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Functionalization and further crosslinking of the Nicalon polycarbosilane based on its metalation with the n-butyllithium–potassium t-butoxide reagent

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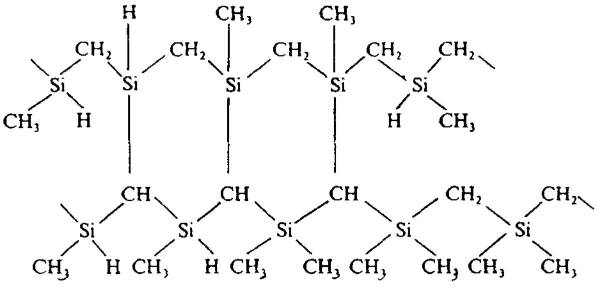
Reaction of the Nicalon polycarbosilane with the n-BuLi/Me_3COK reagent resulted in metalation of approximately one CH_2 group in four. Reaction of the metalated polymer with $Me_2(CH_2=CH)SiCl$ gave a $Me_2(CH_2=CH)Si$-substitued Nicalon polycarbosilane. The polymer was heated with different amounts of the $[(MeSiH)_{\sim 0.8}(MeSi)_{\sim 0.2}]_n$ polysilane in the presence of azobisisobutyronitrile in refluxing benzene. Hydrosilylation by the Si—H-containing polysilane of the CH_2=CH groups of the $Me_2(CH_2$=CH) Si-substituted Nicalon polycarbosilane gave a new hybrid polymer (when appropriate quantities of reactant polymers were used) whose pyrolyis in a stream of argon to 1000°C left a ceramic residue in 77% yield whose elemental analysis indicated a nominal composition of 91% by weight SiC and 9% C.

Keywords: Polycarbosilane, metalation, hydrosilylation, ceramic, Nicalon

INTRODUCTION

We have reported recently concerning the metalation of the polycarbosilane, $[(CH_3)_2SiCH_2]_n$, obtained by ring-opening polymerization of 1,1,3,3-tetramethyl-1,3-disilacyclobutane by the n-BuLi/t-BuOK reagent.[1] Approximately one CH_2 group in four could be metalated, giving a polymer of approximate composition $\{[(CH_3)_2SiCH_2]_3[(CH_3)_2SiCHK]\}_n$. Reactions of such metalated polycarbosilanes with chlorosilanes introduced silyl side groups. Such a reaction with $(CH_3)_2(CH_2$=CH)SiCl gave a polycarbosilane which could be converted to crosslinked systems by appropriate hydrosilylation chemistry.



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The polycarbosilane (PCS) that serves as the precursor for the Nicalon silicon carbide-containing ceramic fibers (henceforth 'Nicalon PCS') contains principally two types of repeat units: $[CH_3Si(H)CH_2]$ and $[(CH_3)_2SiCH_2]$. However, it is not a linear polymer. During its preparation by thermal processing of poly(dimethylsilylene) some ring formation and crosslinking occur and polymer compositions such as **1** have been suggested.[2–4] Linear polymers containing the $[(CH_3)_2SiCH_2]$ or $[CH_3Si(H)CH_2]$ units give only very low ceramic residue yields when they are pyrolyzed in a stream of argon.[1–5] In contrast, such pyrolysis of the uncured Nicalon PCS results in ceramic yields of 55–65%, indicative of a crosslinked system. The nominal composition of the ceramic residue (by elemental analysis) was approximately $1\,SiC + 0.54\,C$, i.e. an excess of free carbon was present.

In view of our successful metalation of the $[(CH_3)_2SiCH_2]_n$ polycarbosilane and the use of the metalated polymer in the preparation of crosslinked materials whose pyrolysis gave much better yields of ceramic residue, it was of interest to study the metalation of the Nicalon PCS. Although the yield of ceramic residue obtained on pyrolysis of this material was reasonable, any improvements would be worthwhile. The presence of Si—H functionality in the Nicalon PCS would be expected to lead to some complications

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since reactive organometallics such as alkyllithium reagents were known to displace hydride from silicon to give an alkysilicon group.[6] We report here the results of such a study.

