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Borate-Catalyzed Thermolysis of Polymethylsilane

Bruno Boury*

UMR 5637, CC 007, Université Montpellier II, Sciences et Techniques du Languedoc,
34095 Montpellier Cedex 05, France

Nathan Bryson and Gérard Soula

Flamel Technologies Parc Club du Moulin à Vent, 33 av. du G Levy, 69390 Venissieux, France

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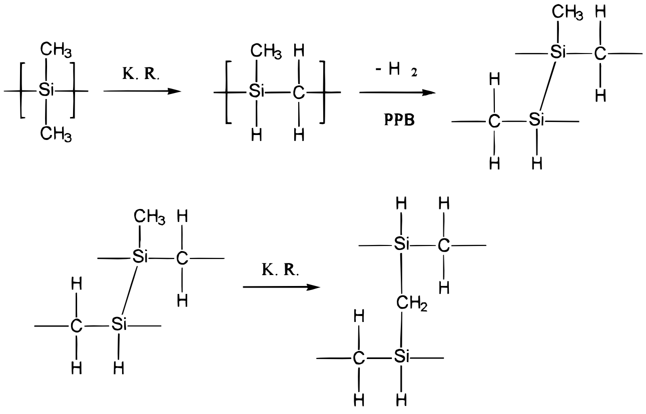
Polymethylsilane (PMS) with a general formula $[-(CH_3SiH)_{1-y}-(CH_3Si)_y-]_n$ has been synthesized by Würtz type polycondensation of methyldichlorosilane. Copolycondensation with dimethylchlorosilane was realized in an attempt to control the viscosity of the PMS. Thermal reactions at 230 °C with small amounts (1 wt %) of boron derivatives such as $B[OSi(CH_3)_3]_3$ serve to cross-link this Si−H-containing organosilicon polymer. As a result, when the products of these reactions are pyrolyzed at 1000 °C under argon, the ceramic residue yields are increased considerably over those obtained with the original polymers.

Introduction

The thermally induced transformation of polydimethylsilane (PDMS) into a polycarbosilane (PCS) is a key step in the production of Nicalon fibers.[1−8] The uncatalyzed reaction is performed at 450 °C in a closed vessel and under pressure. The carbosilane Si−C−Si structure is obtained only after repeated insertion of methyl, methylene, and methyne C−H groups into adjacent Si−Si bonds of the starting polymer; Scheme 1 is a simplified description of this transformation based on the results initally reported by Kumada et al.[9−11] The final polycarbosilane product has been described as a partially dehydrogenated polycyclic network.[12−14]

Scheme 1. Kumada Rearrangement in the Production of Polycarbosilane[a]



[a] K. R. = Kumada rearrangement.

The addition of an organoborate catalyst, such as poly(borodiphenylsiloxane) (PPB), allows the reaction to be conducted at a lower temperature (380 °C) and at ambient pressure.[15,16] According to Ishikawa et al., the boron compound catalyzes the elimination of hydrogen between two Si−H-containing intermediates creating new Si−Si bonds, which further undergo methylene insertion reactions with remaining C−H groups within the polymer.[7,17,18] We thought to use the boron treatment as a means to improve the ceramic performance of liquid polymethylsilane (PMS) based on the repeated structure $[-(CH_3SiH)_{1-y}-(CH_3Si)_y-]_n$ of PMS are easily prepared by Wurtz condensation and exist as liquid and solid precursors, making it possible to use them in numerous applications. These polymers are particularly interesting candidates for the preparation of stoichiometric SiC since they possess a 1-to-1 Si/C ratio in the preceramic state. One drawback, however, is that their low molecular weight leads to low pyrolysis yields (~20%).[19−21] In addition, the obtained ceramic is rich in silicon (C/Si ratio 0.6).

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* E-mail: boury@crit.univ-montp2.fr; Fax number: (+33) 04 67 14 38 88.

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In this respect, cross-linking the polymer into a dense network before pyrolysis should help increase the ceramic yield. In fact, the ceramic yields of PMS have been greatly improved by cross-linking them with vinyl-containing polymers[22,23] or with organometallic catalysts.[24−26] During our investigations on the formulation of PMS with different additives, we found that PMS reacts directly with boron derivatives and that this reaction is useful for increasing the ceramic yield. The results of our study and the characterization of the boron-modified PMS products (B−PMS) are reported herein.

I. Experimental Section

Caution: All of the products are extremely air-sensitive, liquid or viscous oils. In fact, PMS can burn spontaneously in air, particularly when absorbed on paper. We have found previously that the air stability can be improved by the addition of 0.5% 2,6-di-*tert*-butyl-4-methylphenol (BHT) to the polymer mixture, allowing an air stability of 5−10 min. This also decreases the risk of spontaneous ignition.

All manipulations were carried out under nitrogen atmosphere using standard inert-atmosphere techniques. Solvents were distilled from appropriate drying agents under nitrogen prior to use.[27] Commercial methyldichlorosilane was purified by distilling over magnesium under nitrogen. Other reagents were purchased from Aldrich and used as received.

NMR spectra were obtained using a Bruker 300 MHz spectrometer with benzene-d_6 as solvent and internal standard. FTIR spectra were recorded on a Perkin-Elmer PE1700 spectrometer. The products were analyzed neat in KBr pellets. Molecular weights distributions were determined by gel permeation chromatography using a Perkin-Elmer 9010 analyzer and m-Styragel columns (porosity ranges of 100, 500, and 10 000 Å) calibrated with polystyrene standards and with THF as eluent at a flow rate of 0.6 mL/min. Thermal analysis were performed using a Perkin-Elmer TGA 7 with a heating rate of 2, 5, or 10 °C/min under nitrogen at a flow rate of 30 mL/min. Bulk pyrolysis was performed in a Carbolite furnace under nitrogen (30 mL/min).

