Methylhydridopolysilazane and Its Pyrolytic Conversion to Si_3N_4/SiC Ceramics

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The present report explores the use of liquid-state nuclear magnetic resonance (NMR) spectroscopy for characterizing the methylhydridopolysilazane (MHPS) prepared by the Seyferth/Wiseman procedure and compares the structure of this polymer with other ceramic precursors derived from similar synthetic routes. X-ray diffraction, cross-polarization (CP), and single-pulse magic angle spinning (MAS) solid-state NMR spectroscopy were employed for characterizing temperature-induced short-range bonding and phase evolution in MHPS precursors to SiC/Si_3N_4 ceramics. The molecular weight and methyl substitution of the preceramic polymers is shown to affect the ceramic yield and phase development of these polysilazanes during pyrolysis. Ceramic yields approaching 90% are observed in these systems. CPMAS NMR is shown to be uniquely capable of identifying the hydrogen-rich environments and the onset of short-range SiC and Si_3N_4 phase development in these amorphous preceramic materials.

Introduction

The development of inorganic and organometallic polymers as preceramic materials for the synthesis of silicon carbide (SiC) and silicon nitride (Si_3N_4) ceramics is an area of considerable research emphasis in modern materials science. These materials hold potential for a host of applications which include (1) drawing fibers,[1-3] (2) protective coatings for otherwise oxidizable materials, such as carbon or ceramic reinforcement fibers, and parts fabricated from carbon/carbon composites,[4] (3) injection molding or casting of complex shapes,[5] (4) infiltration of porous ceramic bodies, (5) binders for ceramic powder processing,[6] (6) preparation of controlled morphology powders[7] and (7) formation of thin ceramic films for electronics applications. Preceramic polymer routes to ceramics may also allow for tighter control of final product purity[8,9] and deliberate modification of required processing temperatures owing to the minimal diffusion distances afforded by atomic level mixing of the ceramic precursors.[10] For ceramic composites, such as Si_3N_4/SiC, final product phase selectivity and crystallinity may be engineered by deliberate control of the molecular architecture of the preceramic precursors.[11] This sustained development of divergent synthetic and processing routes for ceramic and preceramic materials increases the need for improved characterization techniques to investigate the development and evolution of chemical structure in these systems.

Magic angle spinning solid-state nuclear magnetic resonance (MAS NMR) has emerged as a powerful, nondestructive tool for characterizing ceramic[1,8,9,12-15] and preceramic[2,8-11,17-27] materials. This technique is ideal for investigating the coordination and chemical bonding of NMR active nuclei as well as elucidating phase distributions regardless of crystallite size or degree of crystallinity.

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This type of quantitative, multielemental information is useful for following chemical structure evolution during amorphous polymer/preceramic/ceramic phase transitions and is largely unavailable by other means.

The present report details the synthesis of and liquid-state characterization of methylhydridopolysilazane (MHPS) polymers of the form $[(CH_3SiHNH)_x-(CH_3SiN)_y]_n$ which are precursors for Si_3N_4 and Si_3N_4/SiC ceramics[17,19] and compares the structure of these polymers with other ceramic precursors derived from similar synthetic routes. Cross-polarization and single-pulse ^{29}Si magic angle spinning solid-state NMR experiments are used to explore temperature-induced short-range bonding, phase evolution, and hydrogen incorporation in the products of the pyrolysis of the polymers on the way to the final Si_3N_4/SiC ceramics. Molecular weight is shown to affect both the ceramic yield and phase selectivity of preceramic materials derived from hydridomethylpolysilazane.

Experimental Section

Preceramic Polymer Synthesis.[17,18] All reactions and manipulations were performed under prepurified nitrogen or argon atmosphere using standard Schlenk techniques or were carried out in a nitrogen-filled drybox. Tetrahydrofuran and diethyl ether were distilled under nitrogen from sodium benzophenone ketyl. Potassium hydride (Alfa), obtained as a 20–25 wt % slurry in mineral oil, was washed with hexane, dried, and used without further purification. Methyl iodide (Aldrich) was distilled, under nitrogen, from P_2O_5.

A mixture of cyclic $(CH_3SiHNH)_n$ oligomers was prepared by bubbling ammonia into a diethyl ether solution of methyldichlorosilane (Petrarch), at 0 °C, until an excess of NH_3 was observed condensing in a dry ice/acetone condenser. The reaction mixture was warmed to room temperature and filtered. Trap-to-trap distillation of the ether gave a clear oil in 70% yield.

$[(CH_3SiHNH)_a(CH_3SiN)_b]_n$ polymer was prepared by slow addition of 21.12 g (0.357 mol) oligomer to 0.14 g (3.49 mmol) of potassium hydride in THF at room temperature. The resulting mixture was heated at reflux for 30 min, and then 1.0 mL (16.17 mmol) of methyl iodide was added by syringe, precipitating white KI in 95% yield. The reaction mixture was cooled to room temperature and filtered to remove KI. Evaporation of the solvent gave the low molecular weight (approximately 7800 by GPC) solid polysilazane (called 8K MHPS). A reflux time of 2 h after addition of KH to the silazane oligomer solution gave a polysilazane of higher molecular weight (approximately 31 900 by GPC, called 32K MHPS). All samples were stored under nitrogen in sealed vials.

