MALDI-TOF MS Investigations of Polyamides Synthesized in Autoclave and Microwave Assisted Processes

*Lars Nothdurft, Ralf Bode, Gudrun Schmidt-Naake**

Summary: Due to their excellent physical and chemical properties polyamides (PA) are used in many industrial processes. The most common products are the aliphatic polyamides synthesized by a conventional melt-polycondensation method of AH-salt in an autoclave. High temperatures, high pressure and long reaction times are necessary. On the other hand the polyamide synthesis can conducted as solution polycondensation in a microwave oven. Moreover the higher heating efficiency of microwave irradiation reduces the reaction time to about 20 minutes. The main focus of this study lies on the end group analysis by MALDI-TOF MS (matrix assisted laser desorption/ionization time of flight mass spectrometry) of aliphatic polyamides produced by autoclave – as well as microwave assisted synthesis by AABB-type condensation. The results show differences in the end group formation depending on the chosen reaction conditions. In case of following modification or protecting group chemistry, it is of course important to know the kind of end groups of the polyamide.

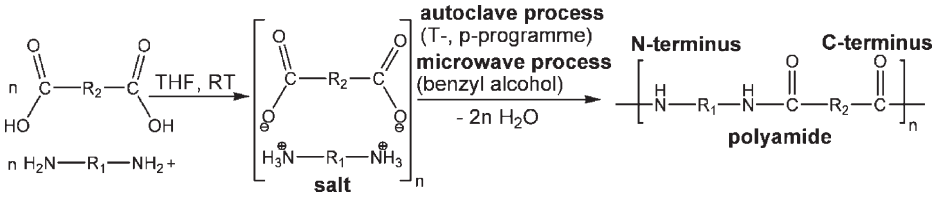
Keywords: esterification; matrix-assisted laser desorption/ionization mass spectrometry (MALDI MS); polyamides; polycondensation; synthesis

Introduction

Polyamides are still one of the major engineering thermoplastics. They can be modified by a number of techniques like copolymerization, incorporation of fillers or blending with other polymers.[1] The class of polyamides offers a huge number of industrial applications in textile, medicine or automobile industry. One of the most investigated polyamides is PA 6 which is synthesized by ring opening polymerization of ω-aminocaprolactame (AB-type condensation).[2] Another important polyamide is PA 6.6 synthesized by AABB-type condensation of adipic acid and hexane diamine.[3,4] AABB-type refers the condensation of bifunctional amines with bifunctional carboxylic acids. The reaction can be carried out in a two-step synthesis. In the first step the diamine and the dicarboxylic acid are converted into a salt. The salt formation is necessary for an equal stoichiometric ratio of the educts. In the second step, the salt is converted into polyamide under condensation conditions realized by a conventional autoclave[5] or a microwave assisted process[6] (Scheme 1).

When using microwave irradiation the reaction mixture is heated directly by stimulation of polar molecules. Due to the more efficient heating of the reaction mixture by microwave irradiation, the reaction times can be drastically reduced.[7] One of the first syntheses of polyamides using microwave irradiation as heating source was described by Imai[8] in 1993. The salt was converted into polyamide in a domestic microwave oven. The process can be described as a polycondensation carried out in solution, because it is necessary to solve the salt in a medium which is able to absorb the microwave irradiation otherwise

Technische Universität Clausthal, Institut für Technische Chemie, 38678 Clausthal-Zellerfeld, Germany
Fax: +49 5323 723655;
E-mail: gudrun.schmidt@tu-clausthal.de



Scheme 1.
Reaction scheme of AABB-type polycondensation; PA 4.9 ($R_1 = (CH_2)_4$), PA 6.9 ($R_1 = (CH_2)_6$), PA 7.9 ($R_1 = (CH_2)_7$); $R_2 = (CH_2)_7$.

it is impossible to heat up the educts. Because of the low solubility of the salt in organic solvents and the requirement of a high boiling point, only a few solvents can be used for the synthesis. Imai obtained good results with *m*-cresol or benzyl alcohol as solvents.[8] By reason of health aspect we prefer benzyl alcohol.

MALDI-TOF mass spectrometry has been proved to be a powerful technique to investigate the end groups of AB-type polyamides (PA 6),[9] as well as AABB-type polyamides like PA 6.6.[10,11] The advantage in comparison to conventional mass spectrometry is that the analyte can be detected without fragmentation. The low solubility of polyamides in organic solvents requires fluorinated alcohols like 2,2,2-trifluoroethanol (TFE) or 1,1,1,3,3,3-hexafluoroisopropanol (HFI) as solvents for MALDI preparation. The most common matrix for polyamides described in literature is 2-(4-hydroxyphenylazo)benzoic acid (HABA).[12] As salt additives sodium trifluoroacetate (NaTFA), potassium trifluoroacetate (KTFA) or lithium chloride (LiCl) are mostly used. Weidner et al. reported the MALDI-TOF analysis of modified PA 6.6.[13] Besides cyclic species (which are formed by inter- or intramolecular condensation), the spectra of unmodified PA 6.6 show various linear structures. Species with free amino and free carboxylic acid end groups were detected as well as species with only amino end groups (NH_2-PA-NH_2) or species with only carboxylic acid functions (HOOC-PA-COOH).

