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Negative Ion Mode Electrospray Tandem Mass Spectrometry of Hydroxy-Terminated Polydimethylsiloxanes Formed upon *in situ* Methanolysis

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Ethoxy-, methoxy- and hydroxy-terminated polydimethylsiloxanes (PDMS) are formed as the result of the methanolysis of diethoxy-ended PDMS during its infusion in electrospray ionization. The negative ion mode permits only hydroxy-ended products to be detected, and isomeric interference is avoided in single stage and tandem mass spectrometry. The routes for the fragmentation of (ethyl, hydroxy)-, (methyl, hydroxy)- and (hydro, hydroxy)-ended PDMS upon collision activated dissociation (CAD) were explored in the negative ion mode using either formate or acetate anion adduction. Symmetrical (hydro, hydroxy)-ended PDMS decomposed to product ions carrying one of the hydroxy terminations through the abstraction of an acidic hydrogen and depolymerization (expulsion of cyclic neutral species) regardless of the adducted anion. Asymmetric (ethyl, hydroxy)-ended (resp. (methyl, hydroxy)-ended) PDMS yielded both ethoxy-ended (resp. methoxy-ended) fragment ions through the abstraction of the only acidic hydrogens and linear product ions carrying both terminations still interacted with the anion. The production of information-rich ethoxy-ended (resp. methoxy-ended) fragment ions was limited by formate but favored when acetate (higher proton affinity) was used in a CAD fingerprint complementary to the positive ion mode.
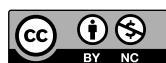
INTRODUCTION

Tandem mass spectrometry (MS/MS) coupled to soft ion sources such as electrospray ionization (ESI) and matrix assisted laser desorption ionization (MALDI) is a powerful analytical technique for the microstructural characterization of polymers.[1] A single stage mass spectrometry (MS) analysis can provide information concerning the nature of the repeat unit, the degree of polymerization (DP) and the sum of the masses of the end-groups.[2,3] Triggering the dissociation of a selected oligomeric chain to detect so-formed product ions in a MS/MS configuration (*e.g.*, triple quadrupole, ion trap, hybrid quadrupole time-of-flight QTOF[4] or TOF/TOF) offers unrivaled insights into the composition of each individual end-group, as well as the architecture of the chain.[5] Among several activation techniques, collision activated dissociation (CAD, also known as collision induced dissocation CID), has been extensively used for the characterization of unknown polymers by applying fragmentation pathways preliminarily elaborated from standards.[6] To account for the importance of this technique in the field of polymer chemistry, Wesdemiotis *et al.* proposed a complete nomenclature to unambiguously name the product ion series formed upon the disruption of backbones from major polymers, such as polystyrenes, polyethers, polyesters and polysiloxanes.[7]

If the literature dealing with the MS(/MS) of polymers is expanding continually year by year, it remains surprisingly unequally distributed in terms of repeat units that are covered and does not reflect the importance of a polymer class in industry. This is particularly true for polysiloxanes (also known as silicones) considering their unlimited applications, while a limited number of reports dealing with MS(/MS) analyses of these polymers have been published.[8,9]

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Reference works are nevertheless mandatory from the early steps of synthesis to the final degradation to ensure a safe life cycle of technical polymers. Given the growing concern about enviromental protection, the degradation step is particularly prominent as it would take part of a recycling process to create new synthons or lower grade products for use in less demanding applications.[10–15] It is also a major topic in the oil industry, since polydimethylsiloxanes (PDMS) derivatives are used as anti-foaming agents and undergo various types of degradation during the refining of fuels.[16–18] Several MS-based multi-technique approaches have been proposed for the characterization of industrially relevant samples[19] but reports dealing with MS/MS analysis continue to be rare. In an attempt to update the literature, a series of articles concerning detailed descriptions of the fragmentation pathways of polysiloxane ions such as PDMS,[20–25] polymethylhydrosiloxanes (PMHS),[26] polymethoxymethylsiloxanes (PMMS)[27] and polyhedral oligomeric silsesquioxanes (POSS) have been published.[28,29] Within the class of PDMS samples, a variety of end-groups such as terminations formed upon the alcoholysis of PDMS chains (ethoxy EtO, methoxy MeO, hydroxy OH) have been found to strongly influence the CAD routes.[30]

As a common thread in all of these reports, polysiloxane ions were transferred in the gas phase in the positive ion mode as alkali adducts (e.g., Li^+, Na^+) or ammonium adducts (NH_4^+). Generally speaking, MS and MS/MS analyses of polymers are mainly studied in the positive ion mode, owing to their high propensity to interact with alkali or metallic cations. However, MS and MS/MS analyses of polymer ions in the negative ion mode—reported only for a few favorable cases where the repeat unit and/or the end-group bear an acidic function that can be readily deprotonated—might nevertheless provide molecular and structural information that compliments their positively charged counterparts.[31–36] The only acidic termination that is commonly found for a PDMS chain is the hydroxy group (OH-ended PDMS) which is used as building block or released as a degradation product.[30]

The present article deals with a) a thorough investigation of the methanolysis of a symmetric diethoxy-ended PDMS during its infusion in an ESI-MS analysis (positive and negative ion modes) in which symmetric and asymmetric hydroxy-ended PDMS chains are produced and b) fragmentation rules for the so-formed hydroxy-ended PDMS chains *adducted* with formate and acetate anions (negative ion mode). In particular, the adduction of formate or acetate in the negative ion mode has been found to be the equivalent of the adduction of ammonium in the positive ion mode,[37] *i.e.*, an indirect deprotonation (resp. protonation), a noteworthy departure from the usual direct deprotonation of acidic polymers.[31–36] The influence of the adducted anion in terms of triggered fragmentation routes as well as the influence of the end-group (symmetric hydroxy/hydroxy, asymmetric ethoxy/hydroxy and hydroxy/methoxy) were also investigated.

