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Analysis of modified polyamide 6.6 using coupled liquid chromatography and MALDI–TOF–mass spectrometry

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Abstract

A new approach of analysis of polyamide 6.6 using the principle of coupling polymer liquid chromatography to matrix assisted laser desorption ionization–time of flight–mass spectrometry (MALDI–TOF–MS) is presented. In contrast to the known technique of two-dimensional chromatography, MALDI–TOF–MS was applied in the 2nd chromatographic dimension. According to the synthesis of polyamide 6.6 various species with different end groups are expected. Due to the capping of the end groups during the synthesis, either performed by the addition of mono-functional amines or acids, additional structures are formed and found. Although the resolution of chromatography applied for separation was poor in comparison to the broad variety of expected species, a complete identification of those components was achieved applying the MALDI–TOF–MS technique. The results were presented in a two-dimensional plot, which can be used as a fingerprint method for the analysis of polyamide 6.6.

Keywords: MALDI–TOF–MS; Liquid chromatography; Coupling methods

1. Introduction

Polyamides (PA) represent one of the most widespread classes of polymers. These polymers show some specific properties, which make them unique. Due to the ability to form hydrogen bonds between the polymer chains, fibers showing extraordinary strength can be made. Polyamides are chemically stable against most organic solvents, alkaline mediums, fuels and concentrated acids. This offers a broad range of applications in medicine, textile and car manufacturing industry.

The most important representatives of the class of polyamides are polyamide 6 (e.g., Perlon®) and polyamide 6.6 (e.g., Nylon®). In contrast to polyamide 6, which is made by a ring-opening polymerization of ω-aminocaprolactame, polyamide 6.6 is synthesized by a condensation of bifunctional acids with bifunctional amines. Thus, the resulting polymer contains additional variation of end groups. Beside cyclic polymers, formed by condensation of chain ends of one linear chain (backbiting) as well as by an intermolecular condensation, various linear structures are expected. The presence of two chemically different end groups (amine and carboxylic groups) offers the possibility to modify certain polymer properties as colour and flammability by attaching specific molecules. The addition of mono-functional acids or mono-functional amines can be simultaneously used for a capping of polymer chain propagation.

The modification causes a strong increase of the number of polyamide species with different end groups and results in PA with much lower molar masses, as well. Beside linear acid-amine, diamine, diacid and cyclic structures three additional end group variations are possible: mono-capped acid-amine structures, mono-capped diamines (or diacids) and di-capped diamines (or diacids). An overview of all

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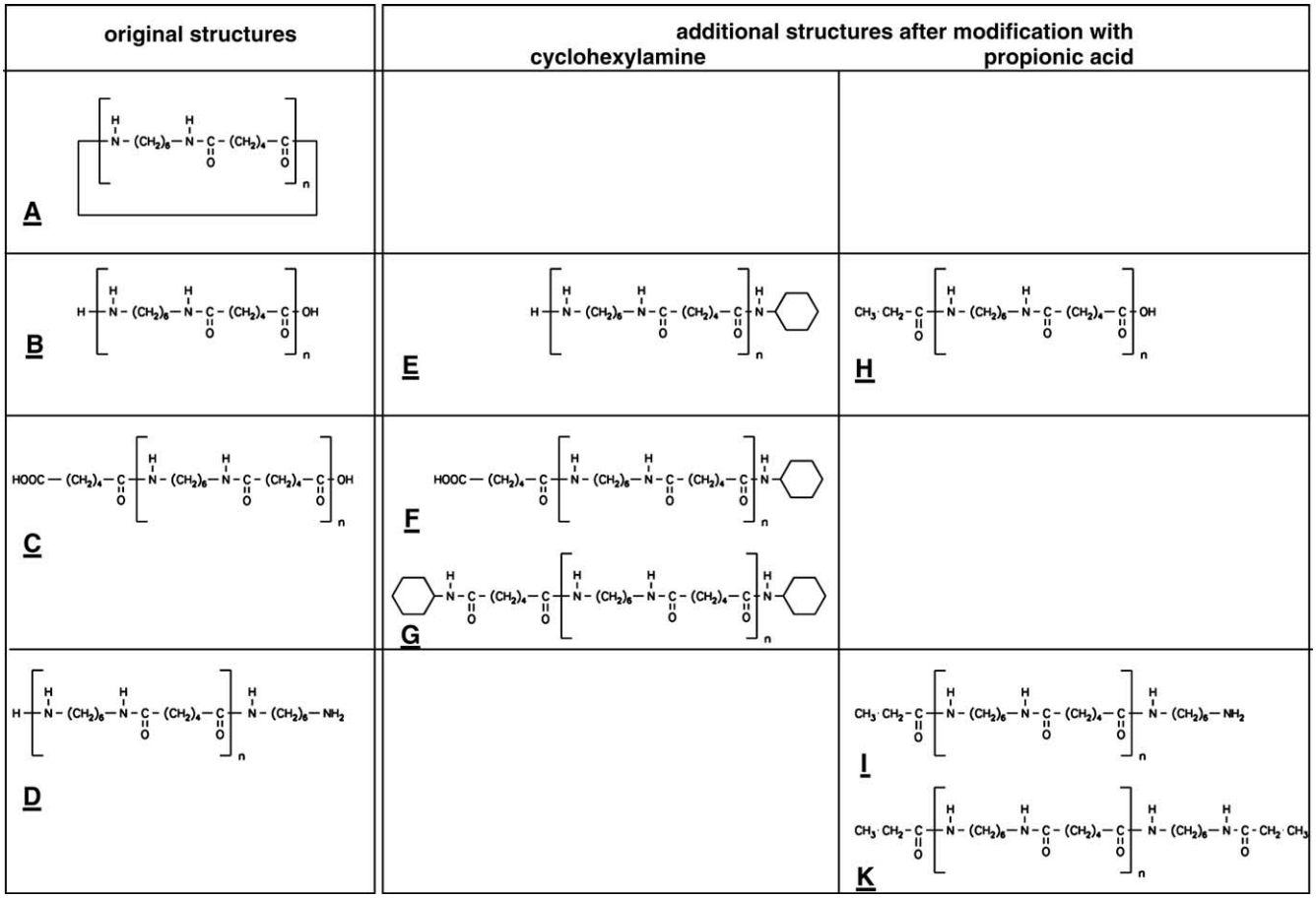

