International Journal of Mass Spectrometry 285 (2009) 78–85

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

ESI-MS investigation of the polymerization of inorganic polymers

Morten E. Simonsen, Erik G. Søgaard*

Aalborg University, Esbjerg Institute of Technology, Section for Chemical Engineering, Niels Bohrs Vej 8, 6700 Esbjerg, Denmark

ARTICLE INFO

Article history:
Received 1 April 2009
Accepted 28 April 2009
Available online 6 May 2009

Keywords:
ESI-MS
Inorganic polymer
Microsilica

ABSTRACT

In this work the polymerization of inorganic polymers synthesized from microsilica and mineral base (KOH or NaOH) was investigated using electro spray ionisation mass spectrometry (ESI-MS). The investigation was conducted in both negative and positive scanning mode enabling detection of both positive and negative charged silicate clusters. Moreover dynamic light scattering (DLS) was used to verify the polymerization model. Similarly, silicate species were identified in the reaction solution of inorganic polymers synthesized from KOH and NaOH. The most intensive peak in the mass spectra was assigned to a dehydroxylated dimer (155 m/z). Moreover a range of different silicate species consisting of 3–5 silicon atoms was identified. These species were found most likely to appear in the reaction solution in the form of polyhedras. The evolution in the intensity of the molecule ions in the reaction solution of inorganic polymers showed that the dissolution/polymerization reaction was slower when NaOH was used compared to KOH.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The development of inorganic polymers is a new promising technology that may be used in many applications. The inorganic polymer reported here has been synthesized by a sol–gel process in which the silica precursor is formed in-situ by dissolution of fumed silica particles in alkaline solution. The silica species are assumed to polymerize through condensation reaction resulting in formation of oligomers (dimers, trimers). The size and number of oligomers in the system increase until they extend throughout the solution resulting in formation of a gel. Another difference between the present inorganic polymer and a standard sol–gel product is the presence of partially dissolved or undissolved particles. Depending on the preparation method, the inorganic polymers can exhibit a wide variety of properties, including high compressive strength, fire resistance and low thermal conductivity [1,2].

The dissolution of fumed silica under alkaline conditions can be expressed by the following reactions depending on pH.

$$SiO_2 + 2H_2O \rightarrow H_4SiO_4 \quad (1)$$

$$SiO_2 + 2H_2O + OH^- \rightarrow H_3SiO_4^- \quad (2)$$

$$H_3SiO_4^- + OH^- \rightarrow H_2SiO_4^{2-} + H_2O \quad (3)$$

$$SiO_2 + 2OH^- \rightarrow H_2SiO_4^{2-} \quad (4)$$

Panagiotopoulou et al. [3] studied the dissolution of different industrial aluminosilicate minerals and by-products and reported that the extent of dissolution was higher when NaOH instead of KOH was used. It was suggested to be due to the smaller size of Na^+ which can better stabilize the silicate monomers and dimers present in the solution, thus enhancing the minerals dissolution [4,5]. The size of the cation is also reported to affect the morphology. Na^+ displays strong ion-pair formation with smaller silicate oligomers, whereas K^+ favors the formation of larger oligomers. As a result more polymer precursors exist resulting in better setting and stronger compressive strength when KOH is used compared to polymers synthesized in NaOH solutions [6]. In addition, the fact that K^+ has a smaller hydration sphere than Na^+ allows denser polycondensation resulting in an increase in the overall strength of the material [7].

In order to control the synthesis of the inorganic polymer, it is necessary to understand the stepwise transition from monomer to oligomers and finally bulk material. Mechanisms of the first steps of sol–gel processes involving silica alkoxide precursors are fairly well known. It is generally argued that hydrolysis proceeds by bimolecular nucleophilic displacement reactions involving pentacoordinate intermediates or transition states [8]. By analogy with carbon chemistry, siliconium ions $Si(OR)_3^+$ have been suggested as possible intermediates [8]. Only very few techniques are suited for such analysis, such as NMR spectroscopy for selected nuclei [9]. However, the data acquisition may in some cases take too long in order to study polycondensation reactions [10]. Mass spectrometry has also successively been used in the investigation of hydrolysis and condensation of different precursors [9,11–15].

In this work the polymerization of inorganic polymers synthesized from microsilica and mineral base was investigated using electrospray ionisation mass spectrometry (ESI-MS). ESI-MS allows acquisition of mass spectra directly from aqueous samples; its

* Corresponding author. Tel.: +45 9940 7622; fax: +45 9940 7710.
E-mail address: egs@aaue.dk (E.G. Søgaard).

