Mass spectrometry has turned out to be a fantastic analytical tool for the micro-structural analysis of polymeric materials. Using soft ionization methods such as electrospray ionization (ESI) or matrix-assisted laser desorption ionization (MALDI) mass spectrometry (MS) leads to the direct measurement of the mass distributions of a given polymeric sample in the MS mode, while the precise nature of the chain ends as well as some insights into the architecture of the backbones could be reached by tandem mass spectrometry (MS/MS mode), providing MS/MS rules are clearly described for the same class of polymers. If mass spectrometry is now recognized as a technique of its own for the analysis of polymers, plasma polymers have been rarely mass-analyzed to reach molecular compositions and structural information about repeating units, molecular weights, end-groups and branching. The passage of a vapor or nanodroplets of a precursor in a plasma discharge leads to the deposition of a thin layer (a few tens of nanometers to a few microns), usually described as poorly soluble, composed of short chains, randomly branched and terminated, with a high degree of cross-linking. This constitutes the so-called plasma polymerization, leading to plasma polymers. Due to their unique properties arising from their particular network organization, plasma polymers have a huge potential for industrial applications: organosilicon plasma polymer coatings deposited from hexamethyldisiloxane (HMDSO, Scheme 1 a) have been found to be good candidates for a wide range of applications such as gas barrier and anticorrosion coatings. The possibility of depositing such materials by atmospheric pressure plasma processes allows the use of low-cost equipment, which can be included in on-line processing at industrial scale. Among various techniques enabling atmospheric pressure non-thermal plasmas, dielectric barrier discharges (DBDs) consist in generating discharges in a gas gap between two plane-parallel metal electrodes, one of them being covered with a dielectric layer. Atmospheric pressure DBDs are considered cold plasmas: despite the electron temperature could reach more than 10000 K, the temperature of the plasma remains dictated by the heavy particles (atoms, molecules, ions and mono-
stable species) around 300 K, making DBDs well suited for the surface treatment of fragile substrates such as textiles or polymers. Extended fragmentation of precursors, free radical and ionic polymerization as well as additional phenomena such as oxidation, photochemistry processes or constant UV irradiation account for the complexity of plasma polymer materials for which a thorough characterization still remains an analytical challenge. Roughly, silicon-containing plasma polymers are hybrid materials formed of both polydimethylsiloxane (PDMS, Scheme 1 b) and more generally polysiloxane chains (the organic part) and silica-like structures (the inorganic part), the latter becoming more and more important with the energy applied to the plasma discharge. In the current literature, analyses by surface techniques (FT-IR, XPS, TOF-SIMS) or bulk techniques at the solid state (solid-state NMR, ssNMR) are mainly reported. In our specific case, where silicon-based precursors were used, $^{29}$Si NMR spectroscopy brings useful data about an elemental composition of the films as well as the evolution of deposits with the plasma conditions. To the best of our knowledge, no studies were nevertheless found dealing with the molecular analysis of plasma polymers using mass spectrometry. This kind of molecular (and structural) analysis could be of great interest for a better description of deposit itself as well as some mechanisms taking place within the plasma discharge, allowing a useful comparison with the literature data built from the plasma phase analysis.

Direct (tandem) MS analysis of silicon-based plasma polymers is however limited to a large extent by the two following issues: 1) fragmentation pathways of polysiloxanes are scarcely reported in the literature; 2) plasma polymers are mainly insoluble, and thus not easily amenable to ionization with the main soft ionization sources. This doctoral work was thus aiming at developing an analytical methodology mainly based on tandem MS to overcome these issues through: 1) the exploration of fragmentation pathways of perfectly defined commercial and self-made polysiloxanes under collision-induced dissociation (CID) to further extrapolate their dissociation behavior for a useful interpretation of plasma polymer MS/MS data and 2) a controlled degradation of the insoluble part of plasma polymers to make them amenable to ESI mass analysis.

