Synthesis and High-Temperature Chemistry of Methylsilsesquioxane Polymers Produced by Titanium-Catalyzed Redistribution of Methylhydridooligo- and -polysiloxanes

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Homogeneous, titanium-catalyzed redistribution of the cyclomers $-[MeHSiO]_x-$ ($x = 4$ or 5) or the linear oligomer $-[MeHSiO]_x-$ ($M_n \approx 2000$ Da) generates $MeSiH_3$ and a copolymer of approximate composition $-[MeHSiO]_{0.3}[MeSi(O)_{1.5}]_{0.7}-$. The high-temperature behavior of this copolymer follows closely that of similar polymers prepared by sol-gel processing. Heating to 900 °C at 5 °C/min in N_2 gives a black glass (75% ceramic yield) with an apparent composition of SiO_2 (70%), SiC (20%), and C (10%). This composition belies the true nature of this amorphous material, which is best described by the various Si-E bonding arrangements (E = O, C, H). The chemical evolution of the copolymer during heating is followed by MAS NMR, TGA, and DRIFT spectroscopies and chemical analysis at selected temperatures up to 1000 °C. Heating to 400 °C results in a loss of 20 wt % of the starting copolymer. Chemical analysis and NMR indicate that this weight loss is associated with the disappearence of most of the $-[MeHSiO]_x-$ portion of the copolymer and that the 400 °C material consists primarily of $-[MeSi(O)_{1.5}]_x-$. Sharp absorption bands in the FTIR and resonances in the various NMR spectra associated with recognizable structural features (e.g., $Si-CH_3$) in the low-temperature polymeric material give way to broad, poorly defined absorptions and resonances at temperatures above 600 °C. The changes are indicative of the transformation from a polymer to a glass. Above 600 °C, the silsesquioxane CH_3 groups react with SiO bonds to generate SiOH bonds, SiH bonds, and new SiC bonds. These reactions illustrate the basic chemistry involved in the carbothermal reduction of SiO_2 and the polymer degradation pathways. The resulting glassy material consists of species containing four, three, or two SiO bonds with the remaining bonds being either SiC or SiH. Heating the copolymers in O_2 gives ceramic yields of >90% of SiO_2. On the basis of this result, silsesquioxanes offer an alternative to sol-gel processing of silica glasses.

Introduction

Silsesquioxanes, $[RSi(O)_{1.5}]_n$, have recently been explored as models for silica surfaces[1] and particles,[2] as precursors to nitrided glasses[3] (in the presence of NH_3) and silicon oxynitride (Si_2ON_2),[4] as precursors to silicon carbide powders[5] and silicon carbide reinforced (black) glass composite matrices,[6] as cladding materials for optical fibers,[7] and as photoresists.[8] The typical synthesis involves the hydrolysis of the corresponding silyl chloride, $RSiCl_3$, in the presence of a catalyst (acid or base) in an appropriate organic solvent:[9]

$$RSiCl_3 + 2\text{-}3H_2O \xrightarrow{\text{catalyst}} 3HCl + -[RSi(O)_{1.5}]_x- \quad (1)$$

Although represented by $-[RSi(O)_{1.5}]_x-$, the products of reaction 1 are normally a mixture of polyhedral polysilsesquioxanes, polyhedral oligosilsesquioxanes, $[RSi(O)_{1.5}]_x$ (generally <40% yield) where $x = 6$, 8, 10, etc., partially condensed polyhedral silsesquioxanes $\{[RSi(O)_{1.5}]_x[RSi(O)(OH)]_z\}$,[1] and polymeric species that contain silsesquioxane units and uncondensed silanols, e.g., $-[RSi(O)_{1.5}]_x[RSi(O)_{0.5}(OH)_2]_y[RSi(O)(OH)]_z-$.[9]

The synthesis of polysilsesquioxanes is of interest to us for a number of reasons. First, alkyl- and arylsilsesquioxanes are uncommonly stable in air at quite high temperatures with $[MeSi(O)_{1.5}]_8$ stable at ≈400 °C, $[PhSi(O)_{1.5}]_8$ stable to 500 °C, and poly(phenylsilsesquioxane) stable to temperatures of 600 °C.[9] Thus, they represent a potential alternative to organic polymers for a wide variety of high-temperature applications, providing useful synthetic routes can be developed that permit the preparation of tractable polysilsesquioxanes.

Second, the synthesis of poly(3-tolylsilsesquioxanes) results in the formation of mesomorphic lamellar microstructures, which indicates that silsesquioxanes may

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serve as a new class of organometallic liquid-crystalline materials.[9] Again, this assumes that useful synthetic routes to tractable materials can be developed.

Third, methylsilsesquioxane, $-[MeSi(O)_{1.5}]-$, is the oxygen analogue of methylsilsesquiazane, $-[MeSi(NH)_{1.5}]_x-$, a type of monomer unit that forms in the synthesis of polysilazane preceramic polymers. Thus, studies of the high-temperature chemistry of $-[MeSi(O)_{1.5}]_x-$ should provide useful comparisons with the analogous chemistry of $[MeSi(NH)_{1.5}]_x$ preceramics.[10]

Fourth, heating poly(methylsilsesquioxane) in air or O_2, at temperatures greater than 600 °C leads to the formation of silica in 90+% ceramic yields. This suggests that methylsilsesquioxane polymers may offer an alternative to sol–gel processing of glass materials.[11]

Consequently, the recent discovery by one of us that Cp_2TiMe_2 can be used to catalyze the redistribution of $MeHSi(OEt)_2$, reaction 2,[12] prompted us to explore the

$$3MeHSi(OEt)_2 \xrightarrow{Cp_2TiMe_2/20\ °C} MeSiH_3 + 2MeSi(OEt)_3 \quad (2)$$

utility of synthesizing methylsilsesquioxanes, $-[MeSi(O)_{1.5}]_x-$, by catalytic redistribution of poly(methylhydridosiloxanes), $-[MeHSiO]_x-$, as illustrated in reaction 3.

$$-[MeHSiO]_x- \xrightarrow{Cp_2TiMe_2} 0.33xMeSiH_3 + -[MeSi(O)_{1.5}]_{0.67x}- \quad (3)$$

Reaction 3 proceeds quite readily at low temperatures and leads to a unique copolymer of $-[MeSi(O)_{1.5}]_x-$ and $-[MeHSiO]_y-$. We describe here studies that focus on the high-temperature chemistry of this copolymer. Our efforts have been guided by the above-cited interests and by the fact that we have recently extended reaction 3 to the polymerization of the oligosilazanes $-[MeHSiNH]_x-$ and $-[H_2SiNMe]_x-$.[11,13]

Experimental Section

General Procedures. The polysiloxanes $-[MeHSiO]_4-$, $-[MeHSiO]_5-$, and $Me_3Si[MeHSiO]_xH$ ($M_n \approx 2000$ Da) were purchased from Petrarch/Hüls Corp. The cyclomers were distilled under N_2 and stored under N_2 prior to use. The polymer was stored over CaH_2, under N_2 prior to use. Cp_2TiCl_2, $CpTiCl_3$, and $Ti(NMe_2)_4$ (Strem Chemicals) were used as received. $NaBH_4$ and MeLi (Alfa Chemicals) were used as received. Cp_2TiMe_2, $CpTiMe_3$, and Cp_2TiBH_4 were prepared according to literature procedures.[14-16] Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Instrumental Characterization Methods. NMR studies: All solution spectra were run in $CDCl_3$ unless otherwise noted and recorded on a Varian 300-MHz instrument. Proton NMR spectra were obtained with the spectrometer operating at 300 MHz and using a 4000-Hz spectral width, a relaxation delay of 1 s, a pulse width of 82°, and 16K data points. $^{13}C\{^1H\}$ NMR spectra were obtained with the spectrometer operating at 75 Hz and using a 16000-Hz spectral width, a relaxation delay of 0.5 s, a pulse width of 60°, and 16K data points. $^{29}Si\{^1H\}$ NMR spectra were obtained with the spectrometer operating at 59.6 MHz and using a 32000-Hz spectral width, a relaxation delay of 15 s, a pulse width of 58°, and 32K data points.