In this study we want to show differences in the end group formation of AABB-type polyamides: PA 4.9, PA 6.9 and PA 7.9 in dependence on different reaction conditions (autoclave/microwave). The analysis of the end groups of polyamides is important in case of following modification or protecting group chemistry. Furthermore we want to demonstrate how the MALDI technique can be used to proof the completeness of a saponification and an esterification of the end groups of polyamides. The potentiometric end group titration was used to determine the numbers of end groups and to estimate the molar masses of the polyamides.[14]

Experimental Part

Synthesis of Salt

Firstly 0.3 mol of the dicarboxylic acid and 0.3 mol of the diamine were solved in 800 mL THF. Subsequently the solutions are combined under strong stirring in which the salt precipitates immediately. Afterwards the solid content was filtered, washed with THF several times and dried at room temperature under vacuum. The synthesized polyamides base on azelaic acid, whereas the chain length of the diamine was varied (1,4-butane diamine, 1,6-hexane diamine, 1,7-heptane diamine). Exemplarily we show the most results of PA 6.9.

Synthesis of Polyamides by Autoclave Process[15]

The melt condensations of polyamides were carried out in an autoclave (BEP 280, Typ 3 BÜCHI). The temperature was controlled by a high temperature thermo-

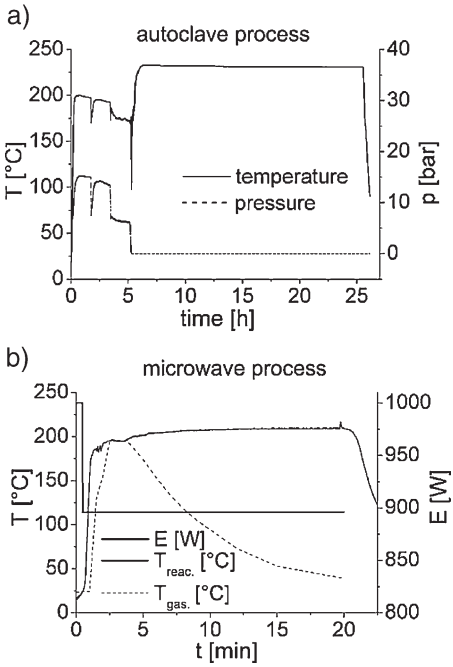
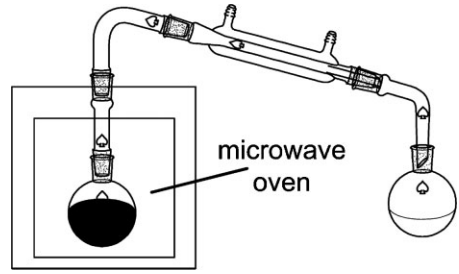


Figure 1.
Reaction profiles a) autoclave process, b) microwave process (E = power in watt).

stat HT30-M1 JULABO equipped by a C.U.-cooling unit. A typical recipe consisted of 50 g salt and 1 g diamine. The reaction mixture was added to 60 wt.-% water. Afterwards a defined pressure-temperature profile was started (Figure 1a). In the first step of the synthesis, the salt was transferred into the melt (5–10 bar, 220 °C). In the last step the reaction mixture was condensed under vacuum for 15 to 19 hours.

Synthesis of Polyamides by Microwave Process

The microwave assisted synthesis was carried out in multimode microwave reactor MicroPrep1500 (MIKROWELLEN LABOR SYSTEM) equipped with a distillation set-up (Scheme 2). Typical reaction conditions comprise 25 g salt solved in 40 mL benzyl alcohol. The reaction mixture was heated up to 200 °C (Figure 1b). During the reaction condition the resulting condensation water and the solvent were distilled. After about 20 minutes a cooling period of



Scheme 2.
microwave oven equipped with a distillation set-up.

10 minutes was started. The polyamide was worked up by two methods.

Method 1

The polyamide was dispersed in methanol and stirred for several hours. Afterwards the dispersion was filtered and washed with acetone.

Method 2

The product was solved in formic acid and kept under reflux for 20 hours and precipitated in acetone. (This treatment leads to a saponification)

Analytical Techniques

Infrared studies were carried out on a FTS 7000 (BIORAD) equipped with a photo acoustic measuring cell (model 300 MTEC).

MALDI-TOF-MS measurements were performed on a BRUKER Biflex III equipped with a 337 nm nitrogen laser. Positive ion spectra were acquired in linear mode with 20 kV acceleration voltage. The mass spectrometer was calibrated with a peptide standard from BRUKER within the mass range from 1000 to 3000 Da. The samples were prepared by mixing a solution of matrix (20 mg/mL in trifluoroethanol), sample (10 mg/mL, in trifluoroethanol) and salt (10 mg/mL in trifluoroethanol) in a ratio of 10:10:2. All results presented here were measured with the matrix 2-(5-hydroxyphenylazo)benzoic acid (HABA) and the salt additives sodium trifluoroacetate (NaTFA), potassium trifluoroacetate (KTFA) and cesium chloride (CsCl). Matrix and salt were used as provided.

