

Synthesis of Ladder Silsesquioxanes by *in situ* Polycondensation of Cyclic Tetravinylsiloxanetetraols

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Abstract Functionalized tetrahydroxy-cyclotetrasiloxanes are very attractive precursors of tetrasiloxane ring systems in linear silsesquioxanes (LPSQs). Vinyl groups are especially important since they can be employed for various chemical transformations (e.g. hydrosilylation, metathesis reactions, thiol-ene addition). However, isolation of such highly reactive species bearing small side substituents at silicon atoms with high yield is challenging. We overcame the problem by *in situ* condensation of 2,4,6,8-tetrahydroxy-2,4,6,8-tetravinyl-cyclotetrasiloxanes, derived from potassium organosiloxanolate $\{(K^+)_4[ViSi(O)O^-]_4\}$ nL (L = EtOH, H₂O). Oligomeric LPSQ materials having a siloxane backbone with ladder structure and functionalized with side vinyl groups were thus prepared. Hexamethyldisilazane was employed for chain termination. The liquid materials show remarkably good solubility in organic solvents. They were isolated and characterized using spectroscopic methods. Information on their structure and molecular masses was derived from MALDI-TOF and MALLS measurements. Size exclusion chromatography (RI detection, volume of elution measurements) was also used. The products were characterized by wide-angle X-Ray diffraction measurements (WAXS) and their thermal characteristics (TGA and DSC) were obtained.

Keywords Ladder oligosilsesquioxanes · Cyclosilanolate · Polycondensation · MALDI-TOF

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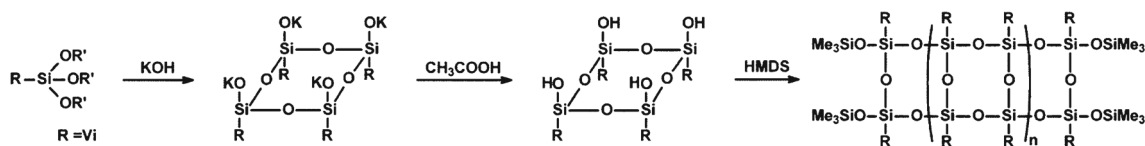
1 Introduction

Linear, ladder-type silsesquioxanes (LPSQs) can be regarded as an intermediate between polyhedral silsesquioxanes (POSS) and single-chain linear siloxanes. They are of increasing interest due to their excellent physicochemical properties, high thermal stability and good mechanical performance. Their hybrid structure (inorganic double chain backbone and organic side groups) results in a low dielectric constant. They are not only thermally- and chemically resistant but also well soluble in organic solvents and show good film-forming properties, so they are attractive as functional materials [1].

The regularity of the LPSQ backbone depends greatly on the methods used for their preparation and can be complicated by uncontrolled side reactions. Ladder-type silsesquioxanes were first reported by Brown et al. [2]. Their synthesis was based on the use of highly reactive trifunctional silanes $RSiX_3$ ($X = Cl$ and OR) as monomers and gave LPSQs with high molecular weight, but of ill-defined architecture. The number of structural defects in polysilsesquioxane materials increases with increasing molecular weight until random networks are formed [3]. The resulting degree of randomness depends both on the nature of the substituent at the silicon atom and the reaction conditions [4]. Several synthetic protocols for the preparation of ladder polysilsesquioxanes have been developed more recently [5, 6]. Efforts are focused on the control of the structure of the double siloxane backbone. The molecular design of the precursor was found to be of special importance. Weak supramolecular interactions (H-bonding or π - π stacking) between silanol groups and/or template molecules help in the synthesis of well-defined LPSQs *via* stepwise coupling and condensation polymerization [7]. The procedure is based on

the template-directed formation of a pseudo-ladder superstructure. It made possible the synthesis of soluble ladder polyphenylsiloxanes having triple [8] and even quadruple [9] chains. High-molecular-weight ladder polyphenylsiloxanes of regular structure were also synthesized by use of “monomer self-organization-lyophilization-surface-confined polycondensation” [7]. Well-defined ladder poly(methylphenylsiloxanes) were obtained as well via nonhydrolytic condensation [10]. Polysilsesquioxanes can be also obtained by condensation of specific tetrasiloxane precursors such as disiloxanes $[\text{RSiX}_2]_2\text{O}$ and cyclotetrasiloxanes $[\text{RXSiO}]_4$ that help the formation of a true ladder structure. Linear ladder silsesquioxanes have been synthesized from sila-functionalized $[\text{RSiXO}]_4$ ($\text{R} = \text{Me}, \text{Ph}; \text{X} = \text{H}, \text{OEt}, \text{NCO}$) [11, 12]. Polycondensation of all-*cis* or *cis-trans-cis* isomers of cyclic tetrasiloxanes [13] or isocyanates [14] gives linear polymers of high regularity and defined tacticity. Unno et al. reported the stepwise stereo-controlled condensation of cyclosilanol for the preparation of tricyclic [15] pentacyclic [16] bi-, tri-, tetra- and pentacyclic ladder siloxanes with an all-*anti* conformation [17], nonacyclic [18] as well as heptacyclic ladder siloxanes and methyl-substituted ladder polysilsesquioxanes [19]. Ladder oligosilsesquioxanes of low molecular weight were also prepared by controlled condensation of an isocyanate functionalized cyclosiloxane precursor: *cis,trans,cis*- $[\text{MeSi}(\text{NCO})\text{O}]_4$ [20, 21].

However, the reported silsesquioxanes obtained with $[\text{RSi}(\text{OH})\text{O}]_4$ bear only simple Me or Ph side groups. The presence of reactive pendant groups would make them more useful as versatile functional materials. Applications of ladder polysilsesquioxanes with vinyl or chloropropyl groups could be of high interest. Our aim was the synthesis of soluble well-defined LPSQs functionalized with vinyl side groups capable of various chemical transformations. We have found that, under specific conditions, condensation of silanol groups in 2,4,6,8-tetrahydroxy-2,4,6,8-tetrafunctional cyclosiloxanes, prepared *in situ* from the respective potassium silanolates, can give oligomeric materials with ladder structure (Scheme 1). Reference materials were prepared by simple hydrolytic condensation of $\text{ViSi}(\text{OEt})_3$ in the presence of K_2CO_3 [1] and stepwise coupling polymerization [22]. The structure and the properties of the resulting materials were analyzed by use of NMR, XRD, TGA, DSC, SEC (MALLS and RI) and MALDI-TOF.



Scheme 1 Synthesis of oligomeric Vi-LPSQs by *in situ* polycondensation method

2 Experimental

2.1 Materials

Reagents [triethoxyvinylsilane (Aldrich, 97 %), trichlorovinylsilane (Aldrich, ≥ 97 %), chlorotrimethylsilane (Fluka Analytical, purum, ≥ 98 %, GC), hexamethyldisilazane (Fluka Analytical, ≥ 98 %, GC), potassium hydroxide (Aldrich, ACS reagent, ≥ 85 , pellets), acetic acid (Aldrich, ≥ 99 %, ReagentPlus[®]), potassium carbonate K_2CO_3 (POCH, pure p.a.), magnesium sulfate (VI) MgSO_4 (Chempur, pure), sodium chloride NaCl (Chempur, pure p.a.)] were used as received. Triethylamine (POCH, pure p.a.) was dried over KOH and distilled before use, p-phenylenediamine (pPDA) (Aldrich, ≥ 99 %, GC/NT) was sublimed before use.

Solvents [ethyl acetate (Chempur, pure p.a.), toluene (Chempur, pure p.a.), hexane (Aldrich, Chromasolv[®] for HPLC, ≥ 97 %, GC), pentane (Chempur, pure p.a.), DMF (Chempur, pure p.a.) acetonitrile (Chempur, pure p.a.) tetrahydrofuran (THF) (Chempur, pure p.a.), dichloromethane (Chempur, pure p.a.), ethanol (Polmos, 95 %), methanol (Chempur, pure p.a.)], were purified according to literature procedures [23].

2.2 Instrumentation

Liquid state NMR (^1H , ^{13}C and ^{29}Si NMR) spectra of the precursors and condensed soluble materials in CDCl_3 were recorded on a Bruker DRX-500 MHz spectrometer, with TMS as the reference. Solid-state ^{29}Si NMR spectra were recorded on a AV-400 Bruker spectrometer at 59.627 MHz with high power decoupling (hpdec) of direct polarization that enabled quantitative integration. The peak positions were referenced to the signal of Q_8M_8 (trimethylsilyl ester of cubic octameric silicate) as standard.

