

Articles

Chemically Designed, UV Curable Polycarbosilane Polymer for the Production of Silicon Carbide

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Despite numerous research efforts, the production of silicon carbide fibers from polycarbosilane polymer precursors requires controlled surface oxidation and oxidative cross-linking for shape retention during inert-atmosphere pyrolysis. As a novel processing solution, a commercial polycarbosilane polymer [Dow Corning (X9-6348)] was chemically modified to provide a precursor of high solubility and latent reactivity. The chemical modification involves the Lewis acid catalyzed chlorination of polycarbosilane and the subsequent substitution of chlorine using sodium acetylide to introduce ethynyl functional groups (e.g., $-\text{C}\equiv\text{CH}$). This ethynyl-modified polycarbosilane undergoes controlled, free-radical initiated cross-linking during UV irradiation. Using this polymerization technique, it is possible to circumvent the need for surface oxidation and to prepare polymer fibers that retain shape during the inert-atmosphere pyrolysis required to produce β -SiC.

Introduction

The production of silicon carbide (SiC) from the pyrolysis of chemically designed, polymeric precursors has been the subject of intense research over the last fifteen years.¹⁻⁶ In general, the precursors developed in these investigations were thermoplastic, low molecular weight polymers which lose shape prior to the thermally activated cross-linking mechanisms that produce SiC/C ceramics. This inability of polycarbosilane polymeric precursors to retain their shape during pyrolysis has severely limited the macroscopic SiC ceramics that can be produced from these polymers.⁷

Despite the inability of polycarbosilane (PCS) precursors to retain their shape during pyrolysis, these polymeric precursors have been successfully used for the production of Nicalon silicon carbide fibers. To provide for shape retention, the commercial production of these β -SiC fibers requires surface oxidation and oxidative cross-linking prior to pyrolysis.^{8,9} Although the oxidation process provides for fiber shape retention, it detrimentally influences the

oxidation resistance and the mechanical properties of the ceramic fibers at high temperatures ($T > 1000$ °C).¹⁰

For several years, investigator's have explored alternative cross-linking techniques (chemical and high-energy irradiative processes) to produce fibers with improved high-temperature properties.¹¹⁻¹³ Unfortunately, only minimal improvements have been achieved because these processes usually involve the oxidation of the PCS precursor. Electron beam irradiative cross-linking is the only technique that does not involve PCS oxidation, but given its experimental complexity, this process is probably economically impractical for commercial development.

To produce β -SiC fibers without surface oxidation, the preceramic polymers should be rigid enough to hold shape up to and exceeding 500 °C where thermally initiated cross-linking will solidify the structure.⁸ One method for accomplishing this is to increase the molecular weight of the initial polymer. Currently, the use of higher molecular weight PCS precursors is being investigated for the production of SiC fibers.^{14,15} The dilemma of using high molecular weight precursors is that their lower solubilities and higher melt temperatures can make melt or solution

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spinning of fibers more difficult, if not possible. As a consequence, these high molecular weight precursors require the addition of vinylic polysilazanes to aid fiber spinning.

As a novel processing solution, we have suggested an economically feasible technique involving the chemical modification of a commercial PCS precursor [Dow Corning (X9-6348)]. This chemical modification includes a Lewis acid catalyzed transchlorination of PCS with trimethylchlorosilane and a subsequent substitution of chlorine with sodium acetylide to introduce ethynyl (e.g., $-\text{C}\equiv\text{CH}$) functional groups. The incorporation of these moieties into the polymer network has numerous advantages, including (1) the substituents can behave as both cross-linking sites and as an intimately dispersed carbon source, (2) cross-linking of the polymers can be initiated thermally or by ultraviolet irradiation to form thermally rigid network polymers, and (3) unsaturated substituents of this type enhance solubility of the polymeric precursor in organic solvents. As a result, a low molecular weight precursor of high solubility is obtained that can be cross-linked, under controlled, non-oxidizing conditions, into thermally rigid solids of high molecular weight.

Noteworthy is that this processing solution will introduce additional carbon impurities into the already carbon rich, SiC ceramic products. However, since these ceramics already contain approximately 20–40 atom % excess carbon, a small increase in the carbon impurity concentration is unlikely to detrimentally influence their mechanical properties.¹⁶ More importantly, the elimination of the oxygen impurities can have a tremendous influence on the physical properties of the ceramic fibers since oxygen contamination is linked to high-temperature crystallization and mechanical property degradation.¹⁰ Furthermore, if this processing solution is viable, it would be possible to modify a silicon-rich, SiC polymeric precursor to result in a more stoichiometric SiC ceramic.

