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Macrocycles. 17. The Role of Cyclization in Kinetically Controlled Polycondensations. 2.[†] Polyamides

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ABSTRACT: Two series of kinetically controlled polycondensations were conducted yielding polyamides of aliphatic dicarboxylic acids. First, the bis(trimethylsilyl) derivatives of 1,3-diaminobenzene, 4,4′-diaminodiphenylmethane, 1,12-diamino-4,9-dioxadodecane, and 1,12-diaminododecane were polycondensed with dicarboxylic acid dichlorides in *N*-methylpyrrodidone below 0 °C. After optimization of the reaction conditions mainly cyclic polyamides were detectable in the MALDI−TOF mass spectra (up to 13 000 Da) of the semiaromatic polyamides in contrast to the Carothers−Flory theory. In the case of silylated aliphatic diamines, side reactions of the acid chlorides prevented a complete conversion of the amino groups, so that the reaction products mainly consisted of cycles and linear chains having two amino end groups. Second, normal interfacial polycondensations were performed either with 1,6-diaminohexane and adipoyl chloride or with 1,12-diaminododecane and decane-1,10-dicarbonyl chloride. When the loss of acid chloride groups by hydrolysis was compensated by an excess of dicarboxylic acid dichlorides cyclic polyamides were again the main reaction products up to masses of 4000−5000 Da. A new version of the “Carothers equation” taking into account the role of cyclization in kinetically controlled step-growth polymerizations is discussed.

Introduction

The fundamental theory of step-growth polymerizations as it is presented in most (probably all) textbooks is mainly based on the experimental and theoretical work of Carothers.[1,2] A further mathematical treatment mainly concerning hyperbranched polymers and networks was contributed by Flory,[3] but neither authors has paid attention to the role of cyclization.

At the same time the “Ruggli−Ziegler−dilution” method (RZDM) was developed[4] as a synthetic strategy for the optimization of the yields of macrocycles. The RZDM is based on the consideration that any difunctional monomer or oligomer having two complementary functional groups has the choice between (poly)condensation or cyclization at every stage of the conversion. High dilution will favor cyclization, because it is an intramolecular and, thus, monomolecular reaction. To the best of our knowledge, the consequences of this concept for polycondensations at high concentration has never been discussed in textbooks or reviews concerning step-growth polymerizations. It is obvious that high monomer concentrations will favor the chain growth, but there is no theoretical or experimental reasons why the tendency of cyclization should completely disappear.

To avoid misunderstandings, it should be emphasized at this point that the RZDM, the further discussion below, and the experiments of this work exclusively concern kinetically controlled polycondensations (KCPs). KCP means that a σ-bond (e.g., amide bond in this work), once it has been formed, will be stable throughout the further polycondensation process. No cyclization by “back-biting” or any other equilibration reactions (e.g., transamidation) will take place.

The problem of cyclization competing with propagation in KCPs has been mathematically treated by several authors. As early at 1934, Stoll et al.[5] have calculated the cyclization probability of ω-hydroxyalkanoic acids (yielding lactones) vs the dimerization step. The same problem was tackeled by Morawetz et al.[6] via another mathematical approach, but in both cases higher cycles were not taken into account. Quite recently, Ercolani et al.[7] calculated the formation of cyclic oligomers in KCPs up to a degree of polymerization (DP) of 12. Another kinetic approach including the entire course of KCPs up to 100% conversion was presented by Stepto et al.[8,9] and Gordon et al.[10] Despite somewhat different mathematical methods both british groups reached the conclusion that all reaction products of an ideal KCP (no side reactions) need to be cycles at 100% conversion. The role of concentration was also considered,[7−10] and thus these calculations represent in principle a quantitative version of the RZDM extended to high concentrations. However, polycondensations confirming these calculation were not reported.

In previous papers of this series,[11−13] it was demonstrated for four different kinetically controlled syntheses of polyesters that high fractions of cyclic oligomers and polyesters were indeed formed, when the reaction conditions were optimized for high molecular weights. The purpose of the present work is 2-fold. First, it should extend the experimental basis of our studies to another group of polymers and prove that the large amounts of cycles found in polyesters does not result from transesterification (including “back-biting degradation”). Second, a mathematic formula should be presented, reflecting the influence of cyclizations on the course of KCPs considering the broadest possible variation of the chemical structure and its influence on the cyclization tendency.

Experimental Section

Materials. 1,3-Diaminobenzene was a gift of Bayer AG (Leverkusen, Germany) and was used as received. 1,6-Diami-

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[†] For part 1, see ref 13.

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nohexane, 1,12-diaminododecane, and 1,12-diamino-4,5-dioxadodecane were purchased from Aldrich Co. (Milwaukee, WI) and used as received. Adipoyl chloride, suberoyl chloride, sebacoyl chloride, and decane-1,10-dicarbonyl chloride were also purchased from Aldrich Co. and distilled in vacuo prior to use. *N,N′*-Bis(trimethylsilyl)-1,4 diaminobenzene and *N,N′*-bis(trimethylsilyl)-4,4′-diaminodiphenylmethane were prepared according to the literature.[14,15] *N*-Methylpyrrolidone (a gift of BASF AG, Ludwigshafen, Germany) was twice distilled over P_4O_{10} in vacuo. Dichloromethane (Aldrich Co.) was once distilled over P_4O_{10}.