Phase transitions of polymers were studied by differential scanning calorimetry (DSC) technique (DuPont 2000 thermal analysis system). Thermograms were taken for samples (sealed in aluminium pans) quenched rapidly from the melt (room temperature) and then heated at the rate of 10 °C/min from -155 °C to 50 °C. The sample was kept at 50 °C for 3 min to destroy any thermal history. Subsequently, it was quenched to -155 °C and heated again at 10 °C/min to 100 °C. Thermogravimetric measurements

were performed using a Hi-Res TGA 2950 Thermogravimetric Analyzer (TA Instruments) in a nitrogen atmosphere (heating rate 10 °C/min, resolution 3, sensitivity 3).

Mass spectrometric measurements (MALDI-TOF) were made on a Voyager-Elite (PerSeptive Biosystems, USA) time-of-flight instrument equipped with a pulsed N₂ laser (337 nm, 4-ns pulse width) and time-delayed extraction ion source. An accelerating voltage of 20 kV was applied. Mass spectra were recorded in the linear positive ion mode using 1,8-dihydroxy-9-anthracenone (ditranol, DT) as the matrix and LiCl or CF₃COOK as the cationization agents.

For size exclusion chromatography (SEC) an Agilent 1100 series chromatograph composed of degasser, pump, and autosampler was used. Two PL Gel 5 μm MIXED-C columns (7.8 x 300 mm) were employed in a series (temperature 27 °C). RI (OPTILAB T-rex, Wyatt) and MALLS (DAWN HEOS, II, Wyatt, λ = 682 nm) were used as detectors. The mobile phase was dichloromethane at a flow rate of 0.8 mL/min. Samples (concentration of polymers: 7 mg/mL) were dissolved in CH₂Cl₂ and passed through 0.2 μm pore size SRP membrane filters. Injection volumes of the sample solutions were 100 μL. Molecular masses were derived from a calibration curve based on polystyrene standards and Astra 4.90.07 software was used to treat the data.

WAXS (wide angle-X-ray scattering) was used for the determination of sample structure. The experiments were made on a Philips X'Pert Pro MD diffractometer with Cu Kα1 line radiation monochromatized by a Ge(111) monochromator and standard Bragg-Brentano geometry with θ–2θ 0.008° step size and 5–90° 2θ range.

2.3 Synthetic Procedures

2.3.1 Potassium Tetravinyltetracyclosiloxanolate

Potassium tetravinyltetracyclosiloxanolate was prepared according to the literature procedure [24]. Triethoxyvinylsilane (0.235 mol) and a mixture of anhydrous ethanol (30 ml) and water (0.4 ml) were simultaneously added drop-wise to a mixture of hexanes (220 ml) and KOH (0.276 mol) in a round-bottom flask equipped with a magnetic stirrer and a thermometer. The rate of addition was adjusted so that the temperature in the reaction flask did not exceed 24 °C. Once the addition was complete, the reaction mixture was stirred for another 1.5 h at room temperature then it was cooled to 0–4 °C in a water/ice bath for 5 hours. The fine white solid that precipitated from the solution was filtered off under reduced pressure, washed with large volumes of n-pentane and dried under high vacuum (1 Torr) at room temperature to constant weight. The white crystalline powder was obtained in a yield of 2.37 g (76 %). It was stable for months at low temperatures.

Elemental analysis: Calculated [%] for {(K⁺)₄[ViSi(O)O-]₄}EtOH 5H₂O, C₈H₁₂Si₄O₈K₄ EtOH 5H₂O: C=18.74; H=4.40; Found [%]: C=19.0; H=5.0.

¹³C CP MAS NMR, δ [ppm]: 129.4 (=CH-); 135.1 (=CH₂)

²⁹Si CP MAS NMR, δ [ppm]: –82.2

2.3.2 Preparation of Oligomeric Vi-LPSQs by *in situ*-Polycondensation of Cyclic Tetravinylsiloxanetetraol

Procedure A Solid potassium tetravinyltetracyclosiloxanolate (15.6 mmol) was slowly added to a cooled (0–5 °C) solution of acetic acid (63 mmol) in ethyl acetate (420 ml). The temperature of the reaction mixture was kept below 10 °C during the addition of cyclosiloxanolate and for another 30 minutes once the addition was completed. Potassium acetate was filtered off and the filtrate was left for 30 minutes to warm up to room temperature. Hexamethyldisilazane (81.5 mmol) and MgSO₄ (10 g) were then added to the reaction mixture, which was stirred under reflux. The progress of reaction was monitored by MALDI-TOF spectrometry. The reaction was continued until condensation of silanol groups was complete. The mixture was then allowed to cool, MgSO₄ was filtered off, the solution was passed through a short silica plug and all volatiles were removed at room temperature under high vacuum. The product was a viscous, colorless liquid.

Procedure B Acetic acid was added dropwise to a cooled (0–5 °C) suspension of potassium tetravinyltetracyclosiloxanolate in a reaction solvent. The temperature of the mixture was kept below 10 °C for another 30 minutes once the addition was completed. Potassium acetate was filtered off and the filtrate was left for 30 minutes to warm up to room temperature. Hexamethyldisilazane and MgSO₄ were added to the reaction mixture, which was then heated under reflux with stirring to achieve complete condensation of silanol groups. The progress of reaction was monitored with MALDI-TOF spectrometry. The reaction mixture was allowed to cool, MgSO₄ was filtered off, the solution was passed through a short silica plug, and all volatiles were removed at room temperature under high vacuum. The product was a viscous, colorless liquid.

¹H NMR (CDCl₃), δ [ppm]: 0.08 (OSiMe₃), 5.91 (–CH=CH₂)

¹³C NMR (CDCl₃), δ [ppm]: 0.3 (OSiMe₃), 129.9 (=CH-), 135.5 (=CH₂)

²⁹Si NMR (CDCl₃); δ [ppm]: –81.0 (H₂C=CH-SiO_{3/2}), 10.5 (OSiMe₃)

2.3.3 Preparation of Vi-LPSQs by Stepwise Coupling Polymerization

Vi-LPSQ polymer of high molecular mass was prepared in 56 % yield using a previously described procedure [22].

^1H NMR (CDCl_3), δ [ppm]: 0.07 (OSiMe_3), 5.92 ($-\text{CH}=\text{CH}_2$)

^{13}C NMR (CDCl_3), δ [ppm]: 0.45 (OSiMe_3), 130.0 ($=\text{CH}-$), 134.9 ($=\text{CH}_2$)

^{29}Si NMR (CDCl_3); δ [ppm]: -81.0 ($\text{H}_2\text{C}=\text{CH}-\text{SiO}_{3/2}$), 10.0 (OSiMe_3)

SEC (RI): $M_n=34\ 000$, $M_w=274\ 000$, $\text{PDI}=8.1$, (MALLS): $M_n=1460\ 000$, $M_w=3330\ 000$, $\text{PDI}=2.3$.

2.3.4 Preparation of Branched Polysilsesquioxane by Polycondensation of $\text{ViSi}(\text{OEt})_3$

The branched analogue of linear Vi-LPSQs was prepared according to the literature procedure [1]. The product was obtained as an insoluble solid (reaction yield: 90 %).

^{13}C CP MAS NMR, δ [ppm]: 130.8 ($=\text{CH}-$), 135.6 ($=\text{CH}_2$)

^{29}Si CP MAS NMR; δ [ppm]: -81.2 ($\text{H}_2\text{C}=\text{CH}-\text{SiO}_{3/2}$)

3 Results and Discussion

3.1 Monomer Synthesis and Polycondensation

The use of hydroxyl-substituted cyclic siloxane stereoisomers is a precondition for the synthesis of linear oligo- and polysilsesquioxanes of stereoregular structure. However, their isolation from the crude reaction mixture is difficult and the product is obtained with a very low yield. For example, a mixture of four stereoisomers was prepared by hydrolysis of the hydride precursor, $[\text{MeSi}(\text{H})\text{O}]_4$ catalyzed by $\text{Pd}/\text{C}_{\text{act}}$ [13]. *Cis-trans-cis*-tetraol was isolated using specific recrystallization protocol with about 8 % yield and polycondensed in the presence of K_2CO_3 as a catalyst, resulting in a ladder-like product of *cis*-syndiotactic conformation [13, 25]. Unfortunately, the method is not suitable for some monomers (e.g. Vi-substituted ones).

