Synthesis and Characterization of Silsesquioxane Prepolymers Bearing Phenyl and Methacryloxypropyl Groups Obtained by Cohydrolysis

Meiser Valencia,[†] Wibke Dempwolf,[†] Fabian Günzler,[‡] Otakar Knöpfelmacher,[†] and Gudrun Schmidt-Naake*[,†]

Institut für Technische Chemie, Technische Universität Clausthal, Erzstrasse 18, 38678 Clausthal-Zellerfeld, Germany, and Institut für Physikalische Chemie, Georg-August-Universität Göttingen, Tammannstrasse 6, 37077 Göttingen, Germany

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ABSTRACT: We studied systems that are built up of a mixture of phenyltrimethoxysilane (PTMS) and (3-methacryloxy)propyltrimethoxysilane (MPTMS). Four different molar ratios on the monomers MPTMS/(MPTMS + PTMS) (0.1, 0.2, 0.3, and 0.5) were co-condensed in bulk using formic acid as catalyst (molar ratio HCOOH/monomers = 3) at 50 °C. The structures of the obtained silsesquioxanes were characterized using matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) and electrospray ionization mass spectrometry (ESI-MS). Cohydrolysis of organoalkoxysilanes can promote cross-condensation as well as self-condensation. A new parameter, the condensation affinity between two organoalkoxysilanes (f_d), is introduced in this study to discuss this effect. Our results indicate that the average amount of methacryloxypropyl groups in the final silsesquioxanes conserves the introduced proportion of MPTMS/(MPTMS + PTMS).

Introduction

Silsesquioxanes are silicon−oxygen structures with an even number of silicon atoms containing an empirical formula of $RSiO_{1.5}$ (R = organic or inorganic group). Each silicon atom is attached to three oxygen atoms $\{SiO_3\}$, forming several rings connected in a finite three-dimensional molecular skeleton and building polyhedral or cagelike structures. These molecules are also called "fully condensed" silsesquioxanes. If there are molecules possessing reactive silanol (Si−OH) groups, then they are named "incompletely condensed" silsesquioxanes. The hydrolysis and condensation of organoalkoxysilanes $RSi(OR')_3$ using a broad variety of synthetic conditions, e.g., bulk[1,2] and solution[3−6] and catalyzed by acids,[4,7,8] bases,[6,7] and salts,[2,3] allow formation of silsesquioxanes, wherein their structures, species distributions, and molecular weights are influenced by the nature of the organic silicon pendant groups.

Structural features of silsesquioxanes vary from branched or ladderlike polymers with formula $T_n(OH)_x$ with $T = RSiO_{1.5-x/2n}$ to perfect polyhedral. The latter are represented by the formula $(RSiO_{1.5})_n$, with n conditioned to even numbers ($n \geq 6$), and denoted as T_n.

There have been considerable efforts in the investigation of silsesquioxanes for using their interesting siliceous−organic structures for building nanomodifiers[9,10] on organic−inorganic materials and also as model compounds for silica surfaces.[11]

Systematic studies on hydrolysis and condensation of organoalkoxysilanes by changing and comparing the nature of organic pendant groups were performed via the sol−gel process.[4,12,13]

Loy et al.[12] studied the hydrolysis of alkyltrialkoxysilanes containing smaller alkyl substituents (R = methyl to octadecyl). Matějka et al.[13] carried out a sol−gel polymerization of trialkoxysilanes with longer pendant groups (poly(ethylene oxide) chains).

The cohydrolysis of organoalkoxysilanes with tetraalkoxysilanes $Si(OR')_4$ has been implemented by the sol−gel process to produce new well-defined hybrid organic−inorganic materials, increasing the possibilities of the material properties compared to inorganic products obtained by the sol−gel process of inorganic oxides. In this case, the obtained structures have shown more random and complex features than those synthesized involving organoalkoxysilanes. The organoalkoxysilanes most used in the cohydrolysis of the tetraalkoxysilanes $Si(OCH_3)_4$ and $Si(OC_2H_5)_4$ contain as organic groups n-alkyl,[14,15] phenyl,[14,15] vinyl,[16] γ-(2-aminoethylamino)propyl,[17] and diphenyl.[18]

So far, only few attempts of cohydrolysis of organoalkoxysilanes without tetraalkoxysilanes have been carried out. Sorarù et al.[19] have investigated the condensation of a mixture of triethoxysilane (TREOS) and methyldiethoxysilane (MDES) by means of solid-state (MAS)NMR ^{29}Si, FTIR, and DSC. The physical properties of sol−gel materials obtained via this cohydrolysis presented a highly condensed network which contains difunctional and trifunctional units which were distributed randomly. The synthesis was carried out in H_2O:EtOH = 1 at room temperature.

In contrast, Su et al.[20,21] reported a silsesquioxane resin synthesis using cohydrolysis of methyltrimethoxysilane (MTMS), phenyltrimethoxysilane (PTMS), and 1,1,2,2-tetramethyl-1,2-divinylsiloxane. In this case high temperature was used, as well as a mixture of toluene/water as solvent. The detailed characterization has been made by means of electrospray ionization mass spectrometry (ESI-MS), showing a mixture containing siloxane and silsesquioxane. A control was obtained over the molecular weight by changing the synthesis conditions.

