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Aliphatic Poly(ether amide)s by Polycondensation of Activated Sebacic Acid Derivatives

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Poly(ether amide)s were prepared by polycondensation of 1,13-diamino-4,7,11-trioxatridecane (DTT) with the bisimidazolide or with the bis N-hydroxysuccinimide ester of sebacic acid. Four different solvents and three different temperatures were compared. The highest molecular weights were obtained with the bisimidazolide in dimethylsulfoxide (DMSO) at 60°C. MALDI-TOF mass spectra revealed the existence of cyclic oligoamides and polyamides in all samples. The molar fraction of cycles considerably increased with higher molecular weights of the entire sample. The polycondensations were repeated under optimum conditions in the presence of α-cyclodextrin to prepare polydisperse catenanes consisting of α-cyclodextrin threaded on cyclic polyamides. Yet, despite broad variation of the reaction conditions, only cylic polyamides free of cyclodextrin were isolated. Furthermore, a pseudorotaxane was prepared from DTT and α-cyclodetrin and polycondensed with bis-(4-chlorophenyl)sebacate. Again, only cyclic polyamides free of cyclodextrin were detectable.

Keywords: cyclics polyamides; α-cyclodextrin; catenanes; polycondensation; MALDI-TOF

1 Introduction

The technical production of aliphatic polyamides is based on polymerizations of lactam or polycondensations of α,ω-diamines with dicarboxylic acids in bulk at temperatures above 200°C. These high temperatures are needed to keep the reaction mixture in the molten state and to enable high conversions. These high temperatures involve transamidation reactions, including cyclization by "back-biting" and they also include side reactions destroying functional groups.

The present work is a continuation of previous studies with the purpose of finding kinetically controlled syntheses of aliphatic polyamides avoiding any kind of equilibration and back-biting reactions. Under mild conditions, kinetically controlled polycondensations (KCPs) may also avoid other side reactions and allow high conversions. In previous studies, we have demonstrated (1, 2) that clean KCPs, conducted up to high conversion, not only give high molecular weights, but also large fractions of cyclic oligomers and polymers. In clean KCPs, cyclization will compete with propagation at any concentration and at any conversion in contrast to the predictions of the classical Carothers-Flory theory of step-growth polymerizations (3, 5). In an ideal case avoiding any side reactions, even 100% cycles will be formed. Therefore, the chain growth is not only limited by the conversion, but also by the competition of cyclization and propagation as summarized in Equation (1).

In this connection, we were interested in syntheses of aliphatic polyamides via a clean KCP. The interfacial polycondensation of aliphatic dicarboxylic dichlorides (ADADs) is unfavorable because of the hydrolysis of acid chloride groups and because of the early precipitation of low molar mass polyamides (6). Polycondensation of ADADs with diamines in dry organic solvents require the addition of HCl acceptors, such as tert. amines, which cause side reactions by elimination of HCl from the ADADs. The use of silylated aliphatic diamines is plagued by the same problem (6, 7).

Therefore, polycondensations of activated esters or amides of aliphatic dicarboxylic acids seemed to be a promising approach. Syntheses of various polyamides via activated esters have been studied a decade ago by Katsarava and coworkers (8–10), but the aspect of cyclization was not taken into consideration. In the preceding part of this series (7), it was demonstrated that the bis(4-chlorophenyl)ester of sebacic acid **1** is, indeed, an useful reaction partner of aliphatic diamines yielding polyamides with high molecular weights and large fractions of cycles under carefully optimized reaction conditions. In the present work, the more reactive bis(N-hydroxy-succinimide)ester **2** and the bisimidazolide of sebacic acid **3** (11) were studied.

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1,13-Diamino-4,7,10-trioxatridecane (DTT) was used as a reaction partner for two reasons. Firstly, this diamine should improve the solubility in organic reaction media, and, thus, enable high conversions. Secondly, the resulting poly(ether amide)s should be suited for threading of various polar macrocycles, such as cyclodextrins or calixarenes. In this way, polydisperse catena compounds may be formed, an interesting aspect currently under investigation in our laboratory.

$$\overline{\mathrm{DP}} = \frac{1}{1 - p(1 - 1/X^{a})} \qquad (1)$$

$\overline{\mathrm{DP}}$= average degree of polymerization; $p =$ conversion; $^{a} = \mathrm{V_p/V_c}$ (rate of propagation versus cyclization); $X =$ factor > 1.0 allowing for an adaption to various concentrations.