Fig. 1. Structures of original polyamide 6.6 (A–D) and possible structures after modification of end groups using propionic acid (E, F, G) and cyclohexylamine (H, I, K), respectively.

possible species is given in Fig. 1. The investigation of these structures is still very complex. Only sophisticated liquid chromatographic and mass spectrometric techniques can be used for separation and additional detection of all functionality's. An appropriate method for the separation of polymers with different end groups, independent of their molar mass, represents the so-called liquid adsorption chromatography at critical conditions (LACCC). At these chromatographic conditions the separation mechanism is characterized by a compensation of entropic and enthalpic contributions. The thermodynamic interpretation is given by the Gibbs–Helmholtz equation for the free enthalpy

$$\Delta G = \Delta H - T\,\Delta S \tag{1}$$

In contrast to the size exclusion mode with $\Delta S < 0$ and $\Delta H = 0$, the adsorption mode is characterized by enthalpic interactions between the stationary phase, eluent and polymer molecules. This can be expressed through $\Delta H < 0$ and $T\,\Delta S \ll \Delta H$. The compensation of enthalpic and entropic interactions (of the repeating units) at the 'critical point of adsorption' leads to $\Delta G = 0$. A more detailed description can be found in refs. [1–4]. In principle, critical separation conditions can be easily found by investigating polymers having different molar masses but identical chain structures and end groups. In size exclusion chromatography (SEC) mode these polymers were separated according to their molar mass. This results in various peaks which can be used for a system calibration. The adjustment of critical conditions for any polymer can be achieved by a variation of the solvent composition and/or temperature. At critical conditions of separation all peaks merge at one retention time. First examples of applying critical chromatography for the analysis of polyamide 6 and polyamide 6.6 [5–7] were recently published by Mengerink et al.

Since the solubility of polyamides in common organic solvents is extremely low, only few solvents can be used for these investigations. Besides hot phenol melts, formic acid [5] and trifluoroethanol (TFE) [8,9] 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) represents a well-suited solvent for PAs. However, the use of HFIP is overshadowed by its costs as well as by serious health risks. Moreover, solvent mixtures have to be found for SEC, liquid adsorption chromatography (LAC) and 'critical' chromatography (LACCC) as well, which enable complete solubility of polyamides combined with a minimal use of HFIP.

MALDI–TOF–MS has been shown to be a well-suited method for the analysis of polymers without fragmentation of macromolecules. First examples of the analysis of end groups and cyclic structures of polyamide 6 by MALDI–TOF–MS were reported by Montaudo et al [8,9] and Mengerink et al. [5]. For these investigations 2-(5-hydroxyphenylazo)benzoic acid (HABA) was exclusively used. Due to the broad molecular mass distribution of polyamides only species up to molar masses of 6000–8000 Da could be observed.

Haba et al. [10] reported the synthesis of hyper-branched aromatic polyamides and their MALDI–TOF–MS analysis using 2,5-dihydroxybenzoic acid (DHB) as matrix. In ref. [11] the synthesis and MALDI–TOF–MS analysis of EDA core-polyamide (PAMAM) dendrimers is described.

In this paper, a comprehensive characterization of polyamide 6.6 capped with amines as well as with acids is presented. Only the consequent coupling of liquid chromatography and MALDI–TOF–MS enables us to identify all possible species. To our knowledge that has not been shown previously.

The coupling of chromatography and MALDI–TOF–MS was performed using an interface, that continuously sprays dissolved analyte and matrix solutions onto the MALDI–TOF–MS target.

2. Experimental

2.1. Chromatography

For chromatographic investigations, a HPLC pump (Shimadzu LC 10 AD) was equipped with different sorts of columns. An evaporative light scattering detector (ELSD) EMD 960 (Polymer Labs), and a UV detector, SPD 10 A (Shimadzu), were used. The eluent flow was adjusted at 0.5 mL/min. The sample concentration was about 1 mg/mL. The composition of the mobile phase was adjusted by weighting of the single solvents. The PA samples were made in the Labs of BASF AG (Ludwigshafen, Germany).

2.1.1. SEC mode

By using HFIP as the mobile phase, silvertrifluoroacetate (AgTFAA) as salt (0.1%) and HFIP gel columns (PolymerLabs, UK), the SEC mode was established.

2.1.2. LAC/LAC_{near} CC mode

Both modes could be realized by adding different polar and/or non-polar solvents to HFIP. The separation was performed using RP-18 polymer columns (PolymerLabs, UK) as well as Bondagel (E-500) columns (Waters, USA).

2.2. MALDI–TOF–MS

A Bruker Reflex III mass spectrometer (Bruker-Daik, Germany) operating at 20 kV acceleration voltage, was used. For ionization/desorption, a UV laser working at a wavelength of 337 nm was applied. The laser pulse length was 3 ns. Typically, 100–200 transients were accumulated for one spectra.

2.2.1. Preparation of matrix–sample spot

2-(5-Hydroxyphenylazo)benzoic acid (HABA) (Aldrich, Germany) was used as the matrix. Matrix solutions with a concentration of 1 mg/mL (in HFIP) were prepared and premixed with polymer solutions (1 mg/mL). The mass spectrometer was calibrated with different standard peptides, as well as by self-calibrating methods using polymers.

