Synthesis of $(PhSiO_{3/2})_{0.35}(MeSiO_{3/2})_{0.40}(Me_2ViSiO_{1/2})_{0.25}$ Resins

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ABSTRACT: Silsesquioxanes are generally prepared by hydrolysis and condensation of a trichloro- or trialkoxysilane with a general formula $RSiX_3$, where X is Cl or an alkoxy group. Initial hydrolysis often resulted in silanol functional oligomers, and these oligomers are then condensed with a catalyst to form silsesquioxanes. Typical condensation catalysts also catalyze Si−O−Si bond rearrangement, so in many cases the structure of the oligomers has little bearing on that of the resins. In the process of synthesizing a silsesquioxane with a formula of $(PhSiO_{3/2})_{0.35}(MeSiO_{3/2})_{0.40}$ $(Me_2ViSiO_{1/2})_{0.25}$ (Ph = phenyl; Me = methyl; Vi = vinyl), we found the reaction conditions during the hydrolysis of $MeSi(OMe)_3$, $PhSi(OMe)_3$, and $(Me_2ViSi)_2O$ (Vi = vinyl) monomers were critical in achieving a high molecular weight resin. To understand this relationship between hydrolysis conditions and final product properties, reaction intermediates at various stages of hydrolysis were characterized using multinuclear nuclear magnetic resonance, size exclusion chromatography, and electrospray ionization Fourier transform mass spectrometry techniques. The analytical data indicated that the cohydrolyzate or oligomers prepared in the presence of toluene contained a large amount of silanol and methoxy groups which undergo facile condensation in the presence of a base catalyst to form a high molecular weight resin. However, when the hydrolysis was conducted by the addition of water to the alkoxysilanes without an organic solvent, the cohydrolyzate formed was of similar size but was more condensed and had fewer condensable groups. Such a reaction intermediate condensed in the presence of a base catalyst produced a relatively low molecular weight resin with a narrow molecular weight distribution. The difference in the molecular weight of the two silsesquioxane products can be explained by preference of intramolecular or intermolecular condensation for the cohydrolyzate, possibly resulting from the difference in interfacial interaction between the alkoxy monomers and water.

Introduction

Silsesquioxane, represented by the $(RSiO_{3/2})_n$ (R = organic group) formulation, is an important class of organic−inorganic hybrids that have been used in many industrial applications such as ceramics,[1−6] low-*k* interlayer dielectric coatings,[7−15] and thermooptical materials for photonic devices.[16−19] The material is generally prepared by the hydrolysis and condensation of trifunctional chlorosilane or alkoxysilane, $RSiX_3$.[20−23] Many of the properties of silsesquioxanes are determined by their compositions and can be modified by selecting an appropriate organic (R) group or by combining two or more $RSiO_{3/2}$ components. For example, with an appropriate combination of organic groups, a $(PhSiO_{3/2})_{0.35}(MeSiO_{3/2})_{0.40}(Me_2ViSiO_{1/2})_{0.25}$ (Ph = phenyl; Me = methyl; Vi = vinyl) resin was demonstrated to produce a SiC ceramic material when pyrolyzed at elevated temperature.[24,25]

Similar to organic polymers, the molecular weight distribution (MWD) of a silsesquioxane has a profound effect on its physical and processing properties and is usually controlled by varying the reaction conditions[22] such as reaction time, choice of catalyst for the condensation, and templating reagent.[26,27] Silsesquioxanes prepared from condensation of chlorosilanes or alkoxysilanes typically have broad, multimodal molecular weight distributions. In our attempt to synthesize a $(PhSiO_{3/2})_{0.35}(MeSiO_{3/2})_{0.40}$ $(Me_2ViSiO_{1/2})_{0.25}$ (Ph = phenyl; Me = methyl; Vi = vinyl) silsesquioxane as a precursor for producing ceramic fibers by a melt-spinning process,[28−30] the presence of an organic solvent during the hydrolysis of $MeSi(OMe)_3$, $PhSi(OMe)_3$, and $(Me_2ViSi)_2O$ (Vi = vinyl) allowed us to achieve a high molecular weight resin. In this paper, we report an investigation of the reaction conditions on the MWD of the final silsesquioxane product. To gain some understanding of the hydrolysis/condensation chemistry, the hydrolysis/condensation intermediates prepared under different reaction conditions were characterized by electrospray ionization Fourier transform mass spectrometry (ESI-FTMS), nuclear magnetic resonance (NMR), and size exclusion chromatography (SEC). The use of state-of-the-art MS techniques for the characterization of silsesquioxanes or intermediates produced during the synthesis has been widely reported.[31−40] Compared with other MS techniques, FTMS offers incomparable ultrahigh resolution and mass accuracy,[41−44] allowing for the unambiguous assignments of compositions for individual oligomeric silsesquioxanes. ^1H and ^{29}Si NMR were used to provide average structural information for the final product as well as that for the intermediates at different stages of reaction. SEC results offered direct comparison of the MWD. The structural and molecular weight information obtained for these reaction intermediates helps us understand the effect of hydrolysis conditions on resin properties and aid in the further development of silsesquioxanes with tailored properties.

Experimental Section

Materials. All organosiloxane materials were obtained from Dow Corning Corp. as intermediates or purchased from Hüls America. Trifluoromethanesulfonic acid was obtained from

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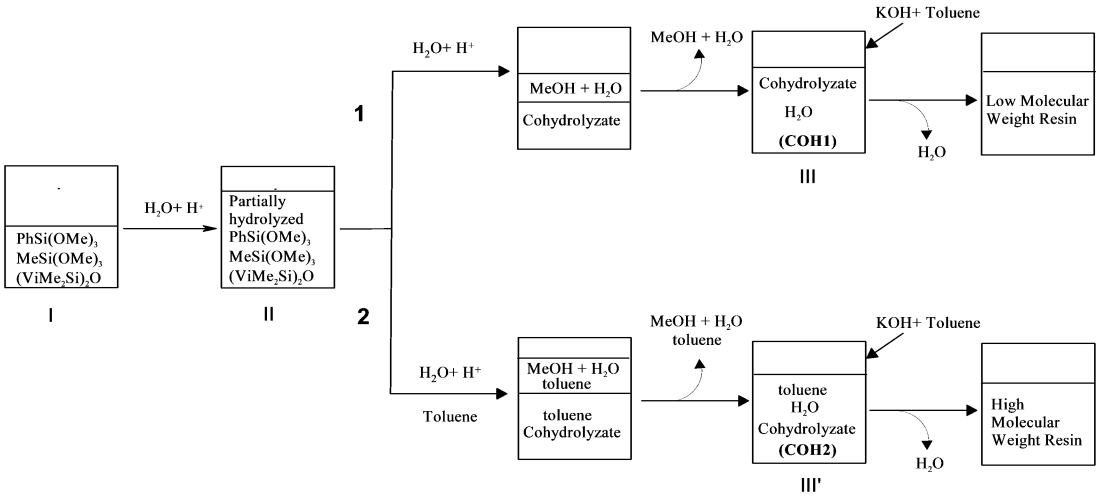
Scheme 1. Schematic Illustration of the Synthesis Processes for a $(PhSiO_{3/2})_{0.35}(MeSiO_{3/2})_{0.40}(Me_2ViSiO_{1/2})_{0.25}$ Silsesquioxane



Aldrich. Toluene, KOH, and calcium carbonate were purchased from Fisher Scientific and used as received. A 3% aqueous KOH solution was prepared before use.

Analytical Techniques. *Nuclei Magnetic Resonance.* Solution NMR spectra were recorded either on a Varian VXR400S or a Varian 200 MHz spectrometer with $CDCl_3$ in a 5 mm switchable probe or a 16 mm Si-free probe. $Cr(acac)_3$ was added for the ^{29}Si spectra to ensure quantitative acquisition.

Fourier Transform Infrared Spectroscopy. FTIR spectra were collected on a Perkin-Elemer 1600 Fourier transform infrared spectrometer with KBr salt plate. The silsesquioxane sample was first dissolved in CCl_4 and then dispersed on a KBr plate. The FTIR spectra were measured from thin films obtained after evaporation of the solvent.