EXPERIMENTAL
Chemicals
Symmetric diethoxy-ended PDMS (noted (Et, OEt)-PDMS) with a weight average molecular weight of 800–900 g

mol^{-1} (kinematic viscosity: 5–10 cSt) was purchased from ABCR GmbH & Co. KG (Karlsruhe, Germany). Ammonium acetate, formic acid and tetrahydrofuran (THF) were obtained from Sigma-Aldrich (St. Louis, MO) and methanol (MeOH) was from SDS (Peypin, France). All chemicals were used as received without further purification. The methanolysis of (Et, OEt)-PDMS to produce symmetric hydroxy/hydroxy-ended PDMS (denoted as (H, OH)-PDMS) and asymmetric hydroxy/ethoxy-PDMS ((H, OEt)- or (Et, OH)-PDMS) and hydroxy/methoxy-ended PDMS ((H, OMe)- or (Me, OH)-PDMS) occurs in methanolic solutions of ammonium acetate within the time frame of the mass analysis with no additional reagent.

Mass Spectrometry
ESI-MS(/MS) experiments were performed in both the positive (noted (ESI(+)) and negative ion modes (noted (ESI(−)) using a QStar Elite hybrid QTOF mass spectrometer from Applied Biosystems SCIEX (Concord, ON, Canada) equipped with an ESI source (capillary voltage at +5500 V/−4500 V, cone voltage at +50 V/−20 V, methanolic solution of ammonium acetate or formic acid and PDMS injected at a 5 μL min^{-1} flow rate in infusion mode). Air was used as the nebulizing gas (10 psi, 0.690 bar) while nitrogen was used as the curtain gas (20 psi, 1.380 bar) as well as the collision gas. Collision energies reported for the tandem mass spectra are in the center of the mass frame $E_{cm}=E_{lab}\times m_{nitrogen}/(m_{nitrogen}+m_{ion})$. Instrument control, data acquisition, and data processing for all experiments was achieved using Analyst software (QS 2.0) provided by Applied Biosystems while mMass[38] was used for artwork.

Pristine (Et, OEt)-PDMS was first dissolved in THF and further diluted in pure MeOH. The last but one dilution was done with a methanolic solution of ammonium acetate to trigger the methanolysis of the polymeric chain and it was allowed to react for 15 min. The mixture was finally diluted once more with MeOH and electrosprayed to produce ammonium (ESI(+)) and acetate adducts (ESI(−)) or diluted in a methanolic solution of formic acid to form formate adducts in ESI(−) (no direct protonation was observed in ESI(+)).

RESULTS AND DISCUSSION
In situ methanolysis of (Et, OEt)-PDMS
The mass spectrum of a PDMS sample that is electrosprayed from a methanolic solution of ammonium acetate tends to vary over time with the supernumerary PDMS distributions differing by the nature of the terminal groups.[6] This property—which has also been reported for POSS structures[28]—constitutes an efficient method to produce special PDMS structures *in situ* that can be further submitted to CAD in a single experiment, thus avoiding their tedious synthesis.[24] It also allows the degradation mechanisms of a PDMS sample to be explored with no need for a preliminary alcoholysis *ex situ* prior to its mass analysis.[20] The alcoholysis of PDMS is simple and the so-formed species are readily predicted, as shown in Scheme 1 for a symmetric (Et, OEt)-PDMS.[39] The nucleophilic attack of a methanoate anion on a silicon atom followed by the capture of a proton by the so-formed negatively charged oxygen atom results in the scission of the chain and the formation of two asymmetric (methoxy, ethoxy)-terminated (denoted
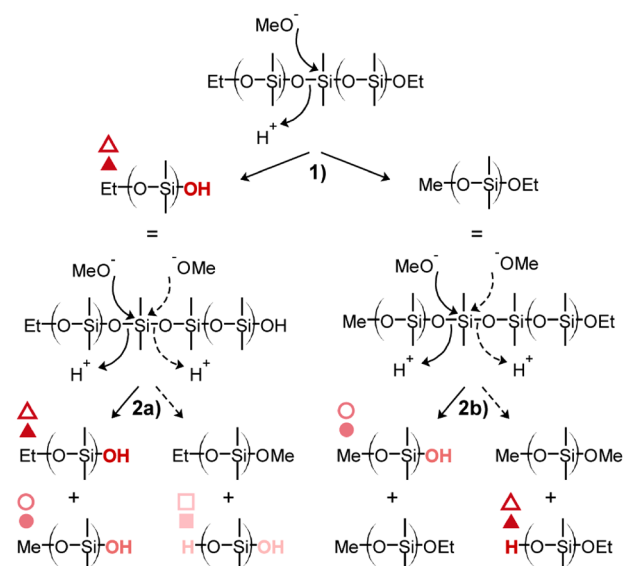
Scheme 1. Methanolysis of a symmetric (Et, OEt)-PDMS producing (Et, OMe)-, (Et, OH)-, (Me, OMe)-, (Me, OH)- and (H, OH)-PDMS chains. The hydroxy terminations are highlighted in pink, light red and red for the symmetric (H, OH)-PDMS and the asymmetric (Me, OH)- and (Et, OH)-PDMS, respectively. Associated symbols (pink squares, light red circles and red triangles) will be used in the ESI(+/−) mass spectra.

