

# Interaction of Polychloromethylsilanes with Ammonia and Ammonium Chloride

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Received September 24, 2003. Revised Manuscript Received January 27, 2004

Polychloromethylsilanes were reacted with ammonia at various temperatures and pressures to achieve shape stabilization of preceramic green fibers. Besides the aspired cross-linking process, other reactions took place due to the interaction with  $\text{NH}_4\text{Cl}$ , deposited as a byproduct at the polymer surface. FT/IR,  $^{13}\text{C}$ ,  $^{29}\text{Si}$ , and  $^{15}\text{N}$  solid-state NMR investigations and X-ray powder diffraction were applied to follow the dynamics of the reaction and to characterize the obtained products. They prove that during annealing under argon back reactions occur. With annealing under ammonia, pressures up to 4 bar and temperatures  $>200^\circ\text{C}$  completely rearrange the polysilane into a polysilazane skeleton. The resulting silazane exhibits a cage-like structure. Reactions causing this rearrangement are discussed.

## 1. Introduction

During the last 2 decades research has been focused on organosilicon precursors for the manufacture of Si–C–N-based materials, especially high-temperature stable silicon carbide and carbonitride fibers.<sup>1,2</sup> For manufacturing silicon carbide fibers the organosilicon polymers are spun into green fibers which have to be transformed into an infusible material before pyrolysis. Several concepts have been developed for this so-called curing step. Methods used so far, such as oxidation in air, where the oxygen introduced reduces the thermal stability of the later ceramic material, or expensive electron irradiation, have obvious disadvantages. Therefore, a curing by cross-linking reactions of highly reactive polymers seems to become the method of choice.

Polychloromethylsilanes represent a material which allow both to obtain green fibers by a melt-spinning process and shape stabilization by a chemical curing step. The cross-linking by  $\text{NH}_3$  is considered a promising method.<sup>3</sup> The introduction of definite and adjustable amounts of nitrogen shifts the onset of crystallization to higher temperatures. Therefore, the thermal stability of the fibers may be improved, too.

The ammonolysis of chloromonosilanes with  $\text{NH}_3$  has been extensively investigated. It created the basis of numerous synthetic routes to polysilazanes and related polymers as precursors for Si–C–N-based ceramics.<sup>1,4</sup> The reaction of  $\text{NH}_3$  with chlorosilanes possessing at least one Si–Si– bond has found only minor interest so far,<sup>5–10</sup> however. There are only a few detailed papers: The potential of polymethyldisilazanes obtained by the reaction of chloromethyldisilanes with hexamethyldisilazane as a ceramic precursor was outlined by Lipowitz et al. more than 20 years ago.<sup>11,12</sup> Burns and Chandra<sup>13</sup> investigated the pyrolysis of polychloromethylsilanes in ammonia, focusing mainly on the composition of the resulting ceramics.

It is the aim of this work to ascertain the chemical steps and related structures caused by the treatment of polychloromethylsilanes with ammonia. Temperatures up to  $290^\circ\text{C}$ , different ammonia partial pressures, and system pressures defined the parameter space for an intended fiber-curing application. The identification and characterization of the relevant chemical reactions

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allow the design of a green fiber-curing process, finally leading to ceramic SiC(N) fibers.

## 2. Experimental Section

**2.1. Polymer Preparation and Treatment of Polymer Samples with Ammonia.** The polychloromethylsilane(copolystyrene) and polychloromethylsilane samples were prepared as described previously.<sup>14</sup> Polymer samples were treated with gaseous ammonia in an autoclave especially constructed for this purpose.<sup>41</sup> The stainless steel vessel was loaded with 1 g of the hydrolysis-sensitive polymer in a glovebox under an argon atmosphere. The flow of dry ammonia (<1 ppm  $\text{H}_2\text{O}$ ) was defined by a mass flow controller. Temperature was measured in the center of the sample. The heating rate was 2 K/min in all cases. During heating a temperature gradient developed between the body of the vessel (hot walls) and the colder top.

The introduction of various amounts of ammonia into the polychloromethylsilane material followed three different regimes:

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(a) Streaming  $\text{NH}_3$  atmosphere, pure or 1:1 mixture with argon.

(b) Low total pressure experiments (below 1 bar):  $\text{NH}_3$  was added to the evacuated vessel at temperatures between 20 and 100 °C.

(c) Experiments at increased overall pressure (1–4 bar):  $\text{NH}_3$  was added to the evacuated vessel to reach the required pressure.

