

Mechanistic Study of Silsesquioxane Synthesis by Mass Spectrometry and in Situ ATR FT-IR Spectroscopy

Paolo P. Pescarmona,[†] Maria E. Raimondi,[‡] John Tetteh,[§] Ben McKay,[‡] and Thomas Maschmeyer^{*,†,||}

Laboratory of Applied Organic Chemistry and Catalysis, DelftChemTech, Technische Universiteit Delft, Julianalaan 136, 2628 BL Delft, The Netherlands, Avantium Technologies B.V., Zekeringstraat 29, 1014 BV, P.O. Box 2915, 1000 CX Amsterdam, The Netherlands, School of Chemical and Life Sciences, The University of Greenwich at Medway, Central Avenue, Chatham Maritime, ME4 4TB, Kent, U.K., and The School of Chemistry, The University of Sydney, Sydney, NSW 2006, Australia

Received: May 27, 2003

The synthesis of cyclopentylsilsesquioxane *a7b3* [(*c*-C₅H₉)₇Si₇O₉(OH)₃] was followed by means of electrospray mass spectrometry (ESI MS) and in situ attenuated total reflection Fourier transform infrared (ATR FTIR) spectroscopy in combination with chemometric analysis methods. This study allowed us to identify silsesquioxane species present in the reaction mixture and to propose a mechanism for the formation of silsesquioxane *a7b3*. The spectroscopic results proved the existence of short-lived, low molecular weight silsesquioxane precursors and indicated that the final product silsesquioxane *a7b3* was only present in very low concentrations in the reaction mixture, suggesting that the high selectivity of the reaction toward silsesquioxane *a7b3* is caused by its low solubility.

1. Introduction

Silsesquioxanes^{1–3} are inorganic–organic hybrid compounds of the general formula (RSiO_{1.5})_a(H₂O)_{0.5b}, where R is a hydrogen atom or an organic group and *a* and *b* are integer numbers (*a* = 1, 2, 3, ...; *b* = 0, 1, 2, 3, ...), with *a* + *b* = 2*n*, where *n* is an integer (*n* = 1, 2, 3, ...) and *b* ≤ *a* + 2. These compounds are usually subdivided into two groups: completely condensed silsesquioxanes, for which *b* = 0, and incompletely condensed silsesquioxanes, for which *b* ≠ 0. Incompletely condensed silsesquioxanes contain silanol groups (Si–OH), which make them suitable model compounds for silica surfaces.³ The incompletely condensed silsesquioxane *a7b3*,^{4,5} which presents three vicinal silanol groups (Figure 1), has proven to be a particularly useful species. It has been reacted with a variety of metal centers and the complexes obtained have been used both as model compounds for heterogeneous catalysts and as homogeneous catalysts.^{1,6–11} Recently, a fast and efficient way to synthesize the cyclopentylsilsesquioxane *a7b3* by means of high-speed experimentation techniques was identified by our group.¹² This new synthetic method produces the pure compound in 64% yield after 18 h of reaction, a considerable improvement over the 29% yield after 3 days reaction known previously.⁵ High-speed experimentation was an efficient means to determine the optimal high selectivity synthesis conditions,¹³ but could not directly be used to elucidate the mechanism of formation of the silsesquioxane.

The aim of the work presented in this paper is to shed light on this mechanism, to identify the species formed during the process and to try to explain the high selectivity toward silsesquioxane *a7b3* of this optimized synthesis method. The

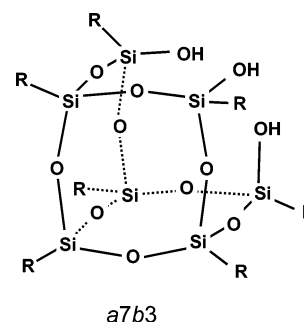


Figure 1. Cyclopentylsilsesquioxane (*c*-C₅H₉)₇Si₇O₉(OH)₃ [R = cyclopentyl].

synthesis of cyclopentylsilsesquioxane *a7b3* was monitored by means of electrospray ionization mass spectrometry (ESI MS)^{2,14,15} and in situ attenuated total reflection Fourier transform infrared (ATR FTIR) spectroscopy.^{16,17} Spectroscopic data from the latter were analyzed using chemometric methods to identify the pure spectra and relative concentration profiles.

2. Experimental Section

The synthesis of cyclopentylsilsesquioxane *a7b3* was performed according to the optimized method discovered by means of high-speed experimentation techniques.¹² Typically, 9.4 mL of deionized water were carefully added to a 100 mL round-bottomed flask containing a solution of 1.4 mL of cyclopentyltrichlorosilane ((*c*-C₅H₉)SiCl₃, 97% purity) in 37.5 mL of acetonitrile.

The homogeneous solution was vigorously stirred and heated under reflux conditions in an oil bath set at 90 °C. A white precipitate was already visible after 1 h. At the end of the reaction, the white precipitate (mainly composed of silsesquioxane *a7b3*) was present on the walls of the flask and a liquid–liquid-phase separation of the reaction solution was observed.¹²

Mass spectrometry (MS) analysis was performed on a Micromass Quattro LC–MS with ESI+ as ionization technique.

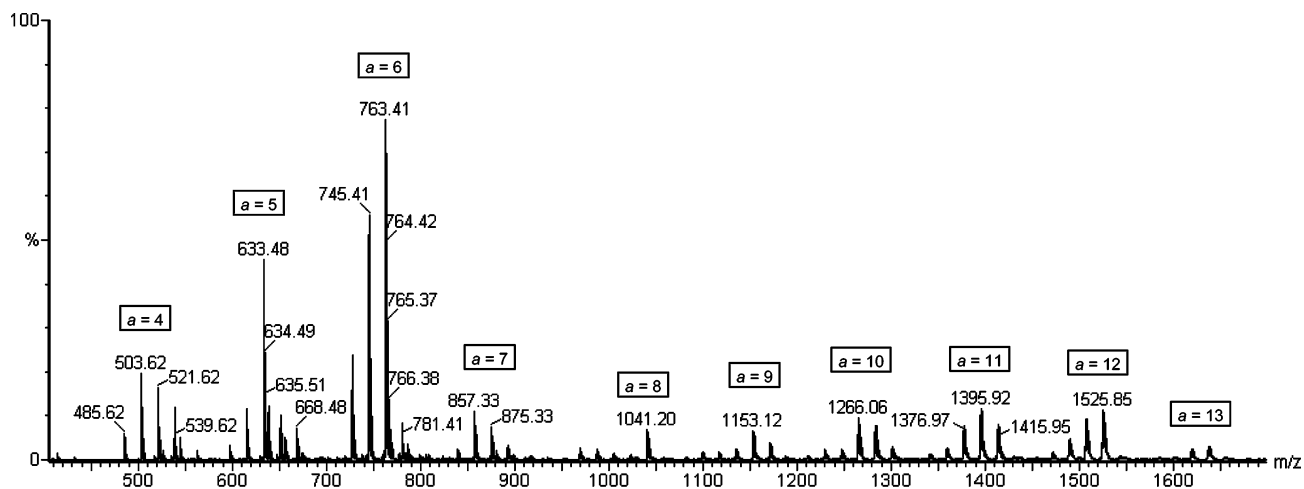
* To whom correspondence should be addressed. Fax: +(31)152784289. E-mail: th.maschmeyer@tnw.tudelft.nl.

