Sonochemical Synthesis of a Poly(methylsilane), a Precursor for Near-Stoichiometric SiC

Paweł Czubarow, Toshiya Sugimoto,† and Dietmar Seyferth*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge Massachusetts

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ABSTRACT: We report a sonochemical process for a single-pot synthesis of high molecular weight poly(methylsilane) (PMS) of composition $[(CH_3SiH)_x(CH_3Si)_y(CH_3SiH_2)_z]_n$, where $x + y + z = 1$ and $0.65 \geq (x + z) \geq 0.23$ by the sodium polycondensation reaction of CH_3SiHCl_2 in a solvent mixture of hexane or toluene and tetrahydrofuran (THF) using ultrasonic activation (47 kHz, 130 W). This polycondensation reaction takes place in two stages: (1) 10−25 h of reaction in which an oligo(methylsilane) (OMS) oil ($0.91 \geq (x + z) \geq 0.83$) is obtained that gives low ceramic residue yields of silicon-rich SiC on pyrolysis in argon and (2) 25−40 h of reaction during which is obtained a PMS solid that gives high ceramic residue yields of near stoichiometric SiC on pyrolysis. PMS also may be prepared by branching of the oligo(methylsilane) with sodium and ultrasonication for ∼5 h in a toluene and THF solvent mixture. PMS is soluble in hexane and toluene and its pyrolysis in argon gives a ceramic residue yield up to 90%. In addition to the main product of the condensation reaction, a high molecular weight PMS may be extracted from large NaCl crystals (the other product of the CH_3SiHCl_2/Na reaction). A comparison of sonochemical and conventional (reflux) activation also is provided. Ceramic fibers, films, and solid monoliths were prepared from PMS without requiring a curing step.

Introduction

A high molecular weight poly(methylsilane) (PMS) that is a single-source precursor to stoichiometric SiC is a worthwhile goal. It is generally believed that branching and cross-linking of a polysilane or a poly(carbosilane) precursor is necessary to afford high ceramic residue yields of SiC when the polymer is pyrolyzed. There are various ways of achieving high molecular weight branched and/or cross-linked polysilanes and, hence, high ceramic yields. One route developed by Bianconi and Weidman[1] and Bortolin[2] involved the reductive coupling of $RSiCl_3$ compounds by Na/K alloy, which yields a soluble polymeric network, $(RSi)_n$. More recently, we[3−5] reported high molecular weight PMSs that were synthesized by reacting an oligo(methylsilane) (OMS), $(CH_3SiH)_n$, with a catalytic amount of an early transition metallocene derivative. Such catalysts induce a dehydrogenative coupling reaction that results in branching and cross-linking and consequently affords a polymer whose pyrolysis gives a high ceramic residue yield of near stoichiometric SiC. Also, Harrod et al.[6,7] utilized $LiAlH_4$ as a cross-linking catalyst for OMS to produce a PMS of high molecular weight.

Several investigators have explored the use of alkali metals for the combined reductive-dehydrogenative coupling of silanes. Schilling and co-workers at Union Carbide[8−10] developed an effective SiC precursor by the reaction of potassium (K) with CH_3SiHCl_2 and vinylchlorosilanes that produced a soluble polysilane-polycarbosilane preceramic network (eq 1).[8−10] When sodium (Na) was used instead of K, only linear polysilanes resulted (eq 2):

$$CH_3SiHCl_2 + ViSiCH_3Cl_2 \xrightarrow{K} (CH_3SiH)_x(CH_2CHSiCH_3)_y(CH_3Si)_z \quad (1)$$

$$CH_3SiHCl_2 + ViSiCH_3Cl_2 \xrightarrow{Na} (CH_3SiH)_x(ViSiCH_3)_y \quad (2)$$

Preceding Schilling's work, Peterson and Arkles[11] reported a synthesis of cyclic oligosilanes by the reaction of chlorohydrosilanes with lithium or lithium-alkali metal alloys. In this process, Si−Si bonds are formed by the action of the alkali metal on Si−H as well as Si−Cl bonds (eq 3):

$$2\ RR'SiHX + 2\ M \rightarrow (RR'Si)_n + 2\ MX + H_2\uparrow \quad (3)$$

Brown-Wensley and Sinclair at 3M,[12−14] Wood at MIT,[15] and more recently Bryson[16] and Noireaux et al.[17] have prepared partly cross-linked PMS by the reaction of CH_3SiHCl_2 with Na in THF (eq 4):

$$CH_3SiHCl_2 \xrightarrow[THF]{Na} [(CH_3SiH)_x(CH_3Si)_y]_n \quad (4)$$

Results and Discussion

In the present work, a single-pot synthesis of high molecular weight PMS and an *in situ* branching or cross-linking of oligo(methylsilane) (OMS) by Na with ultrasonic activation (47 kHz, 130 W) were explored. The use of Na instead of K provides both practical and economic advantages.

Ultrasonic activation differs from conventional energy sources (i.e., reflux conditions) in terms of shorter interaction times, higher pressures, and higher energy per molecule.[18] Implosive collapse of bubbles may produce intense localized heating and high pressure for very short periods of time. The hot spots may reach temperatures of up to 5000 °C and pressures of 500 atm,

† Visiting Scientist, on leave from Sekisui Chemical, Ltd.

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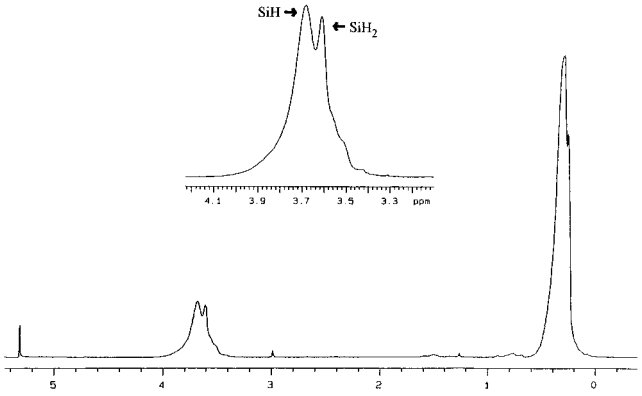

Figure 1. 500 MHz ^{1}H NMR spectrum of oligo(methylsilane) in CD_2Cl_2.

with heating and cooling rates of 10^9 K/s.[19] In the case of heterogenous sonochemistry it is common to find a factor of 10 in enhancement of rates and purity of products.[20]

Sonochemical Synthesis of OMS from CH_3SiHCl_2 and Na. The reaction of CH_3SiHCl_2 with Na in a hexane (or toluene)/tetrahydrofuran (THF) medium using ultrasonic activation takes place in two stages. The first stage takes ~10 h and yields a clear oil with a composition of $[(CH_3SiH)_x(CH_3Si)_y(CH_3SiH_2)_z]_n$, where $x/z \approx 4$, $x + y + z = 1$, and $0.91 \geq (x + z) \geq 0.83$, depending on the reaction conditions, as determined by integration of the proton nuclear magnetic resonance (^{1}H NMR) spectrum of the product. The variable z denotes the mole fraction of end groups of the oligomer, x indicates the mole fraction of difunctional main chain units, and y represents the mole fraction of trifunctional branched units.

The spectroscopic evidence further substantiate the aforementioned composition. The ^{1}H NMR spectrum of the polysilane showed two broad resonances: one between 0 and 1 ppm ($W_{1/2} = 90$ Hz), corresponding to the protons of the methyl group attached to silicon (CH_3-Si), and another between 3.8 and 4.5 ppm ($W_{1/2} = 75$ Hz), corresponding to the protons attached directly to the silicon atom (SiH_x; Figure 1). Integration of these signals in the ^{1}H NMR spectrum of the OMS varies with the reaction conditions used to prepare the oligomer between $SiCH_3/SiH_x = 3.8/1$ for branched and $SiCH_3/SiH_x = 3.2/1$ for oligomers with only a small amount of branching, whereas in theory $SiCH_3/SiH_x$ should be 3.0/1 for $x = 1$. The resonance between 3.8 and 4.5 ppm showed a small upfield shoulder at 3.9 ppm (Figure 1). Based on model compounds,[21] $CH_3SiH_2SiH_2CH_3$ and $(CH_3)_2SiHSiH(CH_3)_2$, resonances for SiH_2 and SiH are expected to be at 3.58 and 3.72 ppm, respectively. This expectation suggested that the shoulder is a part of an SiH_2 signal, which was confirmed by DEPT ^{29}Si NMR and IR spectra (*vide infra*). When deconvolution techniques were applied to the SiH_x signal of the ^{1}H NMR spectrum, the integral ratio of Si**H** protons to Si$\mathbf{H_2}$ protons was 4/1, which indicates a ratio of eight SiH groups to one SiH_2 group. During acquisition of the NMR spectrum care must be taken in choosing a proper relaxation time for Si$\mathbf{H}_x$ and SiC$\mathbf{H}_3$. Because silicon has a long relaxation time, protons attached to it will require longer delays between pulses than will the SiC$\mathbf{H}_3$ protons.[22] A spin−lattice relaxation experiment of OMS in C_6D_6 at ambient temperature showed the relaxation time (T_1) to be 3.5, 4.5 and 1.5 s for Si**H**, Si$\mathbf{H}_2$ and SiC$\mathbf{H}_3$, respectively. The higher the molecular weight

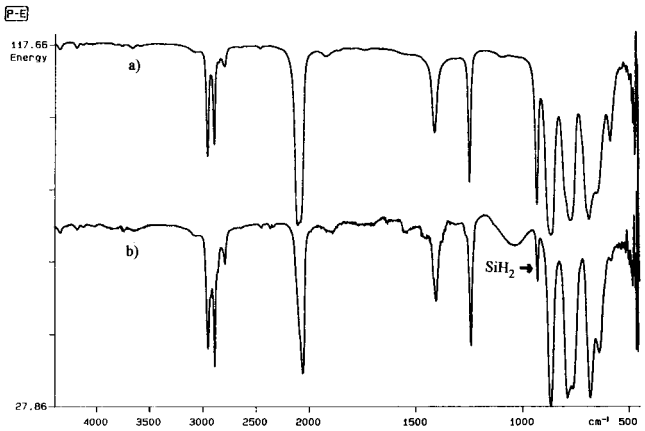

Figure 2. FT-IR spectrum of (a) oligo(methylsilane) oil and (b) PMS-2 (NaCl disk).

becomes, the shorter the relaxation time because there are more degrees of freedom available in the system.