2 Experimental

2.1 Materials

1,13-Diamino-4,7,10-trioxatridecane (DTT) was purchased from Aldrich Co. (Milwaukee, WI) and dried azeotropically with toluene. Sebacoylchloride, imidazole and N-hydroxysuccinimide were also purchased from Aldrich Co. and used as received. Chlorotrimethylsilane and hexamethyldisilazane were gifts of Bayer AG (Leverkusen, Germany) and used as received. N-Trimethylsilyl imidazole was prepared by silylation of imidazole with chlorotrimethylsilane and hexamethyldisilazane in refluxing benzene and isolated by distillation (it is also available from Aldrich Co.). Ultradry dimethylsulfoxide was purchased from Aldrich Co. and used as received.

N-methylpyrrolidone (NMP) and sulfolane were purchased from Aldrich Co. and distilled over P_4O_{10} in a vacuum of 10^{-2} mbar.

2.2 Bis(N-Hydroxy Succin Imide) Sebacate 2

Sebacic acid (0.1 mol) and N-hydroxy succin imide (0.21 mol) were dissolved in dry dioxane (200 mL) and a solution of N,N′-dicyclohexyldiimide (0.21 mol) in dry dioxane (50 mL) was added. The reaction mixture was allowed to stand at 20–22°C for 24 h and then filtered from the precipitated N,N′-dicyclohexyl urea, which was washed with dioxane. The filtrate was concentrated *in vacuo* and the crystallization of the product was completed by the portionwise addition of dry toluene. The product was isolated by filtration and recrystallized from dry tetrahydrofuran/toluene. Yield: 61%, m.p. 160–162°C.

Anal. Calcd. for $C_{18}H_{24}N_2O_8$ (396.40): C 54.54, H 6.10, N 7.07; Found: C 54.07, H 6.17, N 7.09%. ^{1}H-NMR (DMSO-d$_6$/TMS): $\delta = 1.30$–1.36 (m, 8 H), 1.63 (t, 4 H), 2.66 (t, 4 H), 2.81 (s, 8 H) ppm.

2.3 Sebacoylimidazolide 3

N-Trimethylsilylimidazole (0.4 mol) was dissolved in dry toluene (200 mL) and a solution of sebacoylchloride (0.2 mol) in dry toluene (50 mL) was added dropwise with stirring at a temperature around 70–80°C. The reaction mixture was refluxed for 1 h and cooled with ice. The crystallized product was filtered off with the exclusion of moisture, washed with ligroin and dried *in vacuo*. Yield 88% m.p. 153–155°C. Anal. Calcd. for: $C_{16}H_{22}$ N_4O_2 (302.38) C 63.56, H 7.33, N 18.53, Found 63.14, H 7.30, N 18.34 ^{1}H-NMR (DMSO-d$_6$): δ (ppm) = 1.31 (s, 8 H), 1.62 (s, 4 H), 3.00 (t, 4 H), 7.05 (s, 2 H), 7.69 (s, 2 H), 8.41 (s, 2 H).

2.4 Polycondensations

A) with **2** (No. 2, Table 1)

DTT (10.0 mmol) was dissolved in DMSO (22 mL) and the sebacate **2** (10.0 mmol) was dissolved in DMSO (22 mL). Both solutions were mixed by vigorous shaking and thermostated in an oil bath at 60°C for 24 h, whereby a gelation of the reaction mixture was observed. Afterwards, the reaction mixture was precipitated into cold water. The precipitated polyamide was isolated by filtration, washed with warm water and extracted with 300 mL of refluxing diethyl ether with stirring. The isolated polyamide was dried at 80°C *in vacuo*.

B) with **3** (No. 5, Table 2)

DTT (10.0 mmol) was dissolved in DMSO (22 mL) and the solution of **2** (10.1 mmol) in DMSO (22 mL) was added and mixed with vigorous shaking. Both polycondensation and work-up were conducted as described above.

