Cyclic Polyamide-6 by Thermal Polycondensation of ϵ-Caprolactam and ϵ-Aminocaproic Acid[†]

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ABSTRACT: ϵ-Caprolactam (ϵ-CLA) and ϵ-aminocaproic acid (ϵ-ACA) were polycondensed with a molar ratio of 90:10 at 250 °C for 2, 4, 6, 8, 17, and 48 h. The molecular weight increased up to a time of 17 h, and the molar ratio of cycles vs linear chains increased accordingly. After 17 h, only cyclic polyamides were detected in the MALDI−TOF mass spectra (detectable up to 10 000 Da). Furthermore, ϵ-CLA/ϵ-ACA ratios of 0/100, 50/50, and 80/20 were polycondensed at 250 °C for 17 and 48 h. In all cases, the same maximum molecular weight was obtained, suggesting that the chain growth was limited by cyclization. Heating a 99:1 ϵ-CLA/ϵ-ACA mixture yielded a low molar mass product exclusively consisting of cycles. Extraction experiments with various solvents proved that a separation of cyclic and linear polyamides is not feasible in this way. All these results are in perfect agreement with our new theory of thermodynamically controlled polycondensations.

Introduction

Synthesis and technical production of polyamide-6 have been studied by numerous research groups and chemical companies, and these studies have revealed that the formation of the polyamide chains is accompanied by the formation of cyclic oligoamides. Most experimental studies[1−7] and theoretical analyses[8−11] agree in that the content of cyclic oligomers (extracted and identified up to the nonamer) was of the order of 4 ± 1 wt %.[1−9] Most technical syntheses of polyamide-6 are based on copolymerizations (or copolycondensations) of ϵ-CLA and ϵ-ACA (or H_2O) in bulk at 260 ± 15 °C. Under these conditions, transamidation reaction takes place so that the entire polymerization process proceeds under thermodynamic control. These results agree largely with the classical theory of thermodynamically controlled polycondensations (TCPs) elaborated by Flory[12] and Stockmayer.[13,14] According to those authors, polycondensations of monomers in bulk should yield a reaction mixture which at 100% conversion consists of 2.5−3.0 wt % of cycles and one giant linear chain representing 97.0−97.5 wt % of the reaction mixture.

Quite recently, the first author of this work has published[15] a new theory of TCPs, saying that the molar ratio of cycles and linear chains increases with higher conversions and at 100% conversion all reaction products are cycles involved in ring−ring equilibria. According to this theory, the content of cycles in polyamide-6 should vary from 0% at low conversions (<80%) up to 100% at 100% conversion. The discrepancy of this theory and the previously published results of other authors[1−9] prompted us to reinvestigate the role of cyclization in syntheses of polyamide-6 by thermal (co)polymerization of ϵ-CLA and ϵ-ACA.

Experimental Section

Monomers. ϵ-Caprolactam (ϵ-CLA), ϵ-aminocaproic acid (ϵ-ACA), and 2,2,2-trifluoroethanol (TFE) were purchased from Aldrich Co. (Milwaukee, WI) and used as received.

Polymerizations (Tables 1 and 2). A. ϵ-Caprolactam (90 mmol) and ϵ-aminocaproic acid (10 mmol) were weighed into a cylindrical glass reactor equipped with a mechanical stirrer, gas-inlet, and gas-outlet tubes. The reaction vessel was placed into an oil bath preheated to 150 °C. The temperature was rapidly raised to 250 °C, and this temperature was maintained for several hours (see Table 1). Part of the cold reaction product was mechanically removed from the reactor, and the viscosity and MALDI−TOF mass spectra were measured.

All other experiments with ϵ-caprolactam listed in Tables 1 and 2 were performed analogously.

B. ϵ-Aminocaproic acid (100 mmol) was weighed into a cylindrical glass reactor equipped with mechanical stirrer, gas-inlet and gas-outlet tubes. The reaction vessel was placed into an oil bath preheated to 150 °C and the temperature was rapidly raised to 250 °C. After 2 h, the reaction mixture was cooled and a MALDI−TOF ms (Figure 3) and the inherent viscosity in *m*-cresol were measured: $\eta_{inh} = 0.81$ dL/g in *m*-cresol.

