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# Study of the acid hydrolysis of (3-methacryloxypropyl)trimethoxysilane by capillary electrophoresis–ion-trap mass spectrometry

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**Abstract**

The sol–gel method is a widely used technique for the synthesis of various functional coating films. Alkoxysilanes such as (3-methacryloxypropyl)trimethoxysilane (MEMO) are largely used as precursors for inorganic–organic hybrid sol–gel materials. Indeed, these compounds can form complex network, through hydrolysis and condensation reactions. The latter have to be perfectly controlled to obtain the required properties. In such a context, we have studied the potentialities of capillary electrophoresis–ion-trap mass spectrometry (CE–MS) coupling to resolve both separation and characterization of the synthesized compounds as a function of the hydrolysis time. The study of acid hydrolysis of MEMO was carried out as an example. After optimization of the running electrolyte in capillary zone electrophoresis (CZE) with UV detection, we characterized the synthesized compounds in CE–MS by using positive detection mode. The obtained resolution in CZE–UV was not entirely satisfactory because of the very closed charge/mass ratio of formed solute but also because of the interaction between the solutes and the capillary walls. Nevertheless, several oligomers were characterized in CE–MS. The absence of detection with regard to oligomers that possess higher molecular masses than octamer is discussed in this work.


*Keywords:* Methacryloxypropyltrimethoxysilane; Alkoxysilane

## 1. Introduction

Silica-based organic–inorganic hybrid polymers are more and more used as coating material. For example, they are used to obtain chemical sensors or hard optical glasses [1–4]. These polymers are often synthesized by the hydrolysis of alkoxysilanes. The latter involves condensations reactions that lead to complex network [4–6]. The degree of linking and cross-linking of this network influences the mechanical and chemical properties of the polymer. These properties can be controlled, for example, by varying the catalyst used (HCl, HF, $NH_3$, etc.) in the sol–gel process. Nevertheless, it appeared very important to study the evolution of the network as a function of time to obtain the suitable polymer properties [7]. For this purpose, the study of trialkoxysilane hydrolysis was carried out by several techniques like IR [8], Raman [9], NMR [6,10,11], mass spectrometry [10]. Unfortunately, the results obtained by these techniques appeared difficult to analyze because of hydrolysis mixture complexity. In order to characterize more easily the compounds synthesized during hydrolysis, gel permeation chromatography was used but the unsatisfactory resolution obtained did not lead to a good identification of hydrolysis products [5]. With the aim both to resolve separation problems and to characterize the products synthesized during the hydrolysis of alkoxysilane, we used the hyphenation of capillary electrophoresis to mass spectrometry (CE–MS). In this work, we show, as an example, the study of the acidic hydrolysis of (3-methacryloxypropyl)trimethoxysilane (MEMO) by CE–MS. This compound, that possesses chromophoric moieties, enabled us to disconnect separation and MS detection. Indeed, in a first time, we have optimized the resolution of hydrolysis products by CE, by using UV detection, and then we performed the analysis by CE–MS coupling.

## 2. Experimental

### 2.1. Chemicals

All solutions were prepared by using the 18 MΩ water produced by means of an Alpha Q purification system (Millipore, Bedford, MA, USA). (3-Methacryloxypropyl)

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trimethoxysilane (purity 98%) and hydrochloric acid (analytical grade, 37%) were purchased from Acros (Acros, Noisy-Le-Grand, France). The sodium tetraborate, ammonium acetate, sodium acetate, sodium iodide and cobalt acetate were of analytical purity and came from Aldrich (Sigma–Aldrich, Saint Quentin de Fallavier, France). All chemicals were used without further purification. The sodium dodecylsulfate (SDS; purity 98%) was provided by Sigma (Sigma–Aldrich. Methanol and propan-2-ol were of RS-HPLC purity and were obtained from Carlo Erba (Carlo Erba, Val de Reuil, France).