2.3. Coupling of chromatography with MALDI–TOF–MS

The commercially available interface LC 500 (LabConnections, U.S.A.) was used for semi-on-line coupling of liquid chromatography and mass spectrometry. The matrix HABA, which was dissolved in THF (ca. 1 mg/mL), was deposited on the target in a previous run by means of a secondary pump (Knauer, Germany). The flow rate of the matrix solution was 0.4 mL/min. In a second run the eluent was sprayed onto the target and, simultaneously, the solvent was evaporated in a nitrogen gas stream at elevated temperatures. The temperature must be carefully adjusted in order to avoid crystallization of PA on the tip of the needle. The transfer system was controlled by software (LabConnections) which enables the automatic assignment of sample spots to the corresponding retention times.

3. Results and discussion

3.1. Non-modified (original) polyamide 6.6

A typical MALDI–TOF mass spectrum of an original polyamide 6.6 is shown in Fig. 2. Masses up to 9000 Da could be detected. The shape of the peak distribution is typical for polymers with broad molar mass distribution. Only low molar mass polymers can be detected although the maximum of the polymer distribution was determined using different meth-

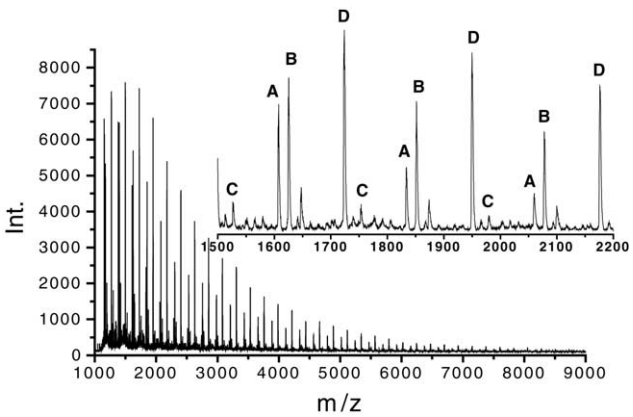

Fig. 2. MALDI–TOF mass spectra of a non-capped polyamide 6.6 (original) solution (matrix: HABA).

Table 1
List of measured and theoretical (calculated) masses and corresponding structures (for $n = 7$ [AcAm] – repeat units) of non-capped polyamide 6.6 (Na^+ adducts)

Series	Molar mass		Corresponding structure
	Measured	Calculated	
A	1606.3	1606.2	$[AcAm]_{cyc}$
B	1624.4	1624.2	$[AcAm]_{lin}$
C	1752.4	1752.2	$[AcAm]_{lin}$-Ac
D	1722.4	1722.3	Am-$[AcAm]_{lin}$

ods (viscometry, end group determination, etc.) to be near 20,000 Da. For A more detailed insight into the fine structure of this spectrum between 1500 and 2200 Da is inserted. It shows four series of peaks, each with a peak-to-peak distance of 226 Da. In Table 1 possible structures and their theoretical (calculated) masses were listed and compared with measured values. The peak at 1606.3 Da corresponds to cyclic structures $[AcAm]_{cyc}$ (series A), whereas the peak at 1624.4 Da (+18 Da, H_2O) represents linear polymers with mixed end groups (series B). Additional peaks at 1752.4 and 1722.4 Da can be attributed to linear polymers either with adipinic acid end groups ($[AcAm]_{lin}$-Ac, series C) or two hexamethylenediamine end groups (Am-$[AcAm]_{lin}$, series D). All *m/z* values correspond to single charged sodium adduct ions. As seen in Table 1, measured *m/z* values are in good agreement with calculated masses. However, a few additional series of peaks could be found, differing by +16, + 22 and +38 Da from the signal representing the linear polyamide with mixed end group. These signals were supposed to be typical for an attachment of one potassium ion (+16 Da) as well as of a second sodium atom (+23 Da) to the polymer. This particular adduct formation only occurs by a simultaneous separation of one hydrogen atom (−1 Da). The most preferred site for that substitution is the acid end group of the PA chain. In order to clarify this formation of a polymer salt structure lithium chloride was successively added to the polymer–matrix mixture. The result is shown in Fig. 3. Additional peaks appear, which can be attributed to various alkali metal–polymer combinations. Beside remaining sodium (PA)Na^+ and sodium-lithium (PA-Na)Li^+ adduct ions, additional lithium (PA)Li^+ and lithium-lithium adduct ions (PA-Li)Li^+ could be found. An increasing lithium ion concentration causes a complete substitution of all sodium adduct and polymer salt ions. Finally, only lithium cationized polyamide (PA)Li^+ and the corresponding lithium salt (PA-Li)Li^+ were detected.

3.2. Functionalization of amine end groups with propionic acid

The modification of amine end groups of polyamide 6.6 with propionic acid was performed during the synthesis of the polymer. As expected, the MALDI–TOF mass spectrum shows two additional peak series (H, and I) (see Fig. 4). Their calculated masses are in good agreement with experimental data. This is shown in Table 2. Polyamide species D (diamine)

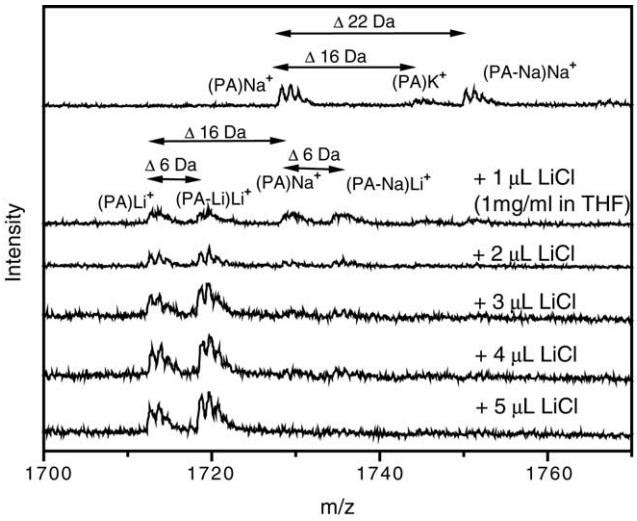

Fig. 3. Changes in adduct formation after adding of lithium salts.

