*Chem. Mater.* **1998,** *10,* 3913−3922 3913

# Solid-State NMR Studies of the Preparation of Si−C−N Ceramics from Polysilylcarbodiimide Polymers

Jörg Schuhmacher,† Markus Weinmann,‡ Joachim Bill,‡ Fritz Aldinger,‡ and
Klaus Müller*,†

*Institut für Physikalische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569
Stuttgart, Germany, and Max-Planck-Institut für Metallforschung and Institut für
Nichtmetallische Anorganische Materialien, Pulvermetallurgisches Laboratorium,
Universität Stuttgart, Heisenbergstr. 5, D-70569 Stuttgart, Germany*

*Received May 14, 1998. Revised Manuscript Received September 28, 1998*

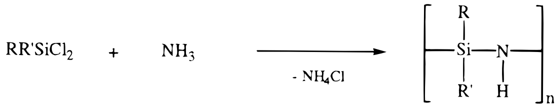
Multinuclear ($^{29}Si$, $^{13}C$, $^{1}H$) solid-state NMR and FTIR spectroscopy are employed to investigate the thermolysis of polymethylsilylcarbodiimide to the amorphous Si−C−N ceramic between room temperature and 1000 °C. During the present work two samples are examined that differ by the preparation route of the precursor polymer. The spectroscopic techniques are used to evaluate the structural intermediates that occur during the various stages of the thermolysis. With the knowledge of the structural components, reaction schemes are proposed that describe the transformation of the precursor polymers to the amorphous ceramic. The formation of the preceramic network is completed at about 500 °C. Above this temperature, a disintegration of the organic structural components takes place. The amorphous ceramics at 1000 °C thus consist of two major contributions: $Si_3N_4$ units and polyaromatic, graphite-like structures. It is interesting to note that even at this temperature the samples contain a considerable amount of hydrogen, partially being located at the boundaries of the graphite-like regions.

## Introduction

Because of their thermomechanical properties, such as creep and corrosion resistance as well as high strength and hardness, silicon nitride- and silicon nitride/silicon carbide-based composites are suitable materials for high-temperature applications. These ceramics are frequently used as cutting tools and are also employed in turbine and motor devices. These ceramics can be prepared by sintering silicon nitride and carbide powders in the presence of additives, such as $Al_2O_3$ and $Y_2O_3$, which segregate at the grain boundaries during the densification process.[1,2] Large amounts of oxide additives can lead to a deterioration of the thermomechanical stability at elevated temperatures due to the softening of these secondary phases incorporated into the microstructure of the ceramics.[3] For that reason, the development of powder technological routes which allow the reduction or even the elimination of the fraction of additives are of great interest.

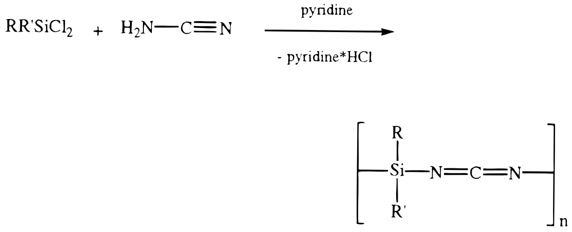
The thermolysis of preceramic polymers provides a means for the preparation of such ceramics without sintering aids. The main objective of this alternative route is the architectural design of ceramics based on well-defined molecular units in order to control the structure and the properties on an atomic scale.[4,5,6,7] The preceramic polymers are at first transformed into amorphous ceramics by thermolysis at temperatures around 1000 °C (ceramization). Subsequently, the obtained amorphous solids crystallize into the thermodynamically stable phases by further heat treatment above 1000 °C.

Ternary Si−C−N ceramics can be obtained by thermolysis of polysilazanes. These preceramic polymers with backbones containing alternating silicon and nitrogen atoms can be synthesized by the reaction of organochlorosilanes with ammonia:



$$RR'SiCl_2 + NH_3 \xrightarrow[-\,NH_4Cl]{} \left[ -\overset{R}{\underset{R'}{Si}}-\underset{H}{N}- \right]_n \qquad (1)$$

Alternatively, ternary Si−C−N ceramics can be obtained by the thermolysis of polysilylcarbodiimides. The corresponding precursors can be synthesized from chlorosilanes with cyanamide in the presence of pyridine:[8]



$$RR'SiCl_2 + H_2N{-}C{\equiv}N \xrightarrow[-\,pyridine{*}HCl]{pyridine} \left[ -\overset{R}{\underset{R'}{Si}}-N{=}C{=}N- \right]_n \qquad (2)$$

---

* Corresponding author. Phone: (711) 685 4470. FAX: (711) 685 4467. E-mail: klaus@b01.chemie.uni-stuttgart.de.

† Institut für Physikalische Chemie.

‡ Max-Planck-Institut für Metallforschung and Institut für Nichtmetallische Anorganische Materialien.

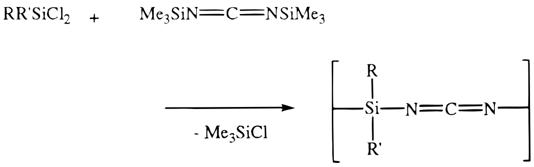
(1) Lange, F. F. *J. Am. Ceram. Soc.* **1973**, *56*, 445.

(2) Greil, P.; Petzow, G.; Tanaka, H. *Ceram. Int.* **1987**, *13*, 19.

(3) Lange, F. F. *J. Am. Ceram. Soc.* **1974**, *57*, 84.

10.1021/cm980719u CCC: $15.00

During both reactions, the byproducts $NH_4Cl$ and pyridine·HCl are formed, which have to be removed from the reaction mixture by additional processing steps in order to prevent contamination of the ceramic material after thermolysis. However, it has been shown that polysilylcarbodiimides can also be prepared in high yields by the salt-free reaction of chlorosilanes with bis(trimethylsilyl)carbodiimide:[9,10]



$$RR'SiCl_2 + Me_3SiN{=}C{=}NSiMe_3 \xrightarrow[-\,Me_3SiCl]{} \left[\begin{array}{c} R \\ | \\ -Si-N{=}C{=}N- \\ | \\ R' \end{array}\right]_n \qquad (3)$$

Here, the liquid byproduct methyltrichlorosilane can be removed by distillation. Moreover, this reaction route can be considered as a non-oxide sol−gel process for the synthesis of Si−C−N preceramic compounds because the carbodiimide unit exhibits pseudochalcogenic character and can act similarly to oxygen atoms in oxide sol−gel processes.

In this contribution we report on the investigation of the transformation of polymethylsilylcarbodiimide into ternary Si−C−N ceramics, of which so far only little is known. Two samples are examined that differ by their preparation routes of the precursor polymers and that are described by reaction routes 2 and 3 with R = H and R′ = $CH_3$. Particular emphasis is given to the characterization of the intermediate stages during the ceramization process, i.e., between room temperature and 1000 °C. The investigations primarily are based on multinuclear solid-state NMR techniques. They represent ideal tools for the characterization of such amorphous structures, as demonstrated by numerous applications.[11,12] Explicitly, $^{29}Si$, $^{13}C$, and $^{1}H$ NMR techniques are employed for the evaluation of the various intermediates that occur during the thermolysis of the precursor polymers.[13,14,15] The fourth potential nucleus, $^{15}N$, has not been used in the present work, since it suffers from a very low natural abundance and a low gyromagnetic ratio and thus requires isotopic enrichment. On the basis of these spectroscopic studies, which are complemented by FTIR experiments, reaction mechanisms for the ceramization of the carbodiimide polymers are proposed.