For the latter experiments different temperature regimes were realized:

(c1) *Room-Temperature Treatment.* The evacuated vessel was flushed by a constant ammonia flow over the sample up to a pressure of 2 bar. The sample was held for 30 min under constant pressure until the detected sample temperature, which had increased during the reaction, had fallen down to room-temperature again. After that the pressure was reduced to 1 bar and the vessel was evacuated and opened in an argon atmosphere.

(c2) *Annealing in Streaming Argon.* Samples were pretreated in the same way as described under (c1). After cooling, the vessel ammonia was replaced by argon and the samples were heated to 150 or 200 °C under streaming argon for 30 min.

(c3) *Annealing in Ammonia Atmosphere.* Samples were pretreated in the same way as described under (c1). After cooling, the vessel was heated to 220, 240, or 290 °C, with the maximal pressures reaching 4.0, 4.2, and 5.2 bar, respectively. If not otherwise mentioned, the samples were held for 30 min at the maximum temperature and then cooled under pressure. At room temperature the vessel was flushed with argon and unloaded. The top of the vessel was found covered by a white layer consisting of several condensed reaction products, especially ammonium chloride.

*Pyrolysis.* Ammonia-treated samples were pyrolyzed in a carbon crucible under argon flow at 1200 °C.

**2.2. NMR Investigations.** All solid-state NMR measurements were performed on a Bruker MSL 300 spectrometer operating at a static magnetic field of 7 T using a 7-mm MAS probe with  $\text{ZrO}_2$  rotors.  $^{13}\text{C}$ ,  $^{29}\text{Si}$ , and  $^{15}\text{N}$  measurements were carried out at resonance frequencies of 75.47, 59.6, and 30.42 MHz, respectively. Typical recycle delays for the cross-polarization (CP) experiments were 3–5 s. If not stated otherwise, the spectra were recorded with a sample rotation frequency of 5 kHz and a contact time of 5 ms.  $^{29}\text{Si}$  and  $^{13}\text{C}$  chemical shifts were determined using the external standards  $\text{Q}_8\text{M}_8$  (octakis(trimethylsiloxy)octasilsesquioxane) and adamantane, respectively. Their values were referred to tetramethylsilane (0 ppm).  $^{15}\text{N}$  chemical shifts were referred to neat liquid nitro methane,  $\delta = 0$  ppm, and determined using  $^{15}\text{NH}_4^{15}\text{NO}_3$  as external standard.

**2.3. FT/IR Investigations.** Samples for FT/IR measurements were mixed and pressed with potassium bromide (dried at 150 °C under vacuum) in a glovebox under an argon atmosphere. The FT/IR spectra were measured on a Nicolet 510 FT/IR spectrometer.

**2.4. Chemical Analysis.** All ammonia-treated fibers were analyzed with respect to their chemical composition. Oxygen and nitrogen were determined by a hot gas extraction method (LECO method) with a halogen trap. Silicon was analyzed after melt combustion by ICP-OES.

**2.5. X-ray Analysis.** Because it is difficult to quantify by chemical analysis the ammonium chloride content in the presence of nitrogen bound in the silazane structure, ammonium chloride contained in the fibers was determined by quantitative X-ray diffraction analysis instead.<sup>43</sup>  $\text{CaF}_2$  was used as internal standard to obtain the crystalline volume share of  $\text{NH}_4\text{Cl}$ .

**2.6. SEM Measurements.** Pictures were taken with a scanning electron microscope, DSM 960 (CARL ZEISS Oberkochen). Low voltage (1–3 kV) was applied for the electron beam to

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**Table 1. Structure Units and Chemical Shifts of Polychloromethylsilane<sup>a</sup>**

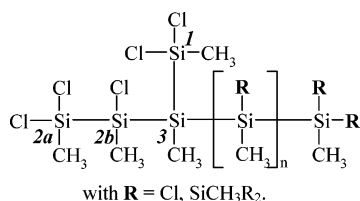
no.	structure elements	$\delta$ /ppm	
		<sup>29</sup> Si	<sup>13</sup> C
<b>1</b>	Cl <sub>2</sub> CH <sub>3</sub> Si– attached to branching units ( <b>3</b> )	36.7	11
<b>2a</b>	Cl <sub>2</sub> CH <sub>3</sub> Si– attached to linear units ( <b>2b</b> )	25.8	2
<b>2b</b>	–SiCH <sub>3</sub> Cl– spacer	14.2	2
<b>3</b>	branching units CH <sub>3</sub> –Si(SiCH <sub>3</sub> R <sub>2</sub> ) <sub>3</sub>	–63	–7.7

<sup>a</sup> The <sup>13</sup>C and <sup>29</sup>Si chemical shifts vary within 0.5 ppm depending on the composition and cross-linking density of the samples.

guarantee nondestructive measurements and to prevent charging of the nonconductive samples.