RESULTS AND DISCUSSION

In a typical metalation experiment, a sample of the Nicalon PCS was dissolved in hexane and the resulting solution was cooled to −74 °C. An equimolar quantity of potassium t-butoxide dissolved in tetrahydrofuran (THF) was added, and subsequently an equimolar quantity of n-butyllithium in hexane. (The reaction of *n*-BuLi with t-BuOK gives *n*-BuK and t-BuOLi.[7-10]) After about one-quarter of the n-butyllithium solution had been added, the partially metalated polycarbosilane separated as a gel. Sufficient THF was added to make the reaction mixture stirrable and more n-butyllithium solution was added until gel formation again made stirring difficult. More THF was then added and this alternating addition of n-BuLi and THF was repeated until all of the n-BuLi had been added. Upon completion of the addition the mixture was stirred for 45 min between −10 °C and 0 °C. (It was found that longer reaction times or higher (>0 °C) reaction temperatures resulted in substantial Si—H substitution by n-butyl and t-butoxy groups.) Subsequently, an excess of a chlorosilane [$(CH_3)_2(CH_2{=}CH)SiCl$, $(CH_3)_2(CH_2Cl)SiCl$, $(CH_3)_2SiCl_2$ or $CH_3(CH_2Cl)_2SiCl$] was added and, after the resulting mixture had been stirred at room temperature for 12–14 h, the volatile materials were removed *in vacuo*. The colorless residue was extracted with a benzene/hexane mixture. Evaporation of the extracts left the silylated Nicalon PCS in the form of white solids in high yield.

The products thus obtained in general had softening points lower than that of the starting Nicalon PCS. They were soluble in common organic solvents and their molecular weights, as determined by cryoscopy in benzene, were in the range 750–1050 (vs 994 for the Nicalon PCS).

When the metalated Nicalon PCS was quenched with gaseous hydrogen chloride (HCl), the original polycarbosilane was not regenerated. The product obtained contained small amounts of n-butyl and t-butoxy groups (by ^1H NMR: signals centered around δ 0.85 due to $Si(CH_2)_2CH_2CH_3$ and around δ 1.3 ppm due to CH_3 groups of the n-butyl and t-butoxy substituents) and had a somewhat lower (ca 890) cryoscopic molecular weight. Thus it appears that reaction of the Nicalon PCS with the n-BuLi/t-BuOK reagent under these conditions resulted in minor substitution reactions at Si—H and also a minor amount of $Si{-}CH_2$ cleavage to give species of lower molecular weight as confirmed by the observed decrease in product molecular weight. Such $Si{-}CH_2$ cleavage also occurred to a greater extent when THF alone was used as reaction solvent or when a threefold excess of the n-BuLi/t-BuOK reagent was used.

Examination of the integrated proton NMR spectra of the silylated PCS produced in these reactions allowed the development of compositions in terms of the structural units present but gave no information about how these building blocks were arranged in the product polymer. Thus, in the reaction in which the metalated Nicalon PCS was treated with an excess of $(CH_3)_2(CH_2{=}CH)SiCl$, the following constitution was obtained:

$$[\mathrm{CH_3SiH}]_{1.0}[\mathrm{n\text{-}BuSiCH_3}]_{0.28}[\mathrm{CH_3SiOBu\text{-}t}]_{0.03}$$

$$[\mathrm{(CH_3)_2SiCH_2}]_{0.88}\text{–}[\mathrm{(CH_3)_2SiCH(Si\{CH_3\}_2}$$

$$\mathrm{CH{=}CH_2})_{0.43}]_n.$$

The C/H analysis of the product polymer was in fair agreement with this formulation. Approximately one CH_2 group in four of the Nicalon polycarbosilane had been metalated, a result similar to that observed in the metalation of the $[(CH_3)_2SiCH_2]_n$ polycarbosilane.[1]

The introduction of $Si(CH_3)_2CH{=}CH_2$ functions as side groups into the Nicalon PCS had very little effect on the ceramic residue yield obtained in the pyrolysis of the product polymer as compared with the Nicalon PCS (Fig. 1). In fact, as can be seen from the TGA traces, the Nicalon PCS has greater thermal stability at temperatures up to 400 °C. Apparently, no significant thermal crosslinking via Si—H to newly introduced $CH_2{=}CHSi$ groups takes place in this temperature range and, in fact, it is likely that some of the $(CH_3)_2(CH_2{=}CH)Si$ side groups are lost.

