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Review

Multidimensional mass spectrometry methods for the structural characterization of cyclic polymers

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ABSTRACT

Several synthetic methods have been developed for the tailored preparation of cyclic macromolecules due to their unique physical and chemical properties. Unequivocal characterization of the macrocyclic architectures has remained challenging, however, because isomeric linear structures often exist, or the spectral features of linear vs. cyclic chains are similar. To address this problem, multidimensional mass spectrometry (MS) techniques have been evaluated for the separation and identification of polymeric macrocycles. Tandem mass spectrometry (MS^2) is found to be ideally suitable for the differentiation of linear and cyclic architectures whose molecular ions exhibit distinct fragmentation characteristics. Conversely, differences in macromolecular sizes and shapes can be exploited to identify the correct architecture by ion mobility mass spectrometry (IM-MS). A third option, chromatographic separation (LC) before MS analysis, is available for the detection of cyclics in complex mixtures. The capabilities of these techniques and combinations thereof are demonstrated with specific covalent or supramolecular (co)polymers.

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1. Introduction

Mass spectrometry (MS) is a sensitive analytical technique, in which analytes are characterized after they have been converted to gas-phase molecular ions. The mass spectrometer acquires the mass-to-charge ratio (m/z) of the molecular ions, and of any fragments formed during the ionization step, and these m/z values are then used to deduce the elemental composition of the analyte and, if fragments are present, to gain information about the analyte structure. Conversion to gas-phase ions (ionization) is the key step in MS analyses. It was not until the late 1980s, when a major breakthrough occurred, the invention of matrix-assisted laser desorption ionization (MALDI) [1,2] and electrospray ionization

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(ESI) [3], which made it possible to ionize and, hence analyze by MS, a wide range of synthetic polymers and biopolymers. MALDI and ESI are soft ionization techniques, creating intact molecular ions and mostly causing no or little fragmentation of the analyte during ionization. Today, MALDI and ESI mass spectrometry are applied widely to determine the compositional heterogeneity of new polymers, to identify their chain end groups, and to ascertain their molecular weight and functionality distributions; such information is essential for identifying or confirming the synthesized structures, for elucidating polymerization mechanisms, and for assessing the commercial viability of the polymeric materials [4,5].

It is noteworthy that the above information is rendered by simple mass measurement which, with modern MS instrumentation, can be performed with high sensitivity and accuracy to unveil the elemental compositions of both major and minor synthetic products. Even though such single-stage (1-D) mass spectrometry has been successfully used to answer questions about polymer composition and structure [4,5], also for macrocyclic compounds [6–10], it faces serious limitations in the analysis of complex synthetic polymers. Polymerizations may create mixtures that are impossible to characterize by single-stage MS due to discrimination effects in the ionization and/or detection steps; this is also true for multicomponent polymer blends. With ESI, multiple charge states and overlapping charge distributions can be formed, obstructing mass determination and compositional assignments. Furthermore, isomeric structures and different polymer architectures cannot usually be distinguished or conclusively identified by m/z measurement alone. As will be shown here [11], these problems can be addressed by utilizing tandem mass spectrometry (2-D MS or MS^2) and by interfacing MS (or MS^2) with liquid chromatography (LC) and/or ion mobility (IM) separation [12–14]. This account is focused on applications of these multidimensional methods to the characterization of cyclic polymers whose unique structures (no end groups) and hydrodynamic volumes (smaller than those of similarly sized linear chains) endow them with physicochemical properties that are ideally suitable for a variety of technological uses.

2. Tandem (2-D) mass spectrometry

Tandem mass spectrometry (MS^2) experiments are performed by selecting one oligomer ion (precursor ion), among those formed by MALDI or ESI (stage MS-1), and by inducing this ion to fragment. The fragment ions generated in this reaction are subsequently mass-analyzed to obtain the corresponding MS^2 spectrum (stage MS-2). The structure, sequence, or architecture of the selected oligomer is (are) determined from the types of fragments observed and their relative abundances [15]. Spectral interpretation is facilitated by the availability of reference spectra or by comparing the fragmentation patterns of isomeric structures or distinct architectures [15]. The use of MS^2 to distinguish cyclic from linear architectures will be illustrated for polystyrene (PS) and polybutadiene (PB) samples, ionized by MALDI and analyzed with either tandem time-of-flight (ToF/ToF) or tandem quadrupole/time-of-flight (Q/ToF) instrumentation (Bruker UltraFlex III and Waters Ultima, respectively) [16].

