–	100	$2^n + 2^r$	5250	1.49	84
13b	HO–	90	$2^n + 3^r$	6100	1.24	86

n = at normal pressure (1 bar), r = at reduced pressure (10^{-2} mbar). M_n and M_w/M_n were determined by GPC in DMAc with polystyrene standards.

Scheme 3 reveals the absence of CH$_2$OH end groups (compare Fig. 4 with Fig. 1(b)). The dependence of theoretically calculated and experimentally determined molecular weight on the value of q is shown in Table 5 (entry 2–5). On increasing the concentration of functional group [PhOCONH–] by adding **7** or **9**, the molecular weight decreases. This indicates that by adjusting the value of q (ratio of functionalities), the molecular weight of the poly(amide urethane)s can be controlled. The α,ω-O-phenylurethane terminated poly(amide urethane) **8b** ($M_n = 5000$) was used to introduce other functional end groups, i.e. –OH and –COOH suitable for chain coupling reactions (Scheme 4). Suitable reaction conditions were elaborated to introduce –OH or –COOH end groups by reacting diphenylurethane **7** as a model compound with sodium ε-aminocaproate **11** or amino alcohol **2**, respectively. A quantitative conversion of the O-phenylurethane groups into carboxyl and hydroxyl groups was obtained at 90–100 °C in DMAc (cf. model reactions in Section 2).
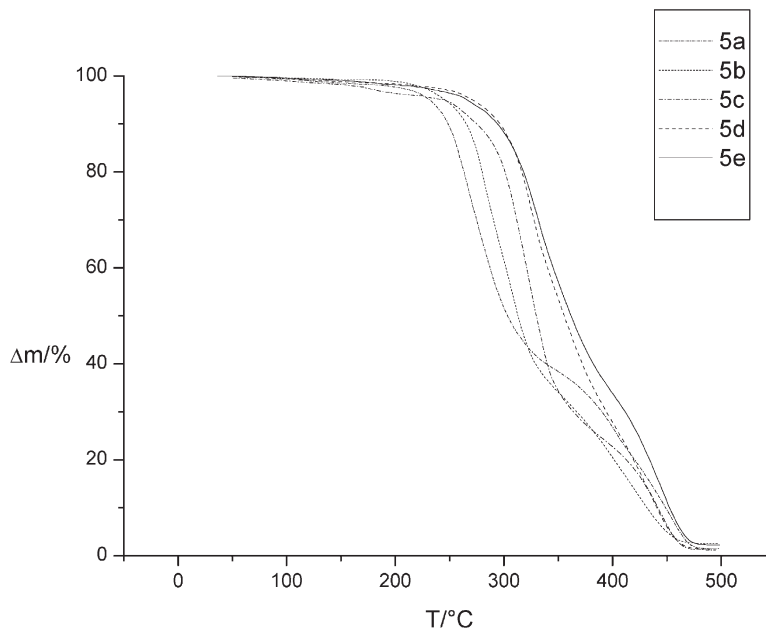
Fig. 5. TGA of the poly(amide urethane)s **5a-e** obtained via polycondensation of α-hydroxy-ω-O-phenylurethanes **4a-e** at 120 °C (heating rate 10 K/min).
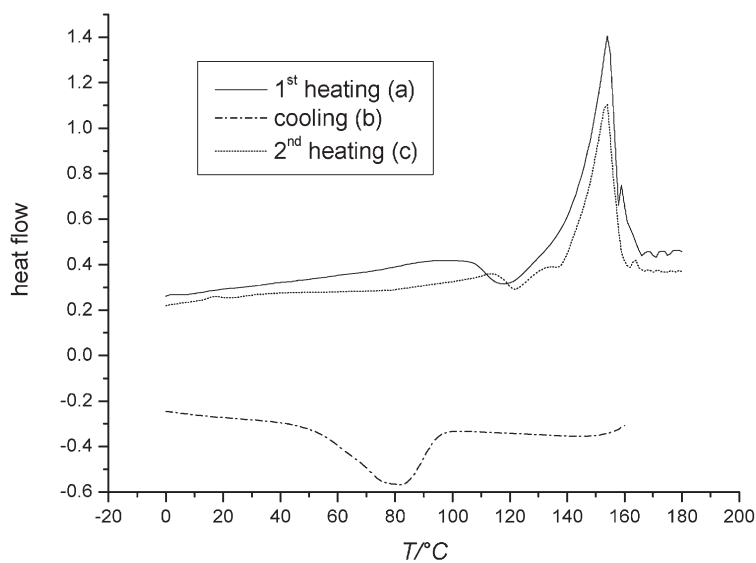

Fig. 6. DSC trace of **5b** prepared via polycondensation of **4b** in bulk at 120 °C (heating and cooling rate: 10 K/min). (a) first heating (b) cooling (c) second heating.

