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Investigation of the Structure of Polymerizable Silsesquioxanes by GPC and MALDI-TOF-MS in Relation to their Viscosity#

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Summary. Hydrolytic condensation of different methacrylate groups containing alkoxy silanes yielded resins which showed interesting properties as a matrix for dental composites. For this purpose, resins of low viscosity are desired resulting in composites with a high amount of inorganic fillers. Our investigations demonstrated that the viscosity of the obtained polycondensates was predominantly influenced by the kind of organic spacer between the methacrylate group and the silicon atom. In addition, the viscosity also significantly changed in dependence of the kind of structure units built. NMR spectroscopic investigations as well as size exclusion chromatography (SEC) and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry showed that the formed structures depended both on the kind of catalyst used for hydrolysis/condensation and the bulkiness of the organic substituent at the silicon atom.

Keywords. Nanostructure; Sols; Polycondensation; Silicon compounds; Dental.

Introduction

Polymerizable inorganic-organic hybrid materials represent a promising alternative to conventional dimethacrylate resins in dental composites [1]. These inorganic-organic hybrid materials can be obtained by the hydrolytic condensation of methacrylate groups bearing trialkoxy silanes in the presence of acids, bases, or other nucleophiles resulting in oligo- or polysilsesquioxanes [2] with inorganic units, like clusters, particles, or a kind of a random polymer network. Reactive organic

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Dedicated to Prof. Dr. *Ulrich Schubert* on the occasion of his 60th birthday

groups are covalently attached to the inorganic units, which can be polymerized in a second step by irradiation of the material with a light source in the presence of a suitable photoinitiator. Organic-inorganic hybrid materials are attractive as filling composite matrix, because they contain inorganic units that reduce the polymerization shrinkage, which frequently causes marginal gaps between the tooth structure (enamel and dentin) and the composite, as well as increase the mechanical properties. Conventional composites suffer from some residual dimethacrylate monomers, which do not polymerize in the curing step, therefore can leach out of the composite upon time and may cause sensibilities or irritations. In the case of oligosilsesquioxanes the methacrylate groups are covalently anchored to the siloxane structure thus increasing significantly the biocompatibility of the material. Dental composite materials are on the market, which are based on organic-inorganic hybrid materials, like Definite®, Ceram X® (Dentsply International Inc., USA), and Admira® (Voco, Germany). Unfortunately, they still contain a certain amount of conventional dimethacrylates as diluent. Therefore, it is a goal of our studies to adapt the viscosity of silsesquioxanes by understanding the influence of the silanes and the reaction parameters on the viscosity. These optimized silsesquioxanes enable the preparation of highly filled composites without the use of conventional dimethacrylates.

We investigated the hydrolytic condensation of different methacrylate-bearing silanes (Fig. 1) at different reaction conditions. With low viscosity resins a high filler load can be realized, but if the applied monomers are too flexible the mechanical properties of the composites can be deteriorated again. Therefore, the structure and flexibility of the silsesquioxane matrix and their viscosity have to be well adapted. Besides the intermolecular polycondensation reaction, cyclization reactions play an important role in the silsesquioxane synthesis process forming polyhedral cyclic oligomers [3]. Larger organic substituents attached to the silicon atom support the formation of cage-like structures by microphase separation and micellar arrangement processes thus preventing gelation [4]. After evaporation of the solvent, soluble polycondensates could be obtained, composed of cyclic polyhedral

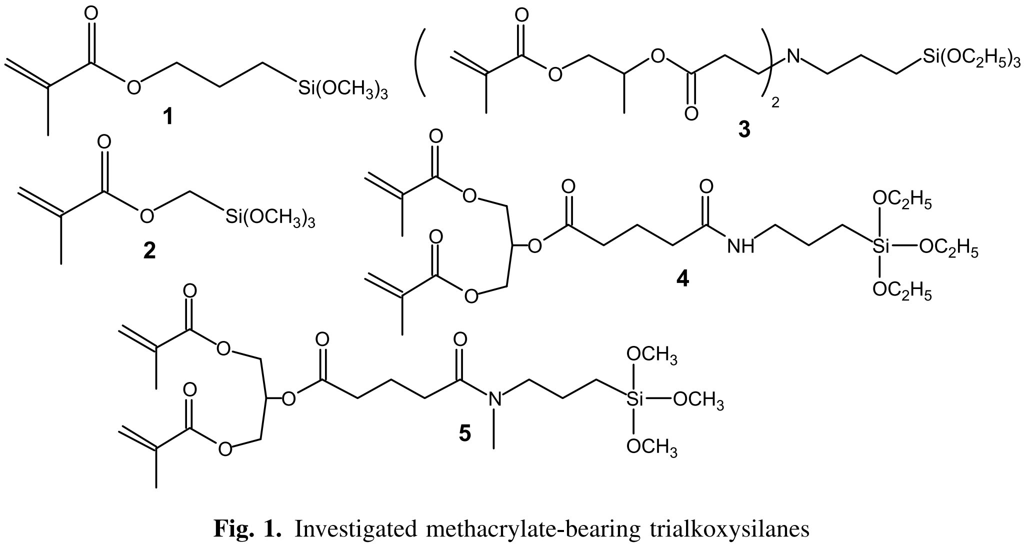

Fig. 1. Investigated methacrylate-bearing trialkoxysilanes

oligomers as well as random branched and ladder polymers. In this work two monomethacrylate silanes (**1** and **2**) with different spacers and three structurally different dimethacrylate silanes (**3**, **4**, and **5**) [5] were investigated.