### 2.2. Apparatus

All analyses were carried out by using a P/ACE 2100 capillary electrophoresis system (Beckman-Coulter, Fullerton, CA, USA) modified for its hyphenation with MS detection. Acquisitions were performed by means of P/ACE 2000 software version 2.0 (Beckman-Coulter). A $HP^{3D}$ CE–electrospray ionization (ESI)-MS interface (Hewlett-Packard, Palo Alto, CA, USA) was used for the coupling. The mass spectrometer was an ESQUIRE-LC ion trap (Bruker, Wissembourg, France) that was controlled by the Esquire-LC NT software version 4.68 (Bruker). A single-syringe infusion pump (Cole-Parmer, Vernon Hills, IL, USA) equipped with 250 or 500 μl Hamilton gastight syringes (Hamilton, Bonaduz, Switzerland) delivered the sheath liquid. The nebulizing gas (nitrogen) was generated by a Nitrox generator model UHPLCMS18 (Domnik Hunter, Durham, UK). The air provided to this nitrogen generator was produced by a JUN'AIR compressor model 2000-40B (Jun-air, Nørresundby, Denmark) equipped with a Cirrus refrigeration dryer model CGB 0025 purchased from Domnick Hunter. Nitrogen was also used as drying gas. It was heated to 300 °C and its flow rate was 300 l $h^{-1}$. The samples were systematically injected in hydrodynamic mode (injection pressure: 0.5 psi, i.e. 3.4 kPa) and their analysis was achieved on fused silica capillaries of 57 cm (50 cm effective length when UV detection is used) × 50 μm i.d. × 375 μm o.d. purchased from Thermo Finnigan (Les Ulis, France). The capillary tips are cut by means of a Shortix capillary column cutter (Hewlett-Packard). In CE–MS coupling, the nebulizing gas was stopped during the injections to prevent aspiration effect. The analyses were carried out at 25 °C and the pH of the running electrolytes was measured before utilization at this temperature with a model Φ pH meter (Beckman-Coulter). Finally, the electrolytes were systematically degassed by sonification by means of an Ultrasonic Cleaner model 2510 (Branson Ultrasonics, Danbury, CT, USA).

### 2.3. Hydrolysis conditions and sample preparation

MEMO was hydrolyzed at 25 °C with 1.5 mol equivalent of water at pH 1.0 with hydrochloric acid as catalyst. Thus, 0.1 M HCl (810 μl) was poured slowly into pure MEMO (2.48 g) by using a 5 ml polypropylene vial as reactor. During this adding, the mixture was rapidly stirred.

A sample was taken after different hydrolysis times and then diluted 200- or 2000-fold with methanol, respectively, for CE–MS analyses or for flow injection analyses (ESI-MS analyses). The use of methanol for the dilutions appears to stop or to slow down hydrolysis and condensation reactions because successive analyses on a given sample prepared, as previously mentioned, lead to the same results in CE or CE–MS. We can note that after about 19 h of reaction, two liquid phases appeared in the hydrolysis mixture but we did not observed any solid material. We have analyzed by capillary electrophoresis (CZE) and CE–MS the supernatant but no oligomer has been found. This phase was containing essentially water but also methanol that is a byproduct of hydrolysis and condensation reactions. The analyzed samples were taken into the other phase that contained only the hydrolysis products.

### 2.4. Rinsing procedure

Some authors used the hydrolysis of alkoxysilane to coat fused silica capillaries and modify the electroosmotic flow in CZE [12,13]. Other works pointed out the potentialities of alkoxysilane hydrolysis to prepare stationary phases for open-tubular electrochromatography by using silica capillaries [14] or even chips [15]. Consequently, the hydrolysis products might modify the electroosmotic flow during the analysis and lead to poor repeatability. So, in order to obtain a satisfactory repeatability of the electroosmotic flow (EOF) we used the following rinsing procedure of the CE capillary:

(i) between each analysis: water (2 min), then running electrolyte (5 min);
(ii) every eight analyses: 0.1 M NaOH (60 min), then water (10 min).

We determined the obtained repeatability on the electroosmosis migration time by injecting eight times 0.05% dimethyl sulfoxide (DMSO) in the considered analytical conditions. This varied from 0.4 to 2% as a function of the analysis except for the analyses carried out after 19 h of hydrolysis. Indeed, this rinsing procedure enabled to regenerate the capillary wall between the analyses but did not prevent the adsorption of some oligomers. By analyzing several times the mixture obtained after 19 h of hydrolysis, we observed more fluctuations of the EOF.