as (Me, OEt)-) PDMS and (Et, OH)-PDMS (annotated with triangles in Scheme 1, step 1). Repeating a similar chain disruption for a (Et, OH)-PDMS chain produces a shorter (Et, OH)-PDMS and a newly formed (Me, OH)-PDMS (denoted with circles) or (Et, OMe)- and (H, OH)-PDMS (denoted with squares) depending on the Si–O bond that is attacked by the methanoate anion (Scheme 1, step 2a). A chain scission conducted over the (Me, OEt)-PDMS chain formed in step 1 produces either (Me, OH)- and (Me, OEt)-PDMS or (Me, OMe)- and (H, OEt)-PDMS chains (Scheme 1, step 2b). Additional methanolysis steps induce only a reduction in chain length, with no alternative terminations. It should be noted that (Me, OMe)- and (Et, OH)-PDMS distributions are isomeric (total mass of the end-groups: $CH_3+OCH_3=CH_3CH_2+OH=46\,Da$) and would not be separated in a single stage ESI-MS analysis.

A 40 min reaction time (more precisely, 15 min *ex situ* and 25 min *in situ* during the infusion of the methanolic solution) was sufficient for the methanolysis of a symmetric (Et, OEt)-PDMS to occur with a reasonable yield. The resulting ESI mass spectrum is first observed in the positive ion mode (Fig. 1A) and discussed based on the available literature. Five distributions of PDMS are detected as ammonium adducts (repeating unit: C_2H_6OSi, 74.0188 Da). Accurate mass measurements, derived elemental compositions and assignments are listed in Table S1 (Supporting Information). The inset in Fig. 1A displays the 10-mer ammonium adducts of
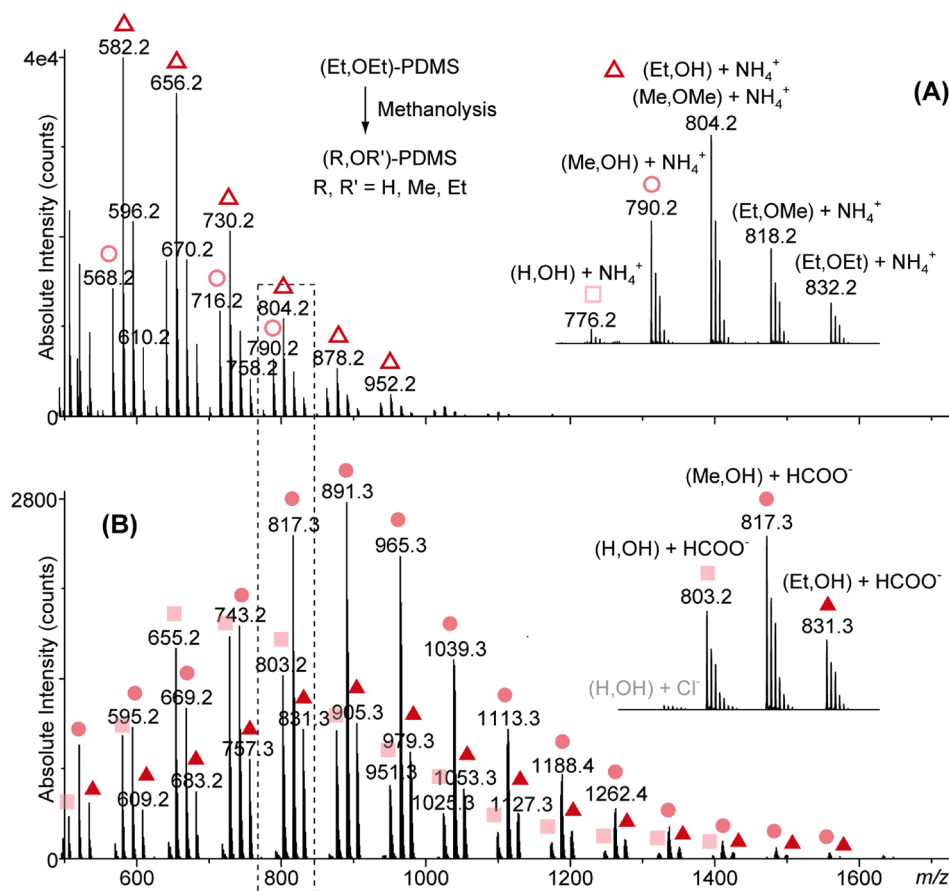

Fig. 1. ESI mass spectra of a symmetric (Et, OEt)-PDMS electrosprayed from (A) a methanolic solution of ammonium acetate and recorded in the positive ion mode and (B) a methanolic solution of formic acid and recorded in the negative ion mode following a 40 min period of methanolysis. Expanded views of the *m/z* 750–850 range are depicted in insets with the peak assignments. Ammonium and formate adducts of (H, OH)-, (Me, OH)- and (Et, OH)-PDMS are marked with pink squares, light red circles and red triangles, respectively (positive ion mode: empty symbols, negative ion mode: filled symbols).

the five PDMS distributions. In descending order, the first peak at m/z 832 is assigned to the pristine (Et, OEt)-PDMS while the −14 Da shifted peak is assigned to a (Et, OMe)-PDMS (Scheme 1, step 1). The two isomeric methanolysis products ending with (Et, OH) or (Me, OMe) could be detected together under the −28 Da shifted peak at m/z 804. Their concomment occurrence will be further assessed by ESI(+)-MS/MS. The last two methanolysis products are detected at m/z 790 ((Me, OH)-PDMS) and m/z 776 ((H, OH)-PDMS) in agreement with the predicted degradation pathway in Scheme 1.

