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Substituent Effects on the Sol−Gel Chemistry of Organotrialkoxysilanes

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Silsesquioxanes are a family of siloxane network polymers that have become important as vehicles for introducing organic functionalities into sol−gel materials. However, there has not been a systematic study of the capacity of organotrialkoxysilanes to form gels through the sol−gel process. In this study, we examined the sol−gel chemistry of organotrialkoxysilanes ($RSi(OR')_3$) with different organic groups (R = H, Me, Et, Pr, *i*-Pr, *n*-Bu, *i*-Bu, *t*-Bu, hexyl, octyl, decyl, dodecyl, hexadecyl, octadecyl, cyclohexyl, vinyl, phenyl, benzyl, phenethyl, chloromethyl, chloromethylphenyl, and tridecafluoro-1,1,2,2-tetrahydrooctyl) with methoxide or ethoxide substituents on silicon, at varying monomer concentrations, and under acidic, neutral, and basic conditions. Gels were obtained from the sol−gel polymerization of the monomers with R′ = Me and R = H, Me, vinyl, chloromethyl, chloromethylphenyl, hexadecyl, and octadecyl and R′ = Et and R = H, Me, Et, chloromethyl, vinyl, dodecyl, hexadecyl, and octadecyl. Formation of gels, even with these monomers, was often circumvented by phase separation phenomena, giving rise to crystalline oligomers, resinous materials, and precipitates. Gels obtained from these polymerizations were processed as xerogels and characterized by solid-state NMR, microscopy, and nitrogen sorption porosimetry.

Introduction

Silsesquioxanes[1] have been the subject of intensive study in the past and are becoming important again as a vehicle for introducing organic functionalities into hybrid organic−inorganic materials through sol−gel processing.[2] Depending on the application, the target hybrid material may be required to be a highly cross-linked, insoluble gel or a soluble polymer that can be cast as a thin film or coating. The former has applications such as catalyst supports and separations media; the latter is an economically important method for surface modification or compatibilization for applying adhesives or introducing fillers.

Polysilsesquioxanes are readily prepared through the hydrolysis and condensation of organotrialkoxysilanes, $R-Si(OR')_3$ (Scheme 1), though organotriaminosilane and organotrihalosilane monomers can also be used. The polymers are composed of a monomer repeat unit, $(R-SiO_{1.5})$, with a single silicon atom attached to other repeat units in the polymer through up to three siloxane bonds. The remaining substituent is an organic group attached to the silicon through a silicon−carbon single bond. Ideally, trifunctional monomers such as the organotrialkoxysilanes would be expected to polymerize to highly cross-linked, network polymers analogous to silica gels. However, cyclization reactions play an important role in the silsesquioxane polymerization process, giving rise to soluble crystalline polyhedral oligomers,[3] amorphous oligomers, and polymers (Scheme 2). There have been numerous reports of gels prepared from methyl- and vinyltrialkoxysilanes[4−6] and a few scattered reports describing gels from hydrido-,[7−9] chloromethyl-,[10] hexadecyl-, and octadecyltrialkoxysilanes.[11] Still, there has not been a systematic study of the propensity of trialkoxysilanes to form (or not form) gels

Scheme 1. Hydrolysis and Condensation of Trialkoxysilanes To Give Polysilsesquioxanes: R = H, Methyl, Ethyl, *n*-Propyl, *n*-Butyl, Isobutyl, *tert*-Butyl, *n*-Hexyl, *n*-Octyl, *n*-Decyl, *n*-Dodecyl, *n*-Hexadecyl, Octadecyl, *n*-Octadecyl, Cyclohexyl, Vinyl, Phenyl, Benzyl, Phenethyl, Chloromethyl, (*p*-Chloromethyl)phenyl, Tridecafluoro-1,1,2,2-tetrahydrooctyl; R′ = Me, Et

$$n\ R{-}Si(OR')_3 + 1.5n\ H_2O \xrightarrow{H+\ or\ OH-} \left[R{-}SiO_{1.5}\right]_n + 3n\ R'OH$$

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(1) Baney, R. H.; Itoh, M.; Sakakibara, A.; Suzuki, T. *Chem. Rev.* **1995**, *95*, 1409−30.

(2) Sanchez, C.; Ribot, F.; Lebeau, B. *J. Mater. Chem.* **1999**, *9*, 35−44.

(3) Voronkov, M. G.; Lavrent'yev, V. I. *Top. Curr. Chem.* **1982**, *102*, 199−236.

(4) Slinyakova, I. B.; Samodumova, I. M.; Voronkov, M. G. *Kolloid Zh.* **1972**, *34*, 574−8.

(5) Reetz, M. T.; Zonta, A.; Simpelkamp, J.; Rufinska, A.; Tesche, B. *J. Sol-Gel Sci. Technol.* **1996**, *7*, 35−43.

(6) Takamura, N.; Taguchi, K.; Gunji, T.; Abe, Y. *J. Sol-Gel Sci. Technol.* **1999**, *16*, 227−234.

(7) Budkevich, G. B.; Slinyakova, I. B.; Neimark, I. E. *U.S.S.R.* **1968**.

(8) Belot, V.; Corriu, R.; Leclercq, D.; Mutin, P. H.; Vioux, A. *Chem. Mater.* **1991**, *3*, 127−31.

(9) Tour, J. M.; Kafka, C. M. *Adv. Mater. (Weinheim, Fed. Repub. Ger.)* **1993**, *5*, 47−9.

(10) Slinyakova, I. B.; Voronkov, M. G.; Krot, I. E. *Kolloid Zh.* **1973**, *35*, 480−5.

(11) Shimojima, A.; Sugahara, Y.; Kuroda, K. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2847−2853.

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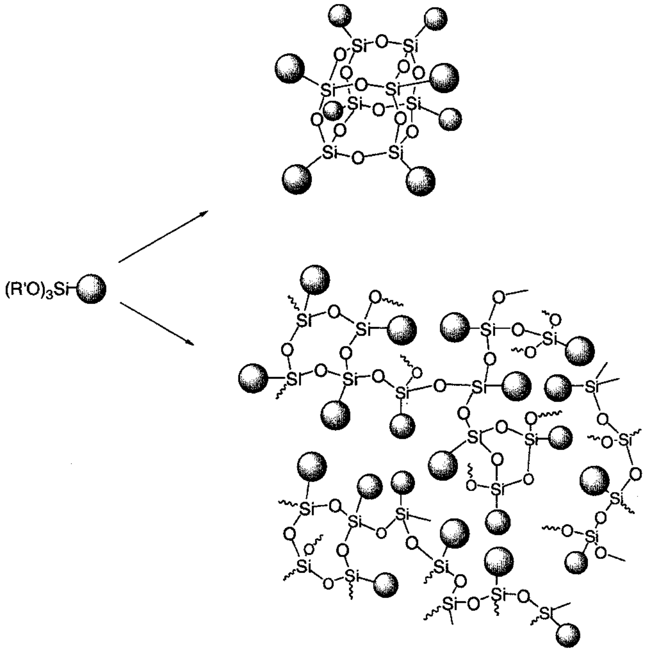
Scheme 2. Polymerization of Organotrialkoxysilanes To Afford Crystalline Polyhedral Oligosilsesquioxanes (Upper Right) or a Range of Amorphous Polysilsesquioxanes from Soluble Oligomers to Insoluble Gels (Lower Right)



through the sol−gel process, save for one study examining the formation of methyl, ethyl, and vinyl polysilsesquioxane gels.[12]