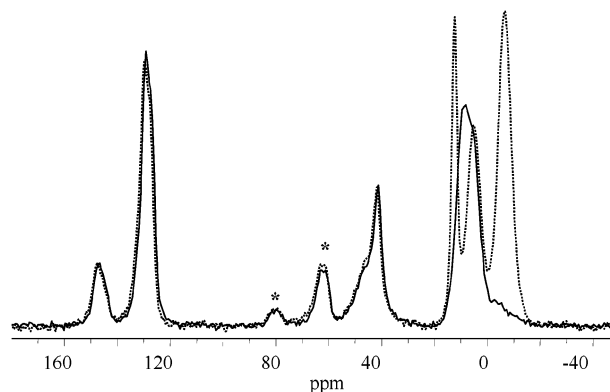
### 3. Results and Discussion

The investigations were carried out with polychloromethylsilane(co-styrene) and pure polychloromethylsilane (PCMS). Polychloromethylsilane(co-styrene), in comparison to pure PCMS, has improved rheological behavior with respect to spinnability. For the synthesis and structure of the polymers see elsewhere.<sup>15–17</sup> The general composition of the polysilane part can be described as



Former investigations<sup>15</sup> showed that <sup>29</sup>Si and <sup>13</sup>C NMR can distinguish between CH<sub>3</sub>Cl<sub>2</sub>Si– end groups **1** bound to silicon-branching units **3**, short linear units CH<sub>3</sub>Cl<sub>2</sub>Si–SiCH<sub>3</sub>Cl– and –SiCH<sub>3</sub>Cl– spacers **2a,b**, and branching units ≡SiCH<sub>3</sub> **3**. As far as branching units are concerned, silicon is bound to three other silicon units, forming a three-dimensional polymer network. Figure 2a includes a typical <sup>29</sup>Si CP/MAS spectrum of the polymer (PCMS); Table 1 gives the <sup>29</sup>Si and <sup>13</sup>C chemical shifts of the structure units. Although the concentration ratio of the characteristic structure units varies with reaction conditions, the overall structure of polysilanes used here is dominated by branching units **3** with 52 ± 5% and consisting furthermore of 15 ± 3% end groups **1** and 33 ± 4% linear groups and spacers **2a** + **b**.

It has been proven previously<sup>17</sup> that the polychloromethylsilane(co-styrene) has to be considered as a polymer blend of PCMS and polystyrene. <sup>13</sup>C CP/MAS NMR (see Figure 1) measurements revealed that the polystyrene part (signals above 20 ppm) is not significantly changed by the ammonia treatment within the pressure and temperature ranges investigated here. Therefore, only the PCMS part and its reactions will be discussed here. For pure PCMS and the PCMS/polystyrene blend differences in the reaction progress but not in the reaction product composition were observed, which may be due to the different morphology of the samples. Pure PCMS was reacted using powder samples, in the case of the PCMS/polystyrene blend so-called green fibers samples (50–100 μm in diameter) were reacted with NH<sub>3</sub>.



**Figure 1.** Part of the <sup>13</sup>C CP/MAS spectra of a PCMS/polystyrene blend before (···) and after (—) treatment with ammonia at 3.8 bar and 290 °C,  $\nu_R$  = 5 kHz. Asterisks mark spinning side bands.

The experiments for monitoring the PCMS/ammonia reactions were designed for fiber-curing application after a melt-spinning process. Therefore, the parameters have been varied as follows:

- (i) System pressure from 10 mbar to 4 bar.
- (ii) Temperature from 20 to 290 °C.
- (iii) Composition of gas phase: pure ammonia and 50% NH<sub>3</sub>/50% Ar.
- (iv) Streaming and static gas phase.

The chemical process steps and related structural changes taking place during the ammonia treatment are analyzed based on representative samples, described in Table 2.

**Experiments at Reduced or Atmospheric System Pressure.** Figure 2a shows the <sup>29</sup>Si CP/MAS spectra of the samples A, B, E, and F (see Table 2) in comparison with the untreated PCMS. Figure 2b gives the FT/IR spectra of the same samples. After reaction with small amounts of ammonia (sample A), a substitution of chlorine by amino groups can be observed. The signal intensity of the –SiMeCl<sub>2</sub> end groups **1** approached zero. In samples with even lower turnover remaining –SiMeCl<sub>2</sub> end groups were observed. The signal intensity at about 15 and –2 ppm increased due to amino substitution.