NCP100 (MW ~ 47 000) and NCP200 (MW ~ 2000) powders (Nichimen Corp., manufactured by the Chisso Corp., Japan, under license of the Seyferth/Wiseman patent[17b]) were used as received.

Bulk Pyrolysis. Samples were placed in high-purity alumina crucibles and pyrolyzed to various temperatures (160, 500, 1000, and 1520 °C) in a microprocessor-controlled tube furnace under a constant flow of argon. All samples were heated to a minimum hold time of 1 h at temperature.

Characterization. Thermal analyses were performed under flowing nitrogen atmosphere using a du Pont Model 9900 TGA at heating rates of 10 °C/min. Gas chromatographic (GC) analyses were performed using a Hewlett-Packard, Model 5890, instrument equipped with a flame ionization detector and capillary jets. Mass-selective detection (GC-MS) was performed using a Hewlett-Packard 5870 mass selective detector. Separations were performed on a 5-m HP 530 μm capillary column at an injector temperature of 250 °C. The GC oven was programmed to an initial temperature of 60 °C and ramped at a rate of 10 °C/min to a final column temperature of 275 °C, with a final temperature hold of 4 min. Samples were prepared as 5–10% solutions in hexane. Direct flash injection volumes of 0.5 μL were used for the GC analyses.

Molecular weight analyses were performed using a Waters Model 712 GPC calibrated with polystrene standands. Samples were dissolved in tetrahydrofuran prior to analysis. The higher molecular weight polysilazanes exhibited limited solubility in a range of solvents. Given the inherently reactive nature of these systems and the wide GPC elution profiles typically observed, the molecluar weights assigned are, at best, relative comparisons of the sizes of these polymers.

NMR analyses were performed using a GE GN-300 wide bore instrument with a 7.05-T cryomagnet and Chemagnetics solids accessories. ^{29}Si and ^{13}C natural abundance spectra were acquired at 59.6 and 75 MHz, respectively. Liquid-state NMR spectra were acquired of solutions in THF-d_8. Quantitative data were ensured by first measuring spin–lattice relaxation times and employing relaxation delays $\geq 5T_1$. All solid-state magic angle spinning (MAS) NMR data were acquired under conditions of gated high power decoupling at sample spinning rates of 4 kHz. The magic angle was adjusted using the ^{79}Br resonance of KBr.[28] All chemical shift values were referenced to external tetramethylsilane.

X-ray diffraction (XRD) was used to determine the crystalline phases present in the same ceramic and preceramic samples used for NMR analyses (i.e., the samples were taken from the NMR sample holders for subsequent XRD). XRD patterns were collected using a Siemans D-500 powder diffractometer using a scan rate of 2°/min from 7° to 87° 2θ (7° to 37° shown) for Cu Kα radiation.

Results

As stated above, MHPS polymer was prepared in the following manner:

$$CH_3SiHCl_2 \xrightarrow[Et_2O,\,0\,^\circ C]{NH_3} \underset{\text{oligomer mixture}}{(CH_3SiHNH)_n} \xrightarrow[THF,\,RT]{[KH]} \xrightarrow[THF,\,RT]{CH_3I} [(CH_3SiHNH)_a(CH_3SiN)_b(CH_3SiHNCH_3)_c]_n$$

The mixture of oligomers $(CH_3SiHNH)_n$, formed from the reaction of CH_3SiHCl_2 with ammonia, may be described as a mixture of cyclic silazanes with $n = 2, 3, 4$, and larger, as illustrated in Figure 1. The ^1H NMR spectrum of this mixture of oligomers, shown in Figure 2a, reflects the symmetry of these structures by evidencing relatively

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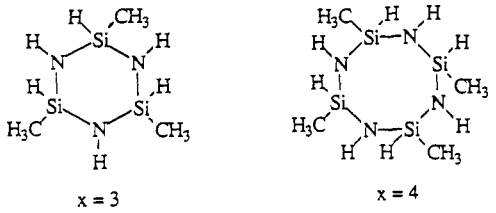

Figure 1. Typical ring systems formed from the oligomer $(CH_3SiNH)_x$, where $x = 3, 4$.