GC-MS (EI) analyses were performed by the Service Central d'Analyse du CNRS (Solaize, France). Elemental analyses were carried out by Galbraith Laboratories, Inc.

Preparation of Polymethylsilane I. In a typical reaction, a 1 L three-necked, round-bottom Pyrex flask was equipped with a reflux condenser, a vacuum line adapter, a thermometer, and a mechanical stirrer. The apparatus was charged with 450 mL of toluene and 85.0 g of Na (3.69 mol). The mixture was heated to 100 °C and stirred vigorously to obtained a sodium dispersion. Addition of 160.0 mL of methyldichlorosilane (1.53 mol) was performed with a syringe at a flow rate of 20 mL/h. The addition of chlorosilane caused the temperature to increase to 104−106 °C, and the surface of the sodium turned brown. After complete addition of the chlorosilanes, the mixture was stirred for 4 h at 104−106 °C and then cooled to room temperature. The solid was eliminated by filtration and washed with toluene. The combined organic layers were mixed and the solvent was removed by trap-to-trap distillation at 30 °C under high vacuum, yielding 44.5 g of a yellow oil, 65.9%. ^{1}H NMR (C_6D_6; 300 MHz; δ, ppm) 3.8−4.4 (0.55 H, br multiplet); 1.4 (0.1 H br multiplet); 0.1−0.9 (3H, br multiplet). ^{13}C NMR (C_6D_6; 50.3 MHz; δ, ppm) 35.0; 31.3; 22.3; −2.0 to −11 (br multiplet). ^{29}Si NMR (C_6D_6; 39.7 MHz; δ, ppm) −35.5 (br multiplet); −32.3 (br multiplet); −50 to −70 (br multiplet). FTIR (neat, cm^{-1}) 2956; 2894; 2799; 2060; 1410; 1247; 931; 870; 766; 687; 588. Proposed formula: $[-(SiH(CH_3))_{0.55}-(Si(CH_3))_{0.45}-]$.

Preparation of Polymethylsilane II. In a typical reaction, a 1 L three-necked, round-bottom Pyrex flask was equipped with a reflux condenser, a vacuum line adapter, a thermometer and a mechanical stirrer. The apparatus was charged with 25 mL of tetrahydrofurane, 140 mL of hexane, and 43.0 g of Na (1.87 mol) cut as small cubes. The mixture was heated to 65 °C and slowly stirred while 95.0 mL of methyldichlorosilane (0.91 mol) were added with a syringe over a period of 3 h. A mild reflux is observed. After complete addition of the chlorosilane, the mixture was maintained at reflux for 6 h and then cooled to room temperature. The salts were separated as a white solid and were filtered and washed with hexane. The combined organic layers were mixed and the solvent was removed by trap-to-trap distillation at 30 °C under high vacuum, yielding 26.2 g of a clear colorless oil (yield 65.2%). ^{1}H NMR (C_6D_6; 300 MHz; δ, ppm): 3.8−4.4 (0.68 H, br multiplet); 1.4 (0.15 H, br multiplet); 0.1−0.9 (3H, br multiplet). FTIR (neat, cm^{-1}) 2956; 2894; 2799; 2060; 1410; 1247; 931; 870; 766; 687; 588. Proposed formula $[-(SiH(CH_3))_{0.68}-(Si(CH_3))_{0.32}-]$.

Preparation of Polymethylsilane III. In a typical reaction, a 1 L three-necked, round-bottom Pyrex flask was equipped with a reflux condenser, a vacuum line adapter, a thermometer, and a mechanical stirrer. The apparatus was purged and charged with 200 mL of toluene, 20 mL of tetrahydrofurane, and 42.0 g of Na (1.83 mol). The mixture was heated to 100 °C and stirred to obtained a sodium dispersion. Addition of 76.0 mL of methyldichlorosilane (0.72 mol) was performed with a syringe at a flow rate of 20 mL/h. It led to an increase of the temperature to 104−106 °C, and the surface of the sodium turned dark blue. After complete addition of the chlorosilane, the mixture was stirred for 4 h at 104−106 °C and then cooled to room temperature. A brown solid was eliminated by filtration and washed with toluene. The combined organic layers were mixed and the solvents were removed by trap-to-trap distillation at 30 °C under high vacuum, yielding 19.4 g of a viscous yellow oil (yield 61.0%). ^{1}H NMR (C_6D_6; 300 MHz; δ, ppm) 3.8−4.4 (0.67 H, br multiplet); 1.4 (0.15 H, br multiplet); 0.1−0.9 (3H, br multiplet). FTIR (neat, cm^{-1}) 2956; 2894; 2799; 2060; 1410; 1247; 931; 870; 766; 687; 588. Proposed formula: $[-(SiH(CH_3))_{0.67}-(Si(CH_3))_{0.33}-]$. Elemental analysis for residual chlorine: 0.45%.