Our silsesquioxanes are obtained through co-condensation of phenyl- and 3-methacryloxypropyltrimethoxysilanes. We studied the changes in the general structure of the obtained silsesquioxanes by changing the molar ratio of the used organoalkoxysilanes. Soft ionization techniques like MALDI-TOF-MS and ESI-MS were used for a careful and detailed structural analysis of the synthesized products. Thus, we were able to examine

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[†] Technische Universität Clausthal.

[‡] Georg-August-Universität Göttingen.

* Corresponding author: Fax +49(0)5323 723655; e-mail gudrun.schmidt@itc.tu-clausthal.de.

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Table 1. Molar Amounts for the Cohydrolyzated Silsesquioxanes Obtained from PTMS:MPTMS Co-condensation in Bulk and the Standard Silsesquioxane P-POSS

designation	HCOOH [mol]	PTMS [mol]	MPTMS [mol]	MPTMS/ (MPTMS + PTMS)
I	0.15	0.025	0.025	0.50
II	0.15	0.035	0.015	0.30
III	0.15	0.040	0.010	0.20
IV	0.15	0.045	0.005	0.10
P-POSS	0.15	0.050		

different features like the influence of the molar ratio between MPTMS and PTMS on the degree of condensation.

We were mainly interested in the control of the appearance of the methacryloxypropyl group in the final silsesquioxanes. This methacryloxypropyl moiety will play an important role in the final silsesquioxane, which will be used as a prepolymer.

Experimental Section

Synthesis. The cohydrolysis was carried out in bulk at 50 °C in open vials with magnetic stirrer. The reaction conditions are shown in Table 1. The cohydrolyzed product with a content of 50% on MPTMS is a very viscous clear liquid, soluble in all common solvents. While increasing the amount of PTMS in the mixture the products became solid, but they were still soluble. The condensation of PTMS to produce the hydrolyzate P-POSS was done keeping the molar ratio 3/1 HCOOH/Si.

The alkoxysilane PTMS (98%) was obtained from ABCR Chemicals and MPTMS (98%) from Sigma. Formic acid (98%) was obtained from Fluka. All of them were used without further purification.

Analytical Techniques. MALDI-TOF-MS measurements were performed on a Bruker Biflex III equipped with a 337 nm nitrogen laser. Positive ion spectra were acquired in linear mode and 20 kV acceleration voltage. The mass spectrometer was calibrated with a peptide calibration standard from Bruker within the mass range from 1000 to 3000 Da.

Several matrix/additive mixtures were tested while analyzing different silsesquioxane structures to find the most suited preparation. According to the literature, 2,5-dihydroxybenzoic acid (DHB),[1,4,6,8] 1,8,9-trihydroxyanthracene (dithranol),[4] 2-(4-hydroxyphenylazo)benzoic acid (HABA),[4,8] and *trans*-3-indoleacrylic acid (IAA)[1,4,8] were used as matrices. Almost always a salt was added. We used sodium trifluoroacetate (NaTFA) and silver trifluoroacetate (AgTFA) to support one sort of ions, making the interpretation of spectra easier. Considering interferences of matrix and additive, best results were obtained using dithranol as matrix with NaTFA as additive. Good experiences with the matrix 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB)[22] while analyzing different polymers[23] led us to try this matrix also here. In the end DCTB was selected as the best matrix leading to high-resolution mass spectra. All results presented here were measured with DCTB and NaTFA.

Samples were prepared from THF solution by mixing matrix (20 mg/mL), sample (10 mg/mL), and salt (10 mg/mL) in a ratio of 10:1:1. All matrices and salts were used as provided by the manufacturer.

ESI-MS experiments were carried out using a Finnigan LCQ ion trap mass spectrometer (Thermo Finnigan, San Jose, CA) equipped with an atmospheric pressure ionization source operated in the nebulizer-assisted electrospray mode. The instrument was calibrated with caffeine, MRFA (L-methionylarginylphenylalanylalanine acetate·H_2O), and Ultramark 1621 (all from Aldrich) in the mass range from 195 to 1822 Da. All spectra were acquired in the positive ion mode over a range of m/z 150−2000 with a spray voltage of 4.5 kV and a capillary temperature of 200 °C. Nitrogen was used as sheath gas (flow: 40 units) and as auxiliary gas (flow: 20 units). Silsesquioxane samples were dissolved in a 3:1 v/v mixture of THF/methanol at a concentration of 0.1 mg/mL. The samples where introduced into the electrospray interface by continuous injection of 3−5 μL/min via a syringe pump. Approximately 200 single spectra were coadded to achieve a high signal-to-noise ratio.

Thermal Analysis. DSC measurements were performed on a DSC 820. Samples were cooled down to −100 °C, and DSC patterns were registered by heating with 10 °C/min up to 250 °C. TGA experiments were carried out on a TGA 850. Both instruments are from Mettler Toledo.

Size exclusion chromatography (SEC) was performed on a system containing a Waters 510 pump with Nucleogel columns (GPC 103-5 and 104-5) from Machrey Nagel using THF (1 mL/min) as eluent at 25 °C. Detection was performed with refractive index detection from Knauer. A calibration curve based on polystyrene standards extended by ethylbenzene for the lower mass range was used for all samples.

Results and Discussion

Thermal Analysis. Thermal stability of P-POSS and the four cohydrolyzates was investigated using thermogravimetric analysis (TGA). The influence of the increase of the PTMS moiety on the different cohydrolyzates in comparison with P-POSS was analyzed by interpreting the initial decomposition temperature (T_d). The initial thermal decomposition temperature is defined as the temperature at which 10% weight loss is observed when heating the sample under air atmosphere.[24] The obtained results are summarized in Table 2. A clear tendency becomes apparent: an increase on T_d is gained by increasing the PTMS moiety. As expected, the standard P-POSS shows with 521 °C the highest decomposition temperature. This result can be ascribed to the higher thermal stability of the phenyl groups in comparison to the methacryloxypropyl groups.