1387-3806/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2009.04.010

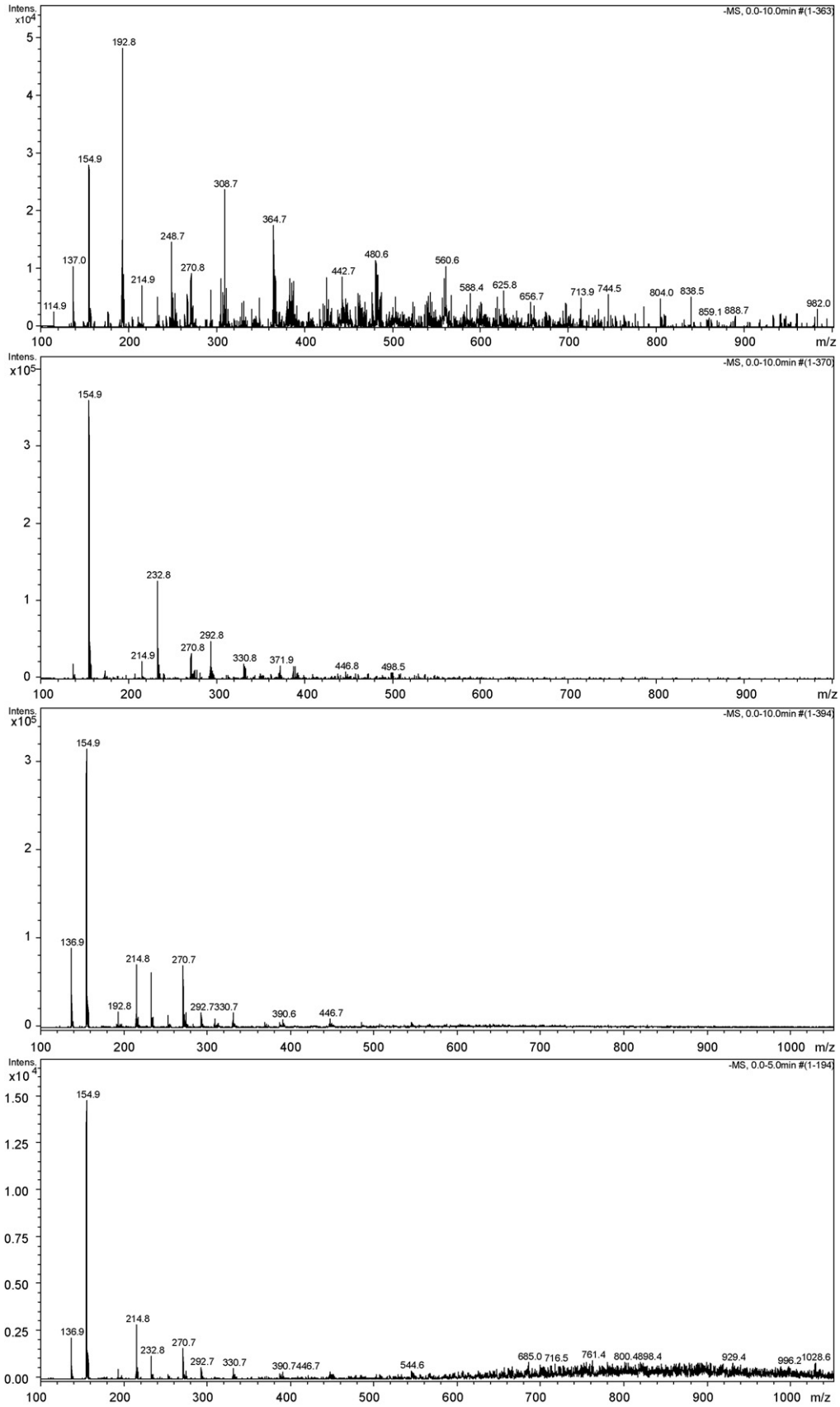

Fig. 1. ESI-MS spectra of the KOH based inorganic polymer reaction solution in negative scanning mode optimized in the spectral region around 500 *m*/*z*, (a) after 15 min, (b) 2 h, (c) 8 h, and (d) after 12 h mixing.

soft character minimizes fragmentation, leaving mostly unaltered species in the solution [16]. The stoichiometries of these species and their relative abundances can be determined from the m/z values and from the relative intensities of the molecular peaks, respectively.

In previous studies, ESI-MS has been used to study the polycondensation of TEOS ($Si(OC_2H_5)_4$). It was found that the polycondensation reaction was initiated by protonated molecules. Furthermore, $Si(OC_2H_5)_3^+$ molecule ions were identified although the intensity was considerably lower [17]. In addition ESI-MS has been used to study the polycondensation reactions of TMOS and TEOS in water. It was found that the formed oligomers were independent on the alkoxy group of the silicate precursor. Moreover, it was reported that the solution changed over time from initially consisting of silicate chains to polyhedras [11]. Similar silicate structures have also been reported in alkaline solutions in the presence of amines acting as a structure directing agent [9]. In that study besides the ESI-MS also ^{29}Si NMR were used to confirm the results.

In this study the polymerization of an inorganic polymer was investigated using ESI-MS. The investigation was conducted in both negative and positive scanning mode enabling detection of both positive and negative charged silicate species.

2. Material and methods

An inorganic polymer was prepared by mixing 250 g amorphous silica (Microsilica U 983, Elkem) with 250 ml 4 M KOH solution. The obtained slurry was mixed using a magnetic stirrer throughout the experiment in order to obtain homogenous samples. The samples for the ESI-MS investigation were obtained by centrifugation of 50 g of slurry for 10 min at 6000 rpm. The liquid part of the sample was filtrated using a 0.45 μm filter and diluted 1:1000 in distilled water in order to avoid clogging of the capillary in the ESI-MS. The pH of the samples after dilution was between 10 and 11. The ESI-MS spectra were recorded using a LC-MSD-Trap-SL spectrometer from Agilent Technology. The dry temperature was set at 325 °C and the dry gas flow (N_2) was 5 L/min. The capillary exit voltage was 166 V. The solution was injected into the ESI-MS at a flow-rate of 0.3 μl/min. The ESI-MS spectra of the inorganic silicate polymers were recorded in both positive and negative scanning mode in the spectral region 50–2200 m/z. ESI-MS spectra of the diluted samples were obtained over a period of 24 h. Similar investigations were conducted with an inorganic polymer synthesized using 4 M NaOH instead of KOH.