The titration of the end groups was carried out with a basic TITRINO 794 device from the firm METRHOM. The polyamides were solved in benzyl alcohol. For the titration an electrode with tetra-*n*-butylammonium bromide 0.4 mol/l in ethylene glycol was used as electrolyte. The amino end groups were titrated by perchloric acid (0.1 mol/l in pure acetic acid) and the carboxylic acid end groups were titrated by tetra-*n*-butylammonium hydroxide (0.1 mol/l in 2-propanol/methanol). The titrations were carried out at 80 °C. The average molar masses were calculated by Equation 1 ($M_{COOH/NH2}$: molar mass [g/mol], m_w: weighted samples [g], $V_{Tit.}$: volume of titration agent [mL], $c_{Tit.}$: concentration of titration agent [mol/L]). The measurements were repeated three times to form an average.

$$M_{COOH/NH_2} = \frac{m_w}{v_{tit.} \cdot c_{tit}} \quad (1)$$

Furthermore the polyamides were investigated after titration. Therefore about 50 mL titrated solvent was transferred into 500 mL acetone. The precipitated polyamide was filtered and dried under vacuum. The residues were analyzed by MALDI-TOF MS.

Results and Discussion

In the following we compare two different reaction conditions of polyamide synthesis (autoclave, microwave). First of all we expect no special effects in case of microwave assisted synthesis but when microwave heating is used the reaction mixture can be heated up more efficiently.

The FTIR spectra (Figure 2) examplarily show the formation of polyamide (PA 6.9). The spectrum of the salt shows the NH_3^+ valence vibration (2180 cm^{-1}) and a sharp COO^- deformation vibration (1390 cm^{-1}). These peaks dissapear in case of the polyamides synthesized by autoclave as well as by microwave process and the resulting spectra show the existence of amide peaks (C=O: 1635 cm^{-1}, N–H: 3298, 3075, 1550 cm^{-1}).

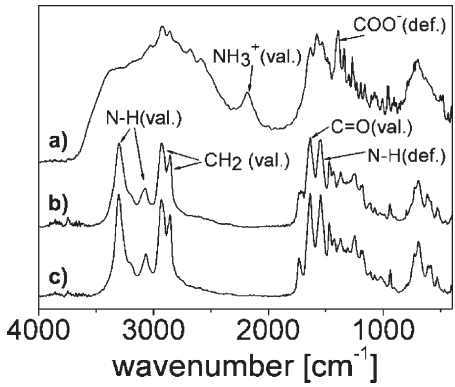


Figure 2.
FTIR spectra of a) salt, b) PA 6.9 produced in autoclave and c) in a microwave reactor.

A special focus of this work lies on the end group analysis of AABB-type polyamides by MALDI-TOF MS. Figure 3 shows the MALDI spectra of PA 6.9 produced by an autoclave (Figure 3a) as well as by a microwave assisted process (Figure 3b). Cesium chloride was used as a salt additive for the MALDI preparation. Thus all detected molecules are observed as cesium adducts [$PA+Cs^+$]. The shapes of the spectra are characteristic for polymers with a broad molar mass. Because of the mass discrimination of high molecular weight species, we are not able to get detailed information of the molar mass distribution. In this study the MALDI-TOF technique is used for a qualitative end group analysis of polyamides.

Each peak in such a distribution represents the molar mass of a species with *n* repetition units and two end groups, one end group at the amino-terminus (N-terminus) and one end group at the carboxyl-terminus (C-terminus) and in addition the salt cation resulting from the MALDI preparation (Equation 2). The spectra of both processes shows distributions with species of 3 to more than 15 repetition units in a mass range of about 1200 to 5000 Da (Figure 3 a,b). Structures and the corresponding abbrevia-

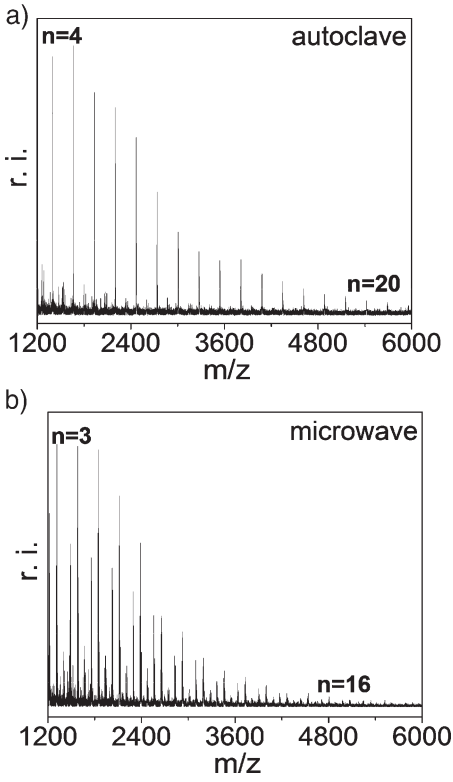


Figure 3.
MALDI-TOF spectra of PA 6.9 a) autoclave process (PA6.9-autoclave-2), b) microwave process (PA6.9-microwave-2a); (matrix: HABA; salt: CsCl; all molecules were observed as cesium adducts [PA+Cs^+]).

tions of possible polyamide species can be taken from Table 1.

$$M_{Peak} = M_{\text{end group N-terminus}} + n\, M_{\text{repetition unit}} + M_{\text{end group C-terminus}} + M_{\text{salt cation}} \quad (2)$$

When comparing both processes, the MALDI spectrum of polyamides synthesized in a microwave process shows a more complex spectrum. The MALDI assignment of polyamide species is done in a range of 2000 to 2500 Da (Table 2).There are differences in the number of series.