## Experimental Section

**Materials.** Polymethylsilylcarbodiimide was synthesized via the two reaction pathways 2 and 3.[16]

*Reaction Pathway 2.* In the first method a solution of 340 mmol (14.3 g) of cyanamide and 680 mmol (53 mL) of pyridine, dissolved in 200 mL of THF, was added dropwise to 340 mmol (39.1 g) of dichloromethylsilane dissolved in 300 mL of THF at 0 °C. Pyridine was used to bind chemically the hydrogen chloride side product. The reaction mixture was then allowed to slowly warm overnight to 25 °C and filtered through a pad of Celite. After evaporation of the volatile components at 25 °C and $10^{-2}$ mbar, 22.6 g (270 mmol; yield, 79%) of $[HSi(CH_3)\text{-}N{=}C{=}N]_n$ was obtained as a colorless viscous liquid. The crude product was then used without any further purification.

*Reaction Pathway 3.* A 260 mmol (30 g) portion of dichloromethylsilane, 260 mmol of bis(trimethylsilyl)carbodiimide (59 mL, obtained from cyamamide, pyridine and methyltrichlorosilane), and 2 mL of pyridine, serving as a catalyst for the trans-silylation reaction, were mixed under vigorous stirring in 100 mL of toluene. Afterward, the mixture was slowly heated to 110 °C and then refluxed for 3 days. The colorless cloudy reaction mixture was then cooled to 50 °C. After the evaporation of all the volatile components in a vacuum ($10^{-2}$ mbar), 14 g (167 mmol; yield, 65%) of $[HSi(CH_3)N{=}C{=}N]_n$ was obtained as a colorless solid.

*Thermolysis.* Samples were prepared by the thermolysis of 2−4 g of the polymeric precursor in a quartz tube under a steady flow (50 mL/min) of purified argon in a programmable tube furnace (Gero HTRV 40−250). Starting at ambient temperature, the following heating program was used: (i) an initial 1 K/min ramp to the desired thermolysis temperature, (ii) a 2 h hold at the desired thermolysis temperature, and (iii) sample cooling with a rate of 2 K/min, during which the sample was allowed to cool to room temperature.

**NMR Measurements.** All NMR experiments were performed on a Bruker CXP 300 spectrometer operating at a static magnetic field of 7.05 T ($^{1}H$ frequency, 300.13 MHz) using a 4 mm magic angle spinning (MAS) probe. $^{29}Si$ and $^{13}C$ NMR spectra were recorded at 59.60 and 75.47 MHz using the single pulse as well as the cross-polarization (CP) technique. In both experiments a $\pi/2$ pulse length of 4.0 $\mu$s was applied. For the single pulse experiment recycle delays up to 30 min were used. During the CP experiment a spin lock field of 62.5 kHz and a contact time of 3 ms were used. Typical recycle delays were 6−8 s. All spectra were acquired using the MAS technique with a sample rotation frequency of 5 kHz. $^{29}Si$ and $^{13}C$ chemical shifts were determined relative to external standards $Q_8M_8$ (the trimethylsilyl ester of octameric silicate) and adamantane. These values were then expressed relative to the reference compound TMS (0 ppm). Inversion recovery cross-polarization (IRCP) measurements[17,18] were done using a modified IRCP sequence with simultaneous phase inversion, as described in ref 19. The $^{1}H$ MAS NMR spectra were measured at 300.13 MHz. Single pulse excitation ($\pi/2$ pulse length 4.0 $\mu$s) with a recycle delay of 2 s was employed. The samples were spun at a frequency of 10 kHz. The $^{1}H$ chemical shifts were directly referenced to TMS as external standard.

**FT IR measurements.** FTIR spectra were obtained using KBr pellets on a Bruker IFS 66 FT IR spectrometer. All experiments were performed under a slight nitrogen flow.

## Results and Discussion

In the following we report on multinuclear solid-state NMR studies of the thermolysis intermediates from

---

(4) Rice, R. W. *Am. Ceram. Soc. Bull.* **1983**, *62*, 916.

(5) Seyferth, D.; Wiseman, G. H. *J. Am. Ceram. Soc.* **1984**, *67*, C-132.

(6) Peuckert, M.; Vaahs, T.; Brück, M. *Adv. Mater.* **1990**, *2*, 398.

(7) Bill, J.; Aldinger, F. *Adv. Mater.* **1995**, *7*, 775.

(8) Kienzle, A.; Obermeyer, A.; Riedel, R.; Aldinger, F. *Chem. Ber.* **1993**, *126*, 2569.

(9) Kienzle, A.; Bill, J.; Aldinger, F.; Riedel, R. Proceedings of Nano 94, the 2nd International Conference on Nanostructured Materials, Germany, October 3−7, 1994. *Nanostructured Mater.* **1995**, *6*, 349.

(10) Bill, J.; Aldinger; F., Kienzle; A., Riedel, R. German Patent DE 4430817, 1997.

(11) Spiess, H. W. *Adv. Polym. Sci.* **1985**, *66*, 23.

(12) Eckert, H. *Prog. NMR Spectrosc.* **1992**, *24*, 159.

(13) Lewis, R. H.; Maciel, G. E. *J. Mater. Sci.* **1995**, *30*, 5020.

(14) Geradin, C. M.; Taulelle, F.; Livage, J. *Mater. Res. Soc. Symp. Proc.* **1993**, *287*, 233.

(15) Seitz, J.; Bill, J.; Egger, N.; Aldinger, F. *J. Eur. Ceram. Soc.* **1996**, *16*, 885.

(16) (a) Riedel, R.; Greiner, A.; Miehe, G.; Dressler, W.; Fuess, H.; Bill, J.; Aldinger, F. *Angew. Chem.* **1997**, *109*, 657. (b) Kienzle, A.; Obermeyer, A.; Riedel, R.; Aldinger, F.; Simon, A. *Chem. Ber.* **1993**, *126*, 2569. (c) Kienzle, A. *Thesis*, Universität Stuttgart 1994. (d) Obermeyer, A.; Kienzle, A.; Weidlein, J.; Riedel, R.; Simon, A. *Z. anorg. Allg. Chem.* **1994**, *620*, 1357. (e) Pump, J.; Rochow, E. *Z. Anorg. Allg. Chem.* **1964**, *330*, 101.

(17) Zumbulyadis, N. *J. Chem. Phys.* **1987**, *86*, 1162.

(18) Cory, D. G.; Ritchey, W. M. *Macromolecules* **1989**, *22*, 1611.

(19) Wu, X.; Zilm, K. W. *J. Magn. Reson.* **1993**, *A 104*, 119.