## 3. Results and discussion

The hydrolysis of alkoxysilane, like MEMO, lead to complex mixture because of the great number of reactions that occur during the sol–gel process. The analysis of this complex mixture can be carried out by using CZE or non-aqueous (NACE) if the synthesized compounds can be ionized or can form charged complex. In these cases, the separation is based on charge/mass ratio. In contrast,

if the hydrolysis compounds cannot be charged or if their charge/mass ratio is too low, the analysis may be performed by micellar electrokinetic chromatography (MEKC). However, electrospray ionization being incompatible with the presence of surfactants, several approaches were developed to prevent the micelles from reaching mass spectrometer. Among them, there is partial-filling MEKC (PF-MEKC) that was first described by Valtchera et al. [16] and used successfully in CE–MS coupling [17–20].

### 3.1. Study of the MEMO hydrolysis by CE–UV detection

#### 3.1.1. NACE analyses

First, we tried to separate the hydrolysis products by NACE because organic media are very interesting as regards MS detection. Moreover, Matejka et al. [10] analyzed the hydrolysis products of a MEMO analog, i.e. glycidyloxypropyltrimethoxysilane (GLYMO) by ESI-MS using such organic media. Indeed the authors performed the MS analyses in positive detection mode by forming adducts with $Na^+$ cation in tetrahydrofuran (THF). The authors used $I^-$ as counter-ion for $Na^+$. So, in this work we wanted to analyze the MEMO hydrolysis medium in NACE by using $Na^+$ or $Co^{2+}$ cations in order to form positively charged complexes within the CE capillary. For this purpose, two electrolytes were prepared by using pure methanol as solvent. One was containing $2 \times 10^{-2}$ M $CH_3COONa$ and the other $2 \times 10^{-2}$ M $Co(CH_3COO)_2$. We can note that in a first approach we used $I^-$ as counter-ion for $Na^+$ cation taking into account the study previously mentioned [10] but when we replaced this anion by $CH_3COO^-$ we obtained the same results. We can note that methanol is a good organic solvent for NACE nevertheless it may react with Si–OH bonds and thus modify the structure of the synthesized compounds. Consequently, the analysis time had to be short to prevent this side reaction.

Non-hydrolyzed MEMO and MEMO hydrolyzed during 19 h were injected at the anodic side of the capillary and analyzed in NACE by using the two electrolytes described earlier. Unfortunately, all the studied compounds migrated with electroosmosis. Consequently, we were not able to form charged complexes in NACE by using these conditions.

#### 3.1.2. CZE analyses

Taking into account these results, we decided to analyze the hydrolysis media in CZE by ionizing the hydroxysilane bond of the synthesized products at higher pH than their p$K_a$. These p$K_a$ values depend on the alkoxysilane substituents. Unfortunately, there are no quantitative published data for deprotonation of alkyl-substituted silanols [21]. Nevertheless, we analyzed the MEMO hydrolysis products at pH >6, i.e. above the p$K_a$ of silicate in aqueous solution. We tested the following two electrolytes: $5 \times 10^{-3}$ M $CH_3COONH_4$ (pH 6.7) and $5 \times 10^{-3}$ M $Na_2B_4O_7$ (pH 9.2).

Although the MS detection sensitivity should be improved by using volatile electrolyte, e.g. $(NH_4)_2CO_3$, we choose the sodium tetraborate to perform the analyses at pH 9.2. Indeed, we wanted to prove that the orthogonal interface used in this work allowed us the utilization of non-volatile electrolytes without polluting the mass spectrometer. Samples taken from the hydrolysis medium as a function of reaction time were injected at the anodic side of the CE capillary and analyzed in CZE with the two electrolytes described earlier. The obtained results argued that the synthesized compounds were not ionized at pH 6.7 because they migrated nearly with electroosmosis whatever the reaction time. Consequently, their charge/mass ratio were too low to allow their separation in CZE.

In contrast, when sodium tetraborate was used as electrolyte, three electrophoretic peaks were obtained by studying the hydrolysis medium during the first 19 h of reaction (see Fig. 1): one migrated with the electroosmotic flow and two broad peaks appeared later.

Consequently the products corresponding to these broad peaks were negatively charged at pH 9.2. Unfortunately, the latter were not entirely resolved. Obviously, we verified that these results were not due to the hydrolysis of MEMO during the separation. The electropherogram obtained by analyzing non-hydrolyzed MEMO with sodium tetraborate as running electrolyte argued that no hydrolysis occurred within the capillary at pH 9.2 because this solute migrated with the electroosmotic flow.