Dynamic light scattering (DLS) was used to follow the evolution in particle size during the polymerization. The samples were prepared as described in the case of the ESI-MS investigation. The particle size was measured using a DLS instrument obtained from Photocor Instruments, Inc. consisting of a photon counting unit (PMT), photocorrelator, and a 633 nm 35 mW laser (JDS Uniphase).

3. Results and discussion

3.1. KOH based inorganic polymers

The mass spectrum recorded 15 min after mixing in negative scanning mode is shown in Fig. 1a. The initial mass spectrum shows numerous peaks in the region from 100 to approximately 1000 m/z. The two most intensive peaks in the mass spectra located at 155 and 193 m/z can be assigned to dehydroxylated dimers ($Si_2O_3(OH)_3^-$ and $Si_2O_3(OK)(OH)_2^-$). The assigned molecule ions were confirmed by the isotopic pattern of the elemental composition of the ion. The fact that the distance between the lines in the isotopic pattern is 1 m/z suggests that the clusters have a unit negative charge ($z = -1$). All molecule ions were found as single negatively charged species,

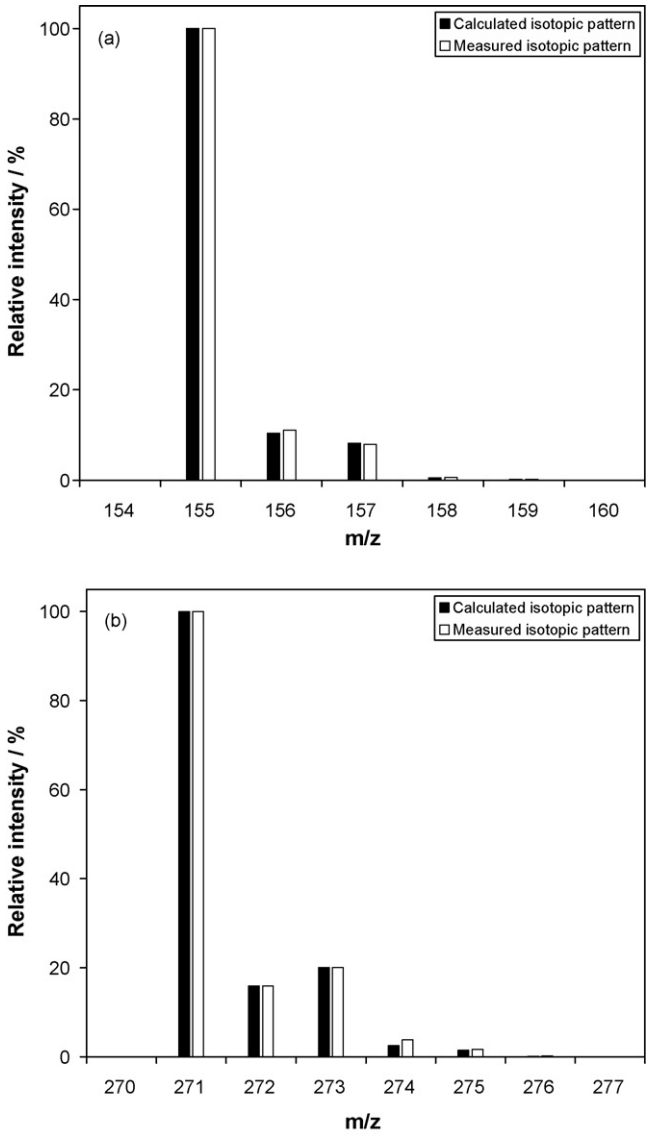

Fig. 2. Comparison between the theoretical and experimental isotopic pattern for the molecule ions located at 155 m/z ($Si_2O_3(OH)_3^-$) and 271 m/z ($Si_3O_4(OK)(OH)_4^-$), respectively. The theoretically isotropic pattern is obtained using Sheffield Chem-Puter [19].

which were obtained by removal of a proton (H^+) from the molecule, thus leaving an anion that was subsequently detected.

The theoretical isotopic pattern for the dimer at 155 m/z is shown in Fig. 2a in comparison to the experimental isotopic pattern. From Fig. 2a it is seen that there is a good agreement between the theoretical and experimental isotopic patterns. The parent molecule of the two dimers found at 155 and 193 m/z a fully hydroxylated dimer ($Si_2O_2(OH)_5^-$) appear to be quite instable in the gas phase of the mass spectrometer, because only a small peak at 173 m/z is seen in Fig. 1a. A second dehydroxylation step results in the peak located at 137 m/z (Fig. 3). This kind of water elimination leads to a Si=O double bond (oxo group) as shown in Fig. 3. This type of water elimination only occurs at Q_0, Q_1, and Q_2 sites in decreasing proportions [18]. However, a series of fully hydroxylated dimers, trimers, and tetramers were identified in the mass spectra. The most dominant peaks were found at 249, 365, 443, and 481 m/z.