Mass Spectrometry. The ESI-MS data were collected using a Bruker Apex II Fourier transform mass spectrometer (FTMS) equipped with a 4.7 T superconducting magnet and an external Analytica electrospray ionization (ESI) source. A Cole-Parmer series 74900 syringe pump was used to continuously infuse samples into the ESI source at a flow rate of 0.3 mL h^{-1}. The external electrospray ion source was operated with a 45° off-axis sprayer. High-purity (99.995%) nitrogen gas was used as a nebulizing gas at ambient temperature and as a drying gas at 105 °C. An electrostatic potential of ca. −4.7 kV (relative to the grounded needle) was applied to the metal-capped glass capillary. Ions were accumulated in a hexapole ion guide, adjacent to the external ESI source, and were subsequently injected into the INFINITY cell using the patented Sidekick method. Data acquired in the broadband mode were typically collected using 512K data points. The reaction intermediates were prepared in 1:1 (v/v) mixture of $CHCl_3$ and MeOH with 1 mM NH_4OAc present in the MeOH solution used to assist in the ionization of siloxane species. In the positive-ion mode, the ions detected in the ESI-FTMS experiment are typically $[M+ NH_4]^+$ ions with little or no fragmentation.

Size Exclusion Chromatography. SEC data were obtained on a Waters SEC instrument equipped with two mixed bed series D PL gel columns, a model 600E systems controller, and a model 410 differential refractometer detector. The SEC columns were calibrated with polystyrene standards using THF as the mobile phase.

Elemental Analysis. CHN analysis was performed on a Perkin-Elmer 2400 analyzer. Silicon analysis was determined by a fusion technique that involved converting the solid to a soluble form and analyzing the solute for total silicon by Arl 3580 ICP-AES analysis.

Softening Point Measurement. The softening point was measured on a Dupont 940 thermomechanical analyzer under argon. The heating rate used was 5 °C/min.

Synthesis of $(PhSiO_{3/2})_{0.35}(MeSiO_{3/2})_{0.40}(Me_2ViSiO_{1/2})_{0.25}$ (Ph = Phenyl; Me = Methyl; Vi = Vinyl). Two synthetic routes used for synthesis are described in Scheme 1. Route 1 used a direct hydrolysis of the alkoxysilanes with water whereas route 2 involved the hydrolysis of monomers with water in the presence of toluene. Detailed reaction conditions are given in the following sections.

Silsesquioxane Synthesis via Route 1. In a typical procedure, 933.8 g (6.86 mol) of $MeSi(OMe)_3$, 1189.8 g (6.0 mol) of $PhSi(OMe)_3$, and 402.6 g (2.16 mol) of $(Me_2ViSi)_2O$ (Vi = vinyl) were charged into a 5 L flask and equilibrated with 85 mL of water with 5.0 g of trifluoromethanesulfonic acid as a catalyst. After refluxing for 100 min, 800 mL of water was added slowly (30 min), and the mixture was refluxed for another hour. A 12 g sample of $CaCO_3$ was then added to the solution, and methanol was distilled until the overhead temperature reached 92 °C. The cohydrolyzate was then cooled to room temperature and used as a stock material.

In a typical bodying experiment, a portion of this cohydrolyzate was charged into a 1 L three-neck flask fitted with a Dean−Stark apparatus and a magnetic stir bar. Toluene was added to obtain a solution with desired nonvolatile siloxane content as measured by weight retention (wt %) after heating a solution sample at 150 °C for 2 h in an air circulated oven. A KOH solution (3 wt %, 15 mL per mole of alkoxysilanes) was added, and the water was azeotropically removed. After the reaction mixture was dried of water, small polymer samples (10 mL) were periodically removed from the reaction flask and neutralized with 0.01 mL of chlorodimethylvinylsilane in preparation for molecular weight analyses. After the reaction was complete, chlorodimethylvinylsilane was added, and the solution was stirred at room temperature overnight. The solution was first filtered through a Celatom filter aid, followed by further filtration through a 0.45 μm membrane. A 20 mL aliquot of this solution was vacuum-dried to yield a soft solid resin. Spectroscopic data for a typical resin prepared from route **1**: ^1H NMR ($CDCl_3$, 200.1 MHz, ppm): 0.25 (br, CH_3), 5.8 (CH=CH_2), 6.1 (CH=CH_2), 7.1 (C_6H_5), 7.8 (C_6H_5). $^{29}Si\{^1H\}$ NMR ($CDCl_3$, 79.4 MHz, ppm): −2.0 ($Me_2ViSiO_{3/2}$), −66.0 ($MeSiO_{3/2}$), −79.0 ($PhSiO_{3/2}$), −80.5 ($PhSiO_{3/2}$). IR (KBr, cm^{-1}): 3073 w, 3045 w, 3008 w, 2953 w, 1590 w, 1430 w, 1403 w, 1273 m, 1256 m, 1132 vs, 1049 vs, 957 w, 836 m, 782 s, 738 w, 719 w, 695 m, 482 m.

The reaction intermediates at various stage of reaction were analyzed using spectroscopic techniques. For this study, the cohydrolyzate (**COH1**) was isolated by vacuum evaporation of volatiles from the reaction mixture at 40 °C after completion of the hydrolysis step. Spectroscopic data for **COH1**: ^1H NMR ($CDCl_3$, 200.1 MHz, ppm): 0.19 (br, CH_3), 3.45 ($SiOCH_3$), 5.81 (CH=CH_2), 6.13 (CH=CH_2), 7.20 (C_6H_5), 7.82 (C_6H_5). $^{29}Si\{^1H\}$ NMR ($CDCl_3$, 79.4 MHz, ppm): −0.5 ($Me_2ViSiO_{3/2}$), −2.0 ($Me_2ViSiO_{3/2}$), −55.8 ($Me(ZO)SiO_{2/2}$), −65.0 ($MeSiO_{3/2}$), −70.0 ($Ph(ZO)SiO_{2/2}$), −79.5 ($PhSiO_{3/2}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz, ppm): 138.2 ($SiCH$=CH_2), 133.9 (2C, Ph), 132.0 (1C, Ph),

130.0 (1C, Ph), 127.5 (2C, Ph; Si*C*H=CH_2), 50.3 (O*C*H_3), 49.7 (O*C*H_3), −0.0 (Si(*C*H_3)$_2$Vi), −0.35 (*C*$H_3SiO_{3/2}$), −0.45 (*C*$H_3SiO_{3/2}$).

Silsesquioxane Synthesis via Route 2. In a typical example, samples of $PhSi(OMe)_3$ (277.6 g, 1.4 mol), $MeSi(OMe)_3$ (218.0 g, 1.6 mol), and $(Me_2ViSi)_2O$ (93.6 g, 0.56 mol) were charged into a 3 L flask, equipped with a condenser and a mechanical stirrer under argon. A 6.8 g sample of trifluoromethanesulfonic acid was dissolved in 20 mL of deionized water and added to the reaction flask, whereupon the solution immediately turned yellow. After the mixture was heated to reflux for 90 min, 800 mL of toluene (228 mL per mole of alkoxysilanes) and 300 mL of water were added. The solution was then heated to the reflux temperature for an additional 90 min. Calcium carbonate (12 g, 0.12 mol) was then added to the cohydrolyzate, and the solvent was distilled until the overhead temperature increased to ca. 81 °C (605 mL of toluene was collected). Additional toluene (365 mL) was added to adjust the solid content to 47 wt %. A KOH solution (3 wt %, 40 mL, 0.021 mol) was added, and the water was azeotropically removed using a Dean−Stark apparatus. After the reaction mixture was dried (ca. 4 h), the reflux was continued for 9.5 h before cooling to 50−60 °C. Chlorodimethylvinylsilane (22.1 g, 0.18 mol) was added, and the solution was stirred at room temperature overnight. The solution was filtered through a Celatom filter aid, followed by further filtration through a 0.45 μm membrane. A 20 mL aliquot of this solution was vacuum-dried. Anal. found: C, 43.06%; H, 5.30%; Si, 20.2%. ^{1}H NMR ($CDCl_3$, 200.1 MHz, ppm): 0.25 (br, C*H*$_3$), 3.50 (SiOC*H*$_3$), 5.84 (C*H*=C*H*$_2$), 6.09 (C*H*=C*H*$_2$), 7.10 (C_6H_5), 7.81 (C_6H_5). ^{29}Si{^{1}H} NMR ($CDCl_3$, 79.4 MHz, ppm): −0.5 ($Me_2ViSiO_{3/2}$), −2.0 ($Me_2ViSiO_{3/2}$), −57.5 (Me(ZO)$SiO_{2/2}$), −65.8 ($MeSiO_{3/2}$), −70.5 (Ph(ZO)$SiO_{2/2}$), −79.9 ($PhSiO_{3/2}$), −80.5 ($PhSiO_{3/2}$); IR (KBr, cm^{-1}): 3051 w, 2965 w, 1595 w, 1430 w, 1407 w, 1270 m, 1132 vs, 1049 s, 837 m, 785 m, 719 m, 698 m, 484 m.