[†] Technische Universiteit Delft.

[‡] Avantium Technologies B.V.

[§] The University of Greenwich at Medway.

^{||} The University of Sydney.



<i>a</i>	<i>b</i>	<i>m/z</i>	<i>a</i>	<i>b</i>	<i>m/z</i>	<i>a</i>	<i>b</i>	<i>m/z</i>	<i>a</i>	<i>b</i>	<i>m/z</i>	<i>a</i>	<i>b</i>	<i>m/z</i>
1	3	148.06	4	0	484.16	6	0	726.24	7	1	856.29	8	0	968.32
			4	2	502.17	6	2	744.25	7	3	874.30	8	2	986.33
2	0	242.08	4	4	520.19	6	4	762.27	7	5	892.32	8	4	1004.35
2	2	260.10	4	6	538.21	6	6	780.29	7	7	910.33	8	6	1022.37
2	4	278.11				6	8	798.30	7	9	928.35	8	8	1040.38
			5	3	632.22							8	10	1058.40
3	3	390.14	5	5	650.24									
3	5	408.16	5	7	668.25									

Figure 2. MS plot after 90 min of reaction and list of possible cyclopentylsilsesquioxanes with $1 \leq a \leq 8$. Analytical parameters for MS measurements were set as follows: flow rate (of the syringe pump) = 40 μ L/min, rf lens = 0.31 V, capillary = 3.20 kV, cone = 30 V, extractor = 4 V, source block temperature = 80 $^{\circ}$ C, desolvation temperature = 300 $^{\circ}$ C, nebulizer gas flow = 85 L/h, desolvation gas flow = 450 L/h.

At regular intervals throughout the experiment, 200- μ L samples were taken from the reaction supernatant liquid, ensuring no aspiration of solids into the syringe, and directly injected into the mass spectrometer by means of a syringe pump. The first sample ($t = 0$) was taken straight after adding water to the acetonitrile solution of cyclopentyltrichlorosilane, and subsequent samples were taken after 30, 60, 90, 120, 180, 270, 360, 480, 600, and 1440 min. The presence of water and of acids (hydrochloric and acetic)¹² in the reaction mixture yielded favorable ionization conditions for MS.

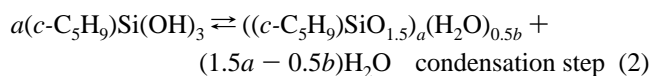
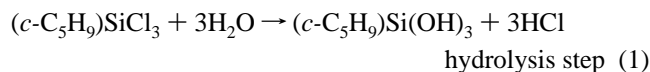
A list of possible silsesquioxane structures and their masses, based on the equations that define the a and b values in the formula $(\text{RSiO}_{1.5})_a(\text{H}_2\text{O})_{0.5b}$ is shown in Figure 2, together with a MS plot of the silsesquioxane synthesis mixture. From MS data,¹⁸ it is possible to determine the number of Si atoms (the value of a in $(\text{RSiO}_{1.5})_a(\text{H}_2\text{O})_{0.5b}$) of the detected species but not their level of condensation (the value of b). The reason for this is that during the ionization process silsesquioxanes can lose water molecules, as confirmed by the fact that the ratio of peak intensities for a given value of a is influenced by the cone voltage applied during the MS analysis.

In situ infrared analysis was performed by means of an ASI ReactIR1000 reaction analysis system, based on attenuated total reflection (ATR) Fourier transform infrared (FTIR) spectroscopy. The spectrometer was equipped with a zinc selenide (ZnSe) crystal cell, a diamond probe, and a mercury cadmium telluride (MCT) detector. During the analysis, the IR diamond probe had to be positioned just below the surface of the reaction mixture in order to avoid coating of the probe by the silsesquioxane precipitate formed during the synthesis. The reaction was carried out under reflux conditions, which led to bubble formation at the surface of the solution. This affected the contact between the probe surface and the reaction mixture, causing

some noise in the recorded spectra. Noisy or spiky data may also be caused by impact on the ATR probe of the precipitate formed during the reaction.

3. Results and Discussion

As described in earlier work,¹² the silsesquioxane synthesis discussed here occurs via the hydrolytic condensation of cyclopentyltrichlorosilane:



3.1. Mass Spectrometry. The MS spectra recorded between $t = 0$ (sample actually analyzed after a couple of minutes) and $t = 1440$ min show peaks corresponding to cyclopentylsilsesquioxane structures with $1 \leq a \leq 13$. Peaks due to $a = 7$ species ($m/z = 839.3, 857.3, 875.3, 893.3$) are present in all the recorded spectra (see Figure 2 for an example). The relative abundance of these peaks compared to that of the peaks of other silsesquioxane species is rather low at any reaction time, indicating a low concentration in solution. Knowing that the precipitate produced by the synthesis is mainly silsesquioxane $a7b3$,¹² it can be inferred that this compound has a low solubility in the reaction mixture and tends to precipitate as it gets formed. Its lower solubility with respect to other cyclopentylsilsesquioxanes is probably due to the tendency of silsesquioxane $a7b3$ to form dimers,^{4,19} which are insoluble in polar solvents such as acetonitrile. This is in agreement with the observed formation of a white precipitate after 1 h of reaction.

