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Young Scientist Feature

Unraveling the architecture of plasma polymers by electrospray tandem mass spectrometry

Thierry Fouquet*

Materials Research and Technology, Luxembourg Institute of Science and Technology, 5 avenue des Hauts-Fourneaux, 4362 Esch/Alzette, Luxembourg

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This feature is dedicated to Pr Laurence Charles, for her continuous support through the years and without whom nothing would have been possible.

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ABSTRACT

This feature article presents the implementation of a controlled chemical degradation (namely ethanolysis) combined with electrospray tandem mass spectrometry (ESI-MS/MS) as an original analytical strategy to gain insights into the molecular composition of insoluble plasma polymers deposited from hexamethyldisiloxane (HMDSO). Dissociation rules were established for poly(dimethylsiloxane) standards (PDMS) holding trimethylsilyl and/or hydroxy and/or ethoxy end-groups, expected to be found as ethanolysis products released after the cleavage of bonds specifically at cross-linking points of the solid plasma polymer network. Mechanistic investigations were performed on the collision-induced decomposition (CID) of ammonium adducts of the selected standards to derive diagnostic ions typical of a given chain termination. Based on the so-listed diagnostic MS/MS features, the MS/MS analysis of the ethanolyzed samples allowed their structures to be deduced and the architecture of the original plasma polymers to be reconstructed.

1. Plasma polymers and mass spectrometry: the pitfall of insolubility

The term “plasma polymer” denotes a thin film that is created as a result of a passage of organic gas or aerosol through a plasma discharge [1]. With unique properties arising from their particular network organization, plasma polymers have a huge potential for industrial applications. In particular, organosilicon plasma polymer coatings formed from hexamethyldisiloxane (HMDSO) were found to be good candidates for gas barrier [2–4] and anticorrosion [5] coatings. The possibility of depositing such materials by *atmospheric pressure* dielectric barrier discharge (DBD) allows surface treatment of fragile substrates (textiles, polymers or precoated surfaces) with low cost equipments, extendable to on-line processing at industrial scale. DBD consists of generating discharges in the gas gap between two plane-parallel metal electrodes, one of them being covered with a dielectric layer [5], leading to plasma polymer deposition when fed with a precursor [6]. DBD plasma polymerization is unanimously considered as involving free radicals and ions generated during collisions of energetic electrons with organic precursors [1]. Additional phenomena such as oxidation (with residual atmospheric oxygen or added oxidative reagent [7]) and photochemistry processes have also been considered to fully embrace the complexity of plasma polymerization. As a result, plasma polymers are composed of short randomly branched chains with a high degree of cross-linking [8,9], hence poorly soluble. Because they exhibit a much more complex structure than macromolecules synthesized by conventional polymerization methods, detailed characterization of plasma polymers still remains an analytical challenge. They escape MS molecular analyses by direct ionization with techniques such as MALDI, as best illustrated by studies showing that MALDI plates coated with plasma polymers for on-probe biomolecules cleanup [10] or affinity capture [11] did not exhibit any background signal. FT-IR and XPS [12], TOF-SIMS [13–15] or solid state NMR [16] remains the most widely used analytical tool. Using these techniques, plasma polymers of HMDSO (*pp*HMDSO) were reported to consist of a mixture of organic polydimethylsiloxanes (PDMS) and inorganic (SiO_x) silica-like species [7,17,18]. Although of asset for pinpointing the functional groups present in a plasma polymer, these techniques provide information on chemical composition rather than molecular structure. The only studies dealing with *molecular* analysis in the field of plasma polymers used gas chromatography–mass spectrometry (GC–MS) to characterize metastable species, oligomers and powders in the

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* Tel.: +352 4259914598.
E-mail addresses: thierry.fouquet@list.lu, thierry.fouquet83@gmail.com

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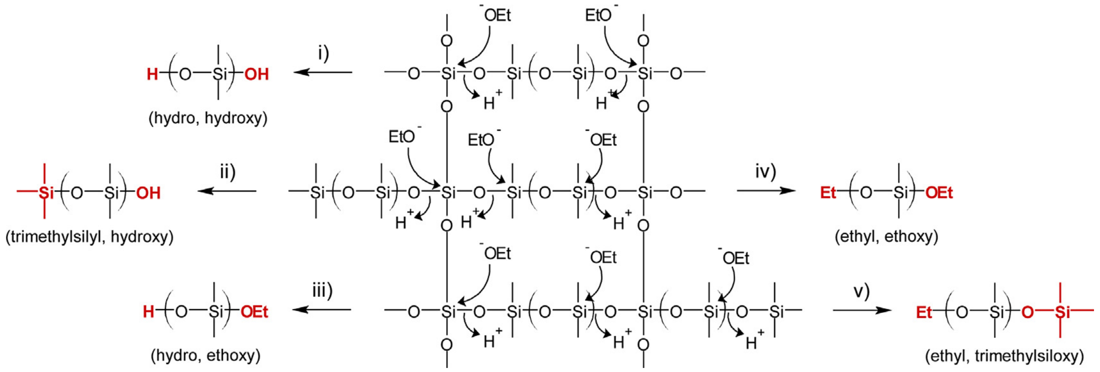