The cohydrolyzate (**COH2**) was isolated by vacuum evaporation of volatiles from the reaction mixture at 40 °C after completion of the hydrolysis step. Spectroscopic data for **COH2**: ^{1}H NMR ($CDCl_3$, 200.1 MHz, ppm): 0.17 (br, C*H*$_3$), 3.41 (SiOC*H*$_3$), 5.81 (C*H*=C*H*$_2$), 6.5 (C*H*=C*H*$_2$), 7.20 (C_6H_5), 7.82 (C_6H_5). ^{29}Si{^{1}H} NMR ($CDCl_3$, 79.4 MHz, ppm): −1.9 ($Me_2ViSiO_{3/2}$), −55.8 (Me(ZO)$SiO_{2/2}$), −65.0 ($MeSiO_{3/2}$), −70.0 (Ph(ZO)$SiO_{2/2}$), −79.5 ($PhSiO_{3/2}$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz, ppm): 138.5 (SiCH=*C*H$_2$), 134.0 (2C, Ph), 132.0 (1C, Ph), 130.0 (1C, Ph), 127.5 (2C, Ph, Si*C*H=CH_2), 50.5 (O*C*H_3), 49.5 (O*C*H_3), −0.10 (Si(*C*H_3)$_2$Vi), −3.8 (*C*$H_3SiO_{3/2}$).

Results and Discussions

The $(PhSiO_{3/2})_{0.35}(MeSiO_{3/2})_{0.40}(Me_2ViSiO_{1/2})_{0.25}$ (Ph = phenyl; Me = methyl; Vi = vinyl) silsesquioxane was synthesized by hydrolysis and condensation of $MeSi(OMe)_3$, $PhSi(OMe)_3$, and $(Me_2ViSi)_2O$ (Vi = vinyl) according to eq 1:

$$0.35PhSi(OMe)_3 + 0.40MeSi(OMe)_3 + 0.25(Me_2ViSi)_2O + H_2O\ (\text{excess}) \xrightarrow{CF_3SO_3H} \text{cohydrolyzate} \xrightarrow{3\%\ KOH} \xrightarrow{Me_2ViSiCl} (PhSiO_{3/2})_{0.35}(MeSiO_{3/2})_{0.40}(Me_2ViSiO_{1/2})_{0.25} \quad (1)$$

The hydrolysis of the alkoxysilane mixture was carried out in the presence of trifluorosulfonic acid, followed by neutralization with $CaCO_3$. The methanol byproduct and excess water were distilled, yielding a viscous oil, which was further condensed in the presence of a base catalyst. The final product obtained after evaporation of the solvent was typically a soft solid. The weight-average molecular weight, M_w, for silsesquioxanes prepared by route 1 ranged from 2000 to 4000 g/mol, whereas those for materials prepared from route 2 were significantly higher (M_w = 8000−55 000 g/mol).

We set out to study the following variables and their impact on the molecular weight of the final product: presence of toluene in the acid-catalyzed hydrolysis, concentration of the cohydrolyzate in the condensation reaction, condensation reaction time, and level of condensation catalyst. The presence of an organic solvent during the acid-catalyzed hydrolysis step was found to have a significant effect upon the MWD of the final product. This was subsequently studied using two sets of designed experiments involving routes 1 and 2 described in detail in the Experimental Section. In the first set of experiments via route 1, the alkoxysilanes were hydrolyzed neat to produce a master batch of cohydrolyzate (**COH1**) after methanol and excess water were distilled. The cohydrolyzate was divided into several portions, diluted with different amounts of toluene, and then condensed by adding 3 wt % aqueous KOH as the condensation catalyst. The solution was heated at reflux temperature (100−112 °C) with continuous removal of water from the reaction flask. When the reaction mixture was "dried" of water or the pot temperature became constant, a small amount of solution was sampled and treated with $Me_2ViSiCl$ (Vi = vinyl) to neutralize the silanolate and then subjected to SEC analysis. The reaction conditions and SEC results are summarized in Table 1. The M_w value ranged from 2000 to 4000 under various conditions through route 1. Silsesquioxane **B** was condensed from a higher concentration of cohydrolyzate (69%), and there was only a small increase in molecular weight when compared to **A**. **C**, prepared with twice the amount of KOH, had similar molecular weights. The result indicates none of the variables (concentration of the cohydrolyzate, condensation time, and amount of catalyst) studied has significant impact on the molecular weight.

In the second set of experiments via route 2, the hydrolysis of alkoxysilanes was first carried out at a fixed concentration in toluene (228 mL toluene per mole of alkoxysilanes) while other reaction conditions were kept identical to route 1. The cohydrolyzate (**COH2**), obtained after the distillation of methanol/water, was divided and dissolved in toluene to form solutions that contained 47% and 66% nonvolatile siloxanes. The nonvolatile siloxane content was measured on the basis of the weight retention after heating a small sample of solution at 150 °C for 2 h in an air-circulated oven. The solutions were then condensed in the presence of a KOH catalyst at reflux temperature. The SEC results shown in Table 1 indicate that in all experiments higher molecular weight materials (M_w > 8000 g/mol) were obtained than when no solvent was used in the hydrolysis. Within the **COH2** series, the most significant increase in molecular weight was observed when the material was condensed at 66% nonvolatile siloxane content. The value of M_w ranged from 23 630 to 54 840 for a 1 and 25 h reflux time, respectively. The polydispersity (D) increased with solids content, and the relatively low number-average molecular weight (M_n = 2500−3600) provided evidence of low molecular weight materials in all the samples.

The effect of solvent in the hydrolysis step on the molecular weight of the final product is easily seen from the overlaid SEC chromatograms shown in Figure 1. The SEC chromatograms for silsesquioxanes (**A**, 19 h; **C**, 15 h) prepared from route 1 exhibit relatively narrow response between 14 and 18 min of retention time. The sharp low molecular weight peaks at 16.3 min likely

Table 1. SEC Results for Final Resins Synthesized under Different Experimental Conditions

expt	synthetic route	reaction scale (mol)	nonvolatile siloxane (%)[a]	mL of toluene per mole of alkoxysilanes during hydrolysis	reflux time (h)	M_n	M_w	M_w/M_n
A	1	1.71	48	0	1	1530	2150	1.41
					5	1530	2130	1.39
					19	1540	2200	1.43
B	1	1.71	69	0	1	1950	3370	1.73
					5	1970	3520	1.79
					19	2060	3940	1.91
C[b]	1	1.70	69	0	4	1940	3440	1.77
					15	2020	3760	1.86
D	2	2.63	47	228	1	2550	8370	3.28
					6.5	2630	8610	3.27
					16.5	2810	9460	3.37
E	2	7.50	47	228	3.5	2840	9940	3.50
					7	2870	10230	3.56
					11	2740	9570	3.49
F	2	7.50	66	228	1	3140	22150	7.05
					5	3410	29490	8.65
					8	3470	38760	11.20
G	2	2.63	66	228	1	3170	23630	7.45
					5	3270	29340	8.97
					10	3540	37540	10.60
					25	3530	54840	15.54
H	2	2.62	47	153	18	2300	6270	2.73
					24	2340	6520	2.79
I	2	2.62	46	76	18	2270	6050	2.67
					24	2310	6300	2.73

[a] Nonvolatile siloxane contents were measured by heating a solution sample at 150 °C for 2 h in an air circulated oven. [b] Double amount of catalyst was used.