Glass Transition Behavior. DSC analyses were made from every sample. For each one of the cohydrolyzates a glass transition temperature was observed, but no one for P-POSS. The same tendency as for the thermal stabilities can be observed. The T_g increases going from cohydrolyzate I with 7 °C to cohydrolyzate IV with 89 °C, as can be seen in Table 2. These results can be explained by the relative bulkiness of the phenyl groups compared to the methacryloxypropyl groups. As a consequence, the silsesquioxane prepolymers with a major proportion of phenyl groups present higher restriction mobility.

According to the SEC results in Table 2, a major growth of the M_w values for the cohydrolyzates I−IV can be seen in comparison to the standard P-POSS. In the latter case a vitrification process takes place, and as a consequence the molar weight growth is hindered.

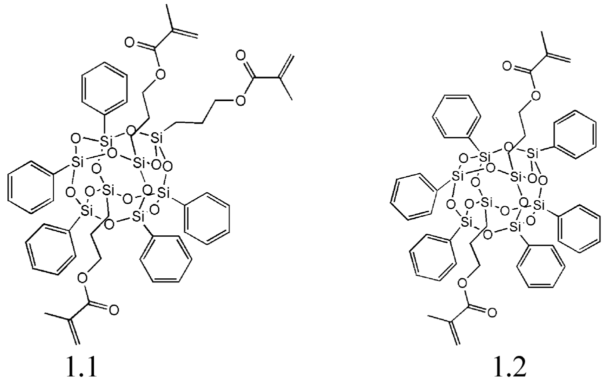
Structural Analysis. Partially hydrolyzed silsesquioxanes are represented by the formula $T_n(OH)_x(OR')_y$, where $T = RSiO_{1.5-(m/2n)}$ and $m = x + y$, x and y being hydroxyl or alkoxy groups, respectively. Intramolecular cycles are formed by reaction between two substituents of the same molecule. For instance, a condensation between two silanol groups produces a new closed ring. The higher the number of m, the lower the degree of condensation for a given n of Si atoms. That means also a lower number of closed rings per molecule. There is a maximum number of intramolecular cycles for a given n of Si atoms which is equal to $(2 + n)/2$ (for n = even) and equal to $(1 + n)/2$ (for n = odd). The actual number of closed rings for a silsesquioxane is $[(2 + n) - m]/2$. Thus, the ratio between the actual number of closed rings and the maximum number of closed rings is given by a parameter (f): $f = (2 + n - m)/(2 + n)$ (for n = even), $f = (2 + n - m)/(1 + n)$ (for n = odd).[1] The higher the f value, the higher the degree of condensation. In our case (R) containing different organic groups should be described by formula $R = M_{a/n}P_{b/n}$, where (P) is standing for phenyl and (M) for methacryloxypropyl. In this study a perfect

Table 2. Weight-Average Molecular Weight (M_w), Number-Average (M_n), Glass Transition Temperature (T_g), and Initial Decomposition Temperature (T_d) of the Cohydrolyzates I−IV and P-POSS

	1 day		3 days		7 days			
designation	M_n	M_w	M_n	M_w	M_n	M_w	T_g [°C]	T_d[a] [°C]
I	1600	2700	1700	3100	2600	4900	7	415
II	1800	3000	2100	4000	2400	5200	47	431
III	1600	2600	1700	3000	2000	4100	67	439
IV	1400	2100	1700	3100	1900	3500	89	459
P-POSS	1400	2000	1600	2600	1600	2700		521

[a] Defined as the temperature at which 10% weight loss is observed when heating the sample under air atmosphere.

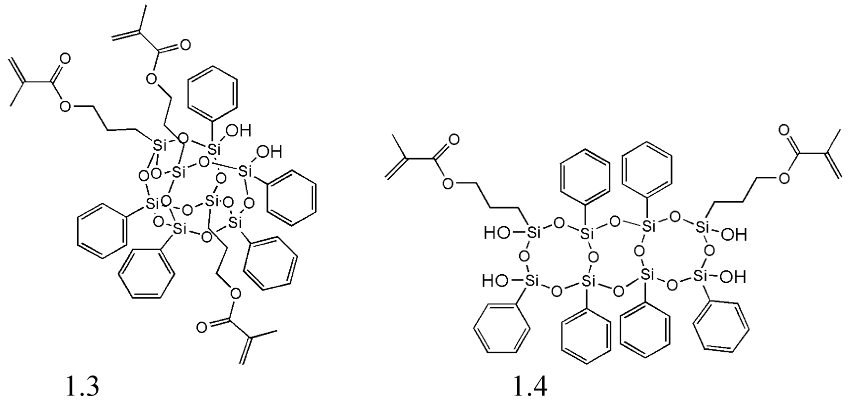
Scheme 1. Possible Structures for a $T_8(OH)_x$ (x = 0, 2, and 4) Silsesquioxane Containing Two Different Organic Groups[a]



1.1

1.2

Scheme	*a*	*b*	OH	c	*f* (c/c$_{max}$)	f_d (a/n)
1.1	3	5	0	5	5/5	3/8
1.2	2	6	0	5	5/5	2/8
1.3	3	5	2	4	4/5	3/8
1.4	2	6	4	3	3/5	2/8



1.3

1.4

[a] *a* = methacryloxypropyl, *b* = phenyl, *c* = actual number of closed rings, *f* = ratio actual number of closed rings and the maximum number of closed rings, f_d = number of methacryloxypropyl over *n*.

polyhedral is written like $T_n = (M_{a/n}P_{b/n}SiO_{1.5})_n$ or $(M_{a/n}P_{b/n}SiO_{1.5-m/2n})_n(OH)_x$ for a non-fully condensed silsesquioxane.