**PDMS standards and soluble part of plasma polymers**

Plasma polymers deposited under soft plasma conditions (i.e., with a reduced energy per particle) exhibit a non-negligible soluble part (around 10%), easily extracted by solvent washing. Despite a potentially reduced representativeness owing to its mass fraction as compared to the whole sample, such a soluble part is easily amenable to ionization using a traditional ESI source. The first part of this doctoral work was thus focused on the exploration of the soluble part from plasma polymerized hexamethyldisiloxane films (further noted ppHMDSO). In particular, the MS analysis highlighted the presence of various polysiloxane chains in the samples, varying by their length and end groups and for which hypothetical structures were postulated. Further study of these species in MS/MS mode was however subjected to the preliminary understanding of the MS/MS behavior of some reference compounds. Fundamental and mechanistic works were thus conducted with high-resolution instruments and ab initio theoretical chemistry as a supporting tool. Trimethylsiloxy-, hydride and methoxy-ended PDMS, additional poly(methylhydrosiloxane) (PMHS) and P(MHS-co-DMS) copolymers, as well as polyhedral oligomeric silsesquioxanes (POSS) cages to mimic highly cross-linked silicons were all thoroughly mass-analyzed and found to be potential models for the species detected in the ppHMDSO soluble parts. This “preliminary” work actually constituted a huge part of the thesis work, but was mandatory for the success of the later studies. However, despite the accuracy in the description of the MS/MS behavior of reference compounds, discrepancies were often detected between MS/MS spectra of reference structures and their plasma equivalent in the soluble parts, regardless of the end groups or reference nature. Such a comparison is depicted in Figure 1 for the case of a trimethylsiloxy-ended PDMS and the isobaric species found in the ppHMDSO aliquot. Discrepancies were found to arise from the presence of randomly branched structures in the plasma samples, without any possibility to avoid their production owing to the random and highly complex nature of the plasma polymerization process. In parallel, another silicon-containing precursor with a cyclic structure (octamethylocycloetrasiloxane, D4, Scheme 1 c) was used to produce silicon-containing plasma polymers, especially because a cyclic precursor should reduce the number of degrees of freedom, that is, the number of isomeric structures. In other words, any unsaturation detected within an oligomeric backbone (based on the elemental composition as measured in the MS mode) will be seen as a D4 cycle. Based on this consideration, new reference compounds synthesized by conventional polymerization methods and bearing a defined number of D4 cycles were mass-analyzed. Self-made reference compounds mimicked in a sat-
isfying extent the plasma oligomers found in the soluble parts of the ppD4 samples. An example of comparison is depicted in Figure 2a for the case of an oligomer containing two cycles as initiating and terminating chain ends. In that case, the standard is of high quality since its MS/MS spectrum perfectly mimics the CID fingerprint of the plasma oligomer. Discrepancies which still exist between reference compounds and plasma oligomer MS/MS spectra were tentatively quantified using a correlation coefficient homogeneous to Euclidian distances. The evolution of this correlation coefficient with the number of repeating units in the reference compound is depicted in Figure 2b. Each point represents the comparison of MS/MS spectra of isobaric species from wet and plasma synthesis. The overall quality of the correlations is very good, but clearly shows a decrease with the length of the reference oligomer. This is in great accordance with the increase of isomeric possibilities with the polymerization degree, as an indirect clue for the presence of isomers in the plasma aliquots.

From these last results, it appeared that the use of a cyclic precursor did not impeach the fragmentation processes to occur in the gas phase during the plasma polymerization. Decrease of correlation and the detection of dimethylsiloxane monomers in plasma oligomers (in MS mode) highlight these dissociation routes. Since HMDSO will lead to fragmentations in a higher extent, linear reference compounds would never satisfactorily approximate the unlimited isomeric variations of branched and cross-linked species.

Despite the huge amount of work to describe these samples, soluble parts of plasma polymers do not represent the whole material, regarding the mass fraction (<10%) and the NMR spectra of both pristine and soluble deposits. Moreover, depositing a ppHMDSO coating under hard conditions (i.e., an excess of energy per particle) will lead to the complete disappearance of any soluble species due to high cross-link density and inorganic character and will find MS analysis impossible by a direct ESI infusion.

Figure 1. a) MS/MS spectrum of an ammoniated 11-mer at m/z 906.3 generated upon ESI of the trimethylsiloxy-terminated PDMS reference compound recorded at a 0.91 eV collision energy (center-of-mass frame). b) MS/MS spectrum of the isobaric species from the soluble part of a ppHMDSO sample recorded under the same conditions. Structure of the standard is depicted as inset.