The Fourier transform infrared (FT-IR) spectrum of OMS (Figure 2) showed the usual C—H absorptions, (ν_{C-H}) at 2957 (antisym), 2894 (sym), and 2796 cm^{-1}, and a large, broad Si—H absorption (ν_{Si-H}) centered at 2107 cm^{-1}. The Si—H absorption is rather broad because it probably consists of at least two overlapping peaks due to SiH and SiH_2.[23] There are strong and sharp absorptions at 1410 and 1248 cm^{-1} assignable to C—H antisymmetric and symmetric bends (δ_{Si-CH_3}) of the methyl groups, respectively.[24] A small but sharp band at 931 cm^{-1} corresponds to the γSiH_2 scissoring mode. The presence of this band provides further evidence for the presence of the -CH_3SiH_2 group. A sharp, strong, and broad absorption at 865 cm^{-1} is due to the ρCH_3 rocking mode.[25] Finally, there are absorptions due to the stretch (ν_{Si-C}) of the methyl group at 770 (antisym), 688 (sym), and 650 cm^{-1}.[24,26] Noteworthy is the absence of residual Si—Cl in the OMS as evidenced by the absence of bands in the 498−525 cm^{-1} region.[27]

Pyrolysis of the OMS thus produced in argon at 1000 °C gives only a low (19%) yield of ceramic residue (Figure 16) that contains a substantial amount of free silicon as well as SiC. The second stage product of the reductive coupling of CH_3SiHCl_2 by Na yields a high molecular weight PMS. This product is obtained by ultrasonication of CH_3SiHCl_2 and Na in hexane/THF or toluene/THF (7/1, v/v) for >22 h at ~47 °C. In addition to the main product that is obtained in these CH_3SiHCi_2/Na reactions (i.e., OMS or PMS), a high molecular weight PMS is also present entrapped in NaCl crystals. A PMS could also be prepared by treating the OMS oil with Na metal by ultrasonic activation for ~6.5 h.

OMS is a very air-sensitive substance. Upon exposure to air it becomes an insoluble solid in a matter of hours. Conflagration occurs when it comes in contact with combustible materials, such as paper or cloth, in air. To prevent the facile air oxidation, a procedure developed by Bryson[16] involving the use of antioxidants was employed. Bryson found that 2,6-di-*tert*-butyl-4-methylphenol (BHT) or its derivatives effectively retard oxidation of very air-sensitive polysilanes such as the Schilling polymer.[8−10] We found that ~5 wt% (~1 mol%) of BHT blended with the OMS prevents its air oxidation for weeks (Figure 3). After ~2 weeks of air exposure, the OMS oil containing BHT still was oily and soluble in common organic solvents.

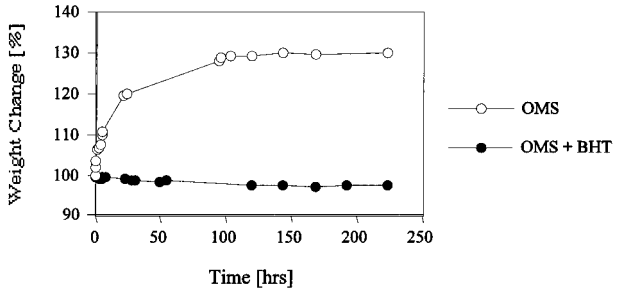

Figure 3. A graph depicting an effect of BHT on oligo(methylsilane) exposed to air. The weight gain due to oxidation results from conversion of Si−Si to Si−O−Si and Si−H to Si−OH.

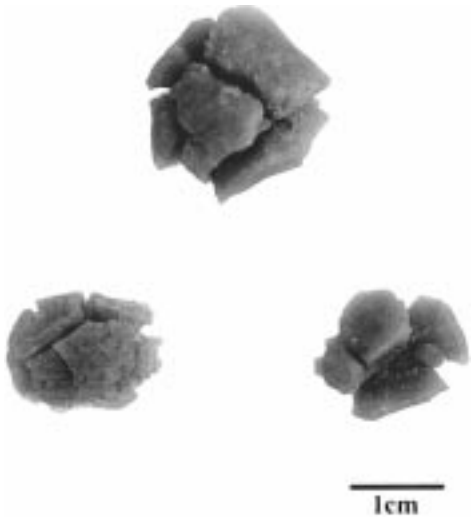

Figure 4. NaCl crystals occluding unreacted sodium particles with encapsulated poly(methylsilane).

Solid Poly(methylsilane) (PMS-1) Extracted from NaCl Crystals. The Wurtz reductive coupling of CH_3SiHCl_2 using Na and ultrasonic activation (130 W, 47 kHz) in its first stage (10−25 h of ultrasonication) afforded the usual 75% yield of OMS clear oil. In addition, during the reductive coupling reaction, a high molecular weight, solid PMS (PMS-1), formed in ∼10% yield, was found entrapped within the large, yellow NaCl crystals that adhered to the unreacted Na (Figure 4). It is known that a variety of inorganic materials, including simple salts, are able to encapsulate organic or organometallic molecules.[28] The PMS-1 polymer was separated from the NaCl crystals (which were previously detached from unreacted Na) by dissolving the latter in oxygen-free water. The polymer was not hydrolyzed and, based on its far IR spectrum, remained free of absorptions due Si−O−Si. Pyrolysis of this polymer in argon at 600 °C afforded a 77% yield of ceramic residue. Based on its elemental analysis, the polymer still contained 0.14% Na. By gel permeation chromatography (GPC), this polymer was shown to have a trimodal molecular weight distribution, with the highest molecular weight $\sim 10^5$ relative to monodisperse polystyrene (Figure 5).

Sonochemical One-Pot Synthesis of High Molecular Weight Poly(methylsilane) (PMS-2) from CH_3SiHCl_2 and Na. The synthesis of high molecular weight PMS (PMS-2) by the CH_3SiHCl_2/Na reaction was examined in some detail. In a 7/1 (v/v) hexane/THF or toluene/THF solvent system, using ultrasonication for >22 h (preferably 25−40 h, the second stage), PMS-2

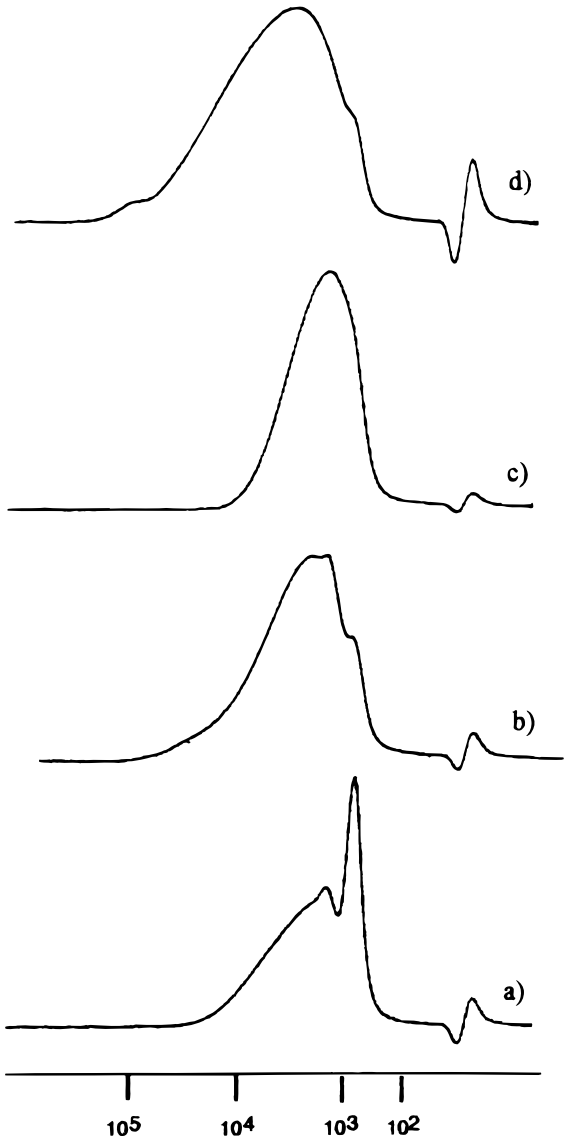

Figure 5. GPC traces (relative to monodisperse polystyrene) of (a) PMS-2 synthesized by prolonged ultrasonication in toluene/THF; (b) NaCl extracted PMS-1 where the main products was PMS-2 depicted in (a); (c) original oligo(methylsilane) clear oil; (d) NaCl-extracted PMS-1, where the main product was an oil depicted in (c).