After 2 h of reaction the mass spectra changed considerably now consisting of fewer and more distinct signals (Fig. 1b). Again the most dominant peak in the ESI-MS spectrum was the dehydroxylated dimer located at 155 m/z. The most dominant peaks in the

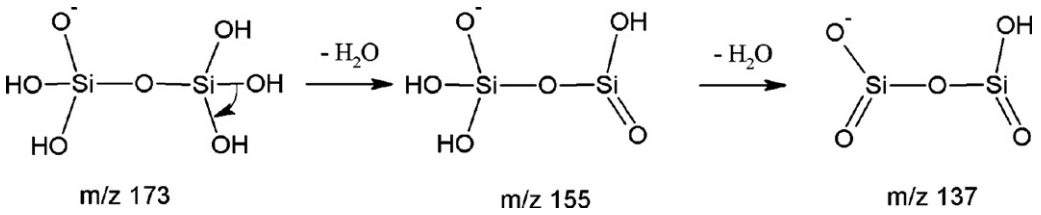

Fig. 3. Dehydroxylation of the silicate species leading to the formation of oxo groups (Si=O).

Table 1
Identified molecule ions in the reaction solution of KOH based inorganic polymers in negative scanning mode. $-H_2O$ denotes dehydroxylation resulting in the formation of an oxo group.

No.	*m/z*	Compound	Intensity	Possible structures
1	77	$SiO_2(OH)^-$	<5	∘ - 1 H_2O
2	95	$SiO(OH)_3^-$	<5	∘
3	137	$Si_2O_4(OH)^-$	29	— -2 H_2O
4	155	$Si_2O_3(OH)_3^-$	100	—-1 H_2O
5	173	$Si_2O_2(OH)_5^-$	<5	—
6	193	$Si_2O_3(OK)(OH)_2^-$	5	—-1 H_2O
7	215	$Si_3O_5(OH)_3^-$	24	△ -1 H_2O ⌒ -2 H_2O
8	233	$Si_3O_4(OH)_5^-$	22	△ ⌒ -1 H_2O
9	249	$Si_2O_2(OK)_2(OH)_3^-$	<5	—
10	253	$Si_3O_5(OK)(OH)_2^-$	<5	△ -1 H_2O ⌒ -2 H_2O
11	271	$Si_3O_4(OK)(OH)_4^-$	22	△ ⌒ -1 H_2O
12	275	$Si_4O_7(OH)_3^-$	<5	□ -2 H_2O ⅄ -2 H_2O ⌒ -3 H_2O
13	293	$Si_4O_6(OH)_5^-$	6	□ -1 H_2O ⅄ -1 H_2O ⌒ -2 H_2O
14	309	$Si_3O_4(OK)_2(OH)_3^-$	<5	△ ⌒ -1 H_2O
15	331	$Si_4O_6(OK)(OH)_4^-$	6	□ -1 H_2O ⅄ -1 H_2O ⌒ -2 H_2O
16	371	$Si_5O_7(OH)_7^-$	<5	
17	387	$Si_4O_5(OK)_2(OH)_5^-$	<5	□ ⅄ ⌒ -1 H_2O
18	391	$Si_5O_8(OK)(OH)_4^-$	<5	
19	425	$Si_4O_5(OK)_3(OH)_4^-$	<5	□ ⅄ ⌒ -1 H_2O
20	443	$Si_4O_4(OK)_3(OH)_6^-$	<5	⌒
21	447	$Si_5O_7(OK)_2(OH)_5^-$	<5	
22	481	$Si_4O_4(OK)_4(OH)_5^-$	<5	⌒

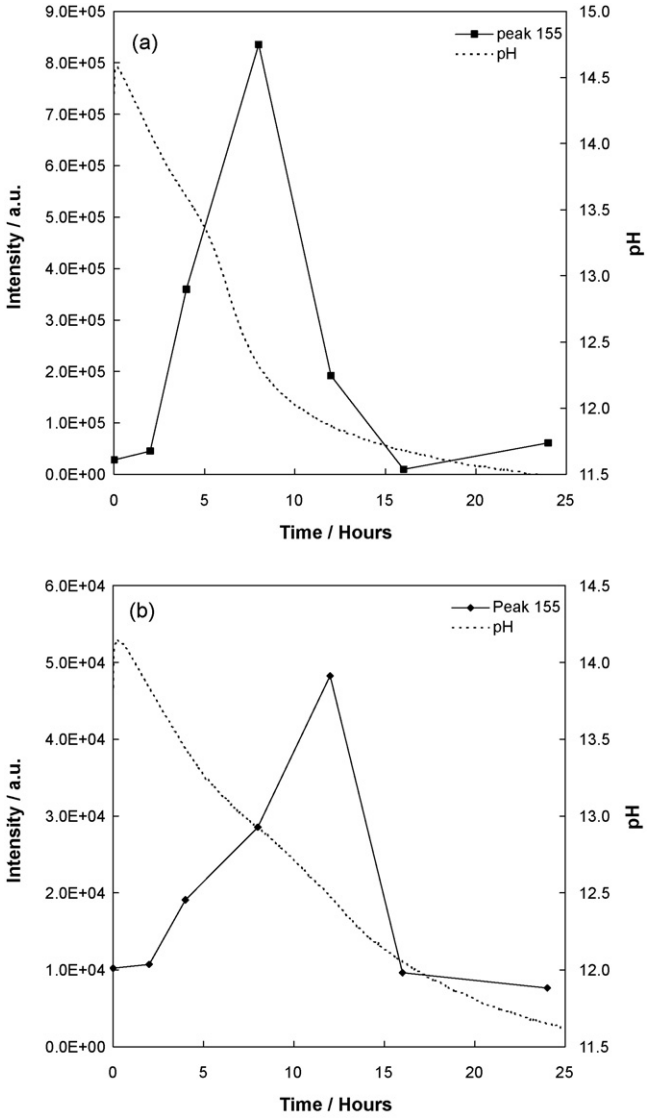

Fig. 4. Evolution of the intensity of the most intensive silicate species for the inorganic polymers reaction solution synthesized using (a) KOH and (b) NaOH in negative scanning mode compared to the change observed change in pH during the reaction.