Figure 2. MS/MS spectra of m/z 892.2 generated upon ESI of a) the soluble part of the plasma polymerized D4 (ppD4) and a2) the self-made reference compound, recorded at a 0.91 eV collision energy. Structure of the standard is given as an inset. b) Correlation coefficients computed from MS/MS spectra to quantify the similarity degree between CID patterns of self-synthesized polysiloxanes and the isobaric plasma species, as a function of the degree of polymerization.
Solubilize the insoluble: controlled degradation of the insoluble part

The second part of the doctoral work was thus devoted to the development of an analytical strategy for the mass analysis of the insoluble plasma polymers, keeping the same instrumental capabilities and thorough characterization expectations. A so-called ethanolysis pretreatment step was developed to specifically cleave silicon–oxygen bonds of the most substituted silicon atoms (i.e., silicon atoms neighbored by three or four oxygen atoms, in other words the cross-linking and branching points) and allow the sample to be dissolved in common solvents, while linear chains are preserved and their average lengths evaluable to gain insights into the architecture of the pristine deposit. According to the expected ethanolysis mechanisms, the so-formed ethanolysis products should bear ethoxy-, hydroxy- or both terminations, depending on the location of the silicon atom submitted to ethanolysis. Since the validation of end groups by MS is only reached by MS/MS experiments, and with the lack of literature on the topic, the MS/MS behaviors of commercially available hydroxy- and ethoxy-ended PDMS were first properly established prior to any plasma polymer ethanolysis. Once applied to ppD4 and ppHMDSO, the ethanolysis pretreatment allowed these plasma polymers to be partly or fully solubilized (depending on the plasma conditions, that is the inorganic character of the deposits), and hence amenable to a molecular and structural description for the first time. An ideal architecture of an insoluble plasma polymer was then reconstructed based on the distributions detected in MS and their micro-structural characterization by MS/MS, as seen in Figure 3. This ideal view of a plasma polymer—a PDMS-like network more or less branched and/or cross-linked via Q or T silicon atoms (neighbored by four or three oxygen atoms respectively)—had then to be faced with several plasma deposition conditions. The analytical methodology based on the ethanolysis pretreatment was thus applied to a series of ppD4 and ppHMDSO samples, varying by the energy delivered over the electrodes. Ethanolysis products were very similar regardless of the plasma conditions, and—quite surprisingly—regardless of the precursor used for the coating, either the cyclic D4 or the linear HMDSO. On the contrary, the relative abundances of these species in the MS spectra of the associated samples were very sensitive to the plasma conditions: the harder the conditions, the more abundant the cross-linked species. This cross-linking degree was conveniently evaluated by the number of cycles (or unsaturations) borne by the ethanolized oligomers, while an average cyclization degree was calculated for each ethanolized sample by computing...
the abundance of the detected species. Despite its simplicity and its inherent errors, this average cyclization degree—a very convenient way to reduce all the data of a MS spectrum to a single point—was found to strongly correlate with the $^{29}$Si NMR data from the whole plasma polymer samples (the NMR data being also easily converted into a single value to evaluate extent of inorganic character of the sample, by computing the relative abundances of the “T” and “Q” signals; Figure 4). Hence, such a correlation for both D4- and HMDSO-related coatings could mean the data extracted from the ethanolysis pretreatment and the related MS results are pertinent and representative of the whole sample, as compared to the NMR data which by nature are macroscopic. Finally, despite a high similarity between species detected in the ethanolyzed ppD4 and ppHMDSO samples, the two precursors do not produce similar deposits, as clearly evidenced by the value of the y-intercept values obtained from the linear regression depicted in Figure 4. These values are in addition and surprisingly a perfect picture of the precursor shape: a “0” value for HMDSO (linear, no cyclization degree) and “1” for D4 (one cycle, hence “1” as the average cyclization degree).

As a conclusion to this PhD thesis, the structural insights obtained for both soluble (direct analysis) and insoluble parts (after the ethanolyzed pretreatment) of a given plasma polymer were compared and allowed the two main mechanisms proposed to occur during the plasma polymerization to be highlighted: both a recombination of “atomized” fragments in the solid phase and “oligomerization” in the gas phase and deposition at the surface. In addition, the usefulness of the soluble part as an aliquot to be analyzed was clearly demonstrated despite its “lack of representativeness”. Its sole analysis first provides some insight into the nature of the species found into the coating, but its comparison with the ethanolyzed insoluble part brings additional data on plasma processes. The whole analytical methodology developed in this PhD thesis is summarized as a workflow diagram in Figure 5. This strategy gave access to a thorough molecular and structural analysis of plasma polymers from silicon precursors. From a more general point of view, the same approach could also be envisaged to be adapted for any other plasma polymers, providing that an appropriate degradation process is developed and any requested relevant models are commercially available or easily synthesized by wet chemistry to deduce useful information from the fragments observed in MS/MS.

Keywords: analytical chemistry · plasma polymerization · polydimethylsiloxane · polymers · tandem mass spectrometry

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Published online on September 26, 2014