ELSEVIER

Polymer 42 (2001) 7095–7099

polymer

www.elsevier.nl/locate/polymer

Electrospray mass spectrometry determination of linear and cyclic oligomers of polyamide-6

U. Klun, S. Andrenšek, A. Kržan*

National Institute of Chemistry, Hajdrihova 19, P.O. Box 3430, 1000 Ljubljana, Slovenia

Received 28 September 2000; received in revised form 9 February 2001; accepted 15 February 2001

Abstract

Analysis of linear and cyclic polyamide-6 (PA-6) oligomer mixtures is an often needed task, that requires expensive equipment and/or chemicals or involved chemical procedures. We present an analytical method using electrospray ionization-mass spectrometry (ESI-MS) that has none of the mentioned difficulties. Measurements were performed on simple acidic aqueous solutions of oligomers. The method allowed qualitative and quantitative characterization of cyclic and linear oligomers up to octamer. Scanning for both the positive, as well as negative ion fragments was used. Signal vs. concentration responses were determined for a number of lower oligomers. The method has the advantage of short analysis times and the use of relatively accessible instrumentation. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Electrospray mass spectroscopy; Polyamide-6; Oligomers

1. Introduction

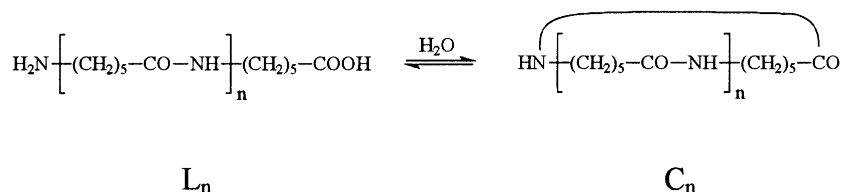
The determination of low molecular mass oligomers of ϵ-caprolactam (C1) is a common requirement in industrial, as well as research laboratories dealing with polyamide-6 (PA-6). During the production of PA-6, oligomers arise as by-products of the equilibrium-polycondensation reaction [1]. Their concentration in the polymer must be known, and controlled in order to avoid adverse effects on polymer properties and its processing characteristics. For example, crystallization of the cyclic dimer (C2) on PA-6 fibers can cause serious problems during the dyeing process. Similarly, exact characterization of oligomers is needed during the chemical recycling of PA-6, which has recently seen its commercial spread. In this process, a mixture of oligomeric products results from the solvolytic depolymerization of PA-6. The product composition must be known in order to allow further use of the products.

The characterization of oligomeric species is marked not only by different characteristics for a line of homologues but also, in addition, each oligomeric species, as well as the monomer has the ability to assume either a cyclic lactam or linear amino-carboxylic acid form that co-exist in equilibrium (Scheme 1). Complete analysis of an oligomeric mixture thus requires the identification and quantification of a relatively large number of chemical species that have markedly different properties between the two homologous lines (linear and cyclic). At the same time the differences within each line of homologues can be quite subtle. A successful analytical method must thus combine a wide detection range with excellent resolution. As a result of these strict requirements methods have been developed for the analysis of either linear or cyclic species, or rather methods that are specific for the monomer in both its forms, but a readily available and cost-efficient complete analysis is still a subject of development.

A number of chromatography methods, including thin-layer chromatography [2], gas chromatography (GC) [3], high-performance liquid chromatography (HPLC) [4,5] and size exclusion chromatography (SEC) [6] have been used for the characterization of PA-6 oligomers. However, each of these methods is marred by at least one serious limitation (limits of detection, extensive sample preparation, duration of analysis, etc.). GC is useful for the determination of both monomer forms, however, very similar elution times prohibit good separation. A further difficulty arises due to partial condensation of ϵ-aminocaproic acid (L1) to C1 in the injector and/or column [7] at high temperatures. The use of SEC is limited by the insolubility of PA-6 oligomers in common solvents used as the mobile phase. By *N*-trifluoroacetylation oligomers can be rendered partially soluble in organic solvents, such as chloroform, dichloromethane and tetrahydrofuran [6] although the derivatization

* Corresponding author. Fax: +386-01-42-59-244.
E-mail address: andrej.krzan@ki.si (A. Kržan).