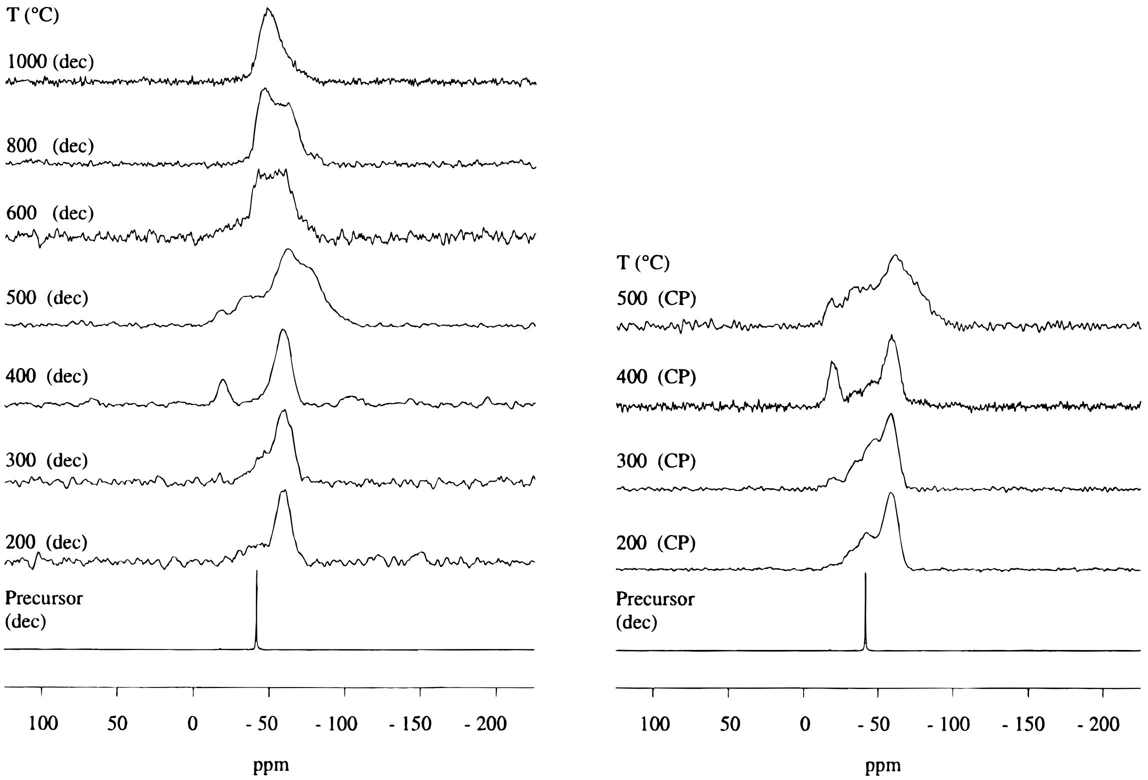


**Figure 1.** Experimental $^{29}$Si NMR spectra of polymethylsilylcarbodiimide obtained via route 2 at various stages of the thermolysis process. The spectra were obtained either via single-pulse excitation (dec, left column) or cross-polarization (CP, right column) at sample spinning rates of 5 kHz.

polymethylsilylcarbodiimide, obtained via two different synthetic routes. The NMR studies are performed at room temperature on various samples that have been heated to a particular thermolysis temperature during the preparation process. The samples examined here cover a temperature range from room temperature to 1000 °C, at which only amorphous intermediates are formed. Structural information from the NMR studies are primarily derived by a comparison of the experimental chemical shift values of the $^{13}$C, $^{1}$H, and $^{29}$Si nuclei with those of well-defined model compounds or structural components. In addition, we will consider the results from a complementary FTIR study performed on the same polymeric and ceramic samples.

**(I) Thermolysis of Polymethylsilylcarbodiimide Obtained via Reaction Route 2.** In this section we present the experimental results of our multinuclear NMR investigations (see Figures 1−3) on the thermolysis process of polymethylsilylcarbodiimide obtained by the reaction of dichloromethylsilane and cyanamide in the presence of pyridine (reaction route 2).

*(a) Polymeric Precursor.* The polymeric precursor prepared via this synthetic route is a colorless liquid of relatively low viscosity. The NMR spectra therefore have been recorded without sample rotation. They show very sharp lines since the anisotropic magnetic interactions, as in a normal liquid, are completely averaged out by molecular tumbling. The $^{13}$C NMR spectrum of the polymeric precursor (shown in Figure 2) exhibits two resonance signals at 121.6 and 1.2 ppm, which can be assigned to the carbon atoms of the carbodiimide unit (NCN) and the trimethylsilyl group (SiCH$_3$), respectively. In the $^{1}$H NMR (see Figure 3) two signals are found at 4.9 and 0.5 ppm. The smaller peak observed at higher frequency can be attributed to the H-atom bonded directly to the Si-atom in the SiH(CH$_3$)(NCN)$_2$

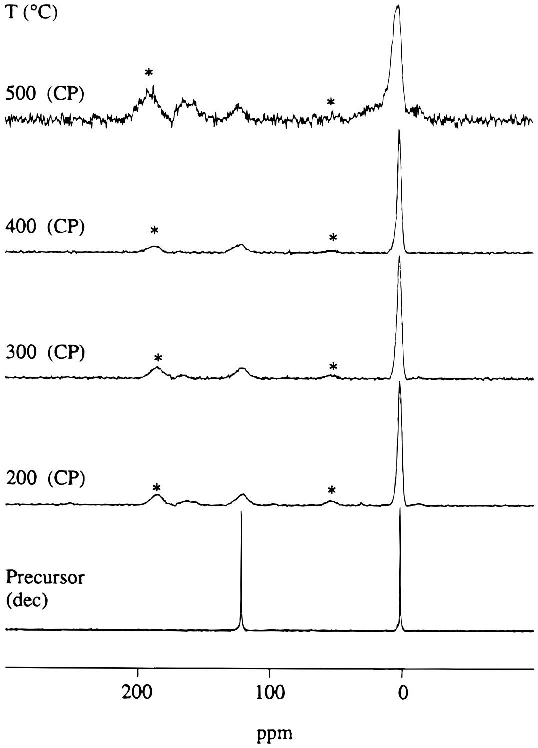


**Figure 2.** Experimental $^{13}$C NMR spectra of polymethylsilylcarbodiimide obtained via route 2 at various stages of the thermolysis process. The spectra were obtained either via cross-polarization (CP) or single-pulse excitation (dec) at sample spinning rates of 5 kHz. Asterisks indicate the MAS spinning sidebands.

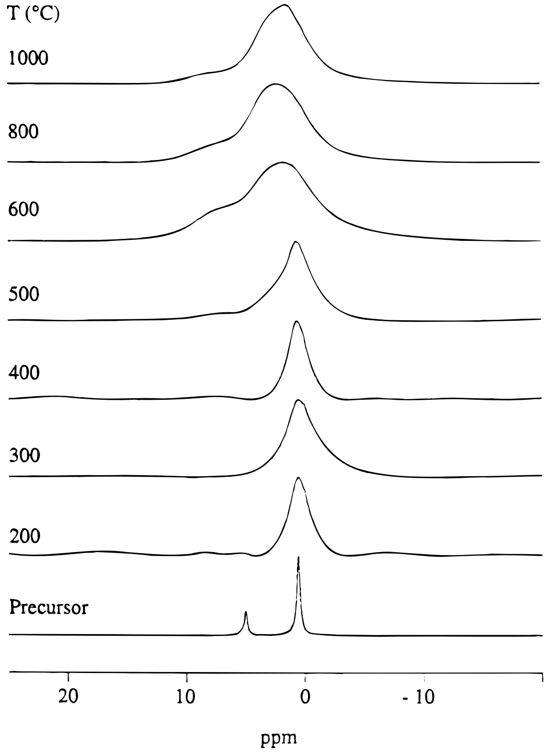


**Figure 3.** Experimental $^1$H NMR spectra of polymethylsilylcarbodiimide obtained via route 2 at various stages of the thermolysis process. The spectra were recorded at sample spinning rates of 10 kHz.

moiety. The signal at 0.5 ppm belongs to the methyl group protons. The 1:3 intensity ratio reflects exactly the amounts of the two chemically different H-atoms in the $SiH(CH_3)(NCN)_2$ unit.