The concentration of the $a = 7$ species in solution can, therefore, be considered approximately constant during the

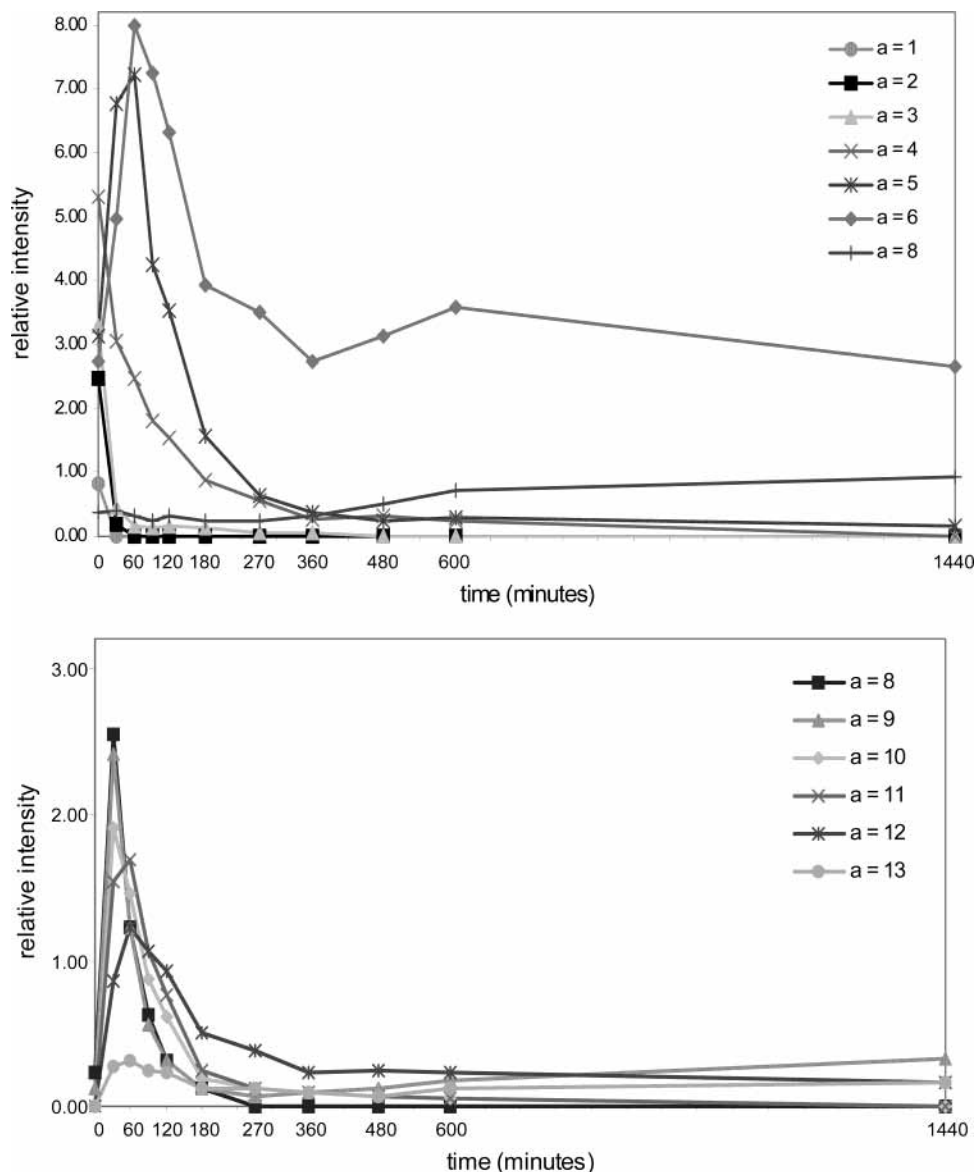


Figure 3. Relative intensity of the MS peaks of the various silsesquioxane species present in solution, as a function of the reaction time. All the intensities are normalized to the intensity of the peaks of $a = 7$ species.

course of the reaction. This assumption allowed us to normalize the intensity of the peaks of the other silsesquioxanes relative to the $a = 7$ peaks, making it possible to compare the spectra measured at the various reaction times.²⁰ The relative concentrations of the principal silsesquioxane species with increasing a values are plotted against reaction time in Figure 3. This plot shows how various silsesquioxane species form and disappear over time. At $t = 0$, silsesquioxane species with $1 \leq a \leq 6$ are present in considerable amounts. No cyclopentyltrichlorosilane was detected, indicating that the hydrolysis step (eq 1) is complete before the first sample is injected in the mass spectrometer.¹⁹ The presence of various species at $t = 0$ shows that the process of condensation of silsesquioxane $a1b3$, ($c\text{-C}_5\text{H}_9$)Si(OH)₃, (step 2) leading to the formation of larger silsesquioxane structures is also very fast. At $t = 0$, species with $a = 4$ are the most abundant. Silsesquioxanes with $1 \leq a \leq 4$ can be seen as the building blocks for larger silsesquioxane structures (see Figure 4 for a proposed scheme for the synthesis of silsesquioxanes). They are likely to be reactive species that tend to condense further, as confirmed by the fact that their concentrations diminish quickly as the reaction proceeds. The smaller the structures, the faster they disappear to form larger

ones. At $t = 30$ min, silsesquioxane $a1b3$ has already disappeared from the reaction mixture. Silsesquioxanes with $a = 2$ disappear after 1 h of reaction and those with $a = 3$ reach a very low concentration after 1 h of reaction and cannot be detected anymore after 6 h. The concentration of silsesquioxanes with $a = 4$ decreases less rapidly. These species are still present in small amounts after 10 h and are only fully consumed close to the end of the reaction, after 24 h.

For $a = 1$, the only possible structure is the trisilanol $a1b3$.¹ For $a = 2$ and $a = 3$, more structures are possible but $a2b4$ and $a3b5$ are the only two that do not present a large geometrical strain. For $a = 4$, two structures are the most likely: $a4b4$ and $a4b6$, the first being a ring and the second a linear structure. The ring structure is part of the structure of the final product $a7b3$, and so it can be assumed that $a4b4$ ²¹ is the precursor species. These structures are schematized in Figure 4, together with their most likely paths of reaction.