0032-3861/01/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(01)00132-X



Scheme 1.

is time consuming and must be performed under strict anhydrous conditions. HPLC is efficient for the determination of C1 and cyclic oligomers, but suffers from problems with UV-detection of linear species, due to their low molar absorption coefficient [8]. Mengerink and coworkers recently reported two HPLC methods that allow detection of linear and cyclic oligomers. First they used a gradient of aqueous formic acid [9] and latter a sandwich injection technique, where the solution of oligomers is placed between two zones of formic acid [10,11]. These successful methods, however still require some elaborate procedures and suffer due to low UV absorption of linear species.

Spectroscopic methods of analysis have been attempted, but in general they are limited by the difficult resolution of signals from homologues [12] (FTIR) and the lack of a good solvent [13] (NMR). NMR analysis was carried out after oligomers had been modified by derivatization [13]. Hommez et al. [14] used mass spectroscopy for the analysis of linear low molecular weight degradation compounds formed during acid-catalyzed glycolysis of PA-6. The method used atmospheric pressure chemical ionization which is a 'hard' ionization method. Very recently, Grigg et al. [15] reported use of MALDI-TOF MS for PA-6 oxidation product analysis. This method remains relatively limited due to high equipment costs, however, it appears to be a very effective method for determination of both linear and cyclic PA-6 oligomers and will likely see a widening group of users in the future.

In this paper, we introduce the use of electrospray ionization-mass spectrometry (ESI-MS) as an analytical tool that allows the simultaneous determination of all ε-caprolactam oligomer forms without the need for elaborate sample preparation. For the purpose of this paper cyclic oligomers are denoted by C# and linear by L#, where # is an integer corresponding to the number of monomer units involved in the particular species.

2. Experimental

2.1. Preparation of samples

The oligomer mixture used in our experiments was obtained through acid hydrolysis of PA-6 using microwave heating in a high pressure closed reaction vessel at 240°C. The method has been fully described in a previous paper [16]. The depolymerization was performed at a constant irradiation power of 200 W and an irradiation time of 12 min, with 90 wt% vs. PA-6 added H_3PO_4. The addition of water was kept constant at 100 wt% vs. PA-6. The water soluble portion of the resulting oligomer mixture was used for analysis. The starting polymer for the depolymerization was commercial grade PA-6 provided by Julon–Aquafil ($M_n = 13.000$ g/mol, $M_w = 59.000$ g/mol). Stock solutions of C1 and L1 standard were prepared by dilution of ε-caprolactam and aminocaproic acid (Sigma-Aldrich Deisenhofen, Germany) in methanol acidified with acetic acid (0.1 vol%). Acetic acid was added for the purpose of ionization in the ESI-MS apparatus. C2 (mp 347°C) was provided by Julon–Aquafil. It was isolated from an industrial oligomer mixture by repeated extraction with water, followed by extraction with toluene to remove any C1 present. A sample rich in cyclic oligomers was provided by DSM (Geleen, The Netherlands). Stock solutions of all samples were prepared in the same manner as those of C1 and L1.

All chemical and solvents used were of at least analytical grade and were used without additional purification. Distilled water was used.

2.2. Experimental conditions

An LCQ ion trap mass spectrometer (Finnigan, MAT, USA) with an electrospray ionization interface was used for detection of positively and negatively charged ions. A degassed mixture of 0.1 vol% acetic acid in methanol–water (1:1, v/v) was used as the mobile phase. The flow rate was 0.3 ml/min with a 10 μl fixed loop at 25°C. Mass detection conditions: capillary temperature was set at 200°C, capillary voltage at 4.0 V, sheath gas flow pressure (N_2) at 0.70 MPa, auxiliary gas flow pressure (N_2) at 0.30 MPa, source voltage at 3.50 kV, source current at 13.5 μA, tube lens offset at 30.00 V, maximum ion time was 300.0 ms and multiplier voltage was set at −950 V. The electrospray ionization interface was used for direct on-line sample introduction into the mass detector.

All quantitative data was obtained by measurements on at least three separate samples.