The polymethylsilylcarbodiimide polymer initially contains silicon atoms in a single chemical environment, i.e., the $SiHC(NCN)_2$ site. As expected, the $^{29}$Si NMR spectrum exhibits a single resonance at a chemical shift value of −41.4 ppm (see Figure 1). It is interesting to compare this value with those reported for $[-SiH(CH_3)-NH-]_m[-Si(CH_3)_2NH-]_n$ and $[(CH_3)_3SiOSiH(CH_3)OSiH(CH_3)]_2O$. In the former polysilazane, the $SiHCN_2$ fragment shows a $^{29}$Si NMR signal at −22 ppm.[15] The $SiHCO_2$ sites of the latter compound are accompanied by two resonances at −35.9 and −35.6 ppm.[20] Obviously, the $^{29}$Si chemical shift of the present polysilylcarbodiimide resembles that of oxygen-bound silicon. This is in agreement with the observation for other polysilylcarbodiimides.[21,22] Table 1 clearly demonstrates the close resemblance of the $^{29}$Si NMR shifts in polysiloxanes and polsilylcarbodiimides. In fact, a recent quantum chemical calculation came up with a similar electronic structure of the H−NCN group of cyanamide and the H−O group of water, as manifested in a very similar electronegativity.[23] The result is of particular importance for the $^{29}$Si NMR shifts in polysilylcarbodiimides, since they are determined by the electronic nature of the bound NCN units. During the discussion of the $^{29}$Si NMR shifts, it therefore is justified to treat the NCN unit as pseudo-oxygen. Furthermore, the FTIR spectrum of the precursor polymer is given in Figure 4. Here, two very strong, overlapping bands at 2256 and 2166 cm$^{-1}$ are found, which are assigned to the asymmetric NCN stretching and the Si−H stretching mode, respectively.

**Table 1. $^{29}$Si Chemical Shift Values of Various Silylcarbodiimides and Siloxanes**

| silylcarbodiimides | | siloxanes | |
|---|---|---|---|
| $Me_4Si$ | $SiC_4$<br>0.0 ppm | $Me_4Si$ | $SiC_4$<br>0.0 ppm |
| $Me_3SiN{=}C{=}NSiMe_3$ | $\mathit{Si}\mathrm{C_3(NCN)}$<br>−0.1 ppm$^a$ | $Me_3SiOSiMe_3$ | $\mathit{Si}\mathrm{C_3O}$<br>4.0 ppm$^{b,c}$ |
| $[Me_2Si(N{=}C{=}N)]_n$ | $\mathit{Si}\mathrm{C_2(NCN)_2}$<br>−22.2 ppm$^a$ | $[Me_2SiO]_n$ | $\mathit{Si}\mathrm{C_2O_2}$<br>−21.7 ppm$^d$ |
| $[MeSi(N{=}C{=}N)_{1,5}]_n$ | $\mathit{Si}\mathrm{C(NCN)_3}$<br>−63.2 ppm$^e$ | $[MeSiO_{1,5}]_n$ | $\mathit{Si}\mathrm{CO_3}$<br>−68.0 ppm$^c$ |
| $Si(N{=}C{=}N)_2$ | $\mathit{Si}\mathrm{(NCN)_4}$<br>−103.0 ppm$^f$ | $SiO_2$ | $\mathit{Si}\mathrm{O_4}$<br>−114.0 ppm$^b$ |

[a] Kienzle, A.; *Thesis*, Universität Stuttgart, 1994. [b] Hunter, B. K.; Reeves, L. W. *Can. J. Chem.* **1967**, *46*, 1399. [c] Horn, H. G.; Marsmann, H. C. *Makromol. Chem.* **1972**, *162*, 255. [d] Lauterbur, P. C. *Determination Org. Struct. Phys. Methods* **1962**, *2*, 511. [e] Gabriel, A.; Riedel, R., private communication. [f] Riedel, R.; Greiner, A.; Miehe, G.; Dressler, W.; Fuess, H.; Bill, J.; Aldinger, F. Angew. Chem. **1997**, *109*, 657.

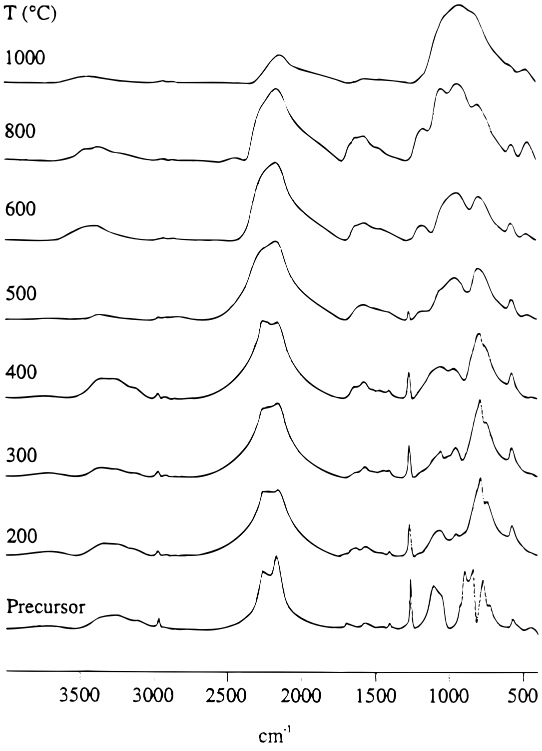


**Figure 4.** Experimental FTIR spectra of polymethylsilylcarbodiimide obtained via route 2 at various stages of the thermolysis process.

*(b) Thermolysis Product at 200 °C.* All thermolysis products—even those obtained at the beginning of the thermolysis, i.e., at relative low temperatures—are solids. Therefore, typical solid-state NMR techniques such as magic angle spinning or cross-polarization and high-power proton decoupling were necessary in order to acquire high-resolution spectra for these specimens. During the $^{29}$Si NMR study both cross-polarization and single-pulse spectra have been recorded which exhibit the same spectral features (see Figure 1). The $^{13}$C CP/

---

(20) Harris, R. K.; Kimber, B. J. *J. Organomet. Chem.* **1974**, *70*, 43.

(21) Greiner, A., Thesis, TH Darmstadt 1997.

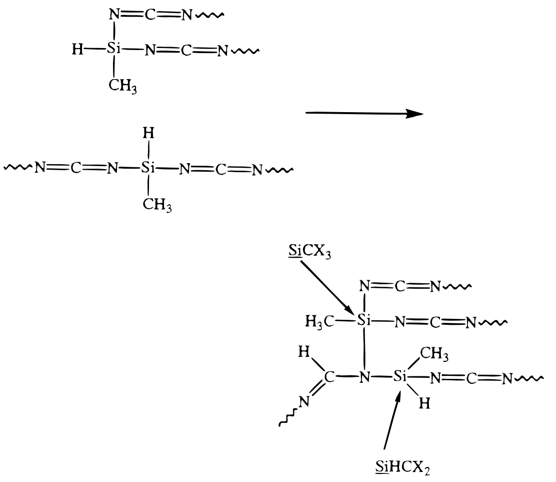
(22) Greiner, A.; Gabriel, A.; Riedel, R. to be published.

(23) Schädler, H.-D.; Jäger, L.; Senf, I. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1115.

MAS NMR spectrum of the thermolysis product at 200 °C again shows two resonances at 121.6 and 0.5 ppm which have already been observed in the $^{13}$C NMR spectrum of the precursor polymer. The signal of the NCN group at 121.6 ppm, however, is significantly broadened. This increase in line width can be traced back to the interaction between a spin-$^{1}/_{2}$ ($^{13}$C) nucleus and a spin-1 ($^{14}$N) quadrupolar nucleus.[24−26] The actual spectral pattern depends on various parameters, e.g. quadrupolar coupling constant, dipolar coupling constant, and sample spinning speed. In favorable cases a splitting of the C−N signal is observed experimentally, which can be analyzed in terms of the above-mentioned magnetic interaction parameters. Such a feature is missing in the present case, most probably due to the inherent heterogeneity of the preceramic samples. Furthermore, two MAS spinning sidebands are observed for the $^{13}$C NMR signals of the NCN units, reflecting a large $^{13}$C chemical shift anisotropy of the carbodiimide group, in agreement with the sp-hybridization of the central carbons.