Preparation of Polymethylsilane IV. In a typical reaction, a 1 L three-necked, round-bottom Pyrex flask was equipped with a reflux condenser, a vacuum line adapter, a thermometer and a mechanical stirrer. The apparatus was purged and charged with 200 mL of toluene, 20 mL of dioxane, and 42.0 g of Na (1.84 mol). The mixture was heated to 100 °C and stirred to obtain a sodium dispersion. Addition of a mixture of 76.0 mL of methyldichlorosilane (0.73 mol) and dimethylchlorosilane was performed with a seringe at a flow rate of 20 mL/h. 1.8 mL and 3.5 mL of dimethyldichlorosilane were used respectively for PMS IVb and PMS IVc; no dimethylchlorosilane was used for PMSIVa. The addition of chlorosilane caused the temperature to increase to 104−106 °C. After complete addition of the chlorosilanes, the mixture was stirred for 4 h at 104−106 °C and then cooled to room temperature. The blue-black solid was eliminated by filtration and washed with toluene. The combined organic layers were mixed and the solvents were removed by trap-to-trap distillation at 30 °C under vacuum, yielding the PMS as a viscous yellow oil; the yield ranged from 70.1 to 77.0%. Spectroscopic characterization of PMS IVa is given below; similar results are observed for PMS VIb and VIc. ^{1}H NMR (C_6D_6; 300 MHz; δ, ppm) 3.8−4.4 (0.67 H, br multiplet); 1.4 (0.15 H, br

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Table 1. Characterization of PMS I, II, III, and IV

PMS	reaction solvent	ratio $(CH_3)_2HSiCl/(CH_3)HSiCl_2$	yield (%)	y	viscosity (cP)	M_n	M_w
I	toluene	0	66	0.45	5500	240	500
II	15% THF−hexane	0	65	0.32	1000	310	1250
III	15% THF−toluene	0	62	0.33	3500		
IVa	20% dioxane−toluene	0	77	0.48	>35000	845	1725
IVb		0.023	71	0.50	3200	650	1300
IVc		0.045	70	0.45	975	790	1350

multiplet); 0.1−0.9 (3H, br multiplet). FTIR (neat, cm^{-1}) 2956; 2894; 2799; 2060; 1410; 1247; 931; 870; 766; 687; 588. Proposed formula: $[-(SiH(CH_3))_{0.67}-(Si(CH_3))_{0.33}-]$. Elemental analysis for residual chlorine: 0.40%

Thermolysis of the Polymethylsilane. All thermal treatments of the different polymethylsilanes were performed similarly, differing only by the duration of the treatment. In all cases, the thermolysis was stopped when the initially liquid mixture solidified and was no more stirrable. An example is given below for the thermolysis of a mixture of PMS I and $B[OSi(CH_3)_3]_3$. Results of NMR analysis are given in the text.

Thermolysis of PMS I with $B[OSi(CH_3)_3]_3$. A Schlenk tube equipped with a magnetic stirrer and a thermometer was charged with 3.52 g of polymethylsilane (44.4 mmol of Si−H) and 0.15 mL of $B[OSi(CH_3)_3]_3$ (0.4 mmol). The mixture is stirred at room temperature for 5−10 min and then heated by plunging into an oil bath at 240 °C. Gas evolution increases slowly during the time course of the reaction. Vapors are observed on the cold part of the Schlenk. After approximatively 40 min, the liquid starts to thicken and is soon after nearly rigid (not stirrable). The reaction is cooled immediately leaving 3.08 g of a yellow solid (yield: 87%). ^1H NMR (C_6D_6; 300 MHz; δ, ppm) 3.8−4.4 (0.40 H, br multiplet); 1.4 (0.1 H, br multiplet); 0.1−0.9 (3H, br multiplet). ^{13}C NMR (C_6D_6; 50.3 MHz; δ, ppm) 35.0; 31.3; 22.3; 1.7; −2 to −11 (br multiplet). ^{29}Si NMR (C_6D_6; 39.7 MHz; δ, ppm) −35.5 (br multiplet); −32.3 (br multiplet); −50 to −70 (br multiplet). FTIR (neat, cm^{-1}) 2956; 2894; 2799; 2060; 1410; 1247; 931; 870; 766; 687; 588. Proposed formula $[-(SiH(CH_3))_{0.40}-(Si(CH_3))_{0.60}-]$.

Thermolysis of PMS I without $B[OSi(CH_3)_3]_3$. Using the same conditions described above, 3.52 g of polymethylsilane (44.4 mmol of Si−H) were thermolyzed over a period of 4 h to give 3.41 g of a yellow oil (97%).

Thermolysis of PMS I with $B[O(CH_2CH_3)]_3$. As described above, 1.65 g of polymethylsilane were thermolyzed in the presence of 0.06 mL of triethylborate (0.3 mmol). After 2 h, 1.49 g of a yellow sticky paste is obtained (90%).

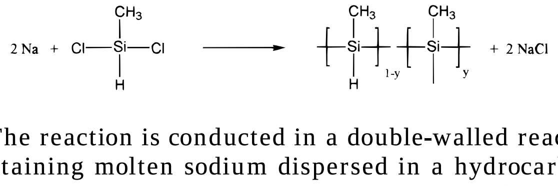
Thermolysis of PMS I with $B(N(CH_3)_2)_3$. Using the same conditions, 2.21 g of polymethylsilane (27.8 mmol of Si−H) were thermolyzed in the presence of tris(dimethylamino)boron (0.08 mL, 0.4 mmol). After 1.5 h, 1.98 g of a yellow solid is recovered (89%).

Thermolysis of PMS I with $B(OCH_2CH_2)_3N$. Using the same conditions, 3.50 g of polymethylsilane (44.1 mmol of Si−H) was thermolyzed in the presence of triethanolamineborate 0.12 mL (0.6 mmol). After 1.5 h, 3.19 g of a yellow tacky solid is recovered (91%).