Solid state spectra were recorded on an MSL 400 Brüker spectrometer operating at 79.5, 100.6, and 400 MHz for ^{13}C, ^{29}Si, and ^1H, respectively. The spinning rate was 4 kHz. For the ^{29}Si and ^1H MAS experiments, pulse widths of 2.5 and 6 μs, respectively, were used with delays between pulses of 60 and 4 s. For the CP MAS experiments, contact times of 2 ms were used for ^{29}Si and 1 ms for ^{13}C. Sample sizes for all solid-state spectra were ≈500 mg.

Weight loss experiments were conducted using a Perkin-Elmer TGA-7 and or a Perkin-Elmer DTA 1700. Samples (20–40 mg) prepared as in the pyrolysis experiments (see below) were placed in a platinum pyrolysis boat in N_2 or synthetic air (80% N_2 and 20% O_2) and heated at 5 °C/min to temperatures of 900 °C.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) studies were performed using an IBM FTIR-44 spectrophotometer. Samples were prepared in the drybox by mixing pyrolysis products with oven-dried KBr (stored in the box) in a Wiggle Bug cup. The sealed cup was then transferred out of the drybox to a Wiggle Bug (dental ball mill) and pulverized. Once pulverized, the cup was opened, and samples were quickly transferred from the cup to the sample holder in air. The sample chamber was flushed with N_2 for a minimum of 15 min before data collection. IR peak positions were identified by using a standard peak searching program.

Mass spectral fragmentation studies: Mass spectral fragmentation data were obtained for the DH_4, DH_5, and the oligo(methylhydridosiloxane) by using a Hewlett-Packard 5890 gas chromatograph (GC) coupled to 5970 mass selective detector (MS). The heating schedule for the GC was 40 °C at 10 °C/min to 280 °C. Injector and detector temperatures were 280 °C. Sample analysis was initiated following a 2–3-min solvent delay. The scan width was 750–50 m/z. The multiplier was 1000. Data are obtained as $m/z = M - 1$ peaks.

Low-temperature mass spectral analysis of the volatile fragments that issue on heating $-[MeHSiO]_{0.3}[MeSi(O)_{1.5}]_{0.7}-$ from 150 to 250 °C were obtained by direct probe inlet techniques using a VG 7070H double-focusing mass spectrometer with 70-eV electron ionization energy. Data are obtained as $m/z = M$ or $M + 1$.

Standard Catalytic Run and Catalyst Survey. An oven-dried, 40-mL pop-bottle glass reactor containing a stir bar and 5 mg of catalyst was sealed under N_2. Alternately, 5 mg of catalyst was dissolved in 100 μL of hexane and added by syringe. $Ti(NMe_2)_4$ was also added by syringe. The oligo(methylhydridosiloxane) (3 mL) was injected through the septum, and the reaction was stirred. Reaction progress was followed qualitatively by noting onset of catalysis indicated by the formation of an intense royal blue color and by noting the time required for complete crosslinking (gelation).

NMR Characterization of Poly(hydridomethylsiloxane). Oligo(methylhydridosiloxane), $Me_3Si[MeHSiO]_xH$ (Petrarch/Hüls Corp.) was characterized by NMR to verify the reported molecular weight ($M_n \approx 2000$ Da). From the ^1H NMR integration studies reported in the results section, we calculate an $M_n \approx 1900$ Da.

Solution Polymerization of Poly(hydridomethylsiloxane). To a 500-mL Schlenk flask are added 50 mL of $Me_3Si[MeHSiO]_xH$ and 250 mL of freshly distilled toluene. The solution is degassed by vacuum pumping followed by flushing with N_2. To the degassed solution is added 0.5 mL (≈5 × 10^{-5} mol) of ≈0.1 M $(\eta^5\text{-}Cp)_2TiMe_2$ in hexane. After 1 h, the solution turns green, and within 2 h the solution turns deep blue. At this point it is allowed to stir for an additional 72 h. Solvent removal by vacuum evaporation results in a viscous liquid, which was characterized by ^1H, ^{13}C, and ^{29}Si NMR (see below).

Standard Pyrolysis Run. Bulk pyrolyses were performed to obtain samples for combustion analysis or for the DRIFT spectra. These pyrolyses were carried out in a Lindberg furnace (Model No. 58114, single zone) equipped with a Eurotherm temperature controller (Model No. 818S). A 5.00-cm-o.d. (4.44-cm i.d.) mullite tube, cooled at both ends by means of water circulated through copper coils, was inserted into the furnace to protect the

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Table I. Polymerization of Methylhydridosiloxane Substrates by Cp_2TiMe_2 at Ambient Temperature

substrate	reaction time	product physical characteristics	ceram yield,[a] wt %
$-[MeHSiO]_4-$	3–4 h	very viscous in 1 h; hard plastic in 3–4 h	78
$-[MeHSiO]_5-$	15 min–1 h	hard plastic	79
$-[MeHSiO]_x-$ ($M_n \approx 2000$ Da)	10–15 min	hard plastic	81

[a] Ceramic yields were determined by using thermogravimetric analysis. Heating rate was 5 °C/min to 900 °C in N_2. Reproducibility of the ceramic yields is ±5%.

heating coils and to provide even heat distribution. Both ends of the tube can be sealed with stainless steel caps and viton O-rings. One cap was fitted with gas inlet and outlet ports to control gas-flow rates and pyrolysis atmosphere. Alternately, pyrolyses were conducted in a 3.8-cm o.d. × 45.7-cm quartz tube, sealed at one end via a quartz cap with a standard O-ring seal. The cap was fitted with gas inlet and outlet ports. The quartz tube was inserted into the mullite tube. This tube was designed for transport of samples in and out of a drybox.

Tared, half-cylinder, stainless steel pyrolysis boats containing weighed amounts of cross-linked polymer precursor were placed in the quartz tube under the desired atmosphere. The quartz tube with sample was then inserted into the mullite tube so that the samples were in the center of the heated zone (approximately 12 cm in length; usually only two or three samples fit in this region). The samples were then pyrolyzed by heating, under the desired atmosphere (N_2 or synthetic air), at 5 °C/min to the desired temperature. The standard gas flow rate was 0.25 m^3/h. Sample sizes were typically 200–800 mg. Sample preparation involved placing the cross-linked polymer under vacuum for 2 h to remove $MeSiH_3$ and traces of hexane.