In this report, we describe the use of an ethynyl-modified polycarbosilane for the production of silicon carbide fibers. The reactions, the products and the UV-initiated cross-linking of the ethynyl-substituted polycarbosilane were characterized using ¹³C and ²⁹Si NMR and IR spectroscopies. The resultant crystalline ceramic fibers were analyzed using X-ray diffraction and electron microscopy.

Experimental Procedures

General Considerations. All reactions and processing were conducted within a nitrogen-atmosphere glovebox or by means of standard Schlenk manipulations. Sodium acetylide, trimethylchlorosilane, and aluminum chloride were purchased from the Aldrich Chemical Co. and used without further purification.

Instrumentation. All ²⁹Si (71.549 MHz) and ¹³C (90.556 MHz) NMR spectra were recorded with a Bruker AM-360 FT NMR spectrometer using relaxation delays of 6.0 and 1.0 s and pulse widths of 10.0 and 12.8 μs for Si and C, respectively. Tetramethylsilane was used as the reference standard for the spectra of both experiments. Transmission IR spectra were obtained using either a Beckman FT-1100 or a Perkin-Elmer 1330 spectrophotometer over respective ranges of 4000–500 and 4000–200 cm^{-1} . The polymeric samples were exposed to ultraviolet radiation (200–600 nm) inside a glovebox under a nitrogen atmosphere. Pyrolyses were conducted in a graphite refractory furnace (Thermal Technology, Series 1000) under a flowing argon atmosphere (99.999% Ar). X-ray diffraction (XRD) spectra were

obtained from a Phillips diffractometer using $\text{CuK}\alpha_{-1}$ radiation at 40 kV and 30 mA. Secondary electron micrographs were obtained for Au sputtered samples using a JEOL 200 scanning electron microscope. Molecular weight and chemical analysis of the polymeric products were performed by Galbraith Laboratories, Inc. in Knoxville, TN.

Preparation of Poly(ethynyl)carbosilane. A 1-L three-necked round-bottom flask, equipped with a teflon-coated magnetic stir bar was dried under vacuum and filled with nitrogen. To this flask, 100 g of polycarbosilane, purchased from DOW Corning ($M_n = 1800$), was added. An excess of trimethylchlorosilane [$\text{ClSi}(\text{CH}_3)_3$] (300 mL) was then added to dissolve the polycarbosilane. Upon dissolution, 5 g of anhydrous aluminum chloride (Al_2Cl_6) was added. An exothermic reaction was observed which caused the solvent to reflux which was maintained for 2 h. Following the reaction, the excess solvent was removed by vacuum distillation. The Al_2Cl_6 catalyst was then removed by sublimation in vacuo at 60 °C ($\sim 10^{-5}$ mmHg). Unreacted polycarbosilane was removed by extraction in hexane, filtration, and drying in vacuo to yield a white polymer (87 g). ¹H NMR (CDCl_3 , 20 °C) $\delta = 0.25\text{--}0.99$ (br s, $-\text{CH}_2\text{Si}$), 0.19 (s, CH_3Si), 3.79–5.05 (br s, SiH). ²⁹Si NMR (CDCl_3 , 20 °C) $\delta = 27.0$ (br s, SiCl), -0.30 (br s, SiCH_3), -18.0 (br s, SiH). FT IR (KBr, cm^{-1}) 2850, 2950 ($\nu_{\text{C-H}}$), 2150 ($\nu_{\text{Si-H}}$), 1450 ($\delta_{\text{H-C-H}}$), 1025 ($\delta_{\text{Si-CH}_2\text{-Si}}$), 1250 ($\delta_{\text{Si-CH}_3}$), 830 ($\nu_{\text{Si-CH}_3}$).