Tetraorganocyclotetrasiloxanates [26] are of interest as precursors of cyclic siloxanetetraols. Removal of metal ions from cyclic tetrametallasiloxanes by dilute aqueous hydrochloric acid is a convenient preparative method resulting in high-yield (80–90 %) formation of stereoregular oligophenylsiloxane polyols: all-*cis*- $[\text{PhSi}(\text{OH})\text{O}]_4$, all-*cis*- $[\text{PhSi}(\text{OH})\text{O}]_6$, *tris-cis-tris-trans*- $[\text{PhSi}(\text{OH})\text{O}]_{12}$ [27]. Analogously, 1,3,5,7-tetramethyl-1,3,5,7-tetrahydroxy-cyclo tetrasiloxane was obtained from all-*cis*-(tetrapotassium tetramethylcyclotetrasiloxanolate) $(\text{K}^+)_4[\text{MeSi}(\text{O})\text{O}^-]_4$ 3L

($\text{L} = \text{EtOH}, \text{H}_2\text{O}$) [28]. Two crystalline isomeric forms (all-*cis* and *cis-trans-cis*) were isolated in good yield (respectively, 29 % and 60 %).

Nevertheless, reports concerning siloxanetetraols functionalized with reactive side groups are scarce as yet. Quite recently, Sparks et al. reported the synthesis of cyclic tetra vinylsiloxanetetraol $[\text{ViSi}(\text{OH})\text{O}]_4$ by acidic hydrolysis of potassium *cis*-tetra vinyltetrasiloxanolate in ethyl acetate [24]. The authors isolated the all-*cis* isomer and described it as reasonably stable, but the yield was not given. The authors presented a ^{29}Si NMR spectrum displaying a single peak at -74 ppm as well as size exclusion chromatography diagrams for the isolated product.

We were not able to obtain pure $[\text{ViSi}(\text{OH})\text{O}]_4$ using the reported procedure. Partial reduction of volume of the crude reaction mixture by evaporation of the liquid components (high vacuum/room temperature) did not give crystalline products but a range of viscous oils. Owing to the silanol functions in the product, the materials were not stable and cross-linked after several days on the bench at room temperature. However, $[\text{ViSi}(\text{OH})\text{O}]_4$ was indeed formed during the acidic hydrolysis of the silanolate, as confirmed by spectroscopic analysis. $[\text{ViSi}(\text{OSiMe}_3)\text{O}]_4$ was detected (NMR, MS- CI^+) as the only derivative after silylation of $[\text{ViSi}(\text{OH})\text{O}]_4$ with an excess of bis(trimethylsilyl)acetamide (BSA) in the crude reaction mixture (Fig. 1).

We thus decided to convert $[\text{ViSi}(\text{OH})\text{O}]_4$ into oligomeric or polymeric ladder vinylsilsesquioxanes, *in situ* in the reaction mixture and block the reactive SiOH groups with SiMe_3 endgroups by treatment with hexamethyldisilazane (HMDS). Potassium siloxanolate $\{(\text{K}^+)_4[\text{ViSi}(\text{O})\text{O}^-]_4\}_n\text{L}$ ($\text{L} = \text{EtOH}, \text{H}_2\text{O}$) was converted into the corresponding cyclosiloxane tetrol by the removal of potassium ion with concentrated CH_3COOH in an anhydrous solvent. The reaction mixture was refluxed

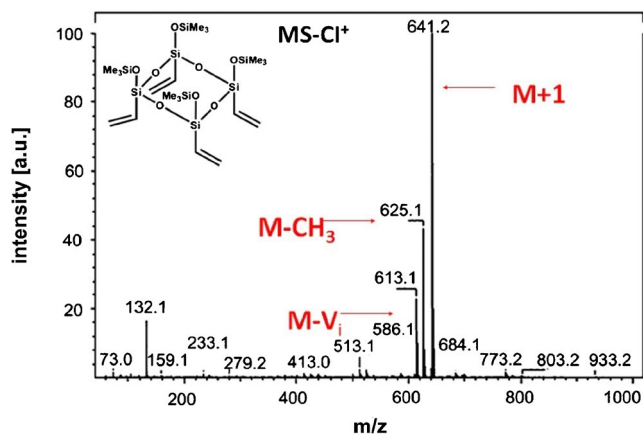


Fig. 1 MS- Cl^+ of $[\text{ViSi}(\text{OSiMe}_3)\text{O}]_4$ obtained by silylation with BSA

Table 1 Reaction parameters and characteristics of the products obtained by *in situ* condensation of tetravinylsiloxanetetraol (molar ratio $[\text{CH}_3\text{COOH}]/[\text{potassium silanolate}] = 4.1$)

Entry	x	y	a_0 [mol/dm ³]	b	Solvent	T [°C]	t [days]	Mn	PDI ₁	Mw	PDI ₂	Y [%]
1–1	A	+	39.0	3.98	toluene	110	7	1100	1.6	6700	1.7	26.7
1–2	A	+	37.1	3.98	CH ₃ COOEt	78	7	1000	1.2	3200	1.6	67.5
1–3	A	+	37.1	3.98	CH ₃ COOEt	78	6	1000	1.4	3000	1.3	71.4
1–4	A	+	32.3	3.98	MeCN	82	4	–	–	–	–	19.4
1–5	B	–	32.3	3.98	CH ₃ COOEt	78	3	800	1.2	3300	1.5	27.4
1–6	B	+	32.3	3.98	CH ₃ COOEt	78	3	300	1.6	–	–	37.9
1–7	B	–	48.5	3.98	CH ₃ COOEt	78	3	400	1.5	4100	1.3	25.8
1–8	B	–	32.3	1.00	toluene	110	3	500	2.3	1500	1.1	87.9
1–9	B	–	32.3	2.00	toluene	110	3	500	2.4	2700	1.1	83.1
1–10	B	–	32.3	3.98	toluene	110	3	1300	1.4	–	–	17.7
1–11	B	+	32.3	3.98	toluene	110	3	600	2.7	1600	2.3	21.0
1–12	B	–	32.3	4.79	toluene	110	4	1200	1.4	–	–	12.9
1–13	B	–	48.5	3.98	toluene	110	3	700	2.1	5900	1.6	19.4
1–14	B	–	97.0	3.98	toluene	110	3	500	2.4	5000	1.4	17.7
1–15	B	+	97.0	3.98	toluene	110	3	600	2.3	1700	1.9	33.1
1–16	B	–	32.3	3.98	hexane	70	3	500	1.7	–	–	9.7
1–17	B	–	74.6	4.95	Et ₂ O	24	13	1100	1.2	–	–	45.2
1–18	B	–	32.3	3.98	THF	66	3	–	–	–	–	32.3
1–19	B	–	32.3	3.98	EtOH	78	3	–	–	–	–	–
1–20	B	–	32.3	3.98	DMF	150	3	–	–	–	–	87.1
1–21	B	–	32.3	3.98	MeCN	82	3	2000	1.2	1400	1.8	40.3

a_0 initial concentration of potassium silanolate $[\text{ViSi}(\text{OK})\text{O}]_4$ in the reaction mixture

b – molar ratio $[\text{HMDS}]/[\text{potassium silanolate}]$

x - synthetic procedure

y - CH_3COOK removed by filtration

T - temperature

t - reaction time

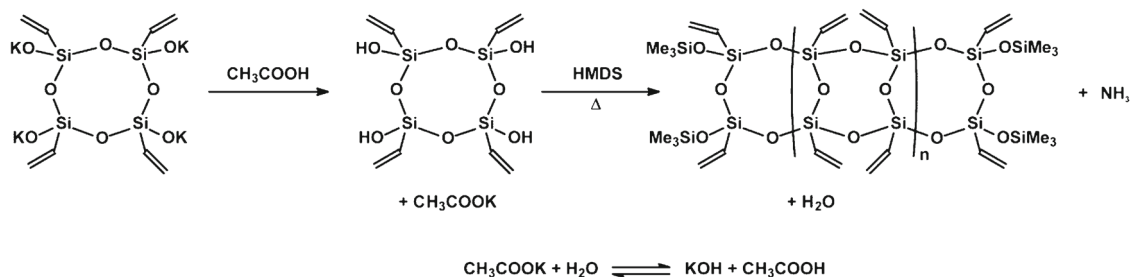
Mn, PDI₁ respectively molecular mass and polydispersity derived from SEC-RI

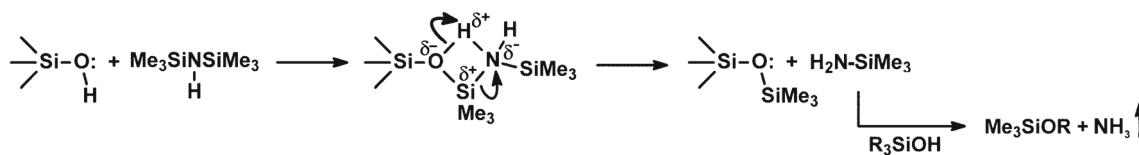
Mw, PDI₂ molecular weight and polydispersity derived from SEC-MALLS

Y - reaction yield calculated for the amount of $[\text{ViSi}(\text{OK})\text{O}]_4$

with HMDS to give the Vi-LPSQs. The condensation was carried out in solvents of various polarities (Et₂O, CH₃COOEt, toluene, hexane, THF, EtOH, DMF, MeCN) (Table 1) and the reaction was followed using MALDI-TOF spectroscopy.

