

# Real-time monitoring of the progress of polymerization reactions directly on surfaces at open atmosphere by ambient mass spectrometry

Asger W. Nørgaard<sup>1,2\*</sup>, Boniek G. Vaz<sup>1</sup>, Frants R. Lauritsen<sup>3</sup> and Marcos N. Eberlin<sup>1</sup>

<sup>1</sup>ThoMson Mass Spectrometry Laboratory, Institute of Chemistry, University of Campinas - UNICAMP Campinas, SP Brazil

<sup>2</sup>The National Research Centre for the Working Environment, Denmark

<sup>3</sup>Faculty of Pharmaceutical Sciences, University of Copenhagen, Denmark

Received 5 August 2010; Revised 20 September 2010; Accepted 20 September 2010

The progress of an on-surface polymerization process involving alkyl and perfluoroalkyl silanes and siloxanes was monitored in real-time via easy ambient sonic spray ionization mass spectrometry (EASI-MS). When sprayed on surfaces, the organosilicon compounds present in commercially available nanofilm products (NFPs) react by condensation to form a polymeric coating. A NFP for coating of floor materials (NFP-1) and a second NFP for coating tiles and ceramics (NFP-2) were applied to glass, filter paper or cotton surfaces and the progress of the polymerization was monitored by slowly scanning the surface. Via EASI(+)-MS monitoring, significant changes in the composition of hydrolysates and condensates of 1H,1H,2H,2H-perfluorooctyl triisopropoxysilane (NFP-1) and hexadecyl triethoxysilane (NFP-2) were observed over time. The abundances of the hydrolyzed species decreased compared with those of the non-hydrolysed species for both NFP-1 and NFP-2 and the heavier oligomers became relatively more abundant over a period of 15–20 min. A similar tendency favouring the heavier oligomers was observed via EASI(-)-MS. This work illustrates the potential of ambient mass spectrometry for the direct monitoring of polymerization reactions on surfaces. Copyright © 2010 John Wiley & Sons, Ltd.

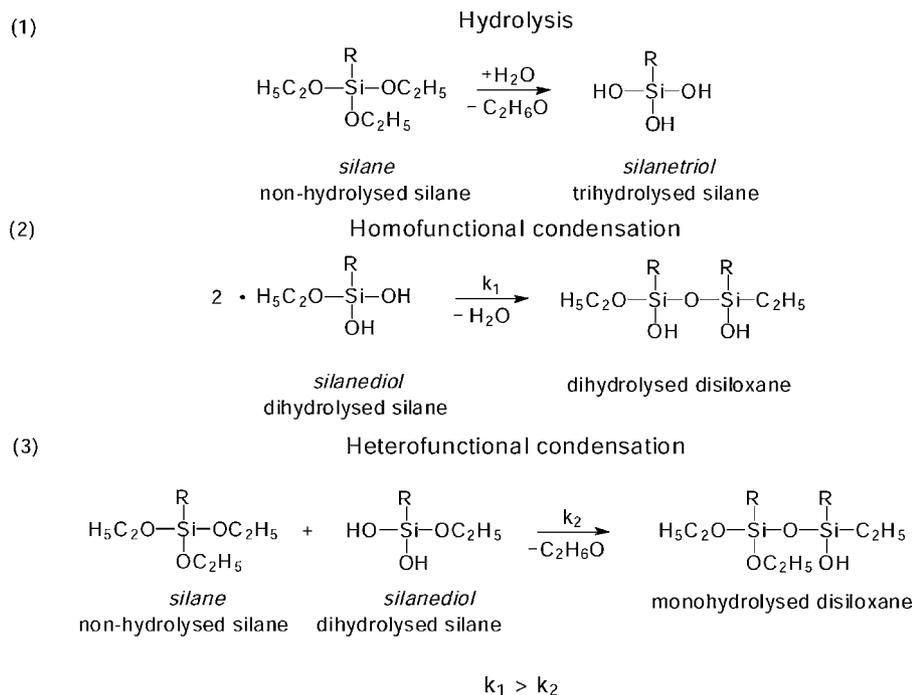
Nanofilm products (NFPs) are a relatively new type of surface coatings for industrial and domestic use. The NFPs are sprayed onto a surface, and a thin film is formed by self-organization during evaporation of the solvent, inducing non-stick properties. The film arises from the sol-gel process<sup>1–4</sup> involving a series of hydrolysis and condensation reactions between organo-functionalized silanes and siloxanes. The process is similar to that used for the preparation of silica sols by polymerization of silicon alkoxides by addition of water and an acid catalyst.<sup>1</sup> The NFPs are available for a wide range of surfaces such as bathroom tiles, floors, textiles, and windows.