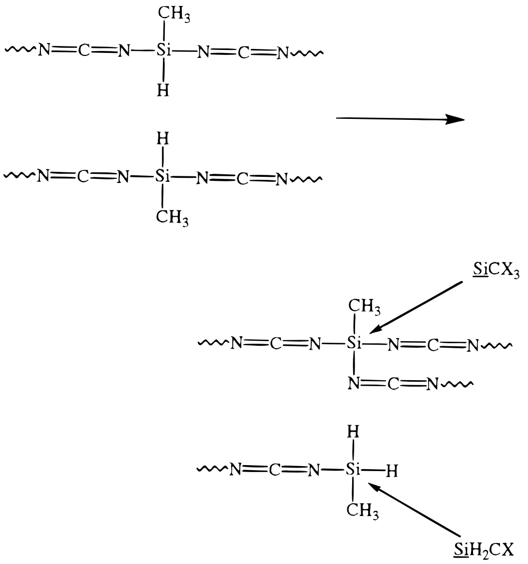
In the $^{1}$H MAS NMR spectrum the Si*H* resonance signal at 4.9 ppm has nearly vanished. This indicates a transformation of the SiH group by polymer cross-linking after heat treatment of the sample to 200 °C. The $CH_3$ signal at 0.5 ppm is very broad due to homonuclear dipolar coupling of the $^{1}$H spins which cannot be suppressed by MAS at spinning rates of 10 kHz.

At 200 °C significant changes are observed in the $^{29}$Si CP/MAS NMR spectrum that are due to the beginning of precursor decomposition. The signal at −41.4 ppm still exists, but a new signal of higher intensity appears at −58.3 ppm. Moreover, there is a weak shoulder at −25 ppm. We assume that, due to the high reactivity accompanied by the thermal instability of the Si−H bond, three major reactions occur. They can be understood as cross-linking steps during heat treatment: (i) a hydrosilylation reaction



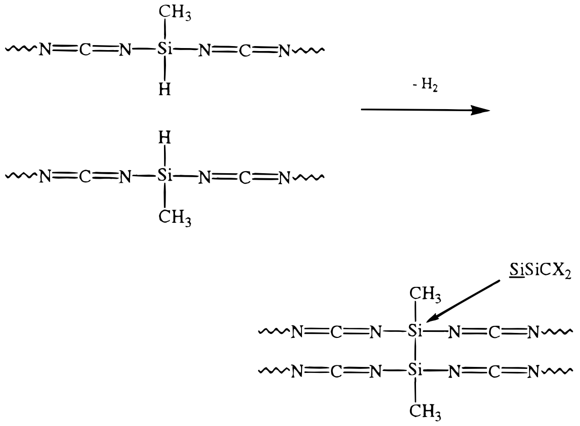
(4)

(ii) a disproportion process of the $SiH(CH_3)(NCN)_2$ moiety



(5)

and (iii) a dehydrogenative coupling route.



(6)

Here, the signal at −58.3 ppm can be traced back to the $SiC(NCN)_2(NCHN)$ and *Si*C(NCN)$_3$ sites that are built up by reaction routes 4 and 5, respectively. In the following we will express these fragments as $SiCX_3$ (X = NCN or NCHN) in order to distinguish NCN and NCHN from amine groups. The above assignment is justified by the chemical shift values of −62.3 ppm for the *Si*C(NCN)$_3$ site in $[CH_3Si(NCN)_{1,5}]_n$ (see Table 1) and of −66.0 ppm for the *Si*CO$_3$ site[27] in $[CH_3SiO_{1,5}]_n$. In a similar way, we can assign the second new resonance at −25 ppm to the *Si*H$_2$C(NCN) signal of the $SiH_2(CH_3)(NCN)$ moiety (or $SiH_2CX$ site) built up in the disproportion process 5. The third signal at −41.4 ppm might stem from the remaining precursor polymer ($SiHCX_2$ site), which so far has not undergone cross-linking reactions and which exhibits a $^{29}$Si NMR signal at −41.4 ppm (see spectrum of precursor), or from *Si*SiC(NCN)$_2$ sites ($SiSiCX_2$ sites), that are formed during the reaction route 6.

The various assignments have been checked independently by $^{29}$Si IRCP measurements that are used to distinguish between protoned and nonprotoned Si

---

(24) Naito, A.; Ganapathy, S.; McDowell, C. A. *J. Chem. Phys.* **1981**, *74*, 5393.

(25) Hexem, J. G.; Frey, M. H.; Opella, S. J. *J. Chem. Phys.* **1982**, *77*, 3847.

(26) Harris, R. K.; Olivieri, A. C. *Prog. NMR Spectrosc.* **1992**, *24*, 435.

(27) Horn, H. G.; Marsmann, H. C. *Makromol. Chem.* **1972**, *162*, 255.

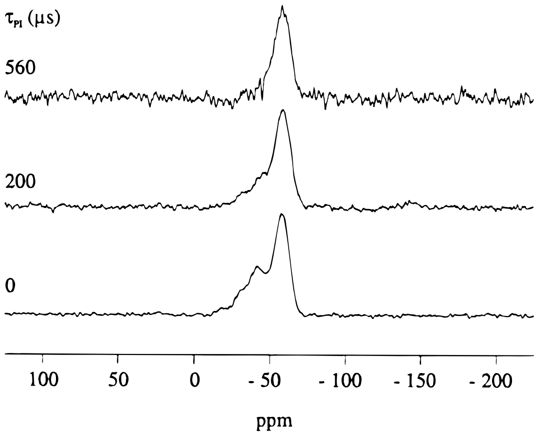


**Figure 5.** Experimental $^{29}$Si IRCP spectra of the thermolysis product at 200 °C of polymethylsilylcarbodiimide obtained via route 2. The phase inversion times $\tau_{PI}$ are given in the figure. The spectra were recorded at a sample spinning rate of 5 kHz and are plotted to the same height.

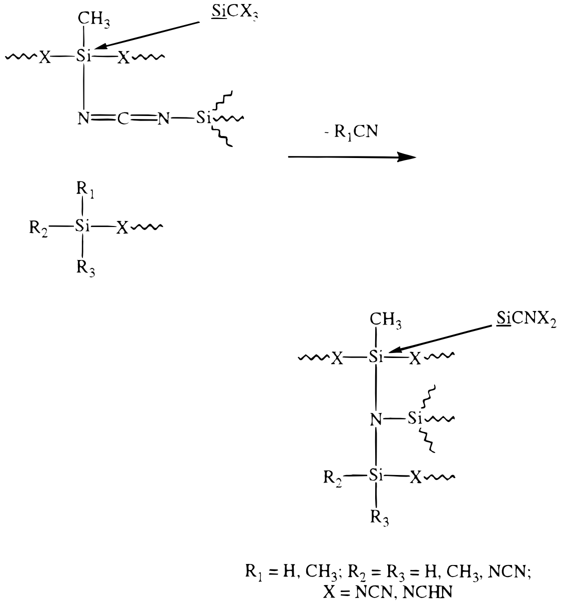
nuclei.[17−19] Representative IRCP spectra are given in Figure 5. They are plotted to the same height in order to emphasize the reduction in relative signal intensity. It can be seen that the high-frequency signals at −25 and −41.4 ppm decrease faster with phase inversion time ($\tau_{PI}$) than the low-frequency signal at −58.3 ppm. This implies that the high-frequency lines in fact refer to protoned Si nuclei ($SiH_2CX$ and $SiHCX_2$), as proposed above on the basis of the reaction schemes 4 and 5. Obviously, the signal at −41.4 ppm is dominated by protoned $SiHCX_2$ sites that stem from the remaining precursor polymer and from reaction route 4. $SiSiCX_2$ sites that would arise from reaction scheme 6 and which are expected to resonate at about −40 ppm cannot be detected. This latter potential reaction scheme therefore seems to play no role in the thermolysis of the present polymeric materials.