The fraction of component (M) is given by the parameter f_d, which is expressed as the ratio $a/(a + b)$ or a/n. This new parameter (f_d), the condensation affinity between two organoalkoxysilanes, is introduced in this study to discuss the grade of co-condensation.

In Scheme 1 some $T_8(OH)_x$ (x = 0, 2, and 4) silsesquioxanes containing different kinds of bearing groups (M and P), represented by values *a* and *b*, are shown. The actual number of closed rings (c) and the *f* parameter are listed also. The parameter of f_d is also presented in Scheme 1, as the ratio between methacryloxypropyl groups and *n*.

P-POSS. In Figure 1 the MALDI-TOF spectrum of P-POSS, the standard silsesquioxane which contains only phenyl groups, is shown in a mass range from 800 to 4000 Da.

The interpretation of mass spectra has been made by comparing the value of molar mass for a possible expected silsesquioxane formula and the experimentally obtained mass. Unless otherwise noted, the monoisotopic peak was used in the case of MALDI and ESI spectra. All the calculations concerning the possible structures were made using a program written in our institute. We were able to identify species containing 6−29 silicon atoms. For higher masses, however, the signal-to-noise ratios or the resolution was insufficient. The most abundant signal was assigned to $T_7(OH)_3$, corresponding to a non-fully

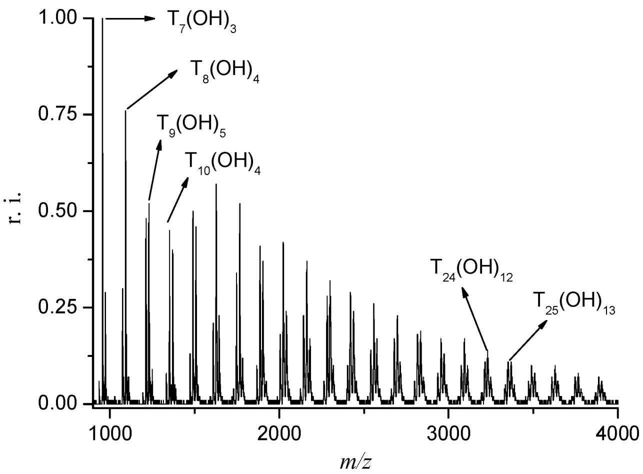


Figure 1. MALDI-TOF-MS of P-POSS.

condensed silsesquioxane bearing three silanol groups. This signal at 953 Da stands in good agreement with the calculated mass of $(M + Na)^+$ at 953 Da. Unfortunately, no analogy can be drawn between the intensity and the actual occurrence of a species within a MALDI- or ESI-MS experiment.

Major clusters can be seen in Figure 1 separated by 138.0 Da, which is the mass of the repeating unit [$C_6H_5SiO_2H$]. Each of these clusters is divided into several peaks, remaining to the same number of silicon atoms. The SEC chromatogram of P-POSS shows a bimodal molar mass distribution. With the assumption that all of these structures are showing the same desorption/ionization probability one maximum can be seen, as stated before, at Si = 7 and another one at Si = 12. This behavior was described before from Williams et al.[1,4] on a more unequivocal example.

A comparison between the results of Kawakami et al.[3] and this work can be done for molecules containing low molecular weights. They identified by means of MALDI-TOF a couple of silsesquioxanes ranging between T_6 and T_9: e.g., $T_8(OH)_2$, $T_8(OH)_4$, and $T_9(OH)_3$ are common structures within Kawakami's work. Their conditions of synthesis (solution: benzene/water/benzyltrimethylammonium hydroxide) afforded molecules with f in a wide range but no preferred value. In contrast, in our study bulk conditions were used.

Our obtained silsesquioxanes are rather non-polyhedral arrangements than open structures, varying from ladderlike to hyperbranched features. The presence of not fully hydrolyzed silsesquioxanes is also remarkable. Some molecules still bearing methoxy groups attached to silicon could be identified: $T_6(OH)_3(OMe)_1$ 847 Da, $T_8(OH)_3(OMe)_1$ 1105 Da, $T_9(OH)_4(OMe)_1$ 1243 Da, and $T_{10}(OH)_5(OMe)_1$ 1381 Da. Pakjamsai also reported a non-fully hydrolyzed silsesquioxane with the formula $T_9(OH)_9(OMe)_2$. It is an indication of stability and a low rate of hydrolysis that these structures can occur regardless of the high concentration of formic acid at the beginning of reaction. Therefore, it is possible to consider that condensation of the oligomers can take place without hydrolysis of every alkoxy group (OR′). Williams et al.[8] reported many of $T_n(OCH_3)_y$ structures obtained after a 3-glycidoxypropyltrimethoxysilane condensation. They stated the high thermal stability as reason for those not fully hydrolyzed silsesquioxane structures even after thermal treatment.

