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New Routes to [*n*]-Polyurethanes. [*3*]-Polyurethane: Synthesis, Characterization, and Polymerization-Depolymerization Equilibrium

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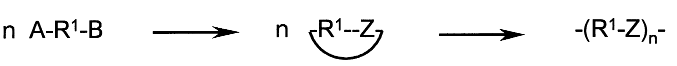
SUMMARY: The ring-opening polymerization of dimethylene urethane (**3**) (systematic name: 2-oxo-1,3-oxazolidine) with methyl trifluoromethane sulfonate as the initiator is inefficient. It was shown that equimolar amounts of dimethylene urethane and trifluoromethane sulfonate result in the expected active species – 2-methoxy-4,5-dihydro-1,3-oxazolium trifluoromethane sulfonate (**5a**) – : propagation, however, does not occur. Poly(dimethylene urethane) (**4**), was obtained by means of polycondensation of a linear monomer, i.e., 2-(2-phenoxycarbonylimino-1-ethoxycarbonylimino)-ethanol (**9**). This [*3*]-polyurethane is a semicrystalline material with a melting point of 200.7 °C. Heating above its melting point leads to dimethylene urethane by ring-closing depolymerization. The thermodynamical data support the experimental results with respect to the polymerization / depolymerization equilibrium.

Introduction

Linear polymers with heteroatoms in the main chain are usually prepared by polycondensation reactions which are typically step growth reactions, i.e., polyesters (PE) by polycondensation of diols with dicarboxylic acid derivatives, polyamides (PA) by polycondensation of diamines with dicarboxylic acid derivatives and polyurethanes (PU) by polyaddition of diisocyanates with diols (Eq. 1). The synthesis of these AA,BB-type polymers or [*m,n*]-polymers, where AA and BB represent the functional groups of the two monomers and *m*, *n* the number of carbon atoms in the main chain of the repeating unit is widely used for technical polymers.

$$n\ A\text{-}R^1\text{-}A\ +\ n\ B\text{-}R^2\text{-}B \longrightarrow A\text{-}(R^1\text{-}Z\text{-}R^2\text{-}Z)_n\text{-}R^2\text{-}B \qquad (1)$$



(2)

An alternative route to the preparation of PE and PA is the ring-opening polymerization (Eq. 2) of suitable cyclic monomers, i.e, *ε*-caprolactone and *ε*-caprolactam. These ring-opening polymerization reactions result in A,B-type polymers or [*n*]-polymers. Beside the advantage

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that this access to PE and PA is by a chain growth reaction, an additional advantage arises if the cyclic monomers are not prepared from linear A-R^1-B precursors, but in a totally different way, i.e., by Bayer-Villiger oxidation of cyclohexanone for ε-caprolactone and by Beckmann rearrangement of cyclohexanone oxime for ε-caprolactam.

Polycondensation of α-amino-ω-alkanols with phosgen or other suitable carbonic acid derivatives leads to polymers with non-uniform microstructures due to the fact that the hydroxy and amino groups show different nucleophilicities in the reaction with carbonic acid derivatives. As a consequence, the α-amino-ω-alkanols are linked head-to-tail with the formation of urethane groups, head-to-head with formation of urea groups, and tail-to-tail with formation of carbonate groups.

In this paper we present results on how to prepare linear polyurethanes with uniform microstructure starting from α-amino-ω-alkanols and carbonic acid derivatives, with special emphasis on amino ethanol.

Recently it was reported that the cationic ring-opening polymerization of cyclic six- and seven membered urethanes yield the corresponding [*4*]- and [*5*]-polyurethanes with uniform microstructure1-3). Further it was reported that by polycondensation of α-amino-ω-alkanols with tert.-butyl tricarbonate [*n*]-polyurethanes are obtained with a high content of urethane groups together with small amount of urea groups. In this latter reaction first α-isocyanato-ω-alkanols are obtained which are polymerized in situ in the presence of zirconium(IV)-acetylacetonate or dibutyltin dilaurate4). In our laboratory [*n*]-polyurethanes were obtained by the polycondensation of α-hydroxy-ω-O-phenyl urethanes5).

Experimental

Reagents

Starting materials and reagents used for syntheses were of high purity. The solvents were stored in an inert gas atmosphere after distillation. Nitrogen was passed over molecular sieves (4Å), finely distributed potassium on aluminium oxide, and BTS catalyst (from BASF) for purification.