The spectrum of polyamides synthesized in autoclave shows one series in a distance of a PA 6.9 repetition unit of 268 Da (Figure 4a). Only carboxylic acid functionalized species (CC1) can be observed, for example the mass of 2199 Da is in good agreement with a COOH/COOH terminated species with seven repetition units (Table 2a). There are some reasons for a formation of a COOH/COOH terminated species. One possibility is the high volatility of diamines during the processes. Hence the diamine concentration may decrease, so that dicarboxylic acid monomer can react with the free amino end group of the polyamide. Another possibility is that an amino-terminated chain turns into a carboxylic acid terminated chain by loss of a hetereocyclic ring. This reaction was described by Roerdink and Warnier on the example of the PA 4.6 synthesis.[16] The free amino end group reacts intramolecular with the neighbouring amide bond by loss of ammonia. In the presence of water the formed pyrolidine ring saponifies and a carboxylic acid end group remains. Both reactions could have happened during the autoclave process and could lead to species with two COOH-end groups. Therefore the propagation reaction is hindered, because no free carboxylic acid monomer can attached to the chain.

The spectrum of polyamide synthesized by microwave irradiation shows more than 5 series (Figure 4b). Besides the CC1-serie, we could detect species with amino end groups (series: AE, AC1, AA). Furthermore microwave conditions can lead to a side reaction. The free carboxylic acid end groups can react with the benzyl alcohol (which is necessary to absorb the microwave irradiation) to form benzyl ester end groups (Scheme 3). Thus new end groups are possible, for example, we detected such monoester (CE1 and AE) and also we could observe diester like series EE (Table 2b).

The polyamide condensation as well as the esterification is favored under microwave conditions. The distillation of the solvent and the condense water during the process shift the equilibrium in both cases to their product sides.

Table 1.

Detected series of polyamides. Abbreviations: C: carboxylic acid end group, A: amino end group, E: ester function. End group formation base on azelaic acid; PA 4.9 ($R_1 = (CH_2)_4$), PA 6.9 ($R_1 = (CH_2)_6$), PA 7.9 ($R_1 = (CH_2)_7$).

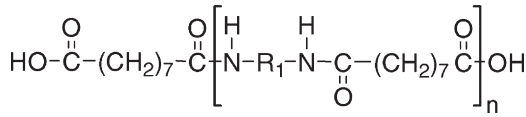
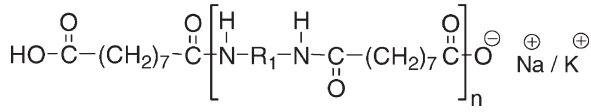
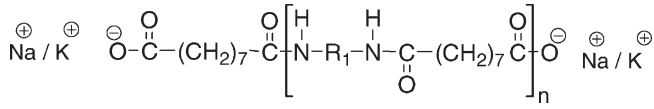
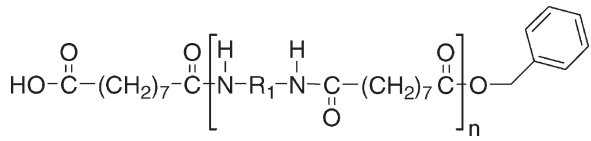
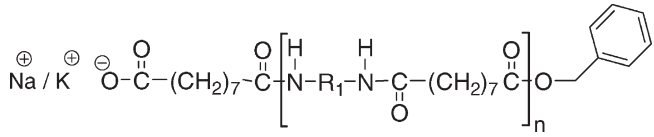
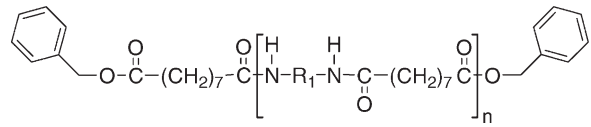
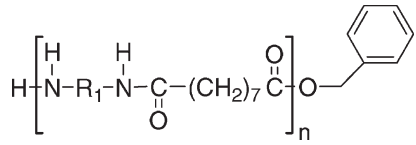
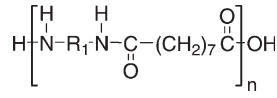
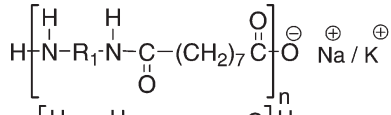
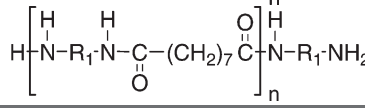
series	N-terminus/C-terminus	species
CC1	COOH/COOH	
CC2	COOH/COO^-	
CC3	COO^-/COO^-	
CE1	COOH/COObenzyl	
CE2	COO^-/COObenzyl	
EE	COObenzyl/COObenzyl	
AE	NH_2/COObenzyl	
AC1	NH_2/COOH	
AC2	NH_2/COO^-	
AA	NH_2/NH_2	

Table 2.
Assignment of MALDI spectra of PA 6.9 in a mass range of 2000 to 2500 Da, **a)** synthesized in autoclave process (PA6.9-autoclave-2), **b)** synthesized in microwave process (PA6.9-microwave-2a).