In this study, we have examined the sol−gel chemistry of a variety of organotrialkoxysilanes with different organic substituents in an attempt to elucidate the requirements for gelation. Most of the organic substituents in this study are hydrocarbons, though a few organofunctional groups, such as chloromethyl- and chloromethylphenyl, were examined as well. The effect of sterics on gelation was examined with the series of saturated, aliphatic substituents: R = H, Me, *i*-Pr, cyclohexyl, *i*-Bu, and *t*-Bu. The effect of the length of a linear alkyl substituent was examined with the series: R = H, Me, *n*-Pr, *n*-Bu, *n*-hexyl, *n*-octyl, *n*-decyl, *n*-dodecyl, *n*-hexadecyl, and *n*-octadecyl. Included with this group was a more rigid fluorinated alkyl chain: R = tridecafluoro-1,1,2,2-tetrahydrooctyl. The effect of olefinic, aromatic, and aromatic-functionalized substituents was examined with R = vinyl, phenyl, benzyl, and phenethyl. We also examined substituents with reactive functionalities that could potentially participate in the sol−gel chemistry: R = chloromethyl and chloromethylphenyl. Because the nature of the alkoxyl group has been shown to affect gelation in alkoxysilanes, monomers with methoxide and ethoxide substituents were studied. In all cases, the monomer concentration used in the polymerizations was increased (from 1 M) until either a gel was obtained or a neat monomer was employed. Aqueous HCl, NaOH, and deionized water were used in the polymerizations of all of the monomers and anhydrous formic acid was used with a few of the monomers that would not form gels with an acid or base. For purposes of comparison, we also prepared silica gels from tetramethoxysilane and tetraethoxysilane under similar conditions.

The polymerization reactions were monitored for the formation of gels, insoluble precipitates, soluble polymers, or crystalline polyhedral oligosilsesquioxanes. In earlier studies, any insoluble material was often referred to as a gel. In this study, a gel refers to a *monolithic* gel that forms from the original polysilsesquioxane solution. To examine the organic substituents' effects on the material properties, the gels were isolated and characterized by ^{13}C and ^{29}Si CP MAS NMR spectroscopies, electron microscopy, and nitrogen sorption porosimetry.

Experimental Section

General Methods. Anhydrous methanol was purchased from Aldrich. Ethanol was distilled from magnesium before use. Triethoxysilane, trimethoxysilane, methyltrimethoxysilane, methyltriethoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane, trimethoxyvinylsilane, triethoxyvinylsilane, *n*-octyldecyltrimethoxysilane, and dodecyltriethoxysilane were purchased from Aldrich. Phenethyltrichlorosilane, cyclohexyltrichlorosilane, *tert*-butyltrichlorosilane, and benzyltriethoxysilane were purchased from Gelest. Isopropyltrichlorosilane was prepared from the Grignard reaction between isopropylmagnesium chloride (1.6 M in Et_2O) and tetrachlorosilane. Treatment with tetramethylorthoformate and tetraethylorthoformate afforded isopropyltrimethoxysilane and isopropyltriethoxysilane, respectively. *tert*-Butyltriethoxysilane and *tert*-butyltrimethoxysilane were prepared from *tert*-butyltrichlorosilane by esterification with ethylorthoformate or methylorthoformate. Similarly, the cyclohexyl-substituted monomers were prepared from their corresponding trichlorosilane precursor. 2-Phenethyltrimethoxysilane and 2-phenethyltriethoxysilane were also prepared by esterification of phenethyltrichlorosilane. Monomer purities were checked by GC and ^{1}H, ^{13}C, and ^{29}Si NMR and distilled if necessary until greater than 96% (GC) was obtained. Because of the importance of using NMR to follow the hydrolysis and condensation of organotrialkoxysilanes, ^{13}C and ^{29}Si NMR chemical shifts for the monomers used in this study are tabulated in Table 1. ^{29}Si NMR chemical shifts are consistent with those reported for alkyl-, vinyl-, and aryl-substituted trialkoxysilanes.

^{1}H, ^{13}C, and ^{29}Si solution NMR spectra were recorded on a Bruker DRX 400 MHz spectrometer at a resonant frequency of 400.16 MHz, using standard single-pulse sequences on a 5-mm broad band probe. The relaxation delay was 5 s, with 8 to 32 K complex points. Experiments were performed at 298 K, using 16−32 scans. Residual solvent peaks or tetramethylsilane was used as an internal reference for ^{1}H and ^{13}C spectra. ^{29}Si NMR spectra were obtained with neat monomer, resulting in a slight (0.2−0.4 ppm) downfield shift from those reported in solution experiments.[13] An external tetramethylsilane (δ = 0.0) sample was used as the reference for ^{29}Si NMR spectra. Infrared spectra were obtained on a Perkin−Elmer 1750 Fourier transform infrared spectrophotometer.

Polymerizations. Monomers were polymerized at 1 M concentration with 1.5, 3.0, or 6.0 equiv of water in the appropriate alcohol (methanol for trimethoxysilanes and ethanol for triethoxysilanes). Aqueous HCl (1 N) and NaOH (1 N) were used as catalysts (2.7 mol/mol % catalyst relative to monomer concentration). Deionized water without added catalyst was also used. All experiments were performed in triplicate. Polymerizations with 3 equiv (relative to monomer) of anhydrous formic acid or with catalytic aqueous tetrabutylammonium fluoride were also examined with select monomers. If gels were obtained at 1 M monomer concentration, the monomer was then polymerized at lower concentra-

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(12) Slinyakova, I. B.; Kurennaya, L. I. *Vysokomol. Soedin., Ser. B* **1972**, *14*, 889−92.

(13) Liepins, E.; Zicmane, I.; Lukevics, E. *Kremniiorg. Soedin. Mater. Ikh Osn., Tr. Soveshch. Khim. Prakt. Primen. Kremniiorg. Soedin., 5th* **1984**, 16−19.