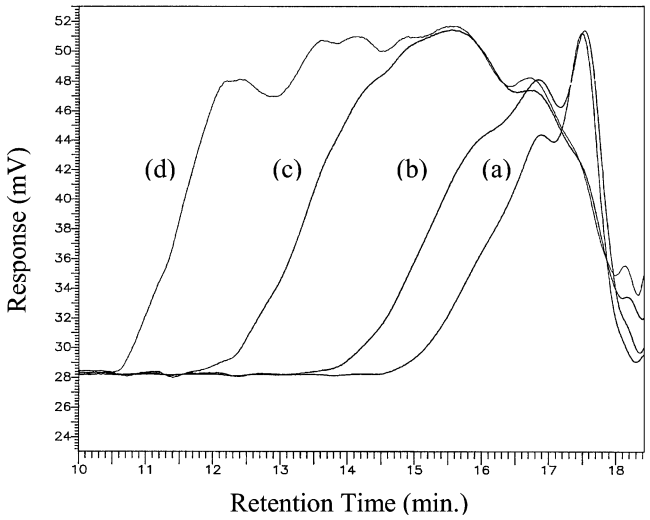


Figure 1. Overlay of the SEC chromatograms of final resins prepared at various conditions: (a) **A** (19 h reflux); (b) **C** (15 h reflux); (c) **E** (11 h reflux); and (d) **G** (10 h reflux).

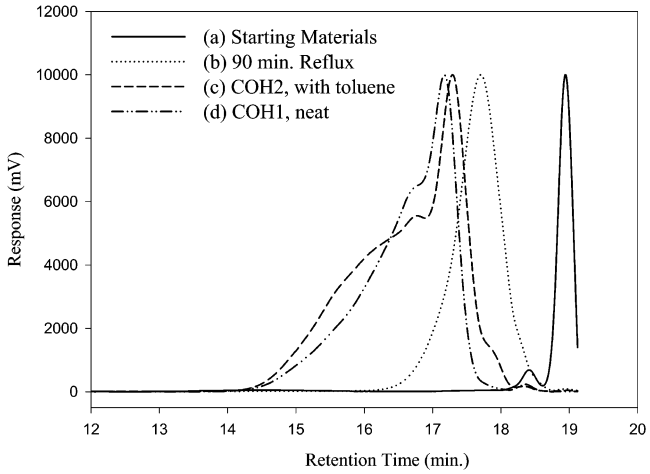


Figure 2. SEC chromatograms of (a) starting materials (I); (b) cohydrolyzate, 90 min reflux (II); (c) **COH1** (III); and (d) **COH2** (III′).

correspond to oligomers of unique structures. The relative higher molecular weight for **C** is attributed to the higher nonvolatile siloxane content (69% for **C** vs 48% for **A**) during the condensation step. The silsesquioxanes prepared from route 2, **E** (11 h, 47% nonvolatile siloxane) and **G** (10 h, 66% nonvolatile siloxane), exhibited broad multimodal distributions. The polydispersity was 3.49 and 10.6 for **E** and **G**, respectively, compared to 1.43 for **A** and 1.86 for **C**.

The dependence of molecular weight upon toluene concentration during hydrolysis was investigated in three small-scale reactions. The nonvolatile siloxane content in the condensation step was held constant (46%−47%) while the amount of toluene added during hydrolysis was adjusted to 228 (**D**), 153 (**H**), and 76 mL/mol (**I**), respectively. As shown in Table 1, the higher the alkoxysilane content or less toluene during hydrolysis, the lower the molecular weight of silsesquioxane produced. On the basis of these results, it appeared that the cohydrolyzates produced in the presence of toluene were quite unique, especially when prepared at high dilutions. The intermediates were more readily condensed to high molecular weight materials than those prepared without toluene. In this case, the characterization of the intermediate species at various stages of the reaction should provide additional information to help better understand the reaction chemistry.

The intermediates were prepared according to Scheme 1. The comonomers were first hydrolyzed with a limited amount of water and an acid catalyst at room temperature for 20 min, followed by refluxing at 60 °C for 90 min. The reaction intermediates were sampled before and after the reflux. Toluene was then added to one reaction flask, and both reaction flasks were cooled to 40 °C. An excess amount of water was then added to both reaction flasks and heated to reflux. After 90 min, the volatile materials in both reactions were vacuum-

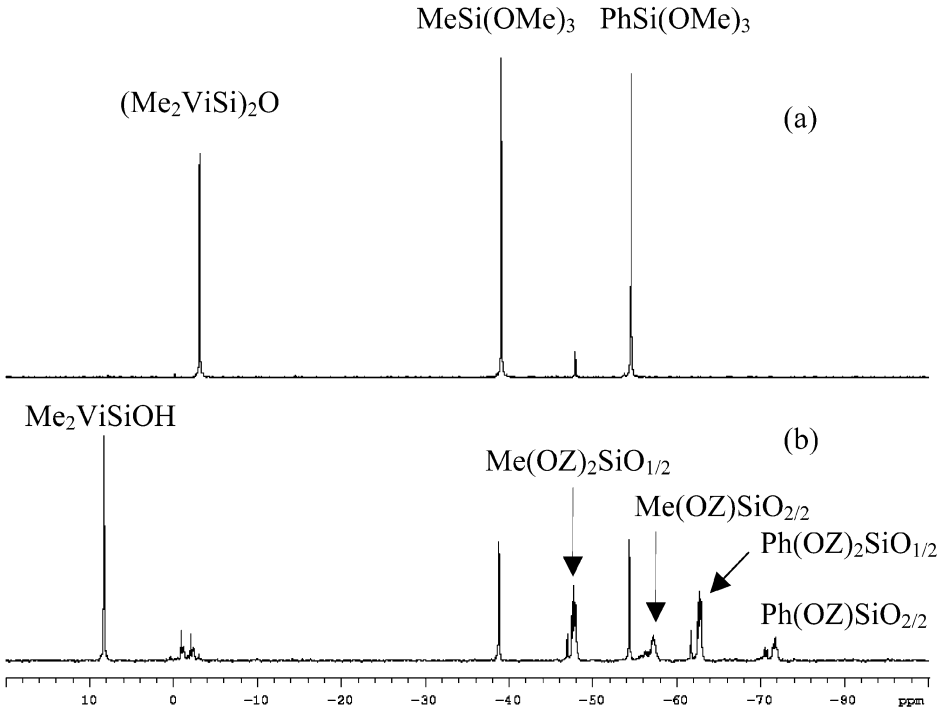


Figure 3. ^{29}Si NMR spectra of (a) starting materials (I) and (b) partially hydrolyzed intermediate (90 min reflux, II).

evaporated at 40 °C, and the two cohydrolyzates (**COH1** and **COH2**) were obtained as viscous oils.

Figure 2 shows SEC chromatograms of the alkoxysilane mixture, partially hydrolyzed intermediate (II), and the cohydrolyzates (**COH1** and **COH2**) after hydrolysis with an excess amount of water. For the starting material, the peak at 18.9 min corresponded to the three starting silanes, and the small peak at 18.4 min was assigned to partially hydrolyzed impurities. The retention time for the partially hydrolyzed alkoxysilanes shifted to 17.7 min, supporting an increase in molecular weight resulting from hydrolysis and condensation. Both **COH1** and **COH2** exhibited multimodal distributions, with an intense peak around 17.0 min and a broad high molecular weight shoulder between 14.3 and 16.8 min. The peak around 17.0 min was assigned to oligomeric species. Note the strong peak for **COH2** appeared to the right of that for **COH1**, indicating that the molecular size of the oligomers present in **COH2** was slightly lower than that for **COH1**. We cannot tell from this analysis whether **COH1** and **COH2** contained either different oligomers or common oligomeric species with different molecular weight distributions. In addition, **COH2** apparently contained more high molecular weight species than **COH1**, as evidenced by the shoulder at a shorter retention time.