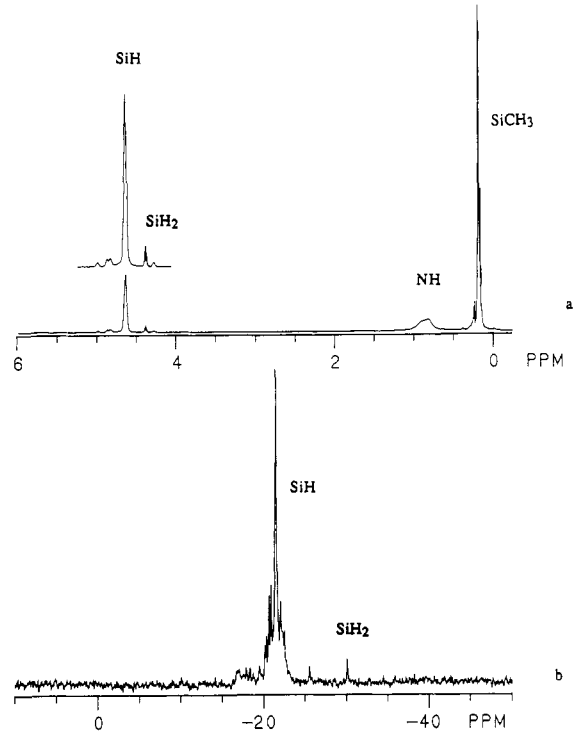

Figure 2. Liquid-state (a) ^1H and (b) ^{29}Si NMR spectra of $(CH_3SiNH)_x$ oligomer.

narrow resonances at 4.65 ppm (SiH) and 0.2 ppm ($SiCH_3$). (NH) functionality gives rise to the broader resonance at1–0.75 ppm. This spectrum supports a cyclic structure, as described above, since no evidence of Si end groups (e.g., CH_3SiH_2NH or $(CH_3)_2SiHNH$) is observed. The relative areas of the resonances defined above are 1:3:1, respectively, consistent with the proposed assignments. The ^{29}Si NMR spectrum of the oligomer mixture, shown in Figure 2b, evidences a narrow resonance at −22 ppm. The fine structure about the main resonance reflects site asymmetry owing to nonplanarity and cis/trans CH_3,H substitution of the silazane rings in solution. ^{29}Si attached proton test (APT) spectra, data not shown,[18] were acquired to confirm the (SiH and SiH_2) assignments discussed above and below, respectively. The minor ^{29}Si peak at −30 ppm confirms the presence of trace amounts of reaction byproducts containing (SiH_2) functionality. This is also reflected by the small peaks observed between 5.0 and 4.3 ppm in Figure 2a.

The NMR assignments discussed above are also supported by GC analyses of the oligomer, shown in Figure 3a. The major species are observed at retention times of 0.72, 2.65, 5.10, 7.32, and 9.30 min. Minor species can be observed, in a similar progression, out to 16 min. The observation of well-defined, narrow peaks at regularly spaced retention time intervals of approximately 2 min is consistent with that expected for $(CH_3SiHNH)_n$ ring systems where ring size is systematically increased, such

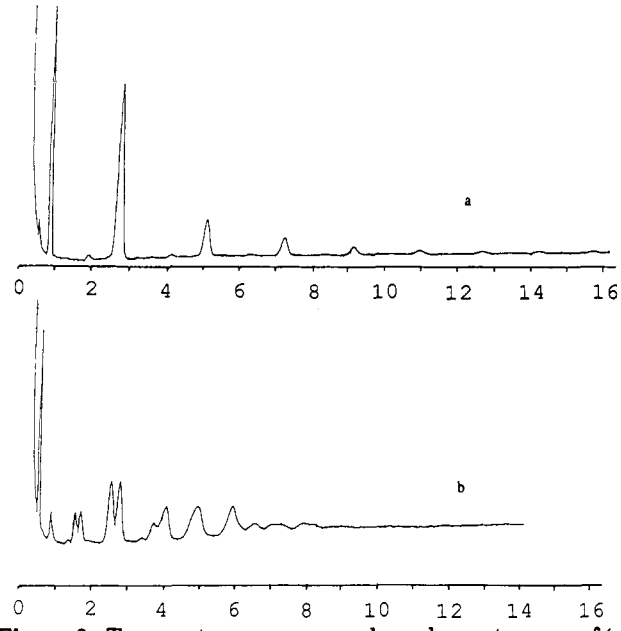

Figure 3. Temperature-programmed gas chromatograms of (a) $(CH_3SiNH)_x$ oligomer and (b) $(CH_3SiNH)_x$ oligomer which had been warmed overnight prior to filtering.

as $n = 2$, 3, 4, etc. Electron impact and mass-selective detection of these GC peaks exhibited parent ions at 177 for the first and 236 for the second major GC peaks. These masses are consistent with cyclic silazanes where $n = 2$ and $n = 3$, respectively. Higher parent ions were not observed for the other GC peaks shown in Figure 3a, suggesting that larger structures may not survive ionization and detection. The higher molecular weight species observed in Figure 3a may result from column or temperature-induced rearrangement or ring condensation reactions. The minor species at retention times of 1.80, 3.55, and 6.36 min may correspond to the (SiH_2) impurity species observed in the NMR data (Figure 2).