Table 1. ^{13}C and ^{29}Si NMR Chemical Shifts for Organotrimethoxysilanes and Organotriethoxysilanes (^{29}Si NMRs Were Performed with Neat Monomer Referenced against an External Tetramethylsilane Standard)

	trimethoxysilyl monomers		triethoxysilyl monomers	
R groups	^{13}C (ppm)	^{29}Si (ppm)	^{13}C (ppm)	^{29}Si (ppm)
H	49.4	−55.4	57.8, 17.6	−59.1
Me	50.0, −9.2	−40.1	58.1, 18.1, −7.3	−44.1
Et	50.1, 5.9, 0.8	−42.1	58.0, 18.1, 6.3, 2.1	−45.7
n-Pr	50.1, 17.7, 16.7, 12.6	−42.8	58.4, 18.6, 17.9, 16.9, 13.5	−46.4
i-Pr	50.7, 16.8, 10.3	−44.4	58.4, 18.3, 17.0, 10.9	47.6
n-Bu	50.2, 25.9, 24.6, 13.4, 10.1, 8.7	−42.6	58.2, 26.1, 24.9, 18.2, 13.7, 10.1	−46.2
i-Bu	50.1, 25.6, 23.6, 19.3	−43.2	58.2, 25.8, 23.8, 20.6, 18.2	−46.9
t-Bu	51.0, 26.2, 17.7	−46.4	58.8, 26.3, 18.4, 17.5	−49.3
n-Hex	50.6, 10.2	−42.7	58.0, 32.7, 31.4, 22.6, 22.4, 18.0, 13.8, 10.2	−45.8
n-octyl	50.1, 33.1, 33.0, 29.2, 29.1, 22.6, 13.9, 10.4, 9.0	−42.3	57.6, 32.8, 31.6, 29.0, 22.5, 22.3, 17.8, 13.6, 10.1	−45.8
n-decyl	50.0, 33.0, 31.8, 29.5−29.0, 22.6, 14.2, 9.0	−42.3	57.9, 33.0, 31.8, 29.5−29.0, 22.6, 22.5, 18.0, 13.8, 10.2	−45.8
dodecyl	50.0, 33.0, 31.8, 29.6−29.2, 22.5, 22.4, 13.8, 9.0	−42.3	57.9, 32.9, 31.8, 29.5−29.1, 22.6, 22.5, 18.0, 13.7, 10.2	−45.7
hexadecyl	50.4, 33.1, 31.9, 29.7−29.3, 22.63, 14.0, 9.1	−42.9	58.0, 32.7, 31.4, 22.6, 22.4, 18.1, 13.8, 10.2	−45.8
octadecyl	50.1, 33.1, 31.8, 29.1, 22.6, 13.9, 10.5, 9.0	−42.9	57.6, 32.8, 31.6, 29.0, 28.9 22.5, 22.3, 17.8, 13.6, 11.2, 10.1	−45.7
cyclohexyl	50.2, 27.3, 26.4, 22.1	−46.3	58.3, 27.6, 26.7, 22.8, 18.2	−49.5
vinyl	137.4, 129.2,50.6	−55.9	135.9, 129.1, 57.8, 17.5	−59.1
phenyl	134.6, 130.5, 129.3, 127.8, 50.6	−55.4	134.7, 130.9, 130.2, 127.7, 58.6, 18.1	−58.6
benzyl	137.7, 129.2, 128.6, 125.0, 50.5, 19.7	−48.1	137.5, 128.8, 128.1, 124.5, 58.6, 20.3, 18.1	−52.2
phenethyl	144.2, 128.2, 127.7, 125.6, 50.3, 28.6, 11.2	−43.7	144.4, 128.1, 127.6, 125.4 58.2, 28.7, 18.1, 12.4	−46.5
$ClCH_2$	50.4, 22.1	−54.8	58.7, 23.2, 17.6	−58.7
$ClCH_2Ph$	139.6, 134.7, 129.6, 127.7, 50.4, 45.6	−55.4		

Table 2. Solid-State CP MAS ^{29}Si and ^{13}C NMR Chemical Shifts for Peaks Observed in Gels[a]

monomer	T^0	T^1	T^2	T^3	^{13}C resonances
$HSi(OMe)_3$	(−55.4)	not obs.	−74.6	−84.7	
$H Si(OEt)_3$	(−59.1)	not obs.	−74.6	−84.9	
$MeSi(OMe)_3$	−39.8 (−40.1)	not obs.	−57.0	−65.2	−4.2
$MeSi(OEt)_3$	(−44.1)	−50.9	−58.8	−65.3	−4.1
$EtSi(OEt)_3$	(−45.7)	not obs.	not obs.	−66.5	−5.8
vinyl$Si(OMe)_3$	(−55.9)	not obs.	−71.4	−80.3	136.0, 130.3
vinyl$Si(OEt)_3$	(−59.1)	not obs.	−71.5		135.8, 130.5
hexadecyl$Si(OMe)_3$	(−42.9)	−49.8	−58.0	−66.7	32.8, 24.1, 14.2
hexadecyl$Si(OEt)_3$	(−45.8)	−49.0	−57.3	−66.5	32.6, 24.0, 14.1
octadecyl$Si(OMe)_3$	−42.2 (−42.9)	−49.3	−58.0	−67.1	32.7, 24.3, 14.2
octadecyl$Si(OEt)_3$	(−45.7)	−50.5	−58.2	−66.0	32.8, 24.3, 14.3
chloromethyl$Si(OMe)_3$	(−54.8)	−59.2	−68.7	−78.4	24.7
chloromethyl$Si(OEt)_3$	(−58.7)	not obs.	−68.2	−78.2	24.7
chloromethylphenylsi$(OMe)_3$	(−55.4)	not obs.	−70.7	−77.5	139.8, 134.2, 127.9, 45.9

[a] Monomer ^{29}Si (solution) chemical shifts are given for the T^0 values in parentheses. T^0 refers to monomeric silanes including monomer and its hydrolysis products. T^1 refers to resonances due to a silicon with a single siloxane bond, T^2 refers to a resonance due to a silicon with two siloxane bonds, and T^3 refers to the fully condensed silsesquioxanes.

tions to determine the practical gelation threshold. If the monomer did not gel within a maximum of 2 weeks, it was then polymerized at as high a concentration as possible (based on the molecular weight and density of the monomer). Soluble polysilsesquioxanes were described as resins. Other nomenclature includes the following: Oils are oligosilsesquioxanes that phase separate from the alcohol−water solvent as a liquid. Precipitates are amorphous materials that phase separate as an insoluble solid rather than form a gel. Molecular weight determinations were conducted by gel permeation chromatography at room temperature in THF using a Polymer Laboratories GPC 210 equipped with a Precision Detectors PD 2040 multiangle detector. Glass transition (T_g) measurements on aryl-substituted polymers were performed with a Perkin−Elmer DSC7 instrument. Gels were described as either colloidal (opaque white) or translucent (blue tinted) or transparent. Gels were prepared for further characterization by crushing and washing in water and diethyl ether and then drying under vacuum at 100 °C overnight.