Results and Discussions

*NMR Spectroscopy of Polycondensates of Silanes **1** to **5***

The hydrolytic condensation of the different silanes resulted in polycondensate resins of high viscosity (Table 1). During the hydrolytic condensation no radical polymerization of the methacrylic groups took place. The complete maintenance of the methacrylate groups in the product was checked by ^{1}H NMR spectroscopy. In the case of silane **1** to **5** no loss of the double bonds was observed. The course of the condensation reaction was followed by ^{29}Si and ^{1}H NMR spectroscopy (residual Si-O*R* units). The reaction conditions were optimized to obtain a high degree of condensation and to ensure the absence of monomers in the product. Using 0.1 *N* ammonium fluoride as catalyst for the hydrolysis and condensation of the trialkoxysilanes (T^0) (subscripts indicate the number of siloxy groups attached to the silicon site [6]), only small amounts of T^2 units and mainly T^3 units were observed in the ^{29}Si NMR spectra. Additionally the amount of residual alkoxy groups per silicon atom was estimated by ^{1}H NMR spectroscopy to be below 0.08 mol/mol silane. If the hydrolysis and condensation reaction was catalyzed by aqueous 0.5 *N* HCl, the maximally possible degrees of condensation were slightly lower, indicated by more intense signals of T^2 in the ^{29}Si NMR spectra and a very small signal for T^1 in the case of **S1b**. The amount of residual alkoxy groups ranged between 2–0.5 mol/mol silane in this case. For the polycondensates of **2** no residual alkoxy groups were found neither with fluoride nor with HCl catalysis. Condensation of **3** was not performed with HCl as catalyst due to the presence of a tertiary amine group in the silane molecule. Besides ethanol as solvent for the

Table 1. Reaction conditions for the prepared polycondensates of the corresponding silanes and their properties

Silsesquioxane resin	Catalyst	Solvent	$\frac{\text{Viscosity}}{\text{Pa} \cdot \text{s}^{a}}$	$\overline{M}_n$/g mol^{-1} by SEC-analysis (PDI)
S1a	NH_4F	ethanol	6	6400 (3 max) (2.49)
S1b	HCl	ethanol	2	1200 (unsymm) (1.37)
S2a	NH_4F	*i*-propanol	2440[b, c]	5800 (3 max) (3.87)
S2b	HCl	*i*-propanol	104	61200 (1.37); 1430 (1.47)[d]
S3a	NH_4F	ethanol	8	4400 (shoulder) (1.11)
S3a*	NH_4F	methanol	2	3500 (shoulder) (1.11)
S4a	NH_4F	ethyl acetate	95600–25100[c]	–
S4b	HCl	ethyl acetate	10380[c]	–
S4aS	NH_4F	–	20800–10900[c]	14200 (2 max) (1.76)
S4bS	HCl	–	480	4800 (2 max) (1.78)
S5a	NH_4F	ethyl acetate	350	7200 (2 max) (1.49)

[a] Measured with the CP system at a shear rate of 1–20 s^{-1}; [b] highly fluctuating; [c] measured with the PP10SS system at a shear rate of 0.1–2 s^{-1}; [d] 2 separated signals

silane (**S3a**), the effect of methanol on the viscosity and structure of the resulting polycondensate was evaluated (**S3a***). The influence of methanol should increase the reaction rate of the hydrolysis and condensation step [7] due to transesterifications [8] and therefore influence the obtained structures [9]. The polycondensate of **4** prepared in the presence of HCl as catalyst was a resin of extremely high viscosity. Therefore, the condensate was additionally silylated with chlorotrimethylsilane in the presence of 2,4,6-collidine to reduce both the amount of residual silanol groups and the high viscosity. The polycondensation of **5** could not be performed with HCl as catalyst. As a consequence the hybrid material was only prepared with ammonium fluoride as catalyst.

Viscosity of Polycondensates

The measured shear viscosities of the silsesquioxane resins varied strongly with the structure of the silanes. Thus, the dimethacrylate silanes with an amide spacer **4** or a methyl amide spacer **5** resulted in materials of extremely high viscosity compared to the other polysilsesquioxanes. This can be explained by the relatively bulky carboxylate bearing spacer and the polar amide group, which is capable of forming hydrogen bonds. These hydrogen bonds can be reduced by methylation of the amide group (**S5a**). Indeed the viscosity of polycondensate **S5a** was reduced to 350 Pa · s, compared to the viscosity of the amid group containing product **S4a** of 95600–25100 Pa · s depending on increase of the shear rate. The viscosity of the silsesquioxane resin can additionally be fine tuned by variation of the reaction conditions for the hydrolytic condensation. For example, by using ammonium fluoride as catalyst the viscosity of the silsesquioxane resin increased compared to the corresponding resin catalyzed by HCl. For **S1** the viscosity increased only by a factor of 3 from 2 (**S1b**) to 6 Pa · s (**S1a**), but for **S2** a dramatic increase was observed from 104 (**S2b**) to about 2400 Pa · s (**S2a**). Comparing the viscosities of **S4**, the viscosity was also significantly increased by using fluoride catalysis (**S4a**). In this case the material showed pseudoplastic behavior. The viscosity decreased from 95600–25100 Pa · s with increasing shear rate from 0–2 s^{-1}. In addition, the silylation capped the residual silanol groups and reduced the viscosity from 95600–25100 to 20800–10900 Pa · s for **S4aS** and from 10380 to 480 Pa · s for **S4bS**. In the former case only 3 mol% trimethylsilyl groups were found in the ^{1}H NMR spectrum of the product, thus confirming the high degree of condensation of alkoxysilane by fluoride catalysis. Therefore, the decrease in viscosity was lower compared to the HCl-catalyzed product, where the condensation degree was less complete and after silylation 26 mol% trimethylsilyl groups were found in the polycondensate. The viscosity was reduced by a factor of $\sim$20 in **S4b**.

SEC Measurements

The molecular weight distributions of the silsesquioxane resins were determined by SEC [10–11]. The lower viscosity of **S1b** in comparison to **S1a** can be explained by the existence of smaller oligomers in the resin, which is detected as a multimodal peak in the chromatogram of the samples. Thus, for **S1a** a $\overline{M}_n$-value of 6400 g/mol was found with three different maxima at 15900, 4000, and 1700 g/mol in the SEC curve (Fig. 2a), resulting in a polydispersity index (PDI) of 2.49. The three different