The chlorinated polycarbosilane polymer (87 g) was dissolved in oxygen-free tetrahydrofuran (THF, 500 mL). To this solution, dry sodium acetylide ($\text{NaC}\equiv\text{CH}$, 30 g) was added in excess. An exothermic reaction ensued and a gray precipitate was observed in the orange colored solution shortly after addition. The insoluble salts and the excess sodium acetylide were removed by filtration. The THF solvent was removed in vacuo to afford a tan, solid polymer (84 g). ¹H NMR ($(\text{CD}_3)_2\text{CO}$, 20 °C): $\delta = -0.28\text{--}2.79$ (br m, $-\text{CH}_2\text{Si}$, CH_3Si), 3.25 (br s, $\text{C}\equiv\text{CH}$), 3.71–4.82 (br s, SiH). ¹³C NMR (THF, 20 °C): $\delta = -5.11\text{--}15.1$ (br s, CH_2Si , CH_3Si), 92.1 (br s, $\text{C}\equiv\text{CH}$), 96.0 (br s, $\text{C}\equiv\text{CH}$). FTIR (KBr, cm^{-1}): 3300 ($\nu_{\text{C-H}}$), 2850, 2950 ($\nu_{\text{C-H}}$), 2150 ($\nu_{\text{Si-H}}$), 2050 ($\nu_{\text{C}\equiv\text{C}}$), 1450 ($\delta_{\text{H-C-H}}$), 1025 ($\delta_{\text{Si-CH}_2\text{-Si}}$), 1250 ($\delta_{\text{Si-CH}_3}$), 830 ($\nu_{\text{Si-CH}_3}$).

Results and Discussion

Poly(ethynyl)carbosilane was conveniently prepared in a two-step process from the Dow Corning polycarbosilane. The first step involves modification of PCS by chlorinating the polymer with $(\text{CH}_3)_3\text{SiCl}$ and catalytic amounts of aluminum chloride. Dunogués *et al.* have described the chlorination of a high polymer obtained from the ring-opening polymerization of 1,1,3,3-tetramethylsilacyclobutane by such methods to realize a brown-oily polymer ($M_n \sim 2000\text{--}2200$).^{17–18} The chlorination of the Dow Corning PCS proceeds in a similar fashion to afford a white polymer powder of comparable molecular weight (eq 1).¹⁹

The chlorination reaction could be followed by spectroscopic methods. The IR spectra obtained during the chlorination reaction are presented in Figure 1. The absorption at 440 cm^{-1} in the spectrum of the reaction product confirms the chlorination of the polymer precursor while the characteristics Si–H stretching vibration (2150 cm^{-1}) continuously decreases in intensity. Since the relative intensity of the Si– CH_3 vibration at 1250 cm^{-1} does not change, it is presumed that the chlorination primarily occurs through the Si–H moieties with the

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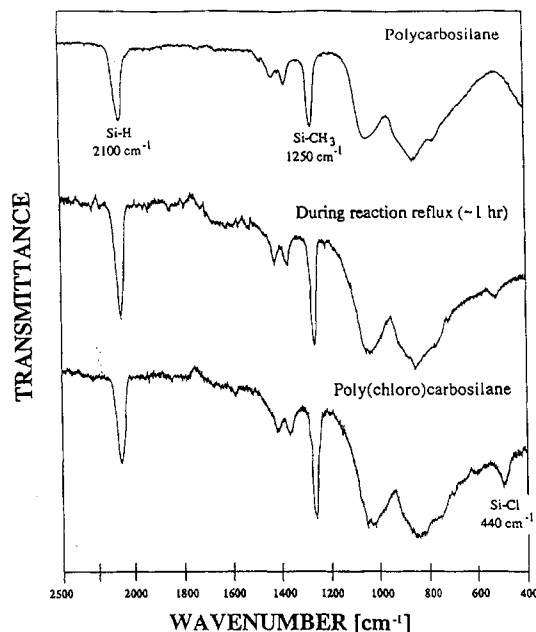
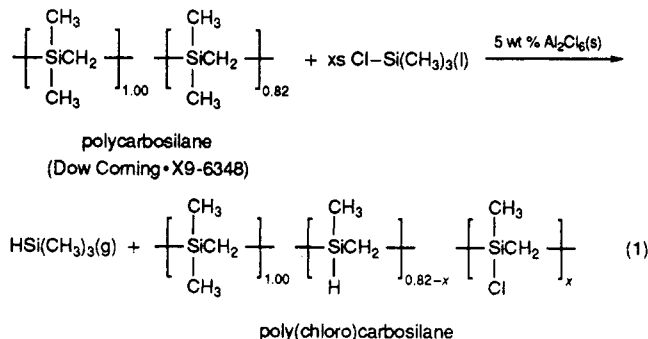


Figure 1. Infrared spectra during the Lewis acid catalyzed chlorination of polycarbosilane.