The resulting xerogels were characterized by solid-state ^{13}C and ^{29}Si CP MAS NMR and the chemical shifts are reported in Table 2 and are typical for hydrido-, alkyl-, and vinylpolysilsesquioxanes. Solid-state ^{13}C and ^{29}Si CP MAS NMR spectra were obtained with a Bruker AMX-400 MHz spectrometer at 100.63 and 79.5 MHz, respectively, and were acquired with magic angle spinning (MAS) speeds of ~5 and ~3−5 kHz, respectively. ^{13}C NMR spectra were acquired using cross-polarization (CP) with a relaxation delay of 1 s and a cross-polarization time of 2 ms. ^{13}C referencing was performed on the carbonyl resonance of solid glycine ($\delta = 176.0$). Because the gels in this study are similar, these parameters were optimized on only one of the gels to obtain spectra with a satisfactory signal-to-noise ratio. ^{29}Si NMR spectra were acquired using single-pulse excitation with a relaxation delay of 480 s. With ^{29}Si T_1 values ranging from 19 to 135 s, the relaxation delay of $\geq 3T_1$ is sufficient for quantitative spectra. ^{29}Si CP MAS NMR spectra were deconvoluted using a Lorentz−Gaussian (50:50) fit. As with other silsesquioxane materials,

Table 3. Range of Products Obtained from Organotrimethoxysilanes, $RSi(OMe)_3$[a]

R Group	Gel	Sol	Crystal	Oil	Resin	Precip.
H	▨				▨	
Methyl	▨	▨	▨		▨	
Ethyl			▨	▨	▨	
Propyl			▨	▨	▨	
n-Butyl			▨	▨	▨	▨
i-Butyl			▨	▨	▨	▨
t-Butyl			▨	▨		▨
Hexyl				▨	▨	
Octyl				▨		▨
Decyl				▨		▨
Dodecyl			▨	▨	▨	▨
Hexadecyl	▨					
Octadecyl	▨					▨
Cyclohexyl		▨			▨	▨
Vinyl	▨		▨		▨	
Phenyl			▨		▨	▨
Phenethyl		▨	▨	▨	▨	
Chloromethyl	▨		▨		▨	▨
(p-Chloromethyl)phenyl	▨		▨		▨	▨
Tridecafluoro-1,1,2,2-tetrahydrooctyl				▨		

[a] Sol refers to a homogeneous solution. Crystalline products were generally minor contributors to the polysilsesquioxane products; most of the product was either in solution or in an oil or resinous phase. Precipitates are insoluble, noncrystalline materials. Gray shading indicates that polysilsesquioxane was observed in the indicated physical form. White indicates that the polysilsesquioxane failed to afford the indicated physical form.

the spectra have peaks progressively upfield from the monomer with higher degrees of condensation.

Porosity was evaluated by nitrogen sorption porosimetry and scanning electron microscopy. Porosimetry measurements were determined using a Quantachrome Autosorb-6 multiport nitrogen porosimeter. Surface areas were determined using the multipoint BET (Brunauer−Emmett−Teller) method. The P/P_0 range was $0.05 \leq P/P_0 \leq 0.35$. The average pore diameter was calculated from d_{av}. Elemental analyses for chlorine were performed by Galbraith.

Microscopy studies were performed using a Hitachi S4500 field emission scanning electron microscope. The samples were coated with 100−200-Å chromium using a Gatan Model 681 high-resolution ion beam coater. Secondary electron images were taken using 5-kV accelerating voltage. The images were acquired digitally from the SEM using a PGT Imix imaging system. Precipitates were examined by microscopy to determine if they were crystalline or amorphous.

Results and Discussion

Hydrolysis and condensation of trialkoxysilanes readily affords oligomeric and polymeric silsesquioxanes in the form of phase-separated oils, resins, and precipitates; gels were only observed with 14 out of 41 (34%) of the monomers in this study (Tables 3 and 4). Only a few of the monomers that did not gel remained as solutions. Phase separation of oligomers and polymers from the solution dominated the polymerization reactions. Crystalline polyhedral oligosilsesquioxanes were observed with many of the alkyl-substituted monomers, despite the high monomer concentrations used. For the most part, the nongel products were not fully characterized. Many of the polysilsesquioxane gels that did form were opaque white and colloidal in appearance.

In addition to screening monomers for gelation, the time required for the gels was noted. These data are useful practically for designing sol−gel experiments with organotrialkoxysilanes. To allow the relative gel times to be compared, gel times for the various monomers were obtained with 1 M monomer concentration when possible. Gel times under these conditions ranged from immediate gelation for octadecyltriethoxysilane under acidic conditions to months for chloromethyltriethoxysilane. Under the same conditions used to polymerize the organotrialkoxysilanes, tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS) form transparent or translucent silica gels. Under acidic conditions, TMOS formed transparent gels in 60 days at 1 M monomer concentration and in 7 days at 5.4 M (neat) monomer concentration. Under basic conditions, TMOS formed transparent gels overnight at 1.0 M. TEOS was less reactive under acidic conditions, going 8 months without forming gels as 1 M solutions and forming only precipitates at 4.0 M. Under neutral conditions, translucent gels formed after 148 days. Base-catalyzed polymerization of TEOS afforded white, opaque colloidal precipitates (rather than gels) overnight. In the group of polysilsesquioxanes that did form gels, gel times were generally much shorter than those for the silica gels prepared under similar conditions (Table 5).

Table 4. Range of Products Obtained from Organotriethoxysilanes, $RSi(OEt)_3$[a]

R Group	Gel	Sol	Crystal	Oil	Resin	Precip.
OEt	▨				▨	▨
H	▨					
Methyl	▨		▨		▨	
Ethyl	▨		▨		▨	▨
Propyl			▨	▨	▨	
i-Propyl						▨
n-Butyl				▨	▨	
i-Butyl		▨	▨		▨	
t-Butyl			▨			▨
Hexyl		▨		▨	▨	
Octyl				▨	▨	▨
Decyl				▨		▨
Dodecyl					▨	▨
Hexadecyl	▨			▨	▨	
Octadecyl	▨			▨		▨
Cyclohexyl		▨				▨
Vinyl	▨	▨	▨			
Phenyl					▨	▨
Benzyl		▨		▨	▨	▨
Phenethyl		▨		▨	▨	
Chloromethyl	▨				▨	▨
Tridecafluoro-1,1,2,2-tetrahydrooctyl				▨	▨	▨

[a] Sol refers to a homogeneous solution. Crystalline products were generally minor contributors to the polysilsesquioxane products; most of the product was either in solution or in a oil or resinous phase. Precipitates are insoluble, noncrystalline materials. Gray shading indicates that polysilsesquioxane was observed in the indicated physical form. White indicates that the polysilsesquioxane failed to afford the indicated physical form.