2.1. Linear polystyrene

Fig. 1 shows the MALDI-MS^2 spectrum of the $[M+Ag]^+$ ion from the 19-mer of a divinyl-terminated polystyrene prepared by living anionic polymerization [17]. This spectrum includes the typical fragments observed from the metal ion adducts of chain-end functionalized, linear polystyrenes: abundant radical ions containing either the initiating (R_α) or terminating (R_ω) chain end ($b_1^\cdot, b_2^\cdot, z_1^\cdot, z_2^\cdot$) and internal ions ($J_2^\cdot, K_3$) in the low-mass region (Fig. 2) as well as two homologous fragment series (a_n, y_n) of lower intensity across the medium-mass region and stretching (with decreasing intensity) into the high-mass region; series a_n and y_n contain one original end group (R_α or R_ω) and one newly produced methylene end group (Fig. 2). This fragmentation pattern arises from random, charge-remote homolytic C—C bond cleavages along the polymer backbone, which create charged radicals carrying one of the original end groups. These radicals decompose further primarily by monomer evaporation, which leads to the small radical ions mentioned above (vide infra), and by backbiting rearrangements (Scheme 1) [18], which coproduce internal fragments as well as series a_n and y_n. Notice that varying the chain-ends or the cationization agent does not change this fragmentation pattern (cf. Figs. 1 and 3) [19].

Fig. 2 explains the nomenclature used and summarizes the structures of the major fragments generated from linear polystyrenes. The initial C—C bond breakup in the PS backbone yields incipient radical ions with both benzylic ($b_n^\cdot, z_n^\cdot$) and primary ($a_n^\cdot, y_n^\cdot$) radical sites at their chain ends. Only very small benzylic radical ions survive intact (mainly $b_1^\cdot, b_2^\cdot, z_1^\cdot, z_2^\cdot$), indicating extensive (for the benzylic) or complete (for the primary radicals) depolymerization by unzipping. The longer lifetimes of the benzylic radicals also permit the occurrence of hydrogen rearrangements that move the radical site to a more stable internal position (backbiting), cf. Scheme 1; subsequent C—C bond cleavages give rise to the terminal series a_n and y_n and to the internal fragments $J_2^\cdot$ and K_3. The same internal ions are produced from all incipient radical ions emerging after the initial PS backbone breakup, which explains their quite high intensities. It is noteworthy that the y_n series is less abundant than the a_n series for the divinyl terminated

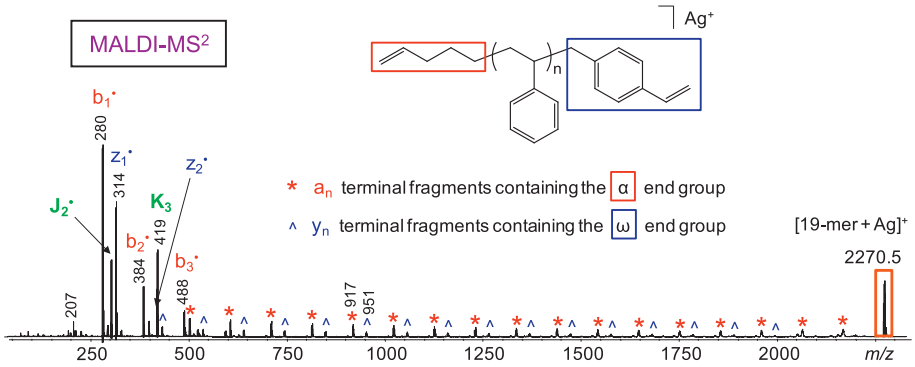

Fig. 1. MALDI-MS^2 spectrum of the linear silverated 19-mer of α-4-pentenyl-ω-(*p*-vinylbenzyl) polystyrene (m/z 2270.5), acquired with ToF/ToF instrumentation; reproduced from Ref. [19] with permission from Springer. See Fig. 2 for the fragment structures and nomenclature.

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