II. Results

II.1. PMS Preparation and Characterization. The polymethylsilanes (PMS) used in this study were prepared by sodium polycondensation of dichloromethylsilane. The reaction is shown schematically as follows:

equation 1 Wurtz polycondensation of methyldichlorosilane



The reaction is conducted in a double-walled reactor containing molten sodium dispersed in a hydrocarbon solvent. In our hands, an ether cosolvent (THF or dioxane) is crucial to ensure the initiation of the polycondensation reaction. In the absence of an ether, the reagents react only after a certain amount of chlorosilane has accumulated in the reaction mixture. As the reaction is initiated, heat is liberated, causing the reaction to reflux. Since the addition of the chlorosilane (or mixture of chlorosilanes) is performed over a period of ~60 min, the temperature must be maintained by simultaneously controlling the rate of chlorosilane addition and the temperature of the outer cooling jacket (50−80 °C). Four different experimental procedures were used to prepare PMS polymers, differing mainly by the choice of the solvent. Relative to PMS I, II, and III, PMS IV was prepared with a mixture of two chlorosilanes; the monomer HMe_2SiCl limits the size of the growing polymer chain.

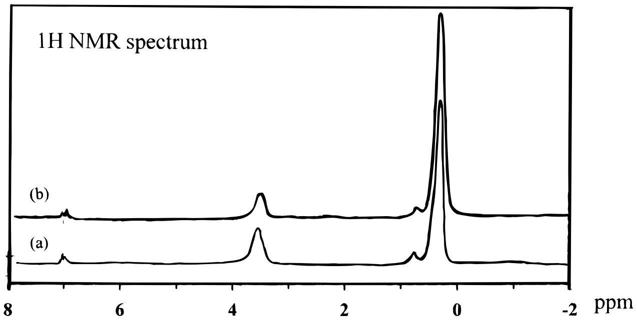


Figure 1. ^1H NMR of PMS I (a) starting PMS I and (b) B−PMS I after 2 h at 240 °C with 3% of $B(OSi(CH_3)_3)_3$.

The polymer is isolated from the reaction mixture after filtration of the insoluble salts and the excess of sodium and evaporation of the solvent. The resulting clear-to-yellow oil is particularly air sensitive and can ignite in the air when absorbed onto paper. We have found that the air stability can be improved by the addition of 0.5% of 2,6-di-*tert*-butyl-4-methylphenol (BHT) to the polymer.[28] The formulated polymer has an air stability of 5−10 min before oxidation begins. This method also decreases the risk of spontaneous ignition of the polymer. The characteristics of the polymers prepared are presented in Table 1.

It should be noted that GC-MS analysis shows methylsilane CH_3SiH_3 in the headspace of the reaction. Thus, care should be taken when handling the byproducts of a large-scale synthesis of PMS.

A typical ^1H NMR spectrum is shown in Figure 1. Resonances are observed in two discrete regions 0.5−1.5 and 3.0−5.0 ppm, corresponding to methyl and hydride functions, respectively. In the case of PMS IV, the Si−H resonance of the chain-end blocker is not distinguishable from the hydride group of the main chain. Integration of the two regions shows that a portion of the Si−H groups are consumed during the condensation reaction. From NMR integration, the

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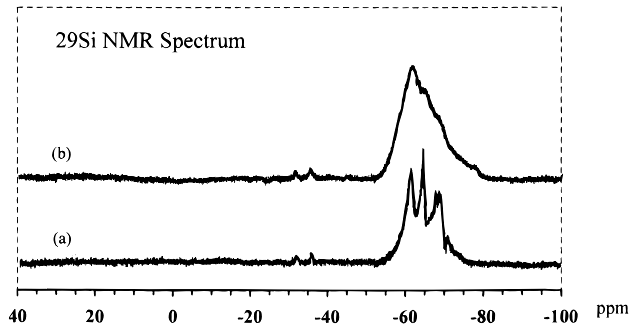

Figure 2. ^{29}Si NMR of PMS I (a) starting PMS I and (b) B−PMS I after 2 h at 240 °C with of 3% of $B(OSi(CH_3)_3)_3$.

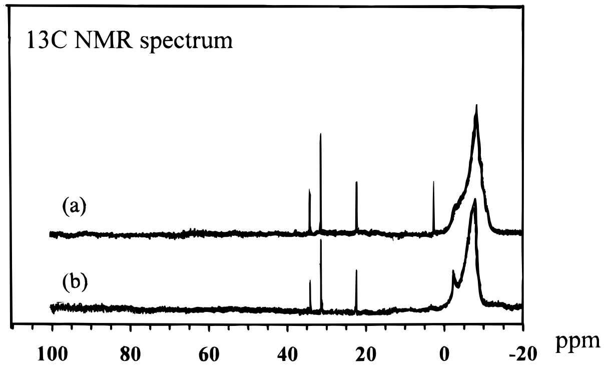

Figure 3. ^{13}C NMR of PMS I (a) starting PMS I and (b) B−PMS I after 2 h at 240 °C with 3% of $B(OSi(CH_3)_3)_3$.