MALDI-TOF and ESI-MS Characterization of Cohydrolyzates I−IV. All of the MALDI-TOF spectra for cohydrolyzates I−IV present a much higher amount of ions compared with P-POSS. This is an evidence for higher molecular feature diversity. We were able to detect and characterize ions in the range from 800 to 2100 Da approximately. Within this range additional ESI-MS measurements were made. The combination of both methods provides a deeper insight into the synthesized structures. Caused by differences in the ionization of each technique a discrimination of special molecules can occur. Both methods combined provide a good picture of the species which are present in the samples within the range mentioned. Above 2100 Da the resolution of the mass spectra did not permit an accurate assignment, and a comparison with the corresponding ESI-MS data was not longer possible. The domain used for the ESI measurements ended at 2000 Da.

Mainly, we found molecules containing 6−14 silicon atoms with a high degree of condensation. Some of them differ also in the value of the parameter f_d. A summary of the possible structures of the identified $T_n(OH)_x$ silsesquioxanes together with their a values for the corresponding cohydrolyzates I−IV is given in Table 3.

Table 3. Composition Assignments of UV-MALDI-TOF and ESI-MS from the Cohydrolyzates I−IV

$T_n(OH)_x$		no. of *a* for the cohydrolyzates			
T	x	I	II	III	IV
T_6	0	3−5	2, 3		
	2	1−6	0−5	0−3	0, 1
	4	1−5	0−5	0−3	0−2
T_7	1	3−5	2−4	1−3	1
	3	1−6	0−5	0−4	0−3
	5	2−4	1−3	0, 1	0, 1
T_8	0	5			
	2	2−7	1−6	0−5	0−3
	4	3−6	1−5	0−3	0−3
	6	3			
T_9	1	5	1		
	3	2−7	1−6	0−4	0−3
	5	4−7	1−5	0−3	0−3
T_{10}	2	5, 6	3, 4	2, 3	1, 2
	4	4−8	1−6	1−5	0−2
	6	4−6	1−5	1−3	0−2
	8			0	
T_{11}	3	5−7	1, 3−5	2, 3	1, 2
	5	5−7	1−5	0−5	0−3
	7	5, 6	2−5	0, 2−4	0−2
T_{12}	4	5−7	4−6		1
	6	4−7	1−6	0−4	0−3
	8		4	2	
T_{13}	5	5−7	3, 4	2, 3	0−3
	7	5−7	2−4	1, 2	0, 2
T_{14}	6				0−3

Because of the complexity of synthesized silsesquioxane structures which are determined by multiple parameters, we have employed a visualization method of the so-called fingerprints. The idea is based on an approach of van Herk et al.[25] in which they analyzed mass spectra of block copolymer polystyrene-*block*-polyisoprene by means of $\langle I_{ij}(cf)_{ij} \rangle$ matrix where the matrix indices i and j are related to the number of repeat units n_j, m_j from which the copolymer is built up, I_{ij} is an intensity peak of MALDI-TOF-MS spectrum which was assigned to a copolymer with a given composition, and $(cf)_{ij}$ is a correction factor. The matrix elements were then graphically presented as a contour plot denoted as the copolymer fingerprint. A series of fingerprints corresponding to different conversion rates enabled to observe the "growth" of copolymer.

In our study, we present fingerprint diagrams constructed in an analogical manner. The structural parameters a and b on the x and y axes represent the number of methacryloxypropyl and phenyl groups, respectively. The color scale in the contour plots expresses the intensity of the MALDI-TOF peak. In Figure 2 we present fingerprints of almost condensed silsesquioxane structures (f higher or equal 0.8), and in Figure 3 structures with f values between 0.5 and 0.6 are shown.

In comparison with block copolymers, fingerprints of silsesquioxane exhibit much complicated patters with multiple high-intensity spots. Those maxima are related to structures with various combination of structural parameters a and b.

The cohydrolyzate I with an equal molar ratio of PTMS and MPTMS shows perfect polyhedral silsesquioxane structures of formula T_8 ($f = 1.00$) and T_6 ($f = 1.00$) with different a values. T_6 exists with 3 ($f_d = 3/6$), 4 ($f_d = 4/6$), and 5 ($f_d = 5/6$) methacryloxypropyl groups at 947, 997, and 1047 Da, respectively. The existence of such structures decreases from cohydrolyzate I (four structures) to cohydrolyzate IV (none).

The fully condensed structures are shown in Figure 2a in a two-dimensional contour plot. A balanced proportion between a and b in the resulting structures can be seen with an emphasis on the proportion equal to the molar ratio of 1:1 employed in the synthesis.