Measurements

Specifications of the instruments used have been described elsewhere in the literature3,5).

Syntheses

Dimethylene urethane (*DU*, **3**): 70.25 g (1.15 mol) amino ethanol (**1**), 270.99 g (1.26 mol) diphenylcarbonate and 642.0 µL ($2.87 \cdot 10^{-3}$ mol) $Bu_2Sn(OMe)_2$ were heated to 145°C. After 4 h first phenol was distilled off at 19 mbar and then dimethylene urethane (**3**) at $1.5 \cdot 10^{-2}$ mbar.

Crystallization from acetone and recrystallization from ethyl acetate lead to a colourless solid. Yield: 75%; m.p. 87-88°C.

$C_3H_5NO_2$ (87.08):	calc.:	C 41.38	H 5.79	N 16.08
	found:	C 41.28	H 5.76	N 16.12

2-O-Phenoxycarbonylimino-1-phenoxycarbonyloxy-ethane (**8**): To a solution of 20.0 g (327.4 mmol) amino ethanol (**1**) and 79.2 mL (982.3 mmol) pyridine in dry THF, 94.5 mL (753.0 mmol) phenylchloroformate was added within 90 min at 50°C. After 12 h stirring at 50°C the suspension was cooled to room temperature, pyridine hydrochloride was filtered off and the solvent was distilled off under vacuum. After purification a colourless solid was obtained. Yield: 81%; m.p. 89-90°C.

$C_{16}H_{15}NO_5$ (301.30):	calc.:	C 63.78	H 5.02	N 4.65
	found:	C 63.53	H 4.96	N 4.69

2-(2-Phenoxycarbonylimino-1-ethoxycarbonylimino)-ethanol (**9**): To a solution of 20.0 g (66.4 mmol) 2-O-phenoxycarbonylimino-1-phenoxycarbonyloxy-ethane (**8**) in dry THF 3.6 mL (60.3 mmol) amino ethanol (**1**) was added within 10 min. After 12 h stirring at room temperature the solvent was distilled off and the product was purified by column chromatography and crystallization. Yield: 72%; m.p. 100°C.

$C_{12}H_{16}N_2O_5$ (268.27):	calc.:	C 53.73	H 6.01	N 10.44
	found:	C 53.53	H 6.25	N 10.35

Polycondensation of 2-(2-phenoxycarbonylimino-1-ethoxycarbonylimino)-ethanol (**9**): 2-(2-Phenoxycarbonylimino-1-ethoxycarbonylimino)-ethanol (**9**) and 1.67 mol% $Bu_2Sn(OMe)_2$ was stirred under nitrogen at 120°C. After 15 min the phenol was distilled off under vacuum. The polymerization was terminated after 3 h by cooling to room temperature. The polymer was dissolved in DMF at 150°C and then precipitated into Et_2O. Yield: 88%; M_n = 8200; M_w/M_n = 1.55 (GPC in DMAc/1.22 $g{\cdot}L^{-1}$ LiCl; polystyrene standards); m.p. 200.7°C.

2-Methoxy-4,5-dihydro-1,3-oxazolium trifluoromethane sulfonate (**5a**): To a solution of 0.87 g (10^{-2} mol) dimethylene urethane in 9 mL CH_2Cl_2 1.64 g (10^{-2} mol), TfOMe was added at room temperature and stirred for 19 h. The solvent was evaporated under vacuum and the residual oil was analyzed by means of ^1H and ^{13}C NMR spectroscopy (Table 1.).

Reaction of 2-methoxy-4,5-dihydro-1,3-oxazolium trifluoromethane sulfonate (**5a**) *with potassium acetate*: To 1.0 g (3.98 mmol) **5** was added a solution of NaOAc/AcOH in excess. After 12 h stirring at 80°C the solvent was removed and the liquid residue was analyzed by means of ^1H and ^{13}C NMR spectroscopy.