was obtained in 42−51% yield. This polymer was isolated as a highly pyrophoric, orange-yellow solid ($(x + z) = 0.33 - 0.41$), which was soluble in toluene and partly soluble in hexane, and afforded a ceramic residue in 80 to 87% yield upon pyrolysis in argon at 1000 °C. The elemental analysis of PMS-2 indicated the presence of 0.6% by weight of residual Na and on pyrolysis of this polymer in argon at 1000 °C, 0.41% Na was retained. After pyrolysis in argon at 1500 °C for 3 h, only 0.14% Na remained. Because NaH decomposes at 800 °C and elemental Na (bp, 882.9 °C) probably would volatilize,[29] it could be assumed that if the pyrolysis of PMS-2 was carried out for longer periods or at higher temperature, the amount of Na would diminish to ppm levels. The products from both stages of the reductive coupling reaction [i.e., oligomer oil, OMS, and solid poly(methylsilane), PMS] have almost identical IR spectra (Figure 2). However, the IR spectrum of the latter showed a diminished absorption due to γSiH_2 at 930 cm^{-1}. The diminished content of SiH_2 was confirmed by a DEPT ^{29}Si NMR spectrum, which is in agreement with its

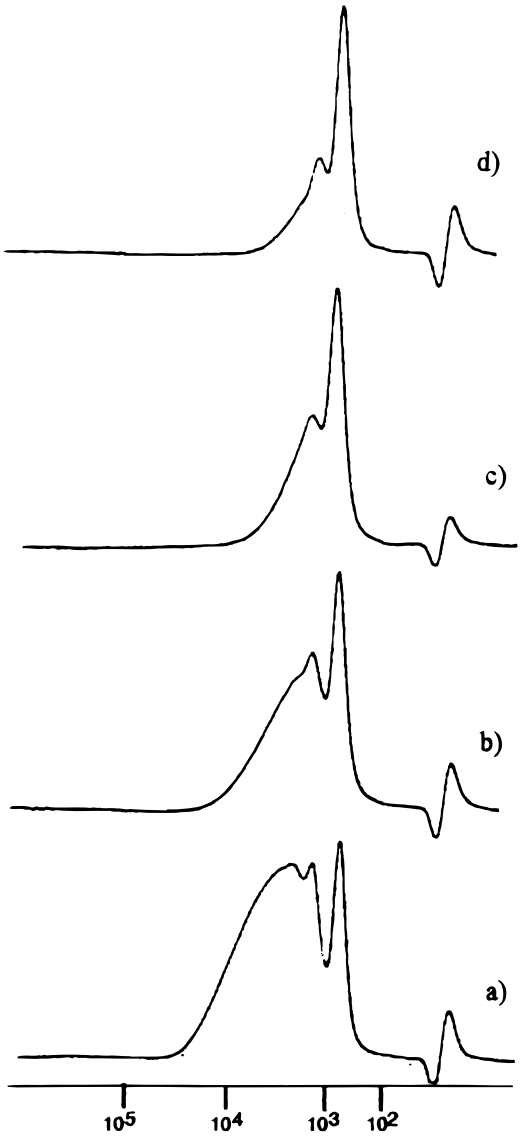

Figure 6. GPC traces (relative to monodisperse polystyrene) of oligo(methylsilane) reacted with (a) Na (PMS-3) and (d) NaH. Poly(methylsilane) synthesized by extensive ultrasonication in (b) toluene/THF system and (c) hexane/THF system.

higher molecular weight. Most of the branching initiates preferentially on SiH_2 groups because they are least hindered in the entire polymer structure.

Different reaction conditions also were investigated. It was observed that the presence of an aromatic hydrocarbon such as toluene affords higher molecular weight polymer (hence higher ceramic residue yields) than when hexane alone was used as reaction solvent (Figure 6). The highest yield of high molecular weight, soluble product was obtained when the duration of ultrasonication was 40 to 65 h. More than 65 h of ultrasonication resulted in formation of some insoluble, fully cross-linked product. Only an insoluble product was formed when the CH_3SiHCl_2/Na mixture was heated at reflux for ~30 h without ultrasonication. Further experiments showed that an excess of Na (≥ 2.5 molar equivalents) was required to obtain the high molecular weight PMS. Use of only a stoichiometric amount of Na resulted in formation of an oily product that still contained Si—Cl bonds, even after 40 h of ultrasonication.

The extended time reductive coupling reaction also afforded large NaCl crystals that contained high molecular weight PMS ($(x + z) = 0.36$) whose pyrolysis gave a ceramic residue yield of 73%.

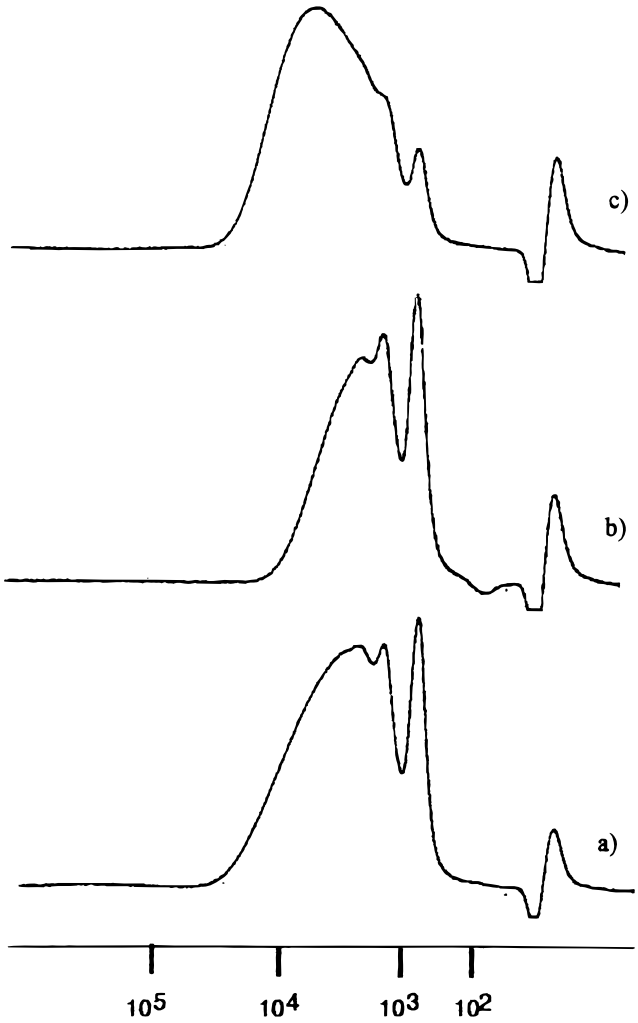

Figure 7. GPC traces (relative to monodisperse polystyrene) of poly(methylsilane) (PMS-3) reacted with Na (a) the entire molecular weight distribution; (b) hexane-extracted fraction (PMS-3H); (c) toluene-extracted fraction (PMS-3T).

Branching and/or Cross-linking of OMS with Na; Synthesis of PMS-3. Another variant of high molecular weight PMS was obtained by the action of Na with ultrasonication on previously synthesized OMS. In this reaction, 0.5 molar equivalent of Na and 1.0 molar equivalent of OMS (based on the CH_3SiH repeat unit) in 7/1 (v/v) toluene/THF were ultrasonicated for at least 5 h. The ethereal (THF) cosolvent was essential for a successful reaction. The product was a toluene-soluble, pyrophoric, pumpkin-yellow-orange solid polymer (PMS-3) ($(x + z) = 0.50 - 0.23$). Upon pyrolysis in argon, this precursor afforded near stoichiometric SiC in ~53−90% yield depending on the length of reaction. The elemental analysis of the ceramic residue from argon pyrolysis at 1500 °C gave 27.07% C and 70.92% Si as compared with theoretical SiC analysis of 29.95% C and 70.05% Si. The GPC trace of this polymer showed a trimodal molecular weight distribution with a broad, high molecular weight region (~10 000) and two narrow low molecular weight regions (~1000 and ~500, respectively; Figure 7a). The low molecular weight fraction can be extracted with hexane (PMS-3H) as shown by the GPC trace (Figure 7b). The high molecular weight fraction is soluble in toluene (PMS-3T; Figure 7c). About 80% of PMS-3 was soluble in hexane. The PMS-3