mass spectra are listed in Table 1. Numerous of the identified silicate species listed in Table 1 apart from silicon, oxygen, and hydrogen also contain potassium.

The presence of potassium in the molecule ion is seen from the isotopic pattern as potassium has three isotopes with the natural abundance: ^{39}K (93.3%), ^{40}K (0.01%), and ^{41}K (6.7%) [19]. The presence of potassium in the molecule ion shifts the intensity ratio between the second and third line in the isotopic pattern as shown in Fig. 2b. From Table 1 it is seen that similar molecule ions in the solution exist only differing by the presence of OK groups instead of OH groups, i.e., $Si_3O_4(OH)_5^-$ (233 m/z) and $Si_3O_4(OK)(OH)_4^-$ (271 m/z).

A series of trimers containing from 3 to 7 OM groups (M=H or K) are found at 215, 233, 253, 271, and 309 m/z. The most intensive of these trimers are found at 233 m/z which can be assigned to linear trimer with one oxo group or a cyclic trimer. The cyclic trimers are usually observed in ^{29}Si NMR investigations of silicate systems. It is not possible to distinguish between these two molecules using ESI-MS because this technique does not give direct information on the interconnectivity of the atoms in the molecule [11]. The peaks at 271 and 309 m/z are derived from the peak at 233 m/z in which 1 and 2 OH groups have been substituted by OK groups, respectively. Moreover dehydroxylation of the peak at 233 m/z leads to the peak at 215 m/z.

Tetramers containing from 3 to 9 OM groups were also identified in the solution. The tetramers were found at 275, 293, 331, 387, 425, 443, 481 and 483 m/z. The most dominate tetramers located at 275, 293, and 331 m/z are assigned to dehydroxylated tetramers or polyhedrons, however the intensity of these peaks is below 10% of the most intensive peak. In addition pentamers and hexamers were also observed but again the intensity of these molecule ions was below 5%. From these results it is observed that no peaks could be assigned to linear trimers or tetramers of the type $Si_xO_x(OM)_{(1+2x)}^-$ as was observed in the mass spectra obtained after 15 min, suggesting that the trimers and tetramers identified in this system under these conditions after 2 h are present in the form of polyhedras.

Similar results have been reported by Eggers et al. who observed a change in the mass spectra obtained during polycondensation reactions involving TMOS and water. The silicate species in solution changed over time from initially consisting of silicate chains to polyhedra [11]. However, it should be noted that Bussian et al. have reported that the tendency of silica species to appear not as the fully hydroxylated ions increase with increasing silicate chain length [9].

In this investigation the reported mass spectra were optimized in the spectra region around 500 m/z in order to observe the polymerization of the silicate species. However, mass spectra were obtained at different spectral optimizations in order to investigate the influence of the optimization. The result of this investigation showed that the peak at 155 m/z was the most intensive peak independent of the spectral optimization at different spectral regions. However, two monomeric species were identified in the mass spectra at 77 and 95 m/z corresponding to $SiO_2(OH)^-$ and $SiO(OH)_3^-$, respectively when the spectra were optimized at 100 and 250 m/z. The intensity of the monomeric silicate species was found to be relatively low (<10%) compared to the peak at 155 m/z. These monomers have also been observed in previous studies of silicate oligomers in aqueous solution [9].

3.1.1. Evolution of silicate species during polymerization of KOH based polymers

The evolution of the intensity of the most dominant silicate species (155 m/z) in the solution is shown in Fig. 4a using the mass spectra obtained from 15 min to 24 h after mixing. Comparison of

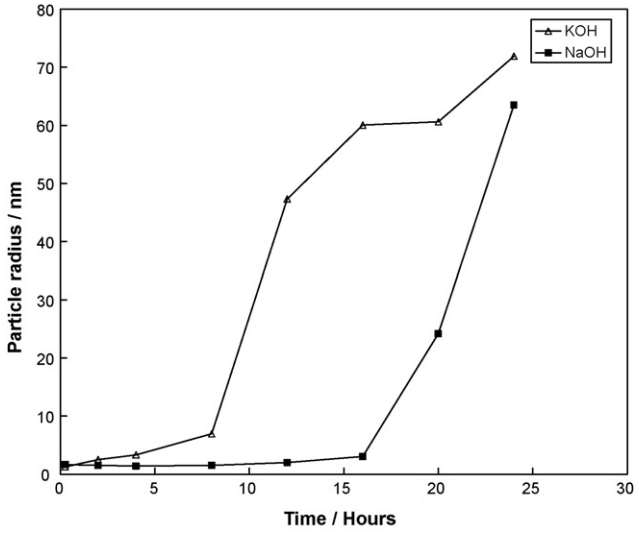

Fig. 5. DLS particle size measurements of the inorganic polymer samples injected into the ESI-MS.