Results

The work presented here focuses on the properties of a copolymer produced from titanium-catalyzed redistribution of methylhydrosiloxanes, $-[MeHSiO]_x-$, reaction 3. Efforts directed toward developing a mechanistic description of the catalytic cycle are reported elsewhere.[12,13] The synthetic methods used to prepare the copolymer are discussed in the Experimental Section. Brief studies were conducted to optimize the rate and extent of cross-linking in reaction 3, as a means of minimizing reaction time and maximizing ceramic yield. These studies explored the effects of simple modifications at the titanium center and changes in the type of $-[MeHSiO]_x-$ precursor on reaction rate and type of product.

These preliminary studies provided sufficient information to choose a "standard polymer" for the subsequent high-temperatures studies.

Oligomeric Precursor Survey. The relative reactivities and extent of cross-linking of the cyclotetramer, (DH_4, $-[MeHSiO]_4-$), the cyclopentamer (DH_5, $-[MeHSiO]_5-$), and the linear oligomer, $Me_3SiO[MeHSiO]_xH$ ($M_n \approx 2000$ Da) were established by using a standard set of reaction conditions (see Experimental Section) and Cp_2TiMe_2 as the catalyst precursor. The results of these studies are recorded in Table I. Chemical analysis of the resulting copolymers are shown in Table II.

The qualitative reactivities shown in Table I indicate that the cyclomers are less reactive than the linear oligomer and that the cyclotetramer reacts slower than the cyclopentamer. However, the chemical analyses (see Table III) and ceramic yields for the final products are, within experimental limits, identical. We conclude that the cross-link densities of the final copolymers are essentially the same.

Table II. Combustion Analysis of Copolymer Formed by Reaction of Oligo(methylhydridooligosiloxane) Precursors with Cp_2TiMe_2 at 21 °C

substrate	C	H	N	Si	O[a,b]
$-[MeHSiO]_4-$	19.45	5.62	0.00	43.60	31.33
$-[MeHSiO]_5-$	20.37	5.98	0.00	45.11	28.54
$-[MeHSiO]_x-$ ($M_n \approx 2000$ Da)	17.93	4.45	0.11	40.66	36.85
$-[MeSi(O)_{1.5}]_x-$	17.90	4.50		41.84	35.76 (calc)
$-[MeHSiO]_x-$	19.98	6.71		46.71	26.61 (calc)

[a] Oxygen is determined by difference.[19]

Table III. Combustion Analyses[19] of the 900 °C Pyrolysis Product of the Copolymer Derived from Various $-[MeHSiO]_x-$ Precursors

substrate	C[a]	H	N	Si	O[b]	ceramic[c,d] composition, %
$-[MeHSiO]_4-$	16.35	0.73	0.14	45.71	37.07	SiO_2 70; SiC 19; C 11
$-[MeHSiO]_5-$	16.43	0.96	0.04	45.00	37.57	SiO_2 70; SiC 21; C 9
$-[MeHSiO]_x-$ ($M_n \approx$ 2000 Da)	15.87	1.18	0.05	46.08	36.82	SiO_2 69; SiC 20; C 10
$MeSi(O)_{1.5}$[e]	14.3			43		

[a] Titanium analyzed in representative samples gave an average value of 0.1%. [b] Oxygen is determined by difference. [c] Pyrolyses were conducted in N_2 at a heating rate of 5 °C/min. [d] Apparent ceramic composition was determined using silicon as the limiting element. [e] Results from Fox et al.[5]

Given these results, $Me_3SiO[MeHSiO]_xH$ was used in all further studies. The proton NMR of this material contains one resonance for the SiH proton at δ 4.69 and two C-H peaks at δ 0.10 (major) and 0.18 (minor). The latter peak is attributed to the Me_3SiO end cap. Proton NMR end group analysis permits calculation of $M_n \approx 1900$ Da, which is somewhat less than the 2000 Da reported by the supplier. The starting polymer exhibits ^{13}C peaks at δ 1.04 (major, by intensity) and at 1.75 (minor). The ^{29}Si NMR shows one peak at δ −34.6 relative to TMS.

Catalyst Survey. A simple catalyst survey was run using the standard set of reaction conditions described in the Experimental Section, with the linear oligomer as substrate. We examined the utility of the titanium complexes $Ti(NMe_2)_4$, $Ti(NEt_2)_4$, Cp_2TiMe_2, $CpTiMe_3$, and Cp_2TiBH_4 as catalyst precursors. $[Cp_2ZrMe(THF)]BF_4$ was also tested for catalytic activity. These complexes were chosen because they are synthesized readily via literature procedures or are available commercially.

Of the precursors tested, only $Ti(NMe_2)_4$, Cp_2TiMe_2, and $CpTiMe_3$ exhibit any activity. The $CpTiMe_3$ precursor gave the most active catalyst of the three precursors, catalyzing complete gelation in a matter of 10–15 min at 0 °C with a ceramic yield of ≈80%. The $Ti(NMe_2)_4$-derived catalyst was the slowest, giving incomplete reaction even after 5 days at room temperature. Cp_2TiMe_2 proved to be the best precursor of all, despite the high activity of $CpTiMe_3$. This is because $CpTiMe_3$ is not stable at room temperature and is even difficult to handle at 0 °C. Solid Cp_2TiMe_2 is also labile and turns black by an autocatalytic decomposition process even under N_2 at −20 °C. However, hexane solutions of Cp_2TiMe_2 remain stable, at liquid N_2 temperatures, for up to 1 week and provide a convenient method of adding the precursor to $-[MeHSiO]_x-$.

Initiation of catalytic redistribution is always preceded by an induction period prior to generation of the active, royal blue catalyst system. This induction period is typ-