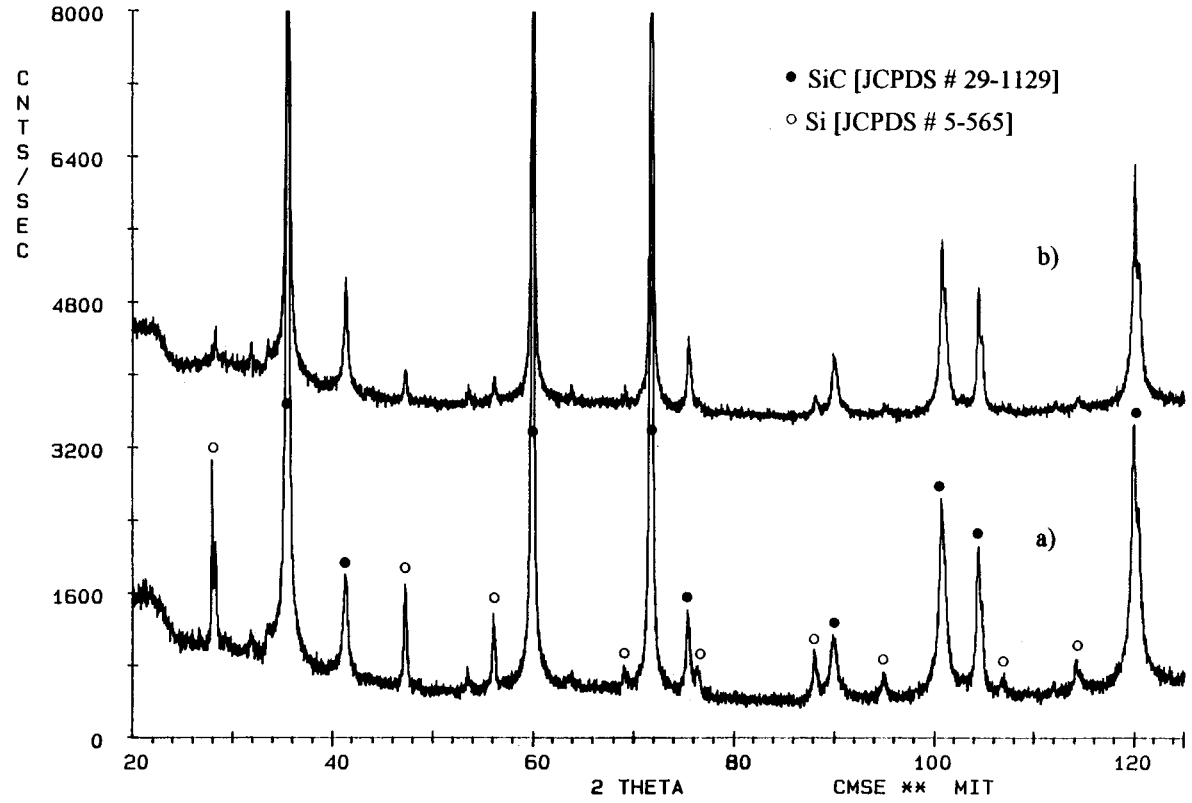

Figure 8. XRD patterns of the ceramic derived from 1500 °C in Ar pyrolysis of PMS-3: (a) hexane-extracted fraction (PMS-3H, low molecular weight); (b) toluene-soluble fraction (PMS-3T, high molecular weight). Both samples fired using the same pyrolysis schedule.

polysilane appeared to have a higher molecular weight than the PMS-2 polymer (Figure 6). It also was observed that, in general, high molecular weight PMS gave higher purity β-SiC on pyrolysis with less elemental Si contaminant compared with the lower molecular weight species, as shown by the X-ray diffraction (XRD) patterns (Figure 8). The elemental analysis of PMS-3 indicated the presence of 1.45% residual Na. The hexane-soluble fraction (PMS-3H), however, contained only 0.1% Na. Pyrolysis of PMS-3 in argon at 1000 °C afforded a ceramic that contained 0.7% Na. After pyrolysis at 1500 °C for 3 h, only 0.06% Na remained.

The residual Na in all of the PMS samples could be due to the presence of silyl-sodium ($\sim CH_3(H)Si{-}Na^+$) end groups. Support for such a possibility was provided by an experiment in which CH_3I was added to a yellow-orange solution of PMS-3 in toluene. The color was discharged immediately. Workup to remove insoluble material and solvent left a white solid. The Na content of the latter (1.1%) was less than that of the original PMS-3 sample (1.7%). The CH_3I-treated polymer was identical to the original PMS-3 sample in molecular weight distribution.

The action of Na on the OMS could involve reaction with Si—H or Si—Si bonds. In either case, silyl anions might be expected to be formed. It is noteworthy in this connection that in the OMS/Na reaction, the SiH_2 groups were almost completely consummed as shown in the DEPT ^{29}Si NMR spectra (Figure 9). In any case, Na is required. Ultrasonication of OMS in 7/1 (v/v) hexane/THF for 90 h gave unchanged starting material.

Various background experiments have been performed to determine the nature of the reaction of OMS with Na. Reflux conditions in place of ultrasonication yielded mostly insoluble products with only a trace of a

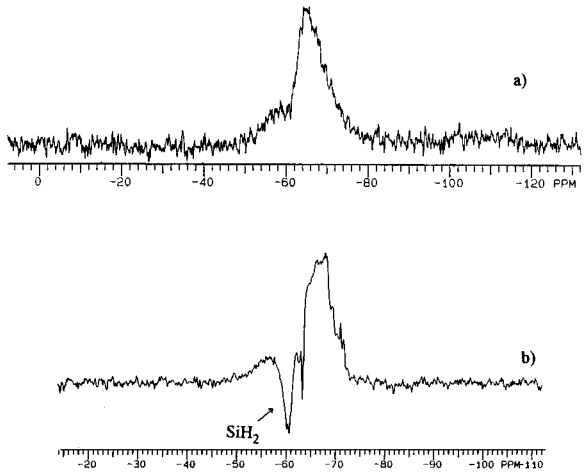

Figure 9. DEPT ^{29}Si NMR (MULT = 1.5) spectrum of (a) PMS-2 and (b) OMS.

soluble, tacky solid. Likewise, a 65.5-h ultrasonication of $(CH_3)_2SiHCl$ with Na yielded only $[(CH_3)_2SiH]_2$ and no high molecular weight polymers. Also, ultrasonication of OMS for 89.5 h in 7/1 (v/v) hexane/THF in the absence of Na did not result in any appreciable structural alteration of the original oligomer. It would appear that the dehydrogenative coupling reaction of silanes with Na is specific only for species having extensive Si—Si linkages.

The high molecular weight PMS also is very air sensitive, to the extent that it is pyrophoric. However, its pyrophoricity can be eliminated with the addition of an antioxidant.[16] Addition of ~5 wt% (1 mol%) of BHT to PMS-3 eliminates its pyrophoricity and inhibits its air oxidation for weeks (Figure 10). After the addition of BHT, the polymer becomes white, probably because

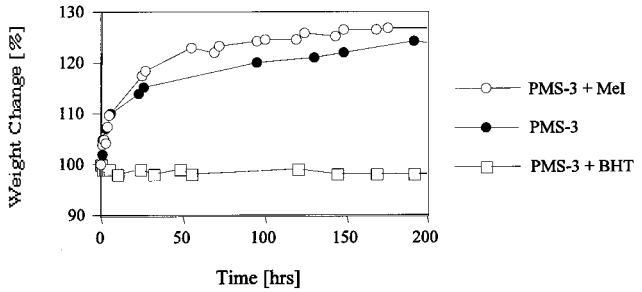

Figure 10. A graph depicting an effect of BHT on poly(methylsilane) exposed to air.

the phenol reacts with the residual silyl anion groups. Spectroscopically, the polymer with and without BHT is identical.

Pyrolysis of High Molecular Weight PMS. The heating program for pyrolysis of PMS is a very important issue. Special attention should be paid to the temperature range at which a transition from polysilane to polycarbosilane takes place. The heat treatment of PMS-3 polymer in a tube furnace in argon showed that a Kumada rearrangement[30] (eq 5) took place between 200 and 300 °C as confirmed in the IR spectrum of the product of such intermediate heating (fingerprint region) by the appearance of the CH_2 deformation band at 1349 cm^{-1}:

$$[\text{-C}\mathbf{H}_3\text{(H)Si-Si(H)CH}_3\text{-}]_n \xrightarrow{\Delta} [\text{-}\mathbf{H}\text{(H)Si-C}\mathbf{H}_2\text{-Si(H)CH}_3\text{-}]_n \quad (5)$$

This observation was in close agreement with recent results of Harrod and co-workers[31] who reported, based on IR spectra, a Kumada rearrangement at ~200 °C of a PMS film cast on a silicon wafer. Consequently, when during the pyrolysis of PMS a 2-h hold was incorporated into the pyrolysis program at ~300 °C, on the way to 1000 °C and higher, the final residual SiC is almost free of elemental silicon based on the XRD patterns (Figure 11).