Table 2
Identified molecule ions in the reaction solution of KOH based inorganic polymers in negative scanning mode. $-H_2O$ denotes dehydroxylation resulting in the formation of an oxo group.

No.	*m*/*z*	Compound	Intensity	Possible structures
1	137	$Si_2O_4(OH)^-$	11	-2 H_2O
2	155	$Si_2O_3(OH)_3^-$	100	-1 H_2O
3	173	$Si_2O_2(OH)_5^-$	<5	
4	177	$Si_2O_3(ONa)(OH)_2^-$	39	-1 H_2O
5	215	$Si_3O_5(OH)_3^-$	8	-1 H_2O -2 H_2O
6	233	$Si_3O_4(OH)_5^-$	8	-1 H_2O
7	255	$Si_3O_4(ONa)(OH)_4^-$	6	-1 H_2O
8	275	$Si_4O_7(OH)_3^-$	<5	-2 H_2O -2 H_2O -3 H_2O
9	277	$Si_3O_4(ONa)_2(OH)_3^-$	8	-1 H_2O
10	293	$Si_4O_6(OH)_5^-$	<5	-1 H_2O -1 H_2O -2 H_2O
11	295	$Si_3O_3(ONa)_2(OH)_5^-$	<5	
12	315	$Si_4O_6(ONa)(OH)_4^-$	<5	-1 H_2O -1 H_2O -2 H_2O
13	355	$Si_4O_5(ONa)_2(OH)_5^-$	<5	-1 H_2O
14	357	$Si_5O_9(ONa)(OH)_2^-$	<5	
15	371	$Si_5O_7(OH)_7^-$	<5	
16	393	$Si_5O_7(ONa)(OH)_6^-$	<5	
17	415	$Si_5O_7(ONa)_2(OH)_5^-$	<5	

the intensity of the 155 *m*/*z* signal in the figure shows that the intensity increases up to 8 h after mixing. The increase in the intensity can be explained by the dissolution of microsilica leading to a greater amount of silicate species in the solution. The pH evolution during the dissolution process reported in previous work [20] indicates that the dissolution process proceeds for approximately 10 h correlating with the observed increase in silicate species. The rapid drop in the intensity observed after 12 h in Fig. 4 is suggested to be due to polymerization of the soluble silica species. A broad band of low intensity signals were observed in the ESI-MS spectra after 12 h in the spectral region from 550 up to 1200 *m*/*z*. These signals were found to consist of silicate species containing 6–12 Si atoms. It is believed that the polymerization lead to silicate species with *m*/*z* values greater than 2200 making detection no longer possible using

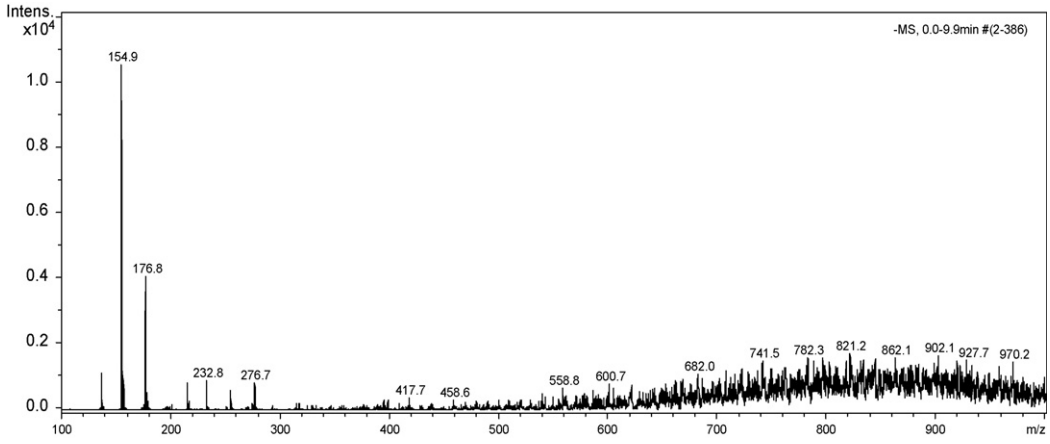

Fig. 6. ESI-MS spectra of the inorganic polymer reaction solution synthesized from NaOH obtained after 12 h.

the ESI-MS method. Thus, when the polymers become greater than approximately 1 nm in size detection is no longer possible using ESI-MS [21].

In this work DLS measurement was used to verify the polymerization model, as DLS enables particle size measurements of particles larger than 1 nm up to 2 μm. In Fig. 5 the size evolution of the polymers/particles is shown. From the figure it is seen that the particle size of the polymer increase rapidly between 8 and 12 h suggesting polymerization. In addition previous studies of the same system have shown that the viscosity changes during synthesis [20]. It was found that the viscosity of the solution started to increase approximately 10 h after mixing also suggesting polymerization. Both the viscosity change and the growth in particle size correlate with the observed decrease in the intensity of the silicate species after 12 h in the present work.

