APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. **13**, 419–430 (1999)

Stoichiometric Silicon Carbide from Borate-catalyzed Polymethylsilane–Polyvinylsilane Formulations

Bruno Boury[1]*, Nathan Bryson[2] and Gérard Soula[2]
[1]UMR 5637, CC 007, Université Montpellier II, 34090 Montpellier Cedex 05, France
[2]Flamel Technologies Parc Club du Moulin à Vent, 33 av. du Docteur G. Levy, 69390 Venissieux, France

Polymethylsilane (PMS) and polyvinysilane (PVS) were prepared by Wurtz condensation of chlorosilanes and characterized by spectroscopy (^{1}H, ^{13}C and ^{29}Si NMR, and infrared), viscosity and GPC analysis. Mixtures of the PMS and PVS were prepared and stabilized with 2,6-di-*t*-butyl-4-methylphenol (BHT; 0.5 wt%) to which was added a catalytic amount of tris (trimethylsilyl)borate, $B(OSiMe_3)_3$ (BTMS; 2 wt% by weight). The resulting liquid materials were pyrolyzed to 950 °C and to 1400 °C under argon. The formulation, composed of 60% PMS / 40% PVS / 2% BTMS, was pyrolyzed and gives nearly stoichiometric silicon carbide in 73% yield. The pyrolyzate was analyzed spectroscopically at intermediate stages in order to study its thermal transformations and the influence of the boron catalyst. The ceramic obtained from the formulation 60% PMS / 40% PVS / 2% BTMS shows good stability at 1500 °C under oxygen. Copyright © 1999 John Wiley & Sons, Ltd.

Keywords: Silicon carbide; borate-catalysed; polysilone; ceromic material

Received 22 June 1998; accepted 6 October 1998

INTRODUCTION

The preparation of silicon carbide from organosilicon polymers has been the subject of intensive research over the past 15 years.[1–3] Often, the ceramic contains unwanted oxygen, carbon or both. For example, the product obtained from the pyrolysis of PCS, a polydimethylsilane-derived polycarbosilane,[4–6] contains as much as 10–20% excess carbon and 10% oxygen. Likewise, polyvinylsilane (PVS)[7,8] gives carbon-rich ceramics (SiC + C), while polymethylsilane (PMS) gives silicon-rich ceramic compositions (SiC + Si).[9–12] For optimal performance of the ceramic at high temperature, the excess of silicon, carbon and/or oxygen must be avoided so as to prevent oxidation and/or carbothermal reduction processes which weaken the mechanical properties of the ceramic, as was demonstrated in the case of Nicalon SiC fiber.[13–15]

The preparation of stoichiometric silicon carbide has been achieved by using sophisticated polymeric precursors, such as polysilaethylene —(—SiH_2—CH_2—)—,[16,17] polymethysilane —(—SiHMe)—,[18,19] polysilethylene —(SiH_2—CH_2—CH_2—)—[20] and polycarbosilane —(—SiMeH—CH_2—)—.[21] These polymeric materials have added to our understanding of the pyrolytic processes which lead to the formation of silicon carbide; however, their syntheses are quite often tedious. More recent work has pointed out the possibility of obtaining stoichiometric SiC by pyrolysis of Yajima-type polycarbosilane (PCS) in a reactive atmosphere such as hydrogen[22], or ozone and borane.[23]

Our aim was to prepare an easily accessible polymer precursor capable of producing stoichiometric silicon carbide in high yield. For the practical purpose of composite formation, it was preferable to identify and synthesize an air-stable and liquid precursor system.

In this respect PMS and PVS, which are both liquid precursors and are completely miscible in all proportions, are particularly interesting candidates. The two polymers are highly complementary. PVS contains an excess of vinyl groups capable of reacting with hydrosilane-containing polymers,

---

* Correspondence to: Bruno Boury, UMR 5637, CC 007, Université Montpellier II, Sciences et Techniques du Languedoc, 34095 Montpellier Cedex 05, France.
E-mail: boury@crit.univ.montpl.fr

CCC 0268–2605/99/060419–12 $17.50

such as PMS. Crosslinking with PVS avoids the formation of foams that often occurs with PMS alone. The previous literature has established that PMS crosslinked with vinylic compounds gives improved ceramic yields,[24,25] and in some case pure silicon carbide.[10–12,26,27] Secondly, a vinylic compound can be used as a means to introduce carbon into the composition and correct the SiC stoichiometry of the ceramic. As PVS alone produces a carbon-rich ceramic, the proper PMS–PVS combination is likely to give a new precursor system which can produce pure or nearly pure SiC.

Synthetically, the two precursors are made using the same standard procedure. Our previous studies have further shown that the viscosity of each of the polymers can be controlled by the use of chain-end blockers during the polymerization.[28] Both polymers, as well as the formulation of the two, can be stabilized by the addition of di-*t*-butyl-4-methylphenol (BHT; 0.5 wt%), which inhibits oxygen-initiated radical chain reactions which cause crosslinking.

Our studies are mainly directed toward the improvement of the synthesis of the precursors and of the ceramic yield of PMS/PVS formulations. In a recent report, we described the use of boron additives, such as tris(trimethylsilyl)borate [$B(OSiMe_3)_3$, or BTMS] to improve the ceramic yield of PMS without modifying the composition of the final ceramic relative to the non-formulated polymer.[28] We thought it might be possible to use the same strategy for upgrading the PMS/PVS mixtures described herein. In this paper we report the results of our studies on the preparation of the precursors, their formulation and transformation into stochiometric silicon carbide, and the role of the boron catalyst. Characterization of the ceramic is given, along with its stability toward oxidation.

EXPERIMENTAL

Caution: Unstabilized, all of the products are extremely air-sensitive, liquid or viscous oils. In fact, PMS can burn spontaneously in air when absorbed on paper. The air stability can be improved and the pyrophoric nature eliminated by the addition of 0.5 wt% of 2,6-di-*t*-butyl-4-methylphenol (BHT). All manipulations were carried out under a nitrogen atmosphere using standard inert-atmosphere techniques. Solvents were distilled from appropriate drying agents under nitrogen prior to use. Commercial methyldichlorosilane was purified by distilling over magnesium, under nitrogen. Other reagents were purchased from Aldrich and used as received. Tris(trimethylsilyl)borate [$B(OSiMe_3)_3$; BTMS] was purchased from Aldrich.