Table 7
Temperature of poly(amide urethane)s **5a-e** at 5, 10, 50 and 90% weight loss measured by means of TGA

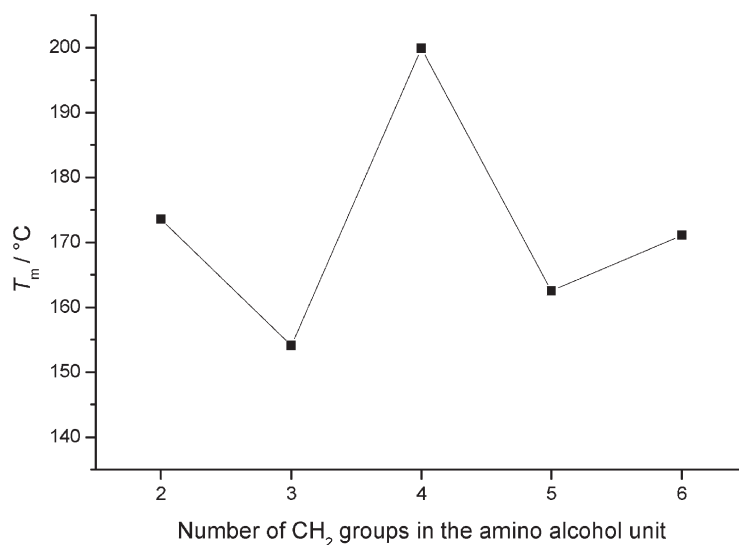| No	M_n-GPC	T (°C at 5% weight loss)	T (°C at 10% weight loss)	T (°C at 50% weight loss)	T (°C at 90% weight loss)
5a	8900	232	249	303	449
5b	7400	245	265	313	432
5c	8300	245	275	329	442
5d	11,500	271	295	356	441
5e	7100	266	294	362	453

Fig. 7. Melting points of the poly(amide urethane)s **5a-e** obtained via polycondensation of α-hydroxy-ω-*O*-phenylurethanes **4a-e** at 120 °C (first heating: 10 K/min).

The synthesis of carboxylic acid and hydroxyl terminated poly(amide urethane)s was carried out in the same way (Scheme 4). The obtained products were characterized by means of ^{1}H NMR spectroscopy. They show no phenyl end groups which confirms the formation of product **12** and **13**. The reaction conditions, molecular weights, polydispersities, and yields of poly(amide urethane)s with different end groups are summarized in Table 6.

3.2. Thermal properties

The thermogravimetric analyses of the poly(amide urethane)s **5a-e** reveal a dependence of the degradation behavior on the chemical structure of the polymer (Fig. 5). The following observations are made: (a) with increasing number of methylene groups in poly(amide urethane)s, the degradation temperature increases. Characteristic values of the weight loss are shown in Table 7; (b) for 1-amino-2-ethanol, 1-amino-3-propanol, and 1-amino-4-butanol in the repeating unit, a clear two-step decomposition is observed in the contrast to 1-amino-5-pentanol and 1-amino-6-hexanol. This indicates a change in the degradation mechanism. Upon degradation, the polymers with repeating

units with lower number of methylene groups decompose to cyclic urethanes while those with higher number eventually result in random chain cleavage with formation of isocyanates, which is characteristic for the thermal decomposition of urethane linkages.

The poly(amide urethane)s **5a-e** obtained by precipitation of a formic acid solution into diethyl ether are semi-crystalline polymers. A characteristic DSC curve (Fig. 6) shows upon first heating a crystallization peak before melting. Upon cooling, a broad crystallization peak is observed. Upon second heating, the trace is similar to that observed in the first heating run. Table 8 summarizes the DSC data obtained for the poly(amide urethane)s **5a-e.** Upon second heating, the melting temperature and the melting enthalpy are lower than upon first heating. By plotting the melting points as a function of the number of methylene groups in the amino alcohol, a pronounced even–odd effect is observed (Fig. 7). This observation was made earlier in the series of [*n*]-polyamides, [*n*]-polyurethanes [8], and [*n*]-poly(ester amide)s [14,15].

Table 8
DSC data of poly(amide urethane)s **5a-e** obtained via polycondensation of α-hydroxy-ω-*O*-phenylurethanes **4a-e** at 120 °C (heating and cooling rates of 10 K/min)

No	First heating		Second heating		Cooling	
	T_m (°C)	ΔH (J/g)	T_m (°C)	ΔH (J/g)	T (°C)	ΔH (J/g)
5a	173.6	54.4	151.5	39.2	No crystallization	
5b	154.1	80.3	153.7	41.8	81.4	−35.9
5c	199.1	54.4	189.4	58.5	154.0	−58.9
5d	162.1	77.2	160.7	64.7	121.4	−68.1
5e	171.1	66.1	169.4	53.7	125.4	−59.2

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