Analytica Chimica Acta 808 (2014) 3–9

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Review

Tandem mass spectrometry of low solubility polyamides

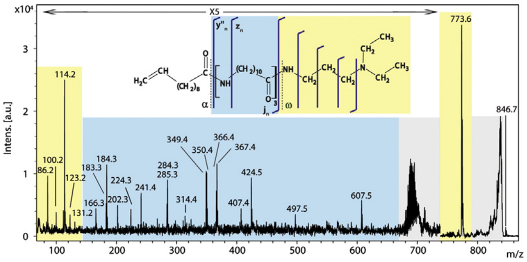
Caroline Barrère[a], Marie Hubert-Roux[a], Carlos Afonso[a], Majed Rejaibi[b], Nasreddine Kebir[b], Nicolas Désilles[b], Laurence Lecamp[b], Fabrice Burel[b], Corinne Loutelier-Bourhis[a,*]

[a] Normandie Université, COBRA, UMR 6014 et FR 3038, Université de Rouen, INSA de Rouen, CNRS, 1 rue Tesnière, 76821 Mont Saint Aignan Cedex, France
[b] Normandie Université, INSA de Rouen, CNRS UMR 6270 PBS & FR 3038, Avenue de l'Université, 76801 St Etienne du Rouvray, France

HIGHLIGHTS

- MALDI-TOF/MS-MS studies of polyamides.
- Orientation of fragmentation processes by end group derivatization.
- Fragmentation rules.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 23 January 2013
Received in revised form 25 March 2013
Accepted 29 March 2013
Available online 8 April 2013

Keywords:
MALDI-MS/MS
Polyamides
Fragmentation rules
Derivatization

ABSTRACT

The structural characterization of polyamides (PA) was achieved by tandem mass spectrometry (MS/MS) with a laser induced dissociation (LID) strategy. Because of interferences for precursor ions selection, two chemical modifications of the polymer end groups were proposed as derivatization strategies. The first approach, based on the addition of a trifluoroacetic acid (TFA) molecule, yields principally to complementary b_n and y_n product ions. This fragmentation types, analogous to those obtained with peptides or other PA, give only poor characterization of polymer end-groups [1]. A second approach, based on the addition of a basic diethylamine (DEA), permits to fix the charge and favorably direct the fragmentation. In this case, b_n ions were not observed. The full characterization of ω end group structure was obtained, in addition to the expected y_n and consecutive fragment ions.

Contents

---

* Corresponding author. Tel.: +33 2 35 52 29 24; fax: +33 2 35 52 24 41.
E-mail address: Corinne.Loutelier@univ-rouen.fr (C. Loutelier-Bourhis).

0003-2670/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.aca.2013.03.064

1. Introduction

Polyamides (PA) constitute an important class of polymer. They are very attractive because of their good chemical resistance, high thermal stability and good mechanical properties that offer a wide range of applications in medicine, textile and car manufacturing industry. Moreover, the interest to extend the application fields of such materials leads to the development of new types of PA, in particular from renewable resources [2–5]. In this context, the structural characterization of original PA is essential to establish structure properties relationship.

PA characterization studies have been reported by matrix assisted laser desorption ionization-time of flight mass spectrometry (MALDI-TOF-MS), widely used as an efficient method to analyze synthetic polymers [6–9]. Montaudo et al. have reported Nylon 6 (M_w = 43 000 Da) analysis after sample hydrolysis with aqueous methanesulfonic acid to decrease the polymer molecular weight [10]. Choi et al. have also reported Nylon 6 and Nylon 6,6 characterization with the same strategy [11]. Other works have shown the characterization of new polyamides by MALDI-TOF-MS [12,13]. In order to facilitate Nylon 6,6 analysis, Weidner et al. have developed semi on-line coupling of liquid chromatography at critical conditions and MALDI-TOF-MS [14]. All these studies have shown that the main difficulty to analyze PA is related to their low solubility. As an alternative to these solvent-based analyses, solvent-free approaches was developed by Skelton et al. to facilitate low soluble PA analysis by MALDI-TOF-MS [15]. Therefore, solvent-free strategy in MALDI sample preparation has a growing interest with the development of the well-known “solvent-free” [16] or “evaporation grinding” methods [17]. A recent study from our group focused on the optimization of MALDI experimental conditions, where solvent-free with different solvent-based approaches for PA11 analysis were compared [18]. This study showed the presence of cyclic oligomers by-products, formed during the polymerization step, which were detected along the expected linear species. Such results were also reported for Nylon 6 in a previous paper of Montaudo [10]. Regrettably, the signals of both cyclic and linear polymers were overlapped preventing precursor selection of a unique species for tandem mass spectrometry experiments (MS/MS). MS/MS data can afford relevant structural information on polymer chain and end-groups. To overcome such interference situation, we performed the chemical modification of the vinylic end-groups of the linear polymer with trifluoroacetic acid (TFA). Such derivation permitted to separate unmodified cyclic from modified linear species in the mass spectrum, and allowed to perform MS/MS experiments. However, only few fragmentation studies have been reported for polyamides in the literature, probably due to the difficulty to analyze these compounds. Yuan et al. have characterized soluble PA, based on N-methylpyrrole and N-methylimidazole, in methanolic solution by electrospray ionization tandem mass spectrometry [19]. Fournier et al. have studied the fragmentation of several protonated nylons (PA6 and PA12) presenting different end-groups by post-source decay (PSD) with a MALDI-TOF-MS instrument [1]. They observed fragmentation pathways similar to those of peptides involving b_n, y_n and z_n ions according to the Roepstorff–Biemann nomenclature [20].