According to these first results, we attempted to improve the resolution of the mixture by decreasing the electroosmotic flow in order to increase the electrophoretic path of the analyzed solutes. For this purpose, we tried two different strategies. The former was based on the increasing of the ionic strength of the electrolyte by varying the tetraborate concentration from $5 \times 10^{-3}$ to $2 \times 10^{-2}$ M. In a second approach, we introduced increasing percentages of propan-2-ol within the electrolyte ($5 \times 10^{-3}$ M $Na_2B_4O_7$). These percentages ranged from 0 to 40% (v/v). On the whole, these two approaches led to the same results. As expected, the electroosmotic flow was decreased, especially when 40% of propan-2-ol was introduced in the electrolyte, but the resolution of the peaks corresponding to the formed products was not improved. Moreover, the decrease of electroosmotic flow led to longer analysis times and so to the broadening of electrophoretic peaks that reduced detection sensitivity. Taking into account these considerations, $5 \times 10^{-3}$ M $Na_2B_4O_7$ appeared to be the best electrolyte for CZE separations. Besides, its low concentration was compatible with MS sensitivity if one considers the CE–MS coupling. So, the study of the MEMO hydrolysis was undertaken by CZE using $5 \times 10^{-3}$ M $Na_2B_4O_7$ as electrolyte.

It is clear from Fig. 1 that the hydrolysis medium changed dramatically during the first minutes of reaction. Thus, after 10 min of hydrolysis, the analyzed mixture contained less than 25% of non-hydrolyzed MEMO if we consider the height of the peak that migrated with electroosmosis. So the hydrolysis kinetic appeared very fast. We detected at least two main compounds despite the poor resolution.

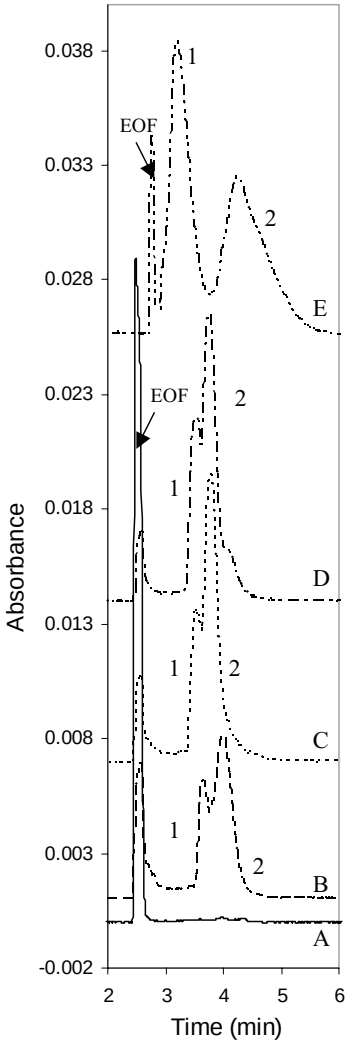


Fig. 1. CZE analyses of the hydrolysis medium as a function of time (EOF: electroosmotic flow; 1 and 2: synthesized oligomers). Operating conditions: sample, hydrolysis medium diluted 200-fold with methanol; hydrolysis times, 0 min (A), 10 min (B), 60 min (C), 120 min (D), 19 h (E); fused silica capillary, 57 cm total length (50 cm effective length) × 50 μm i.d. × 375 μm o.d.; electrolyte, $[Na_2B_4O_7] = 5 \times 10^{-3}$ M (pH 9.2); temperature, 20 °C; hydrodynamic injection during 5 s; applied voltage, +25 kV; cathodic detection at 214 nm.

In contrast, after 10 min of hydrolysis, we were not able to see significant changes between the electropherograms except if one considers the electropherogram obtained after 19 h of hydrolysis (Fig. 1E). Indeed, the compounds detected were much closer to electroosmosis than those detected in Fig. 1B–D. Consequently, these compounds possess smaller charge/mass ratio than the compounds detected for shorter hydrolysis time. This evolution can be due to condensation reactions that form larger oligomers with less hydroxysilane groups. Moreover, the latter can interact with the capillary wall. This adsorption can explain the EOF fluctuations observed by comparing Fig. 1D and E. In order to have a better understanding of this hydrolysis, we attempted to improve the resolution of the hydrolysis medium by using a separation method based on hydrophobicity. We performed the separation by classical MEKC, i.e. by filling the total length of the CE capillary with electrolyte that contained micelles.