Bis(trimethylsilyl)-1,12-diamino-4,9-dioxadodecane. 1,-12-Diamino-4,9-dioxadodecane (0.3 mol) and triethylamine (0.65 mol) were dissolved in azeotropically dried toluene (1 L) and heated to 60−70 °C. Chlorotrimethylsilane (0.65 mol) was added dropwise with stirring, and afterward the reaction mixture was refluxed for 4 h. Afterward the reaction mixture was cooled to approximately 5 °C and filtered under exclusion of moisture. The filtrate was concentrated in vacuo and the product was distilled over a short-path apperatus at a bath temperature of 150−155 °C/10^{-3} mbar. Yield: 61%. Anal. Calcd for $C_{16}H_{40}N_2O_2Si_2$ (348.7): C, 55.12; H, 11.56; N, 9.18. Found: C, 54.98; H, 11.13; N, 8.88.

^{1}H NMR ($CDCl_3$/TMS): $\delta = 0.10$ (s, 18 H), 1.68 (m, 8 H), 2.82 (q, 4 H), 3.43 (m, 8 H) ppm.

Bis(trimethylsilyl)-1,12-diaminododecane was prepared analogously and distilled at a bath temperature of 160−170 °C/10^{-2} mbar. Yield: 63%.

Anal. Calcd for $C_{18}H_{44}N_2Si_2$ (344.7): C, 62.71; H, 12.86; N, 8.13. Found: C, 62.79; H, 12.83; N, 7.99.

^{1}H NMR ($CDCl_3$/TMS): $\delta = 0.10$ (s, 18 H), 1.30 (s, 20 H), 2.72 (s broad, 4 H) ppm.

Polycondensations of Silylated Diamines. The silylated diamine (15 mmol) was dissolved in dry NMP (15 mL, possibly containing 5 wt % of LiCl) and cooled to −10 °C by means of an ice/NaCl mixture. A solution of the dicarboxylic acid dichloride (15 mmol) in dry CH_2Cl_2 was added dropwise (precooled to −10 °C). Afterward the reaction mixture was stirred without cooling for 24 h and precipitated into methanol. The precipitated polyamide was filtered off, washed with water and methanol, and dried at 80 °C in vacuo.

For two experiments, the solution of the silylated diamine in NMP was cooled with a CO_2/MeOH mixture to −70 °C before the solution of the dicarboxylic acid dichloride was added, and the cooling was maintained during the addition.

Interfacial Polycondensations. The diamine (20 mmol) was dissolved or suspended in 0.5 N NaOH (100 mL) containing 5 wt % of KNO_3. The dicarboxylic acid dichloride (20 mmol, possibly 2% or 4% excess) was dissolved in dry CH_2Cl_2 (150 mL). Both solutions were cooled to +5 °C and rapidly mixed in an Erlenmeyer flask with a high speed stirrer ("Ultraturrax") under cooling with ice. After 10 min the high-speed stirrer was replaced by a normal stirrer, and the stirring was continued for 1 h without cooling. The reaction mixture was then precipitated into methanol, and the precipitated polyamide was filtered off, washed with methanol, and dried at 80 °C in vacuo. The polyamide was then dissolved in a mixture of CH_2Cl_2 and trifluoroacetic acid and precipitated into ethanol.

In two experiments, an aqueous 0.25 M Na_2CO_3 solution containing 5 wt % of KNO_3 was used (see Table 2).

Condensation of γ-aminobutyric acid. γ-Aminobutyric acid (0.1 mol) was suspended in 1,2-dichlorobenzene (10 mL) and heated in a glass reactor with stirring to 200−205 °C. The liberated water was removed with a slow stream of nitrogen. The loss of 1,2-dichlorobenzene was compensated for by the injection of additional 1,2-dichlorobenzene (2 mL/h). After approximately 3 h, a clear solution was obtained. After 30 more min, the reaction mixture was cooled to 20 °C, and a ^{1}H NMR spectrum was recorded in $CDCl_3$. This spectrum perfectly agreed with that of pyrrolidone upon precipitation into diethyl ether about 20 mg of oligomers were isolated (yield ~ 2%).

Measurements. The inherent viscosities were measured in *m*-cresol using an automated Ubbelohde viscometer thermostated at 25 °C.

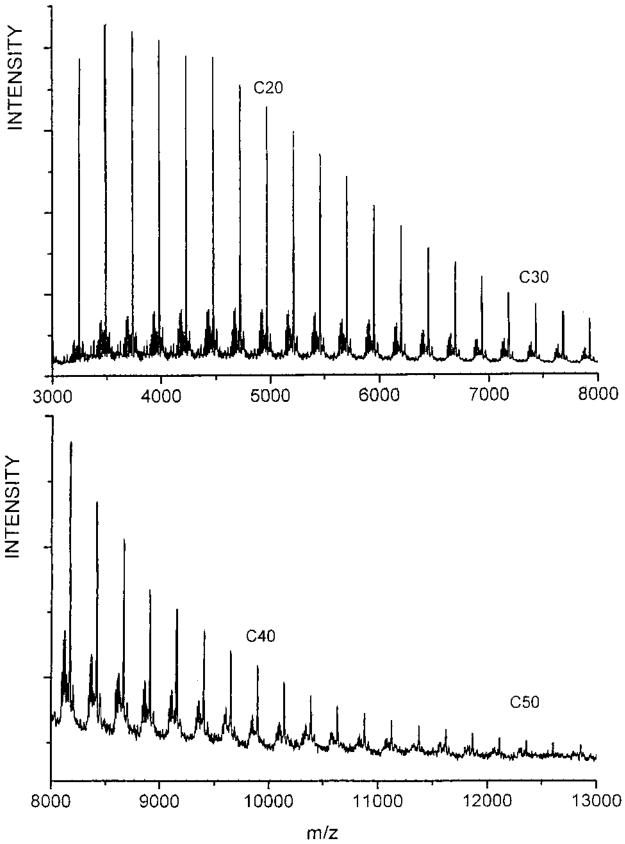


Figure 1. MALDI−TOF mass spectrum of polyamide **1** prepared in NMP/LiCl (no. 1, Table 1) displaying mass peaks of cycles (symbol C) up to DP = 55.