Scheme 1. Ethanolysis of a hybrid PDMS/silica network and structures of the so-expected products depending on the location of the bond cleavages.

exhaust gas [19–22], or implemented MALDI or ESI techniques for mass analysis of *soluble parts* (5–50%, w/w, depending on the polymerization parameters) extracted by solvent washing [23–25]. Before the dissemination of the results summed up in the present feature, no study focused on structural characterization of plasma polymers and usage of *tandem* mass spectrometry had ever been reported. In this context, the analytical strategy proposed here – and which has constituted the thesis topic of the author – first overcame the insolubility issue by performing a controlled chemolysis of insoluble plasma polymers to produce soluble oligomers which would retain, in their end-groups, the memory of their initial location in the solid network. Indeed, providing that the chemical treatment is sufficiently specific, the polymeric skeleton of molecules released from the solid sample is actually that of linear segments between branching points in the original network, and the nature of their end-groups is dictated by the chemical reaction occurring at these cross-linking sites. As a result, the length of linear segments between branching points can be directly determined from the size of released oligomers while their initial connectivity can be deciphered from their end-groups. Both size and end-groups of a polymer are structural features that can be readily characterized by MS techniques. Previously implemented to reconstruct the structure of conventionally polymerized polycarbonates [26], polyesters [27] or polyamides [28], such an approach has been applied to plasma polymers for the first time, in the framework of the author's PhD thesis. Two mandatory requirements need however to be fulfilled:

- ions to be mass analyzed must be formed according to a soft ionization process to ensure the integrity of their end-groups;
- dissociation rules necessary to identify molecule end-groups from their MS/MS data [29] need to be known.

This last point was a major issue when dealing with *pp*HMDSO because no general dissociation rules have ever been established for PDMS molecules typically expected to be produced during the chemolysis of insoluble films. Indeed, in great contrast to most synthetic polymers, fragmentation chemistry of PDMS strongly depends on the nature of the end-groups, as reported in the literature for alkali adducts [29,30]. The nature of the cation adducted to polymer molecules is also known to have a great impact in the production of informative fragment ions under CID conditions. In this work, PDMS ionization via ammonium adduction was found to be of particular relevance [31] because ammonium induced the same major fragmentation pathway regardless of the end-groups held by the precursor ion. Moreover, CID of ammoniated PDMS led to primary product ions containing either one or the other termination of the dissociating oligomer, the key condition to determine each end-group mass. In contrast, secondary dissociation reactions were highly influenced by the oligomer terminations, offering a unique opportunity to validate end-group structure as determined from the primary fragmentation process. This feature is an overview of the fragmentation rules which had to be established for PDMS models holding different end-groups and electrosprayed as ammonium adducts, prior to being applied to the characterization of species released upon ethanolysis of *pp*HMDSO solid networks. Most relevant models were selected based on preliminary MS results obtained for *soluble* parts extracted from *pp*HMDSO, where all PDMS were (trimethylsilyl, trimethylsiloxy) terminated [32], as well as the chemistry of the ethanolysis reaction selected to perform plasma polymer chemolysis. Considering a hybrid PDMS/silica network as the generic structure of the *insoluble pp*HMDSO plasma polymer (Scheme 1), ethanolysis occurring specifically at branching points would release (hydro, hydroxy)-PDMS from segments initially located between two cross-linking points (Scheme 1, i) and asymmetric (trimethylsilyl, hydroxy)-ended chains from pendant arms linked to the plasma polymer network by a single covalent O—Si bond (Scheme 1, ii). In case the treatment is not specific enough or for long reaction where first released species would undergo consecutive nucleophilic substitutions, ethoxy moieties would be produced in lieu of the hydroxy terminations, leading to asymmetric (hydro, ethoxy)-PDMS, symmetric (ethyl, ethoxy)-PDMS or asymmetric (ethyl, trimethylsiloxy)-PDMS, as respectively illustrated by pathways iii–v in Scheme 1. As a result, end-group MS analysis of PDMS species produced upon plasma polymer ethanolysis should allow the architecture of the insoluble network to be reconstructed. Note that this (α,ω) assignment of chain ends is purely arbitrary but will be conveniently kept constant throughout the text.

2. Tandem mass spectrometry of linear PDMS standards

2.1. Nomenclature

According to the nomenclature defined by Wesdemiotis and co-workers [29], only four types of primary product ions can be expected to form from a polymeric skeleton containing two different bonds. As illustrated in Scheme 2a, a_i and b_i product ions retain the α initiating end-group, while y_i and z_i product ions still contain the ω terminating group (where *i* is the number of DMS repeating units, C_2H_6OSi). Owing to the symmetry of the polymeric skeleton, oligomers holding the same moiety as α and ω end-groups will lead to indistinguishable a_i/y_i or b_i/z_i fragment ions, which should be named using letter from the starting of the alphabet (hence a_i and b_i, respectively) [29]. In addition to this nomenclature, the rather official designation of silica structures is also provided (Scheme 2b). From the “Q” notation developed by Lippmaa et al. [33–35] for silicate structures, Glaser et al. [36] and Williams [37] proposed an