Application of PMS in Preparation of SiC Ceramics. Application of the PMS system as a precursor to ceramic fibers, films, and monoliths was explored. Thin SiC films from PMS-3H were prepared on an alumina substrate by dip-coating the substrate into a toluene solution of the precursor. Subsequent pyrolysis of the film at 1000 °C in argon gave an amorphous and mostly uniform ceramic film with the exception of a few flaws, as depicted in Figure 12. Recently, a PMS derived from dehydrogenative coupling of CH_3SiH_3 with $Cp_2Ti(CH_3)_2$ was spun into fibers.[32] Addition of a curing agent was necessary to prevent the fibers from melting during the pyrolysis. In the present study, green fibers were formed by manually pulling them from a viscous toluene solution of PMS-3H; pyrolysis at 1000 °C in argon followed. The resulting ceramic fibers were homogeneous and solid inside (Figure 13). The green fibers did not require prior curing by irradiation or exposure to oxygen before their pyrolysis because PMS-3 does not melt when heated. Monolithic pellets also were prepared from the PMS-3T fraction. The polymer monoliths shrank 70% by volume without a sign of melting on pyrolysis in argon at 1500 °C for 3 h. The density changed from 1.03 g/cc (green body) to 2.27 g/cc (71% of the theoretical of density) for the final monolith. The Vickers microhardness of the monolith was ~2400 HV, which is comparable to the hardness of commercially available SiC.[33] A study of the morphology of the monolith revealed the presence of elemental silicon in the bulk β-SiC matrix. The silicon deposits occurred in regularly arranged veins (~1 μm in diam-

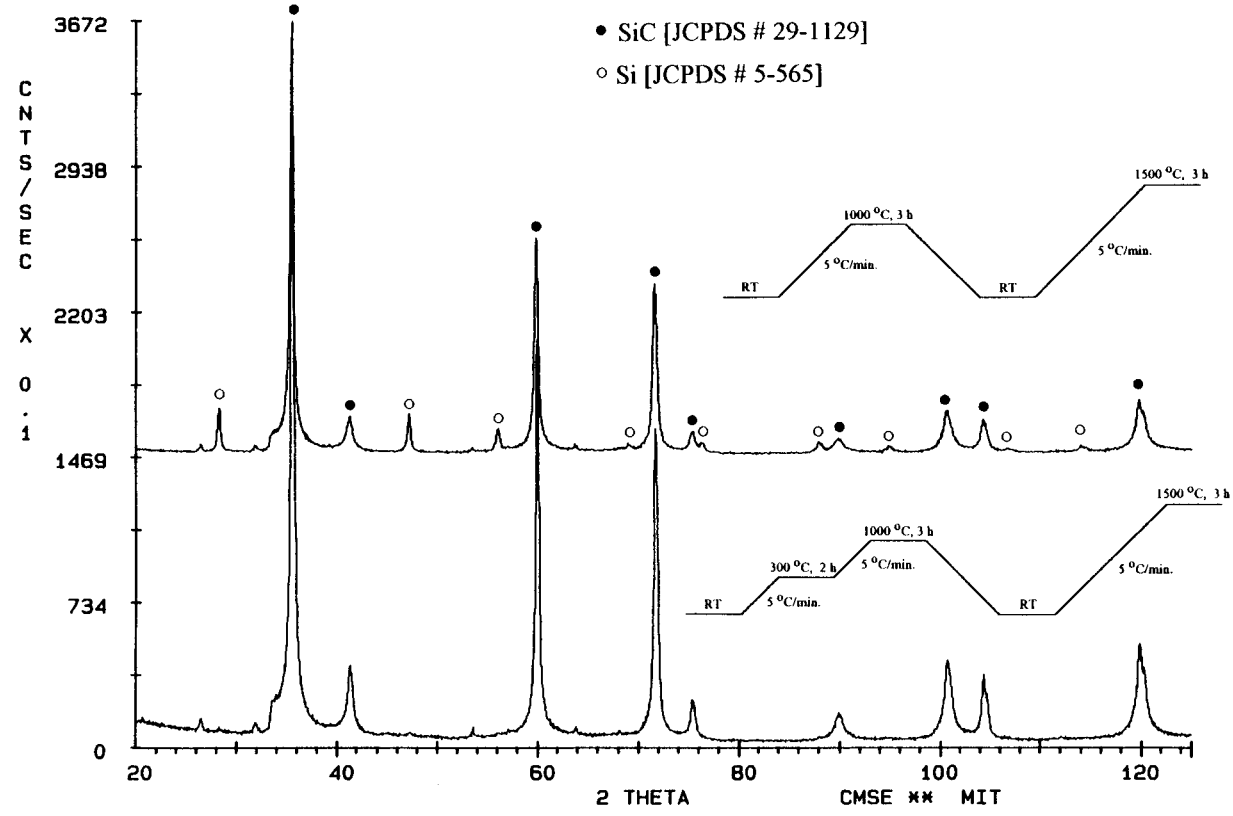

Figure 11. XRD patterns of ceramics derived from pyrolysis of PMS-3.

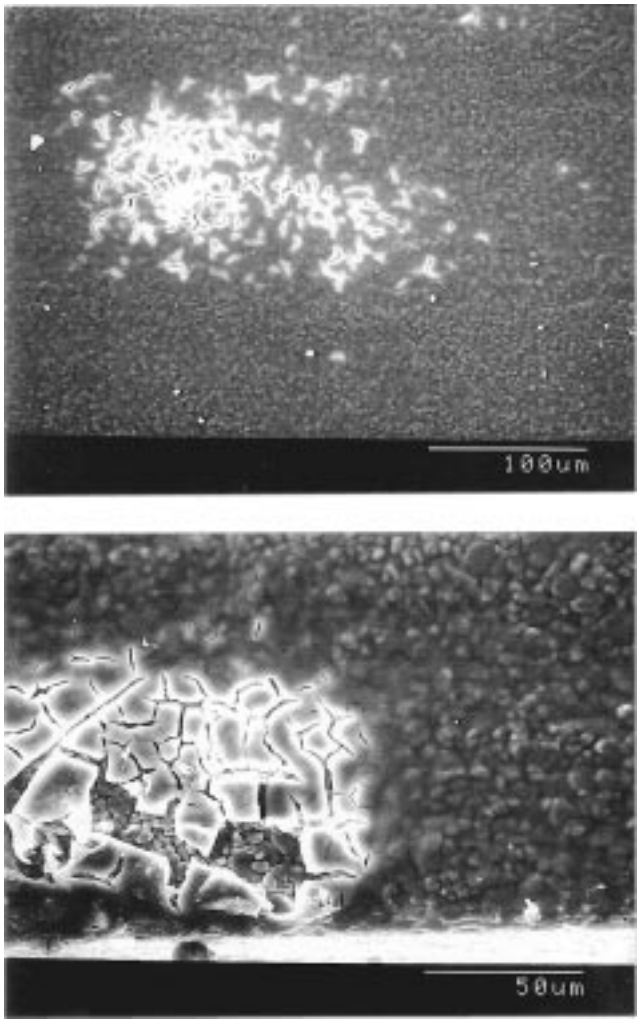

Figure 12. SEM micrographs of SiC film on alumina substrate prepared from PMS-3H and pyrolysis in Ar at 1000 °C.

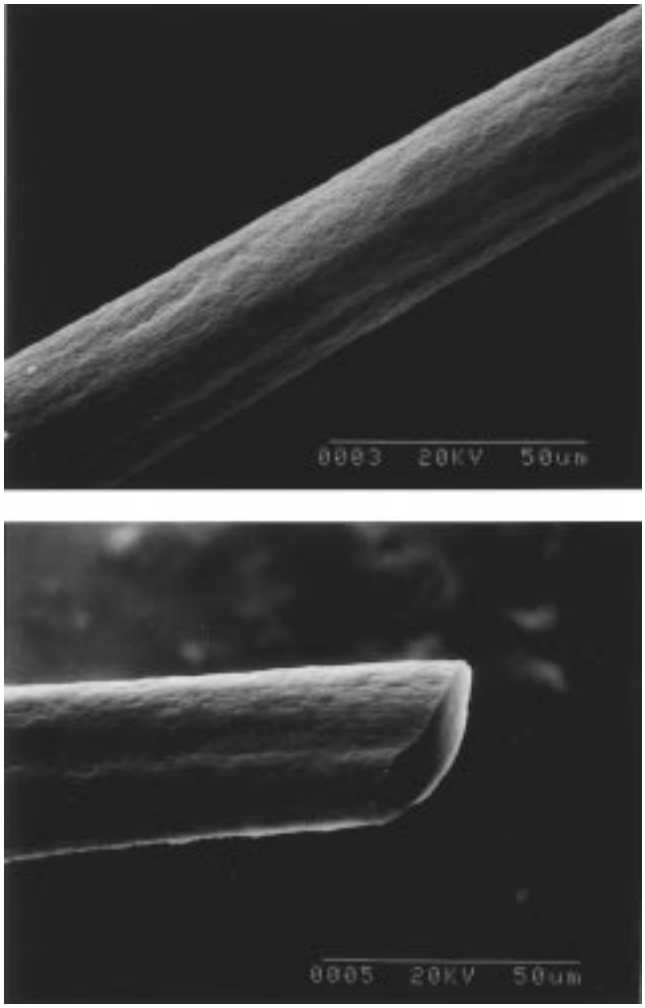

Figure 13. SEM micrograph of SiC fiber span from PMS-3H and pyrolyzed in Ar at 1000 °C.

eter), as depicted in the optical micrograph as well as in the SEM image and its silicon map (Figure 14).

Conclusion

In the current work we have demonstrated the one-pot sonochemical synthesis of high molecular weight precursor for near stoichiometric SiC. The synthesis conditions using ultrasonic activation did not require temperatures in excess of 80 °C. The conversion of monomer to high molecular polymer was the highest reported thus far (up to 65%). PMS-1, PMS-2, and PMS-3 had considerably higher molecular weight than any other PMS polymer known (Figure 15). Current polymers gave higher yields of ceramic residue (up to 90%) than did the polymers obtained using reflux (55%) or room temperature (49%) conditions (Figure 16). The PMS prepared by ultrasonic activation is unique because it exhibited overall shrinkage without melting, bubbling, and spattering during pyrolysis. Properly chosen pyrolysis conditions give essentially stoichiometric SiC.

The action of Na with ultrasonic activation converts OMSs to branched PMS. This method is an inexpensive alternative to the use of transition metal dehydrogenative coupling catalysts whose use leaves transition metal carbides and silicides as unremovable byproducts after pyrolysis.