NMR spectra were obtained using a Bruker 300 MHz spectrometer a 5 mm tube and benzene-d_6 as solvent and internal standard; a trace of $Cr(AcAc)_3$ ($\pm$1 mol%) was added to the sample solution to reduce the ^{29}Si spin–lattice relaxation time (T_1). FTIR spectra were recorded on a Perkin-Elmer PE1700 spectrometer. The products were analyzed neat in a KBr pellet. Molecular weight distributions were determined by gel-permeation chromatography (GPC) using a Perkin-Elmer 9010 analyzer and μ-Styragel columns (porosity ranges of 100, 500 and 10000 Å) calibrated with polystyrene standards and with tetrahydrofuran (THF) as the eluent at a flow rate of 0.6 ml min^{-1}. Thermal analyses were performed using a Perkin-Elmer TGA 7 with a heating rate of 2, 5 or 10 °C min^{-1} under nitrogen at a flow rate of 30 ml min^{-1}. Bulk pyrolysis was performed in a Carbolite furnace under nitrogen (30 ml min^{-1}).

Preparation of polymethylsilane

In a typical reaction, a 1-l three-necked, round-bottomed Pyrex flask was equipped with a reflux condenser, a vacuum line adaptor, a thermometer and a mechanical stirrer. The apparatus was purged and charged with toluene (200 ml), dioxane (20 ml) and sodium (42.0 g, 1.84 mol). The mixture was heated to 100 °C and stirred to obtain a sodium dispersion. Addition of a mixture of methyldichlorosilane (76.0 ml, 0.73 mol) and dimethylchlorosilane (2 ml, 0.023 mol) was performed with a syringe at a flow rate of 20 ml h^{-1}. 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 24.78 g of a viscous yellow oil, yield 77.0%. ^1H NMR (C_6D_6; 300 MHz;δ, ppm): 3.8 to 4.4 (0.67 H, broad multiplet); 1.4 (0.15 H, broad multiplet); 0.1 to 0.9 (3 H, broad multiplet). FTIR (neat, KBr cells, cm^{-1}): 2956; 2894; 2799; 2060; 1410; 1247; 931; 870; 766; 687; 588. Elemental analysis for residual chlorine: 0.40%.

Note that methylsilane (CH_3SiH_3) has been detected in the headspace of the reaction by GC–MS analysis. Care should be taken when handling the gaseous by-products of a large-scale synthesis of PMS.

Preparation of polyvinylsilane

In a typical reaction, a 1-l double-walled reactor was equipped with a reflux condenser, a vacuum line adaptor, a thermometer and a mechanical stirrer. The apparatus was purged and charged with toluene (200 ml), THF (27 ml) and sodium (42.30 g, 1.84 mol). The mixture was heated to reflux (101 °C) and then stirred to obtain a sodium dispersion. The heating was stopped and a mixture of methylvinyldichlorosilane (61 ml, 0.46 mol), methyldichlorosilane (15 ml, 0.14 mol) and trimethylchlorosilane (24.3 ml, 0.19 mol) was added over one hour. **Note**: Because of the exothermic nature of the reaction, it was necessary to cool the reaction vessel during the addition, by the circulation of an inert fluid (Gilotherm hydrocarbon) at *ca* 50 °C in the cooling jacket, in order to maintain a temperature between 98 and 100 °C within the reactor. After approx. 90% of the chlorosilane mixture had been added, the cooling was stopped and the reaction was allowed to heat back to reflux; the reflux was maintained for an additional 5 min after the addition was complete. The reaction mixture was then cooled to 50 °C (5–10 min) via the cooling jacket, and filtered. The blue–black solid containing the sodium chloride and the excess of sodium metal was then washed with toluene. To the filtrate was added BHT (0.22 g, 1.0 mmol). The solvent was eliminated from the combined filtrate by distillation at 50 °C under vacuum, yielding 42.70 g of a viscous yellow oil, yield 81.8%. ^{1}H NMR (C_6D_6; 300 MHz; δ, ppm): 5.4 to 6.5 (3.1 H, broad multiplet); 3.8 to 4.4 (1 H, broad multiplet); -0.2 to 1.0 (7.3 H, broad multiplet). FTIR (neat, KBr cells, cm^{-1}): 2956; 2894; 2799; 2060; 1410; 1247; 931; 870; 766; 687; 588. Elemental analysis for residual chlorine: $<0.10\%$.

RESULTS AND DISCUSSION

Synthesis and characterization of the precursors

Polymethylsilane (PMS, **I**) and polyvinylsilane (PVS, **II**) were prepared by Wurtz condensation of mixtures of dichlorosilanes and monochlorosilanes using molten sodium in excess (25%) (Eqns 1 and 2). Monochlorosilanes were used in the syntheses as an end-blocking agent in the polymerization, so as to produce liquid polymers.

$$(CH_3)SiHCl_2 + 0.32(CH_3)_2SiCl \xrightarrow{\text{5\% excess Na}} \left\{ \begin{array}{ll} x' & \text{—}(Si(CH_3)H)\text{—} \\ y & \text{—}(Si(CH_3)\text{—} \\ x'' & \text{—}(Si(CH_3)_2H) \end{array} \right. \qquad [1]$$

$$x = x' + x''; x + y = 1$$

$$\begin{array}{l} 0.3\,(CH_3)SiHCl_2 \\ +0.4\,(CH_3)SiCl_3 \\ +\,(CH_2CH)SiHCl_2 \end{array} \xrightarrow{\text{20\% excess Na}} \left\{ \begin{array}{ll} w & \text{—}(Si(CH_3)_3) \\ x & \text{—}(SiH(CHCH_2)\text{—} \\ y & \text{—}(Si(CH_3)H)\text{—} \\ z & \text{—}(SiH(CH_2\text{-}CH_2)\text{—}) \end{array} \right. \qquad [2]$$

$$w = 0.35; x = 0.9; y = 0.2; z = 0.1$$

Although various different experimental procedures have been used to prepare the polymers,[28] it is important to respect the experimental procedure, particularly the rate of addition of the chlorosilane mixture and the work-up procedure, in order to obtain stable liquid products. In the present study, PMS was prepared in a 10:1 volume ratio of toluene/dioxane mixture using Me_2SiHCl as the end-blocker chain, at a ratio of $Me_2HSiCl/MeHSiCl_2 = 0.032{:}1$. The ether co-solvent is crucial to ensure the initiation of the reaction. The polymer is isolated after filtration of the salts and evaporation of the solvents. The polymer prepared in this manner is very air-sensitive and should be handled under an inert atmosphere.