Additional information on the average composition and structural features of the intermediates and final resins were provided by NMR spectroscopy. The ^{29}Si NMR spectra of starting alkoxysilanes and the partially hydrolyzed materials are shown in Figure 3. The spectra of the starting materials exhibited three major resonances at −2.0, −38.5, and −54.2 ppm, which correspond to $(Me_2ViSi)_2O$ (Vi = vinyl), $MeSi(OMe)_3$, and $PhSi(OMe)_3$, respectively. The peak at −47.5 ppm suggested the presence of small amounts of hydrolyzed species, such as $Me(MeO)_2Si{-}O{-}SiMe(OMe)_2$ or trimer species, which was consistent with the SEC analysis. Upon addition of limited amount of water and the acid catalyst, the signal at −2.0 ppm completely disappeared while a new sharp singlet at 9.4 ppm was observed, indicating complete conversion to $Me_2ViSiOH$ (Vi = vinyl). The group of resonances centered at −1.2 and −2.2 ppm were assigned to $Me_2ViSiO_{1/2}$ (Vi = vinyl) that were attached to $MeSiO_{3/2}$ and $PhSiO_{3/2}$, respectively. More significantly, species corresponding to partial hydrolyzed/condensed alkoxysilanes were formed, as evidenced by the resonances at −47.9 ppm ($Me(OZ)_2SiO_{1/2}$), −57.0 ($Me(OZ)SiO_{2/2}$), −62.5 ($Ph(OZ)_2SiO_{1/2}$), and −72.0 ($Ph(OZ)SiO_{2/2}$). The only information obtained from the ^1H NMR spectrum was the presence of a broad, weak SiOH proton resonance at 2.42 ppm, confirming the presence of silanol functionality.

When an excess amount of water was added to the reaction mixture, further hydrolysis and condensation occurred. The complete disappearance of the resonance at 9.4 ppm for $Me_2ViSiOH$ (Vi = vinyl) and the appearance of the broad resonance for $Me_2ViSiO_{1/2}$ (Vi = vinyl) attached to the T silicon were the direct evidence of not only the hydrolysis but an ongoing condensation process as well. The ^{29}Si NMR spectra of **COH1** and **COH2** (Figure 4) revealed a significant difference in composition between these two intermediates. The ^{29}Si NMR spectra for both exhibited peaks arising from $Me_2ViSiO_{1/2}$ (2 to −4 ppm), $MeSiO_{3/2}$ (−60 to −68 ppm), and $PhSiO_{3/2}$ (−76 to −84 ppm) silicon nuclei, as well as T_2 species, $Me(ZO)SiO_{2/2}$ (−50 to −60 ppm) and $Ph(ZO)SiO_{2/2}$ (−66 to −74 ppm). The compositions of **COH1** and **COH2** and the final resins derived from these two cohydrolyzates were determined from ^{29}Si NMR spectra and are shown in Table 2. The mole percentage of $Me(ZO)SiO_{2/2}$ (OZ = OH or OMe) groups in **COH1** and **COH2** was 11.1% and 17.2%, respectively. Similarly, the concentration of $Ph(ZO)SiO_{2/2}$ in **COH2** (22.2%) was higher than that in **COH1** (16.0%). Note that in both cases the $PhSiO_{3/2}$/$MeSiO_{3/2}$ ratio (0.74 for **COH1** and 0.58 for **COH2**) was less than the initial $PhSi(OMe)_3/MeSi(OMe)_3$ ratio of 0.88 for the starting materials, suggesting a slower hydrolysis/condensation rate for phenyltrimethoxysilane.

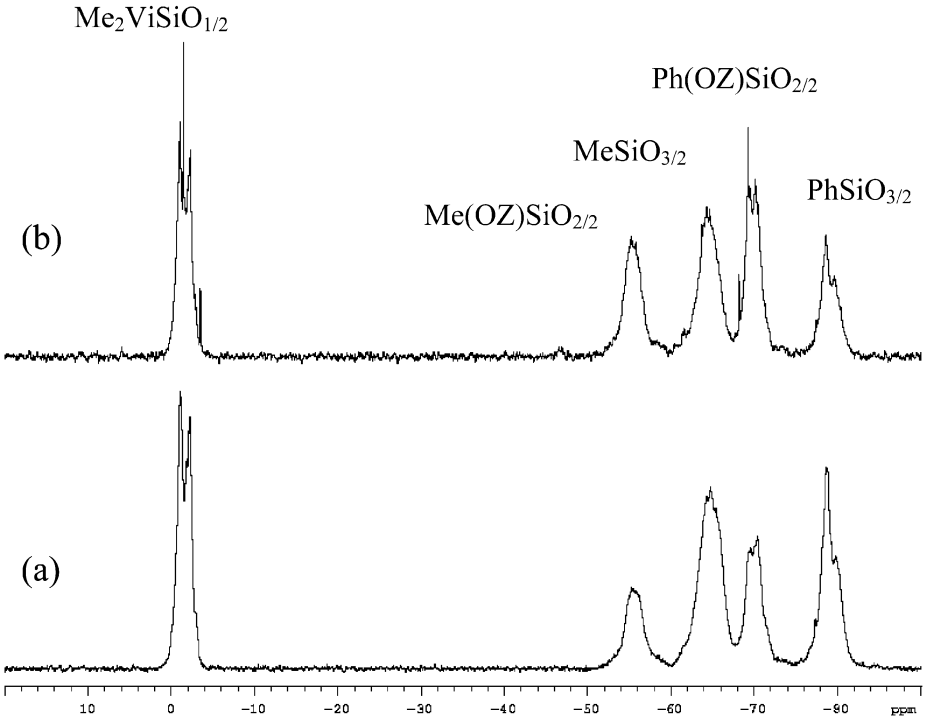


Figure 4. ^{29}Si NMR spectra of cohydrolyzates (a) **COH1** (III) and (2) **COH2** (III′).

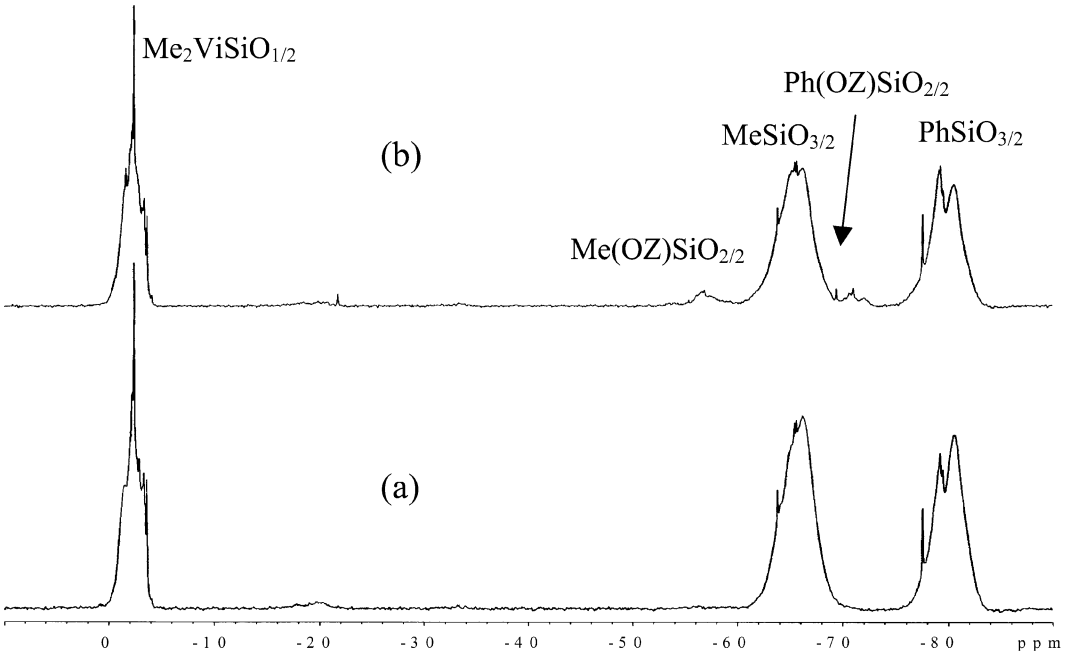


Figure 5. ^{29}Si NMR spectra of final resins (a) **C** (15 h reflux) and (b) **E** (11 h reflux).