### 3.1.3. MEKC analyses

We introduced relatively low concentrations of SDS in $5 \times 10^{-3}$ M $Na_2B_4O_7$ to perform the analyses in nearly the same analytical conditions than those used for PF-MEKC, i.e. with solute–micelle interactions restricted by a small micellar volume. By varying SDS concentration from 0 to $15 \times 10^{-3}$ M, we analyzed the MEMO hydrolyzed during 2 h. The best resolution was obtained by introducing $5 \times 10^{-3}$ M SDS in the electrolyte. This concentration was probably below the SDS critical micellar concentration in such a medium. So, the change of resolution compared to CZE might result from solvatophobic interactions between SDS and the analyzed solutes. Unfortunately, the obtained resolution was only a little better than the one obtained in CZE.

So, taking into account the difficulties to optimize PF-MEKC and the low resolution improvement compared to CZE, we decided to use CZE for the CE–MS analysis of the hydrolysis medium.

## 3.2. Study of the MEMO acidic hydrolysis by CE–MS

The separation of the compounds synthesized during the MEMO hydrolysis was carried out by CZE without any organic modifier in the running electrolyte. First we optimized the MS signal by flow injection analysis before performing the analyses by CE–MS. For this purpose, we prepared the following solutions: solution A, $5 \times 10^{-3}$ M $Na_2B_4O_7$ (pH 9.2) (background salt); solution B, water–propan-2-ol (50:50, v/v); and solution C, the hydrolysis medium diluted 200-fold or pure methanol.

The solutions analyzed by ESI-MS were obtained by mixing the solutions A, B and C, respectively, in a 9:9:2 (v/v/v) ratio.

We have delivered theses solutions to the nebulizer under a 3 μl $min^{-1}$ flow rate in the proportions reported previously then we have optimized the MS conditions. Although the compounds formed during the hydrolysis might be negatively charged in basic medium, only positive detection gave significant signal. All detected compounds appeared as cationic adducts with $Na^+$ cation. The optimized MS conditions were used to study by CE–MS the evolution of the hydrolysis medium during 1 week. This coupling is used to avoid competition problems during electrospray ionization and to simplify the MS spectra. The analyses corresponding to the more significant changes of the hydrolysis mixture composition are reported in Fig. 2. The proposed structure of the compounds detected during these analyses is presented in Fig. 3.

In Fig. 2, the electroosmosis was marked in accordance with the evolution of the current intensity measured in CE. Its migration time was about 4 min so peak 1 seems to