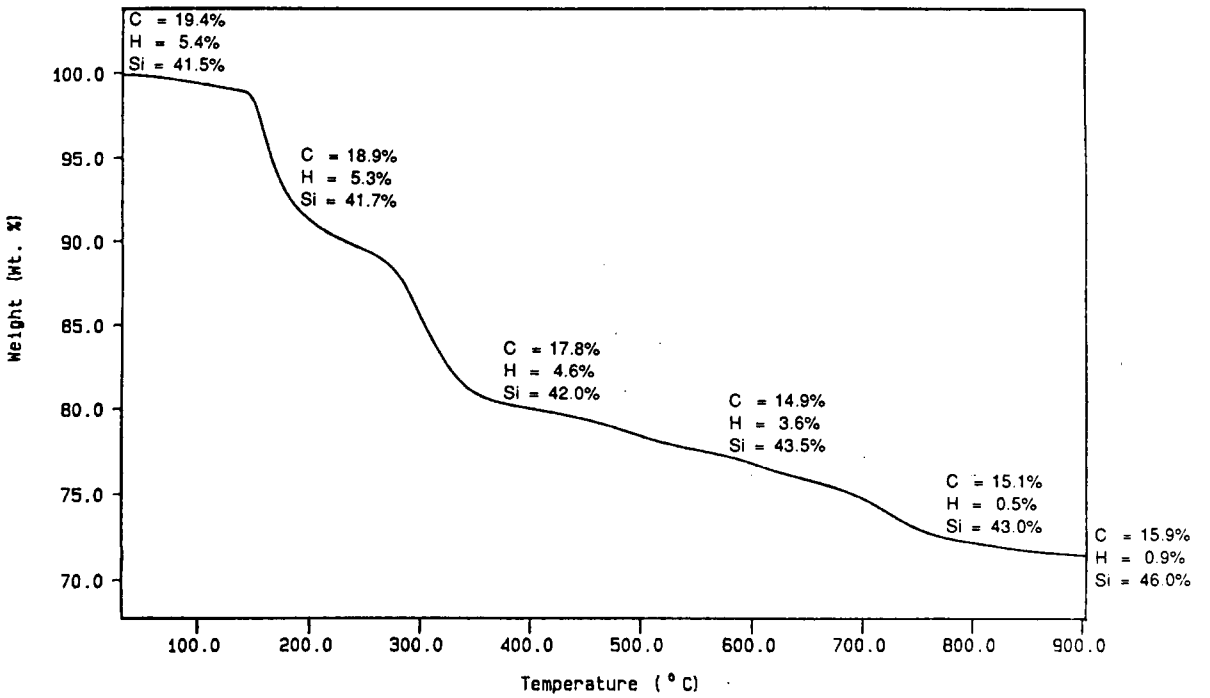

Figure 1. Thermogravimetric analysis of $-[MeHSiO]_{0.35}[MeSi(O)_{1.5}]_{0.7}-$ as a function of temperature. The TGA heating schedule was 5 °C/min in N_2. Bulk samples for the analyses were heated in a similar manner.

ically 30–45 min if one uses freshly prepared, recrystallized Cp_2TiMe_2. Thorough degassing of the precursor solutions or liquids is mandatory before reproducible initiation can be obtained.

The standard reaction used to obtain the data in Tables I–III and for most of the studies described below leads directly to intractable gels that cannot be further characterized by solution techniques. To complement the extensive solid-state NMR studies described below, we attempted to prepare soluble forms of the methylsilsesquioxane polymer as a prelude to solution NMR studies. To this end, we find that soluble polymers can be obtained by running the reactions in toluene, if sufficient dilution is used. Initial experiments with 1:1, 3:1, and even 4:1 toluene:$-[MeHSiO]_x-$ volume ratios led to gellike products. However, at 5:1 volume ratios and 72 h of reaction at room temperature (following initiation), stable solutions of a copolymer (primarily poly(methylsilsesquioxane)) were obtained. Vacuum evaporation of the toluene leads to a semitractable polymer that slowly "sets" to a rigid solid. If this polymer is immediately redissolved in $CDCl_3$, then NMR characterization can follow.

NMR Characterization. NMR characterization of a wide variety of siloxane units has already been described in the literature.[17] The studies described here will use the standard literature nomenclature and peak assignments as listed in Table IV.

The ^{29}Si spectrum for solution-polymerized $-[MeHSiO]_x-$ contains broad peaks at δ −33.5, −34.4, and −35.9 for $MeHSiO$ and, δ −57.2 and −65.5 for $MeSi(O)_{1.5}$. The ^{13}C spectrum exhibits peaks at δ 1.68 $[(CH_3)_3SiO]$, 0.66 (CH_3HSiO), and −3.27 $[CH_3Si(O)_{1.5}]$. The proton NMR shows peaks at δ 4.68 $MeHSiO$, 0.18 $[(CH_3)_3SiO]$, 0.13 $[CH_3Si(O)_{1.5}]$, and 0.10 CH_3HSiO. The NMR results indicate that the product is a copolymer whose composition is $[MeHSiO]_{0.3}[MeSi(O)_{1.5}]_{0.7}$.[18] This compares well with the gel composition established by solid-state NMR as presented below. The results are supported by the combustion analyses listed in Table II.

Table IV. ^{29}Si Chemical Shifts for Common Si Units[17]

Si unit	chem shift (vs TMS), ppm	Si unit	chem shift (vs TMS), ppm
Me_3SiO- (M)	+6 to 7	$-[MeSi(OH)O]-$	−55
HMe_2SiO- (MH)	−5 to 7	$-[MeSi(O)_{1.5}]-$	−65 to −67
$HOMe_2SiO-$ (MCH)	−11 to −12	$-[HSi(O)_{1.5}]-$ (TH)	−85
		$-[Si(O)_2]-$ (Q)	−100 to −110
$-[Me_2SiO]-$ (D)	−20		
$-[MeHSiO]-$ (DH)	−35 to −37		

High-Temperature Studies of Copolymer $-[MeHSiO]_{0.30}[MeSi(O)_{1.5}]_{0.70}-$. $-[MeHSiO]_{0.3}[MeSi(O)_{1.5}]_{0.7}-$, henceforth copolymer, was chosen as a "standard polymer" for these studies because it is easily and reproducibly prepared by titanium-catalyzed redistribution of neat $-[MeHSiO]_x-$ or toluene solutions of $-[MeHSiO]_x-$.

The copolymer was further characterized by TGA (Figure 1), DTA, FTIR, and NMR. Chemical analyses were obtained for the polymer at room temperature and after heating to 200, 400, 600, 800, and 900 °C at 5 °C/min under N_2 and following a 1-h hold at each temperature. The analysis at each temperature is shown in Figure 1. Within the error limits of analysis, there is no difference between the elemental analyses at 800 and 900 °C. The 900 °C analysis is very similar to that obtained by Fox et al. for pyrolysis of $-[MeSi(O)_{1.5}]_x-$ prepared by hydrolysis of $MeSiCl_3$.[5]

The DTA data do not suggest any significant events that could be used as further support for the other methods of analysis. Occasionally, a small exotherm is seen at 630–670

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(18) This integration is confirmed by a novel alcoholysis reaction in which methanol is added directly to the active catalyst solution:

$$-[MeHSiO]_x + MeOH \xrightarrow{\text{"Ti"/RT}} H_2 + -[Me(MeO)SiO]_x-$$

^1H NMR integration of this polymer shows $[Me(MeO)SiO]:[MeSi(O)_{1.5}]$ ratio of 3:7 in keeping with the solid state results. Rahn, J. A.; Laine, R. M.; Zhang, Z.-F. *Mater. Res. Soc. Symp. Proc.* **1990**, *171*, 31.

Table V. Selected Infrared Absorptions for Copolymer at Various Pyrolysis Temperatures[a]

temp, °C	ν(OH)	ν(CH)	ν(SiH)	ν(C=O)	ν(SiC)	ν(SiO)
RT[b]	3729 vw?	2969 s	2166 s		1266 vs	1039 vs
		2910			781 vs	
200	3734 vw?	2969 s	2167 s		1267 vs	1041 vs
		2910			783 vs	
400		2971 s	2166 w		1269 s	1132 vs
		2915			778 vs	1039 vs
600		2969 m		1732 w	1269 m	1047 vs
		2913 w			791 vs	
800	3644–3324 mvbr	2925 w	2257 w	1732 w	1269 sh	1037 vs
			2200 w			1049 vs
1000	3644–3324 mvbr	3028 w	2266 w			1053 vs
		2925 w	1890 w			
		2857 w				

[a] All absorptions are reported as cm^{-1}. Pyrolyses were conducted in N_2 at a heating rate of 5 °C/min [b] Room temperature.