The procedure (Scheme 2) does not involve addition of any catalysts used typically for the condensation of silanols. However, there are many basic species in the reaction mixture. HMDS is a very mild base, much weaker than most organic amines [29]. It has low Lewis basicity ($\text{pK}_a=7.55$)

**Scheme 2** Formation of basic species in the course of *in situ*-polycondensation of $[\text{ViSi}(\text{OH})\text{O}]_4$



Scheme 3 Silylation of silanols with hexamethyldisilazane *via* formation of a bimolecular four-centered “O...H...N...Si” transition state

due to steric factors and possibly also due to delocalization of the nitrogen lone pair. The silylating effectiveness of HMDS is low and requires forceful conditions and long reaction times. Under anhydrous conditions, silylation by HMDS proceeds *via* replacement of the active hydrogen in SiOH by the trimethylsilyl group. Formation of a bimolecular four-centered “O...H...N...Si” transition state (Scheme 3) in the rate determining step is proposed as a result of nucleophilic attack upon the silicon atom [30]. H_2NSiMe_3 , which is slightly more basic than HMDS, is the source of another trimethylsilyl group and gaseous ammonia is produced as the only by-product in the process. However, HMDS is sensitive to moisture. The hydrolysis results in formation of H_2NSiMe_3 and Me_3SiOH which can then interact to give $\text{Me}_3\text{SiOSiMe}_3$. Thus water (and alcohols) should be excluded from the reaction mixture.

The most important source of basic species in the reaction mixture is CH_3COOK , formed as the product of neutralization of silanolate with acetic acid (Scheme 2). It dissolves in H_2O , which is formed continuously during the polycondensation of SiOH groups (MgSO_4 was added in some experiments to bind H_2O). In consequence a strong base (KOH) is generated. It can be a source of silanolate species, either by reaction with silanol chain ends or by scission of siloxane bonds. KOH thus determines the reaction course, but is not a cause of random cross-linking.

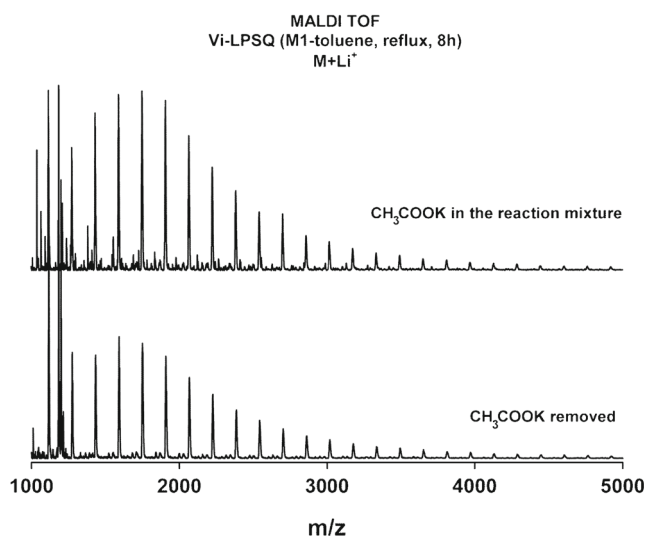


Fig. 2 MALDI-TOF spectra recorded for products obtained according to the procedure B in the presence of CH_3COOK (above) and without it (below)

Several modifications of the general procedure were introduced, but the ratio $[\text{CH}_3\text{COOH}]/[\text{salt}]$ was adjusted to ensure that the reaction medium was always acidic. In order to generate free monomeric tetrols in the reaction mixture, the salt - potassium tetravinyltetracyclosiloxanolate - was added slowly to a cooled solution of concentrated acetic acid in a chosen solvent (procedure A, Table 1). CH_3COOK formed in the neutralization step was either filtered off and the solution containing $[\text{ViSi}(\text{OH})\text{O}]_4$ used for the *in situ* condensation in the presence of HMDS, or the condensation was carried out in a two-phase system in the presence of CH_3COOK . In fact one cannot eliminate partial dissolution of CH_3COOK and formation of KOH even at the earliest stages of the reaction, since molecules of H_2O are present (along with EtOH) in the crystalline structure of $\{(\text{K}^+)_4[\text{ViSi}(\text{O})\text{O}^-]_4\}_n\text{L}$ ($\text{L} = \text{EtOH}, \text{H}_2\text{O}$). In some experiments CH_3COOH was added drop-wise to a suspension of $\{(\text{K}^+)_4[\text{ViSi}(\text{O})\text{O}^-]_4\}_n\text{L}$, (procedure B, Table 1). This did not alter much the structure of the product obtained during the course of the reaction, as indicated by MALDI-TOF MS (Fig. 2) and SEC (RI) (Fig. 3) analyses. However, as one can expect, polycondensation proceeded more effectively in the presence of larger amounts of CH_3COOK .

We have studied (Table 1) the influence of several factors on the course of polycondensation (e.g. the initial concentration of potassium silanolate $[\text{ViSi}(\text{OK})\text{O}]_4$ in the reaction mixture or the molar ratio $[\text{HMDS}]/[\text{potassium silanolate}]$).

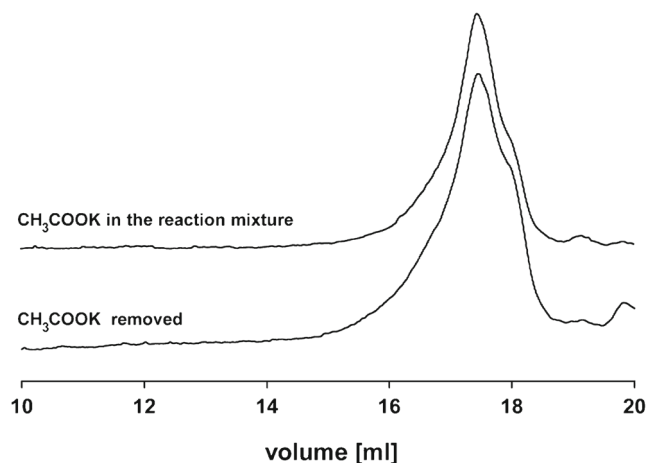


Fig. 3 SEC spectra (RI detection) recorded for products obtained in toluene in the presence of CH_3COOK (above, Table 1, entry 1-10) and after its removal from the reaction mixture (below, Table 1, entry 1-11)

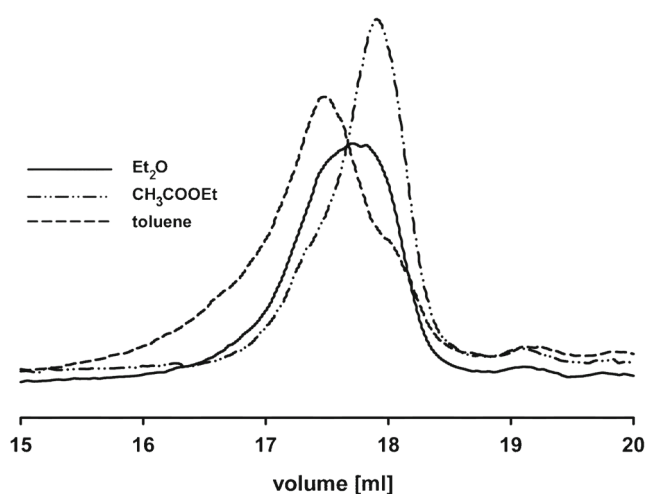


Fig. 4 SEC spectra (RI detection) recorded for products obtained in Et₂O, CH₃COOEt and toluene in the presence of CH₃COOK

Absolute molecular mass measurement (MALLS) was impossible for some samples due to their low Mn. SEC (RI) was used for comparison of volumes of elution of the products (Fig. 4). It was found that among all the reaction parameters (the presence of potassium acetate aside) the temperature of the process and the nature of the solvents are of the highest significance.