The NFPs used in this study, one for coating of floor materials (NFP-1) and one for coating of tiles and ceramics (NFP-2), have been characterized previously by electrospray ionization tandem mass spectrometry (ESI-MS/MS) and gas chromatography/mass spectrometry (GC/MS). They were found to contain hydrolysates and condensates of 1H,1H,2H,2H-perfluorooctyl triisopropoxysilane and hexadecyl triethoxysilane.<sup>5,6</sup>

Recently, a comprehensive set of ambient ionization techniques for mass spectrometry has been introduced allowing the analysis of a variety of samples in the ambient environment without sample preparation (for a recent review, see Alberici *et al.*<sup>7</sup>). These techniques offer therefore unprecedented speed and ease of use and the unique opportunity to screen for chemicals and to monitor chemical reactions directly from surfaces in the open atmosphere. Among the ambient techniques, easy ambient sonic spray ionization (EASI-MS) has proved to be efficient in desorbing and ionizing chemicals from different types of surfaces such as those of drug tablets,<sup>8</sup> thin layer chromatography (TLC) plates,<sup>9,10</sup> and paper.<sup>11–15</sup> EASI-MS was recently shown to be able to desorb and ionize drugs trapped inside the pores of a molecularly imprinted polymer (MIP).<sup>16</sup> EASI is one of the simplest of the ambient ionization techniques. It does not require high voltages or radiation sources; its operation demands only compressed nitrogen (or simply air), a spray solvent and a few common laboratory parts such as stainless steel tubes and matching ferrules.

In this study, using EASI(±)-MS and the NFPs coating agents as a test case, we evaluated the ability of ambient mass spectrometry to monitor in 'real-time' a relatively fast polymerization reaction of a commercial coating product occurring on a surface in open atmosphere.

\*Correspondence to: A. W. Nørgaard, NRCWE, Lersø Parkalle 105, DK-2100 Copenhagen Ø, Denmark.  
E-mail: awn@nrcwe.dk



**Scheme 1.** Hydrolysis (1), homofunctional condensation (2) and heterofunctional condensation (3) reactions of an organosilane.<sup>1,18</sup> The names in italics are according to the nomenclature for organosilicon compounds suggested by Sauer.<sup>19</sup> However, the names in the normal case are used for comprehensibility reasons, e.g. dihydrolysed silane instead of silanediol.

## EXPERIMENTAL

### Chemicals

Methanol (HPLC grade), ammonium acetate (99%), ammonium hydroxide (28–30%) and formic acid (99%), were obtained from Merck SA (Rio de Janeiro, Brazil) and used without further purification. NFP-1 and NFP-2 were obtained from NanoLotus (Odense, Denmark). The NFPs were characterized in a previous study<sup>5</sup> and consist of ca. 1% solutions of hydrolysates and condensates of 1*H*,1*H*,2*H*,2*H*-perfluorooctyl triisopropoxysilane in 2-propanol (NFP-1) and hexadecyl triethoxysilane in ethanol (NFP-2).