C) with **3** in bulk

DTT (20.0 mmol) and **2** (20.0 mmol) were weighed into a cylindrical glass reactor equipped with mechanical stirred gas-inlet and gas-outlet tubes. The reaction vessel was placed into an oil bath preheated to 120°C. The temperature was rapidly raised to 160°C and maintained for 2 h. A vacuum of 10^{-1} mbar was then applied for 20 min to

Table 1. Polycondensations^a of DTT with the bisester **2**

Exp. No.	Solvent	Addition of bases	Temp. (°C)	Yield (%)	η_{inh} (dL/g)
1	DMSO	—	20	80	0.53
2	DMSO	—	60	83	0.64
3	DMSO	—	100	77	0.58
4	DMSO	Pyridine	60	85	0.78
5	DMSO	Pyridine	100	70	0.60
6	DMSO	Triethylamine	60	81	0.84
7	DMSO	Triethylamine	100	72	0.63
8	NMP	—	20	80	0.70
9	NMP	—	60	64	0.64
10	NMP	—	100	0	—

^{a}The reaction time was 24 h for all experiments.

Table 2. Polycondensations of DTT with the bisimidazole **3**

Exp. No.	Solvent	Excess of **3** (mol%)	Temp. (°C)	Time (h)	Yield (%)	η^{a}_{inh} (dL/g)
1	— (in bulk)	—	160	2	93	0.80
2	DMSO	—	60	8	91	0.92
3	DMSO	—	60	24	96	1.20
4	DMSO	—	60	48	97	1.27
5	DMSO	1	60	24	97	1.32
6	DMSO	1	60	48	89	1.38
7	DMSO	—	100	24	90	0.71
8	DMSO	1	100	24	45	0.55
9	Sulfolane	—	60	24	77	0.50
10	Sulfolane	—	100	24	71	0.43
11	NMP	—	60	24	67	0.37
12	NMP	—	100	24	68	0.34

[a] Measured at 25°C with c = 2 g/L in m-cresol.

remove most of the liberated imidazole. Finally, the cold polyamide was dissolved in trifluoroethanol and precipitated into water.

2.5 Attempted Syntheses of Polycatenanes

A) from mixtures of the reactants

Dry α-cyclodextrin (0.1 mmol or 0.4, 0.8, 1.2, 1.6, 2.0, 2.5, 5.0, 10.0 mmol) was dissolved in dry DSMO (44 mL). DTT (20 mmol) was added and bis-(4-chlorophenyl sebacate **1** (20 mmol) or the bis-imidazolide **3** (20 mmol) were added. The reaction vessel was closed by a glass stopper and steel spring thermostated at 60°C and homogenized by stirring with a magnetic bar. After 48 h, the reaction mixture was poured into cold water or acetone, and the precipitated polymer was isolated by filtration.

B) Pseudorotaxane of DTT

DTT (10 mmol) and α-cyclodextrin (50 mmol) were heated with dist. water (100 mL) up to 80°C. The resulting clear solution was rapidly cooled to approx. 5°C (by means of an ice/NaCl mixture), whereby a white precipitate was formed. This precipitate was isolated by filtration, washed with dist. water and dried at 40°C in vacuo. Yield 39% calculated for a pseudorotaxane consisting of two α-cyclodextrin units. No melting point was detectable up to 300°C, whereas α-cyclodextrin melts and decomposes around 278°C. (The ^{1}H-NMR spectrum is presented in Figure 2).

C) polycondensations of the pseudorotaxane

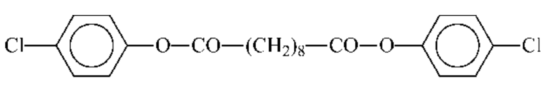
The pseudorotaxane (8 mmol) was dissolved in dry DMSO (50 mL) and diester **1** (3, 8 mmol) was added. The 100 mL Erlenmeyer flask was closed with a glass stopper and thermostated at 60°C for 24 h. The reaction mixture was then poured into acetone (400 mL), and the precipitated polymer was isolated by filtration. Analogous polycondensations were conducted with a suspension of pseudorotaxane (8 mmol) in sulfolane (50 mL).