Extraction Experiments (Tables 3 and 4). A mixture of ϵ-caprolactam (90 mmol) and ϵ-aminocaproic acid (10 mmol) was polycondensed at 250 °C for 17 h as described above. The entire reaction product was then dissolved in 2,2,2-trifluoroethanol and precipitated into methanol. The precipitated polyamide was successively extracted with methanol (3 days), ethanol (3 days), ethanol + TFE (volume ratio 9:1, 3 days), and ethanol + TFE (volume ratio 7:3, 3 days). The isolated polyamide-6 had a weight of 71.6% of the theoretical yield (Table 3).

In a second experiment, the polyamide was precipitated from TFE into methanol and afterward extracted with methanol (3 days) and with a mixture of ethanol and TFE (volume ratio 7:3 for 3 days) (Table 4).

Measurements. The inherent viscosities were measured in *m*-cresol with an automated Ubbelohde viscometer thermostated at 30 °C. The MALDI−TOF mass spectra were recorded on a Bruker Biflex III equipped with a nitrogen laser ($\lambda = 337$ nm). All spectra were recorded in the reflector mode with an acceleration voltage of 20 kV. Most irradiation targets were prepared from hexafluoro-2-propanol solutions using dithranol as matrix and potassium trifluoroacetate as dopant. In selected cases, α-cyanocinnamic acid (CCA) and 2-(4-hydroxyphenylazo)benzoic acid (HPAB) were used as matrices, and the best mass spectra were obtained in HPAB (Figures 2−4). The SEC measurements were conducted in trifluoroethanol (TFE) and evaluated with a triple detector including light scattering.

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Table 1. Polycondensation of ϵ-Caprolactam/ ϵ-Aminocaproic Acid Mixtures[a] in Bulk at 250 °C

expt no.	time (h)	η_{inh}[b] (dL/g)	reaction products[c]
1	2	0.85	C + La
2	4	1.10[d]	C + La
3	6	1.22	C + La
4	8	1.65[e]	C + La
5	17	2.28[f]	C
6	48	2.20	C

[a] Molar feed ratio 90/10. [b] Measured at 30°C with $c = 2$ g/L in *m*-cresol. [c] Based on MALDI-TOF mass spectra below 8000 Da. [d] $M_n \sim 12\,000$ Da, $M_w \sim 27\,000$ Da. [e] $M_n \sim 29\,000$ Da, $M_w \sim 60\,000$ Da. [f] $M_n \sim 43\,000$ Da, $M_w \sim 90\,000$ Da.

Table 2. Polycondensation of ϵ-Caprolactam (ϵ-CLA) and ϵ-Aminocaproic Acid (ϵ-ACA) in Bulk at 250 °C

expt no.	ϵ-CLA/ϵ-ACA[a]	time (h)	η_{inh}[b] (dL/g)	reaction products[c]
1	0/100	17	1.54	C + La
2	0/100	48	2.30	C
3	50/50	17	2.06	C
4	50/50	48		C
5	80/20	17	2.28	C
6	80/20	48		C
7	90/10	17	2.27	C
8	90/10	48	2.20	C
9	95/5	17	1.11	C
10	95/5	48	1.33	C
11	99/01	17	0.12	C
12	99/01	48	0.23	C
13	99/01	96	0.30	C (+ decomp products)

[a] Molar feed ratio. [b] Measured at 30°C with $c = 2$ g/L in *m*-cresol. [c] Based on MALDI-TOF mass spectra below 8000 Da.