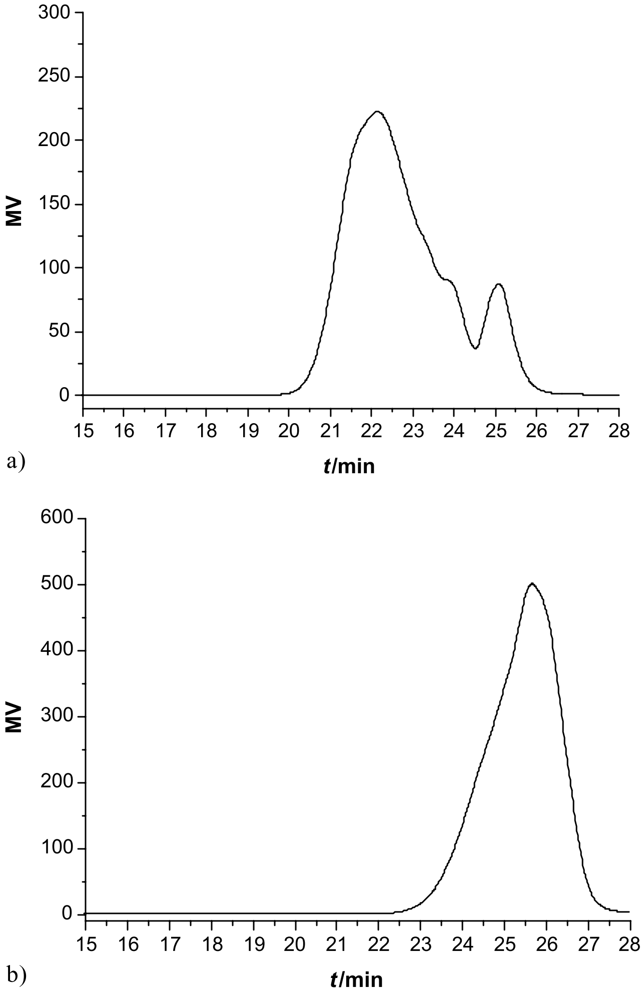

Fig. 2. SEC curves of a) **S1a** and b) **S1b**

maxima were consistent with the results of condensation of **1** with formic acid as reported by *Eisenberg et al.* [11], which were explained by two or three reaction stages. Species were formed with 6–8 Si atoms in the first stage through inter- and intramolecular condensation reactions. The more open and reactive species of this stage reacted among themselves giving the second cluster types (second peak in the SEC). Further intermolecular condensation of reactive species from the first and the second stage resulted in the formation of higher molecular weight products. The maximum at $\overline{M}_n = 1700\,\mathrm{g/mol}$ corresponds to stable species with 8–10 Si units, the second maximum at 4000 g/mol to species with 20–22 Si units, the most intense and broad peak with the maximum at 15900 g/mol (84–85 Si units) indicates higher oligomeric species. The lower viscous resin **S1b**, however, showed a lower $\overline{M}_n$ value of 1200 g/mol (Fig. 2b). The SEC curve was an unsymmetrical peak due to some polymers or oligomers with higher molecular weights. This indicates, that mainly small clusters with 6–7 Si units exist.

S4 resins showed high viscosity. The higher viscosity of **S4aS** compared to **S4bS** can be explained by a larger amount of higher molecular weight oligomers.

For **S4aS** we found an $\overline{M}_n$ value of 14200 g/mol with two maxima at 25000 g/mol and 6000 g/mol (13–14 Si units, "second clusters") and a PDI of 1.76. HCl catalysis resulted in species in **S4bS** with $\overline{M}_n = 4700$ g/mol and the chromatogram showed two maxima at 8500 g/mol (~19 Si units, "second clusters") and 4400 g/mol (~10 Si units, "first clusters"), respectively. The PDI was 1.78 in this case. Surprisingly, for the methylated and fluoride catalyzed **S5a** a $\overline{M}_n$ of 7200 g/mol was measured with two maxima at 10500 (~23 Si units) and 5700 g/mol (12–13 Si units). The $\overline{M}_n$ value was nearly half of the $\overline{M}_n$ of **S4aS**. Besides silylation the molecular structure, especially the H-bonding sites of the silane, seems to have an influence on the oligomers/clusters formed.