Filtration of the reaction mixture containing the silazane oligomers following ammonolysis is a critical step in the synthesis of these ring systems. Overnight storage of the reaction mixture prior to filtration facilitates the formation of measurable amounts of (SiH_2) functionality resulting from base catalyzed isomerization the ring systems. GC data of the oligomer, obtained after it had been warmed to room temperature overnight prior to filtering, are shown in Figure 3b. While the major species from Figure 3a are still observed, a range of structures is evident. Some of these additional structures correspond to the impurity species present in Figure 3a. The ^1H and ^{29}Si NMR spectra of this oligomer mixture are shown in Figure 4. These spectra also reflect a range of structures and evidence an increase in (SiH_2) functionality as shown by the two ^{29}Si resonances at −30 and −32 ppm. Rearrangements of aminosilanes to silazanes[29,30] and isomerization of cyclosilazanes[31–33] in the presence of liquid ammonia have been described previously. Such rearrangements have

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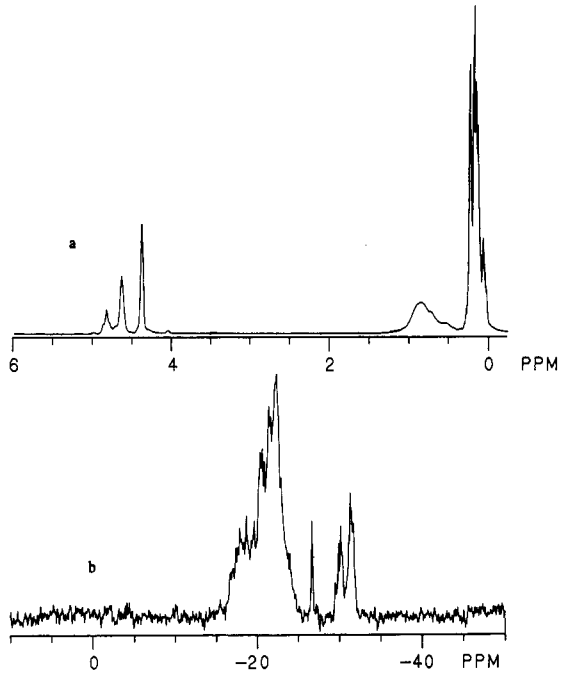

Figure 4. Liquid-state (a) ^1H and (b) ^{29}Si NMR spectra of $(CH_3SiNH)_x$ oligomer which had been warmed overnight prior to filtering.

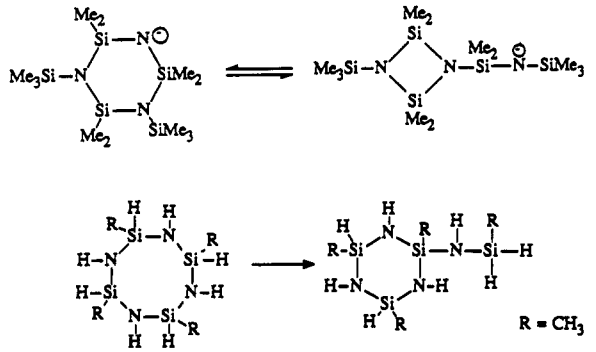

Figure 5. Ring contractions of cyclosilazanes in the presence of liquid ammonia.

been shown to result from intermolecular processes, but these processes are not clearly understood.[30] These rearrangements lead to a variety of straight and branched chain silazanes, as well as ring contractions such as those shown in Figure 5.

The proposed structure of MHPS polymer,[18] a white solid, is that of a mixture of different ring size cyclic and short-chain linear components believed to be bonded via cyclodisilazane linkages, as well as by single Si–N bonds such as those shown in Figures 1 and 5. Obviously, reaction could occur on all sides of the rings, and rings of different sizes could be fused. Polymerization leads to the likely formation of a combination of both ladder, sheet, cage, and linear type structures such as the type shown in Figure 6. The composition of the polymer can be verified using ^1H NMR, as shown in Figure 7a. This spectrum is quite similar to that of polysilazanes prepared by different synthetic routes,[1,8] exhibiting resonances due to SiH, NH,

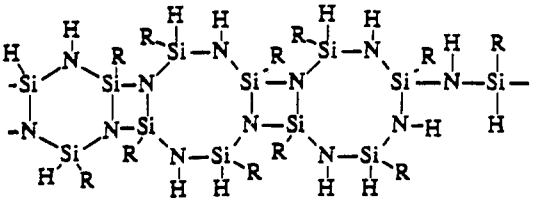

Figure 6. Representative structure of MHPS polymer. Note that a mixture of local structures is supported by this fragment.