Table 2. Structural Analyses from Quantitative ^{29}Si and ^{1}H NMR Analyses

	$Me_2ViSiO_{1/2}$ (Vi = vinyl)	$MeSiO_{3/2}$ (mol %)	$Me(ZO)SiO_{2/2}$ (mol %)	$PhSiO_{3/2}$ (mol %)	$Ph(ZO)SiO_{2/2}$ (mol %)
COH1	23.5	28.3	11.1	21.0	16.0
C, 15 h reflux	24.6	42.1	0.0	33.3	0.0
COH2	22.4	23.9	17.2	13.9	22.2
E, 11 h reflux	21.9	40.6	2.5	33.3	1.6

The ^{29}Si NMR spectrum of final product **E** (Figure 5b) prepared from **COH2** (11 h reflux) showed resonances corresponding to $Me_2ViSiO_{1/2}$ (2 to −5 ppm) $MeSiO_{3/2}$ (−60 to −70 ppm), and $PhSiO_{3/2}$ (−75 to −85 ppm) units as well as weak resonances at −57.5 and −70.5 ppm arising from T_2 silicons: $Me(ZO)SiO_{2/2}$ and $Ph(ZO)SiO_{2/2}$. Because of a similarity in chemical shift, the nature of the OZ group (OH or OMe) cannot be determined from ^{29}Si NMR spectra alone. The presence of residual methoxy groups was supported by ^{13}C NMR (resonances at 49.7 and 50.3 ppm) and ^{1}H NMR (resonance at 3.5 ppm). The amount of $R(ZO)SiO_{2/2}$ in final product **E** was estimated at 4.1 mol %, most of which was due to $R(MeO)SiO_{2/2}$ since no obvious OH stretching

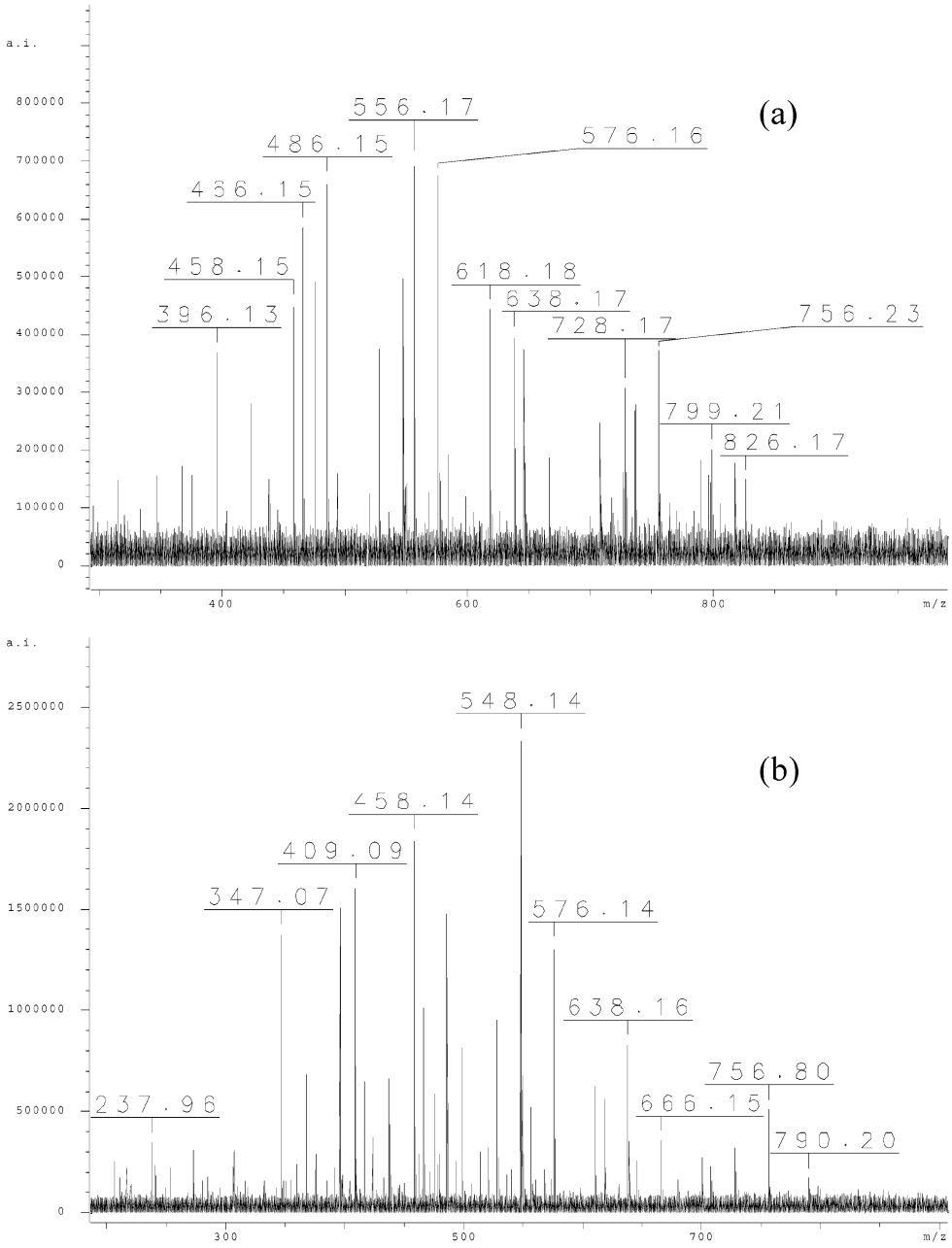


Figure 6. ESI-FTMS spectra of (a) reaction intermediate, 19 min reaction before reflux, and (b) reaction intermediate, 90 min reflux.

band (~3300 cm^{-1} for SiO−H) was detected by FTIR. The ^{29}Si NMR spectra of **C** (Figure 5a) derived from **COH1** (15 h reflux) displayed only three broad peaks corresponding to $Me_2ViSiO_{1/2}$, $MeSiO_{3/2}$, and $PhSiO_{3/2}$. The absence of resonances from T_2 silicon suggested complete consumption of condensable groups in **COH1**. On the basis of the NMR results, the extents of condensation for the cohydrolysates and the final resins were both higher when the hydrolysis step was carried out in the absence of toluene.

The ESI-FTMS spectra of reaction intermediates obtained after 19 min reaction at room temperature after adding less than an equivalent amount of water and at 90 min reflux are shown in Figure 6, spectra a and b, respectively. Close examination of the spectra indicated common species present in two samples with varying intensities. This result supported a fast hydrolysis step whereby water was essentially consumed before reflux. The fast hydrolysis/condensation chemistry was also consistent with a rapid rise in temperature after water addition (1 min to reach maximum 46 °C). The ESI-FTMS spectrum acquired for the sample obtained 3 min after water addition was similar to that for the 19 min sample.

The species identified in the reaction mixture after 90 min of reflux are listed in Table 3. All the identified species were based on a T_nM_{n+2} formula, wherein M was either a $Me_2ViSiO_{1/2}$ or $MeO_{1/2}$ group. This class of molecules should adopt either linear or hyperbranched structures on the basis of simple valence considerations. No composition corresponding to a cyclic structure, denoted by T_nM_n, was observed. The number of methoxy end groups was significantly larger than that of $Me_2ViSiO_{1/2}$ end groups in the partially hydrolyzed material, and there was no silanol-containing species observed.

The ESI-FTMS spectra of **COH1** and **COH2** are shown in Figure 7, spectra a and b, respectively.