evolution of the gaseous byproduct, trimethylsilane [HSi(CH₃)₃]. This observation is consistent with previous work on the chemical modification of PCS by transition metal alkoxides which suggested the preferential reactivity of the Si-H bonds.^{20,21,22}

Additional evidence in support of the proposed reaction mechanism is reflected by the ²⁹Si NMR spectra obtained during the reaction (Figure 2). The ²⁹Si NMR data indicate a continuous reduction in the intensity of the signal at -18 ppm which is assigned to a silicon environment of 1 hydrogen and 3 carbon atoms (C₃-Si-H). Simultaneously, a new peak at approximately 26 ppm appears. The latter peak is assigned to silicon environments with either three carbon atoms and one chlorine atom (C₃-Si-Cl) or two carbon and two chlorine atoms (C₂-Si-Cl₂). The broadness of the signal is consistent with the presence of both, but the position (26 ppm) suggests that a C₃-Si-Cl silicon environment dominates. Intensity is proportional to concentration, so the integration of these signals allows an estimate of the chlorine concentration in the modified polymer to be made. Chlorine concentrations (*x* in eq 1) of 0.20 and 0.62 were obtained for reflux durations of 1 and 2 h, respectively.

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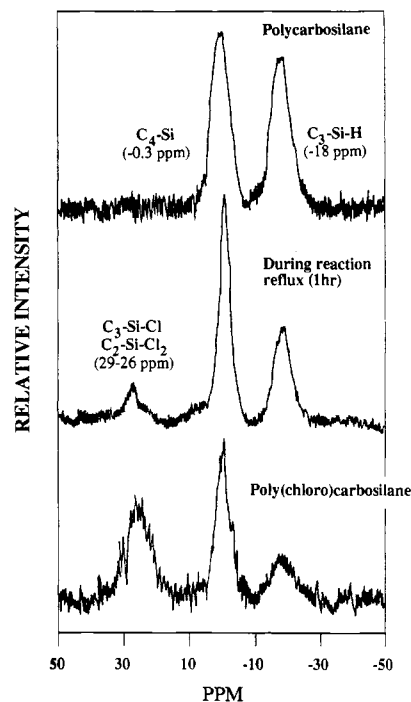
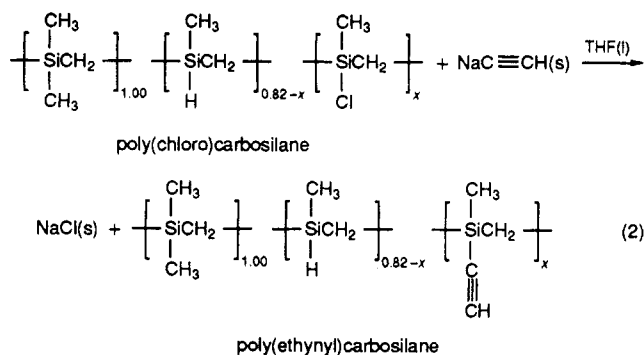


Figure 2. ²⁹Si NMR spectra during the Lewis acid catalyzed chlorination of polycarbosilane.

The chlorinated polymer is soluble in polar organic solvents and in chlorinated hydrocarbons, but it is insoluble in nonpolar organic solvents. This solubility feature was exploited to remove the unreacted polycarbosilane by hexane extraction. The chlorinated polymer is highly reactive as exposure to moist air quickly results in hydrolysis as does direct contact with water or alcohol. Because of its high reactivity, the chlorinated polycarbosilane represents an important synthon for preparing functionalized polycarbosilane derivatives. Several interesting substitution reactions using organometallic reagents have resulted in new chemically modified, polycarbosilanes.²³ In particular, ethynyl functional groups were introduced into the polymeric structure of polycarbosilane as represented by equation 2.



The infrared spectrum of the polymer product from eq 2 indicates the incorporation of ethynyl moieties into the polymer structure as characteristic vibrations are observed at 3300 ($\nu_{\text{C-H}}$) and 2050 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$) (Figure 3). Since the Si-Cl vibration at 440 cm^{-1} is no longer present, it is believed that the substitution occurred through these sites, as designed. Further evidence supporting the proposed

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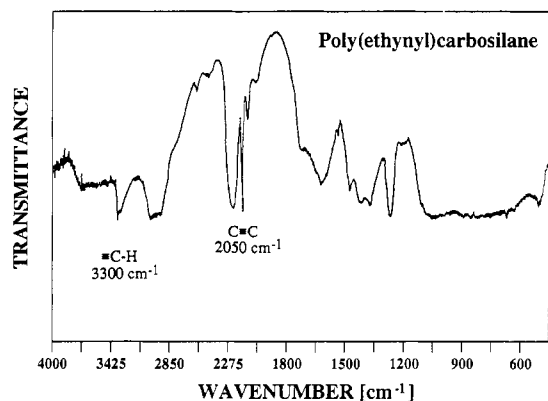


Figure 3. Infrared spectra of poly(ethynyl)carbosilane polymer product.