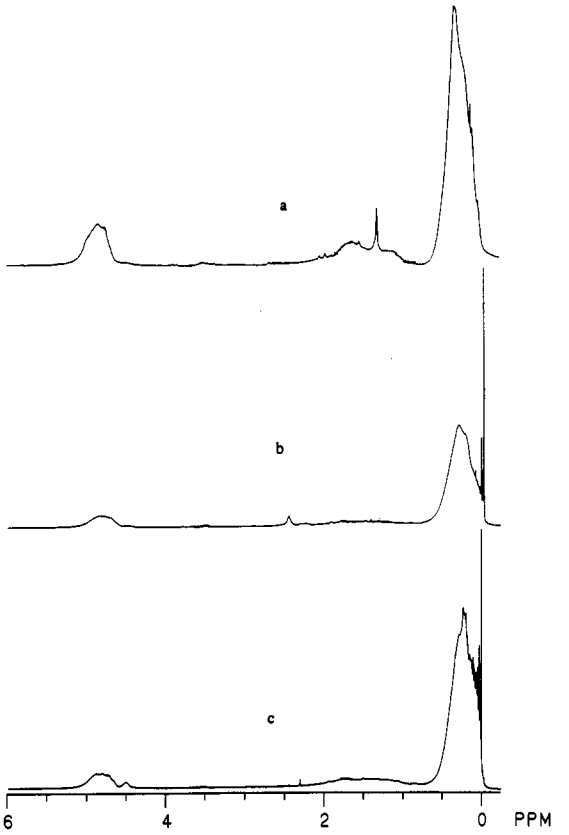

Figure 7. Liquid-state ^1H NMR spectra of (a) 8K MHPS polymer, (b) NCP100, and (c) NCP200.

and CH_3 moieties at 4.9, 2.5–0.75, and 0.75–0.0 ppm, respectively. The spectra of 8K MHPS and 32K MHPS (not shown) are virtually identical. The broad resonances observed confirm that a mixture of structures is present, yet support the general structure $[(CH_3SiHNH)_{0.40}(CH_3SiN)_{0.60}]_n$. It is interesting to compare the ^1H NMR spectrum of MHPS polymer with those of NCP100 and NCP200, shown in Figure 7b,c, respectively. The NCP materials are made by a similar synthetic route as for MHPS; however, $(CH_3)_2SiCl_2$, in addition to CH_3SiCl_3, apparently is used in the ammonolysis reaction. All spectra shown in Figure 7 are quite similar, evidencing only minor differences in peak shape. The NCP materials exhibit a larger resonance at 4.5 ppm and narrow resonances, arising from $Si(CH_3)_2$ functionality, near 0 ppm. Comparative, quantitative ^{29}Si data on these systems, shown in Figure 8, also support the structural assignments discussed above. The MHPS polymers (data only shown for 8K MHPS) exhibit a single, broadened resonance at –22 ppm, while the NCP materials evidence an additional $Si(CH_3)_2$ resonance at –4.6 ppm. The spectra shown in Figure 8 also indicate that NCP200 has a higher concentration of dimethylsilyl groups, relative to NCP100, consistent with the GPC observations of lower molecular weight for this material.

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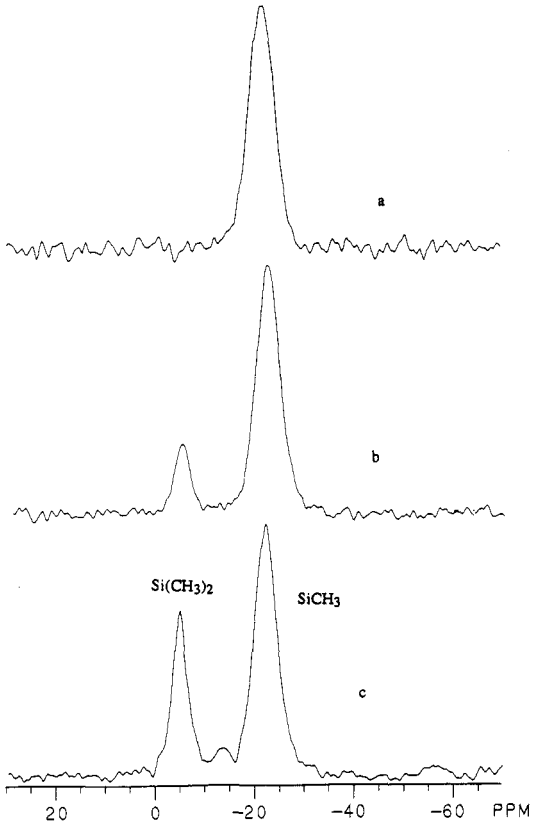

Figure 8. Liquid-state ^{29}Si NMR spectra of (a) 8K MHPS polymer, (b) NCP100, and (c) NCP200.