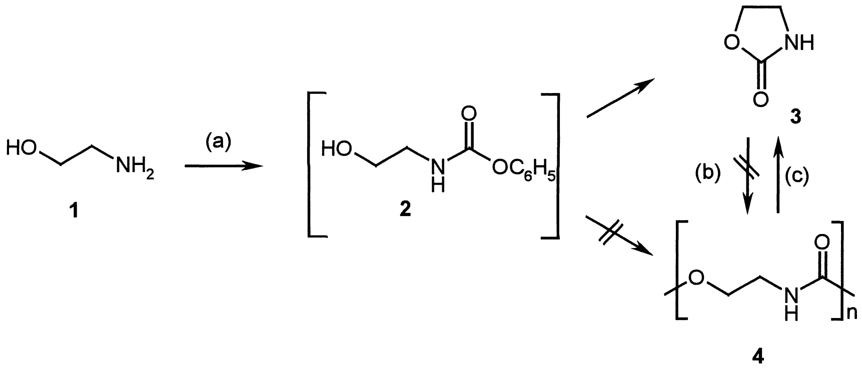
^{1}H NMR (in DMSO-d_6): δ= 7.28 (br.s, NH, 1H), 4.00 (tr, CH_2O, 2H), 3.53 (s, CH_3O, 3H), 3.21 (tr, CH_2N, 2H), 2.00 (s, CH_3CO, 3H).

^{13}C NMR (in DMSO-d_6): δ= 170.36 and 156.83 (C=O, 2C), 62.65 (CH_2O, 1C), 51.30 (CH_3O, 1C), 39.48 (CH_2N, 1C), 20.63 (CH_3, 1C).

Results and discussion

Dimethylene urethane (DU, **3**) was prepared from amino ethanol (**1**), diphenylcarbonate and catalytical amounts of $Bu_2Sn(OMe)_2$. First phenol was distilled off at 145°C and 19 mbar then DU at $1.5 \cdot 10^{-2}$ mbar. In solution and at room temperature the amino ethanol was first converted to O-phenoxycarbonylimino-ethanol (**2**) which, in situ, undergoes cyclization. Obviously the intramolecular process is favored over the intermolecular transurethanization of the hydroxy group with the activated phenyl urethane moiety; [*3*]-polyurethane (**4**) is not obtained.

High purity dimethylene urethane was subjected to bulk polymerization using electrophilic initiators, i.e., methyl trifluoromethane sulfonate (TfOMe) or trifluoromethane sulfonic acid anhydride (Tf_2O) and nucleophilic initiators, i.e., butyllithium or dibutylmagnesium. (For all experiments $[DU]_0/[I]_0$ = 50 to 100, but in all cases the monomer was recovered.) No polymer, nor oligomers were detected (Scheme 1). As will be shown later, [*3*]-polyurethane undergoes ring-closing depolymerization upon heating.



Scheme 1. Synthesis of dimethylene urethane. Ineffective attempts to prepare poly(DU) by polycondensation of **2** and ring-opening polymerization of **3**; ring-closing depolymerization of **4**. (a) $(C_6H_5O)_2CO$, $Bu_2Sn(OMe)_2$, 145°C or $(C_6H_5O)_2CO$, THF, room temperature; (b) TfOMe, 100°C ($[DU]_0/[TfOMe]_0$ = 50 to 100); (c) i. e., heating to 200°C.

Using TfOMe as the initiator, the reason for this result was investigated in more detail. Treatment of DU in methylene chloride solution with equimolar amounts of TfOMe revealed the formation of an 1:1 adduct (Scheme 2). NMR spectroscopic analysis of this adduct revealed the formation of 2-methoxy-4,5-dihydro-1,3-oxazolium trifluoromethane sulfonate (**5a**), by comparison with analogous adducts of TfOMe with trimethylene urethane (TU)[2)] and tetramethylene urethane (TeU)[3)] (cf. Table 1). Special attention was payed to the resonance lines of the CH_3 group in the active species which, due to the high δ value, strongly suggest that it is the carbonyl oxygen and not the nitrogen atom of DU that is methylated, and consequently **5a** and not **5b** is formed.

Table. 1. ^1H and ^{13}C NMR data of the active species of DU, TU, and TeU.