Effect of Trialkoxysilyl Group. The main difference between the *trimethoxysilyl* and *triethoxysilyl* monomers (Tables 3 and 4) is that the trimethoxysilyl-substituted monomers reacted faster and, in some cases (R = methyl, ethyl, and vinyl), so exothermically that the reaction solutions would explosively boil upon mixing and prior to gelation at concentrations higher than 1 M. Under these conditions, gels were obtained that were foamlike in consistency with pores large enough to be visible to the naked eye. In addition, the sol−gels were, with the exceptions of triethoxysilane

Table 5. Gel Times for Organotrialkoxysilanes (Where Possible, Gel Times Are Given for 1.0 M Monomer Concentration; in All Experiments, Monomers Were Reacted with 1.5 equiv of Water)

	trialkoxysilyl group, Si(OR′)$_3$			
	R′ = Me		R′ = Et	
R group	conditions	gel time (±5%)	conditions	gel time (±5%)
OR′	H$^+$, 1.0 M[b]	60 days	H$^+$, 1.0 M	300 days
	OH$^-$, 1.0 M	12 h	H$_2$O, 1.0 M[c]	148 days
	H$_2$O, 1.0 M[c]	64 days		
H	H$^+$, 1.0 M[d]	15 h	H$^+$, 1.0 M	2 days
	H$_2$O, 1.0 M[d]	15 h	H$_2$O, 1.0 M[d]	2 days
methyl	H$^+$[a], 5.9 M	12 h	H$^+$, 4.4 M	9 days
	OH$^-$, 1.0 M[d]	12 h	OH$^-$, 1.0 M[c]	12 h
ethyl			OH$^-$, 2.0 M[c]	12 h
vinyl	H$^+$[a], 5.6 M	12 days	H$^+$, 4.2 M	8 days
	OH$^-$, 1.0 M[c]	4 days	OH$^-$, 1.0 M[c]	7 days
n-hexadecyl	H$^+$, 1.0 M[e]	12 h	H$^+$, 1.0 M[c]	10 min
	OH$^-$, 1.0 M	12 h	OH$^-$, 1.0 M	5 min
	H$_2$O, 2.4 M	12 h		
n-octadecyl	H$^+$, 1.0 M	$<$1 min	H$^+$, 1.0 M[f]	$\ll$1 min
	OH$^-$, 1.0 M[e]	4 min	OH$^-$, 1.0 M[f]	2 days
	H$_2$O, 1.0 M[f]	17 days	H$_2$O, 1.0 M[f]	$\ll$1 min
chloromethyl	H$^+$, 4.35 M	77 days	H$^+$, 1.0 M[g]	172 days
	OH$^-$, 1.0 M[b]	26 days	OH$^-$, 1.0 M[c]	2 h
	H$_2$O, 1.0 M	87 days	H$_2$O, 1.0 M	76 days
p-chloromethylphenyl	H$^+$, 4.0 M	36 days		
	OH$^-$, 1.0 M[c]	$<$1 min		
	H$_2$O, 4.0 M	15 days		

[a] 0.1 M HCl used. At neat concentrations (not shown), these monomers produced the results found in *b*−*g*. [b] Very exothermic, solution sprayed out of vial. [c] Nonhomogeneous gel composed of a mixture of precipitates and gel. [d] Exothermic reaction upon addition of aqueous catalyst caused bubbles throughout gel. [e] Phase separation of heavy oil or gum from solution. [f] Formation of precipitate. [g] Phase separation and formation of hard resin.

and trimethoxysilane (vide infra), more exothermic under acid-catalyzed hydrolysis and condensation conditions than under neutral or base-catalyzed conditions. This increased reactivity has been attributed to inductive stabilization by the organic groups of positively charged intermediates and transition states in the hydrolysis and condensation reactions.[14]

Effect of Monomer: Water Stoichiometry. While most of the monomers were polymerized with 1.5 equiv of water, it is known that the ratio of monomer to water can have pronounced effects on the sol−gel chemistry of tetraalkoxysilanes.[15] For organotrialkoxysilanes, a ratio of 1.5 equiv of water to 1 equiv of monomer is the ideal stoichiometry necessary for complete hydrolysis and condensation. Greater quantities of water increase hydrolysis and, thus, change the monomer composition during the sol−gel polymerization. More water also would be expected to make the solution more polar and, perhaps, less suitable to nonpolar polysilsesquioxanes. Additional sol−gel polymerizations were performed with the phenyl-, benzyl-, and phenethyl-substituted monomers with 3.0 and 6.0 equiv of water under both acidic and basic conditions. In none of the systems did the additional water lead to the formation of gels. It did, however, appear to cause phase separation of oily oligomers and resins. In an attempt to avoid phase separation, the vinyl-, phenyl, ethyl-, *n*-butyl, *n*-hexyl, and decyltriethoxysilanes were reacted neat with 3 equiv of anhydrous formic acid in a nonaqueous sol−gel procedure developed by Sharp and Michaelzak.[16] In all of these cases, no gels were obtained.

Effect of Sterics. The steric effect on gelation was probed with the series of monomers with organic groups of varying sterics. The expectation is that increasing steric bulk at the organic substituent will have an inhibitory effect on the sol−gel polymerization process. Monomers with smaller organic groups, R = H, methyl, and ethyl, should more readily hydrolyze and condense to afford polymers than those with bulkier groups, R = isopropyl, isobutyl, cyclohexyl, and *tert*-butyl, which would be expected to react less quickly and be less prone to form highly cross-linked polymers capable of forming gels. Osterholtz and Pohl[14] revealed that the acid- and base-catalyzed hydrolysis rates and acid-catalyzed condensation rates decreased as the chain length increased from methyl to propyl, suggesting that there was a significant steric effect based on the alkyl group. The inability of *tert*-butyltrialkoxysilanes to afford gels (Tables 3 and 4) and the isolation of the monomeric *tert*-butylsilanetriol indicate that steric inhibition of hydrolysis and condensation reactions by the *tert*-butyl group can effectively prevent polymeric gels from forming. However, one should be cautious about extending the steric effect argument to rationalizing the formation of gels from less sterically hindered monomers. Phase separation of oligomers and polymers from the sol−gel solution, before gelation can occur, appears to be a more important contributor than sterics to the inability of most alkyltrialkoxysilanes to afford gels.

The first monomers in this series are trimethoxysilane and triethoxysilane. Hydrogen-functionalized silsesquioxane gels are of interest because of the reactive nature of the hydrogen group toward bases, radical reactions, and hydrosilation chemistry. While trimethoxysilane and triethoxysilane, R = H, bear the smallest “organic” substituent, the reactive character of the hydrogen group as a reducing agent makes comparison with the aliphatic substituents in the series difficult under basic conditions, where the hydride group reacts with hydroxide to give hydrogen gas and silica gels.[9] In contrast, the monomers polymerized rapidly and exothermically under acidic conditions or even with deionized water (pH 7) to afford insoluble, monolithic gels with at least some of the hydrogen groups intact. Following the reactivity trend observed with the polymerization of tetralkoxysilanes, trimethoxysilane polymerized to form gels more readily and at lower concentrations (0.1 M) than triethoxysilane. The trialkoxysilane monomers (R = H) were the only subgroup of monomers that gave transparent gels of optical quality comparable to silica gels prepared from tetraalkoxysilanes (Table 6).