PMS formula is given as $[\text{-}(CH_3SiH)_{1-y}{-}(CH_3Si)_y{-}]_n$ where *y* gives the proportion of dehydrogenated, trifunctional $=Si(CH_3)-$ units. The silicon units are also observed in the ^{29}Si NMR spectra as shown in Figure 3, three broad signals are observed from −75 to −55 ppm attributed mainly to the different Si units $-CH_3$-$SiH-$ and $-CH_3Si=$. However, ^{29}Si NMR analysis using a DEPT decoupling sequence indicate that some signals in this multiplet might be attributed to the presence of $-SiH_2(CH_3)$ units.

In addition, ^{13}C NMR spectroscopy presentes broad signals centered at −9.2 corresponding to CH_3 groups of the polymethylsilane structure as shown in Figure 2; NMR analyses indicate the presence of other groups albeit in very low proportions: signals at 22, 32, and −35 ppm in the ^{13}C NMR spectrum and signals at −32 and −35 ppm in the ^{29}Si NMR spectrum are possibly attributable to small amounts of $Si-CH_2-Si$, $Si-CH_2-Si$ or $Si-CH_2Cl$ groups. These are neglected in the description of the structure.

The molecular weights of the PMS were determined by GPC using THF as the eluting solvent and polystyrene molecular weight standards. As can be seen in Table 1, the molecular weights of the polymers are quite low, M_n ranging from 200 to 800 (DP ~ 17), while M_w varies from 500 to 1750. The highest molecular weight are obtained for PMS prepared in dioxane/toluene solvent mixture (20/80; PMS IV). Comparison of the different polymers IV, the amount of chain blocker in the synthesis is important for determining the molecular weight and the viscosity of the polymer.

When heated in a Schlenk tube (in the absence of a boron additive), all of the PMS products are stable up to 300 °C. No modification of the mass, viscosity, or the spectra from NMR or IR is observed after 10 h at this temperature. There is however a slight refluxing of oligomers during such a treatment. As a result, when the polymer is heated in a TGA apparatus, having nitrogen which sweeps the pyrolysis zone, a continuous weight loss of ~40% is observed between room temperature and 250 °C due to the distillation of oligomers.

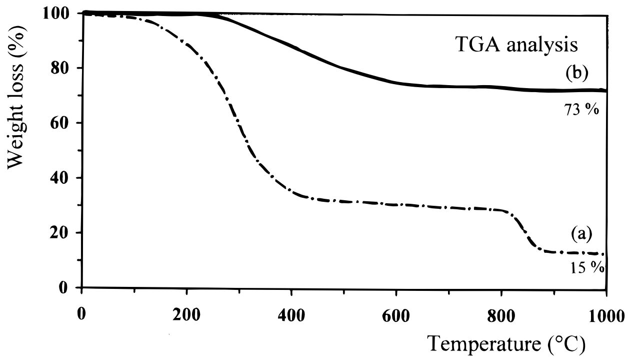

Figure 4. TGA analyses of PMS I before and after thermolysis at 240 °C with 3% of $B(OSi(CH_3)_3)_3$ (a) starting PMS I and (b) B−PMS I after 2 h at 240 °C. Pyrolysis conditions: 5 °C/min, N_2 flow 30 mL/min.

II.2. Thermolysis Catalyzed by Borate Compound. Each of the different PMS products was in turn mixed with borate additives such as $B[OSi(CH_3)_3]_3$, tris(trimethylsilyl)borate ($BTMS_3$). As a general rule, the PMS all form stable homogeneous mixtures with this boron compound, which can be stored, in the absence of air, for several months at room temperature without any significant change in the viscosity or the NMR spectrum. The mixture is also stable up to 200 °C for more than 5 h.

When a ($BTMS_3$ + PMS) mixture is heated to 220 °C, a reaction ensues within 5−10 min. Gas is released from the mixture, causing the material to foam and the polymer progressively becomes viscous, eventually solidifying as the reaction is allowed to continue. From the thermogravimetric analysis presented in Figure 4, weight loss occurs for up to 10 h at 230 °C in the borate catalyzed reaction. The final yield of this thermolysis ranges from 95 to 90% and the resin obtained after 10 h of treatment at 230 °C can be pyrolyzed to give an optimized final ceramic yield of 70−80%.

An identical ceramic yield can also obtained by pyrolyzing the inital boron-PMS mixture (untreated) from room temperature to 950 °C at a heating rate of 1 °C/min or less. It is particularly important to have a slow heating rate in the temperature range where cross-linking occurs and methylsilane is released (200−350 °C). At higher heating rates the yields are somewhat lower; these results are reported in Table 2.

PMS I was used to determine the influence of the concentration of the boron additive on the ceramic yield. The amount of borate was varied over a range of 1−4%. The reaction time necessary for the completion of the thermolysis treatment remained unchanged for all of the samples. The results presented in Table 3, indicate that the variation of the ceramic yields, between 63 and 69%, is rather low for this range of concentration.

We also tested the activity of other boron compounds, such as $B(OCH_2CH_3)_3$, $B(OCH_2CH_2)_3N$ and $B(N(CH_3)_2)_3$, as well as the aluminum compounds $Al(OCH_2CH_3)_3$ and $AlCl_3$. These compounds were reported by Dunoguès et al. to be efficient for the thermal treatment of

Table 2. Ceramic Yields of B−PMS I, II, and III with and without Boron Additive

starting polymethylsilane	ceramic yield of boron-free PMS[a]	ceramic yield of B− PMS[a]	ceramic yield of B− PMS[b]
PMS I	16%	72.1%	77.0%
PMS II	15%	55.0%	62.5%
PMS III	22%	73.0%	77.0%
PMS IVa	18%	72%	
PMS IVb		71%	
PMS IVc		73%	

[a] Bulk pyrolysis in furnace heating rate 5 °C/min from 20 to 950 °C under argon. [b] Bulk pyrolysis in furnace, heating rate 1 °C/min from 20 to 950 °C under argon.