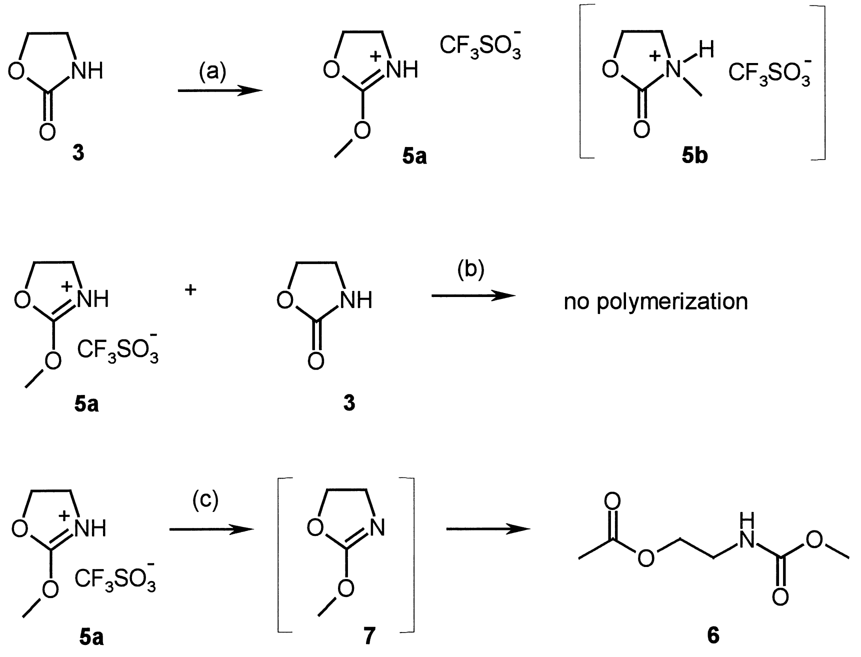
Active species of	NH^+	$O-C(NH^+)-O$	CH_2-O	$O-CH_3$	CH_2-N	$CF_3SO_3^-$
	^1H NMR	data[a)]:				
DU	10.34	---	5.06	4.27	4.13	---
TU	9.77	---	4.80	4.07	3.59	---
TeU	9.67	---	4.85	4.07	3.61	---
	^{13}C NMR	data[a)]:				
DU	---	165.04	71.89	60.89	42.56	119.24
TU	---	160.30	73.10	58.60	38.90	120.80
TeU	---	165.62	78.54	59.50	43.42	123.14

[a)] Solvent CD_2Cl_2; δ-values in ppm.

From this result it was concluded that the initiator reacts with the monomer with formation of the active species expected, however, the propagation reaction did not take place, neither in solution at room temperature nor in bulk at 100°C. Two explanations can be given for this result. First, the DU nucleophile is too weak to induce ring-opening of the active species **5a** and, in terms of thermodynamics, the free energy change of the reaction of DU with the active species is positive. Second, in bulk at 100°C the 2-methoxy-4,5-dihydro-1,3-oxazolium trifluoromethane sulfonate (**5a**) rearranges to form 2-oxo-3-methyl-1,3-oxazolidinium trifluoromethane sulfonate (**5b**) which cannot participate in the ring-opening polymerization. It has been shown in the literature that the kinetically controlled methylation of 2-oxo-3-

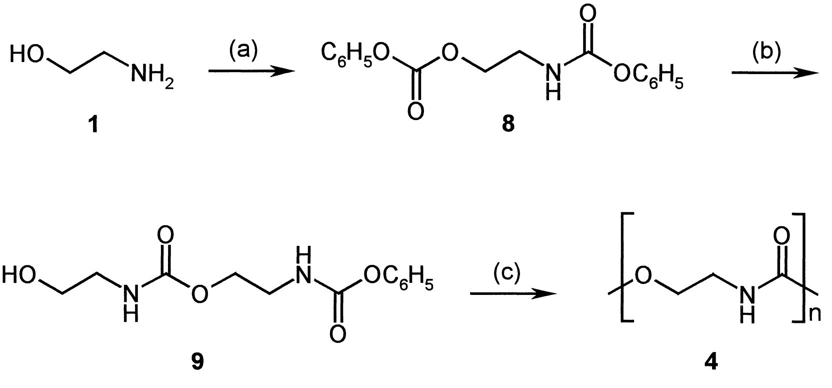
methyl-1,3-oxazolidin with methyl fluorosulfonate leads to the O-methylated product and thermodynamically controlled methylation to the N-methylated product$^{6)}$. Heating of the O-methylated product gives exclusively the N-methylated product.

In order to determine whether the nucleophilicity of the DU monomer is too low to induce ring-opening of the active species by reaction with the most electrophilic center of the active species – the endocyclic CH_2 group adjacent to the oxygen atom – we subjected the active species to a reaction with sodium acetate as the nucleophile. The main product of this reaction was methoxycarbonylimino ethyl acetate (**6**) according to ^1H and ^{13}C NMR analysis. As a consequence, the ring-opening of the active species by a suitable nucleophile is possible. For the formation of **6**, however, two routes are possible. (i) The acetate reacts directly with the active species **5a** or (ii) the acetate first deprotonates the active species with formation of 2-methoxy-4,5-dihydro-1,3-oxazole (7) before ring-opening occurs. Additional experimental results will give more insight into the role of nucleophilicity and basicity of reagents reacting with the active species.