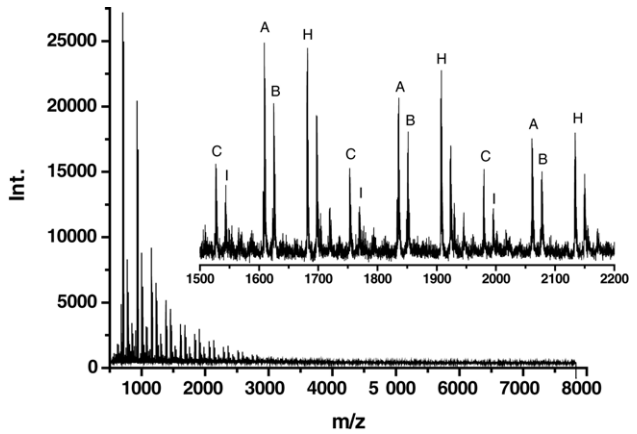

Fig. 4. MALDI–TOF mass spectra of a polyamide 6.6 modified with propionic acid (matrix: HABA).

and, surprisingly, K (diamine, functionalized at both amine end groups) (see Fig. 1) could not be found. Again, additional peaks were detected, which could be attributed to H^+ and K^+ and to (PA-Na)Na^+ adduct ions, as well (Table 3).

As a matter of fact, this intensity ratio of peaks recorded by MALDI–TOF–MS almost never corresponds to their real concentration. This is due to the quite different ionization probability of polymers with identical chain segments but various end groups [12]. Therefore, specifically adapted chro-

Table 2
List of measured and theoretical (calculated) masses and corresponding structures (for $n = 7$ [AcAm] – repeat units) of polyamide 6.6 (Na^+ adducts) with capped carboxylic end groups (in addition to masses given in Table 1)

Series	Molar mass		Corresponding structure
	Measured	Calculated	
E	1707.3	1707.2	Am-$[AcAm]_{lin}$
F	1834.5	1834.3	Am-$[AcAm]_{lin}$-Ac
G	1914.9	1914.5	Am-$[AcAm]_{lin}$-Ac-Am

Table 3
List of measured and theoretical (calculated) masses and corresponding structures (for $n = 7$ [AcAm] – repeat units) of polyamide 6.6 (Na^+ adducts) with capped amine end groups (in addition to masses given in Table 1)

Series	Molar mass		Corresponding structure
	Measured	Calculated	
H	1680.4	1680.2	$[AcAm]_{lin}$-Ac
I	1778.5	1778.2	Am-$[AcAm]_{lin}$-Ac
K	not found	1834.2	Ac-A-$[AcAm]_{lin}$-Ac

matographic methods have to be used for a preliminary separation of modified species.

For that purpose the principle of liquid chromatography at critical conditions (LACCC) was applied. The principle of adjusting critical separation parameters was previously described. In contrast to polyamide 6, where mixed amine-acid end groups were exclusively formed, polyamide 6.6 exhibit three different end group combinations (acid-amine, diacid, diamine). Since the adjustment of critical conditions can only be achieved for one certain end group combination, it becomes clear that a critical mode for polyamide 6.6 could not be obtained. Therefore, these critical conditions obtained for polyamide 6 were applied for the investigation of polyamide 6.6, too.

A resulting chromatogram is shown in Fig. 5. Beside a very sharp peak at 1.59 mL an additional broad peak at higher retention volumes (2.05 mL), showing a shoulder at 3.0 mL can be identified. An assignment of these three peaks to polyamide structures was only possible for non-modified species B, which could be attributed to the peak at 1.59 mL. Hence, the chromatographic run was fractionated by spraying onto the MALDI–TOF–MS target. Due to the very low concentration of species especially in the last fractions of the run, only 11 mass spectra at certain target spots could be recorded. They are shown in Fig. 6.

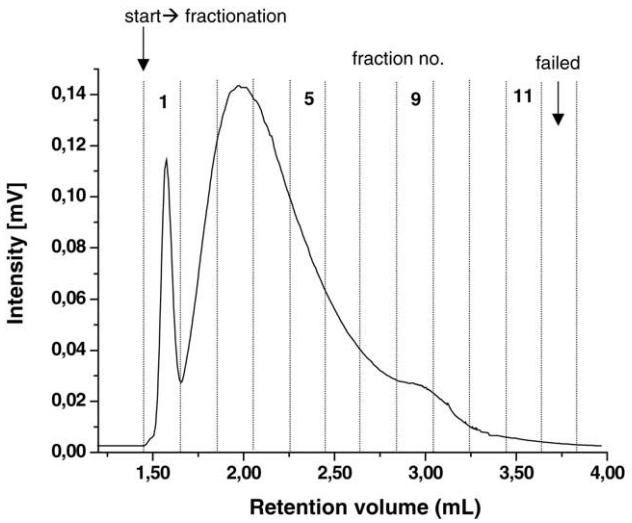

Fig. 5. Chromatogram of PA 6.6 after modification with propionic acid recorded near 'critical' conditions of separation of PA 6 (sample spot positions for MALDI–TOF–MS are indicated by lines and numbers).

Several peaks distributions were detected showing discrete signals with a peak-to-peak distance of 226 Da. Starting from spectrum 1 to 11 the intensity maximum of each distribution shifts towards lower masses, which corresponds to higher retention volumes in the chromatogram. Using the molar mass information given by the corresponding peak maximum, a calibration of the chromatographic system for various species could be performed. These calibration curves are presented in Fig. 7. Depending on the structure of end groups of the modified polyamides calibration curves with different slopes were observed. In contrast to the SEC-like behavior (but still in LAC, according to functional groups!) of series A, C and H seen in Fig. 7 series B and I elute at critical conditions of adsorption. At these particular chromatographic conditions, separation according to molar mass could not be achieved. This result corresponds very well with the shape of the MALDI–TOF mass spectrum 1 (in Fig. 6), which is typical for broad distributed polymers and fits the chromatographic result (sharp peak at 1.59 mL corresponds to fraction 1) as well.