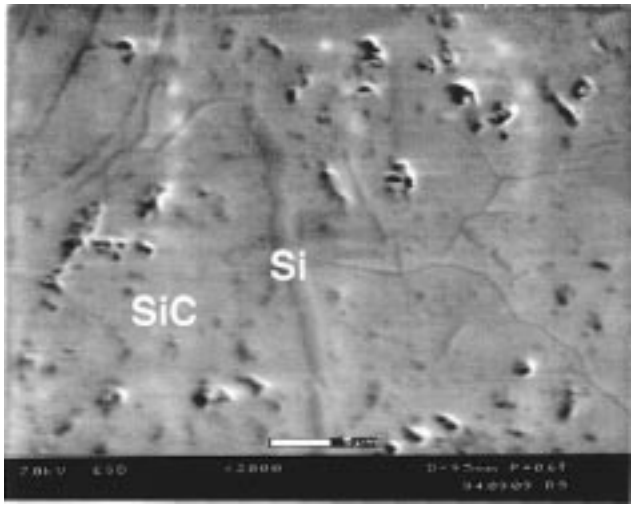

Figure 14. ESEM micrograph image of the morphology of the SiC monolith with vertical Si veins.

Experimental Section

For all the experiments, glassware was oven- or heat gun-dried under vacuum or under a stream of nitrogen or argon prior to use. THF and diethyl ether were distilled from Na/benzophenone. Toluene was distilled from Na and hexane from $LiAlH_4$. Solvents and liquid reagents were deoxygenated by bubbling nitrogen or argon through them for ~30 min to 1 h prior to use. Methyldichlorosilane was obtained from Aldrich,

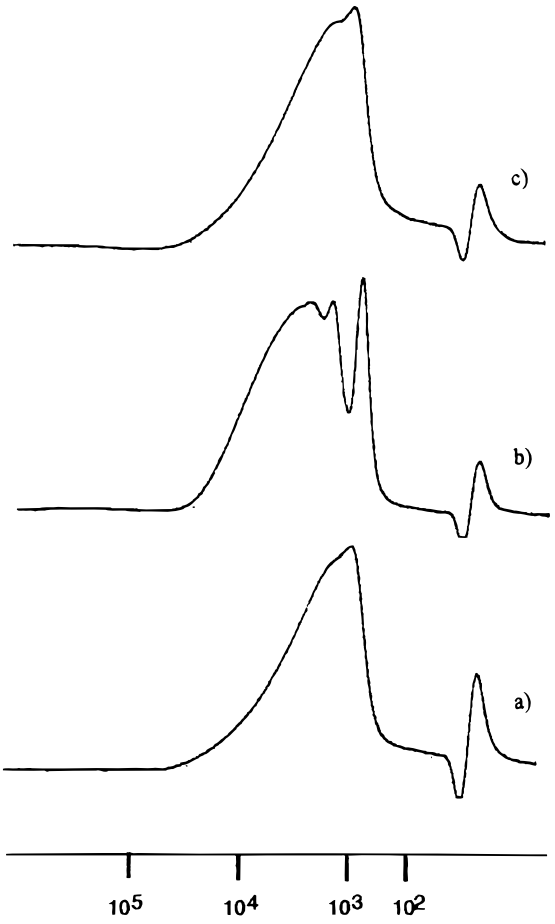

Figure 15. GPC traces (relative to monodisperse polystyrene) of: (a) PMS obtained by reflux in THF of CH_3SiHCl_2 and Na[12,15]; (b) PMS-3; (c) PMS obtained from ultrasonication CH_3SiHCl_2 and Na in THF (in absence of aromatic solvent).

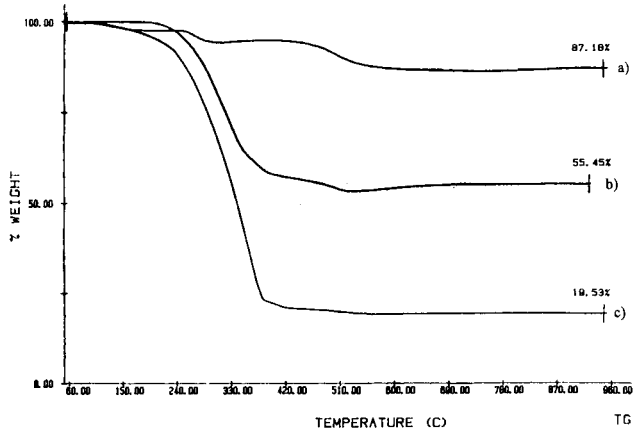

Figure 16. TGA traces of (a) PMS-2 sonochemically synthesized by prolonged reductive coupling; (b) PMS synthesized by reductive coupling in refluxing THF; (c) oligo(methylsilane) (OMS) oil.

Petrarch Systems, Hüls America, or Silar Inc., and was distilled from magnesium under argon prior to use. Reagent-grade Na was further purified by melting it in stirred, refluxing xylene, and allowing it to set in one large mass upon cooling. This process allows for total exclusion of oxide impurities from the bulk of metal. The large piece was then diced to appropriate size shot, which were used in the reactions.

Ultrasonic activation was accomplished with an internally cooled Branson 3200 ultrasonic cleaner operating at 47 kHz, 130 W.

The dip-coating of alumina substrate was effected with a modified syringe pump model 341A (Sage Instrument Division of Orion Research Inc.) with a draw rate of 0.01 mm/s.

GPC was performed with a Waters/Millipore 150-C ALC/GPC instrument, equipped with 10^3 and 10^4 Å Ultrastyragel and 60 Å μ-Porasil columns. Argon-deaerated toluene (HPLC grade) was used as eluent at a flow rate of 1 mL/min at 25 °C. The molecular weights reported are relative to the monodisperse polystyrene standards purchased from Polysciences Inc.

Elemental analyses were performed by the Galbraith Laboratories and Scandinavian Microanalytical Laboratory, Herlev, Denmark (C, H, and N). Estimated error ranges for analysis of ceramic samples are ±1.5% for carbon and ±3.0% for silicon.

Thermogravimetric analysis (TGA) data were obtained with a Perkin-Elmer System 4 connected to a Perkin-Elmer TGS-2 Thermal Analyzer. Samples (3−8 mg) were heated in argon from 50 to 950 °C at a rate of 10 °C/min.

For the elemental analysis calculation, the polymer formula was simplified from $[(CH_3SiH)_x(CH_3Si)_y(CH_3SiH_2)_z]_n$ to $(CH_3SiH_x)_A(CH_3Si)_B$, where subscripts A and B correspond to $(x + z)$ and y, respectively, and the subscript x denotes the number of substituted protons (i.e., one or two).

Procedure for Synthesis of OMS. Reaction Between CH_3SiHCl_2 and 2.5 Na in 7/1 (v/v) Hexane/THF Using Ultrasonic Activation at 47 °C. A 100-mL Schlenk flask was charged with 14.6 g (0.635 mol) of Na shot (∼10 mm in diameter), 7.5 mL of THF, 52.5 mL of hexane, and 26 mL (28.6 g, 0.249 mol) of CH_3SiHCl_2. The flask was placed in the ultrasonic bath for 19 h. Then, the reaction mixture and three 20-mL hexane washings were cannulated into a thick-walled centrifuge bottle and centrifuged for 1 h. The clear supernatant solution was cannulated into a Schlenk flask and trap-to-trap distilled at reduced pressure, leaving 8.2 g (75% yield) of a clear oil that was soluble in most common organic solvents. The rest of the solids (Na + NaCl) weighed 33.0 g. ^{1}H NMR (300 MHz, C_6D_6): δ 0.5 ($W_{1/2}$ = 90 Hz, 3.3 H, SiC**H**$_3$), 4.1 ($W_{1/2}$ = 75 Hz, 1.0 H, Si**H**, Si**H**$_2$); CH/SiH = 3.3; in general CH/SiH = 3.3−3.6. ^{13}C NMR (75.5 MHz, C_6D_6): δ_C −12.2 to −5.1 ($W_{1/2}$ = 230 Hz, Si**C**H$_3$). ^{29}Si NMR (59.59 MHz, C_6D_6): δ_{Si} −71, −67 ($W_{1/2}$ = 300 Hz, **Si**H); −64, −61 ($W_{1/2}$ = 300 Hz, **Si**H$_2$) (Figure 4C). IR (thin film on NaCl, cm^{-1}): 2957(s), 2894(s), 2796(w), 2107(vs), 1918(vw), 1410(s), 1247(vs), 1037(vw), 931(vs), 867-(vs), 770(vs), 685(vs), 584(s). Ceramic residue yield (TGA): 19%.