Under the alkaline conditions present in this work the polymerization is believed to occur through nucleophilic substitution reactions. Partial charge calculations for the polymerization of the inorganic polymer have shown that polymerization at the initial pH of the reaction solution (pH 14) may not be favored since the partial charges of the leaving group and nucleophilic group are similar [20]. In addition the high degree of ionisation of the silicate species at very high pH results in repulsive interaction between the reactants. As the pH drop to below 12, condensations between the silicate species are more favored, since the difference between the partial charge of the leaving group and the nucleophile is greater [20]. Moreover, the overall charge of the silicate species decreases resulting in less repulsion between the reactants. For the investigated system pH evolution experiments have shown that the pH of the solution is 12 after approximately 10 h correlating with the observed decrease in intensity of the silicate species in the present work. Thus, it is suggested that the development of the inorganic polymer is at least partly determined by the alkalinity.

3.2. NaOH based inorganic polymers

Investigation of NaOH based inorganic polymers showed that the silicate species present in the solution were very similar to the silicate species found in the investigation of KOH based polymers. The most dominant silicate species found in the reaction solution are listed in Table 2. Comparison between Table 1 and Table 2 shows that 9 out of the 10 most dominant species are the same apart from the cations K^+ and Na^+. As in the case of the KOH based polymers the dehydroxylated dimer ($Si_2O_3(OH)_3^-$) was found to be the most dominant silicate specie. In Fig. 6 the ESI-MS spectra of the NaOH inorganic polymer reaction solution obtained after 12 h is shown. Comparison between Figs. 1d and 6 shows that the intensity of the peaks assigned to the same molecule ions are similar.

In Fig. 4b the evolution of the intensity of the dehydroxylated dimer ($Si_2O_3(OH)_3^-$) in the reaction solution of NaOH based polymers is shown. From the figure it is seen that the intensity increased up to 12 h after mixing suggesting that the dissolution of amorphous silica particles using NaOH is slower compared to the dissolution using KOH.

The result of the present investigation suggests that the dissolution of microsilica and the following polymerization/gelation of the inorganic polymers synthesized from KOH are faster than inorganic polymers synthesized from NaOH.

The change in the intensity of the most dominant silicate species in the mass spectra suggests that these species may serve as building blocks during the polymerization. It is believed that the polymerization lead to silicate species with m/z values greater than 2200 making detection no longer possible using the ESI-MS method. Another possibility is that the silicate species polymerize on the surface of the undissolved microsilica particles encapsulating the microsilica particles. During gelation the polymer encapsulated sphere of the microsilica particles may increase in size resulting in the formation of a network between the microsilica particles leading to gelation. If the polymerization occurs by addition of monomers it would be expected to see a change in the mass spectra leading to peaks of relatively high intensity at higher m/z values.

The presence of silicate species which serves as building blocks has also been proposed based on ^{29}Si NMR investigation of the synthesis of zeosils and zeolites. In this case up to 20 different building blocks were identified [11].

In positive scanning mode the silicate species were found as single positive charged molecule ions. Comparison of the degree of dehydroxylation between the negative and positive charged molecule ions suggest that the alkali cation (K^+ and Na^+) is attached to the OH groups or the oxo group creating a single positive charge. The high pH of the solution reduces the amount of protons in the solution and thus the formation of protonated silicate cations. The silicate species identified in positive scanning mode were very similar to the observed in negative scanning mode.

All the molecule ions identified in the present investigation were found as single charge molecules. However; partial charge calculation has shown that the charge of silicate species at pH 12 is in the order of −1 per silicon atom in the molecule, suggesting that tetramer has a negative charge of 4. In this case the tetramers will not show up in the ESI-MS spectra, since the m/z will be below 100. It is possible that the ESI-MS method may change the charge of the molecule ion by taking up or delivering an electron or proton. As a consequence, the data obtained by ESI-MS may not represent exactly the properties of the solution under examination prior to the mass analysis [16].

4. Conclusion

In the investigation of the polymerization of inorganic polymers in negative scanning mode all molecule ions were found as single negatively charged species, which were obtained by the removal of a proton (H^+) from the molecule, thus leaving an anion that was subsequently detected. Similar silicate species were identified in the reaction solution of inorganic polymers synthesized from KOH and NaOH. The most intensive peak in the mass spectra was assigned to a dehydroxylated dimer (155 m/z). Moreover a range of different silicate species consisting of 3–5 silicon atoms was identified. These species were found most likely to appear in the reaction solution in the form of polyhedras.

The evolution in the intensity of the molecule ions in the reaction solution of inorganic polymers showed that the dissolution/polymerization reaction was slower when NaOH was used compared to KOH. Moreover a distinct decrease in the intensity of the silicate species in the reaction solution was suggested to be due to polymerization. In this case DLS measurements were used to verify the polymerization model. It was found that the particle size of the polymers increased rapidly between 8 and 12 h of reaction for inorganic polymers synthesized from KOH and between 12 and 16 h for inorganic polymers synthesized from NaOH correlating with the observed decrease in the intensity of the silicate species in the ESI-MS investigation. The difference in reaction time for the inorganic polymers synthesized from KOH and NaOH is suggested to be due to the larger hydration radius of Na^+. The decrease in the intensity of the most dominant silicate species in the mass spectra without the appearing of new higher intensity peaks may suggest that these species may serve as building blocks during polymerization.