Retention of the hydrogen group in the final xerogels increases, with decreasing pH, in the sol−gel polymerization. Examination of the xerogels by solid-state ^{29}Si NMR (CP MAS) spectroscopy reveals a polysilsesquioxane structure for the gels prepared under acidic conditions, but both silica and silsesquioxanes archi-

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(14) Osterholtz, F. D.; Pohl, E. R. *J. Adhes. Sci. Technol.* **1992**, *6*, 127−49.

(15) Brinker, C. J.; Scherer, G. W. *Sol−Gel Science, The Physics and Chemistry of Sol−Gel Processing*; Academic Press: Boston, 1990.

(16) Sharp, K. G. *J. Sol-Gel Sci. Technol.* **1994**, *2*, 35−41.

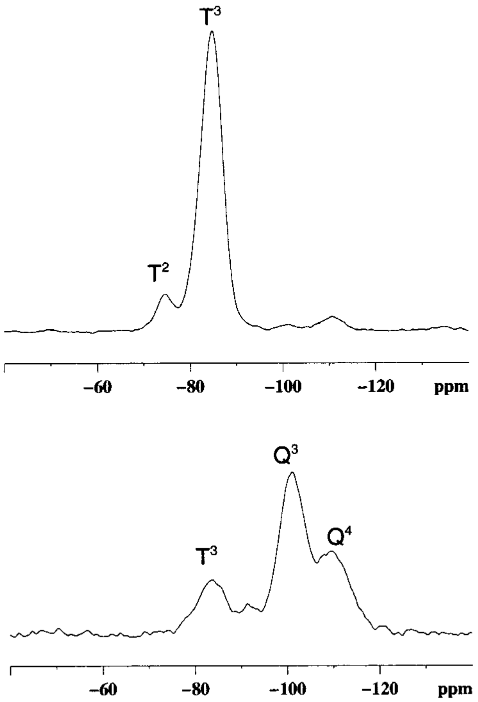

Figure 1. Solid-state ^{29}Si CP MAS NMR of the polyhydrosilsesquioxane xerogel (top) prepared from the HCl-catalyzed sol−gel polymerization of triethoxysilane (1 M, EtOH, 1.5H_2O) and the polyhydrosilsesquioxane silica gel (bottom) prepared under neutral conditons.

Table 6. Appearance of Monolithic Polysilsesquioxane Gels (Entries with Dashed Lines Indicate No Gels Were Obtained)

	$RSi(OMe)_3$			$RSi(OEt)_3$		
R	H^+	OH^-	H_2O	H^+	OH^-	H_2O
H	transl.	transl.	transl.	transp.	transp.	---
CH_3	opaque	transl.	---	transl.	opaque	---
CH_3CH_2	---	---	---	---	opaque	---
dodecyl	---	---	---	opaque	opaque	---
hexadecyl	opaque	opaque	opaque	opaque	opaque	---
octadecyl	opaque	opaque	opaque	opaque	opaque	opaque
vinyl	opaque	opaque	---	transl.	opaque	---
$ClCH_2$	transl.	opaque	transp.	---	opaque	transp.
(*p*-$ClCH_2$)phenyl	---	opaque	opaque	---	---	---

tectures were present from both methoxy- and ethoxy-substituted monomers that were polymerized with deionized water at 1 M monomer concentrations (Figure 1). At higher (neat) monomer concentrations under neutral conditions, the hydrolysis and condensation reactions of the alkoxides lead to gels occurred quickly enough, relative to the rate of Si−H hydrolysis, to minimize conversion to silica. This is evidenced by the fact that only traces of silica were observed from the reaction of the neat monomers with deionized water. With NaOH-catalyzed sol−gels, the hydrolysis of the Si−H occurred quickly and quantitatively. The solid-state spectra for the gels prepared under basic conditions revealed silica (*Q*) resonances with only a trace of a resonance at −85 ppm due to silsesquioxanes. Caution must be exercised in using these monomers, however, as reaction conditions with higher pH and/or longer gel times may lead to significant reduction in the population of hydrogen groups retained in the final materials.

Methylsilsesquioxane gels have been reported elsewhere[5,6,12] and are, perhaps, the most studied of silsesquioxane systems capable of gelation. In this study, gels formed from both trimethoxy- and triethoxy-substituted monomers under basic and acidic conditions, but not at neutral pH. At 1.0 M, methyltrimethoxysilane reacted with acid to give mixtures of tacky resins and crystalline products that phase separated from the solution. At 5.9 M (neat) monomer mixed with water and catalyst, the polymerization was exothermic enough to boil the solution (CAUTION); an opaque white gel was obtained. Under basic conditions, translucent gels formed overnight at 1.0 M monomer concentration and in 5 days at 0.8 M monomer concentration. Methyltriethoxysilane also reacted under acidic conditions to form mixtures of resin and crystalline products that phase separated from the solution at 1.0 M monomer concentration and poorly defined gels with some occluded crystals or precipitates were obtained when 4.4 M (neat) monomer was polymerized. Under basic conditions, yellow-tinted gels were obtained overnight. Only solutions free of crystals were formed under neutral conditions.

Changing the alkyl group from methyl to ethyl resulted in a remarkable reduction in the number of polymerization conditions that would lead to gels. Only the ethyltriethoxysilane monomer formed gels and then only after 8 days with NaOH as the catalyst and at 2.0 M monomer concentration. These gels formed from a white colloidal suspension and, when dry, were opaque white in appearance and insoluble in organic solvents or water. At other concentrations with NaOH catalyst, resins or precipitates were obtained. Under acidic conditions, resins and small amounts ($<$5 wt %) of crystalline products were obtained. With deionized water, phase-separated oils or resins were obtained. The ethyltrimethoxysilane afforded no gels under any conditions. No gels were obtained under any conditions with the *n*-propyl- or *n*-butyltrialkoxysilanes.

Increasing the steric hindrance at the silicon with branched alkyl groups (isobutyl, isopropyl, cyclohexyl, and *tert*-butyl) prevented polymerizations of organotrialkoxysilanes from forming gels under any conditions. Even when neat monomers were mixed with aqueous acid or base in the absence of a solvent, only oligomeric and polymeric materials were obtained through some type of phase separation (separation of oil, resin, precipitation, or crystallization) rather than gel-forming network polymers. These products were generally soluble in more nonpolar organic solvents or at higher dilution in alcohols. In some cases (R = Me, Et, isopropyl, isobutyl), discrete polyhedral oligosilsesquioxanes,[17] such as the cubic octomer (T_8) from isobutyltriethoxysilane (Figure 2), were obtained in sufficient quantities to isolate and characterize. However, the yields of crystalline products are low ($<$10%) compared to those from literature procedures for preparing these compounds because the high monomer concentrations favor a more random assortment of products that generally separate from the solvent as a viscous hydrophobic resin.