Extraction of the High Molecular Weight PMS-1 from NaCl Crystals Obtained in the Synthesis of OMS. A 100-mL Schlenk flask was charged with 25.9 g (1.13 mol) of mirror clean Na metal (∼10 mm in diameter), 90 mL of hexane, 13 mL of THF, and 46.8 mL (51.5 g, 0.45 mol) of CH_3SiHCl_2. The flask was kept in the ultrasonic bath at 48 °C for 16 h. After termination of ultrasonication, the solids were filtered and washed three times with 30-mL portions of hexane. The clear filtrate was trap-to-trap distilled yielding, as residue, 13.9 g (0.32 mol, 71%) of translucent oil, which was soluble in most common organic solvents. The solids (NaCl and Na) weighed 60.0 g. Out of the 60.0 g of solids, 44.0 g of yellow NaCl (removed by detaching NaCl crystals from unreacted Na metal) that contained internally entrapped high molecular weight polymer was placed in a 300-mL round-bottomed flask equipped with a magnetic stir bar. Subsequently, 200 mL of deoxygenated water (argon was bubbled through it for 1 h) was cannulated in *very slowly* to avoid overly exothermic reactions that might be caused by traces of unreacted Na metal. During the water addition, the flask contents warmed to ∼80 °C. The resulting suspension of a fluffy white solid was stirred overnight at room temperature. The solid was filtered and subsequently dried *in vacuo*. The solid was redissolved in 100 mL of toluene to separate it from any remaining NaCl. After filtration, the filtrate was trap-to-trap distilled, leaving 1.9 g (10% yield) of a white, pyrophoric solid that was soluble in most common organic solvents. ^{1}H NMR (300 MHz, C_6D_6): δ 0.6 ($W_{1/2}$ = 90 Hz, 4.6 H, SiC**H**$_3$), 4.1 ($W_{1/2}$ = 75 Hz, 1.0 H, Si**H**, Si**H**$_2$), CH/SiH = 4.6. IR (thin film, NaCl, cm^{-1}): 2955-(s), 2893(s), 2794(w), 2078(vs), 1913(w), 1408(m), 1248(s), 1035-(vw), 931(m), 864(vs), 764(vs), 684(vs), 644(s), 587(m). Ceramic

residue yield (TGA) (10 °C/min, 600 °C, Ar): 77% brown ceramic. Anal. found: C, 23.71; Si, 63.49; H, 8.27; Na, 0.14; $\sum$ = 95.61%; calcd for $(CH_3SiH_x)_{0.65}(CH_3Si)_{0.35}$: C, 27.43; Si, 64.15; H, 8.42. Analysis of ceramic (1500 °C, Ar): C, 27.27; Si, 65.43; $\sum$ = 92.70%; calcd for SiC: C, 29.95; Si, 70.05.

Extended Reaction Time Experiment of CH_3SiHCl_2 and 2.5 Na in 7/1 (v/v) Hexane/THF by Ultrasonic Activation. Synthesis of PMS-2. A 200-mL Schlenk tube was charged with 14.6 g (0.635 mol) of shiny Na metal (~5 mm in diameter), 52.3 mL of hexane, 7 mL of THF, and 26 mL (28.6 g, 0.249 mol) of CH_3SiHCl_2. As soon as the chlorosilane was added, the Na surface turned black. The flask then was placed in the ultrasonic bath operating at 47 °C for 64 h. After termination of ultrasonication, the solids were filtered and washed three times with 50-mL portions of toluene. The yellow filtrate was trap-to-trap distilled leaving 4.6 g (0.104 mol, 42%, rest of the product was insoluble) of a light-yellow solid that was pyrophoric and soluble in most common organic solvents. ^{1}H NMR (300 MHz, C_6D_6): δ 0.5 ($W_{1/2}$ = 60 Hz, 9.0 H, SiC**H**$_3$); 4.2 ($W_{1/2}$ = 90 Hz, 1.0 H, Si**H**, Si**H**$_2$), CH/SiH = 9.0. ^{29}Si NMR (59.59 MHz, C_6D_6): δ_{Si} −64 ($W_{1/2}$ = 400 Hz, **Si**H); −60 (trace peak, **Si**H$_2$). Ceramic residue yield (TGA): 80%. Analysis of ceramics (1500 °C, Ar): C, 26.22; Si, 68.65; $\sum$ = 94.87%; calcd for SiC: C, 29.95; Si, 70.05.

Extended Reaction Time Experiment of CH_3SiHCl_2 and 2.5 Na in 7/1 (v/v) Toluene/THF by Ultrasonic Activation. Synthesis of PMS-2. A 300-mL Schlenk tube was charged with 14.6 g (0.635 mol) of shiny Na metal (~10 mm in diameter), 52.3 mL of hexane, 7 mL of THF, and 26 mL (28.6 g, 0.249 mol) of CH_3SiHCl_2. As soon as the chlorosilane was added, the Na surface turned black. The flask was placed in the ultrasonic bath operating at 47 °C for 43 h. After termination of ultrasonication, the solid phase was filtered and washed three times with 50-mL portions of toluene. The yellow-orange filtrate was trap-to-trap distilled, yielding 5.6 g (0.127 mol, 51%) of yellow-orange solid that was pyrophoric in air and soluble in most common organic solvents. The remaining 49% of the product was insoluble. ^{1}H NMR (300 MHz, C_6D_6): δ 0.5 ($W_{1/2}$ = 60 Hz, 7.35 H, SiC**H**$_3$); 4.2 ($W_{1/2}$ = 120 Hz, 1.0 H, Si**H**, Si**H**$_2$), CH/SiH = 7.35. IR (thin film on NaCl, cm^{-1}): 2953(s), 2889(s), 2790(w), 2065(s), 1893(vw), 1456(w), 1407(m), 1244(s), 1044(s), 930(m), 868(vs), 765(vs), 684(vs), 584(w), 466(m). Ceramic residue yield (TGA): 87%. Anal. Found: C, 25.24; H, 7.21; calcd for $(CH_3SiH_x)_{0.41}(CH_3Si)_{0.59}$: C, 27.67; H, 7.86. Analysis of ceramics (1500 °C, Ar): C, 27.39; Si, 66.93; $\sum$ = 94.32%; calcd for SiC: C, 29.95; Si, 70.05.

Wurtz Coupling Reaction of CH_3SiHCl_2 and 2.05 Na in 7/1 (v/v) Toluene/THF by Ultrasonic Activation and Subsequent Branching of the Oligomer With 0.5 Na. Synthesis of PMS-3. A 300-mL Schlenk flask equipped with an addition funnel containing 64 mL (0.61 mol) of CH_3SiHCl_2 was charged with 29.0 g (1.26 mol) of shiny Na metal (~10 mm in diameter), 105 mL of toluene, and 15 mL of THF. The flask was placed in the ultrasonic bath, and the chlorosilane was added in a dropwise manner over a period of 1.5 h. The mixture was ultrasonicated at 25 °C for 40 h. After termination of ultrasonication, the solids were washed three times with 50-mL portions of toluene, and the washings, together with yellow solution, were cannulated into a thick-walled centrifuge bottle and centrifuged for 1 h. The yellow supernatant solution was trap-to-trap distilled to remove volatiles, leaving 17.1 g (0.39 mol, 64%) of yellow oil as residue. The latter was soluble in most common organic solvents. The oil (17.0 g) was redissolved in 81 mL of toluene and 12 mL of THF. The solution then was cannulated into a 250-mL Schlenk flask containing 4.4 g (0.19 mol) of mirror-clean Na. The flask was placed in the ultrasonic bath at 25 °C for 18 h. After termination of ultrasonication, the solids were washed three times with 50-mL portions of toluene, and the washings, together with yellow-orange solution, were cannulated into a thick-walled centrifuge bottle and centrifuged for 1 h. The yellow-orange supernatant solution was trap-to-trap distilled, leaving 13.2 g (0.30 mol, 77%) of an orange solid that was pyrophoric in bulk and soluble in toluene. Of the toluene-soluble fraction (PMS-3T), ~80% by weight was soluble in hexane (PMS-3H). No melting was observed during pyrolysis of PMS-3. ^{1}H NMR (300 MHz, C_6D_6): δ 0.45 ($W_{1/2}$ = 83 Hz, 9.8 H, SiC**H**$_3$); 4.2 ($W_{1/2}$ = 68 Hz, 1.0 H, Si**H**, Si**H**$_2$), CH/SiH = 9.8. IR (thin film, NaCl, cm^{-1}): 2953(s), 2889(s), 2790(w), 2060(s), 1407(m), 1243(m), 1032(w), 932(w), 864(vs), 760(vs), 680(vs), 638(s). Ceramic residue yield (TGA): 90%. Anal. found: C, 28.54; H, 7.98; Na, 1.45; calcd for $(CH_3SiH_x)_{0.31}(CH_3Si)_{0.69}$:C, 27.66; H, 7.66 (the hexane-extracted polymer (PMS-3H) fraction contained only 0.096% Na); Analysis of ceramics: (1500 °C, Ar): C, 27.07; Si, 70.92; Na, 0.055; $\sum$ = 98.04%; (1000 °C, Ar): C, 24.69; Si, 67.51; Na, 0.68; $\sum$ = 92.88%; calcd for SiC: C, 29.95; Si, 70.05. Analysis of ceramics derived (1500 °C, Ar) from: toluene-extracted fraction (PMS-3T): C, 28.30; Si, 63.27; $\sum$ = 91.57%; and hexane-extracted fraction (PMS-3H): C, 29.34; Si, 66.04; $\sum$ = 95.38%.