The proposed reaction schemes imply that the chemical environment of the carbon nuclei remains almost unaltered. In fact, only the hydrosilylation step 4 requires the formation of a formamidine fragment with a $^{13}$C chemical shift of about 160−170 ppm. The additional broad signal at 164 ppm therefore might be attributed to this latter structural component.

Likewise, the hydrosilylation step 4 and the dehydrogenative coupling 6 should deplete the amount of H-atoms that are bound directly to silicon. In fact, such a behavior is reflected in the corresponding $^1$H MAS NMR (Figure 3) and FTIR spectra (Figure 4). In the former spectra a decrease of the Si*H* signal intensity is registered, while in the latter spectra the intensity of the Si−H vibration band at 2153 cm$^{-1}$ is reduced.

Taking into account the experimental intensities of the $^{29}$Si NMR signals, the hydrosilylation route 4 seems to be the dominant mechanism at such low thermolysis temperatures. A final assignment of the structural intermediates is difficult due to the lack of available reference compounds. It also should be mentioned that Ojima et al.[28] have reported that the addition of hydrosilane to carbodiimides is almost completely suppressed at temperatures below 200 °C. However, how the effiency of the hydrosilylation reaction is affected by the particular reactants and particular reaction conditions, i.e., solvent and reaction temperature, is still unknown.

*(c) Thermolysis Product at 300 °C.* The $^{13}$C CP/MAS NMR spectrum of samples treated at 300 °C does not show any significant changes. The same is true for the $^1$H MAS NMR spectrum that consists of a single broad signal at about 0 ppm. The $^{29}$Si CP/MAS NMR spectrum, however, is different from the previous one at 200 °C. Four signals are found at −58.3, −48.4, −34.0, and −19.6 ppm with decreasing intensities to the high-frequency direction. They can be attributed to $SiCX_3$, $SiCNX_2$, $SiCN_2X$, and $SiCN_3$ sites (X = NCN, NCHN) that are obtained from $SiCX_3$ and $SiH_2CX$ units (see reaction schemes 4 and 5) as well as from residual $SiHCX_2$ groups by elimination of HCN or $CH_3CN$. Reaction scheme 7 illustrates the formation of $SiCNX_2$. A similar elimination of HCN or $CH_3CN$ involving the remaining X-groups of the $SiCX_3$ fragment would give rise to the formation of $SiCN_2X$ and $SiCN_3$ sites.



(7)

Even though carbon-containing gases should evaporate during this reaction route, no significant changes are expected in the chemical environment of the remaining carbons. Therefore, the $^{13}$C CP/MAS NMR spectrum again should be unaffected.

*(d) Thermolysis Product at 400 °C.* For the thermolysis product prepared at 400 °C, again the $^{13}$C CP/MAS NMR and $^1$H MAS NMR spectra are very similar to those described above for the lower thermolysis temperatures. Likewise, the $^{29}$Si CP/MAS NMR spectrum at 400 °C reveals the following features: (i) all resonance signals observed at 300 °C also are present at 400 °C, (ii) the peak at −19.6 ppm now is of higher relative intensity while the relative peak intensities at −34.0 and −48.4 ppm have clearly decreased, and (iii) the signal at −58.3 ppm is still the most intense one. These results indicate that the cross-linking process assumed for the thermolysis at 300 °C is still in progress and the amount of $SiCN_3$ sites increases at the expense of the amounts of $SiCX_3$, $SiCNX_2$, and $SiCN_2X$ sites (X = NCN, NCHN).

---

(28) Ojima, I.; Inaba, S. *J. Organomet. Chem.* **1977**, *140*, 97.

*(e) Thermolysis Product at 500 °C.* For the sample that refers to the thermolysis product at 500 °C, the situation in the $^{13}$C CP/MAS NMR spectrum is slightly different. The resonance line at 1.2 ppm has further broadened. The formamidine signal at 164 ppm now has an increased intensity compared to the residual signals. Moreover, the signal/noise ratio in the spectrum has remarkably decreased. This can be traced back to the reduction of the amount of hydrogen during the thermolysis process, along with a less efficient transfer of the proton magnetization to the carbon and to the silicon nuclei in the cross-polarization experiment. In the $^{1}$H MAS NMR spectrum, again a further broadening of the lines is visible. Apart from that, no further changes can be observed. In the corresponding $^{29}$Si CP/MAS spectrum, the NMR lines are found to be very broad. However, the resonance lines at −19.6 ($SiCN_3$) and −58.3 ppm ($SiCX_3$) are still visible with a lower relative intensity of the high-frequency signal. In addition, a broad signal is found between these two lines and a broad shoulder in the low-frequency region of the spectrum. This again can be understood on the basis of the rearrangement reaction 5 combined with the elimination reaction 7, which is accompanied by the evolution of $SiCNX_2$, $SiCN_2X$, and $SiCN_3$ as well as $SiNX_3$ sites (X = NCN, NCHN). Probably even $SiN_4$ units are formed for the first time at this stage of the thermolysis process.

So far, it was not possible to record $^{13}$C NMR spectra of the thermolysis intermediates above 500 °C, although cross-polarization and single-pulse experiments with recycle delays up to 30 min have been performed. One reason might be the very long relaxation times due to the low mobility of the polymeric intermediates caused by the enhanced cross-linking. Another explanation might be a less effective dipolar coupling between $^{13}$C and $^{1}$H spins—which otherwise provides an efficient relaxation pathway—due to a significant reduction of the proton content at higher thermolysis temperatures. The low proton content is also reflected in the fact that cross-polarization did not work during the $^{29}$Si NMR experiments on the high-temperature samples ($T > 500$ °C). Likewise, paramagnetic centers might be formed during the heat treatment that are located at the C-atoms. In that case, the unpaired electrons would cause a strong dipolar coupling of the $^{13}$C spins along with a remarkable line broadening in the $^{13}$C NMR spectra. At present, the origin for the missing $^{13}$C NMR signal at higher thermolysis temperatures cannot be assigned definitively. This would require additional work comprising other preceramic systems which currently is in progress.

*(f) Thermolysis Product at 600 °C.* The $^{1}$H MAS NMR spectrum of the sample prepared at 600 °C shows an aliphatic signal that now is shifted to higher frequency (about 2 ppm) and that indicates a disintegration of the methyl groups. The additional shoulder, visible at about 8 ppm, is attributed to hydrogen atoms that saturate the boundaries of polyaromatic, graphite-like areas. Unfortunately, in the present case these $^{1}$H NMR results cannot be confirmed by $^{13}$C NMR due to the problems with signal detection, as mentioned above. It should be noted, however, that such graphite-like structures are also observed after heat treatment of other polysilylcarbodiimides at higher temperatures (≥600 °C).[29]

The $^{29}$Si NMR spectra of the samples heated to 600 °C and above were acquired without the cross-polarization technique, since the protons are too diluted for an efficient transfer of the proton magnetization. In the $^{29}$Si NMR spectrum of the sample obtained at 600 °C, the signals at both the high- and low-frequency sides have clearly lost intensity as compared to the central lines at −46 and −58 ppm. The latter signals can be assigned to overlapping lines of $SiN_4$ and $SiCX_3$ sites (X = NCN, NCHN), respectively.

*(g) Thermolysis Product at 800 °C.* In the $^{1}$H MAS NMR spectrum of polymethylsilylcarbodiimide thermolyzed at 800 °C the position of the signals has not changed. Nevertheless, the shoulder at 8 ppm has lost relative intensity, which indicates a further reduction in hydrogen content. Likewise, in the $^{29}$Si MAS NMR spectrum, only a change in relative intensity is observed, i.e., the signal at −46.0 ppm has noticeably increased. This NMR line again can be attributed to the $SiN_4$ site, as found for the Si-atoms in $Si_3N_4$ ($^{29}$Si chemical shifts in $\alpha$-$Si_3N_4$, −46.8 and −48.9 ppm; $^{29}$Si chemical shifts in $\beta$-$Si_3N_4$, −48.7 ppm).[30] At the same time, the remaining carbodiimide units are further decomposed, as can be concluded from the decrease in intensity within the other spectral regions.