In the case of the linear dimethylvinylsilylated poly(dimethylsilene), azobisisobutyronitrile-catalyzed reactions with the liquid $[(CH_3SiH)_x(CH_3Si)_y]_n$ polysilane ($x \simeq 0.8$; $y \simeq 0.2$; obtained by sodium condensation of

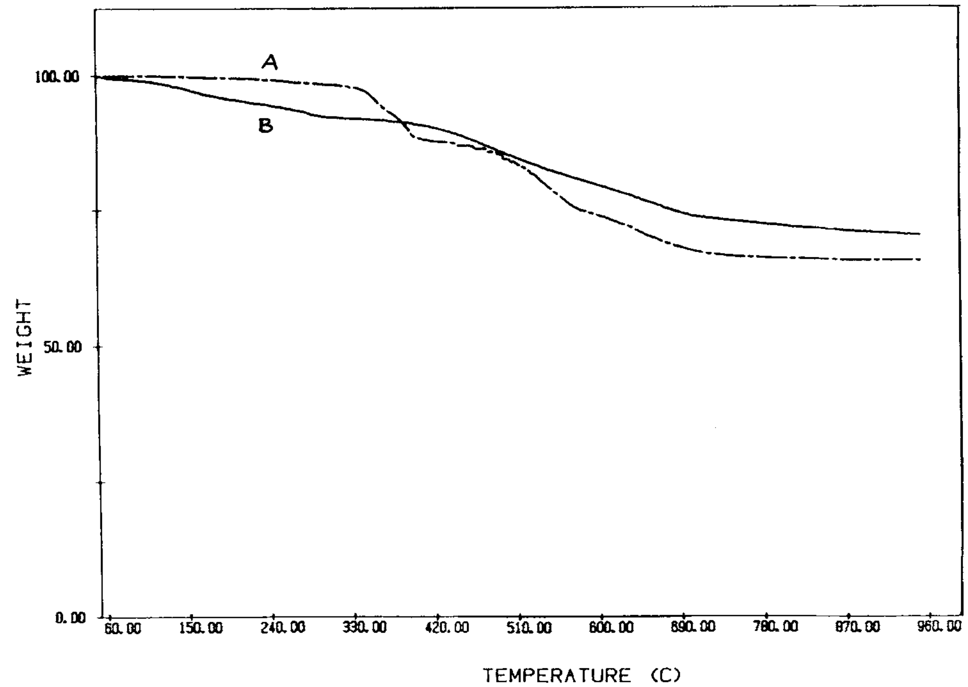

Figure 1 Thermogravimetric analysis traces for commercial Nicalon PCS (curve A) and the Nicalon–$SiMe_2CH{=}CH_2PCS$ (curve B). Heating rate 10 °C min^{-1}, under argon.

CH_3SiHCl_2[11-13]) resulted in formation of a crosslinked system via hydrosilylation and possibly other free-radical processes.[1] Such reactions resulted in two benefits: pyrolysis of the new hybrid polymer gave higher yields of ceramic residue than were obtained for the component polymers alone, and the excess of free carbon obtained in the pyrolysis of the silylated polycarbosilane alone was balanced out (via formation of SiC at higher temperatures) with the excess of free silicon formed in the pyrolysis of the polysilane. This approach could be applied to good advantage in the case of the $(CH_3)_2(CH_2{=}CH)Si$-substituted Nicalon PCS. The reactions with the $[(CH_3SiH)_{0.8}(CH_3Si)_{0.2}]_n$ polysilane were carried out in refluxing benzene solution in the presence of AIBN catalyst (added in portions over the course of 3–3.5 days). The use of 1.9, 3.75 and 6.0 molar equivalents of the polysilane unit per Nicalon–$Si(CH_3)_2CH{=}CH_2$ resulted, respectively, in the formation of white solids **2a** and **2b**, and a waxy solid **2c** that were readily soluble in benzene, toluene and dichloromethane and less soluble in hexane and diethyl ether. Polymer **2a** had a cryoscopic molecular weight of 847; its pyrolysis to 1000 °C in a stream of argon (TGA) gave a ceramic residue yield of 66%. Polymer **2b**, molecular weight 805, gave an 85% ceramic yield (TGA, same conditions). Polymer **2c**, the waxy solid, molecular weight 1275, gave a pyrolysis yield of 64%, possibly because too much of the polysilane had been used. The IR and NMR spectra of these products showed no evidence for residual Si—vinyl groups; Si—H functions still were present. It is clear that the desired hydrosilylation had occurred. However, as noted previously,[1] when a benzene solution of the liquid $[(CH_3SiH)_{0.8}(CH_3Si)_{0.2}]_n$ polysilane and a catalytic quantity of AIBN is heated at reflux for several days, a solid is produced whose yield of ceramic residue on pyrolysis in argon to 1000 °C is 66% (in contrast to the 14% ceramic yield obtained on similar pyrolysis of the untreated polysilane). Thus other crosslinking processes, perhaps via Si—Si bond formation, may be operative when a mixture of the $(CH_3)_2(CH_2{=}CH)Si$-substituted Nicalon PCS and the above-mentioned polysilane is heated in the presence of AIBN.