2.6 Measurements

The inherent viscosities were measured in m-cresol with an automated LAUDA viscometer thermostated at 25°C. The 400 MHz ^{1}H NMR spectra were recorded with a Bruker "Advance 400" FT NMR spectrometer in 5 mm o.d. sample tubes.

The DSC measurements were conducted with a Perkin-Elmer DSC-7 in aluminum pans under nitrogen at a heating (and cooling) rate of 20°C/min.

The MALDi-TOF mass spectra were measured on a Bruker Biflex III mass spectrometer equipped with a nitrogen laser (λ = 337 nm) in the reflectron mode. All spectra were recorded in the reflection mode with an acceleration voltage of 20 kV. The irradiation targets were prepared from hexafluoroisopropanol solution with dithranol as matrix and K-trifluoroacetate as dopant.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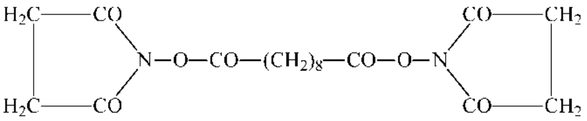
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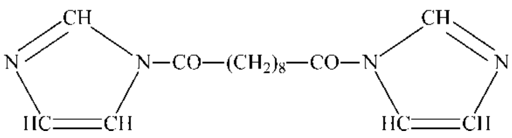
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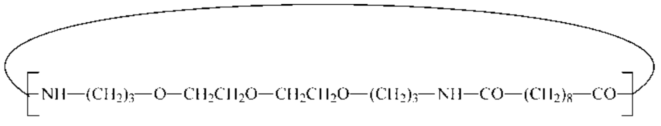
3 Results and Discussion

3.1 Polycondensation of Bis(N-hydroxysuccinimido) Sebacate (2)

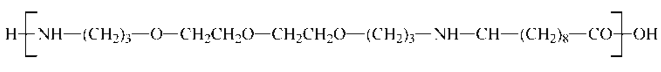
The bis(N-hydroxysuccinimido)sebacate (**2**) was synthesized from sebacic acid and N-hydroxysuccinimide by means of N,N′-dicyclohexylcarbodiimide. Synthesis and reactivity of N-hydroxysuccinimide esters are well documented in peptide chemistry. They are known for a high reactivity (comparable to or higher than that of 4-nitrophenylesters) and the good solubility of the liberated N-hydroxysuccinimide in water or methanol eases the purification of any kind of reaction products.

The polycondensations of **2** with DTT were performed in commercial ultradry DMSO and in dry NMP (Table 1) because in our previous study the best results were obtained in these solvents. When compared with the analogous polycondensations of bis(4-chlorophenyl)sebacate described previously (7), three conspicuous differences were observed. Firstly, due to the higher reactivity the polycondensation of **2** proceeded even at room temperature at a considerable rate (No. 1, Table 1). Secondly, at 100°C, a polyamide was isolated with moderate yield and viscosity (No. 3), whereas no polymer was isolated when the bis(4-chlorophenyl)ester **1** was used (7). Thirdly, all viscosities were considerably lower with the diester **1** despite its higher reactivity. Dry NMP as reaction medium (Nos. 8–10, Table 1) did not have any advantage. This observation proves that the moderate molecular weights obtained in DMSO are not a result of partial hydrolysis of the bishydroxysuccinimide ester. At 100°C the yield was even zero. The best results were obtained when tertiary amines were added to the polycondensation conducted in bulk. This effect suggests that the acidity of the liberated N-hydroxysuccinimide somehow hinders the chain growth process. If protonation of primary amino groups or other side reactions are the main hindrance was not studied in detail. The MALDI-TOF mass spectra revealed the existence of cyclic polyamide in all samples. In agreement with our recently published theory of kinetically controlled polycondensations, the fraction of cyclic oligo- and polyamide increased with the average molecular weight of the sample as demonstrated by MALDI-TOF mass spectrometry. The linear chain detected in these mass spectra had the structures **4Lb** and **4Lc**. In summary, the bis(N-hydroxysuccinimide)ester gave significantly lower molecular weights than the bis(4-chlorophenyl)ester despite its higher reactivity.