The catalytic activity of a base can be affected by the reaction medium. Weakly solvating solvents (e.g. toluene) render naked the nucleophile (e.g. silanolate anion) and thus enhance its reactivity. The use of non-polar toluene facilitates formation of high molecular weight Vi-LPSQ oligomers, but as their PDI and Mw (MALLS) increased their volume of elution and Mn (RI) decreases in a rather anomalous way, especially in experiments carried out following procedure B. It was previously reported that the structure of oligomeric Me-LPSQs changed from linear to

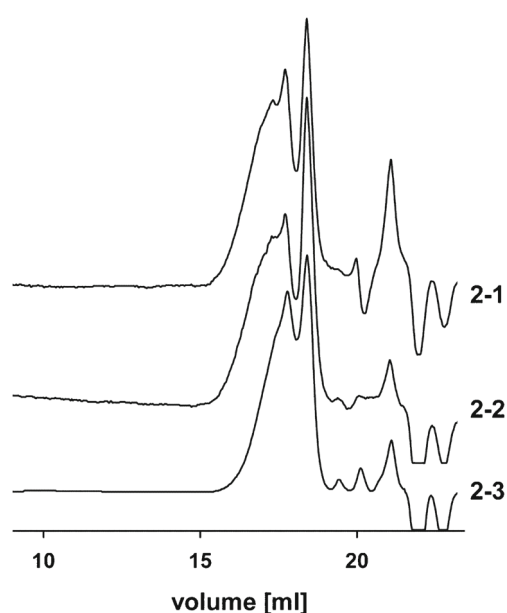


Fig. 5 SEC spectra (RI detection) recorded for products obtained in Et₂O (2-1) and CH₃COOEt (2-2, 2-3) in the presence of Et₃N (Table 2)

branched species, as their molecular weight increased [25]. It seems to be the case for Vi-LPSQs obtained in toluene.

It appears that the solvent should preferably dissolve CH₃COOK, but only to a very small extent. Et₂O would be a good candidate, but its high volatility limited the temperature range of the reaction. Polar-aprotic ethyl acetate was found to be the best solvent for *in situ* condensation of 2,4,6,8-tetrahydroxy-2,4,6,8-tetravinyl-cyclotetrasiloxanes especially conforming to procedure A. It does not cause excessive solvation of potassium ions but is able to take part in hydrogen bonding with silanols. Completely non-polar solvents, such as hexane, did not promote polycondensation of [ViSi(OH)O]₄.

Table 2 Reaction parameters and characteristics of the products obtained by *in situ* condensation of tetravinylsiloxanetetraol carried out in the presence of Et₃N and HMDS

Entry	a ₀ [mol/dm ³]	b	c	d	Solvent	T ₁ [°C]	t ₁ [h]	T ₂ [°C]	t ₂ [h]	Mn	PDI ₁
2-1	0.28	1.32	0.004	0.004	Et ₂ O	RT	18	35	48	2500	1.4
										900	1.1
2-2	0.28	1.32	0.021	0.021	CH ₃ COOEt	RT	18	78	48	2700	1.4
										900	1.1
2-3	0.05	4.10	0.040	0.400	CH ₃ COOEt	RT	170	78	7h	2000	1.3
										700	1.1

a₀ – initial concentration of potassium silanolate [ViSi(OK)O]₄ in the reaction mixture

b – molar ratio [CH₃COOH]/[potassium silanolate]

c – molar ratio [Et₃N]/[potassium silanolate]

d – molar ratio [HMDS]/[potassium silanolate]

T – temperature

t – reaction time

Mn, PDI₁ – molecular mass and polydispersity derived from SEC-RI

Scheme 4 Oligomeric species detected during condensation of $[\text{ViSi}(\text{OH})\text{O}]_4$ in the presence of HMDS

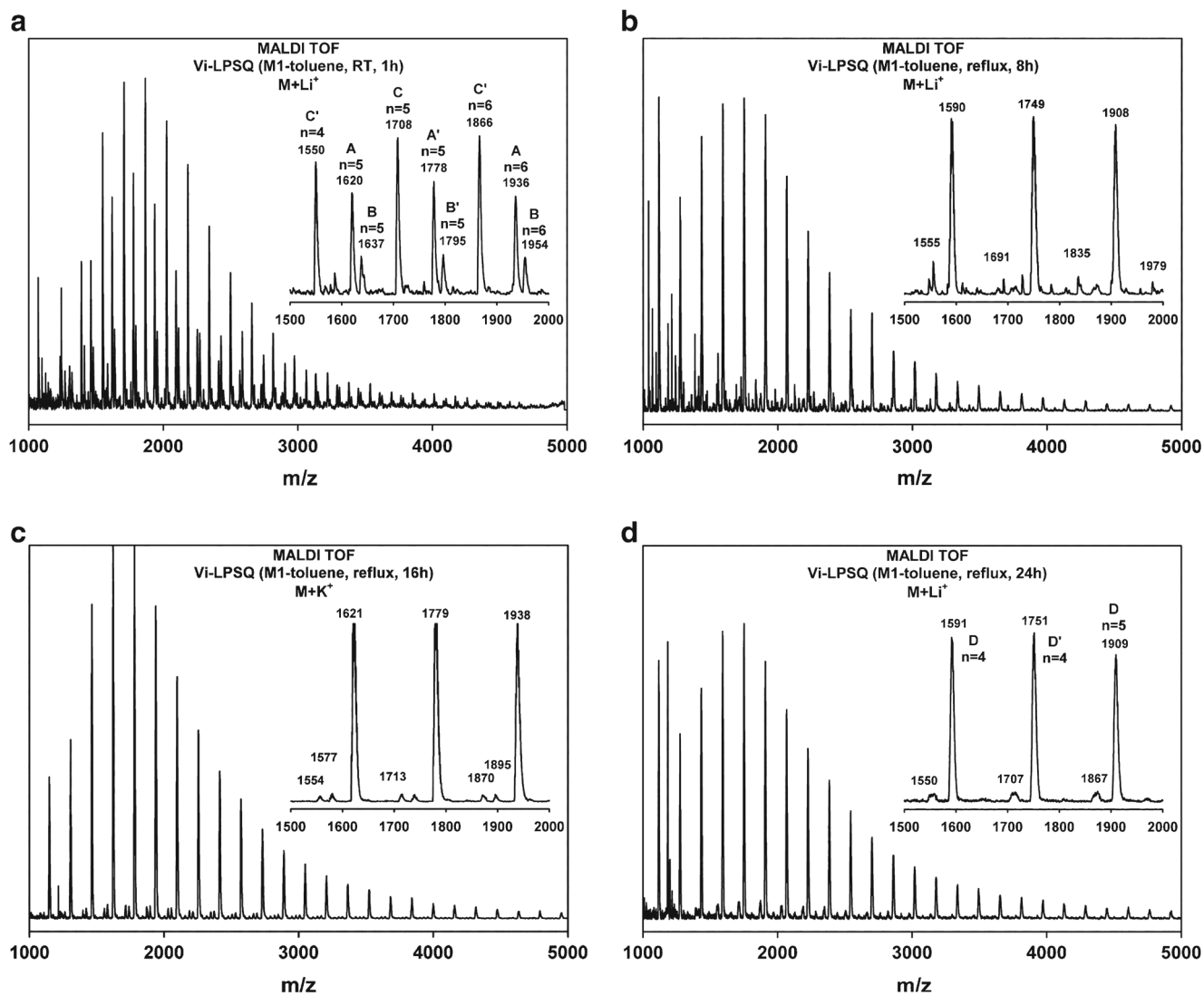
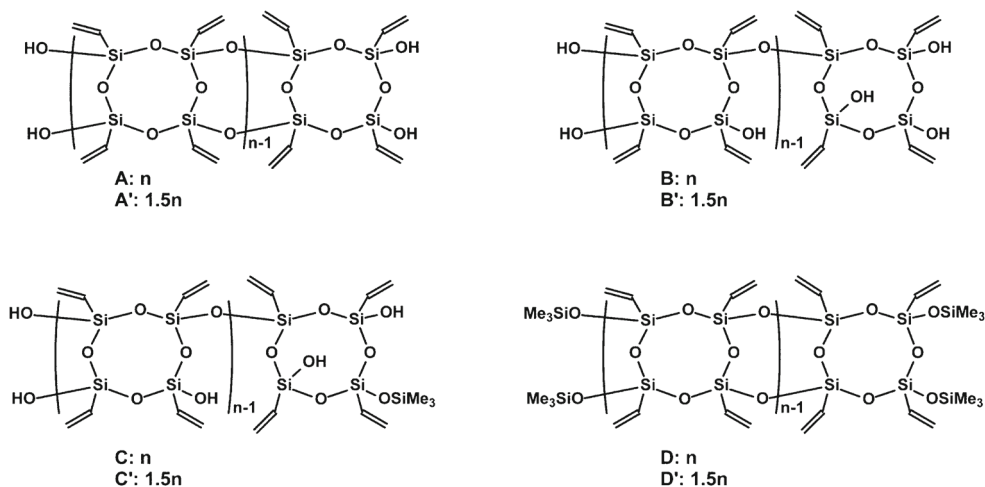