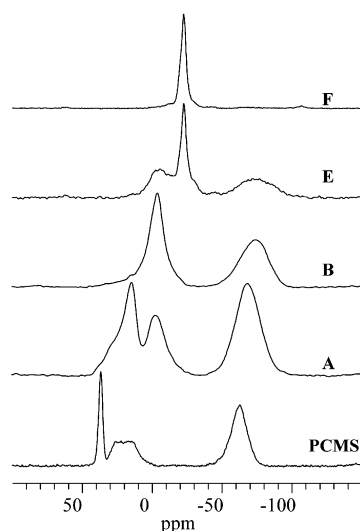
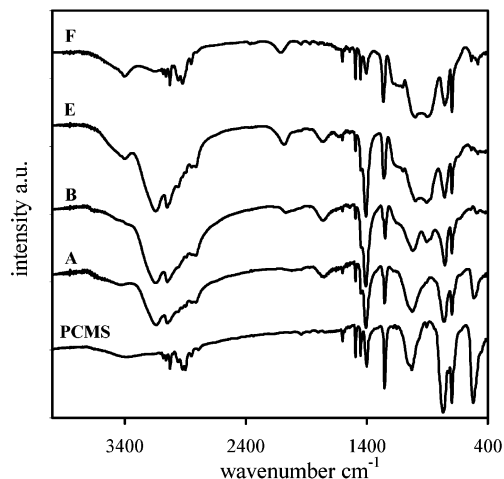
Thus, depending on the reaction conditions—temperature, partial pressure of NH<sub>3</sub>, and total pressure—the chlorine substituents can be exchanged partially or completely by amino groups.

NMR signals of the amino-substituted environments can be assigned based on chemical shifts for chloromethyloligosilanes and their amino derivatives.<sup>18–21</sup> The signal at 15 ppm is assigned to SiMeClN– groups formed by the reaction of **1** with NH<sub>3</sub>. The broad signal at around –2 ppm originates from SiMeN<sub>2</sub>– environments formed by chlorine substitution at **1** and **2a** as well as –SiMeN– spacers resulting from **2b** and SiMeClN– groups as products of **2a**. Unfortunately, the chemical shift differences between the different amino-substituted groups are much smaller than those for the chlorosilyl environments, leading to a strong overlapping of the signals. Furthermore, the signal of the branching units **3** is broadened and shifted to –68 ppm. As a comparison of the chemical shifts of chloro- and amino-substituted oligosilanes indicates, this high field shift is typical for the substitution of chlorine by amino groups.



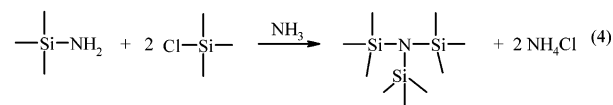
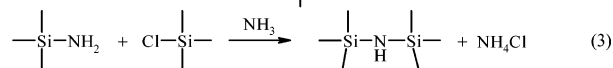
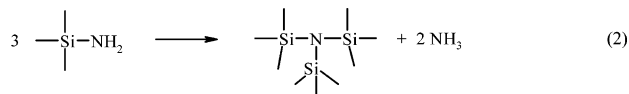
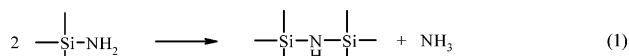
**Table 2. Samples Presented in This Work Together with Reaction Conditions Resulting in Similar Structural Change**