As already mentioned, previous investigations have shown the basic shortcomings of MALDI–TOF–MS to correlate peak intensities to certain concentrations. Therefore, a quantitative interpretation of mass spectra regarding to the amount of a single structure within each spectra could not be performed. The structural information obtained by MALDI–TOF–mass spectrometry can be combined with chromatographic data, leading to quantitative information about the concentration of species. This was exemplarily shown for a single structure (ethyleneoxide–methylene copolymers) in a previous paper [13]. However, if there are more than one structure in a MALDI–TOF spectrum, any correlation between intensity and real amount must be speculative. Therefore, for our combination of methods the relative intensity of peaks of different structures in one MALDI–TOF mass spectrum was disregarded. Nevertheless, impressive two-dimensional plots could be created, which can be used as a fingerprint for the composition of polyamide 6.6. In Fig. 8 the comprising result of the investigation of acid-modified polyamide 6.6 is shown.

In the two-dimensional scheme, four regions of higher intensity can be identified. Using the structural information obtained by MALDI–TOF–MS, these regions can be attributed to different PA structures. Again, the typical SEC-like behavior (in LAC mode!) of species C, H and A can be seen. In contrast to that, species B and I elute in near critical mode. According to theory of 'critical' conditions of separation, this is indicated by a sharp peak eluting nearly independent of the molar mass.

3.3. Functionalization of acid end groups with cyclohexylamine

This functionalization was performed similar to the modification of amine end groups described before. The MALDI–TOF mass spectrum of the non-fractionated

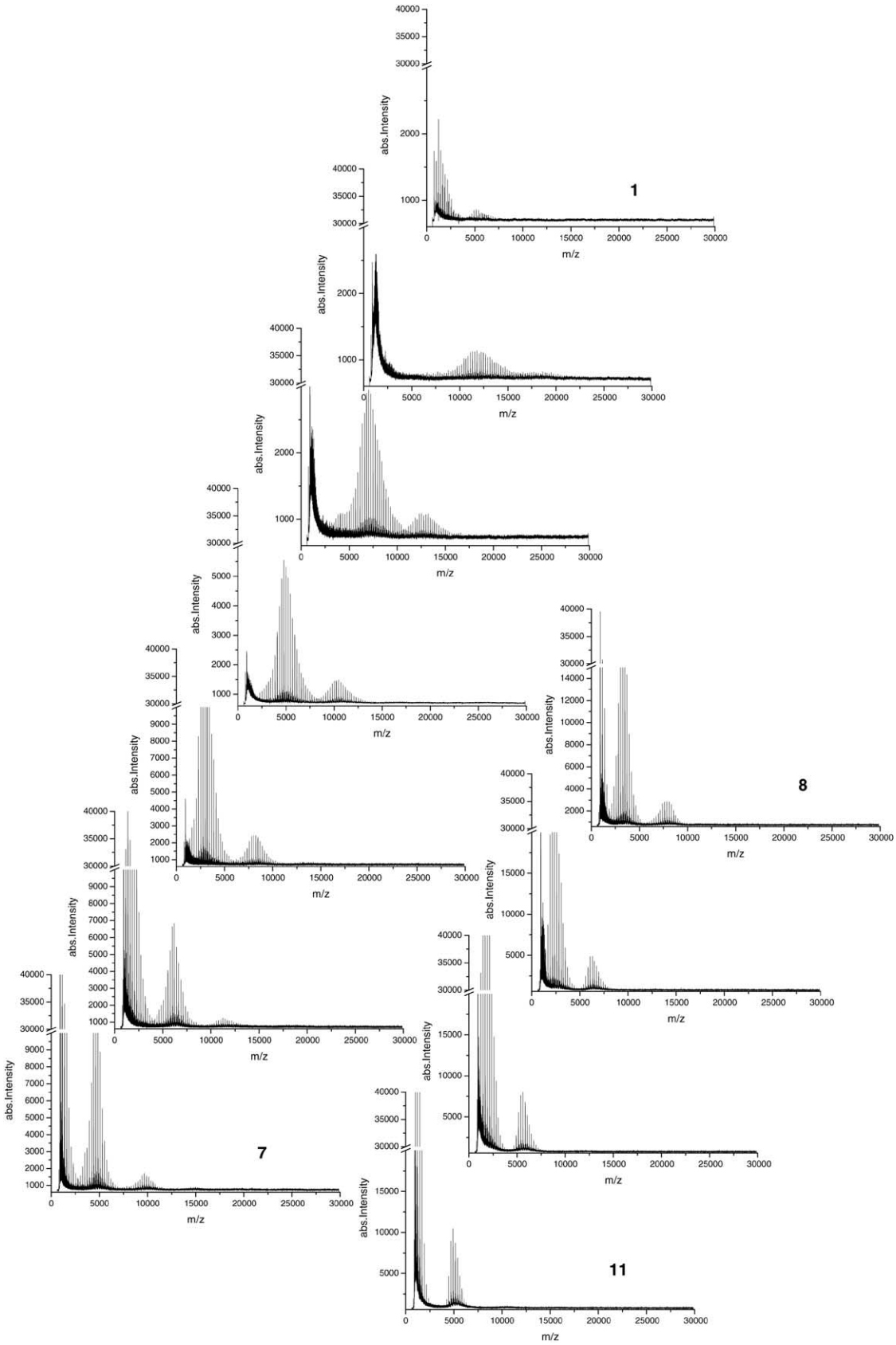

Fig. 6. Series of MALDI–TOF mass spectra of PA 6.6 (modified with propionic acid) after on-line separation and deposition (a correlation of sample spots to retention time can be seen in Fig. 5).