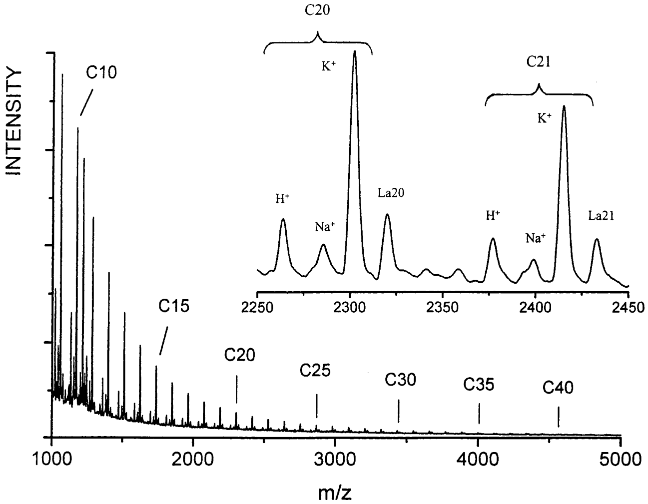


Figure 1. MALDI–TOF mass spectrum of the virgin reaction product obtained from an ϵ-CLA/ϵ-ACA 9:1 mixture after 2 h at 250 °C (no. 1, Table 1) recorded with dithranol as matrix and K-doping.

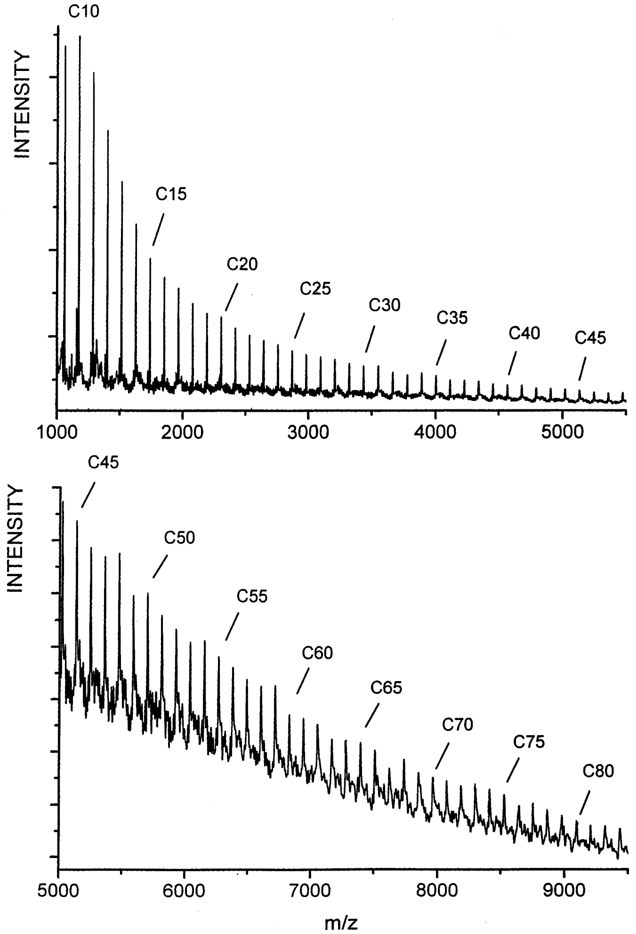


Figure 2. MALDI–TOF mass spectrum of the virgin reaction product obtained from an ϵ-CLA/ϵ-ACA 9:1 mixture after 17 h at 250 °C (no. 5, Table 1) recorded with HPBA as matrix and K-doping.

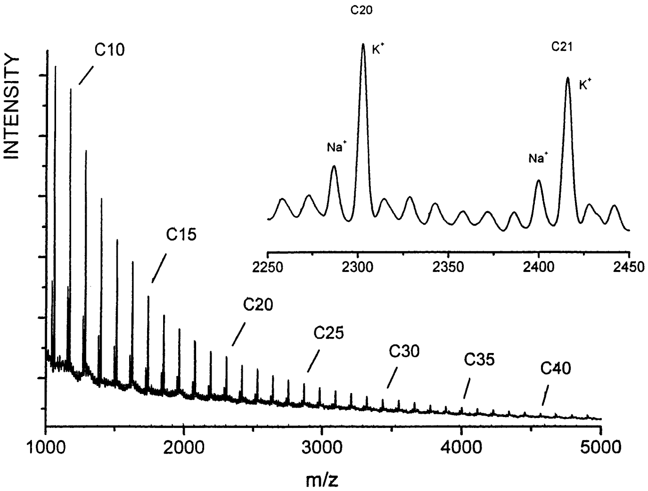


Figure 3. MALDI–TOF mass spectrum of the polyamide-6 remaining after precipitation into methanol followed by four extractions (Table 3) recorded with HPAB as matrix and K-doping.