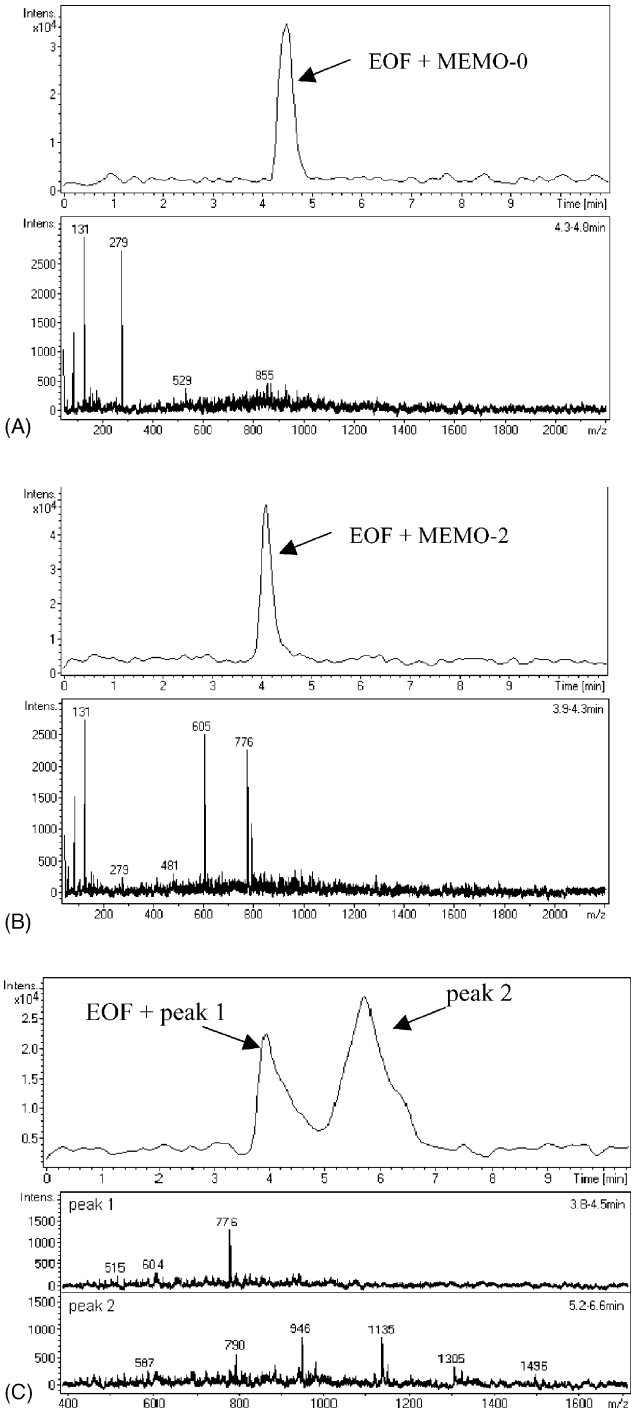


Fig. 2. CE–MS analyses of the MEMO hydrolysis medium as a function of reaction time. Reconstructed ion electropherograms and corresponding mass spectra obtained in positive detection mode. Reaction times: 0 min (A); 2 min (B); 19 h (C). EOF: electroosmotic flow; MEMO-0, MEMO-2, and peaks 1 and 2 correspond to the synthesized oligomers. Operating conditions: CE, fused silica capillary 57 cm × 50 μm i.d. × 375 μm o.d.; electrolyte, $5 \times 10^{-3}$ M $Na_2B_4O_7$ (pH 9.2); temperature, 20 °C; applied voltage, +15 kV; sample, hydrolysis medium diluted 200-fold with methanol; injection time, 5 s (hydrodynamic mode); sheath liquid, water–propan-2-ol (50:50, v/v); flow rate, 3 μl $min^{-1}$; MS, positive detection mode; nebulizing gas pressure, 12 psi; drying gas flow rate, 300 l $h^{-1}$; drying gas temperature: 300 °C; $U_{skimmer1} = 60$ V; $U_{cap} = -4200$ V; scan range, 50–2200.

co-migrate with EOF. So, peaks 1 and 2 mentioned in this figure appeared to correspond, respectively, to the peaks marked 1 and 2 in Fig. 1. Concerning the non-hydrolyzed MEMO (see Fig. 2A), the obtained results were consistent with those obtained from previous CZE analyses. In fact, only one peak was detected on the reconstructed ion electropherogram. However, two compounds were observed on the mass spectrum. The peak at *m/z* 131 appeared to be the methacrylate ion resulting from collision-induced dissociation due to skimmer voltage [22]. This origin was proved by varying skimmer voltage in ESI-MS analyses. The second detected ion at *m/z* 279 might result from a first hydrolysis of methoxysilane group as we can see in Fig. 3. We have noted previously that the experimental conditions used in CZE did not modify the charge of MEMO because the non-hydrolyzed MEMO migrated with electroosmosis. So, in such conditions, the observed first hydrolysis of methoxysilane group, leading to hydroxysilane group, was only due to electrospray ionization.

Concerning the analysis of the reaction mixture obtained after 2 min of reaction (see Fig. 2B), the peak at *m/z* 131 was again observed on the mass spectrum. On the other hand, the two peaks at *m/z* 605 and 776 correspond, respectively, to the structures of trimer and tetramer that are described in Fig. 3. It is important to note that these compounds were not separated in CZE although their masses are different.

At last, the electropherogram corresponding to the analysis of the reaction mixture obtained after 19 h of hydrolysis showed two peaks (Fig. 2C). Several ions with different *m/z* ratio were detected in mass spectrometry for each of these peaks. Keeping with the basis of CZE separation, the second broad peak might correspond to compounds that possessed higher charge/mass ratio than the compounds migrating more rapidly. However, as we can see in Fig. 3, the octamer (*m/z* 1498) was detected at 6 min despite the fact that is was not bearing any charge (no hydroxysilane group). On the contrary, trimer and tetramer migrated at about 4 min although there were bearing potentially charged hydroxysilane groups. To explain this migration order, we assume that the larger oligomers may interact more strongly with the capillary wall than the smaller oligomers. If so, the larger oligomers may have the higher migration times. The interactions between the larger solutes and the capillary wall may explain the decrease of the electroosmotic flow that we have observed in Fig. 1. Nevertheless, it appeared that the nature of the hydrolysis products changed as a function of time although no significant change was observed on migration times. All the ions detected as a function of the hydrolysis time are gathered together in Table 1.