Some bulk furnace pyrolyses of the hybrid polymers **2a**–**2c** were carried out. The following temperature program was used initially: (1) to 300 °C at 10 °C per min; 6 min hold; to 1000 °C at 10 °C per min; 2 h hold; cool to room temperature

Table 1 Ceramic analyses and derived nominal compositions

	Analysis (%)				Nominal composition (wt %)	
Ceramic	C	H	N	Si	SiC	C
Commercial β-SiC	31.10	0.08	0.38	61.54	91.4	8.6
From Nicalon PCS	38.15	—	—	57.88	86	14
From $(CH_3)_2(CH_2{=}CH)Si$–Nicalon PCS	40.34	0.13	—	51.96	80.4	19.6
From polymer **2b**	32.04	—	—	56.95	91	9
From polymer **2c**	29.67	0.32	—	66.01	98.2	1.8

overnight (under argon). The powder X-ray diffraction patterns of the black pyrolysis residues showed only broad, weak features attributable to SiC. To obtain crystalline material, the following temperature program was used: (1) to 1000 °C at 10 °C per min; 1 h hold at 1000 °C; 10 °C per min. to 1500 °C; 7 h hold at 1500 °C; slow cooling under argon to room temperature. Heating to 1500 °C in general resulted in another 3–9% weight loss.

The 1000 °C pyrolysis residues still contained Si—H groups (diffuse reflectance FT IR); these groups were no longer observed when the sample had been heated to 1500 °C.

Table 1 gives ceramic compositions calculated from elemental analyses of ceramic residues from pyrolyses of products generated in this study, as well as of a commercial SiC sample. These compositions were obtained by assuming that all silicon was present as SiC and that the remaining percentage of C represented elemental carbon. These are not 'real' compositions in that crystalline phases were not present. However, those samples that contained an excess of carbon did not show XRD lines due to elemental silicon when they had been heated at 1500 °C. The Nicalon PCS-derived ceramic contained 14% free carbon. The $(CH_3)_2(CH_2{=}CH)Si$-substituted Nicalon polycarbosilane, as expected, on pyrolysis gave a ceramic that contained more (19.6%) free carbon. This free carbon was considerably reduced in the ceramic residues obtained on pyrolysis of the $(CH_3)_2(CH_2{=}CH)Si$–Nicalon PCS/$[(CH_3SiH)_{0.8}(CH_3Si)_{0.2}]_n$ hybrid polymers **2a**, **2b** and **2c**: **2b**: 8.6% C; **2c**: 1.8% C. Hence polymer **2c** is 98% SiC with only a very small amount of excess free carbon, the goal toward which we were striving.

EXPERIMENTAL

General

All manipulations were carried out using oven-dried glassware under an inert atmosphere (argon or nitrogen) following standard techniques. All solvents were distilled from appropriate drying agents under a nitrogen atmosphere prior to use.

NMR spectra were obtained using a Varian XL-300 NMR spectrometer, IR spectra on a Perkin–Elmer Model 1430 spectrophotometer. Ceramic analysis were obtained from Galbraith Laboratories, Knoxville, TN, USA, and C and H analyses on nonceramic materials were obtained from Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Lindberg tube furnaces with Eurotherm controllers were used for all preparative scale (>1 g) pyrolyses (powder and bulk) to 1500 °C. For pyrolyses to 1000 °C, 1.5-inch (3.8-cm) o.d. quartz tubes and fused silica boats were used for all samples; for those to 1500 °C, 1.5-inch o.d. mullite tubes and boron nitride boats supported on alumina dee-tubes were used. All pyrolyses were carried out under an atmosphere of flowing argon. For experiments to 1000 °C the flow rate was *ca* 6–8 $dm^3\,h^{-1}$, for experiments to 1500 °C it was *ca* 16–20 $dm^3\,h^{-1}$.