For most of the reaction silsesquioxanes with $a = 5$ and $a = 6$ are the two major species in solution. Their concentrations increase in the beginning of the reaction to reach a maximum after 1 h and then gradually decrease. This happens more rapidly for species with $a = 5$ that are only present in very small

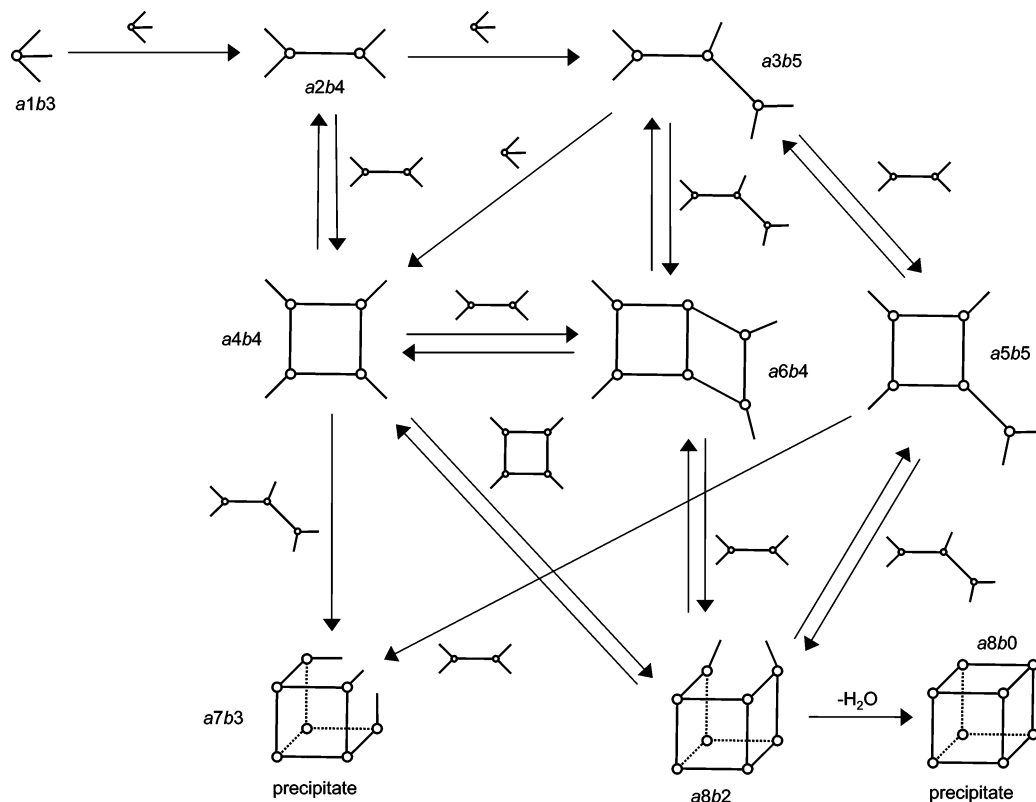


Figure 4. Proposed mechanism for the synthesis of cyclopentylsilsesquioxane *a7b3*. The silsesquioxane structures are represented in a schematic way. Each circle symbolizes a siloxane unit $[(c-C_5H_9)SiO_3]$: silicon atoms are represented by the circles and the oxygen atoms by the lines; nonbinding lines represent the $-OH$ groups. The cyclopentyl groups are not shown.

amounts at the end of the reaction, than for silsesquioxanes with $a = 6$, which are still present in relevant amounts after 24 h of reaction. The two most likely structures with $a = 5$ and $a = 6$ are silsesquioxanes *a5b5* and *a6b4*, which are represented in Figure 4, together with their possible pathways of formation.

For silsesquioxanes with $a = 8$, two groups of peaks with different relative concentration profiles exist. The different behavior as a function of the reaction time suggests that the two groups of peaks belong to two different species with $a = 8$. The first group has a main peak at $m/z = 987.15$, which corresponds to an *a8b2* silsesquioxane. This species has a low concentration during the entire reaction, with only a slightly positive slope toward the end (see Figure 3, top plot). The second group of peaks has a main peak at $m/z = 1041.20$, its intensity reaches a maximum at $t = 30$ min and then decreases rapidly to disappear after 3 h of reaction (see Figure 3, bottom plot). This intensity profile for these species is very similar to those of species with $9 \leq a \leq 13$, indicating a maximum species concentration at $t = 30$ min for $a = 9, 10$ and at $t = 60$ min for $11 \leq a \leq 13$. Given the short lifetime of the species with $8 \leq a \leq 13$ and the fact that they are present in the early stages of the reaction, it can be suggested that these species are instable aggregates of two smaller silsesquioxanes.²² For example, species with $a = 8$ are probably dimers of $a = 4$ species, those with $a = 9$ are constituted by $a = 4$ and $a = 5$ species, and so on.

On the basis of all the information collected from this MS study, it is possible to propose a mechanism for the formation of silsesquioxane *a7b3* (Figure 4). Silsesquioxanes with $1 \leq a \leq 4$ are formed in the early stages of the synthesis and react very quickly to form more condensed species. It is assumed that the very reactive *a1b3* will not be formed again by hydrolysis reactions of more condensed species: this means that

the reactions in which *a1b3* takes part are effectively irreversible and that the compound will only be available for the reactions in the early stages of the synthesis. Silsesquioxanes with $2 \leq a \leq 4$ are then going to react with each other to form the more condensed silsesquioxanes with $4 \leq a \leq 8$. These reactions are more easily reversible, meaning that the structures that are formed by condensation can be hydrolyzed back to the original compounds or to other less condensed species.

As mentioned above, silsesquioxane *a7b3* is less soluble than other silsesquioxanes present in the reaction mixture and precipitates as a white solid. This will influence the equilibrium composition and consequently drive the reactions that involve its formation toward the product; therefore, these reactions are considered irreversible. Silsesquioxanes with $a = 6$ exhibit a maximum of concentration in solution after 1 h of reaction; they are then rapidly consumed up until 3 h of reaction, after which the reaction proceeds more slowly. Since no $a = 6$ silsesquioxane is present in the precipitate, it is inferred that the compound gets slowly hydrolyzed to smaller species which then recombine to give the product *a7b3*.^{5,23} The absence of an $a = 6$ silsesquioxane among the products is, therefore, not due to the instability of the compound but rather to its higher solubility in the reaction mixture. The completely condensed silsesquioxane *a8b0*, obtained by condensation of *a8b2*, is only present in traces in the precipitate. This means that, although silsesquioxane *a8b0* might be expected to be the most thermodynamically favored structure, its formation is unfavorable compared to that of silsesquioxane *a7b3*, suggesting that the reaction is kinetically controlled.