Process	Series	N-terminus/C-terminus	M [PA]		M [PA+Cs$^+$]	M [PA+Cs$^+$]
			theo. [g/mol]	n	theo. [g/mol]	exp. [g/mol]
a) autoclave	CC1	COOH/COOH	2065.6	7	2198.5	2199.1
	CC1	COOH/COOH	2333.8	8	2466.7	2467.5
b) microwave	CE1	COOH/COObenzyl	1887.4	6	2020.3	2021.9
	AC1	NH_2/COOH	1895.5	7	2028.4	2029.9
	EE	COObenzyl/COObenzyl	1977.5	6	2110.4	2111.9
	AE	NH_2/COObenzyl	1985.6	7	2118.5	2119.9
	AA	NH_2/NH_2	1993.6	7	2126.5	2127.8
	CC1	COOH/COOH	2065.6	7	2198.5	2199.6
	CE1	COOH/COObenzyl	2155.6	7	2288.6	2289.8
	AC1	NH_2/COOH	2163.0	8	2296.6	2297.8
	EE	COObenzyl/COObenzyl	2245.7	7	2378.6	2379.8
	AE	NH_2/COObenzyl	2253.8	8	2386.7	2387.8
	AA	NH_2/NH_2	2261.9	8	2394.8	2395.8
	CC1	COOH/COOH	2333.8	8	2466.7	2467.7

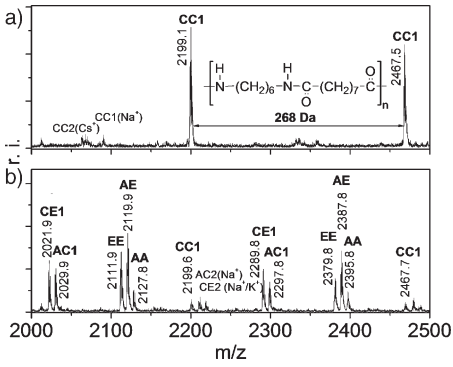
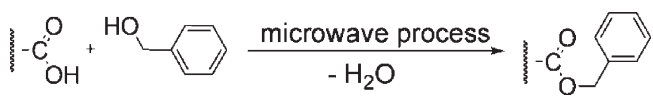


Figure 4.
MALDI-TOF spectra in a range of 2000 to 2500 Da of PA 6.9 synthesized in a) autoclave process (PA6.9-autoclave-2), b) microwave process (PA6.9-microwave-2a); (matrix: HABA; salt: CsCl; all molecules were observed as cesium adducts [PA + Cs$^+$]).

Furthermore, we detected in low intensities some impurities of adducts of other salt cations in the spectra. The pervasive contamination of Na^+ and K^+ ions leads to series like CC1(Na^+) (Figure 4a) or series like AC2(Na^+) and CE2(Na^+/K^+) (Figure 4b). The spectra of the autoclave process also shows series of CC2(Cs^+)-species in low intensities.

The fact that we could only detect carboxylic acid terminated species in case of the autoclave process is confirmed with MALDI measurements with varying salt cations (Figure 5). We tested MALDI preparations without salt, with NaTFA, KTFA and CsCl. In all cases we observed only carboxylic acid terminated species. When samples were prepared without salt (Figure 5a), for the first series we could detect protonated species like [CC1+H^+] as well as sodium adducts [CC1+Na^+]. In the case of preparations with NaTFA and KTFA we observed three series of sodium adducts (Figure 5b) or potassium adducts (Figure 5c). The distances within one repetition unit are in case of sodium adducts 23 Da and in case of potassium adducts 38 Da. One or two carboxylic acid end groups can be detected either as sodium salt or as potassium salt in the spectra (series: CC2, CC3). When MALDI samples are prepared with CsCl the spectra show only one series of a CC1 cesium adduct. It



Scheme 3.
Esterification of a carboxylic acid end group (side reaction during the microwave process).

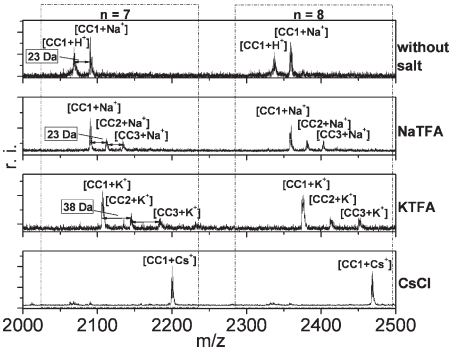


Figure 5.
MALDI-TOF spectra of PA 6.9 synthesized in autoclave (PA6.9-autoclave-2), measured: a) without salt, b) with NaTFA, c) with KTFA, d) with CsCl.

seems that there is a correlation between salt formation and atomic radius (Na^+: 1.9 Å, K^+: 2.4 Å, Cs^+: 2.7 Å). Probably the atomic radius of the cesium ion is too large to form species analogues COO-Na^+ or COO-K^+-salts. The resulting advantage is when samples prepared with CsCl the spectra are clearer than spectra of NaTFA or KTFA and also the signal-to-noise ratio is much better.