3. Results and discussion

Fig. 1 shows a typical MS spectrum of the water soluble oligomers obtained by PA-6 hydrolysis. Peaks at m/z 114, 227 and 340 represent cyclic species C1, C2 and cyclic trimer (C3), respectively. Peaks at m/z 132, 245, 358, 472,

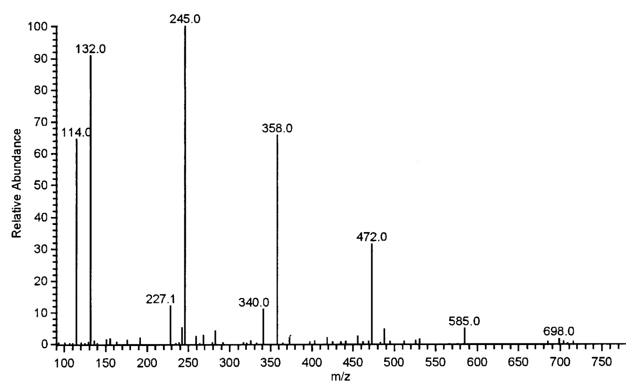


Fig. 1. Mass spectrum of a linear oligomer mixture obtained by PA-6 hydrolysis.

585 and 698 represent linear species ranging from L1 to the linear hexamer (L6). All main *m/z* values correspond to singly charged molecular ions. Peaks for each pair of linear and cyclic species are separated by *m/z* 18 corresponding to one water molecule involved in the ring opening/closing equilibrium. The sample shown in Fig. 1 has a low content of cyclic species, due to the hydrolysis reaction giving rise mainly to linear chain fragments.

During development of the method we observed that it is possible to selectively detect cyclic oligomers by using the negative *m/z* mode (anion detection). The spectrum of a sample rich in cyclic oligomers in Fig. 2 was obtained by this method and shows peaks corresponding to cyclic oligomers up to octamer. The peaks are found at *m/z* values corresponding to the molecular ion of the oligomer plus the anion of acetic acid that was used in the mobile phase ($m/z =$ molecular ion + 59). When acetic acid was replaced by formic acid the peaks shifted to lower values in agreement with the lower mass of the formic acid anion ($m/z =$ molecular ion + 44). Spectrum in Fig. 2 shows that the method allows qualitative characterization of oligomers in the used measuring range $m/z = 100–1000$. It should be noted that the recorded spectra gave no indication of ions

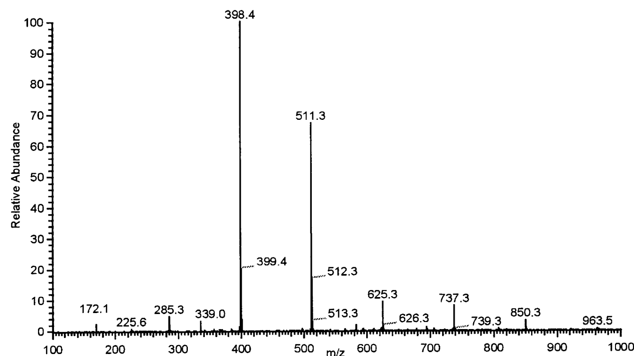


Fig. 2. Mass spectrum of a mixture of cyclic oligomers determined by using the negative *m/z* mode. Peaks at *m/z* 172, 285, 398, 511, 625, 737, 850, 963 correspond to molecular ions + acetate ion. The peak at 225 corresponds to the negatively charged dimer.

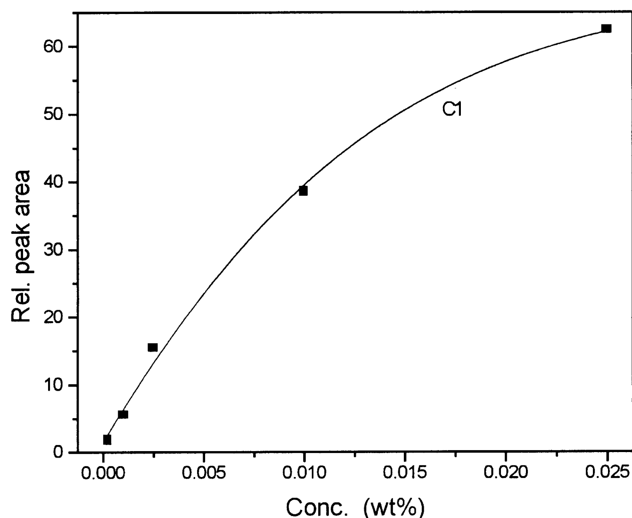


Fig. 3. Peak area vs. concentration dependence for ϵ-caprolactam (C1).

with multiple charges or ions including alkali metal or ammonium cations. Examination of HPLC traces of the recorded ESI-MS peaks showed that the system has proper mass sensitivity.