An alternative way to represent the results of the MS analysis is by plotting the fraction of the total silsesquioxane structures for each value of a (with $1 \leq a \leq 8$), as a function of the reaction time (Figure 5). This graph gives a measure of the

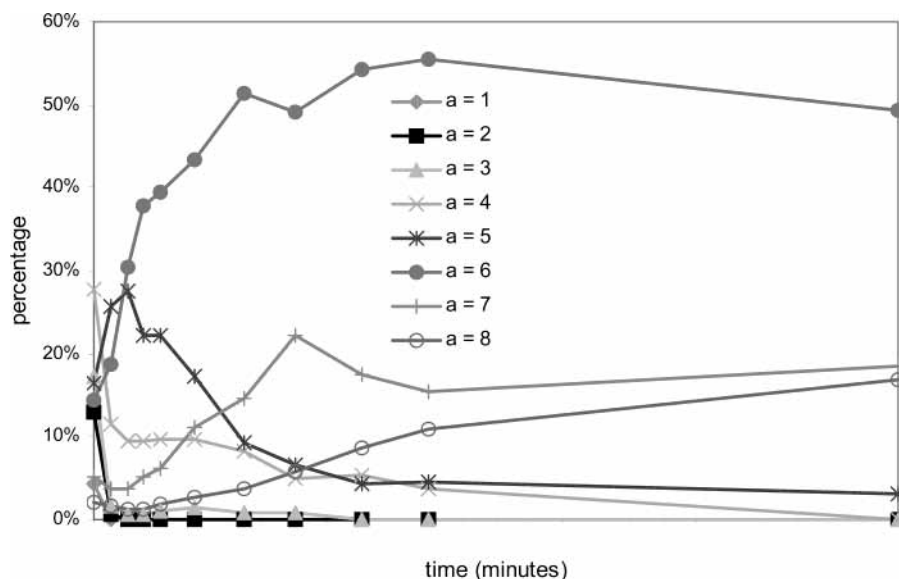


Figure 5. Fraction of the total silsesquioxane structures in solution for $1 \leq a \leq 8$, as a function of the reaction time (based on MS data).

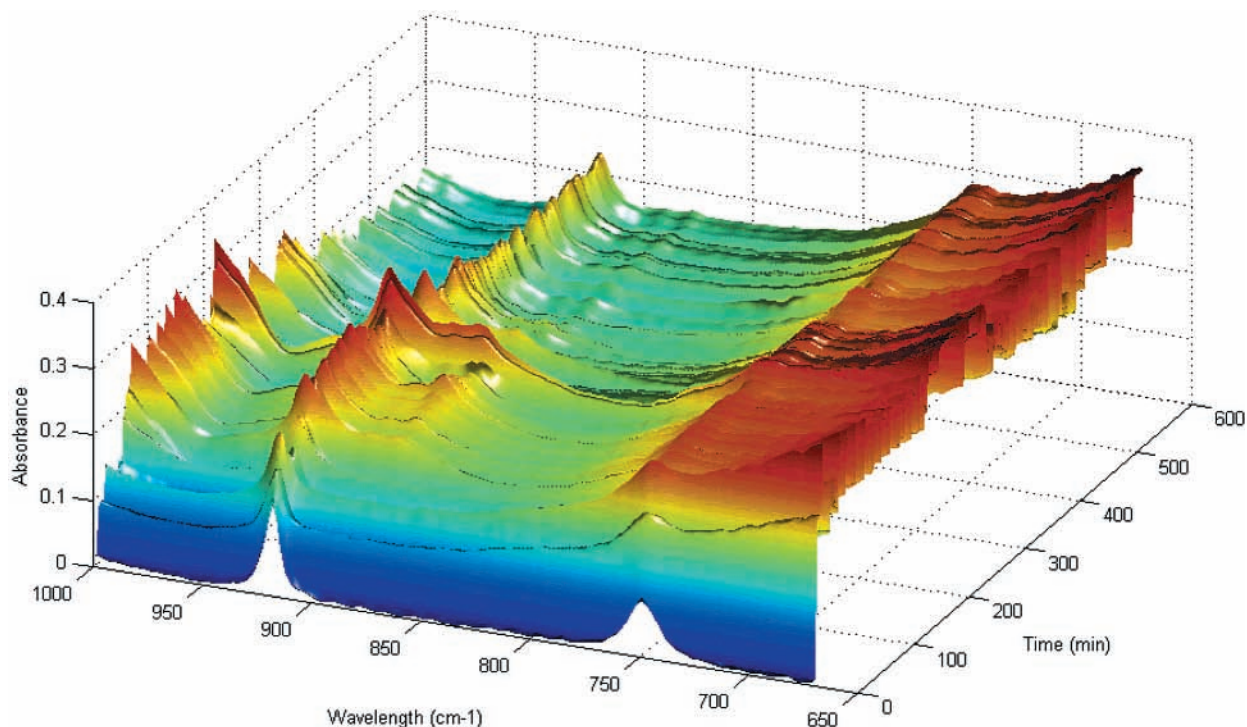


Figure 6. In situ ATR FTIR spectra of the silsesquioxane reaction mixture, as a function of the reaction time for a window of $670\text{--}1000\text{ cm}^{-1}$. Analytical parameters were as follows: IR analysis ($670\text{--}4000\text{ cm}^{-1}$) was performed for 10 h with an acquisition of a spectrum every 2 min, 16 scans per spectrum, and a resolution of 4 cm^{-1} .

distribution of the various species in solution at various stages of the reaction. This plot does not, however, provide any information about the total concentration of silsesquioxane species in solution (the value of which is always set at 100%).²⁰ This graph nicely shows how the smaller silsesquioxane species constitute the main fraction in the early stages of the synthesis and then tend to gradually be consumed in favor of bigger structures as the reaction proceeds. Toward the end of the synthesis, silsesquioxanes with $a = 6$ are the major fraction in solution, though the relative fractions of species with $a = 7$ and $a = 8$ are increasing. This is in agreement with the hypothesis of the concentrations of silsesquioxanes $a = 7$ and $a = 8$ being constant in solution and that of silsesquioxanes a

$= 6$ slowly decreasing upon hydrolysis and consecutive condensation toward silsesquioxane $a7b3$.