Scheme 2: Mechanistic aspects of the reaction of DU with TfOMe and of the DU·TfOMe adduct with sodium acetate. (a) CF_3SO_3Me, CH_2Cl_2, room temperature; (b) 100°C, **3**/**5** = 50 to 100; (c) CH_3COONa/CH_3COOH, 80°C, 12 h.

In order to obtain more information on the thermodynamics of the ring-opening polymerization of DU (**3**) and the ring-closing depolymerization of poly(DU) (**4**) the polymer was prepared by means of polycondensation of a linear dimer **9** (Scheme 3). Starting with amino ethanol (**1**), first 2-O-phenoxycarbonylimino-1-phenoxycarbonyloxy-ethane (**8**) was prepared which, upon aminolysis with amino ethanol, resulted in the linear dimer **9**. This starting material is an ABB' monomer with a nucleophilic species A (OH) and two electrophilic centers B (alkyl-NH-CO-O-alkyl) and B' (alkyl-NH-CO-O-phenyl). The O-phenylurethane carbonyl group is activated by the -I effect of the phenoxy group. In addition, the phenoxide is a good leaving group and therefore it is expected that B' will react preferentially (compared to B). It was shown by means of GPC that the polycondensation of a similar dimer resulted at low conversions, only in oligomers with an even number of repeating units, thus proving the much higher reactivity of B' compared to B7). The polycondensation of the dimer **9** was studied with respect to the monomer conversion and side reactions8). Good results were obtained at 120°C and upon removal of the condensate (phenol) by distillation. After 3 h a polymer yield of 88% was obtained which, after purification showed a molecular weight of M_n = 8200 and a polydispersity index of Q = 1.55 (GPC in DMAc with 1.22 g/L LiCl; calibration with polystyrene). Under these conditions, only traces of DU were detected in the distillate. At longer times the thermodynamic instability of the polymer became evident; DU was formed quantitatively by ring-closing depolymerization.



Scheme 3: Synthesis of [*3*]-polyurethane. (a) C_6H_5O-CO-Cl, THF, Py, room temperature, (b) H_2N-CH_2CH_2-OH, THF, room temperature, (c) $Bu_2Sn(OMe)_2$, 120°C, 3 h, 10^{-2} mbar.

The ^{1}H NMR spectrum (DMSO-d_6) of the polymer revealed three main, well resolved resonance lines at δ = 6.65 (br.s, NH), 3.99 (tr, CH_2O), and 3.24 (d of tr, CH_2N) ppm, which are an indication that head-to-tail linkages dominate the structure of the polymer. No resonance lines for urea-NH ($\delta = 5.5$ ppm) were observed. The signals of low intensity were assigned to HO-CH_2-CH_2-endgroups and to an NH-resonance for a cis conformer. The ^{13}C NMR spectrum showed three resonance lines at $\delta = 155.61$ (C=O), 62.30 (CH_2O), and 39.65 (CH_2N) and no resonance lines of head-to-head structures.

Differential scanning calorimetric measurements indicated a high tendency to depolymerization (Figure 1). Upon first heating two endothermic peaks were observed: one was assigned to the melting transition with a maximum at 200.7°C ($\Delta H_m \approx 50$ J/g) and a second broad peak was assigned to the beginning decomposition process by ring-closing depolymerization. Upon a second heating, an endothermic peak at $T \approx 77$°C was observed which was assigned to the melting of dimethylene urethane contaminated with linear oligomers due to incomplete conversion of poly(DU). The third DSC-plot showed the melting point of a pure DU sample at $T = 95$°C (in the peak maximum). The assumption that ring-closing depolymerization is associated with the melting of the poly(DU) is supported by ^1H NMR analysis of a poly(DU) sample tempered for 20 min at 180°C. The main resonance lines in this spectrum were assigned to DU ($\approx$ 75%), resonance lines of lower intensity were assigned to the linear oligomers by comparison with authentic samples of DU and the linear dimer **9**. Thermogravimetric measurements support the assumption that poly(DU) undergoes decomposition following a ring-closing depolymerization mechanism[5].