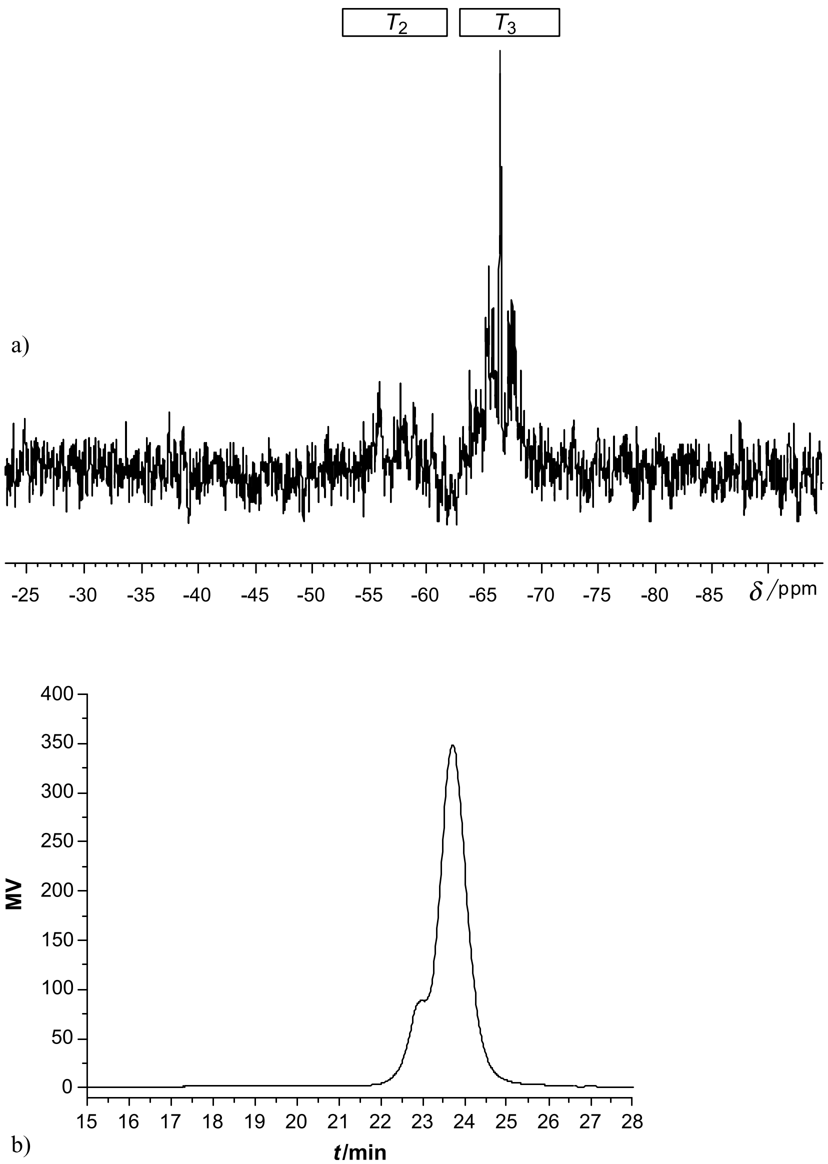

Fig. 3. ^{29}Si NMR spectrum and SEC curve of **S3a**

The influence of the kind of alcohol as solvent on the condensation products was investigated with silane **3**. The lower viscosity of the polycondensate prepared in methanol (**S3a***) can be explained by the lower number-average molecular weight of 3500 g/mol while for **S3a** a $\overline{M}_n$-value of 4400 g/mol was measured. In both cases a small shoulder at higher molecular weight was observed in the chromatogram. Contrary to the other compounds, a narrow molecular weight distribution expressed by a PDI of 1.11 was observed for both samples. The $\overline{M}_n$ value of 4400 g/mol and the shoulder at around 8500 g/mol correspond to species with ~8–9 Si units and ~16–17 Si units, respectively. Similar, the $\overline{M}_n$-value of 3500 g/mol may confirm 6–7 Si units as main product and $\overline{M}_n = 7200$ g/mol corresponds to second clusters with around 14 Si units. The existence of defined polyhedral clusters as main products was also indicated in the ^{29}Si NMR spectrum by individual sharper signals in the T^3 region (Fig. 3).

In contrast to the **S3** products the silsesquioxanes of **2** showed broad molecular weight distributions, especially **S2a** with a PDI of 3.87 caused by 3 different molecular weight maxima (12600 g/mol (~80 Si units), 3700 g/mol (~23 Si units), and 1700 g/mol (10–11 Si units)). Although the overall $\overline{M}_n$ of **S2a** was only 5800 g/mol

Table 2. Found masses in [u] in MALDI-TOF mass spectrum of **S1a** with assignments; repeating unit of **S1** $\Delta r = 188.3$ u, $m/z = (n \cdot \Delta r) + 18 - (t \cdot 18)$

n	t	m/z (exp.)	Species	m/z (th.)
8	5	**1456.0**	T_8	1457.4 (+Na$^+$)
8	5	1471.8	T_8	1473.5 (+K$^+$)
9	5	1644.8	$T_9(\mathrm{OH})$	1645.7 (+Na$^+$)
9	5	1672.3	$T_9(\mathrm{OCH_3})$	1675.8 (+K$^+$)
10	6	**1814.7**	T_{10}	1816.0 (+Na$^+$)
10	6	1830.8	T_{10}	1832.1 (+K$^+$)
10	5	1860.6	$T_{10}(\mathrm{OCH_3})_2$	1862.0 (+Na$^+$)
11	6	2004.3	$T_{11}(\mathrm{OH})$	2004.3 (+Na$^+$)
11	6	2031.4	$T_{11}(\mathrm{OCH_3})$	2034.4 (+K$^+$)
12	7	2173.4	T_{12}	2174.5 (+Na$^+$)
12	7	2192.5	T_{12}	2190.6 (+K$^+$)
12	6	2219.9	$T_{12}(\mathrm{OCH_3})_2$	2220.6 (+Na$^+$)
17		3079.5	$T_{17}(\mathrm{OH})$	3080.0 (+Na$^+$)
18	10	**3249.3**	T_{18}	3250.3 (+Na$^+$)
19	10	**3439.1**	$T_{19}(\mathrm{OH})$	3438.6 (+Na$^+$)
20	11	**3608.2**	T_{20}	3608.9 (+Na$^+$)
etc.				
28	15	5043.0	T_{28}	5043.3 (+Na$^+$)
29	15	5232.2	$T_{29}(\mathrm{OH})$	5231.6 (+Na$^+$)
etc.				
37	19	6667.2	$T_{37}(\mathrm{OH})$	6665.9 (+Na$^+$)
38–44		*etc.*		
45	23	8101.4	$T_{45}(\mathrm{OH})$	8100.3 (+Na$^+$)
46–60		47, 48 more intensive		
etc.				

the viscosity was very high (about 2400 Pa · s), while the viscosity of the HCl catalyzed condensate **S2b** was 104 Pa · s. In the latter case two distinct signals were obtained by SEC. One of the molecular weight maxima $\overline{M}_n$ was at 61200 g/mol with a PDI of 1.37. It was the highest molecular weight maximum we found. The other more intense peak appeared at $\overline{M}_n = 1430$ g/mol (~9 Si units, stable "first clusters")