The enigmatic nature of the structure of these polymers is especially evident when comparing the quality of NMR data obtainable in both liquid and solid state. Figure 9 shows liquid- and solid-state ^{29}Si NMR data for 8K MHPS. The spectra exhibit a single, broad resonance at −22 ppm, which does not undergo any appreciable narrowing or splitting (into discrete resonances) upon dissolution of the polysilazane in solvent. The ^{29}Si MAS NMR spectrum of this material, in the absence of high-power decoupling, is shown in Figure 9c. While some linebroadening and loss of signal/noise is observed, the relatively narrow resonance observed suggests the presence of both H-substituted and -unsubstituted Si sites in the polymer. ^{13}C liquid-state and MAS-NMR data on this system (not shown) are equally uninformative, yielding a single broadened resonance ($Si–CH_3$) centered at 4.4 ppm. Both the ^{29}Si and ^{13}C nuclei of these polymers cross-polarize easily, yielding spectra identical to those discussed above.

While the syntheses of NCP and MHPS oligomers are quite similar, the incorporation of $(CH_3)_2Si$ groups into the NCP polymers leads to dissimilar molecular structures for these polymers. The effects of molecular weight and molecular structure on the ceramic yields of these systems are evident in the TGA data shown in Figure 10. The weight loss profiles suggest the distillation of low molecular weight species from room temperature to 300 °C, side-group elimination, reaction, and cross-linking from 300 to 500 °C (consistent with ^{29}Si NMR data, discussed below) and loss of hydrogen and methyl groups (typical pyrolysis reactions) from 500 to 900 °C.[19] This behavior is consistent with that observed previously for similar preceramic polymer systems.[6,19,34] For both the MHPS and NCP systems, the higher molecular weight polymers give rise

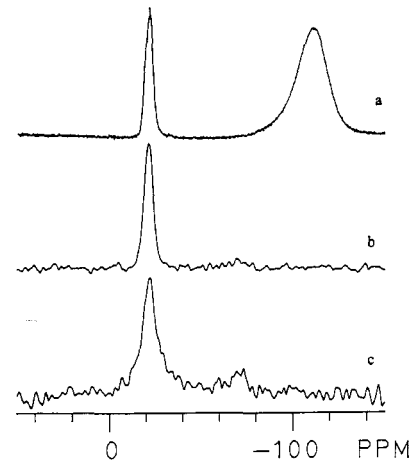

Figure 9. (a) Liquid-state ^{29}Si NMR spectrum of 8K MHPS. Solid-state, (b) proton-decoupled and (c) proton-coupled ^{29}Si MAS NMR spectra of 8K MHPS.

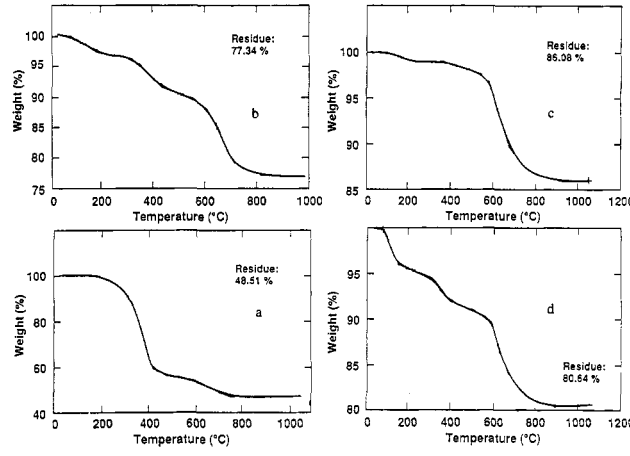

Figure 10. Comparative TGA data for (a) NCP100, (b) NCP200, (c) 32K MHPS, and (d) 8K MHPS.

to higher ceramic yields. This is especially evident for the NCP polymers, since the molecular weight range is wider for this system. It is interesting to note that, for both low and high molecular weight polymers, MHPS systems give significantly higher ceramic yields (81 and 86%, respectively) than the NCP systems (49 and 77%, respectively). This observation is indirect physical evidence for the existence of different molecular structures in NCP and MHPS systems, as stated previously.

The pyrolysis behavior of these four polymers in Ar atmosphere was investigated at four temperatures, 160, 500, 1000, and 1520 °C, using ^{29}Si MAS NMR spectroscopy. The data acquired in these experiments are shown in Figure 11 for NCP200 and 8K MHPS. The NMR spectra were virtually identical for the pyrolysis products of the higher molecular weight NCP and MHPS polymers at the same temperatures (data not shown). The ^{29}Si spectra of NCP200 pyrolysis products evidence a series of changes over this temperature range. At 500 °C, the −22 ppm resonance has broadened and the relatively narrow −4.6 ppm resonance has diminished and split into at least three peaks at 0, −4.6, and −10 ppm, corresponding to $Si(CH_3)_3$, $Si(CH_3)_2$, and $SiCH_3$ functionality, respectively, owing to disproportionation of the original $Si(CH_3)_2$ groups present

(34) Blum, Y.; Schwartz, K.; Laine, R. Preceramic Polymer Pyrolysis. Part 1: Pyrolytic Properties of Polysilazanes. *J. Mater. Sci.* **1989**, *24*, 1707.