The potentiometric titration of end groups of polyamides synthesized in the autoclave is in good agreement with MALDI-TOF results. In case of the autoclave synthesis no amino end groups could be titrated (Table 3b). Hence, the titrated average molar masses of carboxylic acid end groups (Equation 1) counts twice, because the species contains two acid functions. The resulting value can be used for a rough estimation of molar masses (Table 3d). The molar masses are in a range of 2000 to 5000 g/mol. In case of polyamides synthesized in the microwave, carboxylic acid end groups as well as amino end groups could be titrated. Thus the calculation of the average molar masses is based on both titrated values.

Figure 6 shows three examples of polyamides synthesized by microwave assisted synthesis (PA6.9-microwave-2a, PA6.9-microwave-4, PA6.9-microwave-5). These polyamides contain different amounts of amino end groups (Table 3b). The sample **PA6.9-microwave-2a** is an example of a polyamide synthesized in microwave process with a high amount of amino end groups (0.35 mmol/g). The corresponding MALDI spectrum in Figure 6a shows three different series of species with amino end groups (AC1, AE, AA). In case of **PA6.9-microwave-4** we titrate 0.17 mmol/g amino end groups (Table 3b). In the MALDI spectra (Figure 6b) we detected two series of amino terminated species (AC1, AE) and for **PA6.9-microwave-5** the titrated value of amino end groups is 0.15 mmol/g (Table 3b), the generated MALDI spectra shows only one amino terminated species (AE) (Figure 6c). This example demonstrated that MALDI-TOF measurements reflected the results of amino end group titration in good agreement. Furthermore these results show a tendency, when

Table 3.
Results of potentiometric end group titration. (In brackets: uncorrected molar masses, in bold: corrected masses).

Process	Sample	Work-up	Ester	a) Reaction time	b) –NH2 [mmol/g]	c) –COOH [mmol/g]	d) M [g/mol]
autoclave	PA4.9-autoclave-1	–	–	12 h	–	0.54	3800
	PA6.9-autoclave-2	–	–	23 h	–	0.69	3000
	PA7.9-autoclave-3	–	–	12 h	–	0.60	3400
microwave	PA4.9-microwave-1a	Method1	–	25 min	0.24	0.31	(3700)
	PA4.9-microwave-1b	Method2	HCOOH		0.29	**1.45**	**2100**
	PA6.9-microwave-2a	Method1	–	60 min	0.35	0.23	(3700)
	PA6.9-microwave-2b	Method2	HCOOH		0.28	**1.29**	**2200**
	PA7.9-microwave-3a	Method1	–	30 min	0.17	0.29	(4800)
	PA7.9-microwave-3b	Method2	HCOOH		0.18	**1.00**	**3300**
	PA6.9-microwave-4	Method1	–	20 min	0.17	0.17	(5900)
	PA6.9-microwave-5	Method1	–	20 min	0.15	0.23	(5500)

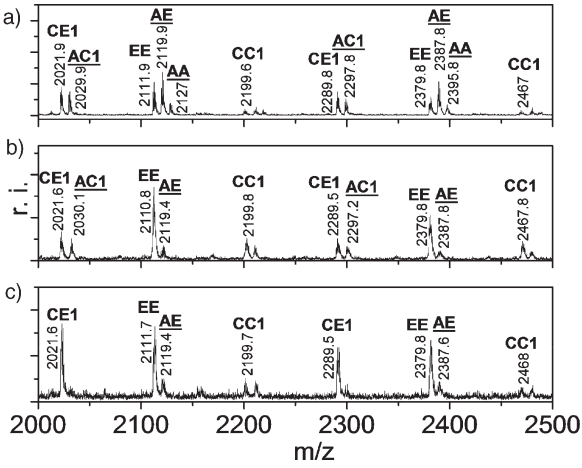


Figure 6.
MALDI-TOF spectra of PA 6.9 synthesized by microwave irradiation, in dependence on the titrated amount of amino groups a) PA6.9-microwave-2a (0.35 mmol/g amino groups), b) PA6.9-microwave-4 (0.17 mmol/g amino groups), c) PA6.9-microwave-5 (0.15 mmol/g amino groups). (All molecules were observed as cesium adducts).

increasing the reaction time from 20 to about 60 minutes (Table 3a) we detect more species with amino end groups in the MALDI spectra. In future further investigations of the optimization of microwave synthesis will follow.