The 100 MHz ^{1}H NMR spectra were recorded with an Bruker AC-100 FT NMR spectrometer in 5 mm o.d. sample tubes. A mixture of $CDCl_3$ and trifluoroacetic acid (volume ratio 4:1) containing TMS as shift reference served as solvent.

The MALDI−TOF mass spectra were recorded on a Bruker "Biflex 3" mass spectrometer in the reflection mode. A nitrogen laser ($\lambda = 337$ nm) and an acceleration voltage of 20 kV were used. Hexafluoro-2-propanol served as solvent and 1,8,9-trihydroxyanthracene as matrix for the preparation of the irradiation targets. The polyamide/matrix ratio was varied between 1:10 and 1:100. The polyamides prepared from silylated diamines were doped with potassium trifluoroacetate. Those polyamides prepared by interfacial polycondensation contained sufficient sodium ions. All mass spectra were recorded with a cutoff limit of 1000 Da and in several cases (e.g., Figure 1) the measurements were repeated with a cutoff limit of 3000 Da.

Results and Discussion

Polycondensations of Silylated Diamines. Two different synthetic methods yielding polyamides via kinetically controlled polycondensation processes are studied in this work: first, polycondensations of silylated diamines with dicarboxylic acid dichlorides (eq 1)

$$\mathrm{Me_3SiNH{-}(A){-}NH{-}SiMe_3} + \mathrm{ClCO{-}(B){-}COCl} \xrightarrow{-\,2\ \mathrm{ClSiMe_3}} \left[\mathrm{{-}NH{-}(A){-}NH{-}CO{-}(B){-}CO{-}}\right] \qquad (1)$$

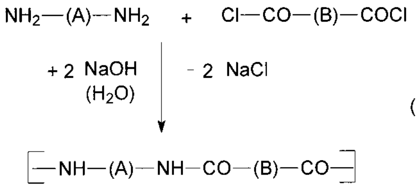
at temperatures ≤ 0 °C; second, interfacial polycondensations of free aliphatic diamines with dicarboxylic acid dichlorides at temperatures ≤20 °C (eq 2). Due to the

Table 1. Reaction Conditions and Results of Polycondensations of Silylated Diamines in Aprotic Solvents[c,d]

polycarboxylate no.	bis TMS derivative of	dichloride of	reaction medium	molar excess of dichloride	yield[a] (%)	η_{inh}[b] (dL/g)
1	1,3-diaminobenzene	suberic acid	NMP + 5% LiCl + CH_2Cl_2	1	69	1.34
2	1,3-diaminobenzene	suberic acid	NMP + 5% LiCl addition of CH_2Cl_2	2	65	1.03
3	1,3-diaminobenzene	suberic acid	NMP + 5% LiCl addition of CH_2Cl_2	4	57	0.68
4	1,3-diaminobenzene	suberic acid	NMP + 5% LiCl addition of CH_2Cl_2	6	49	0.27
5	4,4′-diaminodiphenylmethane	sebacic acid	NMP addition of CH_2Cl_2	1	81	0.98
6	1,12-diamino-4,9-dioxadodecane	suberic acid	NMP addition of CH_2Cl_2	1	75	0.35
7	1,12-diamino-4,9-dioxadodecane	suberic acid	NMP addition of CH_2Cl_2	2	76	0.40
8	1,12-diaminododecane	decane-1,10-dicarboxylic acid	NMP addition of CH_2Cl_2	1	88	0.71
9	1,12-diaminododecane	decane-1,10-dicarboxylic acid	NMP addition of CH_2Cl_2	2	91	0.68
10	1,12-diaminododecane	decane-1,10-dicarboxylic acid	NMP addition of CH_2Cl_2	4	87	0.52

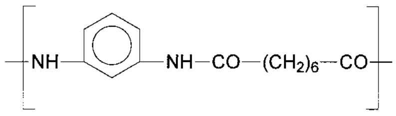
[a] After precipitation into MeOH and reprecipitation into EtOH. [b] Measured at 25 °C with $c = 2$ g/L in *m*-cresol. [c] $M_n \sim 38\,000$ Da by SEC in hexafluoro-2-propanol calibrated with PMMA standards. [d] $M_n \sim 29\,000$ Da by SEC in hexafluoro-2-propanol calibrated with PMMA standards.

high chemical stability of polyamides and the low reaction temperatures it is clear that neither "back-biting degradation" nor any other transamidation reactions will be involved.