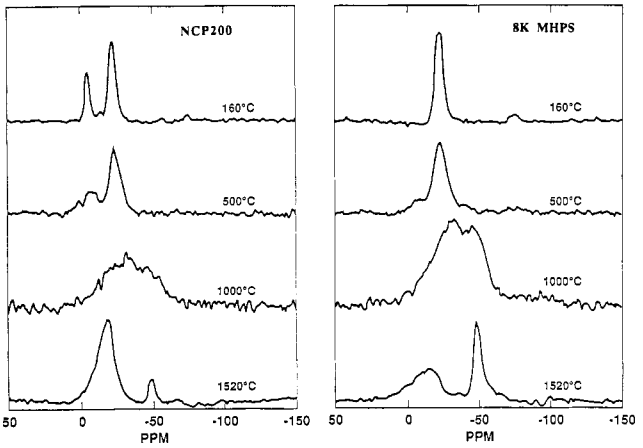

Figure 11. Solid-state ^{29}Si MAS NMR spectra of NCP200 and 8K MHPS following pyrolysis to 160, 500, 1000, and 1520 °C for 1 h.

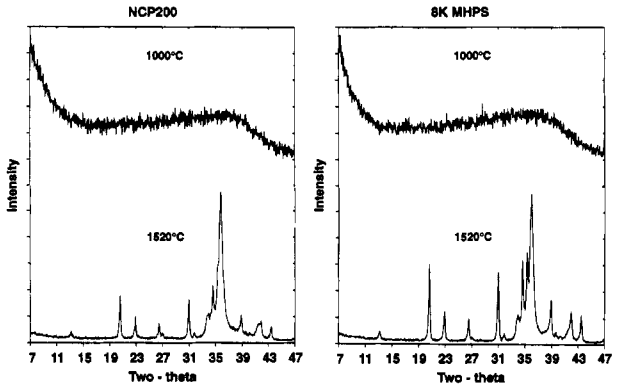

Figure 12. X-ray diffraction data for NCP200 and 8K MHPS following pyrolysis to 1000 and 1520 °C for 1 h.

in the polymer as suggested by the TGA data discussed above. At 1000 °C all fine structure has dissappeared and a broad resonance indicative of a range of Si-to-C and Si-to-N bonding is observed. The 1520 °C spectrum evidences a relatively narrow peak for Si_3N_4 at −49 ppm and a broad, significantly larger peak, covering the entire range of chemical shifts for all known SiC polytypes,[12] at −20 ppm. At 500 °C, the 8K MHPS pyrolsis product exhibits broadening of the −22 pm resonance and growth of a small, broad peak covering the entire range from −5 to −50 ppm. At 1000 °C two broad resonances at −30 and −50 ppm are evident, suggesting that molecular differentiation into SiC-like and Si_3N_4-like domains has occurred. The 1520 °C spectrum of 8K MHPS shows resolved SiC and Si_3N_4 peaks at −20 and −50 ppm, respectively. These latter observations suggests an order–disorder transition, wherein crystal growth and phase separation have changed the amorphous local order of the 500 and 1000 °C solid to one in which microdomains of crystalline SiC and Si_3N_4 coexist in the 1520 °C materials.

XRD diffraction data were acquired over the same temperature series discussed above and are shown in Figure 12 for NCP200 and 8K MHPS following pyrolysis at 1000 and 1520 °C. Both are X-ray amorphous at 1000 °C. This observation, combined with the NMR-based observation of phase differention in the MHPS system at 1000 °C, unambiguously suggests that the 1000 °C phase differentiation is a bulk, local-order transition. The phase differentiation must be a bulk transition to enable the peak separation observed by NMR, while the local order must be of a domain size unobservable by XRD. After

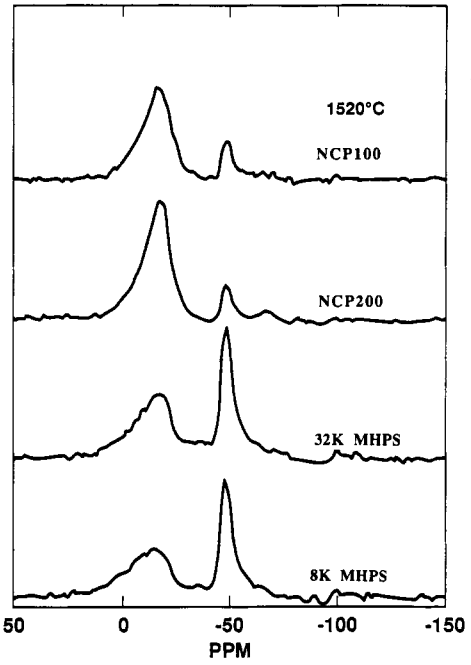

Figure 13. Solid-state ^{29}Si MAS NMR data for NCP100, NCP200, 32K MHPS, and 8K MHPS following pyrolysis to 1520 °C for 1 h.