Results and Discussion

Polymerizations. Most experiments were conducted in such a way that a mixture of ϵ-CLA and ϵ-ACA was heated at 250 °C with stirring under a slow stream of dry and deoxygenated nitrogen. The cold reaction products were characterized by solution (inherent) viscosities and by MALDI–TOF mass spectroscopy. In three selected cases, absolute molecular weights were determined by SEC in TFE. Assuming that the polymerization process proceeds without side reactions, such as oxidation or formation of double bonds (cyclization is considered to be a main reaction), only two types of reaction products should be formed, namely cyclic oligoamides and polyamides (labeled C in Figures 1–4) and linear chains terminated by one amino and one carboxylic end group (La in Scheme 1 and Figure 1). Therefore, NMR and IR spectra are useless for the characterization of the reaction mixtures, whereas MALDI–TOF allows for a distinction between cycles and linear chains and for the detection of small amounts

Table 3. Fractionation of High Molar Mass Nylon-6 (η_{inh} = 2.27 dL/g in *m*-Cresol)

expt no.	method of fractionation	isolated soluble fraction[a] (%)	remainder[a] (%)
1	precipitation into methanol	8.0[b]	88[b]
2	extraction with hot methanol	1.1	73.8
3	extraction with hot ethanol	0.5	73.2
4	extraction with hot ethanol + TFE (9:1)[c]	0.3	72.6
5	extraction with hot ethanol + TFE (7:3)[c]	0.3	71.6

[a] Relative to 100% yield. [b] The difference to 100% mainly results from the sublimation of ϵ-caprolactam. [c] The volume ratio is given in parentheses.

Table 4. Fractionation of High Molar Mass Nylon-6 (η_{inh} = 2.15 dL/g in *m*-Cresol)

expt no.	method of fractionation	isolated soluble fraction[a] (%)	remainder[a] (%)
1	precipitation into methanol	2.5[b]	85.2[b]
2	extraction with hot methanol	1.2	82.6
3	extraction with hot ethanol + TFE (7:3)[c]	0.8	80.4

[a] Relative to 100% yield. [b] The difference to 100% mainly results from the sublimation of ϵ-caprolactam. [c] TFE means 2,2,2-trifluoroethanol; the volume ratio is given in parentheses.

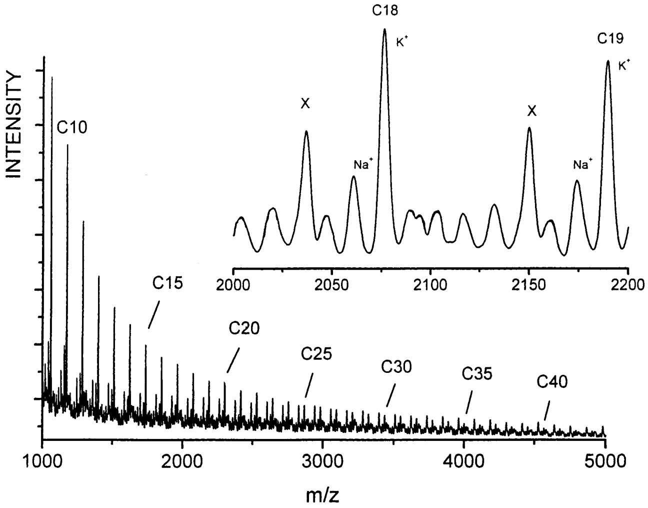
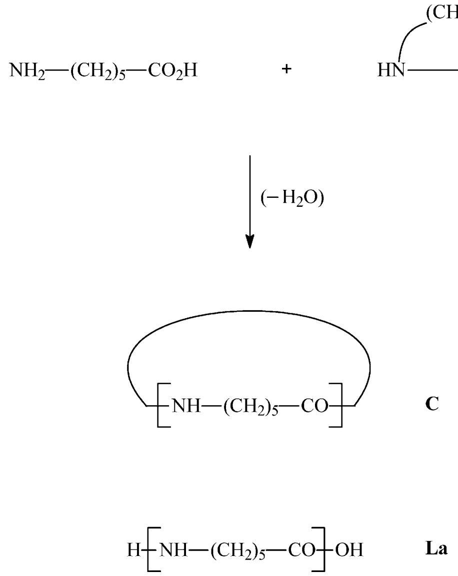