*(h) Thermolysis Product at 1000 °C.* The $^{1}$H MAS NMR spectrum of the thermolysis product prepared at 1000 °C again is dominated by the broad aliphatic peak at about 2 ppm. The additional shoulder at 8 ppm observed in the spectra of the samples obtained at lower temperatures is slightly reduced. Otherwise, no significant changes can be found. The $^{29}$Si MAS NMR spectrum shows a dominant signal at −46.0 ppm that stem from $SiN_4$ units of amorphous $Si_3N_4$, with a slight residual shoulder ($SiCX_3$ sites) in the low-frequency region. This is corroborated by the corresponding FTIR spectrum (see Figure 4). Here, the intensity of the asymmetric stretching band of the NCN group, which has gradually shifted from 2256 $cm^{-1}$ in the precursor polymer to 2131 $cm^{-1}$ at 1000 °C, is significantly reduced. The additional strong vibration band, visible at 800 $cm^{-1}$, is in line with the findings for amorphous $Si_3N_4$.[31,32] This again suggests the presence of $SiN_4$ units, in agreement with the results from the $^{29}$Si MAS NMR measurements. At 1000 °C silicon mainly exists in $SiN_4$ units (i.e. amorphous $Si_3N_4$) while only a small amount of $SiCX_3$ (X = NCN, NCHN) and thus NCN groups remain at such high thermolysis temperatures.

**(II) Thermolysis of Polymethylsilylcarbodiimide Obtained via Reaction Route 3.** In this section we briefly summarize the results from the NMR studies on the thermolysis products of polymethylsilylcarbodiimide prepared via reaction route 3. At first sight the experimental spectra are very similiar to those recorded for the samples from reaction route 2, as described in the previous section. A closer inspection of the experi-

---

[29] Schuhmacher, J.; Weinmann, M.; Bill, J.; Aldinger, F.; Müller, K., to be published.

[30] Carduner, K. R.; Carter III, R. O.; Milberg, M. E.; Crosbie, G. M. *Anal. Chem.* **1987**, *59*, 2794.

[31] Wada, N.; Solin, S. A.; Wong, J.; Prochazka, S. *J. Non-Cryst. Solids* **1981**, *43*, 7.

[32] Luongo, J. P. *Appl. Spectrosc.* **1984**, *38*, 195.

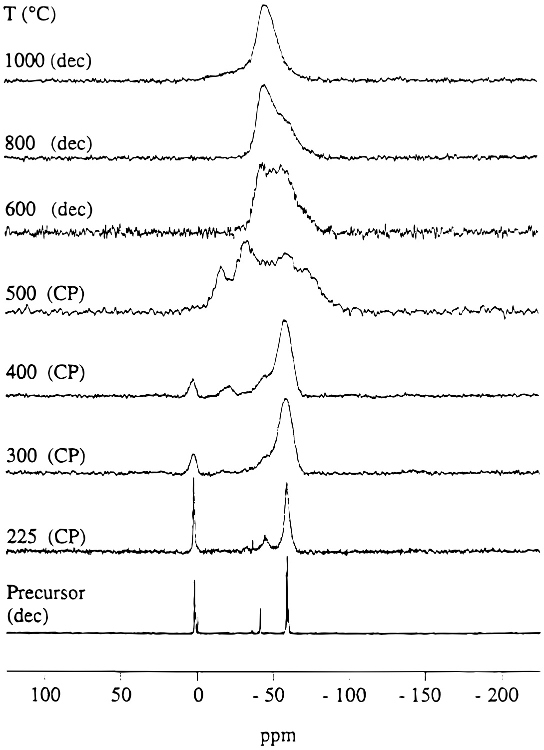


**Figure 6.** Experimental $^{29}$Si NMR spectra of polymethylsilylcarbodiimide obtained via route 3 at various stages of the thermolysis process. The spectra were obtained either via cross-polarization (CP) or single-pulse excitation (dec) at sample spinning rates of 5 kHz.

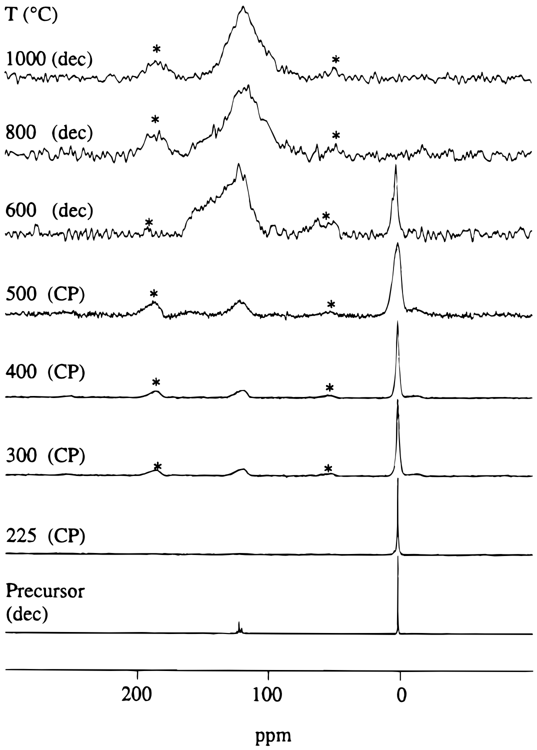


**Figure 7.** Experimental $^{13}$C NMR spectra of polymethylsilylcarbodiimide obtained via route 3 at various stages of the thermolysis process. The spectra were obtained either via cross-polarization (CP) or single-pulse excitation (dec) at sample spinning rates of 5 kHz. Asterisks indicate the MAS spinning sidebands.

mental results, however, reveals some differences in the NMR spectra of the two precursor polymers as well as of the corresponding intermediates during the thermolysis. In the following only the most distinctive features will be presented.

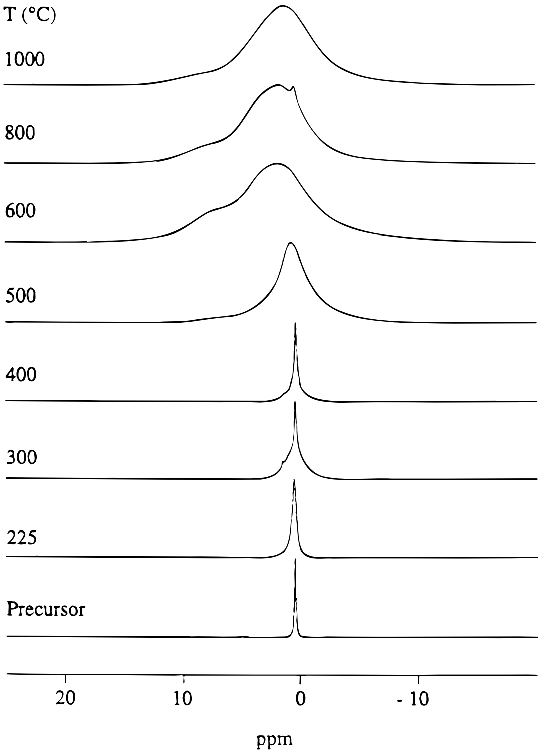


**Figure 8.** Experimental $^{1}$H NMR spectra of polymethylsilylcarbodiimide obtained via route 3 at various stages of the thermolysis process. The spectra were recorded at sample spinning rates of 10 kHz.