3.2. Infrared Spectroscopy. Attenuated total reflection (ATR) FTIR spectroscopy allows in situ monitoring of liquid-phase reactions by collecting the infrared spectra for solution species directly in contact with the infrared probe.²⁴ In the general case of a reaction in which various compounds are present, each ATR FTIR spectrum will consist of the overlapping spectra of all the pure components present in solution at a specific reaction time. During the reaction, the concentration of reagents and products will change, thus influencing the spectrum profile. This may allow appropriate chemometric methods to be used to deconvolute the pure component spectra

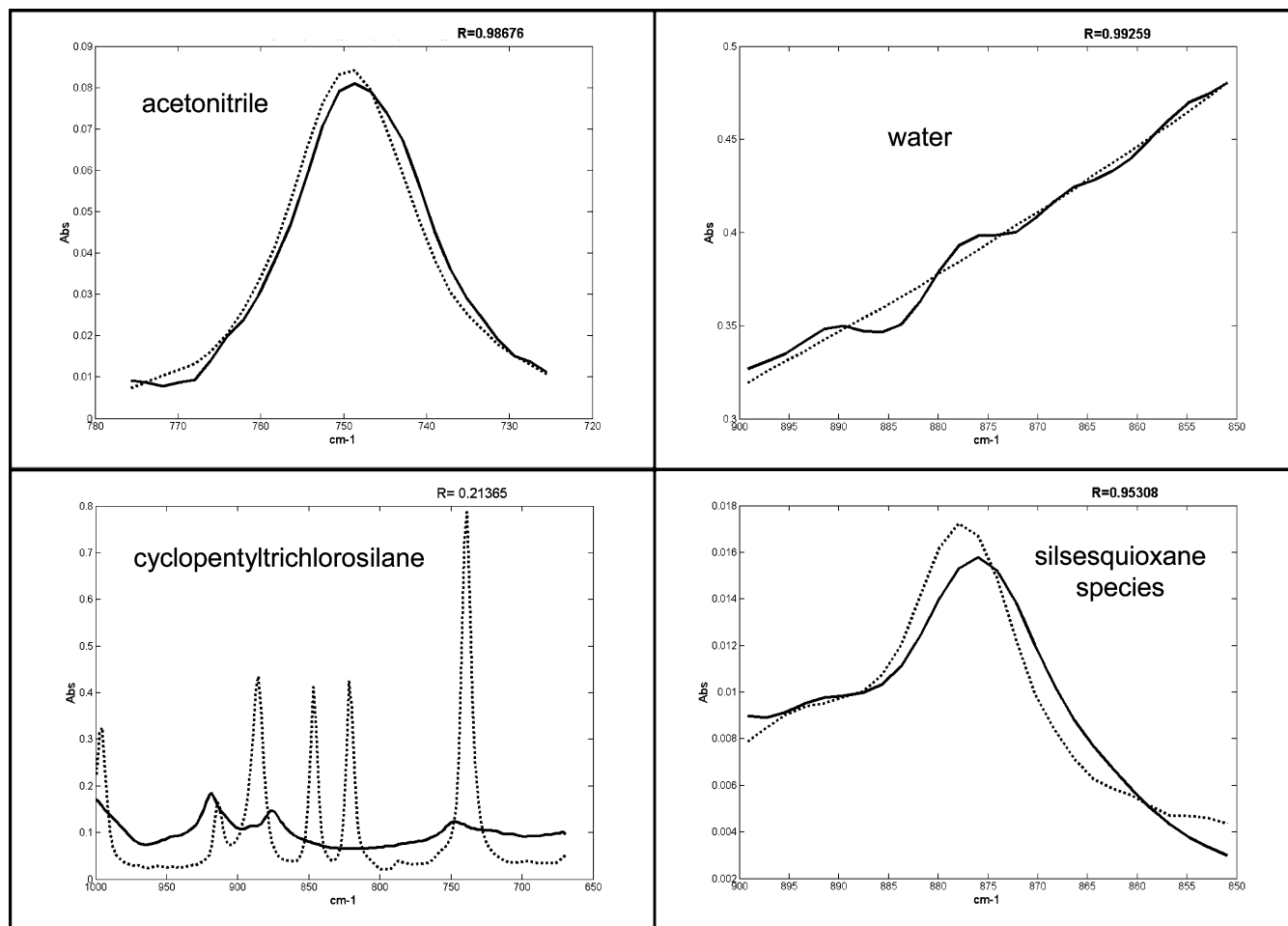


Figure 7. Comparison of the measured reference spectra (dotted line) with the pure component spectra (solid line) obtained by chemometric deconvolution of the complex ATR FTIR spectra reported in Figure 6.

and relative concentration profiles as a function of time. If the IR spectra of some components are known in advance (e.g., the solvent, reagents, and selected products), it is possible to use them as references to improve the fidelity of the deconvolution.

In the ATR FTIR study of the synthesis of cyclopentylsilsesquioxane *a7b3*, in situ ATR FTIR spectra of the reaction mixture were collected every 2 min during the reaction time. The spectra obtained were plotted as a function of the reaction time (Figure 6). The pure component spectra and relative concentration profiles were subsequently recovered using a multivariate curve resolution (MCR)²⁵ technique based on a modified target factor analysis algorithm.²⁶

Principal component analysis (PCA)²⁷ was first used to determine the number of independently varying chemical species present and to provide initial estimates of the spectral shapes resulting from these species and of their concentration profiles. Reference ATR FTIR spectra for a number of components (the solvent acetonitrile and water, the reagent cyclopentyltrichlorosilane and the product *a7b3*) were measured to assist in the deconvolution of the data. Frequency windows were selected that allowed the best discrimination between the reference compounds (725–775 cm^{-1} for acetonitrile; 850–900 cm^{-1} for water and the silsesquioxane). Finally, the MCR technique was applied to the data in the selected frequency windows to find the component spectra and relative concentration profiles that best fit the observed spectra.