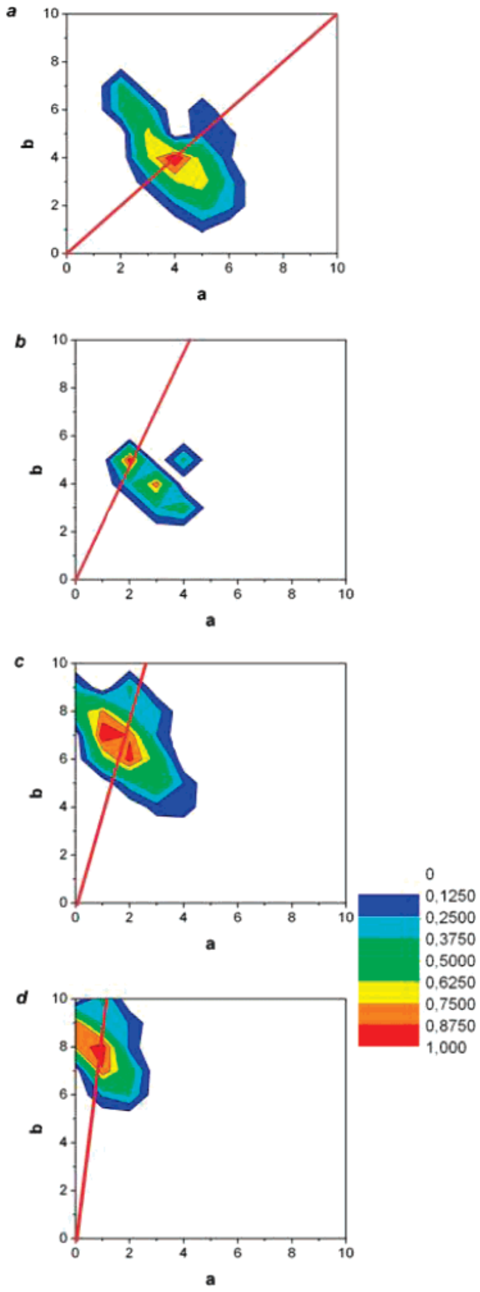


Figure 2. MALDI-TOF intensity diagrams for cohydrolyzates I−IV (a−d) with a higher degree of condensation (f = 0.8−1.0) plotted vs amount of the moieties a (methacryloxypropyl) and b (phenyl). For comparison, reaction mixture ratio of those components is indicated by the straight line.

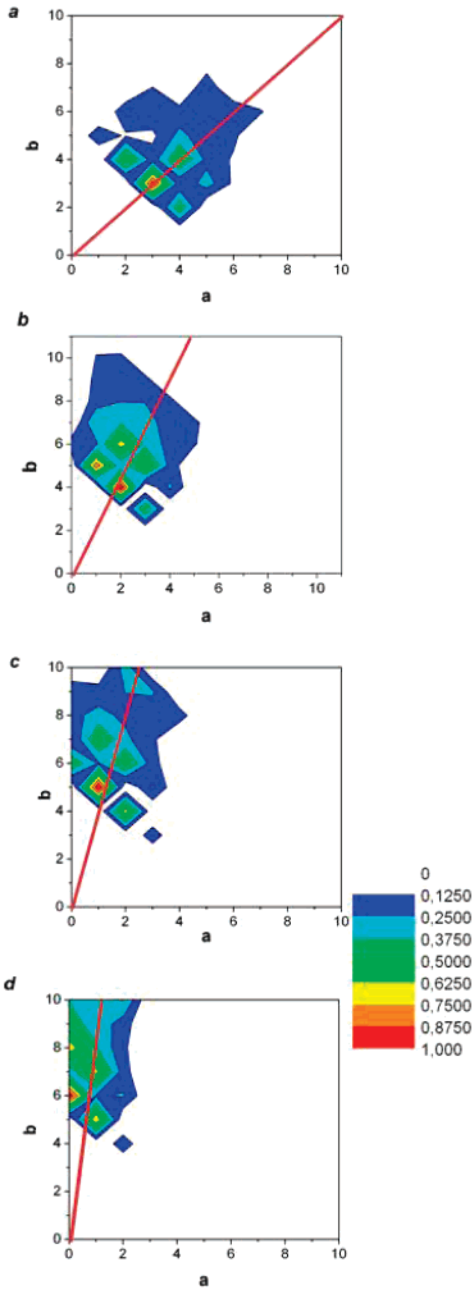


Figure 3. MALDI-TOF intensity diagrams for cohydrolyzates I−IV (a−d) with a lower degree of condensation (f = 0.5−0.6) plotted vs amount of the moieties a (methacryloxypropyl) and b (phenyl). For comparison, the reaction mixture ratio of those components is indicated by the straight line.

Also, fully condensed structures (f = 1.00) are present still bearing a reactive (Si−OH) group, e.g., $T_9(OH)_1$ and $T_7(OH)_1$. $T_7(OH)_1$ is represented by three different structures corresponding to the signals at 1085, 1135, and 1185 Da. Those structures bear 3, 4, or 5 methacryloxypropyl groups, respectively. The existence of these molecules indicates the evidence of a cross-condensation between (3-methacryloxy)propyltrimethoxysilane and phenyltrimethoxysilane, taking place under catalytic conditions.

However, in the majority of cases partially condensed silsesquioxanes are observed. The partially condensed structures vary in the number of silicon atoms n, degree of condensation f, and amount of phenyl as well as methacryloxypropyl groups a. All of them are represented by the general formula $T_n(OH)_x$, where x = 0, 2, 4, 6, 8 for n = even and x = 1, 3, 5, 7 for n = odd. It can be summarized that almost all these structures could be also found within the other cohydrolyzates.

In Figure 3 the cohydrolyzates with a lower degree of condensation (f = 0.5 and 0.6) are shown. The cohydrolyzate I (Figure 3a) shows, besides the structures with a relation of 1:1 of the components PTMS and MPTMS, also structures which are built out of a cross-condensation with a subsequent homocondensation of one of the components.

Changes of f when adding MPTMS to PTMS can be seen by comparing the molecular features of P-POSS and cohydrolyzates I−IV. P-POSS possesses values of f in a range between 0.33 and 0.86, while the diverse cohydrolyzates I−IV presenting values between 0.40 and 1.00. It can be summarized that a large quantity of MPTMS is required for a greater amount of fully condensed structures.