However the microwave synthesis leads also to an esterification of carboxylic acid end groups. We wonder if we are able to cleave the ester group to get free carboxylic acid functions. Therefore we treat the polyamides synthesized in the microwave oven with formic acid. With the help of MALDI technique we can proof the completeness of saponification (Figure 7a). The spectrum of the untreated PA 6.9 shows species with ester end groups (CE1, EE, AE), those series disappear in the MALDI spectrum in case of the treated polyamide. Of course the amino functionalized species as well as the

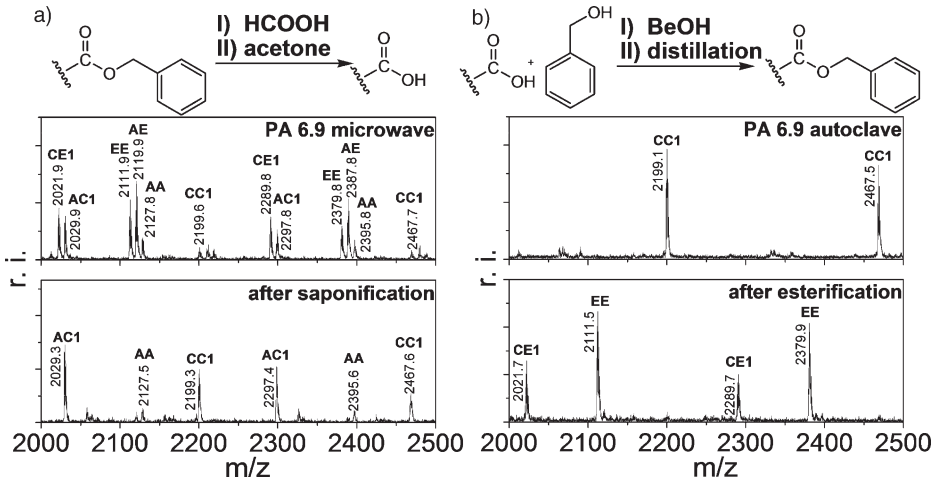


Figure 7.
MALDI-TOF spectra a) saponification of PA 6.9 synthesized in microwave (PA6.9-microwave-2a), b) esterification of PA 6.9 synthesized in autoclave (PA6.9-autoclave-2); (matrix: HABA; salt: CsCl, all molecules were observed as cesium adducts [PA+Cs^+]).

carboxylic acid terminated species will remain in the product.

Another example of end group modification is presented in Figure 7b. It shows the esterification of polyamide synthesized in the autoclave process. The sample was treated with benzyl alcohol with following distillation. Under these reaction conditions the free carboxylic acid end groups changed into ester groups. The MALDI spectrum shows the series CC1 in the spectrum of the untreated polyamide. The CC1 series disappears and the spectrum after the esterification shows series of monoester (CE1) and series of diester (EE).

A problem represents the end group titration of carboxylic acid functions. Especially in case of polyamides which were synthesized in the microwave reactor. Because the resulting species contain ester groups and it is uncertain if the conditions of the end group titration are sufficient to cleave the ester end groups completely. As soon as the ester groups remain, only the free carboxylic acid end groups could be titrated. So the value of carboxylic acid end group titration would lead to an incorrect average of molecular mass. Therefore we investigate the polyamide-residues after potentiometric titration. The solved polyamide in the titrated solution was precipitated in acetone. The MALDI-TOF analysis of the polyamide-residues is shown in Figure 8. The untreated **PA6.9-microwave-2a** shows the series which were mentioned above (Figure 8a). After the titration with tetra-*n*-butylammonium hydroxide, the spectrum of the residue shows series with ester functions (CE1, EE, AE) (Figure 8b). Hence, we can not expect that all carboxylic functions were completely titrated by the base. So the average value of carboxylic acid groups would lead to a wrong molar mass. This is shown at the example **PA6.9-microwave-2a**. Before saponification we found a value of 0.23 mmol/g carboxylic acid groups (Table 3c). This value would lead to a wrong molar mass of 3700 g/mol (Table 3d). After saponification with formic acid, the titrated value of carboxylic acid end groups is 1.29 mmol/g. The correct resulting molar mass is 2200 g/mol

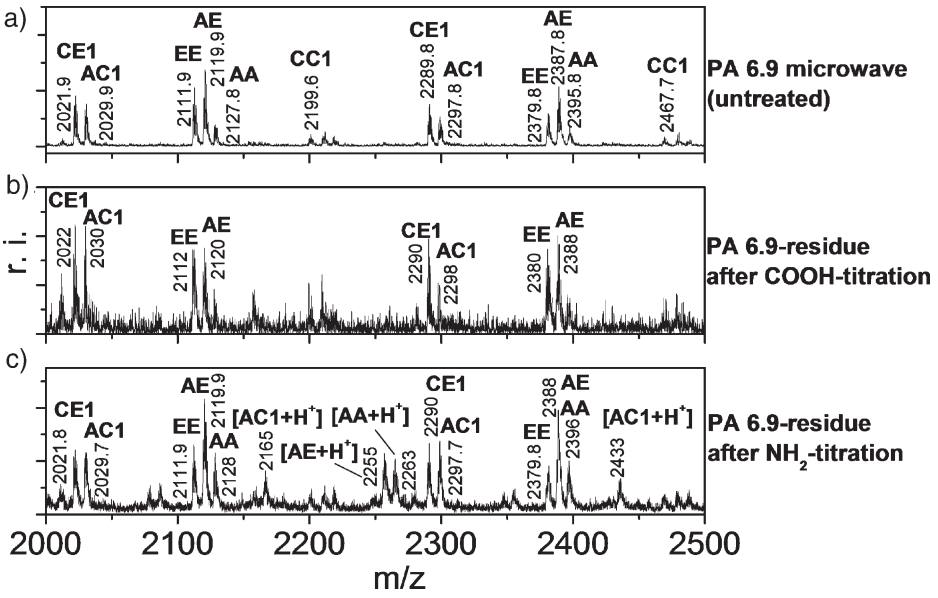


Figure 8.