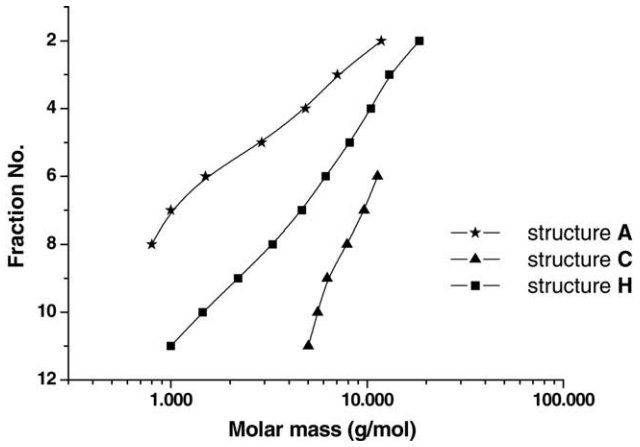

Fig. 7. Calibration curves for linear and cyclic polyamides 6.6 obtained using MALDI–TOF–mass spectrometry.

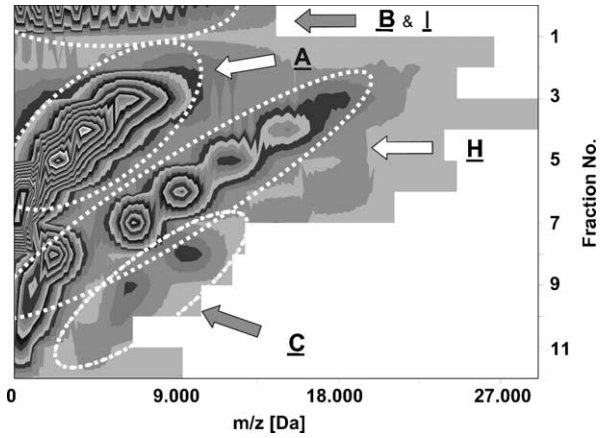

Fig. 8. Two-dimensional plot of polymer composition and corresponding molar masses of a PA 6.6 after modification with propionic acid.

polyamide 6.6 solution is shown in Fig. 9. As listed in Table 2, again three additional structures can be expected. The capping agent cyclohexylamine is able to react with all available carboxylic end groups. Hence, the formation of modified lin-

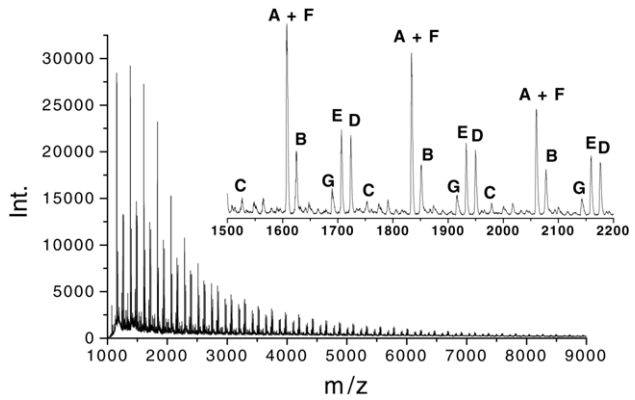

Fig. 9. MALDI–TOF mass spectra of a polyamide 6.6 modified with cyclohexylamine (matrix: HABA).

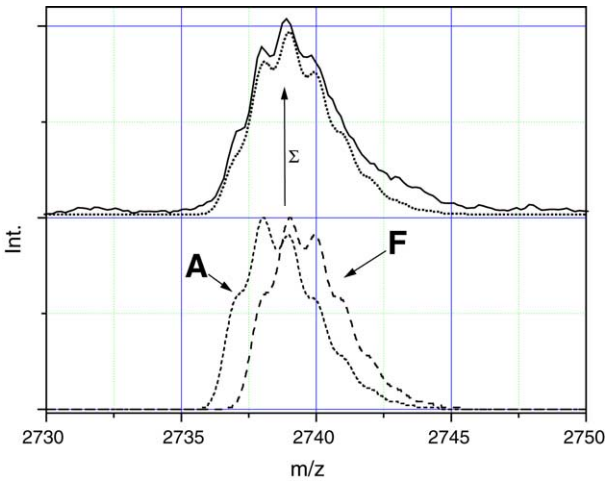

Fig. 10. Comparison of measured isotopic peak pattern of a cyclic structure (straight line) and of the sum (1:1, dotted line) of two theoretically calculated isotopic pattern of cyclic polyamide (structure A) and a linear diacid polyamide 6,6 structure with one capped acid group (structure F; dashed line) – calculation of isotopic pattern was performed at a mass resolution of 3000 using the XMass5.2 – software (Bruker).

ear polymer chains $[AcAm]_{lin}$ as well as mono- and di-capped $[AcAm]_{lin}$-Ac species are theoretically possible (series E, F and G). As seen in the inset of Fig. 9 and in Table 2 as well, additional series of peaks observed in the mass spectrum could be clearly attributed to the expected structures. The mass numbers of polyamide cycles A and of mono-capped di-acid structures F only differ by 1 Da. Thus, the high resolution of the mass spectrometer in the low molar mass region was used to disentangle these two species supposed to overlap in one peak. The results are shown in Fig. 10. In that figure the measured isotopic pattern of the peak at 2736.5 Da which corresponds to a cyclic structure A is explicitly shown. This pattern is overlapped by a second isotopic distribution which

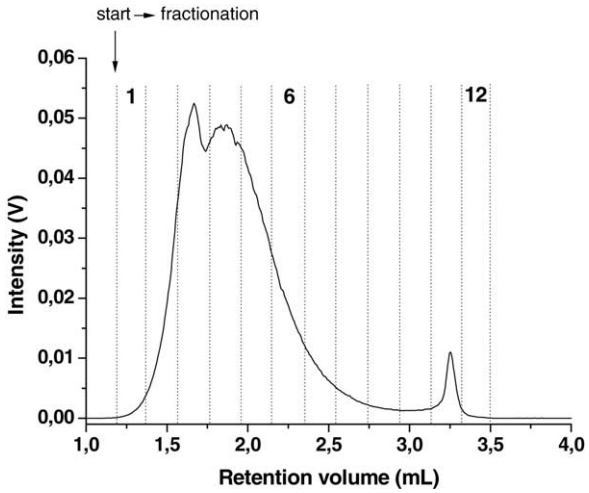

Fig. 11. Chromatogram of PA 6.6 after modification with cyclohexylamine recorded near 'critical' conditions of separation of PA 6 (sample spot positions for MALDI–TOF–MS are indicated by lines and numbers).