A typical ^{1}H NMR spectrum of PMS shows signals in two discrete regions, 0.1–0.9 ppm and 3.0–5.0 ppm, corresponding to methyl and hydride functions, respectively. No attempt was made to distinguish the Si—H resonance of the end-group from those of the main chain. Integration of the Me and H regions shows that a portion of the Si—H groups is consumed during the condensation reaction, and thus the formula of the polymer is written in the simplified form $[(MeSiH)_x(MeSi)_y]_n$, where y gives the proportion of dehydrogenated, trifunctional silicon units formed. Typically, the values of x and y found by ^{1}H NMR integration are $x = 0.63$ and $y = 0.37$. In ^{29}Si NMR spectra, a broad signal that is observed between −75 and −55 ppm is attributed to —MeSiH— and —MeSi═ groups. Using a ^{29}Si DEPT sequence, negative peaks are found in the broad signal within this region, indicating the presence of —SiH_2— groups in low proportions in the polymer. The ^{13}C NMR spectrum shows one broad signal centered at −9.2 ppm, corresponding to CH_3 groups of the polymer; very low-intensity signals are also observed at 22, 32 and 35 ppm and are possibly attributable to small amounts of Si—CH_2—Si or Si—CH_2Cl groups; these are neglected in the description of the structure. The molecular weight of the polymers is typically in the range of M_n 700–800 (DP $\approx$ 17) and M_w 1200–1500. The resulting clear to yellow oil has a viscosity above 1000×10^{-2} P.

PVS was synthesized in a similar manner in a toluene/THF mixture (88:12, v/v). The procedure used here resulted from a slight modification of the reaction described by Schilling.[7,8] A clear, liquid polymer was obtained after filtration of the salts, addition of a small amount of BHT and evaporation of the solvent under vacuum. The spectroscopic analysis of PVS was very similar to that of PMS, with the addition of the vinyl groups near 5.4–6.5 ppm. Interrante has provided a detailed discussion of the spectroscopic characteristics of PVS-type polymers,[29] which can be considered as random polymers. The residual chlorine content of the polymer was 0.05–0.1 wt% and the viscosity was typically between 300×10^{-2} and 700×10^{-2} P directly after the synthesis. The viscosity evolves over a period of 9–12 weeks and stabilizes near 1000×10^{-2}–1500×10^{-2} P; the reason for this evolution is unknown at present.

It should be noted that the polymer solution obtained after filtration of the sodium salts should not be washed with water to eliminate residual chlorine, since this results in an unstable material which slowly hardens to a resin even in an air-free, light-free environment. In this case, the viscosity cannot be stabilized even by the addition of radical inhibitors (or antioxidants). It might appear that the evolution of a water-washed material is a result of residual HCl. In fact, we can induce similar behavior by the addition of HCl gas to a stable material. It could be that the aqueous washing suggested in many publications actually leaves small traces of HCl, or water which slowly consumes unreacted SiCl groups over time. Although the addition of a small amount of an organic base could rectify this problem, we prefer unwashed polymers which have a stable viscosity.

PMS–PVS formulations must be prepared by mixing solutions of pure PMS and PVS. In the absence of solvent, mixing takes a long time at room temperature (more than two days), due to the viscosity of the product. BHT is added and then the solvent is removed by distillation to give a yellow liquid.

Stability of PMS, PVS and PMS/PVS mixtures

It should be noted that all of the PMS/PVS mixtures are somewhat air-sensitive, even with 0.5% BHT in the formulation. When handled under an inert atmosphere, PMS/PVS mixtures are stable. No evolution of their spectral characteristics is observed over a three-month period.

The liquid mixture has a viscosity $<500 \times 10^{-2}$ P at 20 °C; this increases only slightly upon storage at room temperature under nitrogen in the dark, going from 700×10^{-2} P to 1200×10^{-2} P over a period of three months; further aging of the precursors has no effect on its other properties.

Air oxidation of the individual polymers, and of stabilized formulations, has been studied by IR spectroscopy. In order to study the different reactions occuring in the air, a thin polymer film (~100 μm) was spread on a KBr pellet and then exposed to the air. For PMS, oxidation leads to the formation of Si—O ($\nu_{\text{Si—O}} = 1100\ \text{cm}^{-1}$) without a decrease in the intensity of the peaks for Si—H ($\nu_{\text{SiCH}_3} = 2085\ \text{cm}^{-1}$) or Si—Me ($\nu_{\text{SiCH}_3} = 1245\ \text{cm}^{-1}$). After complete oxidation, the infrared spectrum of the oxidized PMS is identical to that of the corresponding commercial siloxane, $(\text{MeHSiO})_n$.

The oxidation of PVS is quite different since the formation of Si–O bonds ($\nu_{\text{SiO}} = 1100\ \text{cm}^{-1}$) occurs simultaneously with the decrease in the intensity of signals related to vinyl groups and Si–H bonds. Furthermore, the changes in the IR spectrum accompany a change in the appearance of the polymer, as it slowly hardens to form a rigid film. BHT retards the onset of the reactions for ~1–2 h. These observations are consistent with oxygen-initiated radical reactions which induce oxidation and crosslinking by polymerization and hydrosilylation.[29,30]

In the case of PMS/PVS mixtures, the situation is similar to that of PVS, but the mixture is apparently more sensitive to the oxygen in the air, as the spectral modifications occur approximately 10 min after exposure to the air even in stabilized samples.

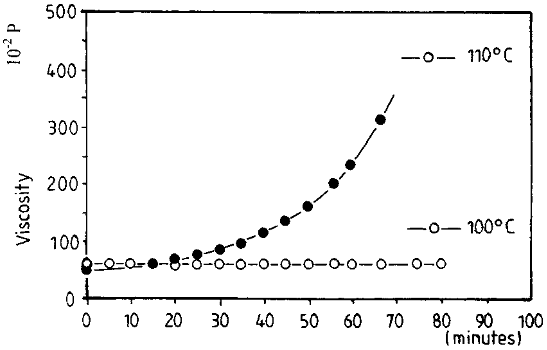


Figure 1 Viscosity of a PMS/PVS mixture at 100 °C and 110 °C.

Crosslinking of the precursors below 200°C

When the mixture is heated to 100 °C, the viscosity decreases below to below 100×10^{-2} P. After 1 h at this temperature, the viscosity increases as crosslinking begins (Fig. 1).

More information was obtained by studying the crosslinking reactions by DSC (Table 1 and the related Fig. 2) and IR analyses of different precursor mixtures (Fig. 3). In these analyses, we defined α as the Si—H/Si—vinyl (SiH/SiVi) molar ratio (from ^{1}H NMR) and β as the number of moles of vinyl per gram of precursor.

The DSC thermogram of PVS alone shows one very broad signal extending from 120 to 220 °C. The IR spectra of PVS after thermal treatment for 1 h at 220 °C show that all of the vinyl groups are consumed during crosslinking. The observations correspond to the loss of Si—H groups (2085 cm^{-1}) and Si—vinyl (3040 cm^{-1}), and the formation of new peaks at 1050 cm^{-1} due to hydrocarbon-type structures, such as —Si—CH$_2$—CH$_2$— or —Si—CH(CH$_3$)— (Fig. 3).[29]

In the case of the PVS, the proportion of vinyl to hydride groups is approximately 3:1 ($\alpha = 0.3$);

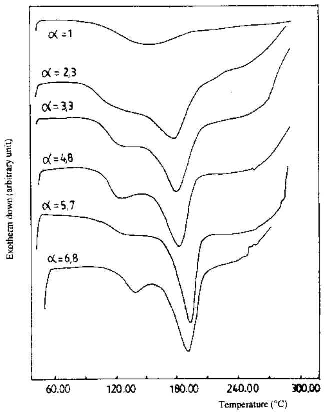


Figure 2 DSC thermograms of PMS/PVS mixtures (from 50 to 250 °C, heating rate 5 °C min^{-1}, nitrogen flow 40 ml min^{-1}).