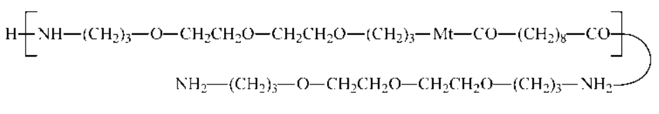
$$\left[NH-(CH_2)_3-O-CH_2CH_2O-CH_2CH_2O-(CH_2)_3-NH-CO-(CH_2)_8-CO\right]$$

4 C



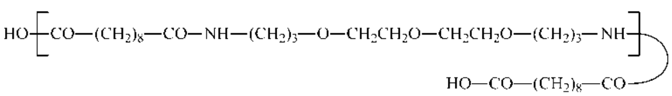
$$H\left[NH-(CH_2)_3-O-CH_2CH_2O-CH_2CH_2O-(CH_2)_3-NH-CH-(CH_2)_8-CO\right]OH$$

4 La



$$H\left[NH-(CH_2)_3-O-CH_2CH_2O-CH_2CH_2O-(CH_2)_3-Mt-CO-(CH_2)_8-CO\right]-NH_2-(CH_2)_3-O-CH_2CH_2O-CH_2CH_2O-(CH_2)_3-NH_2$$

4 Lb



$$HO\left[CO-(CH_2)_8-CO-NH-(CH_2)_3-O-CH_2CH_2O-CH_2CH_2O-(CH_2)_3-NH\right]-CO-(CH_2)_8-CO-OH$$

4 Lc

3.2 *Polycondensations of Sebacic Acid Bisimidazolide (3)*

The polycondensations of DTT with bisimidazolide (**3**) were conducted in three different solvents: DMSO, NMP and sulfolane (Table 2). Since it was expected from previous studies (ref. 7 and Table 1 of this work) that the best results can be obtained in DMSO most polycondensations were performed in this solvent (Nos. 2–8). The viscosity measurements revealed that the highest molecular weights were indeed achieved in DMSO. The molecular weights obtained in NMP and sulfolane were even lower than those obtained with (**2**) in these solvents (Table 1). Yet, it is remarkable that the bisimidazolide **3** yielded polyamide in NMP at 100°C (No. 12, Table 2), whereas no polyamide was found when the bis hydroxy succin imide ester **2** was polycondensed in NMP at 100°C (No. 10, Table 1).

For the polycondensations of **3** again ultradry DMSO was used, because carboxylic acid imidazolides are highly sensitive to moisture at elevated temperatures. Three parameters were varied: temperature, time and stoichiometry. Variation of the temperature revealed that polycondensations at 60°C gave considerable higher molecular weights than polycondensations at 100°C (Nos. 7 and 8, Table 2). Analogous results were found for polycondensations of **2** (Table 1) and of bis(4-chlorophenyl)sebacate (**1**). Even in NMP or sulfolane a temperature of 60°C proved to be advantageous. Variation of the time at 60°C (Nos. 2–4, Table 2) demonstrated that the longest time (48 h) gave the highest molecular weight. This trend was confirmed when the bisimidazolide (**3**) was used in an excess of 1 mol% (Nos. 5 and 6). Furthermore, it was found that this slight imbalance of the stoichiometry gave the highest molecular weights of all experiments of this work. The viscosity values were also slightly higher than the best value obtained in our previous study (7) ($\eta_{inh} = 1.29$ dL/g). The MALDI-TOF m.s. demonstrated that optimization of the molecular weight also involves optimization of the content of cycles in agreement with our theory of polycondensation (2). As demonstrated in Figure 1, even a sample having medium viscosity value almost exclusively exhibits peaks of cyclic polyamides. Unfortunately we were not able to obtain m.s. displaying mass peaks above