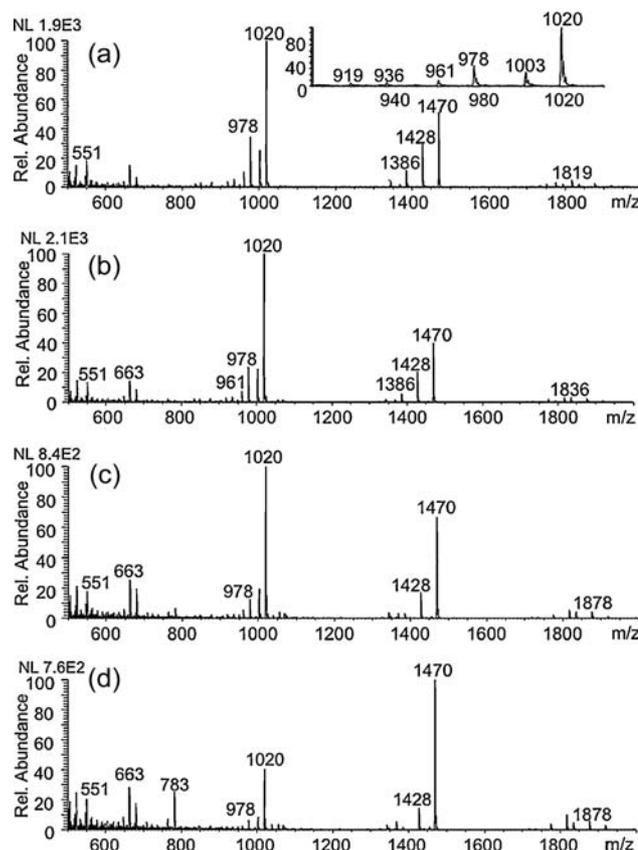
### Instrumentation

Experiments were carried out in both the positive and negative ion mode on a Thermo LTQ linear ion trap mass spectrometer (ThermoScientific, Bremen, Germany) equipped with an in-house built EASI source. The sonic spray solvents were methanol containing 0.1% formic acid and 2–5 mg/mL ammonium acetate for EASI(+)-MS and methanol containing 0.1% ammonium hydroxide for EASI(–)-MS.

Nitrogen was used as the nebulizing gas at a backpressure of ca. 7 bar. More details on the EASI source and its operation are provided elsewhere.<sup>8,17</sup>

For real-time experiments NFP (ca 50  $\mu\text{L}$ ) was applied either to filter paper, cotton or glass<sup>a</sup> and analyzed directly thereafter. Analysis was carried out for 15–20 min during which an area of ca. 2  $\text{cm}^2$  was scanned continuously. All mass spectra are averages over 0.5 min.

<sup>a</sup>When using glass surfaces, the sample was allowed to dry for 1 min before analysis in order to prevent splashing.



**Figure 1.** EASI(+)-MS of NFP-1 on glass 1 (a), 2 (b), 5 (c), and 15 (d) min after spraying on a glass surface. Insert (a): The ions of  $m/z$  1020, 978 and 936 are the ammonium adducts  $[\text{M} + \text{NH}_4]^+$  and those of  $m/z$  1003, 961 and 919 are the protonated molecules  $[\text{M} + \text{H}]^+$  of the non-, mono- and dihydrolysed disiloxane, respectively (Schemes 1 and 2).

## RESULTS AND DISCUSSION

The sonic nitrogen jet may affect the evaporation of the produced water and alcohol and thus accelerate polymerization (see Scheme 1). In order to assess this possibility, a treated surface was analyzed for 30 s every 5 min for a total period of 30 min. The results were compared with those from the scanning experiments. Since no differences between the continuous scanning and the interval scanning methods could be observed, it was concluded that the spray had minimum impact on the condensation reactions taking place. Therefore, continuous scanning was used in order to follow the reactions in real-time.