Fig. 6 Composition of oligomeric species formed during *in situ* condensation of $[\text{ViSi}(\text{OH})\text{O}]_4$ in toluene (a) after 1 hour at room temperature, (b) after 8 hours at 110°C , (c) after 16 hours at 110°C , (d) after 24 hours at 110°C

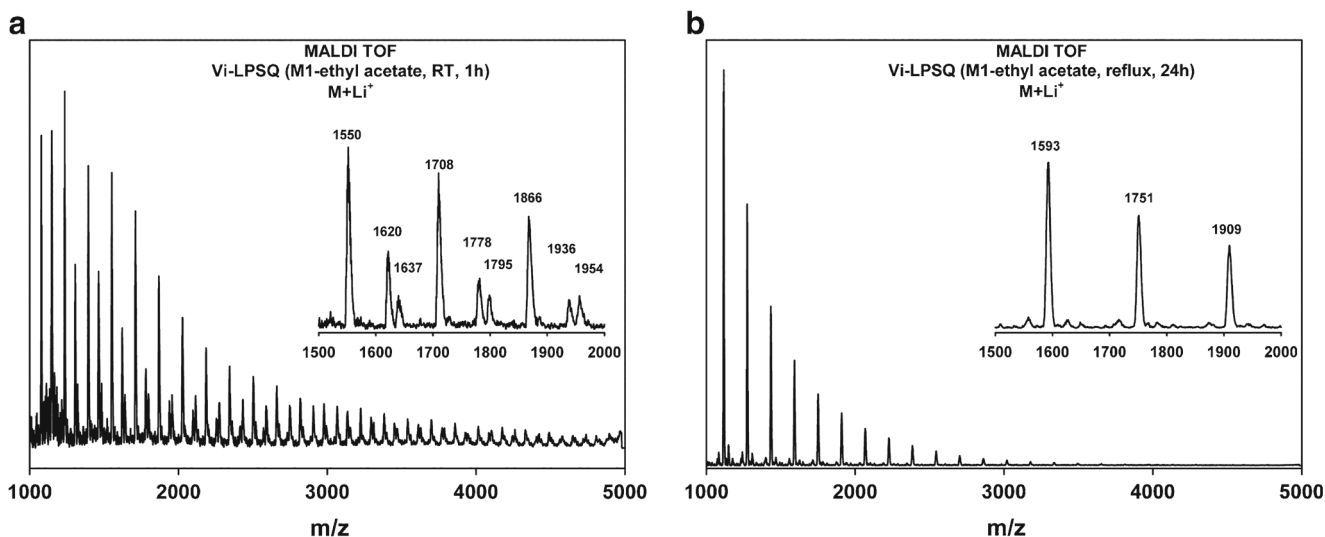


Fig. 7 Composition of oligomeric species formed during *in situ* condensation of $[\text{ViSi}(\text{OH})\text{O}]_4$ in CH_3COOEt (a) after 1 hour at room temperature, (b) after 24 hours at 110°C

Interactions with highly solvating and/or proton donating species reduce the negative charge at a nucleophilic moiety and weaken its nucleophilicity [31]. Redistribution reactions in polysiloxanes are thus usually slowed down in the presence of strong cation solvating agents [32]. However, in the process studied here, the polar and/or proton donating solvents (EtOH, DMF, CH_3CN) tend to promote branching and cross-linking with formation of insoluble materials (Table 1). This can be explained by excessive hydrogen bonding between silanol groups and solvent molecules. We were not able to determine whether redistribution took place.

The concentration of the reaction mixture was found to be of importance. The experiments with higher concentrations of potassium silanolate resulted in products with larger discrepancies between M_n (RI) and M_w (MALLS). The molar ratio $[\text{HMDS}]/[\text{potassium silanolate}]$ had no clear influence on the structure of the Vi-LPSQs although it can be surmised that decreasing the amount of HMDS below a certain limit would give more branched oligomers and polymers. It was also found that the reaction proceeds better without any supplementary catalyst added. Introduction of nucleophilic species, such as Et_3N (Table 2, procedure A, Et_3N added after filtration of CH_3COOK), increased the rate of polycondensation, which resulted in formation of polymers of multimodal structure (Fig. 5).

3.2 MALDI-TOF Analysis

With the right choice of experimental conditions, MALDI-TOF MS can be a useful method for determination of the details of the structure of polymeric chains of LPSQ materials. For example, MALDI-TOF spectrometry was used

to determine the number of uncondensed SiOH groups in Me-LPSQs obtained by polycondensation of *cis-trans-cis* $[\text{MeSi}(\text{OH})\text{O}]_4$ [13]. According to the reported data, linear chains of Me-LPSQs have two uncondensed sites (cycloliner points) which spoil the doublechain structure.

We have obtained satisfactory MALDI-TOF results on the structure of the products formed during the *in-situ* polycondensation of $[\text{ViSi}(\text{OH})\text{O}]_4$. Silanol-terminated Vi-LPSQ oligomers (A, B, Scheme 4, Fig. 6a) are formed in the first stages of condensation in toluene. They undergo silylation with HMDS to give monosilylated species C, and finally D structures at higher temperatures (Scheme 4, Fig. 6b-d). Silylation in CH_3COOEt proceeds effectively and after 1 hour at room temperature silanol-terminated species were detected in a smaller amount than in toluene (Fig. 7a). The degree of condensation varied depending on the type of solvent, but the pattern of oligomeric species detected by MALDI was the same (Figs. 7 and 8).

Along with the expected sequence of oligomers ($n = 2, 3, 4$ etc.), a supplementary series of congener species (A', B', C', D') with $n = 1.5, 2.5, 3.5$ etc., was formed due to base-catalyzed siloxane bond redistribution. The process, under the experimental conditions studied, can be explained in terms of multifunctional interactions of siloxane bonds with silanolate moieties leading to chain redistribution. The species in the reaction mixture consist of tetrameric siloxane rings. The lone pairs of the oxygen atoms in the siloxane bonds of the rings and exocyclic oxygen atoms (e.g. in Me_3SiO end groups) can be involved in the bonding of the alkali ions, acting as electron donors as they do in crown ethers [33]. Similar chain redistribution and cyclization processes due to the interaction of siloxane bonds and silanolate groups, giving assistance to the cleavage