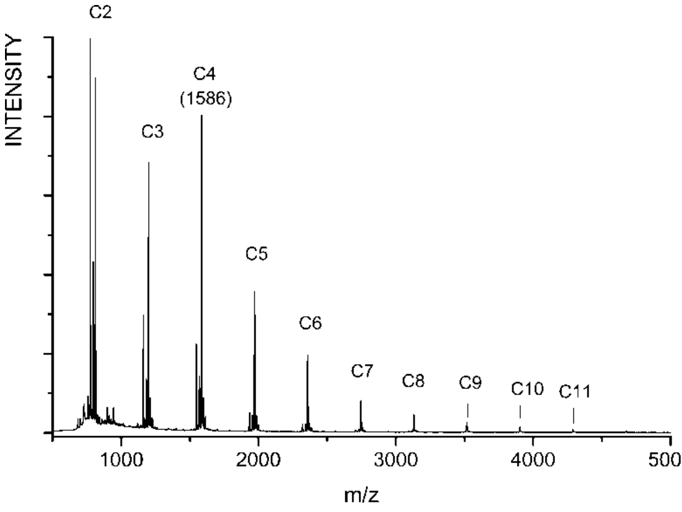


Fig. 1. MALDI-TOF mass spectrum of the poly(ether amide) prepared from DTT and **3** in DMSO at 100°C (No. 7, Table 2).

6 000 Da despite variation of the matrix. The pattern of three closely neighboring mass peaks is the result of $H^{\oplus}$-, $Na^{\oplus}$- and $K^{\oplus}$-doping. Unfortunately, the high molar mass polyamides were neither completely soluble in tetrahydrofuran nor in chloroform nor in dimethylacetamide, and thus, we were not able to perform SEC measurements.

3.3 Syntheses of Catenanes by Means of α-Cyclodextrin

The optimization of the reaction conditions for the preparation of cyclic poly(ether amide)s was also the reason to enable the synthesis of catenanes by threading α-cyclodextrin (or other cycles) on the growing polyamide chain. For this purpose, the polycondensations in DMSO at 60°C were repeated using either the bis(4-chlorophenyl)ester (**1**) or the bisimidazolide (**3**) of sebacic acid as reaction partner of DTT. Prior to the mixing of both monomers α-cyclodextrin was dissolved in DMSO and its concentration was varied between 0.002 mol/L and 0.2 mol/L. The sixteen polycondensations conducted in this way were worked up by precipitation into water. In all cases cyclic polyamides were isolated in yields between 28 and 35%. However, the MALDI-TOF mass spectra did not show any peak of a catenane. It was known from the work of Steinbrunn and Wenz (12) that α-cyclodextrin threads on ω-aminoundecanic acid and a high load of α-cyclodextrin rendered the polyamide-12 soluble in water. To avoid that cyclic poly(ether amide)s containing α-cyclodextrin escaped from detection due to their solubility in water, two polycondensations were performed in such a way that the reaction mixture was precipitated into acetone. Yet, the cyclic polyamides isolated from acetone were again bare of catenanes.

Since DMSO is a good host in the inner void of α-cyclodextrin it was speculated that it hinders the threading on the diamine. Therefore, eight more polycondensations were performed using a suspension of α-cyclodextrin in NMP at 60°C as a reaction mixture. The ring of NMP is too large to penetrate the α-cyclodextrin and to hinder the threading on the poly(ether amide)s. However, no catenanes were detected in the mass spectra.

These negative results prompted us to explore another approach. Wenz et al. (13) reported that α-cyclodextrin threads on α,ω-diaminoalkanes, and the isolated pseudorotaxanes were characterized by ^{1}H-NMR spectroscopy. In the present work, DTT was heated with an excess of α-cyclodextrin in H_2O until a clear solution was obtained which yielded a white precipitate upon rapid cooling. The ^{1}H-NMR spectrum (Figure 2) of the isolated pseudorotaxane confirmed a composition from one DTT and two α-cyclodextrin moieties. This ^{1}H-NMR spectrum measured in D_2O also demonstrates that in water an equilibrium between free DTT + α-cyclodextrin and pseudorotaxane exists. The four signals of CH_2 groups in the range of 0.5-2.0 ppm are characteristic for the pseudorotaxane (12) The isolated pseudorotaxane was then dissolved in DMSO and polycondensed with the activated ester **1** at 60°C. After precipitation into acetone, a polymer was isolated, the MALDI-TOF m.s. of which was almost identical with that of Figure 1. In other words, only cyclic polyamides free of α-cyclodextrin were detected. In two more experiments, the pseudorotaxane was suspended in sulfolane and the polycondensations were performed in this heterocyclic solvent, which in contrast to DMSO, cannot play the role of guest molecule in α-cyclodextrin. Once again, the MALDI-TOF m.s. of the isolated reaction product displayed the mass peaks of cyclic polyamides bar of α-cyclodextrin. In summary, none of the numerous experiments designed to yield polycatenanes gave a positive result. However, it is not clear at this time, if the syntheses were unsuccessful or if polycatenanes were formed and did not "fly" in the mass spectrometer.