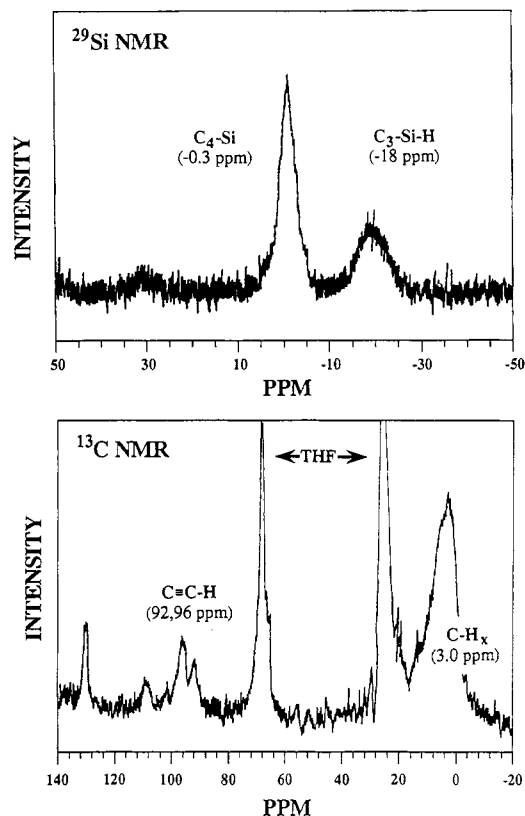


Figure 4. ^{13}C and ^{29}Si NMR spectra of poly(ethynyl)carbosilane.

formation of silicon bonded ethynyl ligands [$\text{SiC}\equiv\text{CH}$] is provided by the ^{29}Si and ^{13}C NMR spectroscopic data (Figure 4). The ^{29}Si NMR spectrum indicates that the replacement of the Si-Cl bonds is essentially complete as reflected by the elimination of the signal at 26 ppm. Unfortunately, the incorporation of ethynyl function groups is not confirmed by the ^{29}Si NMR spectrum. It is believed that the $\text{C}_3\text{SiC}\equiv\text{CH}$ signal is hidden in polycarbosi-lane's broad Si-C_4 peak at -0.3 ppm. More conclusive evidence for the incorporation of ethynyl substituents is provided in the ^{13}C NMR as characteristic ethynyl ($\text{C}\equiv\text{C}$) signals are observed at 92 and 96 ppm. The lack of a discernible peak between 8 and 6 ppm in the ^{29}Si NMR spectrum suggests that oxidation of the modified polymer was avoided during this reaction.

The structure of Dow Corning polycarbosi-lane is described as a highly branched, low molecular weight, gellike

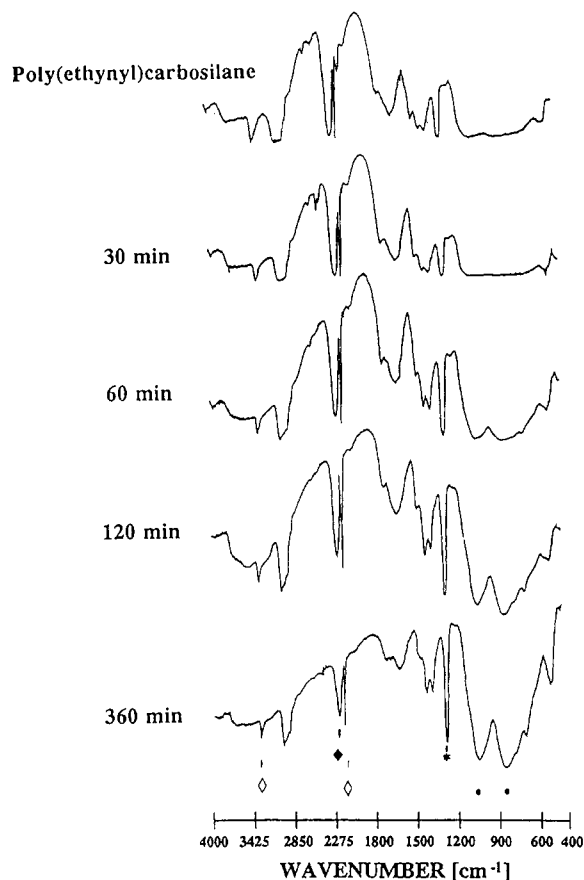


Figure 5. Infrared spectra of poly(ethynyl)carbosilane powders before and after UV exposure.