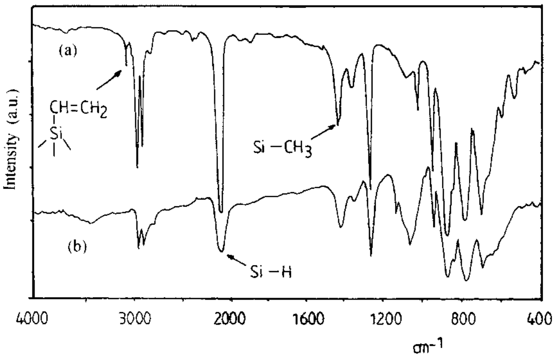


Figure 3 IR spectrum of PMS/PVS (60:40 w/w) mixture: (a) at 20 °C and (b) after thermal treatment at 220 °C.

Table 1. DSC data and ceramic yields of PMS/PVS/BHT mixtures

PVS (wt%)	α	$\beta \times 10^3$	$\Delta H_{\text{react.}}$ (kJ g^{-1})	ΔH_{vinyl}[a] (kJ mol^{-1})	Ceramic yield[b] (%)	C/Si[c]
100	0.3	8.2	−360	−44	62	1.94
70	1.0	5.9	−270	−46	59	1.43
40	2.0	3.7	−210	−57	60	1.07
35	3.3	2.9	−180	−61		
29	4.8	2.2	−150	−68	55	0.95
24	5.7	2.0	−140	−71	54	
20	6.8	1.7	−110	−65		
0					20	0.83

[a] kJ mol^{-1} of vinyl group.
[b] Heating rate 5 °C min^{-1} from 25 to 950 °C; nitrogen flow 40 ml min^{-1}.
[c] Molar ratios in the ceramic calculated from elemental analyses.

therefore stoichiometric hydrosilylation cannot explain the disappearance of all of the vinyl groups which is observed by IR. Crosslinking must be accompanied by vinyl polymerization. For PMS/PVS compositions, similar phenomena are observed. After crosslinking is complete, no vinyl groups remain. However, when an excess of hydride groups is present ($\alpha>1$), a fraction of these is always visible by IR.

When the mixtures are heated in a DSC capsule under nitrogen, two exothermic peaks are observed, at 140 °C and at 190 °C. The combined energy of the exotherm decreases as the proportion of PMS in the mixture increases. Therefore, the heat liberated per mol of vinyl [$\Delta H_{\text{vinyl}} = \Delta H/(\text{mol Vi})$] increases with the amount of PMS, high α (SiH/SiVi) and low β. This can be explained by the fact that the hydrosilylation is more exothermic than vinyl polymerization by $\sim$50 kJ mol^{-1} ($\Delta H_{\text{hydrosilylation}} \approx -135$ kJ mol^{-1}; $\Delta H_{\text{polymerization}} \approx -80$ kJ mol^{-1}) based on the average bond energies.[31–33]

Pyrolysis of PMS/PVS mixtures

Mixtures of PMS/PVS in various proportions were pyrolyzed at 950 °C under argon. When the mixture contains at least 17% PVS, the ceramic yield is better than 50%. The elemental analyses of the ceramic residues show that the carbon content in the ceramic decreases with increasing proportion of PMS, as would be expected (Table 1).

A ceramic with an Si/C ratio of 1:1 is obtained with a starting precursor composed of approximately 60% PMS and 40% PVS. This ratio was used for the major portion of our study, which then centered on the improvement of the ceramic yield and the characterization of this ceramic product.

BTMS-catalyzed crosslinking at 220 °C

We recently reported that a catalytic amount of tris(trimethylsilyl)borate $B(OSiMe_3)_3$ BTMS can cause increases in the ceramic yield of PMS by facilitating a crosslinking reaction at 230 °C.[28] From Table 2, it is evident that the boron catalyst is efficient in improving the ceramic yield of precursors which contain a substantial amount of PMS, and is inactive in the case of PVS.

BTMS was introduced into the polymer precursor formulation, PMS/PVS/BHT (60:40:0.5 by weight) at various concentrations ranging from 1 to 4 wt% in order to assess its effects. The results in Table 2 show that the boron additive had an effect on increasing the ceramic yield of the precursor mixture. However, above 2% no further gain was observed.

Table 2. Ceramic yield[a] at 950 °C of PMS/PVS/BHT/BPMS (60:40:0.5: *x* by wt) mixtures

α	$x = 0$	$x = 1$	$x = 2$	$x = 4$
100% PVS	62		62	
1	62		68	
3	60	69	73	72
5	59		67	
100% PMS	18		73	

[a] Heating rate 5 °C min^{-1} from 25 to 950 °C; nitrogen flow 40 ml min^{-1}.

At a concentration of ±2%, the boron additive had no apparent effect on the mechanism or the temperature of the crosslinking reactions (determined by DSC analyses) which occurred below 200 °C. However, when the PMS/PVS/BHT/BTMS composition was heated at and above 220 °C, thermogravimetric analysis (TGA) showed a weight loss of 5–6% which occurred over a period of 6 h (Figs 4 and 5). With the uncatalyzed precursor, such a weight loss was not observed. The benefit of the boron additive was seen afterwards as the pyrolysis was continued up to 950 °C, where a gain of 20% in the final ceramic yield was observed.

In order to understand the role of the boron additive, the gases emanating from the pyrolyzed sample were analyzed by GC–MS. $MeSiH_3$ was detected as the major species in the gas phase, but

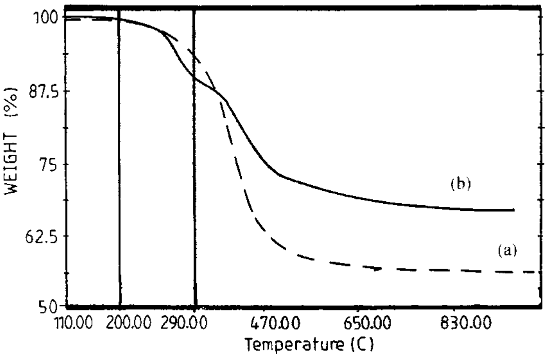


Figure 4 TG curves of (a) PMS/PVS/BHT/BPMS (60:40:0.5:0 by wt) mixture and (b) PMS/PVS/BHT/BPMS (60:40:0.5:2 by wt) mixture. Temperature 50–950 °C, heating rate 5 °C min^{-1}, nitrogen flow 40 ml min^{-1}.