Table 3. Ceramic Yields of B−PMS I with Various Concentrations of $B[Si(O(CH_3))_3]_3$

catalyst concn (weight %)	y^a	yield of preparation[b]	ceramic yield of B−PMS	cumulative ceramic yield[c]
none			16.0%	16%
1.2%	0.65	88%	73.7%	65%
2.1%	0.65	94%	73.1%	69%
3.0%	0.65	87%	72.1%	63%
4.4%	0.60	91%	72.2%	66%

[a] After boron treatment, determined by NMR integration. [b] Treatment 10 h, 230 °C under nitrogen. [c] Cumulative ceramic yield is the product of the yield of the B treatment and the pyrolysis.

Table 4. Ceramic Yields of B−PMS I with Various Catalysts

catalyst	catalyst concn[a]	yield of preparation[d]	y^e	ceramic yield[b]	cumulative ceramic yield[c]
$B(OSi(CH_3)_3)_3$	3.0%	87%	0.59	72%	63%
$B(OCH_2CH_3)_3$	2.9%	90%	0.66	71%	64%
$B(OCH_2CH_2)_3N$	3.1%	91%	0.59	73%	66%
$B(N(CH_3)_2)_3$	3.0%	89%	0.65	73%	65%

[a] Weight %. [b] Bulk pyrolysis up to 950 °C at a heating rate 5 °C/min under argon. [c] Cumulative ceramic yield is the product of the yield of the borate catalyzed thermolysis. [d] Treatment: 3 to 4 h at 230 °C under nitrogen. [e] After Treatment Boron Treatment.

Table 5. Elemental Analysis of PMS and Ceramic

polymer precursor	C %	H %	Si %	total
starting PMS				
PMS I	26.0	8.3	59.0	93.3
PMS thermolyzed[a]				
PMS I without Borate	20.5	6.4	46.5	73.4
B−PMS I	17.7	5.0	43.0	65.8
after pyrolysis[b]				
PMS I	23.9	<0.3	72.7	96.9
PMS I without borate	24.0	<0.3	73.7	98.0
B−PMS I	24.1	<0.3	73.6	98.0
B−PMS II	26.8	<0.3	71.4	98.4

[a] Treatment 3−4 h at 230 °C under nitrogen. [b] Bulk pyrolysis up to 950 °C at a heating rate 5 °C/min under argon.

polydimethylsilane.[16] As can be seen from the results in Table 4, all of the boron compounds effectively increase the ceramic yield relative to boron-free PMS, while the aluminum compounds do not. There is no significant difference in the ceramic yield between the boron catalysts.

Analyses of the ceramic residues obtained from pyrolysis are reported in Table 5, it shows that the elemental compositions are close to those obtained with PMS alone, suggesting that the boron probably does not modify the nature of the ceramic. The level of boron in the final ceramic residue can be estimated to 0.17% if there is a complete conservation of this element during the pyrolysis.

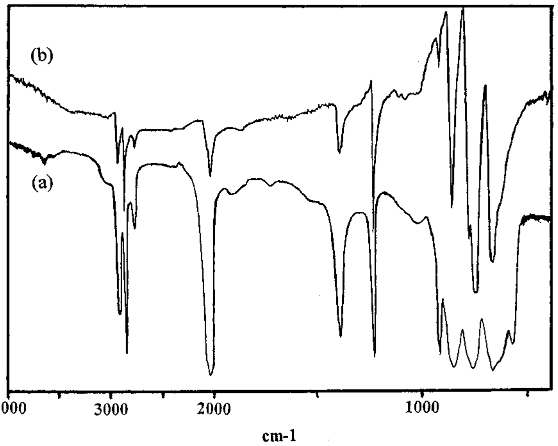

Figure 5. FT-IR spectrum of PMS (a) starting PMS I and (b) B−PMS I after 2 h at 240 °C with 3% of $B(OSi(CH_3)_3)_3$.

To characterize the boron-catalyzed cross-linking reaction, the thermolysis was performed at 230 °C and subsequently at 380 °C in order to identify the mechanisms governing the increases in ceramic yields observed. The products obtained after different thermal treatments were characterized by NMR, FTIR, and GC-MS. When a borate−PMS mixture is heated at 230 °C for 10 h, the resinous material obtained is insoluble in the most common organic solvents and cannot be analyzed by NMR. However, when the reaction is stopped after 2 h at this temperature, the B−PMS obtained can be solubilized in chloroform for analysis.

The ^1H NMR spectra of B−PMS products treated for 2 h with $BTMS_3$ is presented in Figure 1, it shows no new signals when compared with the starting materials. However there is a marked increase in the proportion of $-(CH_3Si)-$ groups corresponding to an increase in y for the formula $[-(CH_3SiH)_{1-y}-(CH_3Si)_y-]_n$, from ∼0.32−0.45 in the starting polymer to nearly 0.6 after 2 h at 230 °C. The final value of y remains relatively constant from run to run. ^{13}C and ^{29}Si NMR spectra of the borate-treated products show similar signals but broadened (Figures 2 and 3). From a qualitative point of view, FTIR analysis of the resin showed a marked decrease in the Si−H peak at 2070 cm^{-1} relative to the other peaks in the spectrum (Figure 5); no other new signal is observed. Finally, the GPC analysis shows a net increase in the molecular weight by a factor of 2−3 and a clear increase of the polydispersity index M_w/M_n.