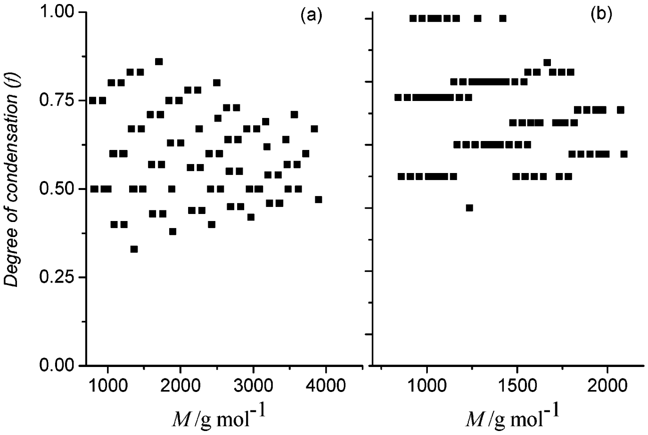


Figure 4. Degree of condensation (f) vs molar mass of (a) P-POSS and (b) cohydrolyzate I.

In Figure 4, the f parameter is plotted against the molar mass of the identified species of P-POSS and cohydrolyzate I. It should be noted, that only one molecule is present with a value of f smaller than 0.50 in the case of cohydrolyzate I. Thus, the f parameter of the cohydrolyzate I is situated in the range between $0.50 \leq f \leq 1.00$, signifying at least 50% of intramolecular cyclization.

Compared to this a broadened range oriented to lower values of f ($0.33 \leq f \leq 0.86$) is shown for P-POSS; this indicates a lower degree of condensation. Furthermore, there are changes in the quantity of molecules having a value f of 1.00. This quantity decreases when PTMS increases in the cohydrolyzates, showing eight fully condensed molecules by cohydrolyzate I and only one by cohydrolyzate IV.

It was not possible to mathematically express the dependency between f and the molar mass. However, regularity on the distribution of dots can be seen: one and the same value of f occurs almost always in the same range of molar mass. For example, molecules with an f of 0.50 exist in two different mass ranges (800−1100 and 1400−1800 Da).

This means that either molecule with higher or lower molar mass presents the same degree of condensation. This distribution can suggest that lower mass oligomers lead to bigger molecules without any further intramolecular condensation. In contrast to molecules with a value f of 0.50, all other molecules with a bigger amount of f show only a single range of molar mass; e.g., the molar mass range between 800 and 1100 Da belongs to molecules having a degree of condensation of 0.75.

Taking into account a comparison of silicon−oxygen pattern between P-POSS and the cohydrolyzates without considering the bearing groups, a distinction of the distribution of silsesquioxanes can be clearly seen from the data, as shown in Figure 4. More opened species are rather present in P-POSS than in the cohydrolyzates, and no variability of species T_n occurs. This comparison can be done for molar masses lower than 2000 Da.

On the other hand, taking into account the degree of condensation (f) and the number of a values, the formation of silsesquioxanes $T_{13}(OH)_x$ or $T_{12}(OH)_x$ via condensation of $T_6(OH)_x$ or $T_7(OH)_x$ oligomers can be explained. According to this evidence, it could be possible to postulate that the degree of condensation of silsesquioxane molecules with higher molar mass depends on the degree of condensations of initial oligomers. However, there is not enough information to state that the formation of silsesquioxanes proceeds after a single condensation via intermolecular silanol reaction between two oligomers and not via another intramolecular condensation.

Cohydrolyzate II which contains a higher proportion of PTMS (70%) presents quite similar features to cohydrolyzate I, but it contains a lower amount of T_n. Within these reaction conditions molecules with smaller values of a compared to cohydrolyzate I with 50% PTMS are observed, as expected. This trend transmits coming to cohydrolyzates III and IV. The formation of structures (either fully condensed or partially condensed) will be influenced by the PTMS to MPTMS proportion. Caused by the reaction condition, some molecules contain no methacryloxypropyl groups ($a = 0$).

Similarly to cohydrolyzate I, the other cohydrolyzates II−IV are showing the same tendency at the fully condensed structures. This means that the incorporation of a and b in the resulting structures is more or less equal to the molar ratio of reaction. Nevertheless, there is a homopolymerization of PTMS in the case of cohydrolyzate IV, as can be seen in Figure 2d.

In the case of the cohydrolyzates II−IV with a lower degree of condensation (Figure 3) a diversification of the resultant species can be seen. As was stated for cohydrolyzate I, a cross-condensation of a and b is followed by a homocondensation of one of the components. The possibility for a condensation of a