Table 3. Composition Assignments for the ESI-FTMS Ions Observed for the Reaction Intermediate Obtained after 90 min Reflux

measured mass $[M + NH_4]^+$	T^{Ph}	T^{Me}	M^{Vi}	OH	OCH_3	theoretical mass $[M + NH_4]^+$	mass error (ppm)	reduced representation[a]
306.11848	1	1			4	306.11875	−0.9	T_2M_4
368.13535	2				4	368.13440	2.6	T_2M_4
376.14387	1	1	1		3	376.14263	3.3	T_2M_4
396.13250	1	2			5	396.13246	0.1	T_3M_5
404.14094		3	1		4	404.14069	0.6	T_3M_5
458.14725	2	1			5	458.14811	−1.9	T_3M_5
466.15877	1	2	1		4	466.15634	5.2	T_3M_5
486.14592	1	3			6	486.14617	−0.5	T_4M_6
494.15311		4	1		5	494.15440	−2.6	T_4M_6
514.14655		5			7	514.14423	4.5	T_5M_7
520.16392	3				5	520.16376	0.3	T_3M_5
528.17022	2	1	1		4	528.17199	−3.3	T_3M_5
548.16144	2	2			6	548.16182	0.7	T_4M_6
556.17067	1	3	1		5	556.17005	1.1	T_4M_6
576.16058	1	4			7	576.15988	1.2	T_5M_7
610.17901	3	1			6	610.17747	2.5	T_4M_6
618.18461	2	2	1		5	618.18569	−1.8	T_4M_6
638.17821	2	3			7	638.17553	4.0	T_5M_7
646.18599	1	4	1		6	646.18375	3.5	T_5M_7
666.17309	1	5			8	666.17358	−0.7	T_6M_8
708.20124	2	3	1		6	708.19940	2.6	T_5M_7
728.19093	2	4			8	728.18923	2.3	T_6M_8
790.20346	3	3			8	790.20488	−1.8	T_6M_8

[a] M = $ViMe_2SiO_{1/2}$ (M^{Vi}), $HO_{1/2}$, or $MeO_{1/2}$.

Table 4. Composition Assignments for the ESI-FTMS Ions Observed for Cohydrolyzate (COH1) Obtained by Hydrolysis in the Absence of Toluene

measured mass $[M + NH_4]^+$	T^{Ph}	T^{Me}	M^{Vi}	OH	OCH_3	OH + OCH_3	theoretical mass $[M + NH_4]^+$	mass error (ppm)	reduced representation[a]
494.16647	2		2	1	1	2	494.16651	−0.1	T_2M_4
516.19138	1	1	3		1	1	516.19038	1.9	T_2M_4
544.11281	2	2	1	2	1	3	544.11253	0.5	T_4M_4
564.19030	2		3	1		1	564.19038	−0.1	T_2M_4
566.13726	1	3	2	1	1	2	566.13641	1.5	T_4M_4
578.20332	2		3		1	1	578.20603	−4.7	T_2M_4
586.21521	1	1	4			0	586.21426	1.6	T_2M_4
614.13553	2	2	2	2		2	614.13641	−1.4	T_4M_4
628.15189	2	2	2	1	1	2	628.15206	−0.3	T_4M_4
642.16693	2	2	2		2	2	642.16771	−1.2	T_4M_4
648.22745	2		4			0	648.22991	−3.8	T_2M_4
690.16873	3	1	2	1	1	2	690.16770	1.5	T_4M_4
698.17483	2	2	3	1		1	698.17593	−1.6	T_4M_4
704.18600	3	1	2		2	2	704.18335	3.8	T_4M_4
712.19117	2	2	3		1	1	712.19158	−0.6	T_4M_4
736.08852	2	5	1	1	1	2	736.08557	4.0	T_7M_3
760.19555	3	1	3	1		1	760.19158	5.2	T_4M_4
762.13934	2	4	2	1	1	2	762.13761	2.3	T_6M_4
766.16726	3	2	2	2	1	3	766.16576	2.0	T_5M_5
774.20940	3	1	3		1	1	774.20723	2.8	T_4M_4
780.18298	3	2	2	1	2	3	780.18141	2.0	T_5M_5
782.21674	2	2	4			0	782.21546	1.6	T_4M_4
824.15300	3	3	2	1	1	2	824.15325	−0.3	T_6M_4
844.23182	3	1	4			0	844.23111	0.8	T_4M_4
850.20814	3	2	3	1	1	2	850.20529	3.4	T_5M_5
864.22275	3	2	3		2	2	864.22094	2.1	T_5M_5
872.23045	2	3	4		1	1	872.22916	1.5	T_5M_5

[a] M = $ViMe_2SiO_{1/2}$ (M^{Vi}), $HO_{1/2}$, or $MeO_{1/2}$.

Compared to the partially hydrolyzed samples, a slight increase in the molecular weight of the oligomers was observed, and the results were consistent with the SEC chromatograms shown in Figure 2. The assigned compositions based on exact mass measurements for **COH1** and **COH2** are listed in Table 4 and Table 5, respectively. Several important observations can be made. First, the presence of silanol is evident in both cohydrolyzates, and the number of $Me_2ViSiO_{1/2}$ end groups in these molecules was higher than that found in the partially hydrolyzed material. The increase in the number of $Me_2ViSiO_{1/2}$ end groups was consistent with the NMR data. These results support the hydrolysis/condensation mechanism that involves the initial hydrolysis of $MeSi(OMe)_3$ and $PhSi(OMe)_3$ to form methoxy-rich species, followed by a reaction with $HOSiViMe_2$. Second, a majority of the oligomeric species identified in both cohydrolyzates had a composition based on T_nM_n which requires a ring structure be present on the basis of valence considerations. These T_nM_n species were likely formed via intramolecular condensations from T_nM_{n+2} species observed in the early stages of hydrolysis. Third, the estimated M_n value for **COH1** seemed to be slightly higher than that for **COH2** on the basis of

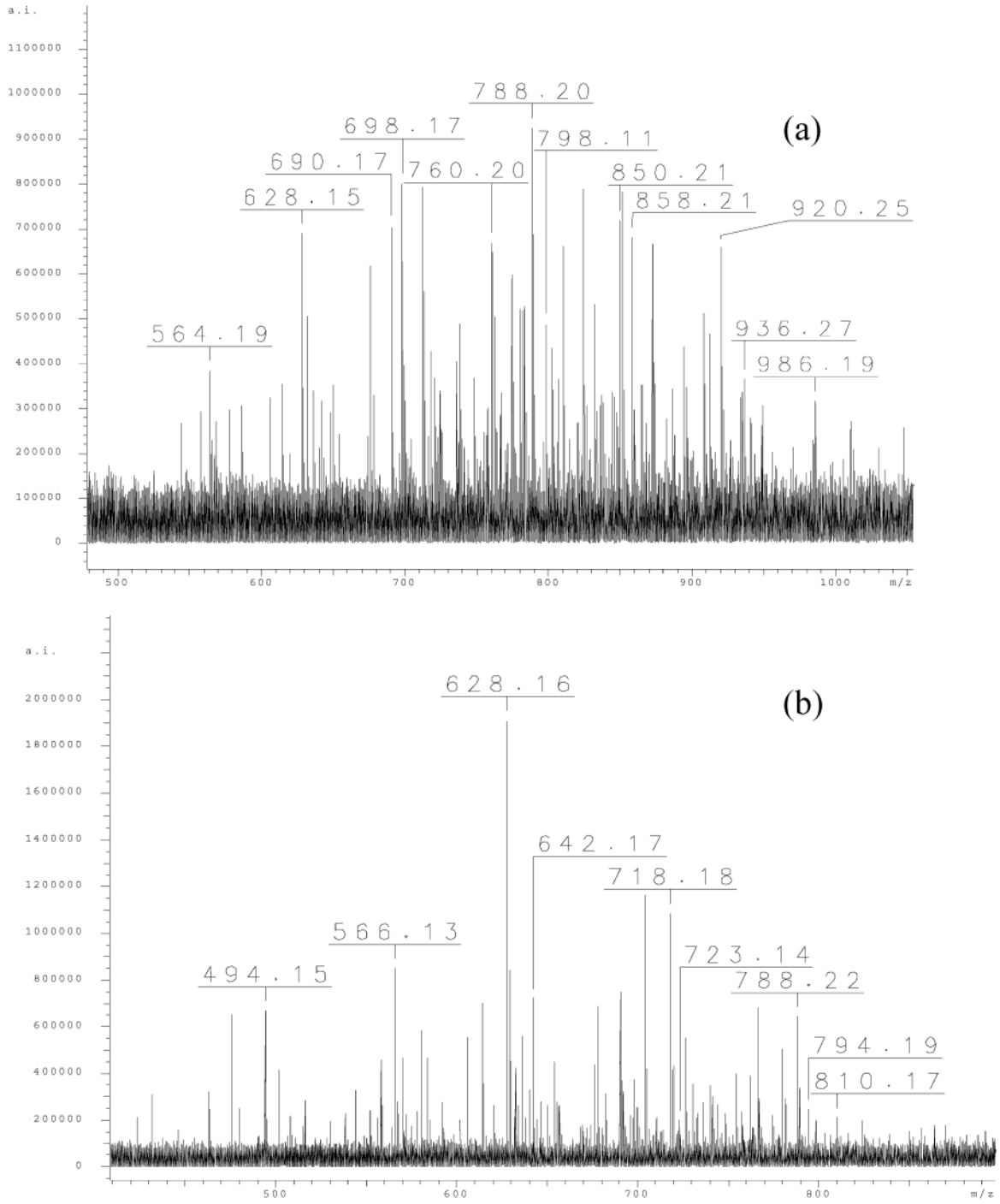


Figure 7. ESI-FTMS spectra of (a) **COH1** (III) and (b) **COH2** (III′).