In order to validate the end-groups assignments, ESI(+)-CAD mass spectra of these 10-mer ammonium adducts were recorded and are depicted in Fig. S1 (peaks and assignments are listed in Table S2). The CAD of all these species has been extensively described elsewhere.[25,30] Briefly, the ethoxy termination ((Et, OEt)-PDMS) is highlighted by the consecutive losses of ethanol and ethylene from the precursor ion at m/z 832 (Fig. S1a). Losses of methanol and ethanol from the precursor ion at m/z 818 account for its asymmetric shape and validates the existence of (Et, OMe) terminations (Fig. S1b). For the more complex case of the ammonium adduct at m/z 804 comprised of two isomeric forms—(Et, OH) and (Me, OMe)-ended PDMS—the detection of the loss of three neutral species from the precursor ion (namely water, methanol and ethanol) confirms the occurrence of these three terminations (Fig. S1c) which cannot be contained within a unique chain according to the accurate mass measurment of the precursor ion. The end-groups of the last two methanolysis products are highlighted by the loss of two neutral species—methanol and water—from the precursor ion at m/z 790, thus confirming its asymmetric (Me, OH) shape (Fig. S1d) and the unique loss of water from the precursor ion at m/z 776 in accordance with a (H, OH) PDMS shape (Fig. S1e).

The positive ion mode allows all of the expected species formed by the methanolysis of a (Et, OEt)-PDMS to be observed but requires the use of both MS and MS/MS modes to ensure that the detected peaks are assigned. To the contrary, using the negative ion mode could be thought as a filter to favor the detection of hydroxy-ended species thanks to their slightly acidic character.[31–36] Shifting from the positive to the negative ion mode using the same methanolic solution of ammonium acetate leads to the detection of several PDMS acetate adducts. The absolute abundance of these species was rather low—even considering the notoriously lower sensitivity of the negative ion mode and the use of formate anions in lieu of acetate anions has been found to dramatically improve the signal-to-noise ratio (Fig. S2, the signal with formic acid is six times higher than the signal with ammonium acetate). For the sake of resolution and improving the accuracy of mass measurements, the ESI(−) mass spectrum depicted in Fig. 1B was therefore recorded from formic acid. Accurate mass measurements are listed in Table S3. Only three PDMS distributions with satisfactory intensities were detected. The inset in Fig. 1B displays the ESI(−) mass spectrum focused around 10-mer formate adducts produced from methanolized PDMS. In ascending order, the peak at m/z 803 is attributed to a (H, OH)-PDMS (denoted with pink square) and the +14 Da shifted peak at m/z 817 is due to the (Me, OH)-PDMS distribution (light red circle). Neither intact (Et, OEt)-PDMS nor partially methanolyzed (Et,

OMe)-PDMS distributions are detected. As expected, only the hydroxy-ended polysiloxane chains are available for interacting with the formate anion and form adducts in the gas phase. *De facto*, this limitation in the third peak at m/z 831 can be assigned to the asymmetric (Et, OH)-PDMS only (red triangle in Fig. 1B). The mass analysis of the methanolyzed PDMS in the negative ion mode therefore allows the isomeric issue mentioned in the previous paragraph to be overcome and permits (Et, OH)-PDMS congeners to be analyzed by MS/MS without any risk of interference. It is worth mentioning that the methanolysis occurs during the electrospray of the solution and the resulting mass spectra can vary over time. The ESI(−) mass spectrum depicted in Fig. 1B is a snapshot at 40 min but the relative abundances of the three distribution change for shorter reaction times as depicted in Fig. S3, highlighting the iterative nature of the methanolysis reaction (Scheme 1).

The formation of acetate and formate adducts in the negative ion mode is somewhat unusual, since acidic polymers have been observed as deprotonated species.[31–36] The absence of deprotonated PDMS chains in the ESI(−) mass spectrum might be accounted for by a fast dissociation during the ionization (in source decay ISD). The detection of intense ions assigned to disrupted PDMS chains in the low mass range (data not shown) is consistent with this hypothesis (deprotonated chains would be actually formed but dissociate faster than the time frame of the MS analysis). On the contrary, anion adducts survive the ionization step thanks to their apparent higher stability. This might be seen as an indirect deprotonation step, since it has been proposed in the positive ion mode with the adduction of ammonium NH_4^+ to indirectly protonate polymer chains (upon CAD, a $[M+NH_4]^+$ adduct dissociates in $[M+H]^+$ and NH_3). Formate and acetate adducts were therefore submitted to CAD to check the reality of the deprotonation step (upon the release of formic acid and acetic acid) and to investigate their fragmentation pathways.