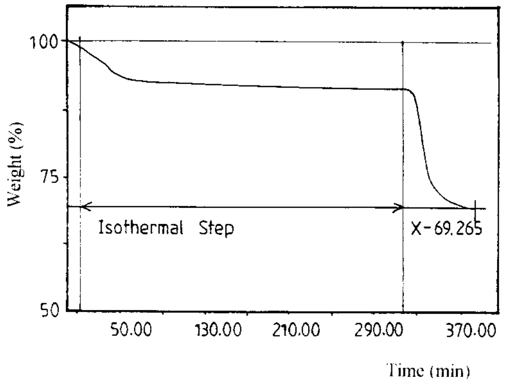


Figure 5 TG curve of the PMS/PVS/BHT/BPMS (60:40:0.5:2 by wt) mixture with an isothermal step at 230 °C. Temperature 50–950 °C under nitrogen, isothermal step at 230 °C for 6 h, heating rate 5 °C min^{-1}, nitrogen flow 40 ml min^{-1}.

low-molecular-weight oligomers $H(MeHSi)_nH$ ($n = 2, 3$) were also observed, in very low proportions. By IR analysis of the crosslinked resin, the decrease in the signal related to Si—H groups of the precursor indicated that these residual groups not consumed by the crosslinking reactions above 200 °C had now reacted. Using the Si—Me absorption (1245 cm^{-1}) as a reference, 60% of the residual Si—H groups were lost during the treatment at 230 °C. A rapid calculation shows that the weight loss observed (5.2%) by TGA is in accordance with the proportion of Si—H groups lost by the formation of $MeSiH_3$.

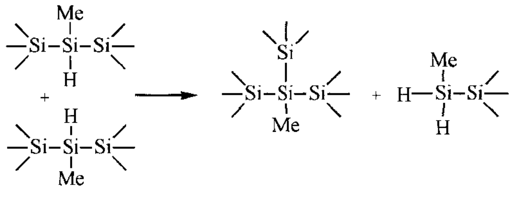
The formation of this gas might result from a disproportionation reaction between Si—Si and Si—H bonds. Similar reactions are well documented in the organosilicon chemistry literature.[34,35] The redistribution of Si—Si and Si—H bonds was investigated by Ring and co-workers,[36,37] and Abedini and MacDiarmid[38] For example, they investigated polysilane [—(SiH_2)—], which they produced by reaction of disilane and alkyldisilane in the presence of a Lewis acid, $AlCl_3$. Without consideration of the catalytic mechanism, the overall balance of the redistribution reaction in the present case is given by Eqns 3 and 4. Here, the boron-catalyzed reaction proceeds within a fairly rigid, crosslinked resin, seemingly with ease.

Table 3. Boron content in the residue from pyrolysis of a PMS/PVS/BHT/BPMS (60:40:0.5:2 by wt) mixture

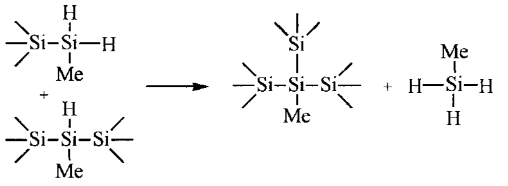
Final temperature of pyrolysis (°C)	Boron content (wt%)[a]
Before pyrolysis	0.079[b]
200	0.089
230	0.06
600	0.05
1000	0.05

[a] From elemental analyses.

[b] Calculated from the formulation of the precursor.



[3]

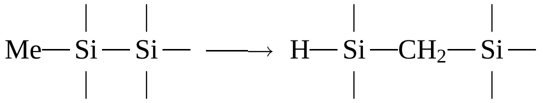


[4]

Elemental analyses were performed on mineralized residues obtained at different temperatures during the pyrolysis procedure. These analyses indicate that the boron is substantially eliminated during the crosslinking treatment at 230 °C (Table 3). We were unable to detect any boron derivatives in the headspace of the resin. Boron derivatives were also eliminated from poly(borodiphenylsiloxane)/polydimethylsilane mixtures during their thermal treatment at 400 °C.[6,39] In that case, the authors speculated on the formation of volatile borane species which distilled from the reaction.

Kumada rearrangement

At temperatures between 350 and 750 °C, at which an important weight loss is observed by TGA analysis (20–22%), a transformation of the polysilane skeleton via the Kumada rearrangement is observed and corresponds to a transformation as described in Eqn 5. Such a mechanism was used to explain the structural changes occurring during pyrolysis of polydimethylsilane,[4,40] polyvinylsilane[29] and polymethylsilane[28] into polycarbosilane polymers. Poly(borodiphenylsiloxane) (PBDPSO) and other boron derivatives, such as BTMS, were found useful for promoting this transformation.[41]



$$\mathrm{Me{-}\overset{|}{\underset{|}{Si}}{-}\overset{|}{\underset{|}{Si}}{-}} \longrightarrow \mathrm{H{-}\overset{|}{\underset{|}{Si}}{-}CH_2{-}\overset{|}{\underset{|}{Si}}{-}}$$

[5]

The presence of this type of transformation and the influence of BTMS in our PMS/PVS precursors were investigated by IR spectroscopy. As can be seen from Table 4, a dramatic increase in the relative amount of SiH groups occurs between 400 and 425 °C, corresponding to the formation of —(MeHSi—CH_2)— carbosilane units, consistent with the Kumada mechanism.

We found that boron-containing and boron-free PMS/PVS precursors gave similar results. In fact, BTMS does not influence the initial temperature or the rate of the Kumada transformation with our formulations and it does not continue to induce methylsilane formation at these temperatures. The starting temperature and the time required for the Kumada transformation were identical for boron-containing and boron-free samples. This would corroborate publications of Ishikawa and Hasegawa and their co-workers, who suggested that boron catalysts facilitate dehydrogenation reactions and not the Kumada transformation.[39,42,43] However, we have no explanations for why the catalyst is not reactivated in our system once new SiH groups are formed. It would thus appear that the difference between the PDMS studied by Ishikawa and PMS-based precursors studied here is related to the reactivity of the Si–H bonds of the polymers. In fact, the SiH groups in our PMS-based precursors react at relatively low temperatures in comparison. For PDMS, there are no SiH groups in the original structure, hydrides are formed as the temperature is increased to 400 °C.

Table 4. Relative amounts of SiH groups of a PMS/PVS/BHT/BPMS (60:40:0.5:2 by wt) mixture

Final temperature of pyrolysis (°C)[a]	SiH / $SiCH_3$[b]
230	0.42
300	0.41
350	0.39
400	0.42
425	0.60
450	0.68
500	1.0

[a] Heating rate 5 °C min^{-1} followed by a plateau at the desired temperature for 30 min, nitrogen flow 40 ml min^{-1}.
[b] Deduced from the intensity ratio of the band absorption (absorbance measurement).