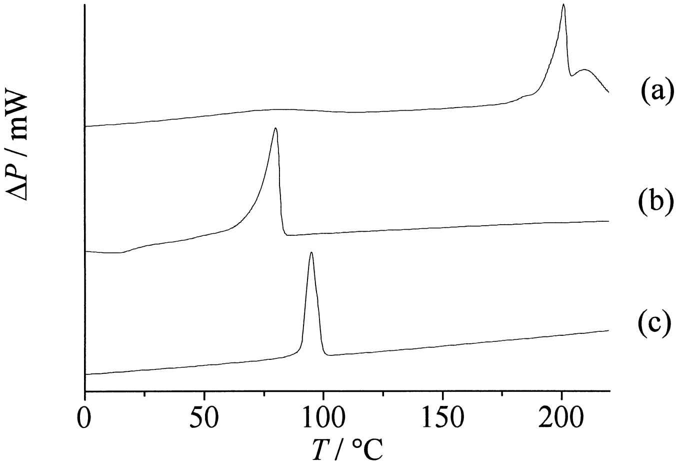


Figure 1. DSC plot of poly(DU). (a) first heating, (b) second heating and of DU (c) first heating.

Calorimetric measurements of DU and poly(DU) were performed between 6 and 335 K to determine the free polymerization enthalpy ΔG^0_{pol}[9]. The molar polymerization enthalpy ΔH^0_{pol} over the entire temperature range had a nearly constant value of between –1 and –2 kJ·mol^{-1} and the polymerization entropy ΔS^0_{pol} had values of between 2 and -5 J·K^{-1}·mol^{-1}. For the free molar polymerization enthalpy a value of $\Delta G^0_{pol} \sim -1$ kJ·mol^{-1} was calculated (Figure 2). From these data a ceiling temperature of ~ 500 K was estimated. The results of the calorimetric measurements were in full agreement with the experimental results: (i) Ring-opening polymerization of DU was not observed; thus under experimental conditions additional factors lead to $\Delta G^0_{pol} > 0$. (ii) Ring-closing depolymerization occured at temperatures ≥ 200°C.

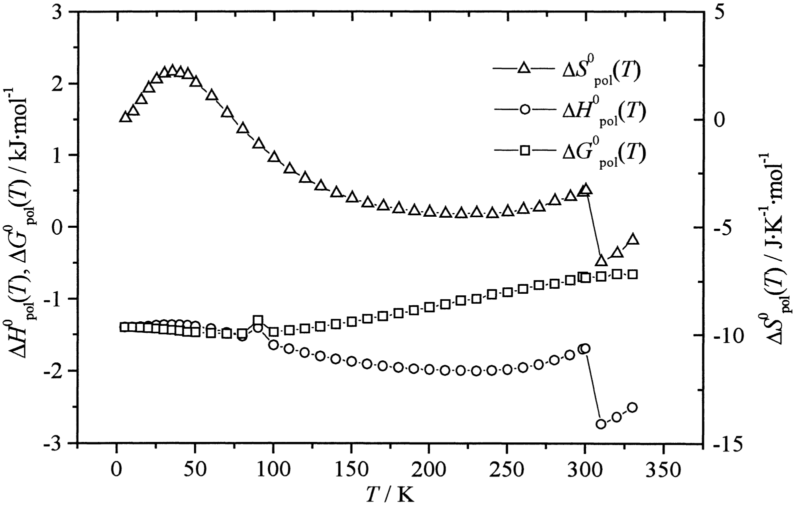


Figure 2. Enthalpy, entropy, and free energy change in the ring-opening polymerization of dimethylene urethane to poly(dimethylene urethane) with uniform microstructure (data obtained from calorimetric measurements)[9].

Conclusions

[*3*]-Polyurethane was prepared by polycondensation of the linear dimer **9** with hydroxy and O-phenylurethane endgroups. The semicrystalline polymer **4** is a high melting material which, upon melting, undergoes ring-closing depolymerization. This thermal instability of the

polymer with respect to its cyclic monomer **3** has thermodynamic reasons: the polymerization / depolymerization equilibrium is completely shifted to the cyclic monomer.

It should be stressed that a thermodynamically instable polymer was prepared by polycondensation of a monomer with a nucleophilic and an activated urethane endgroup, showing that this method has great potential for the preparation of polymers by polycondensation, i.e., of complex polymer architectures like multiblock copolymers.

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