Investigation of the residues after potentiometric end group titration a) untreated PA 6.9 synthesized in microwave (PA6.9-microwave-2a), b) PA 6.9 residues after COOH-titration with tetra-*n*-butylammonium hydroxide **c)** PA 6.9 residues after NH_2-titration with perchloric acid. (All molecules were observed as cesium adducts).

(Table 3d). The examples of PA 4.9 and PA 7.9 show the same tendencies (Table 3d). Thus, to get the correct molecular masses of polyamides synthesized in the microwave process, it is necessary to cleave the ester end groups by treatment with formic acid. The amount of amino end groups were unaffected by this treatment (Table 3b).

For the sake of completeness the spectrum in Figure 8c shows the polyamide after the amino end group titration with perchloric acid. During the titration the free amino groups were protonated by the acid. Besides the cesium adducts we were also able to detect protonated species like [AC1+H^+]; [AA+H^+], [AE+H^+] by MALDI-TOF analysis. Of course the amino end groups were not influenced by the esterification reaction.

Conclusion

The MALDI-TOF investigation of AABB-type polyamides shows spectra with species in a mass range of 1000 to 5000 Da. The MALDI sample preparation works very well with the matrix HABA and the salt additive CsCl. The distributions are typical for polyamides with broad molar masses. Thus we can use the MALDI technique for the analysis of end groups. The detected species of polyamides synthesized in the autoclave process contains only carboxylic acid end groups. The spectra of polyamides which were produced in microwave oven are more complex and show besides carboxylic acid terminated species structures with free amino functions. Furthermore with the help of MALDI-TOF technique we were able to observe a side reaction of the polyamide with the solvent. The benzyl alcohol which is necessary for the microwave process leads to an esterification of free carboxylic acid end groups. We were able to cleave the ester and to show the completeness of saponification by MALDI-TOF MS. The inverse reaction (esterification) works as well.

With the help of MALDI-TOF technique, we can improve the accuracy of the carboxylic acid end group titration for polyamides synthesized in the microwave oven. Therefore we investigated the polyamide-residues of potentiometric end group titration to get information about the titrated species. The results show that in case of polyamides synthesized in the microwave process no complete saponification proceeds during the titration, so that the titrated amount of the carboxylic acid end groups leads to incorrect molar masses. Thus to avoid, it is necessary to cleave the ester end groups by saponification with formic acid.

Acknowledgements: The authors acknowledge the Deutsche Forschungsgemeinschaft for financial support within the European Graduate School ''Microstructural Control in Free-Radical Polymerization''.

[1] M. I. Kohan, *Nylon Plastics Handbook*, Carl Hanser Verlag, München **1998**.
[2] P. Mathies, W. F. Seydl, R. R. Seymont, G. S. Kirschenbaum, *History and Development of Nylon 6*, Elsevie, New York **1986**.
[3] N. Ogata, *Makromol. Chem.* **1961**, *43*, 117.
[4] D. D. Steppan, M. F. Doherty, M. F. Malone, *J. Appl. Polym. Sci.* **1987**, *33*, 2333.
[5] L. Bottenbruch, R. Binsack, In *Technische Thermoplaste – Polyamide, Kunststoff-Handbuch* 3, Carl Hanser Verlag, München Wien **1998**.
[6] F. Wiesbrock, R. Hoogenboom, U. S. Schubert, *Macromol. Rapid Commun.* **2004**, *25*, 1739.
[7] C. O. Kappe, *Angew. Chem.* **2004**, *116*, 6408.
[8] Y. Imai, et al. *Makromol. Chem. Rapid Commun.* **1993**, *14*, 481.
[9] J. P. Katalinic, F. Hillenkamp, *MALDI MS*, Wiley-VCH **2006**.
[10] G. Montaudo, M. S. Montaudo, C. Puglisi, F. Samperi, *J. Polym. Sci: Part A: Polym. Chem.* **1996**, *34*, 439.
[11] C. R. Park, *Bull Korean Chem. Soc.*, **2007**, *28*, 2354.
[12] P. Juhasz, C. E. Costello, K. Biemann, *Am. Soc. Mass Spectrom.* **1993**, *93*, 1044.
[13] S. M. Weidner, U. Just, W. Wittke, F. Rittig, F. Gruber, J. F. Friedrich, *Int. J. Mass Spectrom.* **2004**, *238*, 235.
[14] A. K. Bledzki, T. Spychaj, *Molekulargewichtsbestimmung von hochmolekularen Stoffen*, Hüthig & Wepf Verlag, Basel **1991**.
[15] R. Bode, G. Schmidt-Naake, *Chem. Ing. Tech.* **2007**, *79*, **2099**.
[16] E. Roerdink, J. M. M. Warnier, *Polymer* **1985**, *26*, 1582.