CAD of symmetric (H, OH)-PDMS

Figure 2 displays the ESI(−)-CAD mass spectra of the symmetric (H, OH)-PDMS 5-mer at m/z 433 recorded at a collision energy of 0.25 eV (A) and the 10-mer at m/z 803 recorded at an energy of 0.35 eV (B). Upon CAD at a low collision energy, the 5-mer adduct produced with formate tends to eliminate formic acid (HCOOH, 46 Da) through the abstraction of the acidic hydrogen from one of the two hydroxy terminations by the formate anion, yielding the largest product ion at m/z 387 and denoted a_5^- according to the nomenclature proposed by Wesdemiotis *et al.*[7] The generic nomenclature is summarized in the inset of Fig. 2A with notations of interest for the present study highlighted in red (a^- and y^- ions). Constituting a well-known dissociation pathway,[22,23] PDMS product ions tend to expulse cyclic polysiloxane neutrals, denoted D_n (D=Si$(O_{1/2})_2$(CH$_3$)$_2$ according to the silicon nomenclature[40–43]) with n=3–5 for the most stable cycle. A 3-unit shorter a_2^- product ion is thus mainly formed upon the release of a D_3 neutral (Si$_3$O$_3$C$_6$H$_{18}$ six-membered ring, 222 Da) from the above-mentioned a_5^- product ion. The final expulsion of methane from a_2^- to form a product ion at m/z 165 is negligible. CAD in the negative ion mode does not promote the secondary loss of methane that is observed to a great extent in the posi-
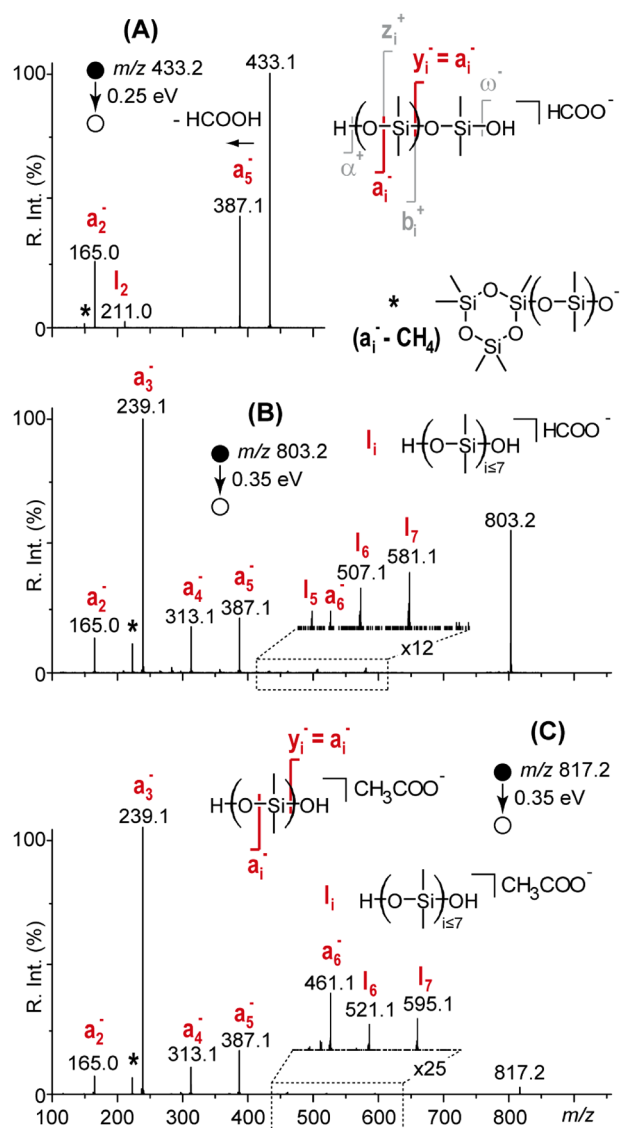
Fig. 2. ESI(–)-CAD mass spectra of the symmetric (H, OH)-PDMS (A) 5-mer formate adduct at m/z 433 recorded at a 0.25 eV collision energy, (B) 10-mer formate adduct at m/z 803 and (C) acetate adduct at m/z 817 recorded at a 0.35 eV collision energy. Structures of a_i^-, a_i^--CH_4 and l_i ions are depicted in insets.

tive ion mode for the ammoniated (H, OH)-PDMS chains (backbiting process with the remaining terminal hydrogen and one methylide group along the polymeric backbone).[30] The two filiations ($-D_3$ and $-CH_4$) were confirmed by MS^3 experiments reported in the Supporting Information (Fig. S4). A last product ion with a very low relative abundance is eventually detected at m/z 211 and found to arise from the direct release of a neutral D_3 species from the precursor ion. Continuing to follow the nomenclature for polymer fragmentation, such a product ion is denoted as l_2, since it carries the two pristine end-groups and is interacting with a formate anion.[7] Increasing the degree of polymerization of the precursor ion to 10, the formate adduct at m/z 803 undergoes a similar dissociation process with the formation of a_i^- congeners (i=2–5) carrying the initial –OH end-group and a negatively charged O atom.

Such a CAD pattern is complementary to the main product ion series detected in the positive ion mode carrying the initial end-group and a positively charged silicon atom (inset of Fig. 2A, grey lines). The domination of low molecular weight congeners of the a_i^- series is also reminiscent of the MS/MS behavior of PDMS in the positive ion mode, with the consumption of the largest b_i^+ congeners under the fast release of D_n neutral species.[25] Similarly, the largest a_{10}^- congener formed upon the loss of formic acid is no longer detected owing to its rapid dissociation. "Linear" fragment ions, l_5, l_6 and l_7, carrying both end-groups and the anion are barely detected at m/z 433, m/z 507 and m/z 581 (inset in Fig. 2B, ×12 magnification). A unique detectable loss of methane is found from the major a_3^- product ion at m/z 239 to yield a poorly seen product ion at m/z 223 that is denoted with an asterisk. Despite the increase in chain length, the elimination of methane, which is the major pathway for large (H, OH)-PDMS oligomers in the positive ion mode[30] is no longer seen in the negative ion mode. This constitutes a definite advantage of ESI(–) over ESI(+) since the resulting MS/MS spectra are free of secondary product ions which tend to complicate the ESI(+)-MS/MS data and provide no additional information. The generic structures of the three product ion series a_n^-, a_n^--CH_4 and l_n are depicted in Fig. 2 aside the mass spectra. The structure proposed for the a_n^--CH_4 series is one isomeric possibility among several other forms but is highly suspected to be preferential, based on a two unit long backbiting process during which a favorable 6-membered ring is formed upon the expulsion of methane. All of the product ions with their accurate mass measurements and assignments are listed in Table S4.