TGA measurements were made on a Perkin–Elmer model TGS2 instrument equipped with a Thermal Analysis System 4 controller in an argon atmosphere with a heating rate of 10 °C min^{-1} to 960 °C.

Molecular weights were measured by cryoscopy in benzene.

The chlorosilanes used in this study were purchased from Petrarch and distilled from magnesium turnings before use.

Nicalon polycarbosilane starting material

The polycarbosilane, a product of Nippon Carbon Co., was purchased from Dow Corning Corp.

Analysis: C, 39.90; H, 8.17%.
Cryoscopic (benzene) molecular weight: 994.
TGA (Ar, 5 °C min^{-1} to 1000 °C): 65% (lit.[2] 55–65%).
IR (KBr, CCl_4): 2940 (m), 2886 (mw), 2098 [s, ν(Si—H)], 1401 (w), 1352 (w), 1244 (s), 1012 (s), 822 (vs), 780 (vs), 750 cm^{-1} (vs).
^{1}H NMR ($CDCl_3$): δ −1.0 to +0.6 (broad m, $SiCH_3$, $SiCH_2$, SiCH), 3.7–5.0 (broad m, SiH; fine structure 3.86, 3.98, 4.06, 4.26, 4.6). Integrated intensity ratio $SiCH_3$,$SiCH_2$,SiCH: SiH = 11.8:1 (lit.[2–4] 11.4:1).
^{13}C NMR ($CDCl_3$): δ_C −5.0 to +15.0 (unstructured m).

Reaction of the Nicalon polycarbosilane with the n-butyl-lithium/potassium t-butoxide reagent

Reactions were carried out in three-necked, round-bottomed flasks of suitable size equipped with a pressure-equalizing addition funnel, a gas inlet/outlet tube connected to a Schlenk line, a rubber septum and a magnetic stir-bar. The reaction flask was flamed out in a stream of nitrogen prior to addition of reagents. All reactions were carried out in a dry nitrogen atmosphere.

The Nicalon polycarbosilane (3 g; 55.47 mmol, if one uses the C, H analysis to calculate the empirical formula to be $Si_{1.0}C_{1.8}H_{4.38}$, mol. wt 54.09) and 150 cm^3 of dry hexane were charged into the reaction flask. The resulting solution was cooled to −74 °C (isopropanol/dry ice) and 5.4 g (48.17 mmol) of potassium t-butoxide in 80 ml of THF was added. To this homogeneous solution was then added, slowly at −74 °C, 19.72 ml of 2.44 *M*-n-BuLi in hexane. After addition of a few drops the initially colorless reaction mixture turned yellow, then yellow–orange, and a waxy material separated from solution. After about one-quarter of the n-BuLi had been added, it became impossible to stir the reaction mixture. Sufficient THF was then added to dissolve the precipitate and make the mixture stirrable. The alternating n-BuLi solution and THF additions were continued until all of the n-BuLi solution had been added (which took 10–15 min). By the end of the additions about equal volumes of hexane and THF were present in the reaction mixture. The yellow to yellow–orange reaction mixture was allowed to warm to −10° to 0 °C over the course of 45 min while stirring was continued. (Temperatures above 0 °C should be avoided in order to suppress reactions of the Si—H units with n-BuK and t-BuOLi.) Then an excess of the respective chlorosilane was added [$Me_2(CH_2{=}CH)SiCl$, 15.74 g, 130.4 mmol; $Me_2(CH_2Cl)SiCl$, 18.47 g, 129.1 mmol; $Me(CH_2Cl)_2SiCl$, 20.43 g, 130.0 mmol). This resulted in discharge of the color and precipitation of LiCl and KCl. The mixture was stirred at room temperature overnight. The volatiles then were removed *in vacuo* and to the solid residue was added a benzene/hexane mixture. Centrifugation gave a clear liquid phase that was separated and evaporated *in vacuo* to leave the air stable solid silylated Nicalon polycarbosilane products. These are soluble in benzene, toluene, chloroform and dichloromethane, less so in hexane.