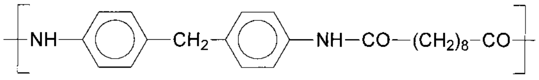


(2)

Four silylated diamines, 1,3-diaminobenzene, 4,4′-diaminodiphenylmethane, 1,12-diamino-4,9-dioxadodecane, and 1,12-diaminododecane were used as reaction partners of suberoyl chloride or decane-1,10-dicarbonyl chloride so that the polyamides **1**, **2,** **3**, and **4** were



1



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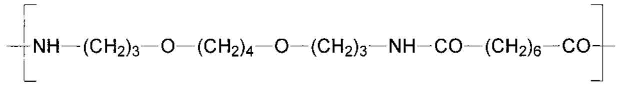
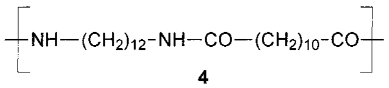


3



4

obtained. These monomers were selected for the following reasons. Aromatic dicarboxylic acid dichlorides are far less reactive than aliphatic dicarboxylic acid dichlorides (ADADs) and, thus, less favorable for complete conversion. However, high conversions are essential for high molecular weights and high yields of cyclic oligomers and cyclic polymers. The long diamines and the meta-substitution of the diaminobenzene were selected to improve the solubility in organic solvents which is again important for efficient propagation and cyclization, because precipitation reduces severely the mobility of the individual polyamide chains. In fact, it turned out that all four polyamides were soluble in NMP which served as the reaction medium. The bis(trimethylsilyl) derivatives of the diamines were used for polycondensations in an inert organic solvent under homogeneous conditions to avoid partial protonation of the diamines by liberated HCl. Basic HCl acceptors are not advisable because they tend to deprotonate the ADADs yielding ketene groups which may undergo a variety of side reactions.

N-Methylpyrrolidone-2 (NMP) is the standard reaction medium for syntheses of aromatic polyamides. Therefore, this solvent was also used for all polycondensations of silylated diamines. LiCl was added to the polycondensations of silylated 1,3-diaminobenzene to improve the solubility of the resulting polyamide (**1**), whereas this addition was not needed for the other polyamides. Since it is known that acid chlorides react with NMP above room temperature, all polycondensations were conducted below 0 °C. Preliminary experiments (not listed in Table 1) have shown that initial cooling to temperatures around −70 °C has no advantages over a cooling to −10/−15 °C. Therefore, all polycondensations listed in Table 1 were performed at an initial temperature ≤−10 °C, and the temperature was kept below −5 °C during the addition of the ADADs.

An excess of 1 mol % of the ADAD was used in most experiments, because it was learned from numerous syntheses of polyesters, that whenever an ADAD is added dropwise to a reaction mixture an excess around 1 mol % gives higher molecular weight than a perfect stoichiometry in the feed. If the slight excess is lost in the glass walls of the pipet or of the dropping funnel or if it is lost by side reactions (e.g., with traces of moisture or solvent) has not been elucidated. In the case of polyamide **1**, the excess of suberoyl chloride was systematically varied and, as expected, both yields and viscosity values decreased with a larger excess of the ADAD (nos. 1−4, Table 1). The MALDI−TOF mass spectra revealed a predominance of the cycles up to masses around 13 000 Da (the technical limit of our measurements) in the case of sample no. 1 Table 1 (Figure 1). As illustrated by Figure 2, the cycles were still predominant (below 8000 Da at least) in sample no. 2, but their fraction had decreased. In sample no. 3 of Table 1, the linear chains were prevailing above masses of 2000 Da, and in the case of sample no. 4 the cycles had almost completely vanished above 1000 Da. These findings perfectly agree with our previous results elaborated from various syntheses of polyesters. Cyclizations are a major and unavoidable component of any KCP in a homogeneous phase. The extent of

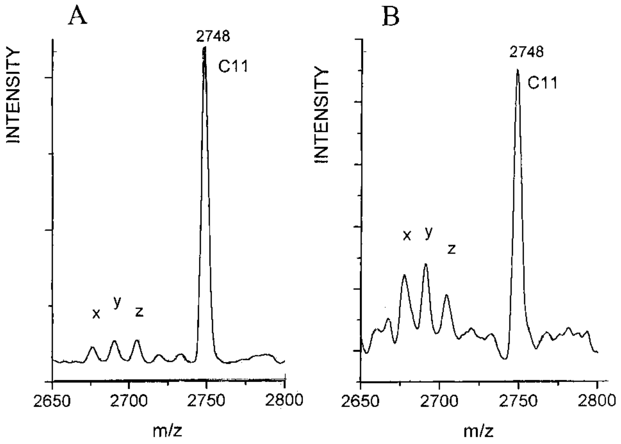
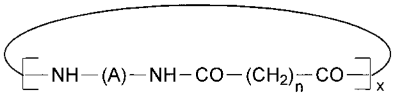


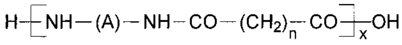
Figure 2. MALDI−TOF mass spectra (segments) of the polyamide **1**: (A) prepared with an excess of 1 mol % of suberoyl chloride (no. 1, Table 1); (B) prepared with an excess of 2 mol % of suberoyl chloride (no. 2, Table 2).

cyclization increases with the molecular weight and is sensitive to any optimization of the reaction conditions.

The MALDI−TOF mass spectra of the polyamide **1** samples also revealed traces of linear chains having the end group combination **U**, whereas no chains with two amine end groups (**V**) were detected in agreements with the addition of excess suberoyl chloride. The majority of the linear chains had the end group combination **X**, **Y**, or **Z** (see Figure 2) resulting from the precipitation of the reaction mixtures into moist methanol. The MALDI−TOF mass spectrum of polyamide **2** was quite similar to that of polyamide 1 (no. 2, Table 1) and displayed the formation of cycles up to 9000 Da (technical limit of the spectrum). The peaks of the cycles were predominant up to 8000 Da.