## NFP-1

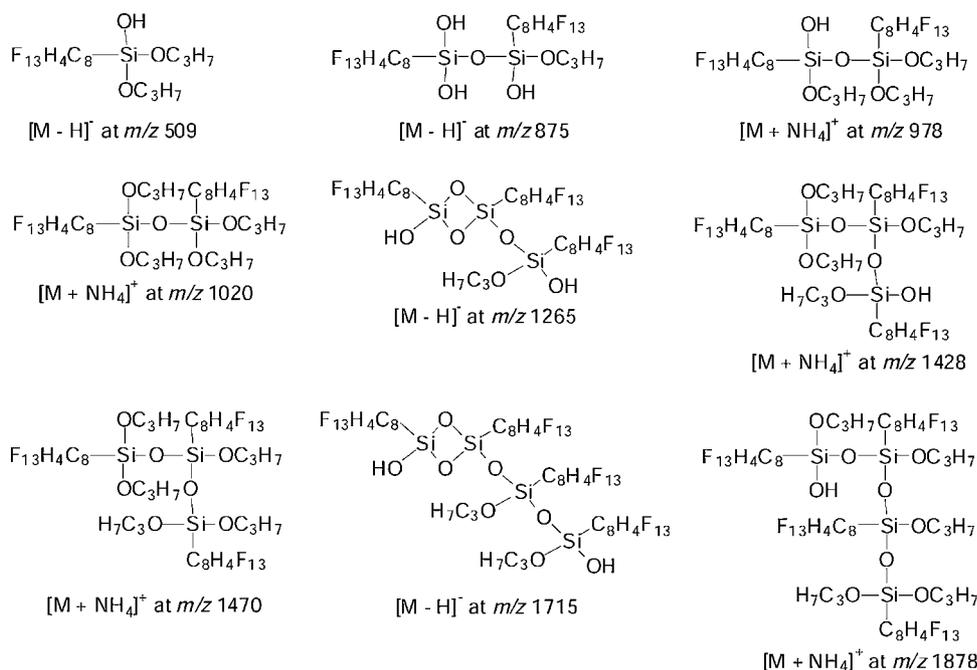
Figure 1(a) shows the EASI(+) mass spectrum of NFP-1 1 min after application to a glass surface. Three clusters of ions are observed around  $m/z$  1020, 1428 and 1819. These clusters

represent the oligomeric disiloxane, trisiloxane and tetrasiloxanes of *1H,1H,2H,2H*-perfluorooctyl triisopropoxysilane with different numbers of hydroxyl groups, respectively (Scheme 2). The insert in Fig. 1(a) shows an expanded view of the disiloxane ion cluster. Two ion series can be observed with intervals of  $42 m/z$  units, consistent with a  $C_3H_6$  repeating unit and corresponding to the hydrolysis of one isopropoxy group.

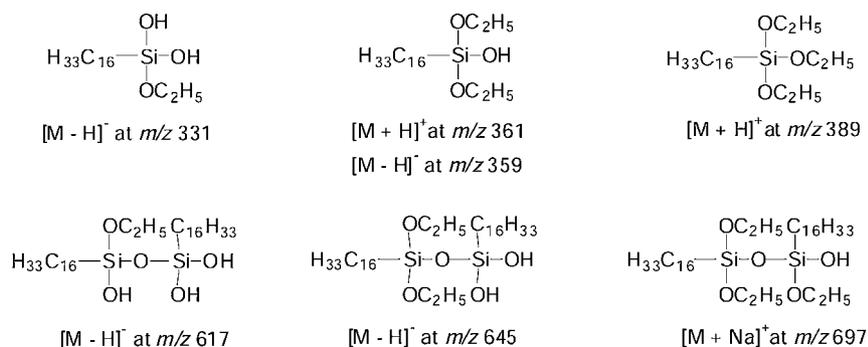
The ions of  $m/z$  1020, 978 and 936 are the ammonium adducts  $[M + NH_4]^+$  and those of  $m/z$  1003, 961 and 919 are the protonated molecules  $[M + H]^+$  of the non-, mono- and dihydrolysed disiloxane, respectively (Schemes 1 and 2).

Figures 1(b)–1(d) show the EASI mass spectra 2, 5 and 15 min after the application of NFP-1. These spectra reveal a clear trend in the course of polymerization; as the reaction proceeds, the abundance of hydrolysed species decreases compared with that of their non-hydrolysed analogues whereas the abundance of the tri- and tetrasiloxanes