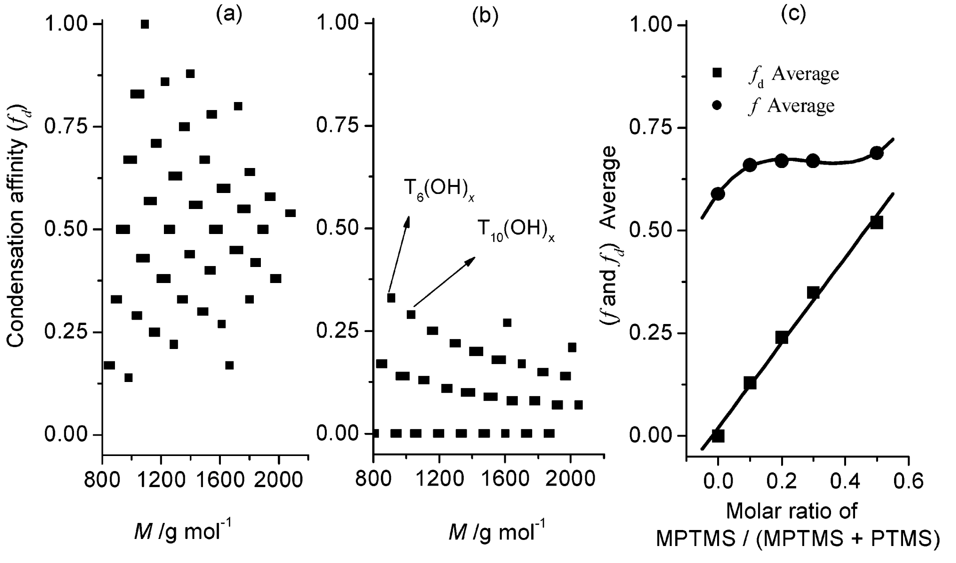


Figure 5. Condensation affinity (f_d) vs molar mass of cohydrolyzate IV (b) and cohydrolyzate I (a). Average degree of condensation (f) and average condensation affinity (f_d) vs molar ratio of the condensate products (c).

decreases for species with lower degree of condensation from cohydrolyzate I to cohydrolyzate IV; this effect can be clearly seen in Figure 3a−d. According to the counter plot of cohydrolyzates I and II (Figure 3a,b), an explanation of the silsesquioxane formation can be stated. Molecules containing *a* and *b* can originate silsesquioxanes with higher molecular weights through addition of *a* or *b*, respectively, but cohydrolyzates III and IV only through a further addition of *b*.

In Figure 5a,b a plot of f_d (a/n) against the molar mass is shown for the cohydrolyzates I (50 mol % MPTMS) and IV (10 mol % MPTMS). A clear distinction can be seen between the distributions of molecules from cohydrolyzates I and IV with decreasing the molar ratio of MPTMS/(MPTMS + PTMS). Using this parameter, the proportion of condensation or self-condensation at different MPTMS/(MPTMS + PTMS) ratios can be visualized. The silsesquioxanes with 0.0 as f_d value indicate only homocondensation of phenyltrimethoxysilane and 1.0 homocondensation of methacryloxypropyltrimetoxysilane, but no co-condensation.

As mentioned above, some molecules were characterized by content of no methacryloxypropyl group ($a = 0$). Those molecules are plotted in Figure 5 with an f_d of 0.0. Their frequency increases from cohydrolyzate II to IV. The distribution of the f_d parameter for the cohydrolyzate IV which contains 90% of PTMS causes molecules bearing a high amount on phenyl groups with a low value of *a* leading to a narrow distribution around 0.10 of the f_d parameter.

An arithmetic average of the f_d parameter was calculated taking into account each f_d value of the identified silsesquioxan structures in a cohydrolyzate. For instance, cohydrolyzates I and IV possess an average of f_d equal to 0.52 and 0.13, respectively. These values are similar to the introduced ratio of the organoalkoxysilane (0.50 and 0.10). This can be seen in Figure 5c, where the plot f_d vs molar ratio of MPTMS/(MPTMS + PTMS) is shown. The plot f_d average and MPTMS/(MPTMS + PTMS) behaves as a straight line. These results indicate that the average amount of methacryloxypropyl groups in the final silsesquioxanes conserves the introduced proportion of MPTMS/(MPTMS + PTMS).

By calculation of an arithmetical average of the *f* parameter for the cohydrolyzate and for P-POSS, it can be stated a slightly increase of the degree of condensation by increasing the MPTMS concentration. This means that, at this reaction condition, the presence of a major amount 3-methacryloxypropyl group leads to higher intramolecular condensations in comparison with the P-POSS standard. As considered before, a major presence of fully condensed silsesquioxan features on the cohydrolyzates take place.

The relationship between the average *f* parameter and molar ratio or organoalkoxysilanes does not resemble the lineal relationship of the former average f_d parameter.

Conclusion

The synthesis of silsesquioxanes bearing two different organic groups was obtained by the co-condensation of two trifunctional organosilanes: phenyltrimethoxysilane (PTMS) and (3-methacryloxy)propyltrimethoxysilane (MPTMS).

Structure determination was made using soft ionization methods, namely ESI and MALDI mass spectrometry. These analysis were carried out for molar masses lower than ∼2100 Da, and the assigned structures have the general formula $T_n(OH)_x$. However, through SEC analysis a presence of molecules with higher molar masses was shown.

The use of *f* and the introduction of the f_d parameters permits a deeper analysis of the distribution of co-condensed and self-condensed silsesquioxanes presented in the four cohydrolyzates. A desired average amount of methacryloxypropyl groups could be introduced into a phenylsilsesquioxane by choosing an adequate ratio of MPTMS/(MPTMS + PTMS). On the other hand, no relationship between the behavior of the degree of condensation and the condensation affinity could be found.

The species presented in the analyzed cohydrolyzates give reason to suppose a monocondensation in order to produce molecules with higher mass than the first formed oligomers. In addition, higher glass transition temperature of the cohydrolyzates was gained by increasing the PTMS amount. It was possible to produce phenylsilsesquioxanes with a controlled average amount of methacryloxypropyl groups which can be used as prepolymers.

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Supporting Information Available: Exact masses of the MALDI-TOF- and ESI-MS experiments and assignments of P-POSS and the four cohydrolyzates. This material is available free of charge via the Internet at http://pubs.acs.org.

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