Despite their lower abundance in ESI(–)-MS, the actual production of acetate adducts permits their CAD to be studied as well. The ESI(–)-CAD mass spectrum of the (H, OH)-PDMS 10-mer acetate adduct is depicted in Fig. 2C and appears to be highly similar to the mass spectrum of the formate adduct. The only noticeable difference concerns the survival yield SY=$I_{precursor}/(I_{precursor}+\Sigma I_{product})$,[44] which is dramatically reduced for the acetate adduct (SY=0.02) as compared to the formate adduct (SY=0.25) when activated at the same 0.35 eV collision energy. The greater proton affinity of acetate as compared to formate[45] induces the abstraction of one of the acidic hydrogens from the hydroxy terminations to be kinetically more rapid and triggers the production of a_i^- product ions.

The dissociation mechanisms accounting for the CAD behavior reported above are depicted in Scheme 2. A Si–O intramolecular bond translocation from the precursor ion favored by the interaction of the end-groups (hydrogen bonding) expulses a D_n neutral (n=3 in Scheme 2A) and yields a l_n product ion that still can interact with the anion, *i.e.*, a shortened chain carrying the same terminations (pathway A in Scheme 2, plain black arrows). On the contrary, the abstraction of one of the two acidic hydrogens by the anion leads to the production of the largest a_n^- congener and the release of an AH neutral species (pathways B and C in Scheme 2, dashed black and grey arrows). Such an a_n^- product ion is then able to dissociate *via* either intramolecular bond translocation or backbiting from the negatively charged oxygen atom on a silicon atom from the backbone, resulting in the expulsion of D_n neutral species and the production of smaller a_n^- product ions. The congeners of the l_n series could further dissociate into smaller l_n or a_n^- product ions upon the release of D_n neutrals or AH and D_n, respectively, which
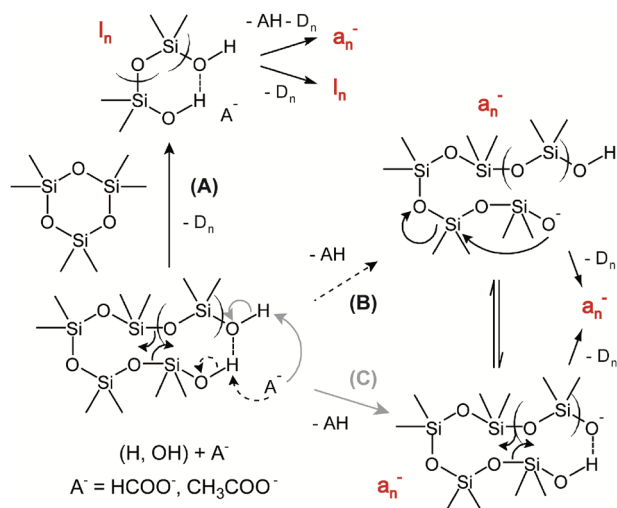
Scheme 2. Fragmentation mechanisms for a (H, OH)-PDMS chain adducted with either formate or acetate anion (noted with A^-). (A) Intramolecular bond translocation to yield l_n product ions. (B) and (C) abstraction of acidic hydrogens from the hydroxy termination by A^- to yield a_n^- product ions. Additional bond translocation and/or elimination of a cyclic D_n neutral through a backbiting process will produce smaller congeners.
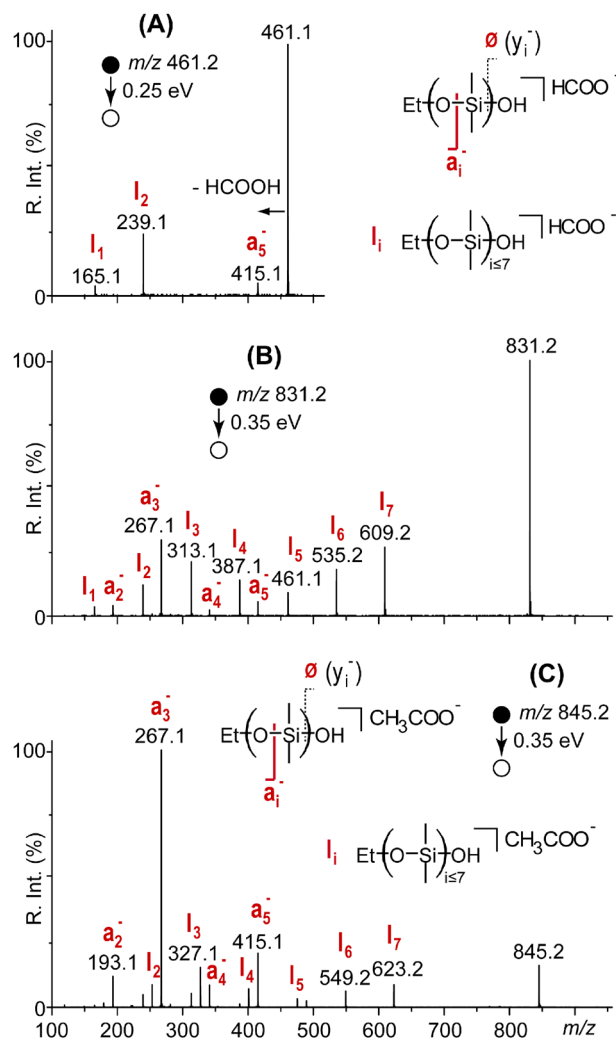

Fig. 3. ESI(–)-CAD mass spectra of the asymmetric (Et, OH)-PDMS (A) 5-mer formate adduct at m/z 461 recorded at a 0.25 eV collision energy and 10-mer (B) formate adduct at m/z 831 and (C) acetate adduct at m/z 845 recorded at a collision energy of 0.35 eV. The structures of a_i^- and l_i ions are depicted in insets.

would deplete the signal of the largest product ions and account for the domination of the short fragment ions. The interaction of the remaining hydrogen with the negatively charged oxygen atom in the a_n^- generic structure (Scheme 2, pathway C) accounts for the limited methane expulsion detected in the negative ion mode, since the hydrogen atom can no longer interact with the methylide groups.