The gases evolved during the thermolysis of PMS I−IV were qualitatively analyzed by FTIR, which shows that the most prevalent product in the gaseous mixture was probably methylsilane $MeSiH_3$. Confirmation was obtained by GC-MS on PMS IV, where this gas was observed along with some $(CH_3)_2SiH_2$, and minor peaks corresponding to dimeric ($(CH_3)_2Si_2H_4$), trimeric ($(CH_3)_3Si_3H_5$), and tetrameric ($(CH_3)_4Si_4H_6$) methylsilanes.

If this boron-treated polymethylsilane is further heated to 380 °C under nitrogen, completely insoluble products are obtained. Their characterization by FTIR spectroscopy presents two new signals at 1344 and 1050 cm^{-1}, simultaneously we note an increase of the inten-

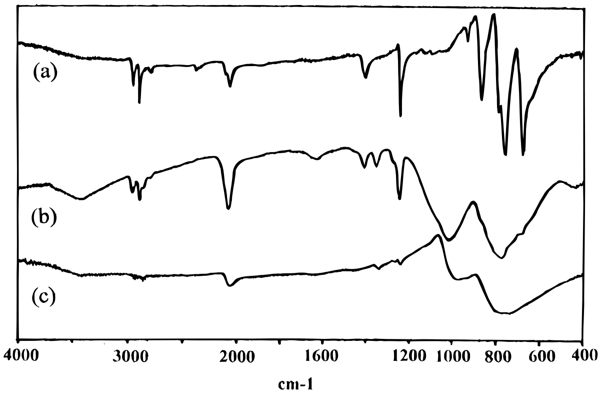

Figure 6. FT-IR spectrum of B−PMS I with 3% of $B(OSi(CH_3)_3)_3$: (a) B−PMS I after 2 h at 300 °C, (b) B−PMS I after 2 h at 300 °C + 1 h at 380 °C, and (c) B−PMS I after 2 h at 300 °C + 1 h at 380 °C + 1 h at 460 °C.

sity of the signal at 2060−2080 cm^{-1} corresponding to Si−H (Figure 6).

III. Discussion

Our research has been oriented toward the optimization of a low-viscosity, liquid precursor with a high ceramic yield. The preparation of polymethylsilane by Wurtz polycondensation of methyldichlorosilane was already reported to give oligomers of general formula $[-(CH_3SiH)_{1-y}-(CH_3Si)_y-]_n$. The formation of gaseous methylsilane during this reaction and accounts for the lack of Si−H function in the PMS. Methylsilane is probably formed by redistribution of silicon−halide and silicon−hydride bonds. This reaction can also explain the presence of $-SiH_2(CH_3)$ units in the PMS as shown by ^{29}Si NMR spectroscopy. For PMS of high viscosity, as with PMS IV, methylchlorosilane mixed to the initial monomer can be used to reduce the viscosity by lowering the molecular weight without substantially modifying y. The type and the concentration of the ether used as cosolvent, dioxane, and THF can modify the viscosity of the PMS and the y value; however, their action is not clearly understood at that time.

$$(-[\mathrm{SiH(CH_3)}]_{0.6}-[\mathrm{Si(CH_3)}]_{0.4}-)_n \rightarrow (-[\mathrm{SiH(CH_3)}]_{0.4}-[\mathrm{Si(CH_3)}]_{0.6}-)_{2n} + 0.1n\mathrm{CH_3SiH_3} \quad (2)$$

Looking at detail into the synthesis and pyrolysis of a typical PMS prepared by Wurtz coupling, it appears that the low ceramic yield is largely due to the distillation of the volatile oligomers from the polymer as it is heated during the pyrolysis. The distillation is further aided by the nitrogen flow in a TGA apparatus. It might thus appear incompatible to have a low molecular weight, fluid PMS product, which does not distill from the pyrolysis zone and which gives high ceramic yields.

To improve the ceramic yields and eventually the ceramic composition of PMS, we have investigated the use of a number of different types of additives that might promote cross-linking of the polymer. For the ease of use of the material, we preferred additives that do not act at room temperature or require UV activation, since both of these ways complicate composite manufacturing processes. Our original tests were performed on PMS to which have been added up to 5 wt % of an organotransition-metal catalyst, such as a metal carbonyl or a biscyclopendadienyl compound.[29] Because these additives were not efficient or their reaction could not be controlled, they were therefore considered uninteresting from the viewpoint of developing a class of stable, liquid polymers for composite infiltration.

In contrast, $BTMS_3$ is totally miscible with PMS and the mixture is very stable at room temperature. The B−PMS mixture can be hardened at 230 °C to give a resin that can be pyrolyzed with very good ceramic yields. This system was thus investigated further in order to identify the mechanisms responsible for the improved performance. When boron-containing PMS is heated at 230 °C over a period of 10 h, the mixture loses up to 10−12% of its weight and the resin becomes insoluble. Intermediate analysis of the B-treated resin shows a decrease in the amount of Si−H groups relative to $-(CH_3Si)_y=$ groups and an increase in molecular weight, both of which are indicative of cross-linking. For different B−PMS the spectroscopic analyses indicate a slightly modified PMS compound $[-(CH_3SiH)_{1-y}-(CH_3Si)_y-]_n$ with y close to 0.6; probably because the reaction is stopped when the mixture starts to solidify which correspond to a certain degree of "cross-linking", we obtain approximately the same for all the B−PMS samples. The loss of hydrogen from the polymer can be attributed predominantly to methylsilane $(CH_3)SiH_3$, as well as di-, tri-, and tetramethylsilanes, all of which are observed in the gas phase over the sample held at 230 °C. When the "loss of hydrogen", which is the change in the value y, is attributed entirely to methylsilane, the balanced eq 2 is in good agreement with the weight loss observed after a 2 h reaction period.