Characterization of the ceramics

The elemental analyses of the ceramic residues obtained by pyrolysis of PMS/PVS/BTMS formulations at 950 °C and at 1400 °C are reported in Table 5. The contents of SiC, SiO_2 and free carbon are deduced from the analyses, assuming that the oxygen is in a silica phase, and any resulting carbon is combined with silicon.

An average Si/C ratio close to 1.1:1 was found for all the precursors, independently of the quantity of boron added. We found that using BTMS results in only a slight increase in the oxygen and carbon content.

X-ray powder diffraction of the ceramics was performed using a Dosophatex system in order to eliminate any artifacts due to the surface structure or the size of the SiC particles.[44] The only crystalline phase detected in the sample was β-SiC (JCPDS 29-1129) (Fig. 6).

The fraction of crystallized sample and the size of the crystallites, presented in Table 6, were determined by standard methods.[45] The 950 °C sample was taken as the reference for an amorphous SiC phase.

As might be expected, increases in the final

Table 5. Elemental analyses (%wt) and formulations of the residues from pyrolysis at 950 °C of a PMS/PVS/BHT/BPMS (60:40:0.5:*x* by wt) mixture

	C	H	O	B	Si	Total[a]	Formulation[b]	SiC (%)	SiO^2 (%)	C (%)
$x = 0$	31.6	0.3	0.8		64.7	98.4	$Si_1\ C_{1.1}\ O_{0.05}$	92.8	1.5	3.7
$x = 2$	32.0	0.3	1.1	0.5	64.7	98.1	$Si_1\ C_{1.1}\ O_{0.05}$	91.0	2.0	4.7
$x = 4$	32.5	0.3	1.6	0.1	64.5	99.2	$Si_1\ C_{1.1}\ O_{0.04}$	90.1	3.0	5.5

[a] Analyses performed by Galbraith laboratories.
[b] Deduced from the elemental analysis.

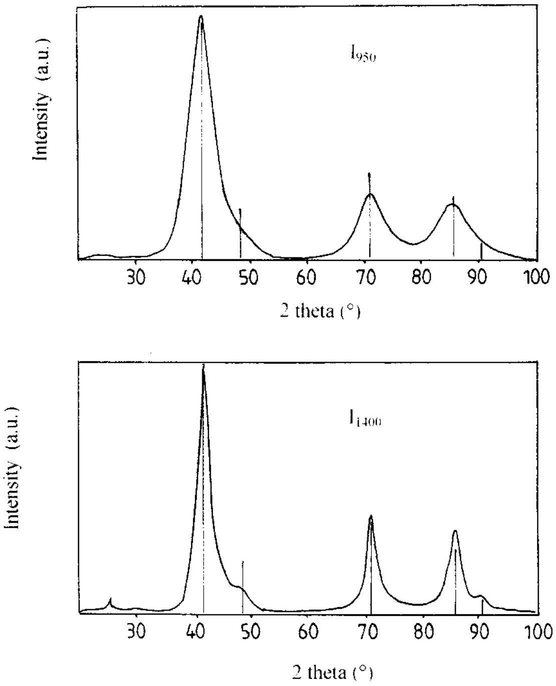


Figure 6 X-ray spectra of ceramics $\mathbf{I}_{950}$ and $\mathbf{I}_{1400}$.

temperature and the amount of boron contribute to a more highly crystalline sample.[46,47] It must be pointed out that the presence of boron is also related to an increase in the free carbon content, and carbon, like boron, is known to promote densification and crystallization of SiC.[48–50]

Oxidation stability of the ceramics

Oxidation of silicon carbide is a spontaneous exothermic reaction with an enthalpy of −840 kJ mol^{-1} at room temperature. The stability of silicon carbide toward air oxidation is the result of a silica barrier at the surface of the SiC particles, which limits the diffusion of oxygen toward SiC. We investigated the stability of our new ceramic compositions by TGA, using pure oxygen as the vector gas.

Oxidation should be accompanied by a weight gain as SiC (mol. wt = 40) is transformed into SiO_2 (mol. wt = 60) according to Eqn 6.[51] It is also possible that an oxycarbide phase is formed initially, corresponding to Eqn 7 and also resulting in a weight gain.[52] The stoichiometry of this phase can change due to further oxidation, and it can finally result in the formation of silica.

$$\mathrm{SiC(s)} + 3\sqrt{2}\mathrm{O_2(g)} \rightarrow \mathrm{SiO_2}(s) + \mathrm{CO(g)} \qquad [6]$$

$$\mathrm{SiC(s)} \xrightarrow{+\mathrm{O_2(g)}} \mathrm{SiO}_x\mathrm{C}_y\mathrm{(s)} + \mathrm{CO(g)} \xrightarrow{+\mathrm{O_2(g)}} \mathrm{SiO}_{x'}\mathrm{C}_{y'}\mathrm{(s)} + \mathrm{CO(g)}$$
$$x' > x; y' > y \qquad [7]$$

Since the rate of oxidation is quantitatively, related to the surface of the material, all the samples were ground and sieved (30–50 μ m) in order to obtain materials with similar specific surface areas (*Ca* 6 m^2 g^{-1}). The samples were heated to 1000 and 1500 °C in a stream of pure, dry oxygen. Figure 7 presents the TGA curve of the ceramic prepared from a PMS/PVS/BHT/BPMS (60:40:0.5:2 by wt) mixture pyrolyzed at 1400 °C. For comparison, the same experiment was performed on a commercial powder of SiC (from ABCR Co.) and on a ceramic from pure PVS pyrolyzed at 1400 °C. For this material, the presence of an excess of free carbon (<20 wt%) leads to significant weight loss starting at ≈650 °C and arising from the oxidation of the free carbon. The weight gain that follows corresponds to the oxidation of the silicon carbide phase. The absence of a large excess of free carbon in the ceramic from the PMS/PVS mixture avoids the weight loss and only a gain in weight is observed, starting at ≈900 °C and arising from the diffusion of oxygen with formation of silica or an oxycarbide phase.