In positive scanning mode the silicate species were found as single positive charged molecule ions. Comparison of the degree of dehydroxylation between the negative and positive charged molecule ions suggest that the alkali cation (K^+ and Na^+) is attached

to the OH groups or the oxo group creating a single positive charge. The high pH of the solution reduces the amount of protons in the solution and thus the formation of protonated silicate cations. The most dominant peak in the mass spectra of the inorganic polymer in positive scanning mode is assigned to a linear trimers with one oxo group or a cyclic trimer.

References

[1] K. Komnitas, D. Zahataki, Geopolymerisation: a review and prospects for the minerals industry, Miner. Eng. 20 (2007) 1261–1277.
[2] P. Duxson, A. Fernández-Jiménez, G.C. Lukey, A. Palomo, J.S.J. Van Deventer, Geopolymer technology: the current state of the art, J. Mater. Sci. 42 (2007) 2917–2933.
[3] C. Panagiotopoulou, E. Kontori, T. Perraki, G. Kakali, Dissolution of luminosilicate minerals and by-products in alkaline media, J. Mater. Sci. 42 (2007) 2967–2973.
[4] H. Xu, J.S.J. Van Deventer, Ab initio calculations on the fivemembered aluminosilicate framework rings model: implications for dissolution in alkaline solutions, Comput. Chem. 24 (2000) 391–404.
[5] H. Xu, J.S.J. Van Deventer, The effect of alkali metals on the formation of geopolymeric gels from alkali-feldspar, Coll. Surf. A: Phys. Eng. Aspects 216 (1–3) (2003) 27–44.
[6] J.W. Phair, J.S.J. Van Deventer, Effect of the silicate activator pH on the microstructural characteristics of waste-based geopolymers, Int. J. Miner. Process. 66 (1–4) (2002) 121–143.
[7] J.W. Phair, J.S.J. Van Deventer, Effect of silicate activator pH on the leaching and material characteristics of waste-based inorganic polymers, Miner. Eng. 14 (3) (2001) 289–304.
[8] C.J. Brinker, G.W. Scherer, Sol–gel Science, the physics and chemistry of sol–gel processing, Academic Press, San Diego, 1990.
[9] P. Bussian, F. Sobott, B. Brutschy, W. Schrader, F. Schüth, Speciation in solution: silicate oligomers in aqueous solutions detected by mass spectrometry, Angew. Chem. Int. Ed. 39 (21) (2000) 3901–3905.
[10] F. Schüth, P. Bussian, P. Ågren, S. Schunk, M. Lindén, Techniques for analyzing the early stages of crystallization reactions, Solid State Sci. 3 (2001) 801–808.
[11] K. Eggers, T. Eichner, J. Woenckhaus, Mass spectrometric investigation of small silicate polyhedra in solution, Int. J. Mass Spectrom. 244 (2005) 72–75.
[12] C. Cristoni, L. Armelao, S. Gross, E. Tondello, P. Traldi, Electrospray ionization in the study of the polycondensation of Ti(O-*i*-C_3H_7)$_4$ and Ti(O-*n*-C_4H_9)$_4$, Rapid Commun. Mass Spectrom. 14 (2000) 662–668.
[13] C. Cristoni, P. Traldi, L. Armelao, S. Gross, E. Tondello, Electrospry ionization in the study of sol–gel processes: the polycondensation of Ti(O-n-Bu)$_4$ in the presence of Si(OEt)$_4$, Rapid Commun. Mass Spectrom. 15 (2001) 386–392.
[14] C. Cristoni, L. Armelao, S. Gross, R. Seraglia, E. Tondello, P. Traldi, Study of polycondensation reactions of Ge(OEt)$_4$ and Ge(OEt)$_4$/Si(OEt)$_4$ by electrospray ionization mass spectrometry, Rapid Commun. Mass Spectrom. 16 (2002) 733–737.
[15] L. Armelao, G. Schiavon, R. Seraglia, E. Tondello, U. Russo, P. Traldi, Electrospray ionisation mass spectrometric study of the hydrolysis-polycondensation process of Sn(OBu^t)$_4$, Rapid Commun. Mass Spectrom. 15 (2001) 1855–1861.
[16] C. Cristoni, L. Armelao, S. Gross, R. Seraglia, E. Tondello, P. Traldi, Matrix-assisted laser desorption/ionization mass spectrometry in the study of polycondensation of Ti(OBu^n)$_4$ in the presence of Si(OEt)$_4$, Rapid Commun. Mass Spectrom. 17 (2003) 2039–2046.
[17] C. Cristoni, L. Armelao, E. Tondello, P. Traldi, Electrospray ionization in the study of polycondensation of Si(OEt)$_4$, J. Mass Spectrom. 34 (1999) 1380–1382.
[18] S.A. Pelster, W. Schrader, F. Schüth, Monitoring temporal evolution of silicate species during hydrolysis and condensation of silicates using mass spectrometry, J. Am. Chem. Soc. 128 (2006), 4310-4217.
[19] http://www.shef.ac.uk/chemistry/chemputer/isotopes.html.
[20] M.E. Simonsen, C. Sønderby, E.G. Søgaard, Synthesis and characterization of silicate polymers, J. Sol–Gel Sci. Technol. 50 (2009) 372–382.
[21] S.A. Pelster, R. Kalamajka, W. Schrader, F. Schüth, Monitoring the nucleation of zeolites by mass spectrometry, Angew. Chem. Int. Ed. 46 (2007) 2299–2302.