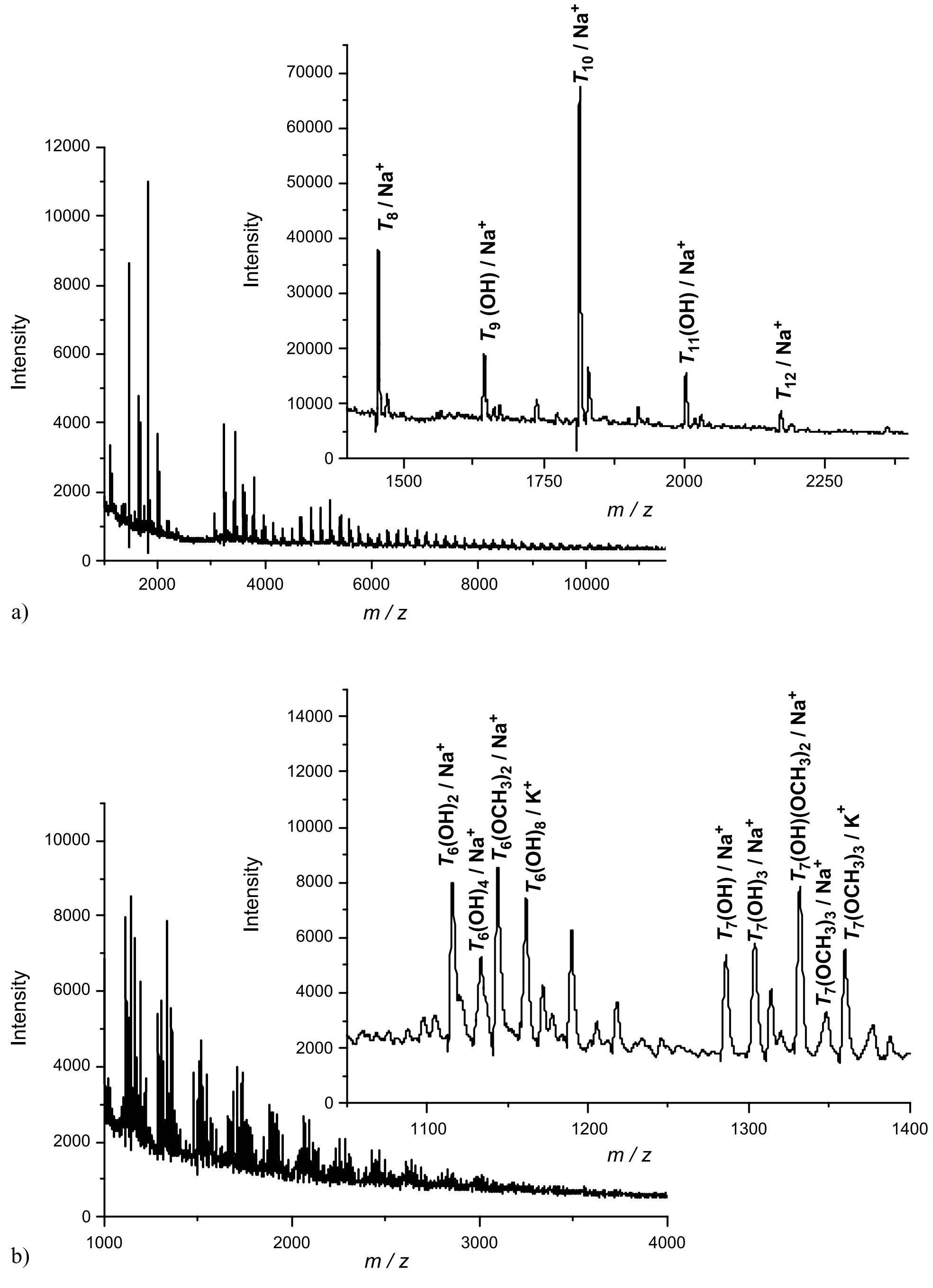

Fig. 4. MALDI-TOF mass spectra of a) **S1a** and b) **S1b**

with a PDI of 1.47. The unsymmetrical peak was faded to higher molecular weights, probably hiding second cluster type species. Although there were higher molecular weight oligomers the viscosity was lower than in **S2a**. This means, in this case there was no direct relationship between the molecular weight distribution of the formed species and the viscosity of the polycondensates of the same silane.

MALDI-TOF Mass Analysis

MALDI-TOF mass analysis from selected samples gave us more information on the structure of the silsesquioxane species. Polycondensation products of **1** have already been investigated and published in recent literature [11–15], but as far as we know, no such products from fluoride catalysis were studied, yet. We found that by condensation of **1** with ammonium fluoride highly condensated species were obtained with no or only one hydroxy group left as can be seen from Table 2, where the main peaks of the spectra were dedicated to the different clusters. A completely condensated cluster of 8 Si units $(R\mathrm{SiO}_{1.5})_8$, for example, is named T_8, unsymmetrical clusters having one condensable group left (OH or OR), for example T_9(OH). The theoretical masses of the clusters were calculated according to the literature [14] considering the repeating units and the intramolecular cycles. In the case of **S1a** structures of more than 60 Si units can be detected (Fig. 4). Preferred clusters were built of 10, 17, and 18 Si units, 28 and 29 Si units, 37 as well as 47 and 48 Si units, where the peaks reached maxima in intensity. Oppositely, peaks for 14–16 Si units were not found, and peaks for 24, 34, and 44 Si units were relatively small in size. *Eisenberg et al.* [11] also detected high molecular weight species,

Table 3. Found masses in [u] in MALDI-TOF mass spectrum of **S1b** with assignments

n	t	m/z (exp.)	Species	m/z (th.)
6	3	1115.6	$T_6(\mathrm{OH})_2$	1116.8 (+Na$^+$)
6	3	1143.9	$T_6(\mathrm{OCH_3})_2$	1144.8 (+Na$^+$)
6	2	1133.3	$T_6(\mathrm{OH})_4$	1134.8 (+Na$^+$)
6	0	1189.9	$T_6(\mathrm{OH})_8$	1186.9 (+K$^+$)
7	4	1285.9	$T_7(\mathrm{OH})$	1287.1 (+Na$^+$)
7	4	1314.0	$T_7(\mathrm{OCH_3})$	1317.2 (+K$^+$)
7	3	1303.9	$T_7(\mathrm{OH})_3$	1305.1 (+Na$^+$)
7	3	1331.9	$T_7(\mathrm{OH})(\mathrm{OCH_3})_2$	1333.1 (+Na$^+$)
7	3	1348.0	$T_7(\mathrm{OCH_3})_3$	1347.1 (+Na$^+$)
		1360.0	$T_7(\mathrm{OCH_3})_3$	1363.2 (+K$^+$)
8	4	1473.9	$T_8(\mathrm{OH})_2$	1475.4 (+Na$^+$)
8	3	1519.9	$T_8(\mathrm{OH})_2(\mathrm{OCH_3})_2$	1521.4 (+Na$^+$)
9	5	1662.1	$T_9(\mathrm{OH})$	1661.8 (+K$^+$)
9	4	1679.7	$T_9(\mathrm{OH})_3$	1679.8 (+K$^+$)
9	4	1707.9	$T_9(\mathrm{OH})(\mathrm{OCH_3})_2$	1707.8 (+K$^+$)
9	3	1736.0	$T_9(\mathrm{OH})(\mathrm{OCH_3})4$	1737.8 (+K$^+$)
etc.				
13	6	2424.3	$T_9(\mathrm{OH})(\mathrm{OCH_3})_2$	2425.0 (+K$^+$)
etc.				
16...				

for example, $T_{52}(OH)_8$, but not of every size and most of them were not fully condensated structures. Despite of these high molecular weight species in **S1a,** the mixture was of low viscosity, and the viscosity can be reduced to some extend by condensation with hydrochloric acid (**S1b**). In this case only clusters up to 8 Si units were found in the mass spectrum. They were more open and they contained some residual methoxy groups (Table 3). This was consistent with the results of the SEC analysis with the only maximum at about 1200 g/mol in **S1b**.