To begin with, we discuss the $^{29}$Si NMR spectrum of the precursor polymers (Figure 6). Here, three groups of resonance lines, centered at 1.5, −41.3, and −59.6 ppm, are visible. It should be recalled that in the corresponding $^{29}$Si NMR spectrum of the precursor polymers from reaction route 2 only the signal at −41.4 ppm shows up that can be ascribed to the $SiHCX_2$ site (see Figure 1). The additional signal at 1.5 ppm refers to $Si(CH_3)_3$ end groups that exist also in the intermediates up to 400 °C. This latter assignment is confirmed by the corresponding $^{13}$C NMR spectrum (Figure 7), where the $SiCH_3$ signal at 1.6 ppm also gains in intensity. The $^{29}$Si NMR signal at −59.6 ppm reflects a cross-linking of the precursor polymer due to the specific preparation conditions: refluxing of the reaction mixture for 3 days at 110 °C. It should be noted that in the case of reaction route 2 the latter NMR signal, which has been attributed to $SiCX_3$ (X = NCN, NCHN) units from the processes 4 and 5, only is found at moderate thermolysis temperatures ($T \geq 200$ °C, Figure 2). The presence of a cross-linked polymer also is evident from the corresponding $^{1}$H NMR spectrum (Figure 8). Here, a strong signal at 0.5 ppm due to $SiCH_3$ groups shows up, while the SiH signal of the un-cross-linked polymer at 4.9 ppm hardly can be detected. Inspection of the $^{1}$H NMR spectra between 200 and 400 °C reveals the presence of a rather narrow resonance at 0.5 ppm. This again can be traced back to the $Si(CH_3)_3$ end groups, which also are evident from the corresponding $^{29}$Si NMR spectra (Figure 6). Above 400

°C the $^{1}$H NMR spectra broaden, in close analogy with the observations for the polysilylcarbodiimide obtained via reaction route 2 (see Figure 3).

Another significant difference of the samples from reaction routes 2 and 3 can be found in the $^{13}$C NMR experiments, in particular at temperatures above 500 °C. In the case of reaction route 3, we were able to detect $^{13}$C NMR spectra via single-pulse excitation, while for the samples from reaction route 2 such experiments failed (see above). The most probable explanation is a higher proton content in the samples of reaction route 3 that also would promote carbon spin relaxation. The higher proton content also can explain the observation that during the $^{29}$Si NMR study the cross-polarization technique was applicable for all samples from the reaction route 3, while for reaction route 2 single-pulse experiments had to be used for those samples prepared above 500 °C. Nevertheless, in Figure 6 the $^{29}$Si NMR spectra above 500 °C refer to single-pulse experiments since they provide a better signal/noise ratio.

The $^{13}$C NMR spectra recorded for the thermolysis intermediates at temperatures above 500 °C exhibit a broad signal at about 120 ppm along with a large chemical shift anisotropy, as can be taken from the spinning sidebands. This implies the presence of polyaromatic, graphite-like regions that also are visible in the corresponding $^{1}$H NMR spectra (see Figure 8) by a broad resonance centered at about 8 ppm and that are in line with the observation for the samples from reaction route 2. Obviously, such polyaromatic regions are a general phenomenon for the high-temperature intermediates and are independent of the actual preparation route of the precursor polymer.

Inspection of Figure 6 reveals that at 1000 °C silicon again exists almost exclusively as $SiN_4$ (i.e. amorphous $Si_3N_4$). The $^{29}$Si NMR spectrum shows a single broad resonance at −46 ppm. An additional shoulder or resonance at about −60 ppm, which is visible in the spectrum of the sample from reaction route 2 (see Figure 1), is absent in the present case. Additional support is given by the FTIR measurements (Figure 9). Here again a strong absorption is registered at 800 $cm^{-1}$ due to the $SiN_4$ units while only a weak stretching band of the NCN group remains. Both the $^{29}$Si NMR and the FTIR data indicate that the relative amount of $SiN_4$ is somewhat higher for the sample corresponding to reaction route 3. Whether this difference is due to the actual preparation route of the precursor polymers that results in a different degree of cross-linking so far is unknown. Here, more work is necessary, comprising studies on a series of samples with precursor polymers prepared under different conditions (e.g. reaction time, temperature).

## Conclusions

The thermolysis of polymethylsilylcarbodiimide to amorphous Si−C−N ceramic was investigated by multinuclear solid-state NMR and FTIR spectroscopy. In the present work two samples have been investigated that differ by the preparation route of the precursor polymer. Both spectroscopic techniques have been used for the determination of the structural intermediates that are formed during the polymer thermolysis. From this, reaction schemes were proposed that occur during the transformation of the precursor polymers to the amorphous ceramics. At low temperatures (110−200 °C) various cross-linking reactions take place which primarily are accompanied by changes in the chemical environment of the $^{29}$Si nuclei. The underlying rearrangement and condensation reactions are effective up to about 500 °C, yielding various structural components such as $SiCNX_2$, $SiCN_2X$, $SiCN_3$, and $SiNX_3$ sites (X = NCN, NCHN). Obviously, at this temperature the formation of the preceramic network is completed. Between 600 and 1000 °C, a further disintegration of the NCN units takes place along with a build-up of amorphous $Si_3N_4$ regions. The amorphous ceramic at 1000 °C thus is characterized by silicon that is mainly incorporated in $SiN_4$ units, although the absolute amount was found to depend on the reaction scheme for the preparation of the precursor polymer.

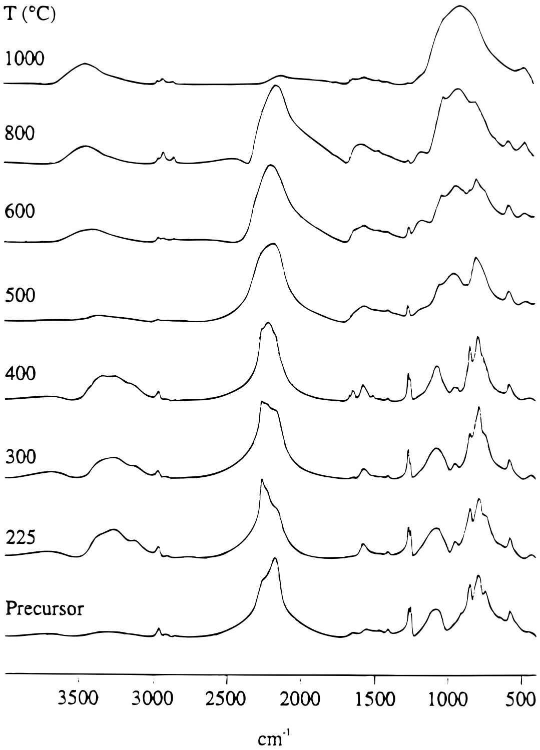


**Figure 9.** Experimental FTIR spectra of polymethylsilylcarbodiimide obtained via route 3 at various stages of the thermolysis process.

From the $^{13}$C NMR studies there is strong evidence that above 600 °C polyaromatic, graphite-like domains are formed which remain up to 1000 °C. At the same time the $^{1}$H NMR spectra suggest the presence of aromatic protons in such samples. It is very likely that these protons are located at the boundaries of such graphite-like regions.

It should be noted that X-ray and electron microscopy studies have been performed on the ceramic materials that were obtained by heating to 1400 °C.[33] Both studies

---

(33) Dürr, J.; Schempp, S.; Lamparter, P.; Bill, J.; Steeb, S.; Aldinger, F. *Solid State Ionics* **1997**, *101−103*, 1041.

reveal the presence of polyaromatic (carbon) regions as well as $Si_3N_4$ domains. Obviously, these structural components are preformed in the amorphous ceramic phase below 1000 °C and are retained in these samples up to the crystallization.

**Acknowledgment.** Financial support for this project by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

CM980719U