Preparation of PMS-3 by Reaction of OMS with 0.5 Na in 7/1 (v/v) Toluene/THF Using Ultrasonic Activation and Subsequent Quenching of the Polymer with CH_3I. A 250-mL Schlenk flask was charged with 14.3 g (0.325 mol) of OMS (CH/SiH = 3.6) clear oil, 3.7 g (0.161 mol) of shiny Na shot, 10 mL of THF, and 75 mL of toluene. The flask was placed in the ultrasonic bath at 25 °C for 20 h (after ~1.5 h, the initially clear solution became yellow-orange). After termination of ultrasonication, the solid were washed three times with 50-mL portions of toluene and the washings, together with yellow-orange solution, were cannulated into a thick-walled centrifuge bottle and centrifuged for 3 h. The yellow-orange supernatant solution was trap-to-trap distilled, leaving 8.5 g (0.19 mol, 60%) of an orange solid as residue was soluble in toluene. The remaining portion of the product was an insoluble gel. ^{1}H NMR (300 MHz, C_6D_6): δ 0.45 ($W_{1/2}$ = 90 Hz, 13 H, SiC**H**$_3$); 4.2 ($W_{1/2}$ = 70 Hz, 1.0 H, Si**H**, Si**H**$_2$), CH/SiH = 13. IR (thin film, NaCl, cm^{-1}): 2951(m), 2889(s), 2057(s), 1405(m), 1242(s), 1032(m), 930(w), 866(vs), 760(vs), 681(vs), 518(w). Anal. Na, 1.72. Ceramic residue yield (TGA): 88%.

In another reaction in which the same ratio of oligomer to Na was used, after only 4.5 h of ultrasonication at 30 °C in a 7/1 (v/v) hexane/THF solution, a 98% yield of yellow-orange solid product, which was soluble in hexane and toluene, was obtained. ^{1}H NMR (300 MHz, C_6D_6): δ 0.5 ($W_{1/2}$ = 90 Hz, 6.0 H, SiC**H**$_3$); 4.1 ($W_{1/2}$ = 105 Hz, 1.0 H, Si**H**, Si**H**$_2$), CH/SiH = 6.0. Ceramic residue yield (TGA): 53%.

In a third reaction in which the same ratio of oligomer to Na was used, after 6.5 h of ultrasonication at 19 °C in a 7/1 (v/v) toluene/THF solution, a 100% yield of yellow-orange solid product, which contain 1.09% Na and which was soluble in hexane, toluene, and benzene, was obtained. ^{1}H NMR (300 MHz, C_6D_6): δ 0.5 ($W_{1/2}$ = 90 Hz, 6.1 H, SiC**H**$_3$); 4.1 ($W_{1/2}$ = 90 Hz, 1.0 H, Si**H**, Si**H**$_2$), CH/SiH = 6.1. Ceramic residue yield (TGA): 83%.

In a fourth experiment in which the same ratio of oligomer to Na was used, after 17.5 h of ultrasonication at 30 °C in a 7/1 (v/v) hexane/THF solution, a 84% yield of yellow-orange solid, which was soluble in hexane and toluene, was obtained. The rest of the product was insoluble. ^{1}H NMR (300 MHz, C_6D_6): δ 0.6 ($W_{1/2}$ = 75 Hz, 8.3 H, SiC**H**$_3$); 4.1 ($W_{1/2}$ = 90 Hz, 1.0 H, Si**H**, Si**H**$_2$), CH/SiH = 8.3. Ceramic residue yield (TGA): 87%.

Quenching of The Living Polymer With CH_3I. A 100-mL Schlenk flask was charged with 2.35 g (0.053 mol) of PMS (CH/SiH = 13) yellow-orange solid prepared as already described and 50 mL of toluene. The flask then was charged with 5.0 mL of CH_3I, and the solution was stirred for 0.5 h at room temperature. The solution and the fine dispersion of NaI, together with three 20-mL toluene washings were cannulated into a thick-walled centrifuge bottle and centrifuged for 1 h. The clear supernatant solution was trap-to-trap distilled, yielding 2.30 g (0.052 mol, 99%) of a white solid, which was soluble in toluene and pyrophoric in bulk. The amount of NaI was <1 mg. The polymer did not show any melting behavior upon pyrolysis. ^{1}H NMR (300 MHz, C_6D_6): δ 0.45 ($W_{1/2}$ = 90 Hz, 10 H, SiC**H**$_3$); 4.2 ($W_{1/2}$ = 70 Hz, 1.0 H, Si**H**, Si**H**$_2$), CH/SiH = 10. IR (thin film, NaCl, cm^{-1}): 2951(m), 2888(s), 2057(s), 1406(m), 1242(s), 1032(w), 930(w), 867-

(vs), 760(vs), 682(vs), 640(s). Anal. C, 23.61; H, 7.01; Si, 63.55; Na, 1.11; $\sum$ = 95.28%; calcd for $(CH_3SiH_x)_{0.30}(CH_3Si)_{0.70}$: C, 27.71; H, 7.62; Si, 64.67. Ceramic residue yield (TGA): 79%. Analysis of ceramics (1000 °C, Ar): C, 23.67; H, < 0.5; Si, 73.34; Na, 0.45; $\sum$ = 97.46%; (1500 °C, Ar): C, 25.64; H, < 0.5; Si, 72.77; Na, < 0.10; $\sum$ = 98.51%; calcd for SiC: C, 29.95; Si, 70.05.

Coating of an Alumina Substrate With PMS-3H. An alumina substrate was treated at 1000 °C in air for 3 h prior to coating to assure all possible phase changes on its surface. The substrate then was suspended on a wire and submerged into 1 M hexane solution of PMS-3H. The substrate was withdrawn using 0.01 mm/s draw rate (with a modified syringe pump). A uniform yellow film was achieved. The coated substrate was pyrolyzed in argon starting at room temperature and ramping at 5 °C/min to 1000 °C, and held at that temperate for 3 h. After pyrolysis, a brown film was obtained. The film was mostly uniform based on the SEM analysis and was resistant to the scotch tape test.

SiC Fibers from High Molecular Weight PMS (PMS-3H). A viscous solution of PMS-3H in hexane was prepared in the glove box. A spatula was used to manually pull 2−3-cm fibers. The fibers were directly (not requiring curing step) pyrolyzed in an open tube furnace in argon at a rate of 10 °C/min to 1000 °C, where they were kept for 3 h. After pyrolysis, the black fibers were between 1−2 cm in length.

Preparation of Monolithic SiC from PMS-3T. Dry powder of PMS-3T was compressed in a IR KBr press. The yellow-orange pellet (ρ = 0.96 g/cc) was placed in the furnace that was programmed with a heating rate of 10 °C/min an 3 h of dwell at 1000 °C (in argon). After pyrolysis, the pellet (ρ = 2.27 g/cc) had shrunk 70% by volume but retained its shape without any signs of melting. Vickers microhardness of the monolith was 2400 HV.

Reductive Coupling Reaction of CH_3SiHCl_2 and 2.5 Na in Refluxing THF[15]. A 250-mL Schlenk flask equipped with a magnetic stir-bar and a reflux condenser was charged with 7.3 g (0.32 g atom) of mirror-clean Na metal shot (~10 mm in diameter), 30 mL of THF, and 13 mL (0.124 mol) of CH_3SiHCl_2. The reaction mixture was stirred for 16 h at room temperature and was heated at reflux for 48 h. After cooling to room temperature, the solids were washed three times with 20-mL portions of hexane, and the washings, together with blue solution, were cannulated into a thick-walled centrifuge bottle and centrifuged for 1 h. After centrifuging, the supernatant solution became clear and was trap-to-trap distilled, leaving 2.2 g (0.05 mol, 40%) of white solid that was soluble in hexane and toluene. ^{1}H NMR (300 MHz, C_6D_6): δ_H 0.6 ($W_{1/2}$ = 120 Hz, 6.6 H, SiC**H**$_3$), 4.1 ($W_{1/2}$ = 90 Hz, 1.0 H, Si**H**, Si**H**$_2$); poly(THF) impurity 1.7, 3.3 (0.015 H, 0.010 H respectively, C**H**$_2$). IR (thin film, NaCl, cm^{-1}): 2954(s), 2890(s), 2790(w), 2100(vs), 1913(w), 1453(w), 1408(s), 1246(s), 1079(m), 930(s), 865(vs), 769(vs), 683(vs), 587(m), 490(w). Ceramic residue yield (TGA): 55%. Anal. C, 26.96; H, 8.32; calcd for $(CH_3SiH_x)_{0.45}(CH_3Si)_{0.55}$: C: 28.16%; H: 7.47%. Analysis of ceramics (1000 °C, Ar): C, 25.21; Si, 64.20; $\sum$ = 89.41%; calcd for SiC: C, 29.95; Si, 70.05.

Preparation of PMS According to US Patent # 4 537 942 (using CH_3HSiCl_2, Na, in THF and Stirring at Room Temperature)[12]. A 300-mL Schlenk flask equipped with a magnetic stir bar and a reflux condenser was charged with 10.0 g (0.43 g atom) of mirror-clean Na metal shot (~10 mm in diameter), 150 mL of THF, and 20.8 mL (0.198 mol) of CH_3SiHCl_2. The reaction mixture was stirred for 4 days at room temperature. The solids then were washed three times with 20-mL portions of hexane, and the washings, together with blue solution, were cannulated into a thick-walled centrifuge bottle and centrifuged for 1 h. After centrifuging, the clear supernatant solution was trap-to-trap distilled, leaving 3.2 g (0.072 mol, 37%) of white solid that was soluble in hexane and toluene. ^{1}H NMR (300 MHz, C_6D_6): δ_H 0.6 ($W_{1/2}$ = 150 Hz, 5.7 H, SiC**H**$_3$), 4.1 ($W_{1/2}$ = 90 Hz, 1.0 H, Si**H**, Si**H**$_2$); poly(THF) impurity 1.7, 3.3 (0.17 H, 0.18 H respectively, C**H**$_2$). Ceramic residue yield (TGA): 49%.

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