Table 6. Crystallite size and crystallinity in the residues from pyrolysis of a PMS/PVS/BHT/BPMS (60:40:0.5:*x* by wt) mixture

	Final temperature of pyrolysis (°C)	Ceramic	Crystallite size (Å)	Crystallinity (%)
$x = 2$	950	$\mathbf{I}_{950}$	44	as ref.
$x = 2$	1400	$\mathbf{I}_{1400}$	65	26
$x = 4$	950	$\mathbf{II}_{950}$	383	77
$x = 4$	1400	$\mathbf{II}_{1400}$	462	82

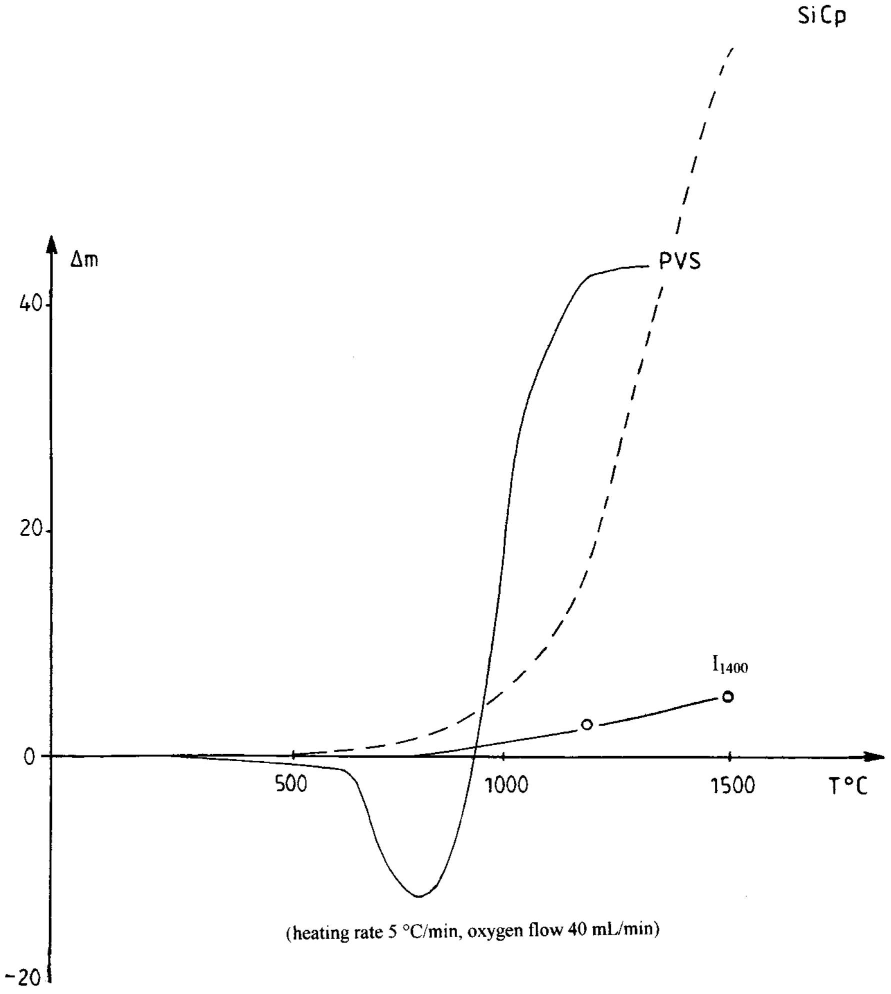


Figure 7 TGA curves of commercial SiC powder (SiCp), ceramic from PVS (PVS) and ceramic $\mathbf{I}_{1400}$, from 50 to 1500 °C in pure oxygen.

Quantitatively, the diffusion of oxygen through the initial silica layer at the surface was interpreted from the TGA according to the rate law: $\Delta\text{wt} = k(t^{1/2})$.[53,54] The TGA curves obtained for different ceramics obtained from the PMS/PVS mixture are reported in Tables 7 and 8.

The rate of oxidation of the SiC prepared from our PMS/PVS/BTMS polymer formulation is comparable with that of a commercial sample. It was established that crystalline SiC prepared from PMS/PVS/BHT/BPMS (60:40:0.5:2 by wt) at 1400 °C is much more stable than amorphous SiC prepared at 950 °C. This is probably related to the densification resulting from the crystallization of the sample when it is prepared at 1400 °C.

Apparently, the use of 4% BTMS in the formulation has little consequence for the rate of oxidation. One might expect that higher concentrations of boron could lead to higher rates of oxidation,[54] but this was not observed in that case. The high amount of boron catalyst used for the preparation of the ceramic increases the crystallite size and the crystallinity, which probably explains this result.

CONCLUSION

PMS/PVS mixtures, stabilized by BHT and formulated with BTMS, are a class of interesting new liquid polymer precursors for the preparation of

Table 7. Oxidation rates of the ceramics

Sample ceramic	Temperature (°C)	k^{b} ($\mathrm{min}^{-1/2}$)
SiC[a]	1000	0.254
$\mathbf{I}_{950}$	1000	0.104
$\mathbf{I}_{1400}$	1500	0.321

[a] Commercial samples purchased from ABCR Co.
[b] Slope of the curve of weight change versus $t^{1/2}$.

Table 8. Oxidation rate of the ceramics at 1000 °C

Sample Ceramic	k^{a} ($\mathrm{min}^{-1/2}$)	Weight gain, 10 h at 1500 °C (%)
$\mathbf{I}_{950}$	0.992	15
$\mathbf{I}_{1400}$	0.321	6
$\mathbf{II}_{1400}$	0.394	9

[a] Slope of the curve of weight change versus $t^{1/2}$.

near-stoichiometric silicon carbide. This study further confirms the benefit of the use of boron additives for increasing the ceramic yields of Si—Si and Si—H containing polymers by inducing a disproportionation reaction which leads to cross-linking. The silicon carbide produced is of a quality similar to commercial powder SiC, being as stable in pure oxygen above 1000 °C, but with the added advantage of processability inherent to polymer precursors.

Acknowledgements We wish to thank M$^{\mathrm{me.}}$ Levy (DRET) and Mr Parlier (ONERA) for financial and technical support and Professor Goeriot (L'Ecole des Mines de St. Etienne) for the oxidation and crystallographic studies performed on the ceramic materials.