oligomer.²⁴ During the chlorination of polycarbosi-lane, a slight increase in molecular weight was observed [$1800\rightarrow 2430$, $\Delta M_n = 630$]. This increase was expected due to the relative weight difference between hydrogen and chlorine. Following the substitution, a slight decrease in molecular weight was observed as expected for the ethynyl substitution of the heavier chlorine atoms [$2430\rightarrow 2284$, $\Delta M_n = 146$]. Since the molecular weight change is not large in either reaction, it is assumed that extensive cross-linking between the polycarbosi-lane oligomers does not occur and that the structural framework of the modified polymer is essentially unchanged.

UV Cross-Linking of Poly(ethynyl)carbosilane Fibers. To determine the extent of cross-linking in the ethynyl-functionalized polycarbosi-lane upon exposure to ultraviolet radiation, bulk polymer samples were analyzed with FT IR spectroscopy during irradiation (Figure 5). UV-initiated cross-linking of the functionalized polycarbosi-lane is supported by the intensity decrease of the Si-H (2150 cm^{-1} , \blacklozenge) and ethynyl vibrations (3300 cm^{-1} , 2050 cm^{-1} , \blacklozenge) in relation to the Si-CH_3 vibration (1250 cm^{-1} , \ast). In addition, Si-C overtone vibrations [$(\delta_{\text{C-Si-C}}, 1160\text{ cm}^{-1}, \bullet)$; $(\delta_{\text{C-Si-C}}, 860\text{ cm}^{-1}, \bullet)$] continuously increase in intensity confirming that cross-linking has occurred. Since the ethynyl ($\text{SiC}\equiv\text{CH}$) and the Si-H vibrations decrease proportionally, it is assumed that the cross-linking of the PCS chains occurs primarily through hydrosilylation reactions at these sites.

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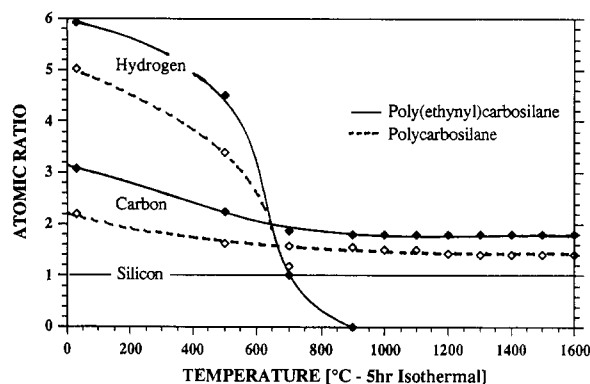


Figure 6. Thermogravimetric analysis of the Dow Corning polycarbosilane precursor and of the functionalized precursor, poly(ethynyl)carbosilane, before and after UV irradiation.

Due to the poor sensitivity of IR spectroscopy, a large degree of polymer cross-linking was required for detection. As a consequence, extremely long exposure times were needed to obtain evidence of cross-linking in these bulk samples. Fortunately, these long exposure times are probably not required since a small degree of polymer cross-linking should sufficiently increase the molecular weight to provide for thermal rigidity. Even after long exposure times, a large concentration of unpolymerized ethynyl groups exist as characteristic stretching vibrations are still observed at 3300 and 2050 cm^{-1} . A limited UV penetration depth would reasonably account for this observation. For the production of ceramic fibers, the penetration depth of the UV radiation should not be a drawback as only surface polymerization is required. Cross-linking of the surface should occur rapidly and result in a thermally rigid coating that allows shape retention during pyrolysis. Since PCS is not prone to thermal decomposition, it is unlikely that cross-linking of the surface would result in the formation of hollow SiC fibers.