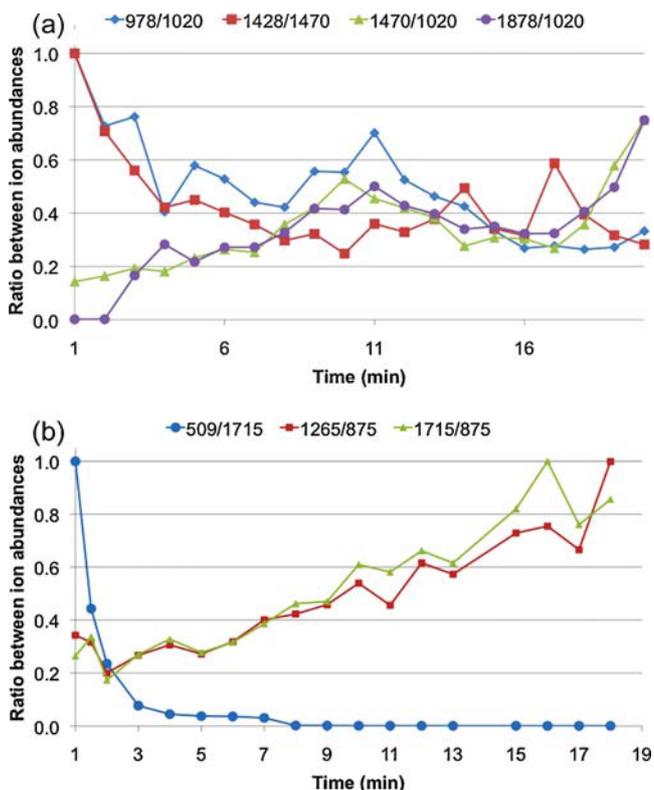
## NFP 1



## NFP 2



**Scheme 2.** Tentative structures of selected hydrolysates and condensates of *1H,1H,2H,2H*-perfluorooctyl triisopropoxysilane (NFP-1) and hexadecyl triethoxysilane (NFP-2) observed via EASI( $\pm$ )-MS monitoring.

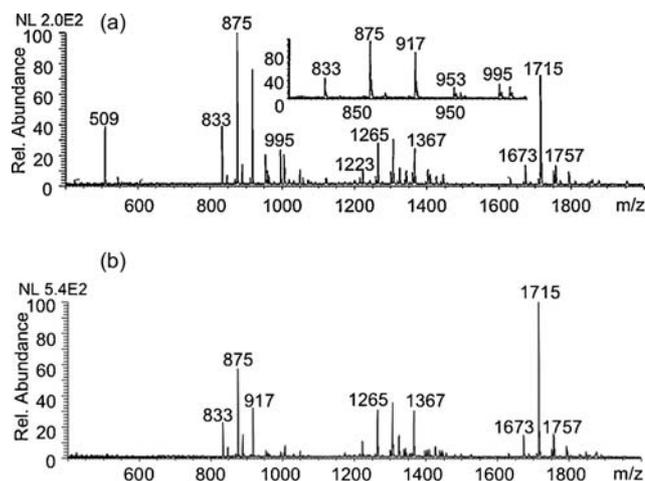


**Figure 2.** Plots for ion ratios as a function of time from (a) EASI(+)-MS and (b) EASI(-)-MS data of NFP-1 on glass. The ratios were normalized to 1 for the maximum ratio for each individual series.

increases compared with that of the lighter disiloxanes. Figure 2(a) illustrates this trend via the ratio between the abundances of the ions for the di-, tri- and tetrasiloxanes as a function of time. The abundance ratio of the ion of  $m/z$  978 for the monohydrolysed disiloxane to its non-hydrolysed analogue of  $m/z$  1020 decreases by about 70% over a period of 20 min. A similar tendency can be observed for the trisiloxanes via the abundance ratio between the ion of  $m/z$  1428 (monohydrolysed) and that of  $m/z$  1470 (non-hydrolysed). In addition, the ratio between the abundances of the trisiloxanes ( $m/z$  1470) or tetrasiloxanes ( $m/z$  1878) and the disiloxanes ( $m/z$  1020) increases by ca. 60–70%. The total ion abundance, designated as normalization level (NL) in the mass spectra, is fairly constant at around  $10^3$  counts throughout the experiment.

Figure 3 shows the EASI(-) mass spectra for the monitoring of the polymerization of NFP-1 on glass. In the negative ion mode, silane ( $m/z$  509), disiloxane ( $m/z$  875), trisiloxane ( $m/z$  1307) and now also tetrasiloxane ions ( $m/z$  1715) are clearly observed 1 min after application (Fig. 3(a)). The insert in Fig. 3(a) shows an expanded view of the disiloxane ion cluster where several types of ions can be observed.