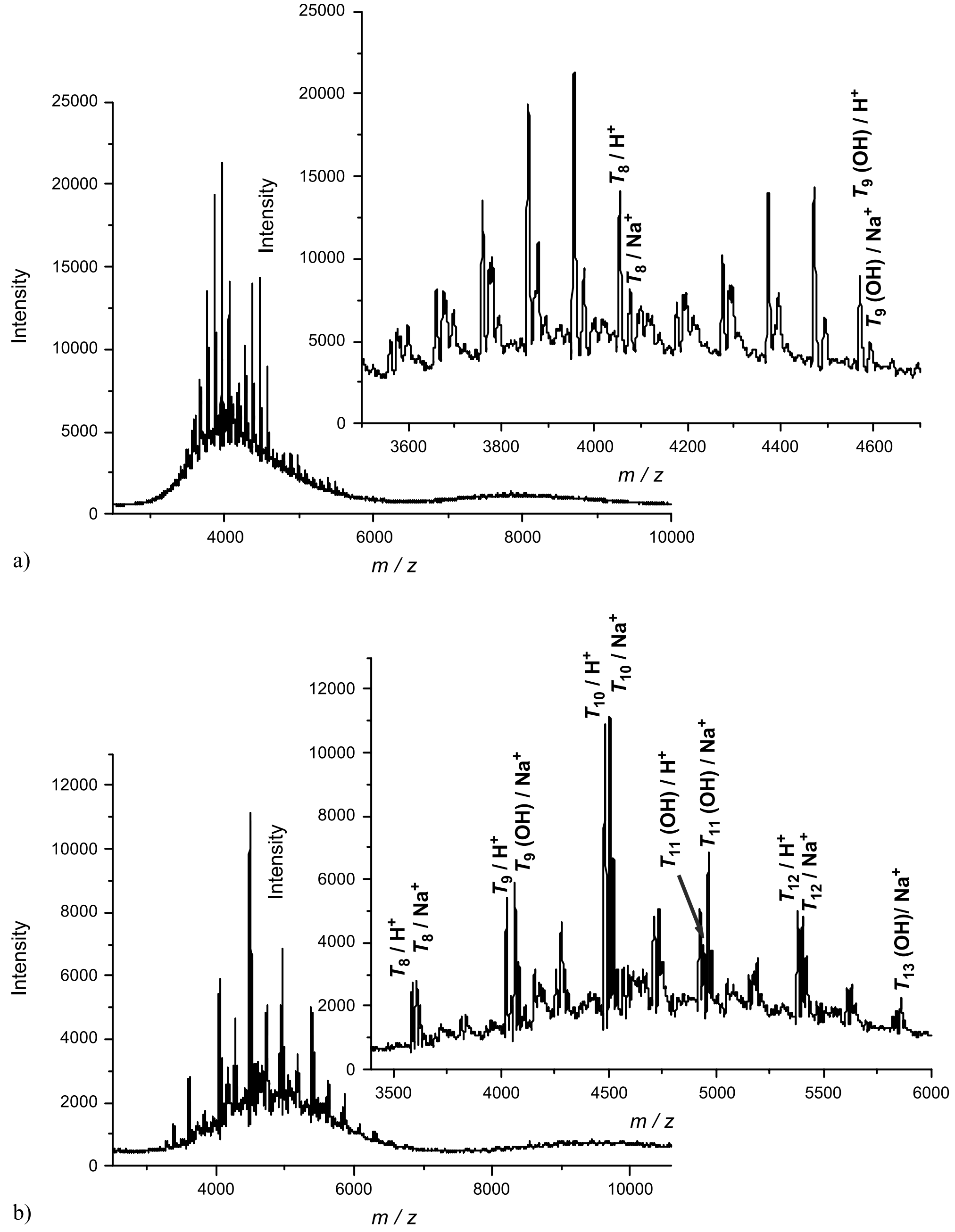

Fig. 5. MALDI-TOF mass spectra of a) **S3a** and b) **S5a**

Investigation of **S3a** confirmed the bimodal and narrow distribution of the molecular weight from the SEC experiment. The clusters T_8, T_9(OH), T_{10}, T_{11}(OH), T_{15}(OH), and T_{16} were found in the MALDI-TOF mass spectrum (Fig. 5). Additionally, fragmentations of these species occurred by subsequently loosing 4 fragments of 98 u, which corresponded to the methacrylate fragment $CH_2{=}C(CH_3)COOCH_2^+$ (98.1 u).

S5a showed a MALDI-TOF mass spectrum (Fig. 5) with mainly the clusters T_8 until T_{13}(OH). A small bump could be recognized between 7000 and 10000 u, which might hide a small amount of second cluster type species as found in the SEC. No higher molecular weight species were detectable, thus the high viscosity was not caused by high molecular weight oligomers. Due to the bulky organic substituent a kind of micellar arrangement of the silane during hydrolysis might favor the built up of only small clusters in contrast to **S1a** [4, 16].

In conclusion, polymerizable resins of varying viscosity were obtained by the hydrolytic condensation of different methacrylate group bearing trialkoxy silanes. High condensation degrees were reached by ammonium fluoride catalysis. The viscosity was mainly determined by the organic substituent, but also by residual silanol groups, which can increase the viscosity due to hydrogen bonding. This can be prevented by a subsequent silylation step. On the other hand, the viscosity was increased to some extent by using ammonium fluoride as catalyst, because higher molecular weight species were formed, although the amount of residual silanol groups was reduced compared to HCl catalysis. With silanes **3**, **4**, and **5** with bulkier organic substituents smaller Si-cluster sizes were obtained compared to **1** or **2**. But this was not the determinant parameter for the viscosity of the silsesquioxane resins. For the application as a matrix for dental composites a well adapted silsesquioxane or a mixture could be used, fine tunable by the reaction conditions chosen for the condensation step.