Note that under the conditions described here, no reaction was observed between $BTMS_3$ and polydimethylsilane $-((CH_3)_2Si)_n-$ or with other polysilane devoid of Si−H groups. Furthermore, when the ($BTMS_3$ + PMS) mixture is heated below 300 °C, we were unable to find any sign that could be attributed to methylene insertion as could be attributed to the Kumada reaction. In fact, for both boron-cross-linked PMS and boron-free PMS, the Kumada rearrangement occurs at 380 °C, where the FTIR analyses indicate an increase of the Si−H signal intensity, and the simultaneous presence of two new signals corresponding to the $Si-CH_2-Si$ deformation (1050 cm^{-1}). These results indicate that the boron has little or no influence on the course of this reaction. In addition, the borate-catalyzed thermal treatment has almost no effect on the elemental analysis of the ceramic material obtained at 1000 °C.

It thus appears that boron compounds catalyze the disproportionnation reaction between Si−Si and Si−H bonds which leads to the formation of "hydrogen-rich" gaseous silanes and dehydrogenated resins. Similar reactions are well documented in the organosilicon chemistry literature.[30,31] The redistribution of Si−Si and Si−H bonds was investigated by Ring et al.[32,33] and

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[29] Boury, B.; Bryson, N.; Soula, G., unpublished resulted.

[30] Chvalovsky, V. *Organometallic reactions*; Becker, E., Tsutsui, M., Eds.; Wiley-Interscience: New York, 1971; Vol. 3, p 199.

[31] Moedritzer, K. *Organometallic Reactions*; Becker, E., Tsutsui, M., Eds.; Wiley-Interscience: New York, 1971; Vol. 2, p 1.

[32] Ingle, W.; Groschwitz, E.; Ring, M. *Inorg. Chem.* **1967**, *6*, 1429.

[33] Morrison, J.; Ring, M. *Inorg. Chem.* **1967**, *6*, 100.

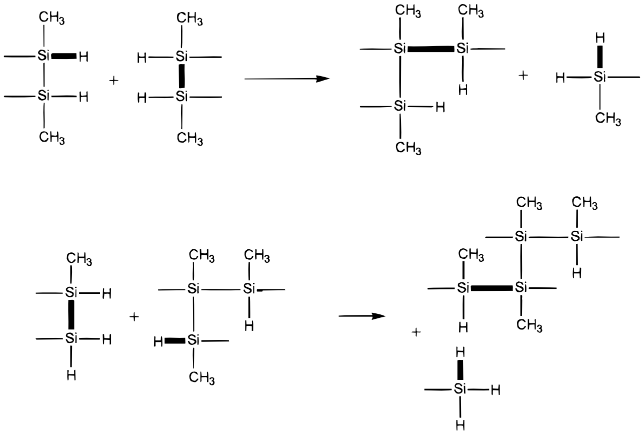
Abedini et al.[34] As an example, polysilane $-(SiH_2)-$ was produced by reaction of disilane and alkyldisilane in the presence of a Lewis acid, $AlCl_3$. Similar exchange between Si−Si and Si−Cl bonds were previously described and used by Baney et al. and Dunoguès et al. for the preparation of polycyclic preceramic polysilanes.[35,36] In these studies, a Lewis acid or a nucleophilic reagent reacts with a disilane to produce polysilane and monomeric silane products, the latter being distilled from the equilibrium mixture as they are formed. The reaction described here transforms the liquid PMS into a resinous material within the pyrolysis zone while distilling gaseous methylsilane. Scheme 2 is a simplified description of the transformations that occur within the PMS structure.

In this manner, a typical PMS that gives a ceramic yield of 16−20% under uncatalyzed conditions can give a ceramic yield better than 60% when 2% $BTMS_3$ is added. Furthermore, the B−PMS borate preceramic mixture is stable for an extended period of time and can be used directly in an application without pretreatment (mixing, thermal, UV, or other).

Conclusion

Boron additives effectively lead to an increase in the ceramic yield of PMS polymers, without modifying the ceramic composition. $BTMS_3$ provokes a hardening of the polymer at the same time as gas elimination occurs. Thus, the appearance of the polymer during the treatment is that of a foam. The redistribution reaction described herein leads to the elimination of mainly methylsilane which does not change the C/Si ratio in the precursor prior to its thermal decomposition. In the hope of preparing a precursor to pure SiC, the addition of $BTMS_3$ is helpful but insufficient.

Scheme 2. Redistribution Reaction between Si−Si and Si−H



To counterbalance these effects, our research efforts are presently directed toward the formulation of PMS, not only with a boron additive, but also with vinyl cross-linking agents. This second type of additive could ensure a dense, cross-linked resin before outgasing of methylsilane begins. The incorporation of a vinyl compound also provides a means of adjusting the carbon content of the precursor system in hopes of attaining pure SiC. The results of these studies will appear in a subsequent article.

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(35) Baney, R.; Gaul, J.; Hilty, T. *Organometallics* **1983**, *2*, 859.
(36) Calas, R.; Dunogues, J.; Deleris, G. *J. Organomet. Chem.* **1974**, *371*, 71.