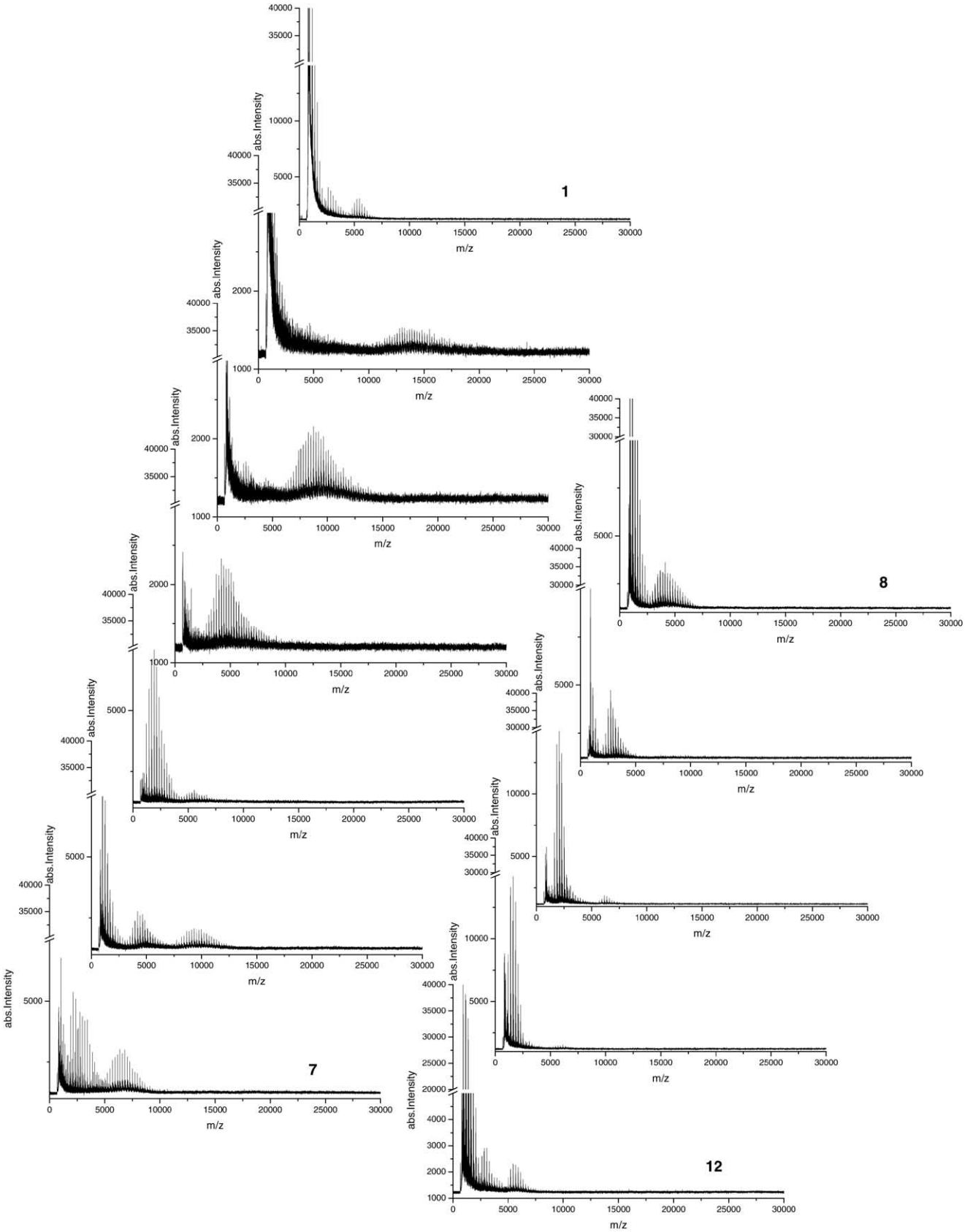

Fig. 12. Series of MALDI–TOF–mass spectra of PA 6.6 (modified with propionic acid) after on-line separation and deposition (a correlation of sample spots to retention time can be seen in Fig. 11).

represents the sum (1:1) of the calculated isotopic patterns of structure A and F. Their isotopic resolutions are shown at the bottom of Fig. 10. The 1:1 sum of these two patterns matches very well the recorded pattern.

For this particular polyamide 6.6 the chromatographic conditions had to be changed, since the separation in the previously used system was very poor. For that purpose, the amount of the polar component had to be increased significantly. Possibly, the tendency of forming hydrogen bonds is much higher and/or the interaction between stationary phase on the one hand and end groups on the other hand is much stronger for polyamides with amine end groups than for those with acid end groups. A higher amount of polar solvent is able to prevent the formation of hydrogen bonds and/or reduces interactions by blocking the polar centers on the stationary phase. The recorded chromatogram is shown in Fig. 11. In contrast to the chromatogram of that polyamide, modified with propionic acid (shown in Fig. 4), a quite different elution behavior was observed. A broad peak with two maxima at 1.65 and 1.8 mL and an additional smaller, but very sharp peak at 3.25 mL were observed.