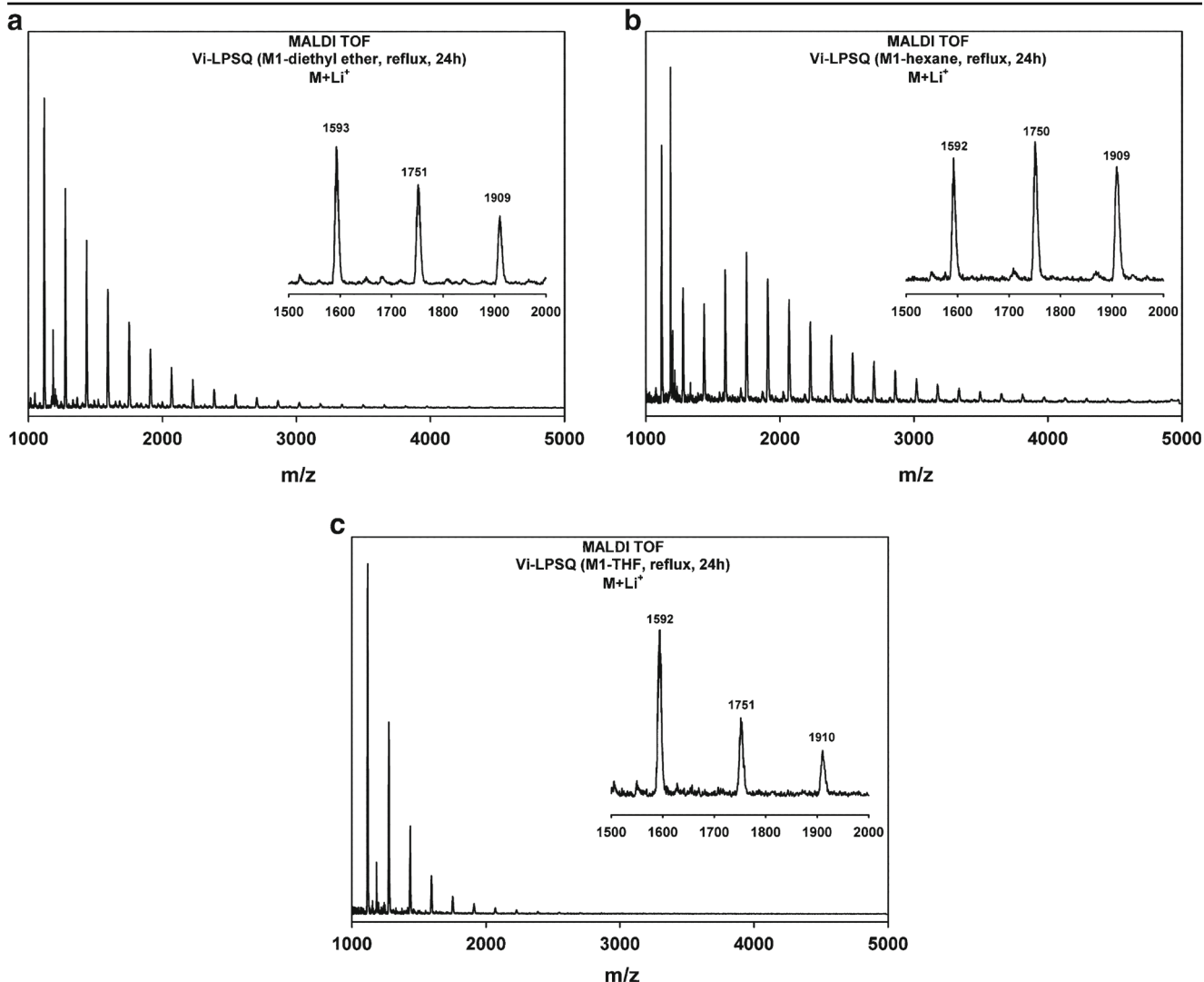


Fig. 8 Composition of oligomeric species formed during *in situ* condensation of $[\text{ViSi}(\text{OH})\text{O}]_4$ after 24 hours of reflux in Et_2O (a), hexane (b) and tetrahydrofuran (c)

of siloxane bonds, were observed during anionic polymerization of siloxanes [32] and disproportionation of α, ω -dihydroxy(polydimethylsiloxanes) in the presence of alkali metal alkoxides or NaOH [34]. A rapid exchange between the protons of SiOH groups of organosilanols and cations of alkali-metal organosilanolates along with disproportionation of siloxane bonds was observed during copolymerization of α, ω -dihydroxy(oligodimethylsiloxane) with 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane [35]. Disproportionation of α, ω -(oligomethylsiloxanols) and redistribution of siloxane bonds occurred in the presence of superbases [31]. Simultaneous cleavage of two siloxane bonds was also proposed to explain the formation of specific stereoisomers during acidic hydrolysis of $(\text{K}^+)_4[\text{MeSi}(\text{O})\text{O}^-]_4$ [28]. Such reactivity enhancement and disproportionation of siloxane bonds can be explained by a mechanism combining elements of bimolecular nucleophilic substitution and elimination-addition with formation

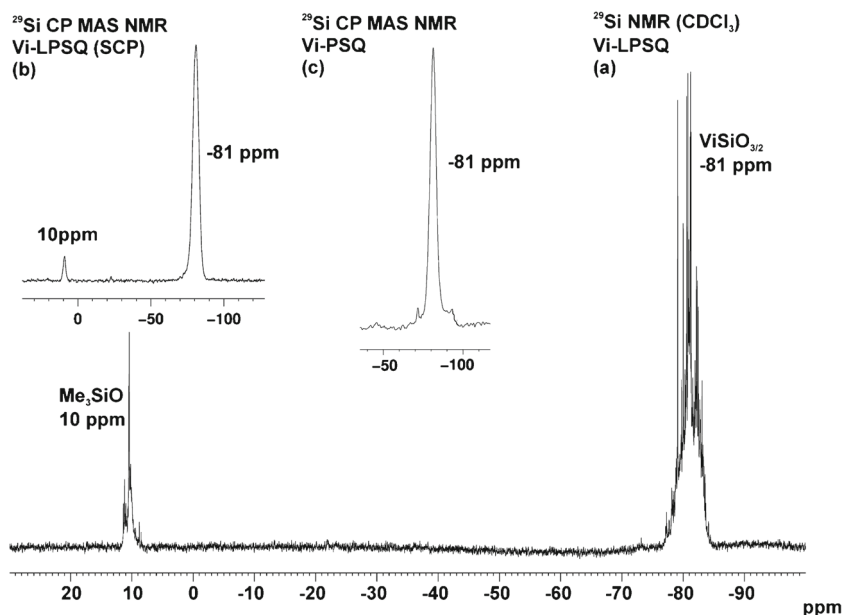
of pentacoordinate silicon transition state/intermediate [31, 32, 34].

However, not only siloxane bonds close to the terminal SiOH groups seem to be affected. Siloxane bonds in double-strand chains can be also broken in the presence of potassium ions. Simultaneous disruption of siloxane bonds at the parallel threads of silsesquioxane ladders can be explained by the cleavage of several siloxane bonds weakened by interactions with potassium ions, and thus more prone to nucleophilic attack.

3.3 Structural Analysis and Physicochemical Properties

The Vi-LPSQs were characterized by NMR, SEC with RI and MALLS (for samples of high molecular mass) detection, X-ray diffraction, DSC and TGA of liquid and solid materials. For comparison of structure and properties, Vi-functionalized silsesquioxanes were also obtained by

Fig. 9 ^{29}Si NMR of vinyl-polysilsesquioxanes (liquid state spectrum of oligomeric Vi-LPSQs in CDCl_3 (a)) and CP MAS spectra of polymeric Vi-LPSQs (SCP) (b) and cross-linked Vi-PSQ (c)



other preparative procedures. Synthesis of Vi-LPSQs by stepwise coupling polymerization resulted in a soluble product of high molecular mass. Hydrolytic condensation of $\text{ViSi}(\text{OEt})_3$ catalyzed with K_2CO_3 gave insoluble, cross-linked condensed solids (Vi-PSQ). ^{29}Si NMR analysis can be an indicator of high degree of regularity of the polymer

structure [7]. It is generally accepted that the narrower the peaks corresponding to $\text{RSiO}_{3/2}$ the less the structural defects in the architecture of the polymer backbone. This is not always the case, since peak widths at half-height for cross-linked sample of Vi-PSQ and highly regular Vi-LPSQs (SCP) in their ^{29}Si CP MAS NMR spectra are almost the same (Fig. 9 insert c and b respectively). The ladder siloxanes obtained via in situ polycondensation of $[\text{ViSi}(\text{OH})\text{O}]_4$ are a mixture of stereoisomers of different chain length, and thus resonances corresponding to $\text{ViSiO}_{3/2}$ are rather broad and composed of several components (Fig. 9a).