From Figure 7, it can be seen that the pure component spectra obtained by the MCR technique closely match the reference spectra for acetonitrile (with a correlation coefficient $R = 0.987$), water ($R = 0.993$), and silsesquioxane ($R = 0.953$). A poor match ($R = 0.214$) is obtained for the cyclopentyltrichlorosilane reference spectra, indicating that cyclopentyltrichlorosilane cannot be detected at any stage during the reaction. This supports the MS results that also suggest that trichlorosilane is immediately hydrolyzed once water is added to the solution.

Relative concentration profiles for the identified species are given in Figure 8. The concentrations of acetonitrile and water are reasonably constant during the reaction, reflecting the fact that both acetonitrile and water are present in large quantities, and that any change in concentration is effectively negligible.

The relative concentration profile of the silsesquioxane component, which has a slightly less accurate fit to the silsesquioxane *a7b3* reference spectrum ($R = 0.953$), reaches a maximum after 2 h and becomes approximately constant after 4 h of reaction. From the MS study (see subsection 3.1), it is inferred that silsesquioxane *a7b3* has a very low and approximately constant concentration in solution throughout the entire reaction, since the compound is only sparingly soluble, and precipitates at higher concentrations. This suggests that the silsesquioxane monitored by ATR FTIR is not represented by structure *a7b3*. Other incompletely condensed cyclopentylsilsesquioxanes are expected to have infrared spectra very similar to that of *a7b3* in the studied spectral regions.^{2,19,28} Therefore, it is proposed that the species identified by MCR is an $a = 5$

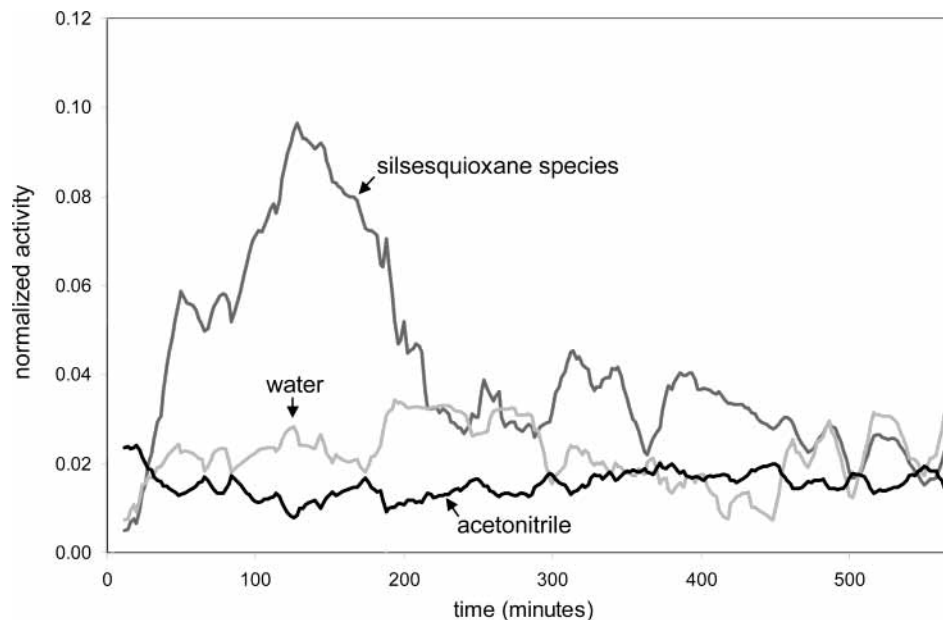


Figure 8. Relative concentration profiles of the three species identified by chemometric deconvolution of the complex ATR FTIR spectra reported in Figure 6.

or an $a = 6$ structure, which presents an MS concentration profile similar to that obtained by ATR FTIR, or a mixture of more silsesquioxane structures. The hypothesis of an $a = 6$ structure is supported by the fact that the ATR FTIR concentration profile for the silsesquioxane species as a function of time is rather similar to the MS concentration profile obtained for the $a = 6$ silsesquioxane (compare Figures 3 and 8). The slightly different position of the maximum in the two plots is considered to be due to the longer time required in the ATR FTIR experiment to reach the reflux temperature.²⁹

The combined MS and ATR FTIR results point to the fact that the concentration of the silsesquioxane species in solution becomes almost constant after 4 h of reaction. This might imply that a reaction time shorter than 18 h could be sufficient to obtain silsesquioxane *a7b3* in high yield. Therefore, the synthesis was repeated with the same conditions but with a reaction time of 6 h: a final yield of 54% in silsesquioxane *a7b3* (after purification) was obtained. After collection of the precipitate, the reaction mixture was allowed to react for 12 h more, yielding more precipitate, and a total yield of 64% was achieved. Although the yield after 6 h is lower than that obtained after 18 h of reaction, the experiment confirmed that most of the yield of the desired *a7b3* structure is generated within the first hours of reaction. This finding would certainly be of practical importance for a potential up-scaling of silsesquioxane *a7b3* production.

4. Conclusion

By coupling the two analytical techniques (MS and ATR FTIR), it was possible to obtain detailed information on the time-resolved mechanism of silsesquioxane formation, with the ATR FTIR results being consistent with the mechanism based on the interpretation of the MS data. The study has shown that the formation of the desired silsesquioxane *a7b3* follows a complex pathway, via initial formation of smaller oligomers. The final, high selectivity for the *a7b3* species is ascribed to its lower solubility, which impedes redissolution and equilibrium reactions yielding other silsesquioxanes.

Acknowledgment. Jan Kees van der Waal is kindly acknowledged for fruitful discussion.