Based on the MALDI–TOF–mass spectra of the original solution, it was evident that seven structures were 'hidden' behind these three peaks. Again, a chromatographic run was transferred onto the MALDI–TOF–MS target and 12 spectra were recorded. They are shown in Fig. 12.

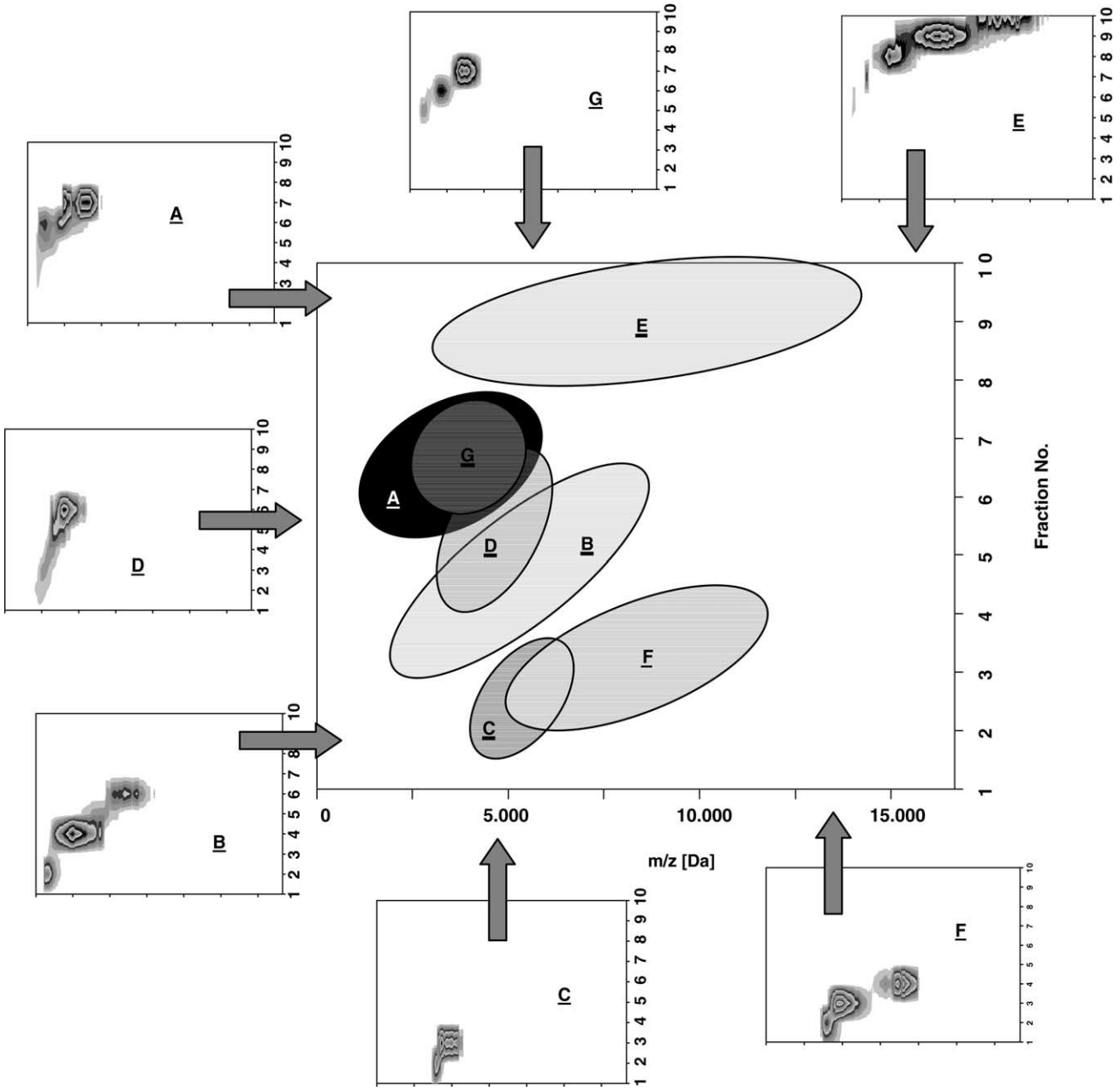

Fig. 13. Two-dimensional plot of polymer composition and corresponding molar masses of a PA 6.6 after modification with cyclohexylamine.

In particular in spectra 4–9, the presence of various polyamides with different end groups and their shift towards lower masses can be seen. However, especially these spectra clearly show the difficulties to get quantitative results. The signal intensities of three different PA species (e.g., presented in spectra 6) cannot be compared to each other and do not correspond to their real concentration. Any quantitative information can only be given by chromatography. Especially in the low mass region a disproportional intensity can be assumed. Therefore, for creating of two-dimensional plots which combine the structural information given by MALDI–TOF–MS and the quantitative intensity information from chromatography, the maximum intensity of each individual peak distribution was scaled to an arbitrary intensity of 1.

The resulting two-dimensional plot is shown in Fig. 13. For a better overview, a schematic presentation is given. In contrast to the two-dimensional plot shown in Fig. 8, this schematic presentation does not contain any intensity information.

Considering the previously stated limitations of MALDI–TOF–mass spectrometry, this shape of a graph gives a more useful fingerprint characterization of modified polyamides.

4. Conclusions

A new chromatographic coupling method was presented and applied for the investigation of end group modified polyamide 6.6. Using the principle of chromatography near ‘critical’ separation conditions in combination with MALDI–TOF–mass spectrometry, limits in chromatographic resolution could be overcome. Two-dimensional plots, showing the molar mass and end group distribution of polyamide 6.6 as well, were created. Although the intensity information (third dimension) in these plots is not correct, they can be used as a fingerprint method in order to get more information on the degree of end group functionalization and for a better comparison of polymer batches in the synthesis of polyamides.

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