We can make the following comments on these tabulated results:

(1) First, methacrylate ion (*m/z* 131) was detected whatever the hydrolysis time. As mentioned previously, it resulted from collision-induced dissociation. Nevertheless, its abundance decreased with the hydrolysis time.

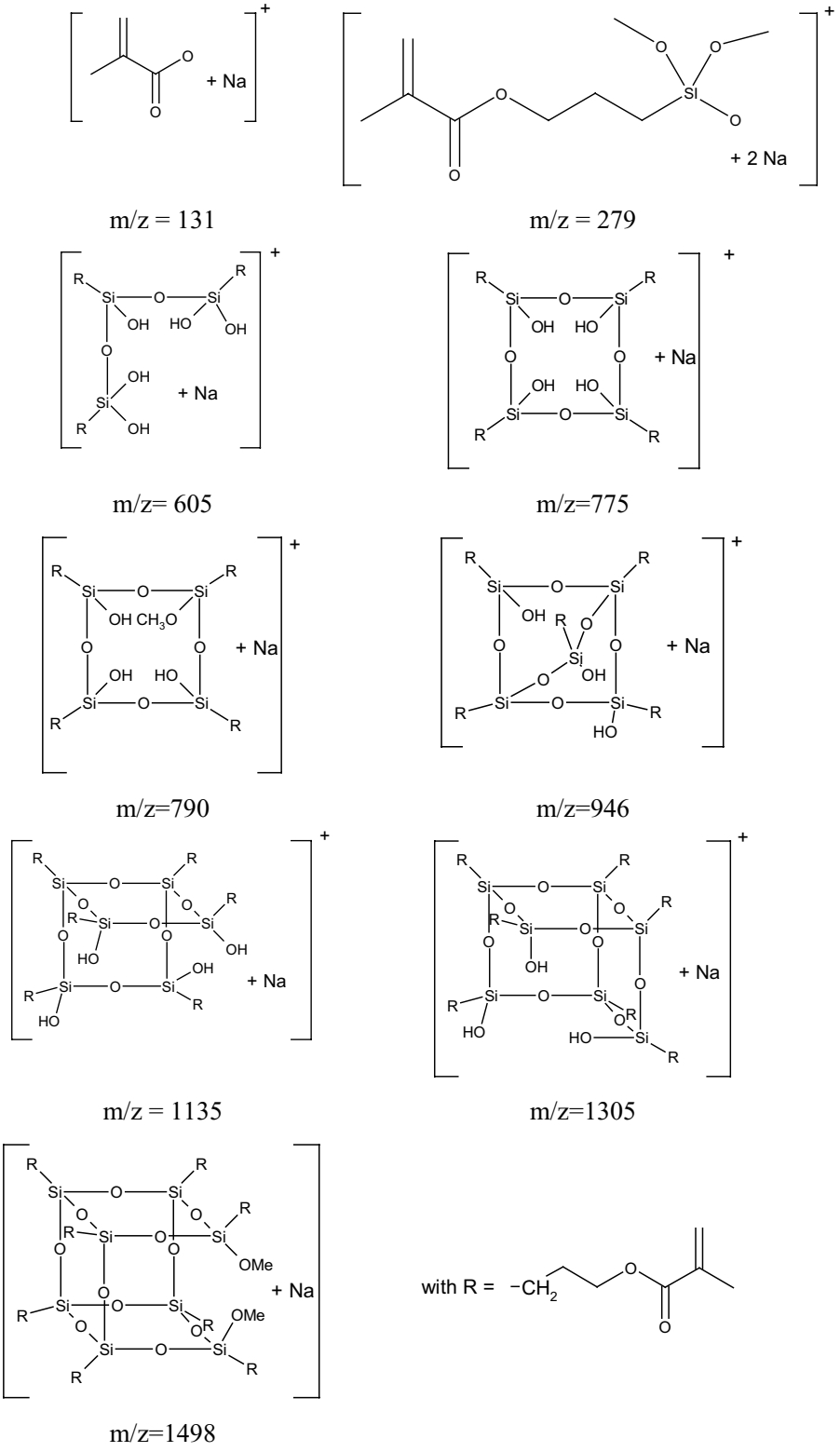


Fig. 3. Proposed structures corresponding to the peaks observed by CE–MS.