Experimental

^{1}H NMR (400 MHz) and ^{29}Si NMR (79 MHz) spectra were recorded with a DPX-400 spectrometer (Bruker) using *TMS* as standard. The ^{29}Si NMR spectra were recorded with INEPT technique to increase the selectivity and sensitivity. The viscosity was measured with a rotational viscosimeter (Bohlin CVO-120HRNF) at 23°C either with a cone plate-system (2.5°/20 mm, gap 0.07 mm) or a plate–plate system (10 mm, gap 0.5 mm). Molecular weight distributions of the silsesquioxane oligomers were measured by SEC in *THF* using linear polystyrene standards (Waters system including a 515 HPLC pump, 717 autosampler, PSS GPC PHASE SDV 50/100/10E5A columns, 2410 differential refractive index detector, Millenium^{32} software). MALDI-TOF mass spectrometry was carried out on a Bruker Reflex III. 0.5 mm^3 of a solution of the sample (1 mg/cm^3 in *THF*) and 0.5 mm^3 of the matrix solution (20 mg/cm^3 of dithranol in *THF*) were mixed on a stainless steel sample slide. The solvent was evaporated in a stream of air at ambient temperature. Poly(ethylene oxide)s were used for calibration. Conditions for the measurements: polarity: positive; flight path: reflection; 20 kV acceleration voltage; nitrogen laser ($\lambda = 337$ nm).

The solvents ethanol, methanol, isopropanol, and ethyl acetate as well as *THF* and *tert.*-butyl methyl ether were dried over molecular sieves. 0.5 *N* HCl (Aldrich, Switzerland), H_2O (puriss, pa), and NH_4F (Fluka, Switzerland) were used as received. 2,4,6-Collidine and chlorotrimethylsilane (Fluka, Switzerland) were distilled before use. 3-Methacryloxypropyltrimethoxysilane (**1**) (Fluka, Switzerland) and methacryloxymethyltrimethoxysilane (**2**) (Geniosil® XL33, donated from Wacker-Chemie, Germany) were used without further purification. The syntheses of bis[2-(2(1)-methacryloyloxypropoxycarbonyl)ethyl)]-3-triethoxysilylpropylamine (**3**) and 1,3(2)-dimethacryloyloxypropyl [4-(3-triethoxysilyl)propylaminocarbonyl]butyrate (**4**) were carried out as described previously [5]. 1,3(2)-Dimethacryloyloxypropyl[4-(3-triethoxysilyl)propyl-*N*-methylaminocarbonyl]butyrate (**5**) was synthesized analogous to **4** with *N*-methylaminopropyltrimethoxysilane (ABCR, Germany) instead of aminopropyltriethoxysilane as starting silane.

Preparation of the Silsesquioxanes

S1a and **S1b**

In 748.8 g ethanol 83.2 g (335 mmol) **1** were dissolved. Then 36.22 g (2.01 mol referred to H_2O) of either a 0.1 *N* NH_4F solution (**S1a**) or a 0.5 *N* HCl solution (**S1b**) were added to start the hydrolysis. The degree of condensation was observed by ^{29}Si NMR spectroscopy. After stirring at room temperature for 48 h (**S1a**) or 72 h (**S1b**) the solvent was removed under reduced pressure to obtain the silsesquioxane resin **S1a** as clear, slightly yellow viscous oil or **S1b** as clear and colorless viscous oil.

S1a: ^1H NMR ($CDCl_3$): $\delta = 0.71$ (br, $SiCH_2$), 1.20 (q, $OCH_2C\underline{H}_3$, residual alkoxy), 1.77 (br, $SiCH_2C\underline{H}_2$), 1.93 (s, $=CCH_3$), 3.71–3.88 (m, $OC\underline{H}_2CH_3$, residual alkoxy), 4.11 (br, $COCH_2$), 5.54, 6.09 (2br, $=CH_2$) ppm; ^{29}Si NMR ($CDCl_3$): $\delta = -71$–-63 (m, T_3), -62–-56 (m, T_2) ppm.

S1b: ^1H NMR ($CDCl_3$): $\delta = 0.72$ (br, $SiCH_2$), 1.21 (q, $OCH_2C\underline{H}_3$, residual alkoxy), 1.80 (br, $SiCH_2C\underline{H}_2$), 1.93 (s, $=CCH_3$), 3.72–3.90 (m, $OC\underline{H}_2CH_3$, residual alkoxy), 4.13 (br, $COC\underline{H}_2$), 5.55, 6.10 (2br, $=CH_2$) ppm; ^{29}Si NMR ($CDCl_3$): $\delta = -71$–-63 (m, T_3), -62–-53 (m, T_2), -52–-47 (m, T_1) ppm.

S2a and **S2b**

Compound **2** (44.06 g, 0.2 mol) was dissolved in 102.8 g isopropanol, then 10.81 g (0.6 mol referred to H_2O) of either a 0.1 *N* NH_4F solution (**S2a**) or a 0.5 *N* HCl solution (**S2b**) were added. The mixture was stirred at room temperature for 24 h (**S2a**) or 48 h (**S2b**). After evaporation of the solvent at reduced pressure the silsesquioxane resin **S2a** was obtained as a clear and colorless highly viscous resin, **S2b** was obtained as a slightly yellow, clear viscous resin.

S2a: ^1H NMR ($CDCl_3$): $\delta = 1.89$ (br, $=CCH_3$), 3.58–4.02 (br. m, $SiCH_2$), 5.51, 6.03 (2br, $=CH_2$) ppm; ^{29}Si NMR (79 MHz, $CDCl_3$): $\delta = -84$–-74 (m, T_3) ppm.

S2b: ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.91$ (br, $=CCH_3$), 3.80 (br, $SiCH_2$), 5.53, 6.06 (2br, $=CH_2$) ppm; ^{29}Si NMR ($CDCl_3$): $\delta = -82$–-73 (m, T_3), -73–-62 (T_2) ppm.

S3a and **S3a***

Compound **3** (100 g, 0.16 mol) was dissolved in 233.3 g ethanol (**S3a**) or methanol (**S3a***). To start hydrolysis and condensation 11.53 g (0.64 mol referred to H_2O) of a 0.1 *N* NH_4F solution were added and the mixture was stirred at room temperature for 24 h. The sol was filtrated through a frit and the solvent was evaporated under reduced pressure. **S3a** and **S3a*** were obtained as clear and colorless viscous resins. **S3a**/**S3a***: ^1H NMR ($CDCl_3$): $\delta = 0.57$ (br, $SiCH_2$), 1.28 (m, 2 $CHC\underline{H}_3$), 1.51 (br. m, $C\underline{H}_2CH_2Si$), 1.93 (s, 2 $=CCH_3$), 2.42 (m, $C\underline{H}_2CH_2CH_2Si + 2\ CH_2C\underline{H}_2N$), 2.76 (t, 2 $C\underline{H}_2CH_2N$), 4.03–4.26 (2m, 2 $C\underline{H}_2CH(CH_3)$), 5.17 (br, 2 $CH_2C\underline{H}(CH_3)$), 5.58, 6.10 (2s, $=CH_2$) ppm; ^{29}Si NMR ($CDCl_3$): $\delta = -70.0$–-62.5 (m, T_3), -62.0–-53.0 (m, T_2) ppm.