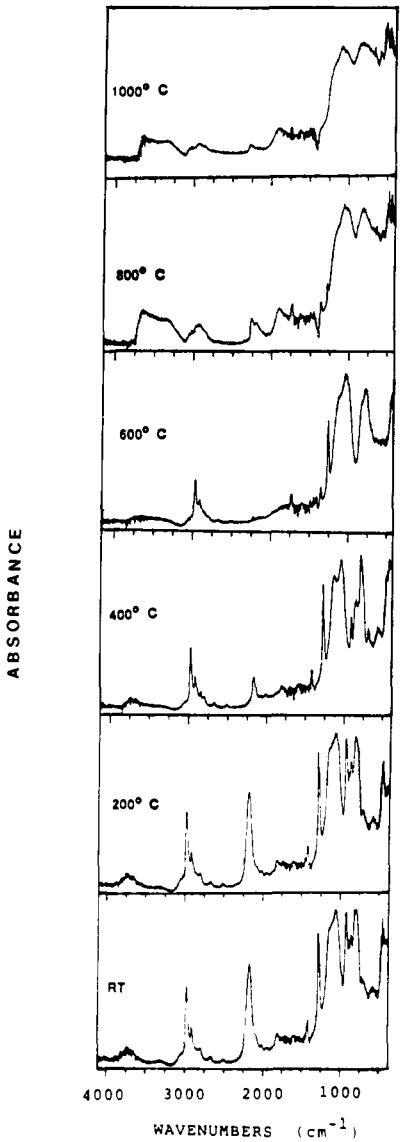

Figure 2. Diffuse reflectance infrared Fourier transform spectra (DRIFTS) of $-[MeHSiO]_{0.3}[MeSi(O)_{1.5}]_{0.7}-$ following heating to selected temperatures. Samples heated at 5 °C/min in N_2 to the desired temperature, mixed with KBr (under N_2). Spectra taken under N_2.

°C (in air), although this exotherm is not found in aged polymer. This exotherm most likely arises from oxidation of residual SiH bonds.

Diffuse reflectance infrared spectra (DRIFTS) were also taken both at room temperature and for the 200, 400, 600, 800, and 1000 °C samples. The DRIFTS data are presented in Figure 2. The pertinent IR absorptions for the DRIFTS data are recorded in Table V. ^{29}Si, ^{13}C, and ^{1}H magic angle spinning (MAS) and cross polarized (CP) NMR spectra were also recorded at each temperature. The solid-state proton spectra reveal very little, except the presence of SiMe and SiH at lower temperatures and a small peak of SiH plus a broadened peak for saturated CH adjacent to Si at temperatures ≥800 °C. The ^{29}Si MAS and CP spectra and the ^{13}C spectra for the various temperatures are shown in Figures 3–5. Figure 6 shows the quantitative evolution of the various species based on the ^{29}Si MAS spectra. The peaks in Figures 3 and 4 can be readily assigned to different silicon units on the basis of the literature values listed in Table IV.[17]

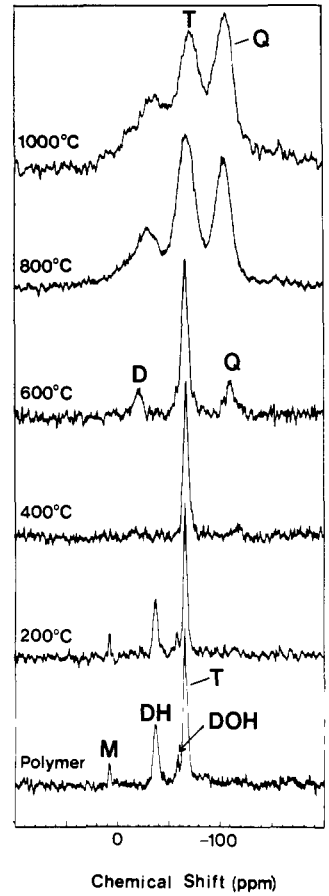

Figure 3. ^{29}Si MAS NMR spectra of $-[MeHSiO]_{0.3}[MeSi(O)_{1.5}]_{0.7}-$ following heating to selected temperatures. Samples were heated at 5 °C/min in N_2 to the desired temperature, crushed under N_2, and transferred to NMR rotors under drybox conditions.

General Observations. The TGA reveals that much of the weight loss (20%) occurs below 400 °C. The chem-

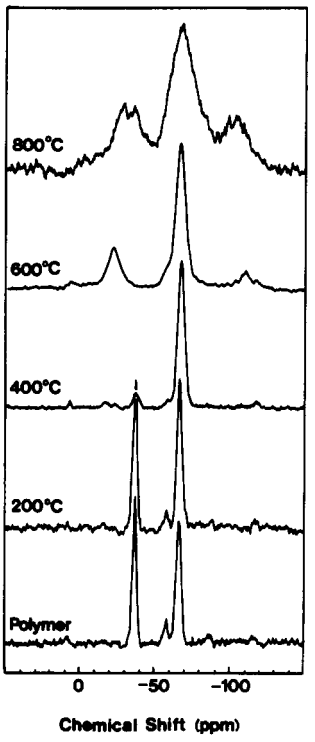

Figure 4. ^{29}Si CP MAS NMRs of $-[MeHSiO]_{0.3}[MeSi(O)_{1.5}]_{0.7}-$ following heating to selected temperatures. Samples were heated at 5 °C/min in N_2 to the desired temperature, crushed under N_2, and transferred to NMR rotors under drybox conditions.

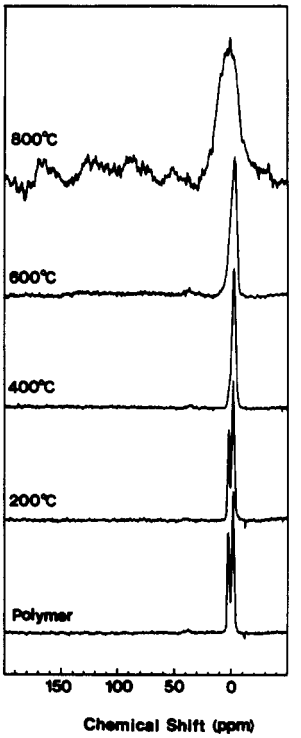

Figure 5. ^{13}C CP MAS NMRs of $-[MeHSiO]_{0.3}[MeSi(O)_{1.5}]_{0.7}-$ following heating to selected temperatures. Samples were heated at 5 °C/min in N_2 to the desired temperature, crushed under N_2, and transferred to NMR rotors under drybox conditions.

ical composition for the 400 °C product is identical with that calculated (Table II) for pure $-[MeSi(O)_{1.5}]_x-$. Thus, the low-temperature weight loss can be ascribed to the disappearence of the $-[MeHSiO]_x-$ copolymer segments by depolymerization and volatilization. However, the calculated weight loss resulting from complete volatilization of all of the $-[MeHSiO]_x-$ groups would be ≈28%.