Figure 4. MALDI−TOF mass spectrum of a “BAYER polyamide-6” (η_{inh} = 0.91 dL/g in *m*-cresol) prepared with addition of a chain terminator (the peaks of linear chains containing the chain terminator were labeled X) and recorded with HPAB as matrix and with K-doping.

of byproducts resulting from side reactions. Yields were not determined because they were meaningless. They are influenced by the sublimation of ϵ-CLA (increasing with longer times) and by fractionation upon precipitation (which depends on the average molecular weight). Therefore, yields of precipitated and isolated polyamides do not provide accurate information on the conversion.

In a first series of polymerizations, a 9:1 mixture of ϵ-CLA and ϵ-ACA was performed with variation of the time. The results listed in Table 1 demonstrate that the reaction mixture approaches the maximum molecular weight around 17 h. The MALDI−TOF MS of the virgin reaction product recorded after 2 h (Figure 1) displays intensive peaks of cyclic polyamides, but the peaks of linear chains (La) are still detectable, despite the relatively low feed ratio of ϵ-ACA. After 17 h, the peaks of linear chains have completely vanished, at least in the mass range below 9000 Da (Figure 2). At this point it should be mentioned that it proved difficult to obtain good MALDI−TOF MS of polyamide-6, despite variation of matrix and dopant. Figure 2 represents the best spectrum obtained in this work and demonstrates that high molecular weight polyamide-6 contains large cycles which were detected in the original mass spectrum up to a degree of polymerization around 90. These results are in perfect agreement with our theory of TCPs and prove in contrast to the literature[1−6,12,13] that the fractions of cycles and their average DPs increase with higher conversions.

Scheme 1



In a second series of experiments, either neat ϵ-ACA or various mixtures of ϵ-CLA and ϵ-ACA were heated to 250 °C for 17 and 48 h (Table 2). In the case of neat ϵ-ACA, an additional experiment was conducted and stopped after 2 h (see Experimental Section). In the MALDI−TOF of this 2 h experiment the mass peaks of the linear La chains were observable with an intensity similar to that of the ϵ-CLA/ϵ-ACA 9:1 mixture (Figure 1). This finding suggests that even after 2 h a thermodynamically controlled equilibrium was achieved. Both the viscosity and the MALDI−TOF MS of the product obtained after 48 h were almost identical with those of the 9:1 mixture after 48 h (Figure 2). The experiments with 5:5 and 8:2 ϵ-CLA/ϵ-ACA mixtures gave again similar results. At least after 48 h the same inherent viscosities (2.25 ± 0.5 dL/g in *m*-cresol) were obtained, and the MS exclusively displayed the mass peaks of cycles. This finding suggests that, regardless if a neat polycondensation or mainly a ring-opening polymerization is performed, the final reaction product is the same, namely a mixture of small and large cycles. The thermodynamic properties of these ring−ring equilibria limit the chain growth as outlined in eqs 1−3

$$[\mathrm{M}]_x + [\mathrm{M}]_y \rightleftharpoons [\mathrm{M}]_{xy} \tag{1}$$

$$K = \frac{[\mathrm{M}]_{xy}}{[\mathrm{M}]_x[\mathrm{M}]_y} \tag{2}$$

$$\overline{\mathrm{DP}} = \frac{1}{1 - p(1 - X^{-K})} \tag{3}$$

and in a previous publication.[15] Molecular weight measurements in TFE evaluated with a triple detector (including light scattering) suggest that the number-average molecular weight (M_n) of the highest molecular weights ($\eta_{inh} \approx 2.27-2.230$ dL/g in *m*-cresol) are around 40 000−45 000 Da and the weight-average molecular weights (M_w) around 80 000−90 000 Da (see footnotes in Table 1).