Polymer fibers were prepared by dissolving the functionalized PCS polymer in THF to produce solutions whose viscosity allowed simple wire fiber pulling. These polymer fibers were irradiated with UV light for 10 min and then pyrolyzed in an inert atmosphere. The influence of this UV curing on the ceramic yield is represented in Figure 6. With a 10-min exposure, the modified polymer resulted in an 85% ceramic yield which is significantly better than the results obtained with the uncured polymer (74%) and the original PCS polymer (63%). The chemical analysis results for the modified PCS precursor and the original PCS precursor after 5 h of isothermal pyrolysis at temperatures between 30 and 1600 °C are represented in Figure 7. The increased carbon impurity concentration in the modified polymer system is consistent with its increased ceramic yield.

After pyrolysis at 1000 °C, broad peaks characteristic of small β -SiC crystallites were observed in the X-ray diffraction spectra (Figure 8). At this temperature, an X-ray diffraction, peak-broadening analysis suggests that the average crystallite size is approximately 35 Å. After pyrolysis to 1300 °C, a similar analysis suggests an average β -SiC crystallite size of approximately 62 Å. Since these results are similar to that of the original polycarbosilane precursor, it is reasonable to assume that the modification does not significantly alter the crystallization kinetics.²⁵

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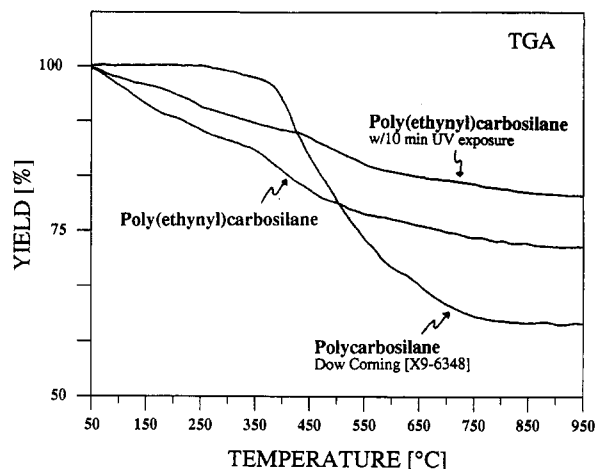


Figure 7. Chemical analysis of poly(ethynyl)carbosilane and Dow Corning polycarbosilane during inert-atmosphere pyrolysis.

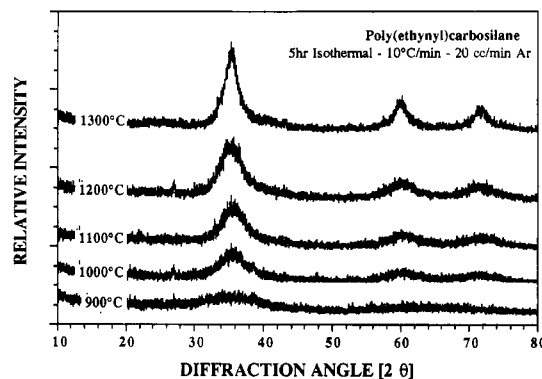


Figure 8. X-ray diffraction spectra of the β -SiC prepared from poly(ethynyl)carbosilane.

In Figure 9, scanning electron micrographs of the crystalline, β -SiC fibers prepared via UV cross-linking of the modified polymer are presented. For comparison, micrographs of commercial Nicalon silicon carbide fibers are included. It is apparent that this new process yields fibers which retain their shape during inert atmosphere pyrolysis without surface oxidation. The β -SiC fibers obtained had diameters ranging between 40 and 100 μm .

From the SEM micrograph, it is evident that the UV cured ceramic fibers do not contain the surface oxide contaminants. These fibers, however, contain interior porosity as observed in the fiber cross section shown in Figure 10. This is a result of either solvent entrapment during fiber drawing or poor densification during pyrolysis. The ceramic fibers prepared via solution drawing are inferior to the melt-spun Nicalon fibers because of the interior porosity observed in the fiber cross section (Figure 10). It is expected that spindle extrusion of smaller diameter fibers will eliminate these problems and allow the production of dense β -SiC/C fibers.