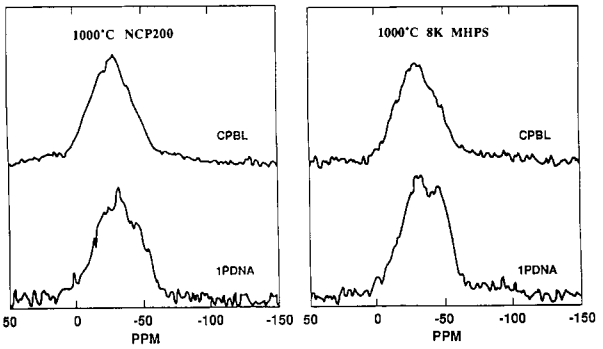

Figure 14. Cross-polarization, proton-decoupled (CPBL), and Bloch decay, proton-coupled spectra solid-state ^{29}Si MAS NMR spectra of NCP200 and 8K MHPS following pyrolysis to 1000 °C for 1 h.

pyrolysis to 1520 °C both the NCP and MHPS materials exhibit diffraction patterns consistent with a-Si_3N_4 and polymorphic SiC.

It is interesting to note the different selectivities towards ceramic products in these two systems. The 1520 °C ^{29}Si NMR data for all four polymer pyrolysis products are shown in Figure 13. The MHPS systems clearly form more Si_3N_4 than do the NCP systems. This observation results from differences in the molecular structures of the starting polymer and the higher carbon loading in the NCP polymers, owing to $Si(CH_3)_2$ incorporation in this system.

As mentioned above, the ^{29}Si MAS NMR spectrum of 8K MHPS polymer pyrolysis products (Figure 11) suggests that phase differentiation begins to occur by 1000 °C. If Si_3N_4 and SiC bonding environments are formed in this system, the domain size must be on the atomic to molecular scale, since the MHPS-derived pyrolysis products are X-ray amorphous to 1400 °C.[17] Figure 14 shows ^{29}Si one-pulse and CP-MAS NMR spectra for NCP200 and 8K MHPS systems after pyrolysis to 1000 °C. The NCP200 one-pulse and CP spectra are virtually identical, indicating that this amorphous preceramic still contains hydrogen and the hydrogen present is not isolated to any particular

phase in this material. The 8K MHPS one-pulse and cross-polarization spectra are clearly different. The one-pulse spectrum of the 8K MHPS exhibits the two peak signal described above while the cross-polarization spectrum clearly exhibits a single resonance centered at −30 ppm. This difference in hydrogen disproportionation behavior is also observed between the NCP100 and 32K MHPS systems (^{29}Si CP NMR data not shown).

Interrogating pyrolysis-dependent phase evolution using CP-MAS NMR affords a unique capability to assess phase separation and hydrogen disproportionation in the pyrolysis of preceramic polymers. The lack of a −50 ppm resonance in the CP-MAS NMR spectra of the MHPS systems is unambiguous evidence for phase separation and isolation of hydrogen to the SiC-like domains of this system. If phase separation were not present or was limited to several bond distances or hydrogen was incorporated in the Si_3N_4-like phase of this system, cross- polarization enhancement would not be limited to the SiC-like phase, as is evident in Figures 13 and 14. The observation that hydrogen incorporation is limited to the SiC-like (or carbon rich) domains of these preceramics suggests that residual hydrocarbon fragments still remain after pyrolysis in N_2 to 1000 °C. This observation is consistent with previous CP-MAS NMR investigations of plasma-produced SiC[12] as well as with proposed structures of the amorphous SiC phases obtained from the pyrolysis of polycarbosilanes.[25,26]

The MHPS and NCP polymer pyrolysis products also were characterized over the temperature range 160–1520 °C using diffuse reflectance Fourier transform infrared spectroscopy (DRIFT) to further define the pyrolysis behavior of these systems. The spectra obtained (not shown) were virtually identical to those shown in previous reports,[10,19,22] evidencing substantial but incomplete loss of SiH and CH functionality by 1000 °C. This observation is in agreement with the obvious retention of hydrogen in the SiC-like domains of these polymers up to 1000 °C, as evidenced by the CP-MAS NMR data.

Conclusion

The synthesis of the preceramic precursors was followed using liquid- and solid- state NMR spectroscopy. ^{29}Si liquid-state NMR was particularly useful for unambiguously showing the cyclic nature of the oligomer formed in the ammonolysis of methyldichlorosilane. Cross-polarization and single-pulse ^{29}Si MAS NMR experiments were used to explore temperature-induced short-range bonding, phase evolution and hydrogen incorporation in these materials as a function of pyrolysis to Si_3N_4/SiC ceramics. MAS NMR is shown to be uniquely sensitive to microdomain phase separation, particularly when these domains are amorphous or microcrystalline. CP-MAS NMR is shown to offer added capabilty for assesing hydrogen distribution, even at low levels, in ceramic materials. Molecular weight is shown to affect both the ceramic yield and phase selectivity of preceramic materials derived from methylhydridopolysilazane.

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