References and Notes

- (1) Pescarmona, P. P.; Maschmeyer, T. *Aust. J. Chem.* **2001**, *54*, 583.
- (2) Voronkov, M. G.; Lavrent'yev, V. I. *Top. Curr. Chem.* **1982**, *102*, 199.
- (3) Abbenhuis, H. C. L. *Chem.—Eur. J.* **2000**, *6*, 25.
- (4) Feher, F. J.; Newman, D. A.; Walzer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 1741.
- (5) Feher, F. J.; Budzichowski, T. A.; Blanski, R. L.; Weller, K. J.; Ziller, J. W. *Organometallics* **1991**, *10*, 2526.
- (6) Feher, F. J.; Budzichowski, T. A. *Polyhedron* **1995**, *14*, 3239.
- (7) Buys, I. E.; Hambley, T. W.; Houlton, D. J.; Maschmeyer, T.; Masters, A. F.; Smith, A. K. *J. Mol. Catal.* **1994**, *86*, 309.
- (8) Liu, J.-C. *Chem. Commun.* **1996**, 1109.
- (9) Crocker, M.; Herold, R. H. M.; Orpen, A. G. *Chem. Commun.* **1997**, 241.
- (10) Maschmeyer, T.; Klunduk, M. C.; Martin, C. M.; Shephard, D. S.; Thomas, J. M.; Johnson, B. F. G. *Chem. Commun.* **1997**, 1847.
- (11) Thomas, J. M.; Sankar, G.; Klunduk, M. C.; Johnson, B. F. G.; Maschmeyer, T.; Attfield, M. P.; Bell, R. G. *J. Phys. Chem. B* **1999**, *103*, 8809.
- (12) Pescarmona, P. P.; van der Waal, J. C.; Maschmeyer, T. *Eur. J. Inorg. Chem.*, in press.
- (13) Pescarmona, P. P.; van der Waal, J. C.; Maxwell, I. E.; Maschmeyer, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 740.
- (14) Bussian, P.; Sobott, F.; Brutschy, B.; Schrader, W.; Schüth, F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3901.
- (15) Bakhtiar, R.; Feher, F. J. *Rapid Commun. Mass Spectrom.* **1999**, *13*, 687.
- (16) Harrick, N. J. *J. Phys. Chem.* **1960**, *64*, 1110.
- (17) Fahrenfort, J. *Spectrochim. Acta* **1961**, *17*, 698.
- (18) Main MS peaks for the different values of a . For $a = 1$, m/z : 257.55 (H^+ , $a1b3 + 6H_2O$), 275.61 (H^+ , $a1b3 + 7H_2O$), 293.62 (H^+ , $a1b3 + 8H_2O$), 316.67 (H^+ , 275.61 + CH_3CN). For $a = 2$, m/z : 261.59 (H^+), 279.59 (H^+), 302.65 (H^+ , 261.59 + CH_3CN), 320.65 (H^+ , 279.59 + CH_3CN). For $a = 3$, m/z : 373.64 (H^+ , 391.64 - H_2O), 391.64 (H^+), 414.64 (H^+ , 373.64 + CH_3CN), 432.64 (H^+ , 391.64 + CH_3CN). For $a = 4$, m/z : 485.57 (H^+), 503.57 (H^+), 521.57 (H^+), 544.56 (H^+ , 503.57 + CH_3CN). For $a = 5$, m/z : For $a = 5$, m/z : 597.49 (H^+ , 633.49 - $2H_2O$), 615.49 (H^+ , 633.49 - H_2O), 633.49 (H^+), 638.48 (H^+ , 597.49 + CH_3CN), 651.43 (H^+). For $a = 6$, m/z : 727.42 (H^+), 745.36 (H^+), 763.36 (H^+), 781.36 (H^+). For $a = 7$, m/z : 839.28 (H^+ , 857.28 - H_2O), 857.28 (H^+), 875.28 (H^+), 893.28 (H^+), 911.22 (H^+), 929.22 (H^+), 947.22 (H^+ , 911.22 + CH_3CN). For $a = 8$, m/z : 969.20 (H^+), 987.20 (H^+), 1005.19 (H^+), 1023.20 (H^+), 1041.20 (H^+). For $a = 9$, m/z : 1099.06 (H^+), 1117.12 (H^+), 1135.19 (H^+), 1153.12 (H^+), 1171.13 (H^+). For $a = 10$, m/z : 1211.05 (H^+), 1229.00 (H^+), 1247.05 (H^+), 1265.05 (H^+), 1282.99 (H^+), 1301.00 (H^+). For $a = 11$, m/z : 1340.91 (H^+), 1358.91 (H^+), 1376.97 (H^+), 1394.91 (H^+), 1412.91 (H^+). For $a = 12$, m/z : 1470.90 (H^+), 1488.90 (H^+), 1506.84 (H^+),

1524.84 (H⁺), 1542.84 (H⁺). For $a = 13$, m/z : 1600.82 (H⁺), 1618.76 (H⁺), 1636.76 (H⁺), 1654.76 (H⁺).

(19) Brown, J. F.; Vogt, L. H. *J. Am. Chem. Soc.* **1965**, *87*, 4313.

(20) A normalization of the MS data is necessary because the mass spectrometer produces plots in which the intensities of the peaks are not absolute but normalized to the most intense peak, the value of which is set at 100%.

(21) Haddad, T. S.; Moore, B. M.; Phillips, S. H. *Polym. Prepr.* **2001**, *42*, 196.

(22) A similar effect can be seen measuring a mass spectrum of pure cyclopentylsilsesquioxane *a7b3* with similar experimental conditions but at two different cone voltages: with cone = 30 V two main peaks are present, at $m/z = 875.33$ and at $m/z = 1749.89$; with cone = 65 V, the peak at $m/z = 1749.89$, due to the *a7b3* dimer, disappears.

(23) Feher, F. J.; Terroba, R.; Ziller, J. W. *Chem. Commun.* **1999**, 2153.

(24) Harrick, N. J. *Internal Reflection Spectroscopy*; John Wiley & Sons: New York, 1967.

(25) Tauler R.; Kowalski, B.; Fleming, S. *Anal. Chem.* **1993**, *65*, 2040.

(26) Metcalfe, E.; Tetteh, J. *Polym. Mater. Sci. Eng.* **2000**, *83*, 88.

(27) Jackson, J. E. *A users guide to principal components*; John Wiley & Sons: New York, 1991.

(28) This similarity was confirmed by measuring and comparing the transmission IR spectra (KBr pellet) of cyclopentylsilsesquioxane *a7b3* with that of the mixture of silsesquioxanes (mainly containing $a = 5$ and $a = 6$ species) obtained by removing the solvent from the reaction mixture after 18 h of reaction at 50 °C (instead of reflux conditions). The two spectra present corresponding sets of peaks (within 6 cm⁻¹) in the region 670–1000 cm⁻¹.

(29) This hypothesis was confirmed by repeating part of the MS study of the synthesis of silsesquioxane *a7b3* at 50 °C (instead of reflux temperature). In these conditions the hydrolytic condensation is slower and, though the same silsesquioxane species are present in solution, species with $1 \leq a \leq 4$ disappear more slowly and those with $a = 5$ and $a = 6$ reach the maximum of the concentration profile after a longer reaction time.