Additionally, chlorine adducts of (H, OH)-PDMS barely observed in the ESI(–) mass spectrum (Fig. 1B, noted in grey) were submitted to CAD and their MS/MS patterns are reported in the Supporting Information (Fig. S5 and Table S5). The signal-to-noise ratio is poor but the informative a_n^- product ion series is clearly detected and echoes the results found for the acetate and formate adducts in the negative mode as a complimentary fragmentation route to the positive ion mode fingerprint (b_n^+ product ion series[22]). The absence of chlorine adducts for the two asymmetric (Et, OH)- and (Me, OH)-PDMS prevented us from pursuing this investigation further and the fragmentation pathways for only formate and acetate adducts were examined.

CAD of asymmetric (Et, OH)- and (Me, OH)-PDMS

To the best of our knowledge, the fragmentation route for asymmetric (Et, OH)- and (Me, OH)-PDMS structures in the negative mode has not yet been reported. The nature of the initiating termination (*i.e.*, Et or Me) was found to have no impact on the MS/MS fingerprint and associated dissociation mechanisms. For the sake of simplicity, the CAD mass spectra of the (Et, OH)-PDMS distribution are discussed in the main article, while results regarding (Me, OH)-PDMS are reported in the Supporting Information. Figure 3A displays the ESI(–)-CAD mass spectrum of a (Et, OH)-PDMS 5-mer formate adduct. Upon activation, the precursor ion expulses a formic acid neutral species (46 Da) to form the largest congener of an a_n^- product ion series carrying an

ethoxy termination (inset in Fig. 3A for the generic structure and nomenclature). Alternatively, the precursor ion also expulses D_3 and D_4 neutral species (cyclic PDMS neutrals containing three and four dimethylsiloxane units, respectively) to yield the so-called l_1 and l_2 product ions at m/z 165 and m/z 239. Those product ions still carry the two pristine end-groups and the formate anion. A striking difference in terms of relative abundances of these two ion series is readily evidenced between the (H, OH)- and (Et, OH)-PDMS 5-mers (Figs. 2A and 3A). Indeed, the intensities of the l_i ions are significant in the case of (Et, OH)-PDMS, while only one congener of the l series is barely seen in the spectrum of (H, OH)-PDMS. To the contrary, the a_5^- product ion is formed with a low abundance from (Et, OH)-PDMS while it is the main product ion from (H, OH)-PDMS. Replacing one hydroxy end-group with an ethoxy (or methoxy) termination thus drastically modifies the CAD pattern and tends not to favor the abstraction of the terminal hydrogen (*i.e.*, the route to yield a_n^- product ions).

Increasing the degree of polymerization from five to ten does not drastically affect the MS/MS behavior of (Et, OH)-PDMS. Both a_i^- and l_i product ion series are detected,
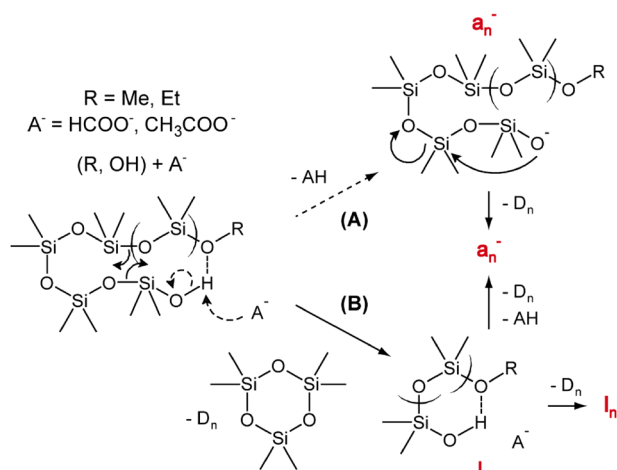
Scheme 3. Fragmentation route for an asymmetric (R, OH)-PDMS (with R=Me, Et) adducted with anion A^- (with A=HCOO, CH_3COO). (A) Abstraction of the acidic hydrogen from the hydroxy termination by A^- to yield a_n^- product ions. (B) Intramolecular bond translocation to yield l_n product ions. Additional bond translocations and/or elimination of cylic D_n neutral through a backbiting process would produce smaller congeners.

from a_2^- at m/z 193 to a_5^- at m/z 415 and from l_1 at m/z 165 to l_7 at m/z 609. The absence of larger l_i congeners (i=8, 9) is rationalized by considering the fact that the neutral D_3 is the smallest stable cycle to be released from the precursor ion. D_2 would be a four-membered ring with a high string tension, while D_1 is a single dimethylsiloxane unit with a Si=O double bond, which would be unlikely to be produced in the gas phase. The nearly entire l_n series is thus observed for (Et, OH)-PDMS and (Me, OH)-PDMS, Supporting Information) with high intensities when only three congeners were seen for (H, OH)-PDMS with magnification of the spectrum. The below-depicted Scheme 3 is an attempt to rationalize such a variation. A noticeable difference between the MS/MS spectra of the 5- and 10-mer is largely due to the disappearance of the $a_{n\ max}^-$ product ion, $i.e.$, the largest a_i^- congener formed upon the release of formic acid. A similar trend was found for (H, OH)-PDMS in the negative ion mode (previous section) and in the positive ion mode CAD for trimethylsilyl and hydride terminated PDMS.[22,23] All of the accurate mass measurements and peak assignments are listed in Table S6. Owing to the ionization route and fragmentation mechanisms, no signals from a product ion series carrying the intact hydroxy termination were observed, $i.e.$, so-called y^- product ions (inset in Fig. 3). Even if the hydroxy termination cannot be highlighted in the ESI(−)-CAD mass spectra of asymmetric PDMS oligomers, there is no loss of information compared to the positive ion mode. The presence of a –OH end-group is indeed intrinsically highlighted by the detection of oligomers in ESI(−) (mandatory for a succesful ionization by promoting adduction with formate/acetate anions) while the EtO- (or MeO-) termination is readily evidenced thanks to the a_n^- series.