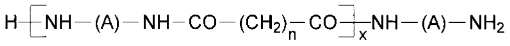


C



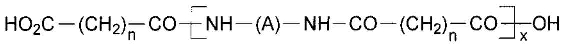
$$H-\left[NH-(A)-NH-CO-(CH_2)_n-CO\right]_x-OH$$

U



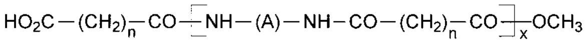
$$H-\left[NH-(A)-NH-CO-(CH_2)_n-CO\right]_x-NH-(A)-NH_2$$

V



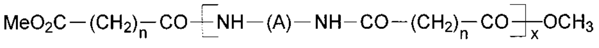
$$HO_2C-(CH_2)_n-CO-\left[NH-(A)-NH-CO-(CH_2)_n-CO\right]_x-OH$$

X



$$HO_2C-(CH_2)_n-CO-\left[NH-(A)-NH-CO-(CH_2)_n-CO\right]_x-OCH_3$$

Y



$$MeO_2C-(CH_2)_n-CO-\left[NH-(A)-NH-CO-(CH_2)_n-CO\right]_x-OCH_3$$

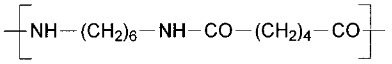
Z

At this point the problem of quantification of the cyclic oligomers and polymers deserves a short discussion. Since cycles and linear chains coexist over a broad range of molecular weights (from 500 up to presumably 20 000 Da) fractionation by SEC does not separate cycles from linear species. Furthermore, it should be taken into account that for an evaluation of the chemistry of polycondensation processes the molar fractions and frequency distributions of the reaction products are of interest and not the mass distribution. A "translation" of the mass distributions obtained by SEC measurements into frequency distributions requires identification and quantification of all species up to the highest molecular weights. For this purpose 50 or more fraction are required when polycondensates with M_ns 30 000 Da should be characterized. The main problem is then the quality of the MALDI−TOF mass spectroscopy of the fractions, because identification and quantification of individual reaction products in fractions with M_ns up to 10^5 Da is needed. To the best of our knowledge such an analysis is technically not feasible at the current state of art. A crude estimation to what extent the MALDI−TOF mass spectra of polycondensates are useful for an evaluation of the major chemical reactions can be obtained by consideration of eq 3 representing

$$n_x = p^{x-1}(1-p) \qquad (3)$$

(at least roughly) the frequency distribution of polycondensates. The maximum of the distributuion curve is the dimer. For polycondensates having a M_n around 10 000 Da, approximately 50 mol % of all species fall into the mass range below 6 500 Da. For a polycondensate of M_n 20 000 Da, approximately 50 mol % are below 11 000 Da, for a polycondensate of M_n 38 000 Da (footnote *c* of Table 1), 50 mol % fall into the mass range below 20 000 Da, and approximately 35 mol % are below 13 000 Da (Figure 1). Almost all technical polycondensates have M_ns below 25 000 Da and all polycondensates studied in the present work (see footnotes of Table 1) or in our previous studies[11−13] have M_ns below 40 000 Da. Therefore, MALDI−TOF mass spectra covering the mass range up to 13 000 Da represent at least 30−35 mol % of all species in the polycondensates under investigation.

In the case of the aliphatic polyamides **3** and **4**, the MALDI−TOF mass spectra revealed again a predominant formation of cyclic oligo- and polyamides (detectable up to 6000 Da). However, mass peaks of linear chains having two amino end groups (formula **V**) were also observable (Figure 3). Therefore the syntheses of both polyamides **3** and **4** were repeated using an excess of 2 mol % (or 4 mol %) of dicarboxylic acid dichlorides, but the peaks of the linear-chain decreased only little. This result proves that the amino terminated chains were not a consequence of a coincidential imbalance of the stoichiometry. Obviously the basic aliphatic amines deprotonated a small fraction of acid chloride groups in α-position and the liberated HCl protonated and blocked amino groups. This hypothesis is support by two observations. First, the peaks of the amine terminated linear chains were not detectable when the less basic silylated aromatic diamines were used as monomers. Second, in the case of interfacial polycondensations, which avoid protonation of amino groups, a slight excess of dicarboxylic acid dichlorides dramatic lowers the yield of linear-chains in favor of more cycles (see below). Anyway, a detailed study of the side reaction consuming acid chloride groups was not intended in this work.



$$-\left[NH-(CH_2)_6-NH-CO-(CH_2)_4-CO\right]-$$

5

Table 2. Reaction Conditions and Results of Interfacial Polycondensations

polycarboxlate no.	acid chloride of	% excess of acid chloride	diamine	content of the aqueous solution	yield[a] (%)	η_{inh}[b]
1	adipic acid	0	1,6-diaminohexane	NaOH (+KNO_3)	46	0.84
2	adipic acid	2	1,6-diaminohexane	NaOH (+KNO_3)	35	0.76
3	adipic acid	4	1,6-diaminohexane	NaOH (+KNO_3)	33	0.84
4	adipic acid	0	1,6-diaminohexane	Na_2CO_3 (+KNO_3)	29	0.86
5	decane-1,10-dicarboxylic acid	0	1,12-diaminododecane	NaOH (+KNO_3)	73	0.66
6	decane-1,10-dicarboxylic acid	2	1,12-diaminododecane	NaOH (+KNO_3)	94	0.81
7	decane-1,10-dicarboxylic acid	4	1,12-diaminododecane	NaOH (+KNO_3)	68	0.71
8	decane-1,10-dicarboxylic acid	0	1,12-diaminododecane	Na_2CO_3 (+KNO_3)	45	0.41

[a] After precipitation into MeOH and reprecipitation from EtOH. [b] Measured at 25 °C with $c = 2$ g/L in *m*-cresol.