Solution ^{29}Si NMR studies have revealed that hydrolysis and condensation of alkoxysilanes are generally slowed by the steric effect. *tert*-Butyltrialkoxysilanes are sterically hindered enough that while complete hydrolysis eventually occurs, condensation reactions are inhib-

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(17) Voronkov, M. G.; Vlasova, N. N.; Pestunovich, A. E. *Russ. J. Gen. Chem.* **1998**, *68*, 770−774.

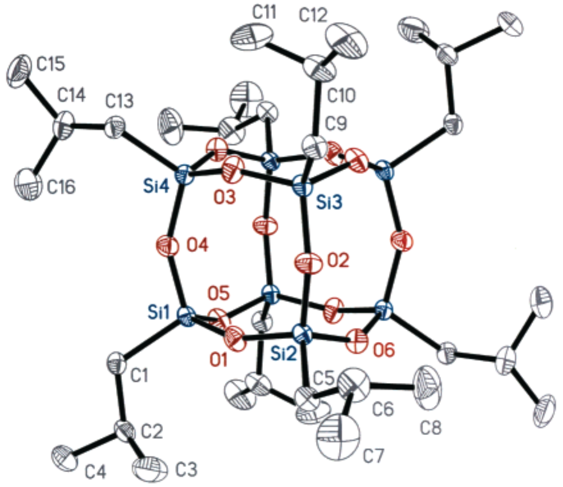

Figure 2. Ortep drawing for the crystal structure of a T_8 cube obtained from the polymerization of isobutyltriethoxysilane.

ited such that even oligomers form only slowly. Solution ^{29}Si NMR of the polymerization reaction of *tert*-butyltriethoxysilane under acidic conditions reveals only hydrolysis products (T^0) after 18 h and only minor resonances from T^1 (1 siloxane bond) and T^2 (2 siloxane bonds) peaks under basic conditions. Even after 3 months, T^1 peaks dominate the ^{29}Si NMR spectra for the acid-catalyzed system. Thus, the *tert*-butyl monomers are suitable for forming some discrete oligomeric products or for surface functionalization of surfaces, but not for forming resins and gels.

Effect of Substituent Length. With increasing length of alkyl substituents, the silsesquioxanes become less prone to form gels. The reluctance of the ethyl-substituted monomers and the inability of the *n*-propyl, *n*-butyl, *n*-hexyl, *n*-octyl, *n*-decyl, *n*-dodecyl, and tridecafluoro-1,1,2,2-tetrahydrooctyl monomers to form gels may be more of a physical phenomenon than one of chemical reactivity. In every case, phase separation of a dense oil, resin, or precipitate from a less dense alcoholic phase was observed. Even performing nonaqueous sol−gel polymerizations with anhydrous formic acid failed to prevent phase separation and resin formation. Surprisingly, with very long alkyl groups (hexadecyl and octadecyl) gelation is again observed, possibly due to supramolecular organization of the long alkyl groups.[11] Hexadecyl- and octadecyltrimethoxysilanes polymerized to form opaque white gels under acidic, basic, and neutral conditions. Hexadecyl- and octadecyltriethoxysilanes also formed opaque white gels under acidic, neutral, and basic conditions. Gels formed by phase separation of a colloidal species, followed by gelation. In both cases, gels formed at concentrations as low as 0.2 M. Below that concentration, the colloids precipitated. We were unable to observe any of the lamellar structures reported by A. Shimojima et al.[11] in the gels we prepared. Furthermore, the gels were discovered to melt between 46 and 61 °C for the hexadecylsilsesquioxanes and 55−75 °C for the octadecylsilsesquioxanes. These results suggest that phase separation is occurring to form colloidal species in a fashion similar to that observed with shorter alkyl-substituted monomers, but that the long-chain hexadecyl and octadecyl substituents provide sufficient nonbonding interactions between colloids to facilitate gelation. Interestingly, the dried gels dissolve in hot benzene to form transparent solutions that, when cooled to room temperature, form transparent gels.

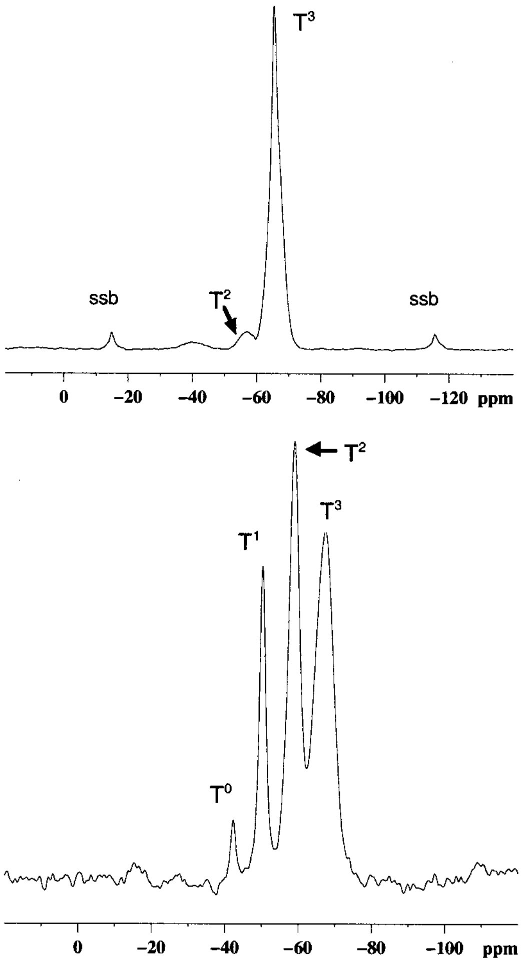

Figure 3. Solid-state ^{29}Si CP MAS NMR of the polymethylsilsesquioxane xerogel (top) prepared from the NaOH-catalyzed sol−gel polymerization of methyltrimethoxysilane (1 M, EtOH, 1.5H_2O), showing that the material is highly condensed with its large T^3 peak. In contrast, the polyoctadecylsilsesquioxane gel (bottom) prepared with NaOH as the catalyst has much greater contributions of lesser condensed silsesquioxane silicons as evidenced by the greater contributions of the T^1 and T^2 resonances.

Effect of Aryl and Vinyl Substituents. Aryl-containing substituents (phenyl, benzyl, and phenethyl) also formed soluble resinous oligomers with molecular weights under 10 K (by gel permeation chromatography). Even with heating to 200 °C, the molecular weights (M_w) of the oligomers remained under 20 K and no gels were obtained. Unlike the alkyl-substituted oligomers and polymers, it was possible to prepare aryl-substituted polysilsesquioxanes with glass transition temperatures above room temperature. The low molecular weight phenyl, benzyl, and phenethyl-substituted polysilsesquioxanes prepared by normal sol−gel techniques and dried without heating exhibited glass transition temperatures below −25 °C.[18] Heat treating the polymers at 100 or 200 °C significantly increased the T_g's to near room temperature or above.[19] The phenyl-substituted monomer produced materials with the high-

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(18) Rahimian, K.; Loy, D. A.; Wheeler, D. R. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1998**, *39*, 593−594.