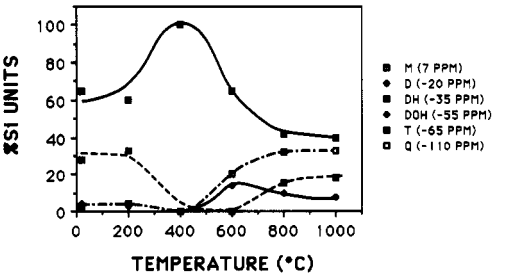

Figure 6. Changes in quantities of various silicon species as a function of temperature. Determined by ^{29}Si MAS NMR spectra following heating of $[MeHSiO]_{0.3}[MeSi(O)_{1.5}]_{0.7}$ to selected temperatures.

Therefore, the disappearence of all of the $-[MeHSiO]_x-$ segments is likely due to some further redistribution together with volatilization. These results have been confirmed by mass spectral analyses (vide infra).

Further heating to 900 °C results in an additional weight loss of about 5–7%. The elemental analyses suggest that this loss is due to in part to hydrogen loss above 400 °C as this drops from 4.6% to <1% at 900 °C. Some loss of carbon is also observed (≈1.8%).

The following sections focus on the chemical evolution of the polymer as it is heated to specific temperatures up to 1000 °C by using the data contained in Figures 1–6 and Tables II–VI.

Room temperature: The composition of the "standard" polymer precursor, based on MAS solid-state ^{29}Si NMR, is $[MeSiO_{1.5}]_{0.65}[MeHSiO]_{0.28}[MeSi(OH)O]_{0.04}[Me_3SiO]_{0.03}$. The proton MAS NMR also reveals the presence of SiH groups at 4.5 ppm. The ^{13}C MAS spectrum shows two peaks at 1.1 and −2.9 ppm that can be assigned to the DH and T units, respectively. These results confirm the solution ^{29}Si NMR studies. The DRIFT spectrum also confirms part of this assignment in that there is a strong ν(SiH) peak at 2200 cm^{-1}. In addition, the DRIFT spectrum shows sharp ν(CH) peaks at 2800–2950 cm^{-1} normal for $SiCH_3$ and a sharp ν(SiC) absorption (for $SiCH_3$) at 1260 cm^{-1}. The presence of Me_3SiO and SiOH moieties cannot be confirmed by DRIFTS because ν(CH) of the M group is lost in the ν(CH) of the T and DH units, and the small contribution to the spectrum from ν(SiOH) (3200–3400 cm^{-1}) is lost in the background noise. However, the presence of both is expected given that one can prepare a well-defined ($M_n \approx 2000$ Da) oligomer of $-[MeHSiO]_x-$ only by ring-opening polymerization of the cyclotrimer, $-[MeHSiO]_3-$, using Me_3SiO^- and a water workup.

It would be reasonable to confirm the NMR-determined composition by chemical analysis; however, the error limits for the analysis of preceramics are somewhat higher than for typical organic molecules and do not permit a reliable calculation.[19] All that can be said from the data presented in Table II is that the polymer composition does lie between those calculated for $-[MeHSiO]_x-$ and $-[MeSi(O)_{1.5}]_x-$.

200 °C: Heating the polymer to 200 °C appears to have little effect on the polymer composition as seen in Figure 1. One might expect the SiOH groups to condense with each other or with Me_3SiO groups or react with SiH bonds to form SiOSi bonds and release H_2O, Me_3SiOH, or H_2. However, the concentrations of these species and their diffusivities are too low for significant condensation to

(19) (a) Combustion analyses for preceramics are less accurate than those obtained for organic compounds. Typical error ranges are C (±1–1.5%), H (±1%), N (±1–1.5%), Si (±3%). Hutchinson, G. Galbraith Laboratories, private communication. (b) Wu, H.-J.; Interrante, L. V. *Chem. Mater.* **1989**, *1*, 564, and references therein.[13]

Table VI. Mass Spectral Fragmentation Patterns and Intensities for DH_4, DH_5, $Me_3SiO(MeHSiO)_xH$, and Fragments Found on Heating $[MeHSiO]_{0.3}[MeSi(O)_{1.5}]_{0.7}$ to 150 and 250 °C

fragment	m/z	DH_4[a]	DH_5[a]	oligomer[a]	$[MeHSiO]_{0.3}$-$[MeSi(O)_{1.5}]_{0.7}$ 150 °C[a]	250 °C[a]
$MeSiH_2$	45					40
$MeSiH_3$	46				≈3	36
MeHSiO	60	10	18	15	17	67
Me_2SiO	74				100	98
$(MeSiH_2)_2$	90					30
$(MeHSiO)_2$	120	12	06	≈2	8	100
DH_3	180	20	17	13	5	60
DH_4	240	61	100	100		
DH_5-Me	285		78	82		

[a] All intensities are relative to highest peak in each spectrum.

occur. The weight loss in the TGA at 200 °C is not reflected by changes in the NMR spectra. This is expected given that the weight loss is approximately 10%, which tests the limits of solid-state NMR sensitivity. There also are no significant changes in the DRIFT spectrum.

The data shown in Table VI list the major (by intensity) fragments observed for electron impact fragmentation of DH_4, DH_5, and the oligomer. These are compared with the fragments that issue from the copolymer as it decomposes between 150 and 250 °C in the solid probe inlet of the mass spectrometer. The species suggested to be responsible for the individual m/z fragments are based on literature and our previous studies.[20,21]

All of the DH_x species provide fragments indicative of $-[MeHSiO]_x-$, where x = 1–3. For x = 4, we see evidence for M – CH_3 only, and nothing identifiable or of significant intensity is seen for $x > 4$. In the solid probe experiments, with the copolymer heated to 150 °C, we also see the same fragments for $-[MeHSiO]_x-$ where x = 1–3. However, the fragment of major intensity is m/z = 74, found frequently for M – CH_3 for the Me_3SiO group. At 250 °C, the decomposition products from the copolymer include the same set of fragments for $-[MeHSiO]_x-$ where x = 1–3 as found at 150 °C but with much less contribution from the m/z = 74. The x = 2 fragment (m/z = 120) now predominates in the spectrum. Also of importance is the appearence of fragments m/z = 45, 46, and 90. These can be attributed to MeH_2Si, $MeSiH_3$, and $(MeH_2Si)_2$ and are products likely to arise from redistribution of –[MeHSiO]– groups. Consequently, they offer evidence that low-temperature weight loss (<400 °C) results because of coincidental depolymerization and redistribution, as suggested above.

400 °C: At this temperature, the TGA indicates a weight loss of 20% and the chemical analysis data suggest that the only material remaining is $-[MeSi(O)_{1.5}]_x-$. Chemical analysis is insufficiently accurate to permit one to draw indisputable conclusions concerning chemical makeup;[19] however, the DRIFTS data are in keeping with the almost complete elimination of SiH bonds as witnessed by the significant loss of intensity of the ν(SiH) absorption in the DRIFTS. This loss, as discussed above, is due to both depolymerization and redistribution of $-[MeHSiO]_x-$ segments.

The less sensitive ^{29}Si MAS and ^1H NMR spectra suggest that the 400 °C sample is composed entirely of $-[MeSi(O)_{1.5}]_x-$. The use of cross polarization techniques (Figure 4) confirms the DRIFT spectrum by revealing remnants of $-[MeHSiO]_x-$ and a very small amount of –[MeSi(OH)O]–. The ^{13}C spectrum has changed somewhat in that the peak at 1.1 ppm is reduced to a shoulder on the major peak, which has shifted somewhat from –2.9 to –3.5 ppm.