The value of the method for quantitative determinations was verified for C1, L1 and C2 for which pure samples could be obtained. Solutions of C1 with concentrations between 2.5×10^{-4} and 0.025 wt% gave a concentration vs. peak area dependence as shown in Fig. 3. The dependence is linear at concentrations below 0.01%. At higher concentrations the response levels out logarithmically. No side products were detected at temperatures up to 200°C.

A similar examination of L1 solutions (0.001–0.025 wt%) gave a peak area vs. concentration dependence that is almost identical to that of C1 shown in Fig. 3. Upon closer inspection the spectra showed that approximately 40% (by peak area) of L1 was converted to C1 during the measurement. The extent of conversion was stable (40–43%) over the examined concentration range. Fig. 4 shows the dependence of peak areas for L1, C1 and their sum on concentration. Examination of L1 stock solutions for C1 presence by HPLC showed no conversion at room temperature even over extended periods. It is likely that elevated temperatures and the absence of water inside the MS instrument cause L1 to undergo condensation, losing a molecule of water and conversion to the cyclic form C1. This leads to the conclusion that it is possible to determine L1 either in the absence of C1 or when C1 concentration is known. The total L1 concentration can then be obtained as a sum of the signals for L1 and C1.

Examination of C2 behavior during the measurement was determined by using anion detection described above. The peak corresponding to C2 complexed to a negatively charged acetate ion at $m/z = 285$ was obtained without any interferences or additional peaks. The dependence of peak area vs. concentration is linear in the concentration range 0.001–0.02 wt%. C2 solutions gave a very poor response using the positive measuring mode. This result

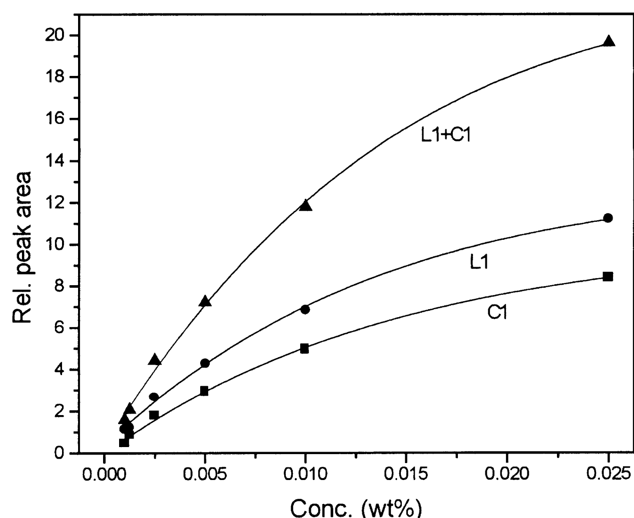


Fig. 4. Dependence of peak area vs. concentrations for ϵ-aminocaproic acid (L1) stock solutions. ϵ-Caprolactam (C1) resulting from conversion in the spectrometer, as well as the sum of both species are also indicated.

can be explained by the weak ionization of the very stable cyclic dimer.

The lack of pure standards for other oligomers did not allow us to make absolute evaluations of their behavior during the measurement. Nevertheless, we determined the response of peak area vs. concentration in oligomer mixtures of linear, as well as cyclic forms. The dependence of signals vs. concentration for linear oligomers from L1 to L4 in Fig. 5 is uniform and should allow easy quantitative interpretation. A similar examination (cation detection) of cyclic species C3 and C4 gave a linear response over the concentration range 2.5×10^{-4}–2.5×10^{-2} wt% (R^2 values 0.9976 and 0.9955 for C3 and C4, respectively). Using the negative *m*/*z* mode, peak areas were found to be lower and the concentration dependence resembled the logarithmic form seen for the linear species.