Table 1
Comparative study of ions detected in the hydrolysis medium as a function of hydrolysis time

| m/z | Hydrolysis time | | | | | | | Migration time of the main observed ions |
|---|---|---|---|---|---|---|---|---|
| | 0 min | 2 min | 5 min | 10 min | 30 min | 1 h | 19 h | |
| 131 | X | | | | | | | 4 and 6 min |
| 279 | X | | | | | | | 4 min |
| 605 | | X | | | | | | |
| 776 | | X | | | | | | |
| 946 | | | X | | | | | 6 min |
| 1135 | | | | X | | | | |
| 1305 | | | | | X | | | |
| 1496 | | | | | X | | | |

X: present at the considered hydrolysis time.

Table 2
Evolution of relative abundance of the synthesized oligomers as a function of hydrolysis time

| Hydrolysis time | Relative area (%) | | | | | |
|---|---|---|---|---|---|---|
| | Trimer | Tetramer | Pentamer | Hexamer | Heptamer | Octamer |
| 2 min | 44 | 56 | 0 | 0 | 0 | 0 |
| 5 min | 43 | 57 | 0 | 0 | 0 | 0 |
| 10 min | 28 | 61 | 11 | 0 | 0 | 0 |
| 30 min | 25 | 55 | 20 | 0 | 0 | 0 |
| 60 min | 20 | 72 | 4 | 4 | 0 | 0 |
| 19 h | 1 | 21 | 25 | 23 | 23 | 8 |

(2) Secondly, the adduct corresponding to the first hydrolysis of a methoxy group (*m*/*z* 279) disappeared from the hydrolysis medium after 5 min of reaction. It suggested that non-hydrolyzed MEMO disappeared very quickly from the mixture showing that the hydrolysis reaction is very rapid.
(3) Thirdly, ions corresponding to the hydrolysis of more than one methoxysilane group were not detected in the reaction medium. It may argue that condensations occurred during hydrolysis and led rapidly to oligomers. Two of them at *m*/*z* 605 and 776 were detected after only 2 min. After 10 minutes of hydrolysis, pentamers were observed through an ion at *m*/*z* 946. In contrast, hexamer (*m*/*z* 1135) appeared about 1 h later. Lastly, heptamer (*m*/*z* 1305) and octamer (*m*/*z* 1496) appeared after 19 h of hydrolysis.

We wanted to quantify the main changes within the hydrolysis medium despite: (i) the possible total adsorption of some larger oligomers; (ii) the difference of ionization process as a function of the oligomer structure; and (iii) and the variation of the detection sensitivity as a function of the *m*/*z* ratio for a given scan range with an ion-trap spectrometer. Thus, we tabulated together the obtained results as regards the evolution of the relative abundance of the formed compounds in Table 2.

As we can see in Table 2, until 60 min of hydrolysis, tetramer was the more abundant ion. Consequently, condensation reactions appeared very rapid in a first time but led to rather small oligomers like trimers and tetramers. Then, these condensations carried on to form pentamer after about 10 min. The synthesis of higher-molecular-mass oligomers was obviously slower because we were able to detect significant amounts of heptamers and octamers only after 19 h of hydrolysis.

## 4. Conclusion

CE–MS coupling was used to study the hydrolysis of MEMO. The separation optimization of the synthesized compounds was first performed by CE–UV detection. Despite the unsatisfactory resolution, CE–MS coupling appeared to simplify the mass spectra obtained elsewhere by flow injection analysis (ESI-MS). Thus, our results evidenced that MEMO hydrolysis was very rapid and involved condensation reactions. These reactions led to oligomers that possess at most eight MEMO units. In fact, we were not able to detect oligomers larger than octamers even after 1 week of hydrolysis. We assume that the absence of detection of these compounds originated from: (i) competition phenomena during ESI that we can attribute to the co-migration of the formed compounds; (ii) from the low volatility of higher-molecular-mass oligomers; and (iii) or from their strong interactions with the capillary wall that not allow their migration. In order to prevent competition problems during ESI, the resolution should be improved. Nevertheless, if the hydrolysis lead to oligomers of different

molecular mass, these compounds have probably about the same charge/mass ratio that is relatively low. Consequently it appeared very difficult to separate these compounds by CZE. We attempt now to separate and characterize larger formed compounds than octamers within the hydrolysis medium by capillary electrochromatography–MS coupling in order to have a better understanding of this hydrolysis process.

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