Table 7. Surface Areas and Mean Pore Diameters for Different R Groups in $RSi(OMe)_3$-Based Polysilsesquioxane Xerogels

	surface area (m^2/g)/(pore diameter (Å))					
catalyst	OMe	H	Me	vinyl	$ClCH_2$	$ClCH_2Ph$
H^+	246/22[a]	617/67[a]	nonporous[c]	nonporous[c]	nonporous[c]	nonporous[c]
H_2O	342/50[a]	393/45[a]	no gels	no gels	28/380[a]	nonporous[c]
OH^-	212/65[a]	566/40[b]	566/45[a]	70/407[a]	20/750[a]	nonporous[a]

[a] Gels were obtained at 1.0 M monomer concentration. [b] Monomer reacts violently, boiling the solution. [c] Gels were obtained at neat monomer concentration.

Table 8. Surface Areas and Mean Pore Diameters for Different R Groups in $RSi(OEt)_3$-Based Polysilsesquioxane Xerogels

	surface area (m^2/g)/pore diameter (Å)				
catalyst	OEt	H	Me	vinyl	$ClCH_2$
H^+	no gels	766/40[a]	226/56[c]	nonporous[c]	nonporous[c]
H_2O	637/84[a]	662/41[a]	no gels	no gels	51/240[a]
OH^-	no gels	502/49[b]	281/214[a]	140/338[a]	63/478[a]

[a] Gels were obtained at 1.0 M monomer concentration. [b] Monomer reacts violently, boiling the solution. [c] Gels were obtained at neat monomer concentration.

est T_g's, ranging from 45 to 76 °C. The polybenzylsilsesquioxanes (a single methylene spacer between the phenyl ring and the silicon) exhibited T_g's between 4 and 40 °C and the polyphenethylsilsesquioxanes (an ethylene spacer between the phenyl and the silicon) had the lowest T_g, at -10 °C or below. Polysilsesquioxanes prepared with base catalysts exhibited T_g's of about 20 °C higher than those prepared with acid catalysts.

In contrast to the aryl-substituted monomers, the vinyl-substituted monomers reacted to afford monolithic polysilsesquioxane gels. Colloidal white gels were obtained from the NaOH-catalyzed polymerization of trimethoxyvinylsilane at concentrations ranging from neat monomer (immediate gelation) to as low as 0.6 M (after 1 week). Under acidic conditions, spongy opaque gels were obtained at neat monomer concentrations. Resins and crystals were obtained at lower monomer concentrations. All of the HCl-catalyzed polymerizations of the trialkoxyvinylsilanes were exothermic. In many cases, the solution would boil upon mixing. Furthermore, triethoxyvinylsilane would only form translucent gels at the highest (4.2 M) monomer concentration used when the reaction was HCl-catalyzed. No gels were obtained under neutral conditions. Under basic conditions, opaque white gels were obtained with monomer concentrations as low as 0.8 M. The smaller steric bulk of the vinyl group compared to that of the phenyl may have contributed to gelation by allowing polymerization to higher molecular weights.

Effect of Organofunctional Substituents. Most organofunctional trialkoxysilanes reacted to form oils and polymeric products. Notable exceptions that readily formed gels were the chloromethyltrialkoxysilanes[10] and chloromethylphenyltrimethoxysilane. These chloromethyl groups might be expected to undergo nucleophilic substitution reactions with hydroxide ions present under basic conditions. However, under the sol–gel conditions used in these experiments, the chloride substituents in the chloromethyltrialkoxysilanes and chloromethylphenyltrimethoxysilane did not react, even when basic catalysts were used. Both solid-state ^{13}C NMR and chlorine elemental analysis showed that little, if any, of the chlorine (>90% retained) was lost during the sol–gel process.

Polysilsesquioxane Xerogels. Structural characterization of the xerogels using solid-state ^{29}Si NMR revealed two different families of materials. The first was polysilsesquioxanes whose spectra revealed mostly fully condensed T^3 and lesser contributions from T^2 resonances (Figure 1). These spectra are consistent with what has been observed by others for polysilsesquioxanes. The second group was the thermoreversible hexadecyl- and octadecylsilsesquioxane gels that were not insoluble network polymers, but oligomers. As one would expect, the ^{29}Si NMR spectra of these materials exhibited greater contributions from T^2 resonances as well as T^1 resonances (Figure 3).

Xerogels with R = H or Me exhibited the highest surface areas (>500 m^2/g) and pores in the lower mesopore range (<100 Å) (Tables 7 and 8). Most of the polysilsesquioxanes with organic groups had lower surface areas and larger pores than the polysilsesquioxanes with R = H or were completely nonporous. Xerogels prepared under acidic conditions were often nonporous, whereas those prepared under basic conditions were generally porous. Exceptions to this were the chloromethylphenyl-substituted polysilsesquioxane xerogels that were nonporous regardless of the experimental conditions used in their preparation. Xerogels prepared from sol–gel polymerizations, run at higher monomer concentration, generally possessed lower surface areas or were nonporous.

Conclusions

Polysilsesquioxane gels were prepared by the sol–gel polymerization of organotrialkoxysilanes, $RSi(OR')_3$, with R′ = Me and R = H, Me, vinyl, chloromethyl, chloromethylphenyl, hexadecyl, and octadecyl and R′ = Et and R = H, Me, Et, chloromethyl, vinyl, dodecyl, hexadecyl, and octadecyl. The other substituents studied led to the formation of oligomers and polymers in the form of oils and resins. Formation of gels from trialkoxysilanes is significantly hindered by phase separation of oligomeric or polymeric silsesquioxanes and, to a lesser extent, by sterically bulky organic substituents. Crystalline products were obtained, despite the high monomer concentrations used, from a few alkyl-substituted trimethoxysilanes and a variety of triethoxysilyl monomers under acidic conditions. The majority of the gels were opaque and colloidal in appearance. The gels with R = H, Me, and chloromethyl were the most transparent. Most of the gelations were irreversible, but dodecyl-, hexadecyl-, and octadecylsilsesquioxane gels were thermoreversible between 45 and 75 °C.

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(19) Schneider, D. A.; Loy, D. A.; Baugher, B. M.; Wheeler, D. R.; Assink, R. A.; Alam, T. M.; Saunders, R. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1998**, *39*, 513–514.

The porosity of the xerogels was characterized by nitrogen porosimetry and scanning electron microscopy. Xerogels prepared from trimethoxysilane and triethoxysilane had the highest surface areas. Many of the remaining organotrialkoxysilanes formed porous polymeric gels, but the surface areas were lower and the mean pore sizes were larger. Some of the xerogels, especially those prepared under acidic conditions, were nonporous. Future efforts will be focused on the formation of gels from polar organotrialkoxysilanes that are more typically used for coupling agents.

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for the octaisobutylsilsesquioxane cube depicted in Figure 2 (PDF). This information is available free of charge via the Internet at http://pubs.acs.org.

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