S4a and **S5a**

The silane (40 mmol) was dissolved in 90 wt.-% ethyl acetate. H_2O (120 mmol) was added as a 1 *N* NH_4F solution and stirred for 48 h at room temperature resulting in a cloudy solution. After filtration through a frit the solvent was evaporated under reduced pressure. The products **S4a** an **S5a** were left as a slightly yellow, clear and highly viscous resins.

S4a: ^1H NMR ($CDCl_3$): $\delta = 0.63$ (br, $SiCH_2$), 1.11–1.28 (m, $Si{-}OCH_2C\underline{H}_3$, residual alkoxy), 1.61 (br, $SiCH_2C\underline{H}_2$), 1.94 (br, 2 $CC\underline{H}_3$, CH_2), 2.20–2.48 (m, $NH(CO)C\underline{H}_2 + O(CO)C\underline{H}_2$), 3.21 (br, NCH_2), 4.12–4.47 (m, $({-}C\underline{H}_2)_2CH$), 5.37 (br, CH), 5.61, 6.11 (2s, $CH{=}$), 6.13–8.55 (br, NH) ppm; ^{29}Si NMR ($CDCl_3$): $\delta = -71$–-63 (m, T_3), -62–-52 (m, T_2) ppm.

S5a: ^{1}H NMR ($CDCl_3$): $\delta = 0.58$ (br, $SiCH_2$), 1.58 (br, $SiCH_2C\underline{H}_2$), 1.94 (m, 2 $C\underline{C}\underline{H}_3$ + CH_2), 2.31–2.49 (m, $NH(CO)C\underline{H}_2 + O(CO)C\underline{H}_2$), 2.88, 2.98 (2s, NCH_3, 2 isomers), 3.32 (br, NCH_2), 3.67 (s, OCH_3, residual alkoxy), 4.17–4.48 (m, $(-C\underline{H}_2)_2CH$), 5.38 (br, CH), 5.61, 6.11 (2s, CH=) ppm; ^{29}Si NMR ($CDCl_3$): $\delta = -73$–-63 (m, T_3), -60–-58 (m, T_2) ppm.

S4b

Compound **4** (109.1 g, 0.2 mol) was dissolved in 981 g ethyl acetate. After addition of 32.4 g (1.8 mol) H_2O as a 0.5 *N* HCl solution the mixture was stirred for 2 h. Afterwards, the solvent was removed under reduced pressure. A clear, slightly yellow highly viscous resin was left. The resulting material (**S4b**) was silylated with chlorotrimethylsilane in the presence of 2,4,6-collidine in *THF*. After solvent exchange (*MTBE*) the organic phase was washed with a saturated NaCl/HCl solution (0.5 mol/l) (1/3), dried (Na_2SO_4), the solvent was removed, and the product was dried in vacuum. **S4b** was obtained as clear slightly yellow highly viscous resin. The product contained 29 mol trimethylsilyl groups per mol trialkoxysilane. **S4b**: ^{1}H NMR ($CDCl_3$): $\delta = 0.10$ (br, $Si(CH_3)_3$), 0.58 (br, $SiCH_2$), 1.11–1.28 (m, residual $Si{-}OCH_2C\underline{H}_3$), 1.55 (br, $SiCH_2C\underline{H}_2$), 1.93 (br, 2 $CC\underline{H}_3 + CH_2$), 2.26 (br, $NH(CO)C\underline{H}_2$), 2.39 (br, $O(CO)CH_2$), 3.18 (br, NCH_2), 3.64 (br, residual $SiOC\underline{H}_2CH_3$), 4.12–4.45 (m, $(-C\underline{H}_2)_2CH$), 5.37 (br, CH), 5.61, 6.12 (2s, CH=) ppm; ^{29}Si NMR ($CDCl_3$): $\delta = -71$–-63 (m, T_3), 9–11 (m, M_1) ppm.

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References

[1] Moszner N, Klapdohr S (2003) Int J of Nanotechnology **1**: 24

[2] Baney RH, Itoh M, Sakakibara A, Suzuki T (1995) Chem Rev **95**: 1409

[3] Matejka L, Dukh O, Hlavatá D, Meissner B, Brus J (2001) Macromolecules **34**: 6904

[4] Loy DA, Baugher BM, Baugher CR, Schneider DA, Rahimian K (2000) Chem Mater **12**: 3624

[5] Moszner N, Völkel T, Cramer von Clausbruch S, Geiter E, Batliner N, Rheinberger V (2002) Macromol Mater Eng **287**: 339

[6] Glaser RH, Garth LW, Bronnimann CE (1989) J Non-Cryst Solids **113**: 73

[7] Aelion R, Loebel A, Eirich F (1950) J Am Chem Soc **72**: 5705

[8] Brinker CJ, Keefer KD, Schaefer DW, Assink RA, Kay BD, Ashley CS (1984) J Non-Cryst Solids **63**: 1

[9] Brinker CJ (1988) J Non-Cryst Solids **100**: 31

[10] Piana K, Schubert U (1994) Chem Mater **6**: 1504

[11] Eisenberg P, Erra-Balsells R, Ishikawa Y, Lucas JC, Nonami H, Williams RJJ (2002) Macromolecules **35**: 1160

[12] Eisenberg P, Erra-Balsells R, Ishikawa Y, Lucas JC, Mauri AN, Nonami H, Riccardi CC, Williams RJJ (2000) Macromolecules **33**: 1940

[13] Wallace WE, Guttman CM, Antonucci JM (2000) Polymer **41**: 2219

[14] Mori H, Lanzendörfer MG, Müller AHE, Klee JE (2004) Macromolecules **37**: 5228

[15] Falkenhagen J, Jancke H, Krüger RP, Rikowski E, Schulz G (2003) Rapid Commun Mass Spectrom **17**: 285

[16] Fasce DP, Williams RJJ, Erra-Balsells R, Ishikawa Y, Nonami H (2001) Macromolecules **34**: 3534

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