REFERENCES

1. R. M. Laine and F. Babonneau, *Chem. Mater.* **5**, 260 (1993).
2. M. Birot, J. M. Pillot and J. Dunoguès, *Chem. Rev.* **95**, 1443 (1995).
3. W. Toreki, *Polymer News* **16**, 6 (1991).
4. S. Yajima, J. Hayashi, M. Omori and K. Okamura, *Nature (London)* **261**, 683 (1976).
5. S. Yajima, Y. Hasegawa, K. Okamura, T. Matsuzawa and T. Shishido, *Nature (London)* **279**, 706 (1979).
6. S. Yajima, T. Shishido and H. Kayano, *Nature (London)* **273**, 525 (1978).
7. C. L. Schilling, J. P. Wesson and T. C. Williams, *Am. Ceram. Soc. Bull.* **62**, 912 (1983).
8. C. L. Schilling and T. C. Williams, *Polym. Prepr.* **25**, 1 (1984).
9. D. Seyferth and Y. Yu, *Design of New Materials*, Plenum Press, New York, 1987.
10. D. Seyferth, G. Wiseman, J. Schwark, Y. Yu and C. Poutasse, *Inorganic and Organometallic Polymers*, M. Zeldin, and H. Allcock, (eds), American Chemical Society, Washington DC, 1988, p. 143.
11. C. Brown-Wensley, *Organometallics* **6(7)**, 1590 (1987).
12. K. Brown-Wensley and R. Sinclair, US Patent 4,537,942 (1984). C.A.: 104-512780.
13. S. M. Johnson, R. D. Brittain, R. H. Lamoreaux and D. J. Rowcliffe, *J. Am. Ceram. Soc.* **71**, p. C132 (1988).
14. T. Mah, N. L. Hecht, D. E. McCullum, J. R. Hoenigman, H. M. Kim, A. P. Katz and H. A. Lipsitt, *J. Mater. Sci.* **19**, p. 1191 (1984).
15. K. L. Luthra, *J. Am. Ceram. Soc.* **69**, p. C231 (1986).
16. H. Wu and L. V. Interrante, *Polym. Prepr.* **33**, p. 210 (1992).
17. H. Wu and L. V. Interrante, *Chem. Mater.* **1**, p. 564 (1989).
18. Z. F. Zhang, F. Babonneau, R. M. Laine, Y. Mu, J. F. Harrod and J. A. Rahn, *J. Am. Ceram. Soc.* **74**, p. 670 (1991).
19. Y. Mu, R. H. Laine and J. F. Harrod, *Appl. Organometal. Chem.* **8**, p. 95 (1994).
20. B. Boury, L. Carpenter and R. J. P. Corriu, *Angew. Chem.* **102**, p. 818 (1990).
21. A. T. Hemida, M. Birot, J. P. Pillot, J. Dunogues, R. Pailler and R. Naslain, *J. Mater. Sci.* **32**, p. 3485 (1997).
22. A. T. Hemida, R. Pailler and R. Naslain, *J. Mater. Sci.* **32**, p. 2359 (1997).
23. A. T. Hemida, H. Tenailleau, L. Bardeau, R. Pailler, M. Birot, J. P. Pillot and J. Dunogues, *J. Mater. Sci.* **32**, p. 5791 (1997).
24. Z. F. Zhang and R. M. Laine, *Mater. Res. Soc. Symp. Proc. (Covalent Ceramics II: Non-Oxides)*, volume 327, Gottschalk, R. (ed.), TIRS, Pittsburg (1994), p. 207.
25. Z. F. Zhang, S. Scotto and R. M. Laine, *Ceram. Eng. Sci. Proc.* **15**, p. 1529 (1994).
26. D. Seyferth, H. Lang, C. A. Sobon, J. Borm, H. J. Tracy and N. Bryson, *J. Inorg. Organometal. Polym.* **2**, p. 59 (1992).
27. M. F. Gozzi and I. V. P. Yoshida, *Eur. Polym. J.* **33**, p. 1301 (1997).
28. B. Boury, N. Bryson and G. Soula, *Chem. Mater* **10**, p. 297 (1998).
29. W. R. Schimdt, L. V. Interrante, R. H. Doremus, T. K. Trout, P. S. Marchetti and G. E. Maciel, *Chem. Mater.* **3**, p. 257 (1991).
30. N. Bryson, *French Patent* 92 00 369 (1992). C.A. 120-198710u.
31. J. March, *Advanced Organic Chemistry* 3rd edn. John Wiley, New York, 1985.
32. F. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry* 4th edn, John Wiley, New York, 1980.
33. *Comprehensive Organic Chemistry*, volume 3, Pergamon: New York, 1979, p. 567.
34. V. Chvalovsky, *Organometallic Reactions*, volume 3, E. Becker, and M. Tsutsui, (eds), Wiley–Interscience, New York, 1971, p. 1.

35. K. Moedritzer, *Organometallic Reactions*, volume 2, Becker, E. and M. Tsutsui, (eds), Wiley–Interscience, New York, 1971, p. 1.
36. W. Ingle, E. Groschwitz and M. Ring, *Inorg. Chem.* **6**, p. 1429 (1967).
37. J. Morrison and M. Ring, *Inorg. Chem.* **6**, p. 100 (1967).
38. M. Abedini and A. MacDiarmid, *Inorg. Chem.* **2**, p. 608 (1963).
39. Y. Hasegawa and K. Okamura, *J. Mater. Sci.* **15**, p. 720 (1980).
40. S. Yajima, M. Omori, J. Yayashi, K. Okamura, T. Matsuzawa and C. F. Liaw, *Chem. Lett.* p. 551 (1976).
41. F. Duboudin, M. Birot, O. Babot, J. Dunoguès and R. Calas, *J. Organometal. Chem.* **341**, p. 125 (1988).
42. H. Ishikawa, F. Machino, S. Mitsuno, T. Ishikawa, K. Okamura and Y. Hasegawa, *J. Mater. Sci.* **24**, p. 1177 (1989).
43. T. Ishikawa, M. Shibuya and T. Yamamura, *J. Mater. Sci.* **25**, p. 2809 (1990).
44. P. Fillit, A. J. Perry, J. P. Dodelet, G. Perrier and R. Phillip, *Non-destructve Characterization of Material* Volume IV, Plenum Press, New York, 1991.
45. J. G. M. Van Berkum, A. C. Vermeulen, R. Delhez, T. H. deKeijer and E. J. Mittemeijer, *J. Appl. Crystallogr.* **27**, p. 345 (1994).
46. S. Prochazka and R. M. Scanlan, *J. Am. Ceram. Soc.* **58**, p. 72 (1975).
47. S. Prochzak, *Ceramics for High Performance Applications*, J. J. Burke, A. E. Gorum and R. N. Kayz, (eds), Brook Hill Chestnut Hill, 1974.
48. W. Van Rijswijk and D. J. Shanefield, *J. Am. Ceram. Soc.* **73**, p. 148, (1990).
49. Y. Tajima and W. D. Kingery, *J. Am. Ceram. Soc.* **65**, p. C-27 (1982).
50. C. Greskowich and J. H. Rosolowski, *J. Am. Ceram. Soc.* **59**, p. 336 (1976).
51. R. Warren and C. H. Andersson, *Composites* **15**, p. 101 (1984).
52. R. Pampush, W. Ptak, S. Jonas and J. Stoch, Vol. 6 of *Materials Science Monographs (Energy and Ceramics)*, Elsevier, Amsterdam - Oxford - New York, 1979, p. 435.
53. R. F. Adamsky, *J. Phys. Chem.* **63**, p. 305 (1959).
54. *Silicon Carbide* suppl Vol. 3B to *Silicon Gmelir Handbook of Inorganic Chemistry*, Springer, New York, 1986.