The ion of  $m/z$  1005 is the formic acid adduct  $[M + \text{HCOO}]^-$ ; the ions of  $m/z$  995 and 953 and their respective A + 2 isotopologues are chlorine adducts  $[M + \text{Cl}]^-$  whereas the ions of  $m/z$  959, 917, 875 and 833 are the deprotonated molecules  $[M - \text{H}]^-$  of the mono-, di-, tri- and tetrahydrolysed disiloxanes, respectively. Figure 3(b) shows the spectrum 15 min after spraying. Significant changes can again be observed; the silane ion of  $m/z$  509 is



**Figure 3.** EASI(-)-MS of NFP-1 on glass 1 (a) and 15 (b) min after spraying on a glass surface. Insert (a): The ion of  $m/z$  1005 is the formic acid adduct  $[M + \text{HCOO}]^-$ ; the ions of 995 and 953 are chlorine adducts  $[M + \text{Cl}]^-$  of the mono- and dihydrolysed disiloxanes, while the ions of  $m/z$  959, 917, 875 and 833 are the deprotonated molecules  $[M - \text{H}]^-$  of the mono-, di-, tri- and tetrahydrolysed disiloxanes, respectively. Spectra obtained 2 and 5 min after spraying are shown in Fig. S-1 (Supporting Information).

no longer detected after 15 min whereas the abundance of the tri and tetrasiloxane ions of  $m/z$  1265 and 1715 have increased significantly over time (note that the total signal is increasing by a factor of ca. 3 during the experiment). The changes between the proportion of hydrolysed siloxanes and that of their non-hydrolysed analogues, as clearly seen via EASI(+)-MS monitoring, could not be followed by EASI(-)-MS since the non-hydrolysed oligomers do not seem to ionize well in the negative ion mode.

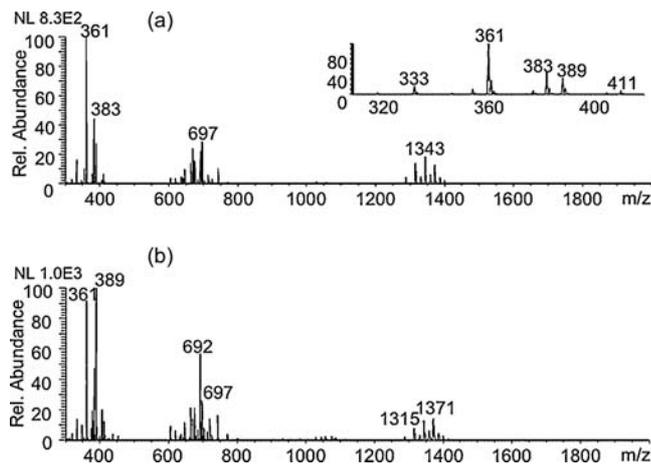
Figure 2(b) shows trends for the ratios between the abundances of selected ions from EASI(-)-MS data as a function of time. The ratio of the monohydrolysed silane ion ( $m/z$  509) to that of a dihydrolysed tetrasiloxane ion ( $m/z$  1715) decreases from 100 to 0 within the first 8 min of open atmospheric polymerization. The formation of heavier siloxanes is clearly visualized by a ca. 60% increase in the  $m/z$  1715/875 ratio.

Similar results for EASI( $\pm$ )-MS monitoring of NFP-1 were observed for other surfaces, namely filter paper and cotton (Figs S4–7, Supporting Information), but with an overall 2–4 times decrease in total ion abundance over time which is probably due to the absorbing nature of these two surfaces.