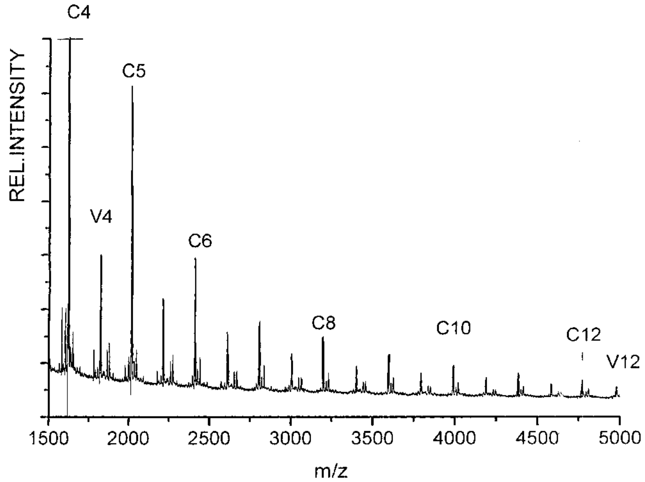


Figure 3. MALDI−TOF mass spectra of polyamide **4** prepared in NMP (no. 8, Table 1). V means linear chains of structure **V**.

Interfacial Polycondensations. Two polyamides were prepared by interfacial polycondensations, namely nylon-6,6 (**3**) and nylon-12,12 (**4**). The nylon 6,6 was selected because it is from the historical point of view the first commercial and most important polyamide at all. Nylon-12,12 was selected for its higher solubility in the organic phase and for comparison with the polycondensations conducted of silylated 1,12-diaminododecane.

For both polyamides, a first pair of polycondensations was performed to evaluate the usefulness of NaOH in comparison to Na_2CO_3. No difference was found for nylon-6,6, whereas a considerably lower solution viscosity was found when nylon-12,12 was prepared with aqueous Na_2CO_3 solution. Therefore, aqueous NaOH was used for all further polycondensations. These polycondensations were conducted with an excess of ADADs. It is well-known and obvious that a small fraction of acid chloride groups is hydrolyzed by the attack of hydroxide ions, and the loss of acid chloride groups limits the chain growth. Interestingly neither an excess of 2 nor an excess of 4 mol % of adipoyl chloride had a significant influence on yield or viscosity of nylon-6,6 (nos. 1−3, Table 2). This finding may be explained with the assumption that the early precipitation and immobilization of the nylon-6,6 chain is the main factor limiting the chain growth. In the case of nylon-12,12, which should be more soluble in the organic phase, the viscosity increased with a 2% excess of decane-1,10-dicarbonyl chloride, but fell to a somewhat lower value with an excess of 4%.

The MALDI−TOF mass spectra revealed the same trends for both polyamides (**3** and **4**). Cyclic oligo- and polyamides were found in all samples. The fraction of cycles was relatively low, and the fraction of amine terminated chains (structure **V**) was particularly high, when excactly equimolar amounts of monomers were used (nos. 1 and 4, 5 and 8, Table 2) as illustrated by Figure 4A. The mass spectrum of Figure 4B demonstrated that the fraction of cycles considerably increased, when an excess of ADADs was added. In other words, the extent of cyclization paralleled the optimization of the conversion. In the case of nylon-12,12 the fraction of cycles seemed to be higher than in the case of nylon-6,6, probably because a higher solubility of the oligomers in the organic phase delayed precipitation and immobilization. With an excess of 4 mol % of decane 1,10-dicarboxyl chloride the cycles were detectable up to approximately 7000 Da (Figure 5) and were the

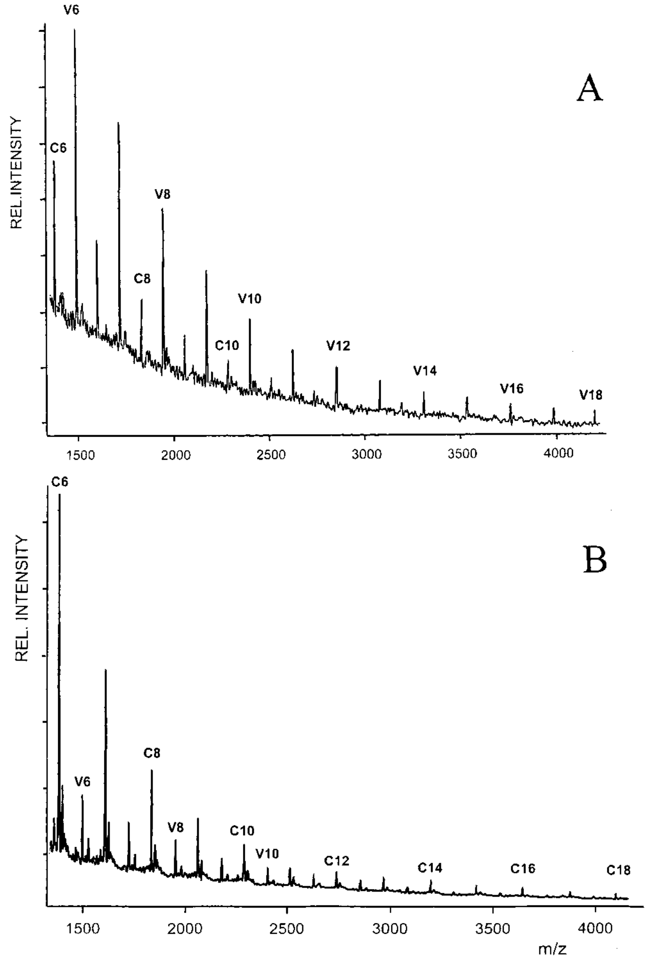


Figure 4. MALDI−TOF mass spectra of nylon-6,6 prepared by interfacial polycondensation in CH_2Cl_2/0.5 N NaOH: (A) 1:1 stoichiometry (no. 1, Table 1); (B) 2% molar excess of adipoyl chloride (no. 2, Table 2).