The stability of poly(methylsilsesquioxane) is not unexpected given that $[MeSi(O)_{1.5}]_8$ is stable to ≈415 °C.[9]

600 °C: The transition between 400 and 600 °C results in some chemical changes in the 400 °C polymer structure. The ^{29}Si spectrum reveals a decrease in the number of T units to approximately 65% (from ≈100%), coincident with the appearence of peaks for D-type $[MeSi(CH_x)O]$ units (14%) and Q (20%) units (see Figure 6). Given that the relative amounts of each are reasonably close, these species most probably arise by direct redistribution of the T groups. Partial oxidation by adventitious oxygen could account for the slightly higher abundance of the Q groups. This is supported by the slight reduction in carbon content in the chemical analysis (Figure 1).

The ^{13}C NMR spectrum shows some changes as the peak attributable to $SiCH_x$ species broadens, shifts to –4.2 ppm, and becomes asymmetric. This is in keeping with the formation of new D-type units in the polymer matrix. In the DRIFT spectrum, the ν(CH) absorptions are still fairly sharp, although diminished compared to the ν(SiO) absorptions. The $\nu(SiCH_3)$ peak at 1260 cm^{-1} is still sharp, although somewhat diminished in intensity. Careful inspection of the region adjacent to $\nu(SiCH_3)$ reveals the appearence of a small peak at ≈1360 cm^{-1}. Yajima et al.[22] have shown that this peak,[19b] which is never very intense, corresponds to the formation of the $SiCH_2Si$ linkage, which corroborates the appearence of new D-type units in the polymer matrix. Neither the DRIFT spectrum nor the NMR studies provide evidence for either SiH or SiO–H bonds.

Although the 600 °C material has reacted in part, the evidence still suggests that much of the 400 °C structure is retained. This conclusion is supported by contrast with the very drastic changes that occur on further heating to 800 °C.

800 °C: At this temperature, all the analytical tools reveal major changes in the structure of the material. The chemical analysis in Figure 1 shows that most of the hydrogen has been driven off, although the C:Si ratio remains essentially unchanged. In the NMR spectra, all of the peaks broaden greatly. The presence of Q units becomes significant, and the number of T units continues to decrease (42%). The most important observation is the reappearence of DH units in the ^{29}Si spectrum and in the ^1H NMR spectrum (SiH). The ^{13}C spectrum provides limited information at this stage because the peak becomes extremely broad (typical of a disordered material) and shifts its center to 5 ppm. Furthermore, slight peaks begin to appear at higher field that are indicative of amorphous or graphitic carbon.[23–25] Cross polarization cannot be used

(20) *Silylation of Organic Compounds*; Pierce, A. E., Ed.; Pierce Chemical Co.: Rockford, IL, 1968.

(21) (a) Schwartz, K. B.; Rowecliffe, D. J.; Blum, Y. D.; Laine, R. M. *Mater. Res. Symp. Proc.* **1986**, *73*, 407–412. (b) Blum, Y. D.; Schwartz, K. B.; Laine, R. M. *J. Mater. Sci.* **1989**, *24*, 1707.

(22) (a) Yajima, S.; Hasegawa, Y.; Hayashi, J.; Iimura, M. *J. Mater. Sci.* **1978**, *13*, 2569. (b) Yajima, S. Silicon Carbide Fibers. In *Handbook of Composites*; Watt, W., Perov, B. V., Eds.; Elsevier: New York, 1985; Vol. 1, pp 201–237. (c) See also: Carlsson, D. J.; Cooney, J. D.; Gauthier, S.; Worsfold, D. J. *J. Am. Ceram. Soc.* **1990**, *73*, 237.

(23) The ^{13}C NMR relaxation times for carbon without hydrogen attached can be on the order of minutes to hours (especially for graphitic carbon, ≈120 ppm). Consequently, identification of these species using NMR techniques is difficult without a dedicated instrument.

(24) Resonance Raman can be used to distinguish between amorphous and graphitic carbon: Exharos, Dr. G., Pacific Northwest Laboratories, private communication.

(25) Babonneau, F.; Thorne, K.; Mackenzie, J. D. *Chem. Mater.* **1989**, *1*, 554.

to enhance these signals because the average number of protons that remain in the sample have dropped considerably, as noted above. Efforts to distinguish between graphitic and amorphous carbon using Raman spectroscopy are under way.[24]

The DRIFT spectrum confirms the reappearance of the SiH bonds (ν(SiH) at ≈2200 and 2254 cm^{-1}). In addition, the 800 °C DRIFT spectrum exhibits well-developed absorptions for ν(SiOH) at ≈3200–3400 cm^{-1}. These absorptions were readily confirmed by exposing a sample of the pyrolyzed material to D_2O overnight. Following exchange of D for H, the absorption at 3200–3400 cm^{-1} is considerably diminished, and new absorptions appear at 2200–2400 cm^{-1} that correspond to ν(SiO–D).

1000 °C: The DRIFTS and the ^{29}Si MAS NMR spectra show that this sample has essentially the same chemical organization as the 800 °C material. The only significant difference is in the hydrogen content of the material as revealed by our inability to obtain good CP MAS ^{29}Si spectra. The ^{29}Si MAS NMR spectrum indicates that the composition of this material is SiO_4 (35%) and SiO_3C (42%) with some SiO_2C_2 (<10%) and SiO_2CH (<20%) units. *Given the fact that the Si:C ratio has not changed in the 800 or 900 °C chemical analyses and remains approximately 1:1, we must conclude that some of the carbon is no longer bonded directly to silicon and has segregated to form small pockets of graphitic or amorphous carbon.*[23-26]

The formation of free carbon during pyrolysis of silsesquioxanes has been discussed by Fox et al.[5] and Baney et al.[6] and is in keeping with Babonneau et al.'s[25] studies on the pyrolytic evolution of D/Q copolymers produced by sol–gel processing. It also is in keeping with our results on the pyrolytic evolution of $-[MeNH_2Si]_x-$ (under N_2) at temperatures above ≈600 °C, wherein ^{29}Si NMR shows evidence for exclusive formation of Si_3N_4 and ^{13}C NMR provides evidence for free carbon.[26]

Black Glass. SEM images of fragments of a bulk sample of the standard polymer that has been heated to 900 °C according to the standard heating schedule reveal essentially featureless materials that are amorphous and pore free at the highest magnifications possible. XRD analyses of crushed samples of this material are also featureless in keeping with its amorphous nature.

Discussion

Titanium-catalyzed redistribution of either cyclomeric or oligomeric methyldihydridosiloxanes neat or in toluene produces a *copolymer* of almost constant composition $\{-[MeHSiO]_{0.3}[MeSi(O)_{1.5}]_{0.7}-\}$ if the reaction is run neat or long enough (72–96 h) in toluene. The 5:1 toluene solutions are normally stable for at least 120 h. Beyond this period, gelation is observed occasionally, especially if excess catalyst is used.

The fact that the system does not attain complete redistribution is predictable. As the degree of cross-linking increases, the mobility of the catalyst in the polymer decreases significantly, and the concentration of reactive monomer units, –[MeHSiO]–, available for cross-linking and redistribution decreases accordingly. Therefore, the reaction must slow and eventually stop short of completion.