the mass spectra shown in Figure 7. In Figure 7b, the most abundant ion was located at *m*/*z* 628.15, and the same ion was less abundant in Figure 7a. One would expect that the calculated M_n value for **COH2** would be close to the molecular weight of the most abundant ion on the basis of a somewhat symmetrical molecular weight distribution. Overall, this observation was consistent with the slight shift of the strong peak for **COH1** and **COH2** in the SEC chromatograms shown in Figure 2. Fourth, the total number of hydrolyzable/condensable groups (SiOMe and SiOH) in **COH2** was higher than that in **COH1**, consistent with the NMR results (Table 2). The higher number of condensable groups in **COH2** renders more intermolecular condensations, and it was likely the cause for the higher molecular weight components observed in **COH2** relative to **COH1** on the basis of the SEC analysis.

In summary, the hydrolysis of alkoxysilanes in the presence of toluene yielded the cohydrolyzate (**COH2**) containing more condensable groups, as confirmed by NMR and ESI-FTMS, and a higher concentration of large molecules, as observed by SEC. Further condensation in the presence of a base catalyst resulted in a high molecular weight silsesquioxane with some residual T_2 structure. In contrast, the cohydrolyzate (**COH1**) derived from the neat hydrolysis of alkoxysilanes was found to contain oligomers with less condensable groups, and the materials subsequently obtained had lower molecular weights and did not have T_2 structure. Relatively more "open" average structures are expected

Table 5. Composition Assignments for the ESI-FTMS Ions Observed for Cohydrolyzate (COH2) Obtained by Hydrolysis in the Presence of Toluene

measured mass $[M + NH_4]^+$	T^{Ph}	T^{Me}	M^{Vi}	OH	OCH_3	OH + OCH_3	theoretical mass $[M + NH_4]^+$	mass error (ppm)	reduced representation[a]
432.15121	1	1	2	1	1	2	432.15086	0.8	T_2M_4
446.16407	1	1	2		2	2	446.16651	−5.5	T_2M_4
454.17271		2	3		1	1	454.17474	−4.5	T_2M_4
480.15316	2		2	2		2	480.15086	4.8	T_2M_4
494.16771	2		2	1	1	2	494.16651	2.4	T_2M_4
502.17355	1	1	3	1		1	502.17473	−2.4	T_2M_4
508.18428	2		2		2	2	508.18216	4.2	T_2M_4
516.19139	1	1	3		1	1	516.19038	1.9	T_2M_4
530.09686	2	2	1	3		3	530.09688	0.0	T_4M_4
544.11135	2	2	1	2	1	3	544.11253	−2.2	T_4M_4
544.14425	3		1		2	2	544.14577	−2.8	T_3M_3
552.12366	1	3	2	2		2	552.12076	5.3	T_4M_4
558.12747	2	2	1	1	2	3	558.12818	−1.3	T_4M_4
566.13849	1	3	2	1	1	2	566.13641	3.7	T_4M_4
570.16414	2	1	2	2	1	3	570.16456	−0.7	T_3M_5
572.14568	2	2	1		3	3	572.14383	3.2	T_4M_4
584.18322	2	1	2	1	2	3	584.18021	5.1	T_3M_5
592.19194	1	2	3	1	1	2	592.18844	5.9	T_3M_5
606.12737	3	1	1	2	1	3	606.12818	−1.3	T_4M_4
606.20232	1	2	3		2	2	606.20409	−2.9	T_3M_5
614.13765	2	2	2	2		2	614.13641	2.0	T_4M_4
620.14511	3	1	1	1	2	3	620.14383	2.1	T_4M_4
628.15065	2	2	2	1	1	2	628.15206	−2.2	T_4M_4
636.15708	1	3	3	1		1	636.16028	−5.0	T_4M_4
642.16489	2	2	2		2	2	642.16771	−4.4	T_4M_4
654.20424	2	1	3	1	1	2	654.20409	0.2	T_3M_5
656.14818	1	4	2	1	2	3	656.15012	−2.9	T_5M_5
676.15414	3	1	2	2		2	676.15205	3.1	T_4M_4
690.17246	3	1	2	1	1	2	690.16770	6.9	T_4M_4
704.15338	2	3	2	2	1	3	704.15011	4.6	T_5M_5
718.16790	2	3	2	1	2	3	718.16576	3.0	T_5M_5
740.11250	3	3	1	2	1	3	740.11373	−1.7	T_6M_4
762.13739	2	4	2	1	1	2	762.13761	−0.3	T_6M_4
766.16820	3	2	2	2	1	3	766.16576	3.2	T_5M_5
780.18298	3	2	2	1	2	3	780.18141	2.0	T_5M_5
788.18764	2	3	3	1	1	2	788.18964	−2.5	T_5M_5
794.16064	2	4	2	2	2	4	794.16382	−4.0	T_6M_6
810.13249	3	3	2	2		2	810.13760	−6.3	T_6M_4

[a] M = $ViMe_2SiO_{1/2}$ (M^{Vi}), $HO_{1/2}$, or $MeO_{1/2}$.

for the species in **COH2** than in **COH1** since they can accommodate more uncondensed groups. The more opened structural features for **COH2** allowed for the formation of high molecular weight material to progress primarily via intermolecular condensation. On the other hand, intramolecular condensation could play a more significant role for **COH1** on the basis of its relatively "closed" structural features. The complete consumption of condensable groups for material derived from **COH1** appeared to support this assumption. The difference in the structures of cohydrolyzates and their respective preference for inter- or intramolecular condensation is in fact unexpected, since intramolecular reaction is generally favored when the concentration of the reactants is low. The adverse trend observed in this study is likely attributed to the interfacial interaction of monomer with water. In the absence of an organic solvent, the hydrolysis of alkoxy monomers proceeds at the "oil"−water interface, and the surface property in this case might facilitate intramolecular reaction. This assumption is supported by previous work that surfactant molecules can be used to mediate silsesquioxane synthesis and afforded resin with controlled molecular weight distribution.[27]

Compared to a one-step synthesis, in which the hydrolysis and condensation are carried out either under acidic or basic conditions, the two-step chemistry described here was shown to be quite unique. The initial hydrolysis step under acidic conditions with or without the participation of organic solvent was utilized to set up the "prestructures", and subsequent fast condensation under basic conditions[45] allowed molecular growth from these prebuilt oligomeric structures. The two-step process described here will allow more control over the structure and the molecular weight distribution of final silsesquioxane by taking advantage of the reaction kinetics.

Conclusions

In this paper, we demonstrated that the reaction conditions, especially the hydrolysis conditions, have a significant effect on the molecular weight distribution of a $(PhSiO_{3/2})_{0.35}(MeSiO_{3/2})_{0.40}(Me_2ViSiO_{1/2})_{0.25}$ (Ph = phenyl; Me = methyl; Vi = vinyl) resin. The presence of toluene in the hydrolysis step was found to be critical in achieving high molecular weight material. The difference in the final products was attributed to the preferential intra- or intermolecular condensations for the cohydrolyzates, possibly due to different interfacial interactions between the alkoxy monomers and water phase. This finding is important since it could be used to guide future design of resins with desired properties. In a separate paper, we reported compositional and structural analysis of $(PhSiO_{3/2})_{0.35}(MeSiO_{3/2})_{0.40}(Me_2ViSiO_{1/2})_{0.25}$ resin (Ph = phenyl; Me = methyl; Vi = vinyl).[46]

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