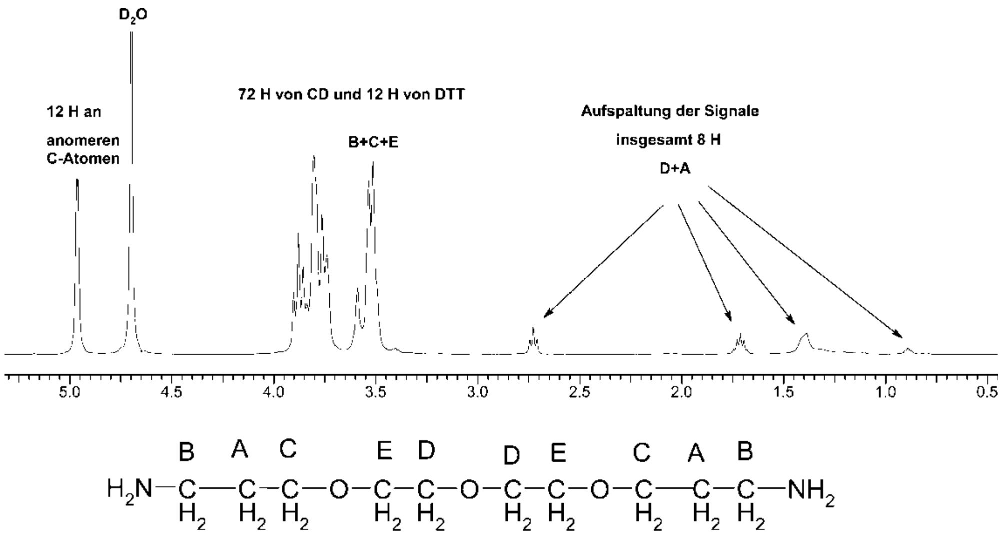


Fig. 2. 400 MHz ^{1}H NMR spectrum of the DTT-α-cyclodecxtrin complex measured in D_2O.

4 Conclusion

The polycondensations studied in this work allow for the following conclusions. Firstly, regardless which sebacic acid derivative was used, the highest molecular weights were obtained in DMSO at 60°C in perfect analogy to previous experiments based on bis(4-chlorophenyl)sebacate. Secondly, the highest molecular weights of this work were obtained from polycondensations of the bisimidazolide **3** favored by the use of ultradry DMSO (Nos. 5 and 6, Table 2). The highest molecular weights of this work were slightly higher than the best result obtained previously with bis(4-chlorophenyl)sebacate. Thirdly, cyclic polyamides were formed in all experiments, and their fraction increased with higher molecular weights of the entire polyamides. Only cyclic polyamides were detected in the MALDI-TOF m.s. of the samples with the highest molecular weights (Nos. 5 and 6, Table 2). This observation suggests that under optimum conditions the chain growth was mainly limited by end-to-end cyclization. These findings are in perfect agreement with our new theory of kinetically controlled polycondensations (1, 2).

Repetition of polycondensations under optimum conditions, but in the presence of α-cyclodextrin did not yield catenanes in amounts detectable by MALDI-TOF mass spectrometry. Although, it is known that α-cyclodextrin can thread on poly(ethylene oxide) (13, 14) and polyamides (12) efficient threading was obviously hindered under the given reaction conditions. Yet, even when a preformed pseudorotaxane was used as monomer, the formation of polycatenanes was not detectable by mass spectrometry. Clearly part of the DTT had lost the α-cyclodextrin in the reaction mixture. Yet, the low sensitivity of the mass spectra may be another reason why the detection of polycatenanes has failed.

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