Product characterization

$(CH_3)_2(CH_2{=}CH)Si$-substituted Nicalon PCS
Analyis: Found: C, 47.35; H, 8.85%; Cl, not detectable
Softening range: 165–170 °C.
Molecular weight: 1050.
Ceramic yield (TGA): 70%.
IR(KBr, CCl_4): ν(SiH) 2092, ν(C=C) 1588, ν(Si—C) 1247 cm^{-1}.
^{1}H NMR ($CDCl_3$): δ −1.0 to +2.0 (broad m, maximum intensity between −0.4 and +0.5, peaks in the multiplet at 0.1, 0.18, 0.25, 0.5, 0.83 (CH_2 of n-BuSi), 1.25 (CH_3 of n-BuSi and t-BuOSi), 3.8–4.9 (m, Si—H), 5.4–6.4 (m with peaks at 5.6, 5.9, 6.15, $CH_2{=}CH$). Integrated intensity ratio: SiH:$CH_2{=}CHSi$: CH_3Si,CH_2Si,CHSi = 1:1.3:19.5.

If the integrated intensities of the 0.83 and 1.25 signals are considered, an NMR-derived 'formula' for the constitution of the product can be written:

$$[(CH_3SiH)_1(CH_3SiBu\text{-}n)_{0.28}(CH_3SiOBu\text{-}t)_{0.03}(\{CH_3\}_2SiCH_2)_{0.88}(\{CH_3\}_2SiCHSi(CH_3)_2(CH{=}CH_2))_{0.43}]_n.$$

The calculated C and H values for this 'formula' are: C, 47.71; H, 10.57%.

^{13}C NMR ($CDCl_3$): broad resonances at δ_C −4.0 to +15.0 (CH_3Si,CH_2Si,CHSi),132(=CH_2) and 141(—CH=).

$(CH_3)_2(CH_2Cl)Si$-substituted Nicalon PCS

Analysis: Found: C, 41.53; H, 8.01%.
Softening range: 95–115 °C.
Molecular weight: 674.
Ceramic yield (TGA): 58%.
IR (KBr, CCl_4): ν(SiH) 2091 cm^{-1}.
^{1}H NMR ($CDCl_3$): δ −0.7 to +1.9 (broad m, maximum intensity between −0.2 and +0.6, with considerable fine structure, and 0.86 (CH_2 of n-BuSi), 1.2–1.3 (CH_3 of n-BuSi and t-BuOSi), 2.7–2.8 (m, $SiCH_2Cl$), 3.8–5.0 (m, SiH).

The integrated intensities of these signals allowed the calculation of an approximate 'formula':

$$[(CH_3SiH)_1(CH_3SiBu\text{-}n)_{0.18}(CH_3SiOBu\text{-}t)_x\text{-}(\{CH_3\}_2SiCH_2)_{0.9}(\{CH_3\}_2SiCHSi\{CH_3\}_2\text{-}CH_2Cl)_{0.2}(\{CH_3\}_2SiCH_2Si\{CH_3\}_2CH_2OBu\text{-}t)_y]_n$$

($x+y=0.08$). C, H calcd for $x=0$, $y=0.08$: C, 42.82; H, 0.46%.

$CH_3(CH_2Cl)_2Si$-substituted Nicalon PCS

Analysis: Found: C, 40.59; H, 7.26; Cl, 7.11%.
Softening range: Begins to soften above 175 °C.
Molecular weight: 743.
Cermic yield (TGA): 60%.
IR (KBr, CCl_4): ν(SiH) 2092 cm^{-1}.
^{1}H NMR ($CDCl_3$): δ −0.8 to +1.9 (broad m, maximum intensity between −0.2 and +0.5, CH_3Si, CH_2Si, CHSi, CH_2 and CH_3 of n-BuSi, CH_3 of t-BuOSi), 2.7–3.0 (m, $SiCH_2Cl$), 3.6–4.7 (m, SiH); integrated intensity ratio, SiH:$SiCH_2Cl$:$SiCH_3$,$SiCH_2$,SiCH = 1:0.9:17.

AIBN-catalysis of the reaction of the $(CH_3)_2(CH_2{=}CH)Si$-substituted Nicalon PCS with the $[(CH_3SiH)_{0.8}(CH_3Si)_{0.2}]_n$ polysilane

The $(CH_3)_2(CH_2{=}CH)Si$-substituted Nicalon PCS (above; 2 g), xg of the $[(CH_3SiH)_{0.8}(CH_3Si)_{0.2}]_n$ polysilane ($x=2.60$ g (giving polymer **2a**), 5.18 g (giving polymer **2b**) and 8.2 g (giving polymer **2c**), respectively, were charged into a 300 ml Schlenk flask and 200 ml of benzene was added. To the resulting solution was added 50 mg of AIBN. The reaction mixture was shielded from the light (by wrapping the flask with aluminum foil) and heated at reflux for one day. Then the solution was cooled to room temperature and another 50 mg of AIBN was added; reflux was continued for another day, at which point another 50 mg of AIBN was added. Total heating time was 3–3.5 days. The reaction mixture was filtered through Celite and the filtrate was evaporated at reduced pressure. The residue was dried in high vacuum at 30 °C for several days.