In this study, we propose two derivatization strategies involving chemical modification of either the initiating (α) or terminating (ω) end-groups of linear PA11 to allow MS/MS experiments. The fragmentations of the resulting polymers will be studied and dissociation rules established. Moreover, a comparative study of the different derivatized polymers (showing different end-groups) would permit to understand the influence of PA11 end-groups on fragmentation pathways.

2. Experimental

2.1. Chemical

11-Aminoundecanoic acid (CAS no. 2432-99-7), 10-undecenoic acid used as chain limiter (CAS no. 112-38-9), trifluoroacetic acid (reagent plus 99%), N,N-diethyl propanediamine (DEPDA) (CAS no. 104-78-9) and 2,5-dihydroxybenzoic acid (2,5-DHB) were purchased from Sigma Aldrich (St. Louis, MO). Sodium iodide (Ultrapure) was from Prolabo (Vitry sur Seine, France).

2.2. Polymer synthesis

500 mg of 11-aminoundecanoic acid and 25.4 mg of 10-undecenoic acid as chain limiter were introduced in a 50 mL two-necked flask fitted with a magnetic stirrer, a Dean–Stark topped by a condenser, and a switchable inlet for nitrogen. A molar ratio of 1:18 between chain limiter and monomers was used. The reaction mixture was placed under nitrogen flow for 20 min before the two-necked flask was immersed in an oil bath at 220 °C. After melting of the reactants, the mixture was stirred magnetically for 2 h 30 min. The reaction took place under stream of nitrogen. At the end of the reaction, the synthesized product was allowed to cool completely at room temperature for at least 1 h under a nitrogen purge. The resulting polymer was recovered by cooling with liquid nitrogen to obtain a solid polymer which was broken in pieces and crushed into a white powder.

2.3. Chemical modification

TFA modification was performed dissolving the polymer (5 mg mL^{-1}) in neat TFA. The mixture was stirred under magnetic agitation at room temperature for 4 h.

Diamine modification was carried out using a three-necked flask fitted with a magnetic stirrer, a Dean–Stark topped by a condenser. A solution of initial polymer (490 mg) in dimethyl sulfoxide (10 mL) was added to 20 mL of N,N diethyl-1,3-propanediamine. The mixture was heated to 190 °C under magnetic stirring during 3 h. Then the mixture was cooled to ambient temperature and the modified polymer was filtered under vacuum conditions and dried in an oven during 2 h under vacuum conditions.

2.4. Mass spectrometry

MALDI-TOF-MS and MALDI-TOF/TOF-MS experiments were performed on an Autoflex III time-of-flight mass spectrometer (Bruker Daltonics, Bremen, Germany) equipped with a frequency-tripled Nd:YAG laser emitting at 355 nm. FlexControl (3.3) and FlexAnalysis (3.3) software package (Bruker Daltonics, Bremen, Germany) were used for data acquisition and processing. Spectra were acquired in the positive-ion reflectron mode at 50 Hz laser shot frequency. The acceleration voltage was set to 19 kV and the extraction delay time used was set to 220 ns in MS mode. Samples were prepared using the thin-layer method by spotting successively 1 μL of 2,5-DHB as matrix (10 mg mL^{-1} in methanol)