When the 90:10, 95:5, and 99:1 experiments are compared (nos. 7−12, Table 2), it becomes obvious that the total reaction rate slows down with lower feed ratios of ϵ-ACA, which plays the role of a catalyst (in addition to the role of monomer). In the mass spectra of all 95:5 and 99:1 polymers only mass peaks of cycles were detectable (up to 6000 Da), indicating that these polymerizations may be understood as ring-equilibration processes.

Extraction Experiments. In previous studies of other research groups,[1−6] polyamide-6 samples were extracted with hot water or methanol and cyclic oligomers up to the nonamer were identified. These extractions were considered to be exhaustive in such a sense that all cyclic oligomers were extracted from the polyamide-6 samples. The formation of significant fractions of cyclic polyamides having DPs above 10 was not taken into account, and analytical methods allowing for the detection of cyclic polyamides in virgin reaction products did not exist at that time.

In this work, two samples having inherent viscosities around 2.25 dL/g (in *m*-cresol) were fractionated. In the first case, precipitation into methanol was followed by four extractions. The extracts exclusively contained cyclic oligo- and polyamides, and in the fourth extract (ethanol/TFE = 7/3) cycles up to 5000 Da were detectable. This means that cycles of much higher DP were extracted than expected from the literature.

However, the most interesting result concerns the remaining insoluble polyamide which made up 71.6% relative to a theoretical yield of 100% (Table 3). The MALDI−TOF MS of this remainder is presented in Figure 3. It exclusively displays mass peaks of cycles (up to 6000 Da in the original spectrum, the technical limit of this mass spectrum). In other words, the MS of the remainder was almost identical with that of the virgin reaction product, so, as if no extraction had occurred. This finding was confirmed by a second analogous experiment. After precipitation into methanol, the second polyamide was extracted with methanol and with a ethanol/TFE mixture (7/3 by volume). The remaining 80% of the polyamide showed a MALDI−TOF MS which displayed mass peaks of all cycles between 800 and 6000 Da. Again, no significant change relative to the original polyamide was detectable. Therefore, these experiments suggest that a nearly quantitative extraction of cyclic polyamide and, thus, separation from linear chains is not feasible.

Conclusion

The results obtained in this work from polymerizations of ϵ-CLA and (co)condensations of ϵ-ACA suggest the following conclusions. Both the molar fraction of cyclic oligo-/polyamides and their average DP increase with higher conversions, so that in the MS of the polyamides with the highest molecular weight linear chains are not detectable below 10 000 Da. Regardless of the feed ratio of ϵ-CLA/ϵ-ACA with sufficiently long reaction time (i.e., 48 h in most cases), all reaction products achieve the same molecular weight. Fractionation of two high molecular weight polyamides revealed that after removal of 20−28% of the virgin product (by sublimation, precipitation, and extraction) the MALDI−TOF MS still displays the same number and molar masses of cyclic polyamides as before the fractionation. All these results together are in good agreement with our theory of TCPs which postulates that a clean polycondensation approaching 100% conversion produces nothing else but ring−ring equilibria which limit the chain growth (eqs 1−3). Side reactions on the order of 0.01% (relative to all chain growth steps) which are not detectable by MALDI−TOF mass spectrometry may, of course, also contribute to the limitation of the chain growth.

Finally, it should be mentioned that three polyamide-6 samples of Bayer AG were characterized by MALDI−TOF mass spectrometry ($\eta_{inh} = 0.91$, 1.46, and 1.78 dL/g in *m*-cresol). High fractions of cycles were found in all three samples. Most interesting is the sample having $\eta_{inh} = 0.91$ dL/g because in this case molecular weight was limited by addition of a chain terminator. Nonetheless, cyclic polyamides were detectable up to masses of 4000 Da (Figure 4). Above 3000 Da the peaks of linear chains containing the chain terminator (labeled X in Figure 4) prevail over the mass peaks of cycles. The MALDI−TOF MS of the high molar mass samples exclusively displayed the mass peaks of cycles. These findings were in perfect agreement with our results and their interpretation.

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