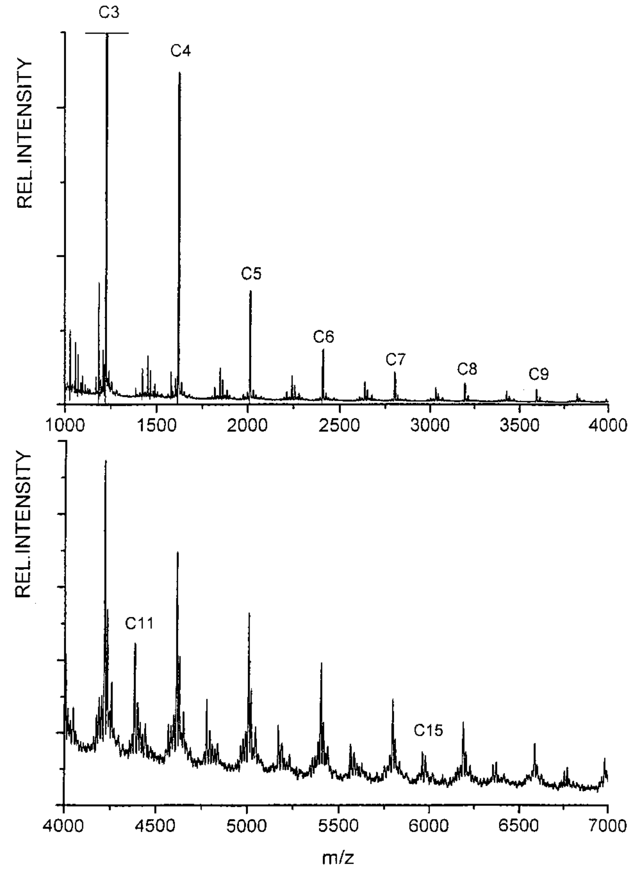


Figure 5. MALDI−TOF mass spectrum of the nylon-12,12 prepared by interfacial polycondensation with a 4% molar excess of decane-1,10-dicarbonyl chloride (no. 7, Table 2).

predominant mass peaks up to 4 500 Da. Although the molar fraction of cycles in these nylon samples were probably not much higher than 10% these results demonstrate a high tendency of cyclization under the extremely unfavorable conditions of interfacial polycondensations.

Theoretical Aspects. The above-mentioned results demonstrate that the role of cyclization in kinetically controlled syntheses of polyamides is the same as in kinetically controlled syntheses of polyesters.[13] Any optimization of the reaction conditions in direction of higher molecular weights automatically enhances the extent of cyclization. The MALDI−TOF mass spectra presented in this work also confirm that cyclization is not limited to low molar mass oligomers, but involves polymers having molecular weights at least above 10 000 Da. These results perfectly agree with the principles of the RZDM and its interpretation in direction of high concentration. Cyclization of difunctional oligomers and polymers can compete with propagation at any stage of the polycondensation process. The rate of cyclization certainly decreases with the length of the polymer chain. However, the cycles are inert reaction products, and their fraction continuously increases with the conversion, whereas the cyclization depletes the pool of reactive linear species. As calculated by Stepto et al.[8,9] and Gordon et al.[10] all reaction products will finally be cycles in the ideal case of quantitative conversion.

The Carothers−Flory theory of step-growth polymerization is certainly a correct description of what happens between reactive species as expressed in the so-called “Carothers equation” (eq 4).[2] However, the condensation steps alone are not a complete and representative description of the entire field of kinetically controlled polycondensation processes. Cyclization is an

$$\overline{\mathrm{DP}} = \frac{1}{1-p} \qquad (4)$$

p = conversion of the functional groups

unavoidable component of almost all kinetically controlled step-growth polymerizations. The course of all kinetically controlled polycondensation including the competition between cyclization and propagation is expressed by eq 5). This equation includes two ex-

$$\overline{\mathrm{DP}} = \frac{1}{1-p(1-\frac{1}{X^{a}})} \qquad (5)$$

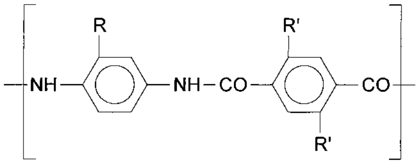
X > 1 (factor which can be adjusted different concentrations)

tremes: (a) a chain growth without any cyclization ($\nu_{cy} = 0$) or (b) cyclization without any propagation ($\nu_{pr} = 0$) (eq 6).

$$a = \frac{v_{pr}}{v_{cy}}; \text{ with } v_{pr} = k_{pr}\,[\mathrm{M/O/P}]^2 \text{ and } v_{cy} = k_{cy}\,[\mathrm{O/P}] \qquad (6)$$

[M/O/P] = total molar concentration of monomers, oligomers and polymers

The first extreme corresponds to the classical “Carothers equation” (eq 4). Syntheses of extremely stiff chains such as poly(*p*-phenylene terephthalamide)s **6**