Conclusions

The aluminum chloride catalyzed transchlorination of polycarbosilane with trimethylchlorosilane results in a reactive, chlorinated polycarbosilane derivative which readily undergoes substitution in the presence of sodium acetylide introducing ethynyl functional groups ($\text{SiC}\equiv\text{CH}$). This chemical modification does not significantly increase the molecular weight of the polymer precursor allowing

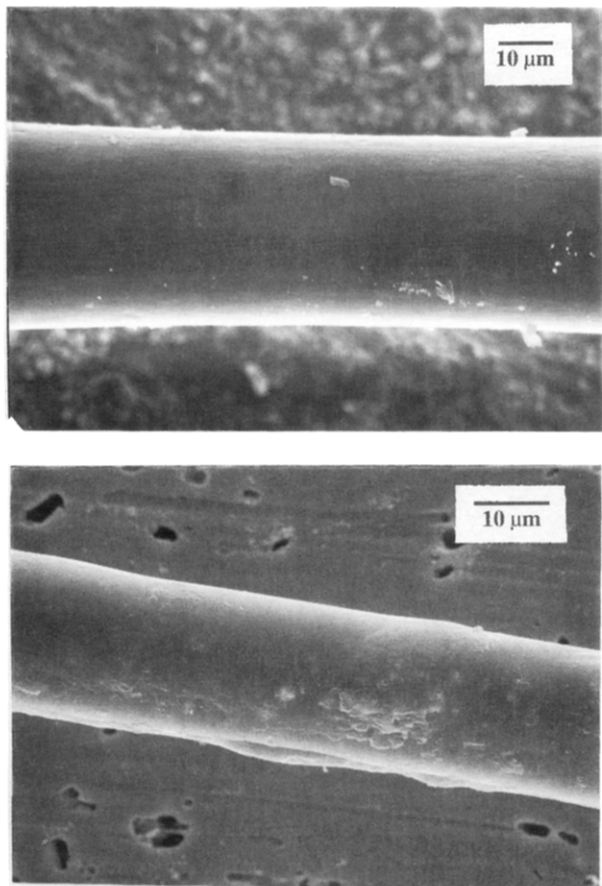


Figure 9. Scanning electron micrographs of (a) a β -SiC fiber prepared via UV-irradiated poly(ethynyl)carbosilane (1000 °C, 2 h) and (b) a commercial Nicalon β -SiC fiber.

for high polymer solubility. The primary advantage of this modification is that the ethynyl functional groups enable polymer cross-linking via UV irradiation. Through controlled cross-linking of this type, it is possible to prepare polymers that maintain their shape and dimension during inert atmosphere pyrolysis into SiC without the use of oxidation curing. Through refined processing of the polymer fibers, it is believed that oxide and pore-free, high-

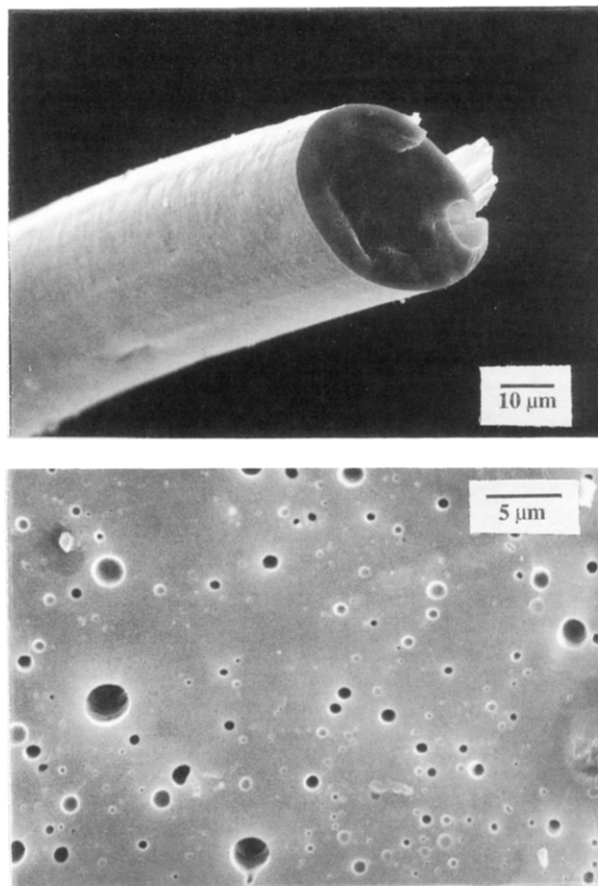


Figure 10. Cross-sectional, scanning electron micrographs of a β -SiC fiber prepared via UV-irradiated poly(ethynyl)carbosilane (1000 °C, 2 h).

quality β -SiC fibers can be produced using this technique.

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