WAXS confirmed the formation of ordered structures in linear Vi-LPSQs (Fig. 10b-c), comparable to that of highly regular Vi-LPSQs (SPC) prepared *via* supramolecular template polymerization (Fig. 10d). A slight difference in the

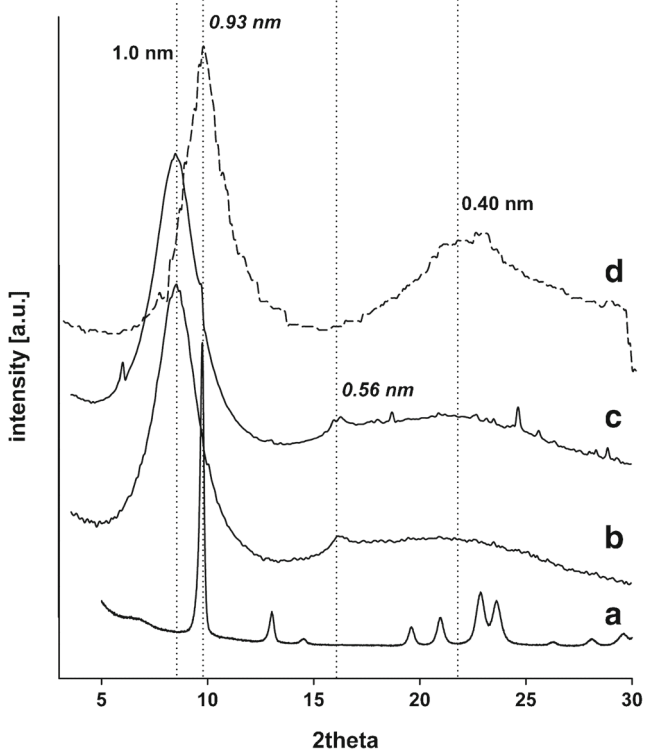


Fig. 10 WAXS diffraction patterns recorded for model T_8 Vi (a), Vi-LPSQs obtained in CH_3COOEt (b), Vi-LPSQs obtained in toluene (c), Vi-LPSQs (SPC) (d)

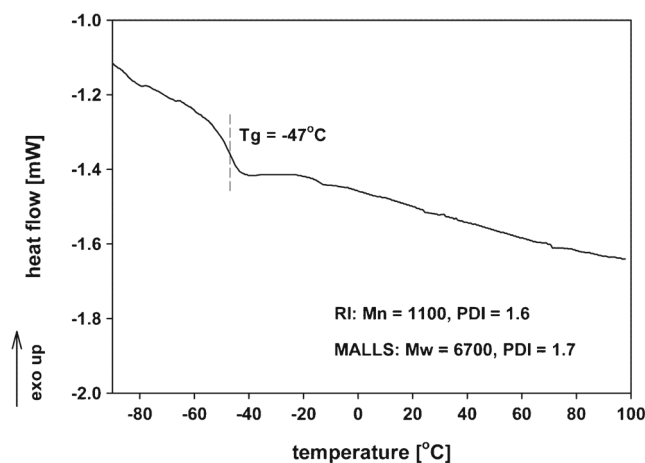


Fig. 11 DSC trace of a Vi-LPSQs prepared in toluene

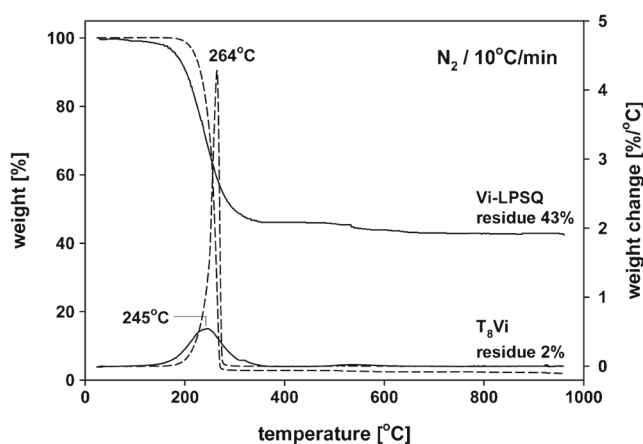


Fig. 12 Comparison of thermal stability of $T_8\text{Vi}$ and Vi-LPSQs ($M_{n(\text{RI})} = 1100$, $\text{PDI} = 1.6$, $M_{w(\text{MALLS})} = 6700$)

position of the major diffraction peak can be explained in terms of different arrangement of silsesquioxane frameworks and the disposition of vinyl groups [*cis-syndiotactic* conformation in Vi-LPSQs (SPC) and random in Vi-LPSQs obtained by *in situ* condensation]. This suggestion is supported by the fact that the cross-linked and insoluble Vi-PSQ obtained by polycondensation of $\text{ViSi}(\text{OEt})_3$ (with ordered structures confined in the network) exhibits similar diffraction peaks at $d_1 = 0.71$ nm and $d_2 = 0.29$ nm. The formation of polyhedral species can also be examined. Octahedral silsesquioxane ($T_8\text{Vi}$) was not obtained during the synthesis (Fig. 10, trace **a** shows WAXS diffraction pattern of the original compound). But if the condensation was carried out in toluene the linear product was admixed with a small amount of a crystalline material that could not be isolated from the mixture of oligomers. The data obtained with MALDI-TOF in the low molecular weight region (Supporting information, Figs. 1–6SI), can suggest that incompletely

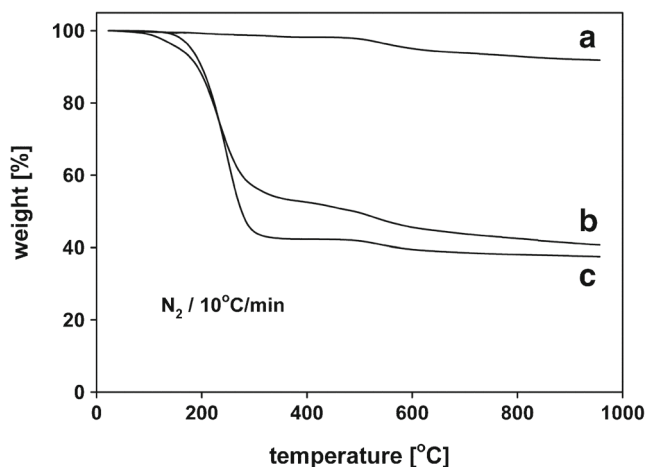


Fig. 13 Comparison of thermal stability of cross-linked Vi-PSQ (**a**) and Vi-LPSQs prepared in CH_3COOEt (**b**) and THF (**c**)

condensed but silylated polyhedral species $T_{10}\text{Vi}(\text{SiMe}_3)_2$ and $T_{12}\text{Vi}(\text{SiMe}_3)_2$ (Supporting information, Scheme 1-SI) may be formed during the reaction. However, the same MALDI-TOF patterns were found in samples prepared in CH_3COOEt , which did not show admixture of crystalline species in their WAXS diffraction patterns. Other molecules of m/z 1275, 1433 and 1591 could be also ascribed to the series of incompletely condensed silylated species, but they probably should be attributed to linear oligomers. This is supported by the fact that they form a coherent sequence with oligomers of higher molecular weight, whereas condensed polyhedral molecules would give peaks at completely different m/z . Moreover, the shape of SEC traces obtained for Vi-LPSQs resembles those of polymers with a statistical distribution of chains. A sequence of polyhedral molecules would give a set of separate sharp peaks.

The obtained materials are viscous liquids and the only phase transition they exhibit is devitrification at low temperatures (Fig. 11). They are thermally stable and decompose to leave about 40 % residue in N_2 (Figs. 12 and 13). Comparing TGA traces of $T_8\text{Vi}$ and Vi-LPSQs (Fig. 12) one can notice a significant difference. $T_8\text{Vi}$ sublimes quite rapidly under the analysis conditions at 260–265 °C to leave 2 % residue. The weight of a sample of Vi-LPSQs decreases rapidly in the temperature range 200–300 °C, which suggests evaporation of the shortest and volatile oligomers. At about 500 °C one can notice a small change of weight that can be related to polymerization of vinyl groups in the less volatile material. The same process was reported in the literature for poly(vinylsilsesquioxanes) [36] as well as for Vi-PSQ and Vi-LPSQs synthesized in CH_3COOEt and THF (Fig. 13a–c). The sample prepared in THF contains mostly oligomeric species (MALDI-TOF analysis, Fig. 8c) and the corresponding weight decrease due to their volatilization is more pronounced.

4 Conclusions

We have found that soluble oligovinylsilsesquioxanes can be obtained via condensation of cyclic organosiloxane tetraols obtained *in situ* from their alkali metal cyclosiloxolate precursors. The use of a silanol group blocking agent – hexamethyldisilazane – is crucial for the formation of linear and bench-stable Vi-LPSQs by condensation of $[\text{ViSi}(\text{OH})\text{O}]_4$. The ladder structure of the materials was confirmed by analytical methods.

We have studied the influence of reaction conditions on the structure of LPSQs. It was found that the reaction medium can induce structural changes in the LPSQ product. In some solvents incompletely condensed linear oligomers were formed at the initial stage of the reaction,

to be subsequently silylated by HMDS. The process of condensation is catalyzed by K^+ ions present in the reaction mixture. However, the potassium derivatives cause at the same time redistribution of siloxane bonds and formation of congeneric series of linear oligomers.

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