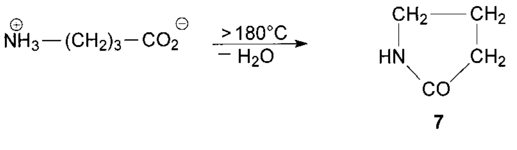


6

R, R' = H, Alkyl, Aryl, Alkoxy, Aryloxy, Alkylthio, Arylthio

are examples of real polycondensations which obey almost perfectly this extreme ($\nu_{cy} = 0$). Such aromatic polyamides are usually prepared from *p*-phenylene diamines (or their *N*,*N*′-bis(trimethylsilyl) derivatives) and terephthaloyl chlorides in NMP below 0 °C. Under these conditions rotations about the CO−N-double bond are almost absent, because the rotational barriere corresponds to a temperature in the range of +30 to −60 °C.[16,17] Taking into account that thermodynamical factors favors a quasi linear conformation of the polyamide chains, cyclization is kinetically and thermodynamically hindered. For this work we have extracted two previously prepared[18,19] substituted polyaramides of structure **6**, with a chloroform 2,2,2-trifluoroethanol mixture and characterized the extracts by MALDI−TOF mass spectrometry. In agreement with the theoretical expectations, no cycles were detected.

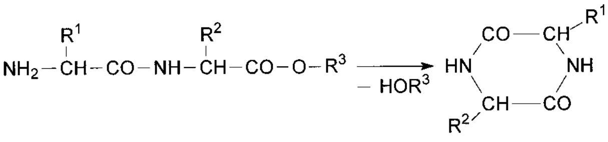
The following (poly)condensations come close to the second extreme ($\nu_{pr} = 0$). When a concentrated suspension of γ-aminobutyric acid was heated in refluxing 1,2-dichlorobenzene the reaction products almost completely consisted of pyrrolidone-2 (eq 7). Furthermore, it has



7

(7)

been known for more 100 years[20-24] that (poly)condensations of dipeptide esters (eq 8) yield large fractions of



(8)

cyclic dipeptides (**7**) in combination with small amounts of cyclic tetrapeptides. In the case of proline peptides, the formation of cyclic dipeptides may be almost quantitative. Even tripeptide esters may yield high fractions of cyclic hexapeptides.[23,24] The syntheses of polyamides summarized in Tables 1 and 2 fall somewhere between these extremes. Therefore, all these aforementioned examples and eq 5 demonstrate that there is no gap and no borderline between syntheses of smaller or larger heterocycles as they were elaborated in organic chemistry, on one hand, and kinetically controlled polycondensations, on the other.

Furthermore, the influence of the conversion on the course of kinetically controlled polycondensations needs a short discussion. Whereas, the rate constant of the propagation (k_{pr} in eq 6) may be nearly constant over a broad range of conversion, k_{cy} will continuously decrease with the lengths of the polymer chains, and thus, with increasing conversion. For a certain group of flexible chains, k_{cy} may decrease with DP$^{-3/2}$ [6-10] but this relationship is not necessarily valid for all chains. Another difference between v_{cy} and v_{pr} concerns the influence of the concentration. v_{pr} decreases rapidly with increasing conversion, despite constant k_{pr} due to its dependence on the square of the concentration of the reactants. In consequence, any polycondensation beginning at high concentration will end as polycondensation under high dilution (with the cycles as solvent). This is one important reason cyclization can compete with propagation even at high conversion and for long chains. A low initial concentration of the reactants favors cyclization even more as illustrated by the RZDM.

Finally, it should be emphasized that all curves described by eq 5 with exception of the extreme $v_{cy} = 0$ have in common that they hit the ordinate at a certain $\overline{DP}$ characterization for an individual polycondensation. This is the maximum $\overline{DP}$ a polycondensation can achive under ideal conditions. In a real polycondensation with less perfect stoichiometry and incomplete conversion, the $\overline{DP}$ will, of course, be somewhat lower. This aspect represents a significant difference between eq 5 and the classical "Carothers equation" (eq 4) which predicts unlimited chain growth under ideal conditions.

Conclusion

Four different polyamides were prepared by two different polycondensation methods. The first method is based on the polycondensation of silylated diamines in a homogeneous organic phase whereas the second method is the well know heterogeneous interfacial polycondensation. All syntheses have in common that cyclic oligo- and polyamides were formed in amounts not compatible with the Carothers–Flory theory. These results confirm that cyclization is an integral and unavoidable reaction in kinetically controlled step-growth polymerizations. Particular important is the observation that polycondensations of silylated aromatic diamines and ADADs in a homogeneous organic phase may approach the ideal case (no side reactions, high conversions) and mainly cyclic oligo- or polyamides were detectable in the MALDI–TOF mass spectra up to 13 000 Da. Linear chains certainly prevail in the high molecular weight fraction, because an ideal stoichiometry and 100 % conversion were never achieved. Two important conclusions may be drawn from these results. Cyclization competes with propagation even for long chains (>10 000 Da), and under (nearly) ideal conditions, cyclization reactions are decisive for the limitation of the chain growth. Therefore, any kinetically controlled polycondensation in a homogeneous phase is characterized by a maximum $\overline{DP}$. A mathematical equation summarizing these results and conclusions is presented in the form of eq 5 which includes the classical "Carothers equation" as a borderline case of chain growth without any competing cyclization. However, eq 5 also includes a second extreme, namely the formation of cycles without significant chain growth, and thus represents a bridge between the synthesis of small (hetero)cycles from linear precoursers, on one hand, and polycondensations yielding cyclic and linear polymers, on the other.

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