The fact that it stops in essentially the same place for the cyclomeric and oligomeric reactants is not unexpected. The only likely difference with the cyclomeric reactants is the initial ring-opening step, which accounts for their exhibiting slightly poorer rates of reaction as compared with the oligomeric reactant.

High-Temperature Studies of Copolymer $-[MeHSiO]_{0.30}[MeSi(O)_{1.5}]_{0.70}-$. The high-temperature studies described here were conducted to (1) develop an understanding of the stability of the methylsilsesquioxane copolymer produced via reaction 3, (2) identify modes of decomposition for comparison with the decomposition patterns of $-[MeHSiNH]_x-$ and $-[H_2SiNMe]_x-$, and (3) detail the chemical transformations that the copolymer undergoes during heating to temperatures to 1000 °C for comparison with previous studies on the pyrolysis of sol–gel-derived $-[MeSi(O)_{1.5}]_x-$ polymers.[5]

On heating to 400 °C, the copolymer loses approximately 20 wt %, which is associated with the disappearence of almost all of the starting monomer units. At this point, the polymer consists almost entirely of methylsilsesquioxane or T units as supported by all of the characterization methods employed. Consequently, all of the chemistry that occurs above 400 °C can be ascribed to reactions of T groups. This chemistry is directly associated with the conversion of the polymer to an amorphous $Si_xO_yC_z$ network, "black glass",[5,6] and free carbon. These same methods suggest that little chemistry occurs below or at 600 °C.

Above 600 °C, e.g., at 800 °C, all of the characterization techniques, except elemental analysis, indicate a drastic change in the solid-state structure of the polymer. The 800 °C spectra all show very significant broadening of peaks. One explanation for the observed broadening is that the polymer is transformed from a partially cross-linked material, where relatively free motion of individual chain segments is possible, to a highly cross-linked network where motion is very restricted. This leads to diminished degrees of freedom for specific chain segments and therefore a larger distribution of absorbing species. This explanation is reasonable if the polymer structure remains intact; however, the 800 °C infrared spectrum suggests otherwise. For example, ν(SiC) (1260–1270 cm^{-1}) is a sharp, easily identified absorption feature common to all methylpolysiloxanes. It is clearly visible in all of the spectra below 800 °C but visible only as a shoulder in the 800 °C spectrum. Consequently, highly restricted chain segment motion as a cause of spectra broadening can serve only as a partial explanation.

The loss in the intensity for ν(SiC) suggests an alternate explanation wherein the T groups react almost completely with each other on heating to 800 °C. The resulting spectral changes must then be associated with a multitude of solid-state reaction products wherein only some part of the original polymer structure is maintained. This reorganization occurs coincident with a significant loss (≈ 3%) in hydrogen content (Figure 1).

The chemical changes associated with reorganization include the reappearence of both SiH and SiOH units and formation of quantities of Q- and D-type or $[MeSi(CH_x)O]$ units. To form new bonds, we must break either CH, SiC, or SiO bonds. To form SiH and SiOH bonds and new SiC bonds (D units), we must break both CH and SiO bonds. Clearly, we must also cleave SiC bonds to make Q groups. The exact bond-breaking and bond-making sequence(s) whereby these reactions occur is not immediately evident. That is, does SiC bond cleavage occur as a consequence of the formation of new SiH and/or Si–OH bonds or after the fact?

Without detailed labeling and kinetic studies it is not possible to delineate the exact reaction pathways whereby T groups react with each other at elevated temperatures. However, it is possible to make several basic observations

(26) Youngdahl, K. A.; Rahn, J. A.; Laine, R. M.; Babonneau, F.; Drobny, G.; Dumais, J., manuscript in preparation.

based on literature precedent.

To begin with, at temperatures above 600 °C, the ^{29}Si and ^{13}C NMR and DRIFT spectra (≈1360-cm^{-1} deformation) indicate that one reaction pathway open to T groups leads to the formation of $SiCH_xSi$ units. On the basis of Yajima et al.'s work with poly(carbosilanes), these linkages will likely lead to the formation of SiC on heating to higher temperatures.[19b,22] Fox et al.[5] report that heating methylsilsesquioxanes to 1500 °C does indeed lead to the formation of SiC.

The ^{29}Si integration data plotted in Figure 6, when considered in terms of the elemental compositions for the bulk materials, indicate that a second major reaction pathway must exist for the disappearence of T groups. At the highest temperatures, we observe that the quantity of Q groups (≈35%) is more than twice the number of D groups (<10%). Furthermore, the bulk analyses of the materials at 800 and 900 °C are essentially identical (Table III), and the silicon to carbon ratio does not change significantly from 400 to 900 °C. The appearence of Q groups indicates that SiC bonds are cleaved without being reformed. The fact that the carbon content does not coincidently drop off is further support for the formation of free carbon as suggested above.

This free carbon probably derives from initial coupling of methyl groups as observed during vapor pyrolysis of tetramethylsilane.[27] The exact nature of this carbon (graphitic or amorphous)[23,24] cannot be deduced in the present study by MAS ^{13}C NMR; however, we have observed a similar product in pyrolysis studies of the $-[H_2SiNMe]_x-$ polymers.[26]

At present, we would like to suggest that the materials formed on heating poly(methylsilsesquioxanes) to temperatures in the range 600–1000+ °C are best described as glasses or solid solutions. These glasses may, on extended heating in the same temperature range or heating to higher temperatures, form known ceramic materials. We will explore this concept again in another paper that focuses on the high-temperature chemistry of poly(methylsilazanes).[26]

Comparison with Sol–Gel-Derived Poly(methylsilsesquioxanes). Pyrolysis of the cross-linked polymers of Table I in nitrogen to 900 °C permits us to compare our poly(methylsilsesquioxane) with that prepared by Fox et al.[5] We find, as does Fox et al., that pyrolysis produces a "black glass". The compositions of the 900 °C materials produced in both studies are listed in Table V with the apparent ceramic compositions. Within the error limits of the analytical technique, the compositions and the ceramic yields of the black glasses produced by both methods are very similar.

We have also examined the pyrolysis of the poly(methylsilsesquioxane) in an oxygen atmosphere to determine the effects of oxidation on the type of product obtained. As expected, the product is primarily SiO_2 with some excess hydrogen. The ceramic yields for all the polymers are 91 ± 1%. Calculated ceramic yields for reaction 4 are 90%.

$$-[MeSi(O)_{1.5}]_x- + O_2 \xrightarrow{\Delta} SiO_2 + 1.5H_2O + CO_2 \quad (4)$$

Consequently, we note that the titanium-catalyzed cross-linking and redistribution reactions of $-[MeHSiO]_x-$ cyclomeric and oligomeric polysiloxanes lead to inorganic polymers that have numerous similarities to those produced by typical sol–gel processing. Moreover, pyrolysis of these preceramics leads to ceramic products apparently identical with those obtained by pyrolysis of the sol–gel-processed material.

Future work in this area will examine the utility of titanium-catalyzed redistribution for the synthesis of other silsesquioxanes.

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(27) See, for example: *Carbosilanes, Synthesis and Reactions*; Fritz, G., Matern, E., Eds.; Springer-Verlag: Berlin, 1986.