Mechanistically speaking, there is no difference between the symmetric (H, OH)-PDMS and the asymmetric (R, OH)-PDMS with R=Et or Me. The capture of the acidic H from the hydroxy termination by the anion leads to the release of AH and the production of the largest a_n^- product

ion, which is itself prone to form a_i^- congeners upon the release of stable D_n cyclic neutral species (with n=3–5 as the more stable neutrals) (Scheme 3, pathway A). Relying on a favorable interaction between the proton of the hydroxy termination and an oxygen atom located along the polymeric chain or from the methoxy/ethoxy terminal group, an intramolecular bond translocation would produce a D_n neutral species and a l_n product ion—still carrying the two pristine terminal groups and the anion. The l_n product ions are further liable to produce smaller l_n congeners or a_n product ions in the case of the release of D_n or AH and D_n, respectively. However, compared to the symmetric (H, OH)-PDMS structure, only one acidic hydrogen could be abstracted from the (Et, OH)-PDMS backbone ($vs.$ two possibilities for the dihydroxy ended chain), while the probability for intramolecular bond translocation to occur remains unchanged. This undoubtedly accounts for the higher abundance of the l_n series in the MS/MS spectra of the (Et, OH)-PDMS and (Me, OH)-PDMS congeners.

The linear product ion series is nevertheless not very informative in terms of microstructure, since the congeners still contain the two end-groups. Tandem mass spectrometry is usually employed to gain insights into the chemical nature of each end-group separately, thanks to the disruption of the polymeric skeleton while the MS stage provides the sum of the end-groups masses as the sole result. The adduction of acetate has been found to trigger the abstraction of an acidic hydrogen in the case of the symmetric (H, OH)-PDMS with a dramatically decreased survival yield (Fig. 2C). Using acetate in lieu of formate should, therefore, allow information-rich a_n^- ions to be formed with better statistics by forcing the (unique) abstraction of H. Despite a poor signal to noise ratio in the MS mode, acetate adducts of (Et, OH)-PDMS have been produced in the gas phase and submitted to CAD. Figure 3C displays the ESI(−)-CAD mass spectrum of a (Et, OH)-PDMS 10-mer adducted with acetate anions, recorded at the same 0.35 eV collision energy in the center-of-mass frame. All of the product ions detected in the spectra of the 10-mer adducted with formate and acetate are the same (Table S6 for the mass measurements). However, the influence of the anion is highlighted by a change in the survival yield (at ~0.41 and ~0.07 for formate and acetate anion adduction, respectively) as well as a dramatic increase in the relative abundances of the a_3^- and a_5^-. The higher gas phase basicity of the acetate anion compared to formate leads to a higher propensity for the anion to capture an acidic hydrogen atom from the hydroxy termination, triggering the production of a_i^- congeners, detrimental to the l_i series. The mass spectra of the (Et, OH)-PDMS congeners adducted with acetate are thus comparable to spectra recorded for the symmetric (H, OH)-PDMS with the targeted a_n^- fragment ions dominating. Similar results were obtained for the other asymmetric (Me, OH)-PDMS as reported in the Supporting Information (Fig. S6 and Table S7 for accurate mass measurements).

CONCLUSION

The $in\ situ$ methanolysis of a diethoxy-ended PDMS can be readily deciphered using MS and MS/MS. The positive ion mode leads to the detection of all of the methanolysis products but two series are interfering owing to the presence

of inseparable isomers. Switching to the negative ion mode removes this interference by filtering the non-acidic species and allows the chains bearing only hydroxy terminations to be detected, thus simplifying the MS and MS/MS data. Contrary to other acidic polymers which are readily deprotonated in the gas phase, hydroxy-ended PDMS are detected as formate adducts in the negative ion mode, which involves an indirect deprotonation step. The ESI(–)-CAD fingerprint of a dihydroxy-ended PDMS is simpler than its positive ion mode counterpart due to a limited secondary methane expulsion. The ESI(–)-CAD of asymmetric hydroxy/ethoxy- and hydroxy/methoxy-ended PDMS display l_n product ions (not observed in the positive mode except with lithium adduction) to a great extent, the unique acidic termination decreases the probability of producing a_n^- information-rich fragment ions bearing one end-group only. The intensity of the latter fragment series could nevertheless be dramatically increased by using an anion with a higher proton affinity (namely acetate in lieu of formate) as a way to trigger the abstraction of hydrogen from the hydroxy end-group in spite the poor signal to noise ratio in MS. In other words, formate adduction would be preferred in case of an MS analysis that demands sensitivity, while acetate adduction allows both a lower collision energy to be used and activates the production of informative a_n^- product ions.

Supporting information

Additional supporting information can be found in the online version of this article at the publisher's website.

Acknowledgements

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