## NFP-2

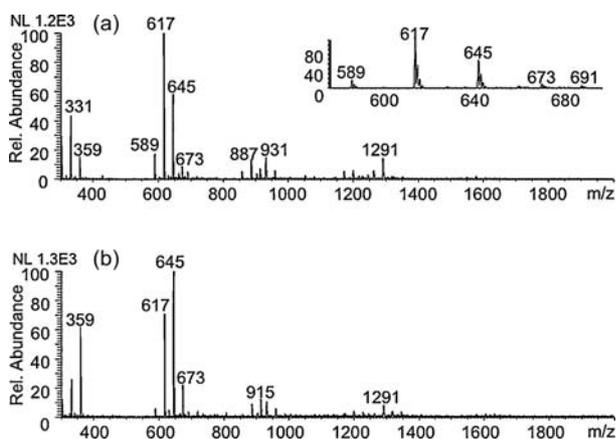
Figure 4(a) shows the EASI(+) mass spectrum of NFP-2 after application (1 min) to a glass surface. The ion clusters around  $m/z$  361 and 697 are assigned as the silanes and disiloxanes of hexadecyl triethoxysilane (Scheme 2). The ion cluster around  $m/z$  1343 are sodiated dimers  $[2M + \text{Na}]^+$  of the disiloxanes. The insert (Fig. 4(a)) shows an expanded view of the silane ion cluster; two ion series are observed with intervals of 28  $m/z$  units ( $\text{C}_2\text{H}_4$ ) corresponding to hydrolysis of an ethoxy group.

The ions of  $m/z$  411, 383 and 355 are  $[M + \text{Na}]^+$  species whereas those of  $m/z$  389, 361 and 333 are  $[M + \text{H}]^+$  forms of



**Figure 4.** EASI(+)-MS of NFP-2 on glass 1 (a) and 22 (b) min after spraying on a glass surface. Insert (a): The ions of  $m/z$  411, 383 and 355 are the sodium adducts  $[M + Na]^+$  whereas those of  $m/z$  389, 361 and 333 are  $[M + H]^+$  forms of the non-, mono- and dihydrolysed disiloxane, respectively. Spectra obtained 7 and 13 min after spraying are shown in Fig. S-2 (Supporting Information).

the non-, mono- and dihydrolysed disiloxane, respectively. No siloxanes higher than disiloxanes could be observed in the positive ion mode. Figure 4(b) shows the spectrum 22 min after application. The changes for NFP-2 are not as significant as for NFP-1 (Fig. 1) and seem to take place at a slower rate. For the silanes, the non-hydrolysed silane ( $m/z$  389) becomes dominant over time at the expense of the monohydrolysed analogue ( $m/z$  361). In addition, the abundance of the monohydrolysed disiloxane ( $[M + Na]^+$  of  $m/z$  697 and  $[M + NH_4]^+$  of  $m/z$  692) increasing relative to that of the silanes suggesting the formation of disiloxanes over time.



**Figure 5.** EASI(-)-MS of NFP-2 on glass 1 (a) and 22 (b) min after spraying on a glass surface. Insert (a): The ion of  $m/z$  691 is the  $[M + HCOO]^-$  adduct of the dihydrolysed disiloxane whereas those of  $m/z$  673, 645, 617 and 589 are the deprotonated molecules  $[M - H]^-$  for the mono-, di-, tri- and tetrahydrolysed disiloxanes. Spectra obtained 7 and 13 min after spraying are shown in Fig. S-3 (Supporting Information).

Figure 5(a) shows the EASI(-) mass spectra of NFP-2 1 min after application; the spectrum shows four ion clusters around  $m/z$  331, 617, 931 and 1291 representing the silanes, di-, tri- and tetrasiloxanes, respectively. The insert in Fig. 5(a) shows an expanded view of the disiloxane ion cluster; the ion of  $m/z$  691 is the  $[M + HCOO]^-$  adduct of the dihydrolysed disiloxane whereas those of  $m/z$  673, 645, 617 and 589 are the deprotonated molecules  $[M - H]^-$  for the mono-, di-, tri- and tetrahydrolysed disiloxanes, respectively. The spectrum after 22 min (Fig. 5(b)) shows that, for both the silanes and the disiloxanes, the monohydrolysed species ( $m/z$  359 and  $m/z$  645) are becoming increasingly more abundant whereas the dihydrolysed analogues are decreasing correspondingly. No indication of the formation of larger siloxanes could be observed.

The EASI-MS total ion current was also fairly constant in both positive and negative ion modes for NFP-2. EASI-MS monitoring for NFP-2 on cotton and filter paper surfaces was unsuccessful since it appears that the silanes and siloxanes in NFP-2 are much less prone to desorb and ionize via EASI( $\pm$ ) from these surfaces.