Polymer **2a** and polymer **2b** were white solids, polymer **2c** a faint yellow waxy material (from which long fibers could be hand-drawn).

Characterization data

Polymer 2a

Analysis: Found: C, 35.60; H, 8.45%.
Softening range: 90–9 °C.
Molecular weight: 847.
Ceramic yield: 66%.
IR (KBr, CCl_4): ν(SiH) 2096 cm^{-1}.
^{1}H NMR ($CDCl_3$): δ 0.0 to 1.6 (m, peaks at 0.33, 0.85, 1.25, 1.52, CH_3Si, CH_2Si, CHSi, the 1.52 peak due to Me_2(CN)C), 3.4–4.1 (m, maximum peak at 3.68, SiH). Integrated intensity ratio SiH/all other hydrogens = 1:8.6.

Polymer 2b

Analysis: Found: C, 34.37; H, 7.91%.
Softening range: The polymer does not melt, only softens up to 250 °C.
Molecular weight: 805.
Ceramic yeild (TGA): 85%.
IR (KBr, CCl_4): ν(SiH) 2093 cm^{-1}.
^{1}H NMR ($CDCl_3$): δ −0.6 to +1.5 (m with maximum intensity between −0.1 and +0.22, further peaks at 0.85, 1.15, 1.45, CH_3Si, CH_2Si, CHSi and Me_2\{CN\}C), 3.3–3.9 (m, maximum peak at 3.55, SiH).

Polymer 2c

Analysis: Found: C, 31.30; H, 8.44%.
Softening range: 75–80 °C.
Ceramic yield (TGA): 64%.
IR (KBr, CCl_4): ν(SiH) 2098 cm^{-1}.
^{1}H NMR ($CDCl_3$): δ 0.0 to 1.6 (m, maximum peak at 0.35, CH_3Si, CH_2Si, CHSi, 1.55, Me_2(CN)C), 3.3–4.3 (m, SiH).

Control experiments

(a) The action of AIBN on the $(CH_3)_2(CH_2{=}CH)Si$-substituted Nicalon PCS in refluxing benzene (3 g of the polymer, three 50 mg portions of AIBN, total reaction time 3 days) was examined. The polymer isolated after this treatment showed no change in ceramic yield on pyrolysis under the standard TGA conditions. IR and ^1H NMR spectroscopy showed vinyl groups still to be present.

(b) In the case of the commercial Nicalon PCS, such treatment resulted in an increase in ceramic yield from 65% (untreated) to 75% (AIBN-treated).

(c) In the case of the $[(CH_3SiH)_{0.8}(CH_3Si)_{0.2}]_n$ polysilane, such AIBN treatment increased the ceramic yield from 14% (untreated) to 66%.

Bulk pyrolyses

In a typical experiment, 1.500 g of polymer **2b** was weighed out in the inert atmosphere box into the porcelain boat. This was transferred into a quartz tube in the tube furnace and subsequently flushed with argon for 20–30 min. The pyrolysis program involved heating (in a stream of argon) to 300 °C at 10 °C min^{-1}, a 6-min hold at 300 °C, and then heating to 1000 °C at 10 °C min^{-1}, with a 2-h hold at that temperature. Slow cooling to 25 °C followed. The black ceramic residue was transferred to the inert atmosphere box; it weighed 1.150 g (77% ceramic yield). Its powder X-ray diffraction pattern (Cu-Kα, Ni filter) showed only weak, broad peaks attributable to SiC.

A 500 mg sample of the ceramic thus obtained at 1000 °C from polymer B was heated to 1000 °C at 10 °C min^{-1} and, after a 1-h hold at 1000 °C, was heated to 1500 °C at 10 °C min^{-1}. The residue weighed 455 mg; thus another 9% weight loss had occurred. The powder X-ray diffraction pattern now showed strong, sharp lines due to β-SiC.

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