The described quantitative responses were found to be quite reliable and useful in analyses performed in our laboratory, despite their lack of linearity. The weak point of the method, as we see it, is the reaction of L1 during the measurement, which we hope to avoid by manipulating experimental conditions. It is our experience, however, that in practical use the concentration of L1 in particular is not always the most vital piece of information. The linear response of C2 should not come as a surprise, since it is well established that the compound has aberrant properties, due to its high stability. The most significant limitation for the use of this technique for absolute quantitative determinations is most likely the difficulty of obtaining pure standards for oligomers higher than the dimer.

We are currently working on the details of a validation method for the determination of linear and cyclic monomer forms by the ESI-MS method. In addition we plan a comparison between an established HPLC method and the ESI-MS method described here, using the same samples.

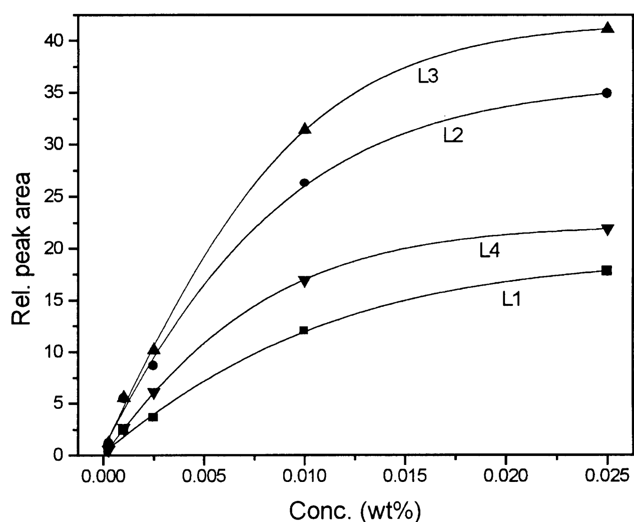


Fig. 5. The dependence of peak area vs. concentration for linear oligomers from ϵ-aminocaproic acid (L1) to tetramer (L4).

4. Conclusions

Our experiments show that ESI-MS is a useful method for the analysis of acidic aqueous solutions of lower cyclic and linear ϵ-caprolactam oligomers. Complex mixtures can be analyzed without the need for prior separation or elaborate sample preparation. The signal vs. concentration relations for several species indicate that absolute or relative quantitative determinations are possible. Selective detection of cyclic species was obtained by using the negative *m*/*z* mode and peaks corresponding to particular component complexed to a negatively charged acetate ion were obtained without any interferences.

Acknowledgements

The authors wish to express their gratitude to Dr Ynze Mengerink of DSM, for generously supplying the cyclic-species rich sample.

References

[1] Hermans PH. Recueil 1953;72:798.
[2] Rothe M, Dunkel WJ. J Polym Sci Part B 1967;5:589.
[3] Mori S, Furusawa M, Takeuchi T. Anal Chem 1970;42:661.
[4] Krajnik V, Božek P, Kondelikova J, Kraliček J. J Chromatogr 1982;240:539.
[5] Bonifaci L, Frezzotti D, Cavalca G, Malaguti E, Ravanetti PJ. J Chromatogr 1991;585:333.
[6] Veith CA, Cohen R. E Polym 1989;30:942.
[7] Sarbach C, Postaire E, Sauzieres J. J Liq Chromatogr 1994;17(12):2737.
[8] Mori S, Takeuchi T. J Chromatogr 1970;50:419.

[9] Mengerink Y, van der Wal Sj, Claessens HA, Cramers CA. J Chromatogr A 2000;871:259.
[10] Mengerink Y, Peters R, Kerkhoff M, Hellenbrand J, Omloo H, Andrien J, Vestjens M, van der Wal Sj. J Chromatogr A 2000;876:37.
[11] Mengerink Y, Peters R, Kerkhoff M, Hellenbrand J, Omloo H, Andrien J, Vestjens M, van der Wal Sj. J Chromatogr A 2000;878:45.
[12] Mori S, Okazaki K. J Polym Sci Part A 1967;5:231.
[13] Girardon V, Correia I, Tessier M, Marechal E. Eur Polym J 1999;34:363.
[14] Hommez B, Goethals E. J Macromol Sci Chem A 1998;35:1489.
[15] Grigg M, Hunt S, George G. Proceedings of MoDeSt 2000, Palermo.
[16] Klun U, Kržan A. Polymer 2000;41:4361.