## CONCLUSIONS

Ambient mass spectrometry, as demonstrated here using EASI( $\pm$ )-MS to study the commercially available NFP coating products, is a useful tool for the direct and real-time monitoring of polymerization reactions occurring on surfaces at open atmosphere. Consumption of the monomers and the formation of heavier oligomers could be followed continuously over time, and reactive trends for different classes of reactants were also seen. EASI( $\pm$ )-MS has shown that, for both NFP-1 and NFP-2, polymerization in the open atmosphere makes the non-hydrolysed silanes/siloxanes dominant over time at the expense of their hydrolysed analogues. This polymerization trend can be rationalized by assuming a faster reaction rate for the homofunctional condensation reaction involving silanes with two hydroxyl groups than for the heterofunctional condensation reaction involving silanes with a hydroxyl group and an alkoxy group<sup>18</sup> (Scheme 1). A relatively constant ion current was observed during EASI( $\pm$ )-MS monitoring for both NFP-1 and NFP-2. This result seems to indicate, as expected, that the EASI spray samples chemicals from the very top layer of the nascent nanofilm. The polymeric nanofilm probably first forms at the area in direct contact with the glass surface leaving therefore a residual layer of less condensed material on top, which is then monitored by EASI-MS.

## SUPPORTING INFORMATION

Additional supporting information may be found in the online version of this article.

## Acknowledgements

We thank the Brazilian science foundations FAPESP, CNPq, FINEP, CAPES and the Working Environment Research Fund, Denmark for financial support.

## REFERENCES

1. Hench LL, West JK. *Chem. Rev.* 1990; **90**: 33.
2. Schmidt H. *J. Sol-Gel Sci. Technol.* 2006; **40**: 115.
3. Brinker CJ. *J. Non-Cryst. Solids* 1988; **100**: 31.
4. Schmidt H, Scholze H, Kaiser A. *J. Non-Cryst. Solids* 1984; **63**: 1.
5. Nørgaard AW, Wolkoff P, Lauritsen FR. *Chemosphere* 2010; **80**: 1377.
6. Nørgaard AW, Jensen KA, Janfelt C, Lauritsen FR, Clausen PA, Wolkoff P. *Environ. Sci. Technol.* 2009; **43**: 7824.
7. Alberici R, Simas R, Sanvido G, Romão W, Lalli P, Benassi M, Cunha I, Eberlin M. *Anal. Bioanal. Chem.* 2010; **398**: 265.
8. Haddad R, Sparrapan R, Eberlin MN. *Rapid Commun. Mass Spectrom.* 2006; **20**: 2901.
9. Haddad R, Milagre HMS, Catharino RR, Eberlin MN. *Anal. Chem.* 2008; **80**: 2744.
10. Eberlin LS, Abdelnur PV, Passero A, de Sa GF, Daroda RJ, de Souza V, Eberlin MN. *Analyst* 2009; **134**: 1652.
11. Haddad R, Catharino RR, Marques LA, Eberlin MN. *Rapid Commun. Mass Spectrom.* 2008; **22**: 3662.
12. Sawaya ACHF, Abdelnur PV, Eberlin MN, Kumazawa S, Ahn M-R, Bang K-S, Nagaraja N, Bankova VS, Afrouzan H. *Talanta* 2010; **81**: 100.
13. Alberici RM, Simas RC, de Souza V, de Sa GF, Daroda RJ, Eberlin MN. *Anal. Chim. Acta* 2010; **659**: 15.
14. Abdelnur PV, Eberlin LS, de Sa GF, de Souza V, Eberlin MN. *Anal. Chem.* 2008; **80**: 7882.
15. Simas RC, Catharino RR, Cunha IBS, Cabral EC, Barrera-Arellano D, Eberlin MN, Alberici RM. *Analyst* 2010; **135**: 738.
16. Figueiredo EC, Sanvido GB, Zezzi Arruda MA, Eberlin MN. *Analyst* 2010; **135**: 726.
17. Haddad R, Sparrapan R, Kotiaho T, Eberlin MN. *Anal. Chem.* 2008; **80**: 898.
18. Kazmierski K, Chojnowski J, McVie J. *Eur. Polymer J.* 1994; **30**: 515.
19. Sauer RO. *J. Chem. Ed.* 1944; **21**: 303.