sample	sample treatment	reaction conditions giving similar structural changes
A	sample heated to 99 °C, autoclave-evacuated, 3 L of $\text{NH}_3$ added (60 min with 50 mL/min)	-reduced system pressure and small ammonia amounts at temperatures from 80 to 100 °C or -streaming $\text{NH}_3$ — atmosphere
B	room-temperature treatment, autoclave-evacuated, $\text{NH}_3$ added up to $p = 2$ bar; for further details, see Experimental Section	-samples treated with $\text{NH}_3$ without preheating, $\text{NH}_3$ pressures from 1 to 4 bar
C	sample preparation according to B, in addition, annealing at 150 °C for 30 min under <i>streaming argon</i>	-samples treated with $\text{NH}_3$ with preheating, $\text{NH}_3$ pressures from 1 to 4 bar
D	sample preparation according to B, in addition, annealing at 200 °C for 30 min under <i>streaming argon</i>	-samples treated with $\text{NH}_3$ without preheating, $\text{NH}_3$ pressures from 1 to 4 bar and after that annealing under argon at temperatures up to 200 °C
E	experiment at increased pressure, $p = 3$ bar $\text{NH}_3$ , $\vartheta = 220$ °C for 16 h	experiments under increased pressure up to 4 bar, -high-temperature treatment $\vartheta \leq 240$ °C, annealing in $\text{NH}_3$
F	experiment at increased pressure high-temperature treatment at 290 °C, $p = 3.8$ bar $\text{NH}_3$	experiments under increased pressure up to 4 bar and -high-temperature treatment above 240 °C and -long-time treatment 2 to 24 h at $\vartheta \geq 220$ °C in $\text{NH}_3$

**(a)****(b)****Figure 2.** (a)  $^{29}\text{Si}$  CP/MAS NMR spectra of ammonia treated samples in comparison with the starting material (PCMS). (b) FT/IR spectra of ammonia treated samples in comparison with the starting material (PCMS). For reactions see Table 2.

$^{15}\text{N}$  CP/MAS investigations validated that  $\text{NSi}_3$ — and  $\text{NSi}_2\text{H}$ — environments built up at the nitrogen atoms. This means cross-linking reactions have already taken

place to a significant extent. Relevant processes are formulated in reactions (1)–(4), with (3) and (4) being most probable.



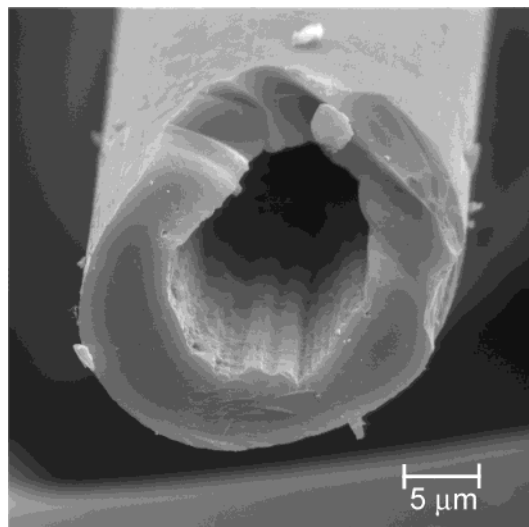
The interpretation of the FT/IR spectra is complicated due to the formation of  $\text{NH}_4\text{Cl}$ . The latter exhibits strong vibrations between 2900 and 3300  $\text{cm}^{-1}$ , a region interesting also to indicate the formation of  $\text{NH}_2$ — groups and  $\text{NH}$ — bridges. So only a strong reduction of the  $\text{Si—Cl—}$  vibration at 520  $\text{cm}^{-1}$  is observed together with a very weak vibration around 900  $\text{cm}^{-1}$  attributed to  $\text{Si—NH—Si—}$  groups.

Actually, the pyrolysis of the thus-obtained fibers showed that, despite of the cross-linking, the hardening of the fiber was unsatisfactory or resulted in hollow fibers (Figure 3).

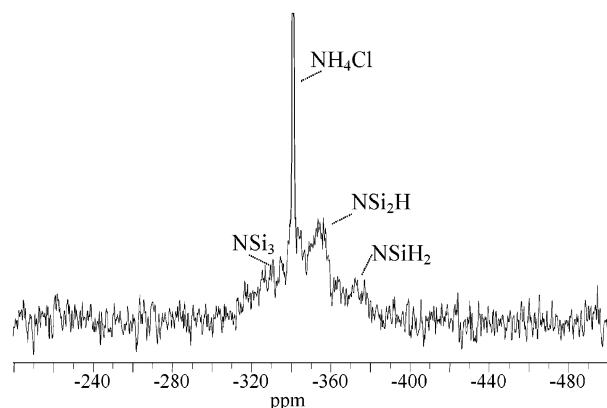
The latter should originate from a decreasing cross-linking density from the fiber surface to the inner region.

#### Experiments at Increased System Pressures.

(a) *Room-Temperature Treatment.* Experiments at increased pressure were designed to extend the cross-linking reaction into the fiber center, with sample B as a representative example. Its  $^{29}\text{Si}$  NMR spectrum shows a complete conversion of the chlorine-containing PCMS groups. Besides the signal of the polysilane backbone only one broad signal at  $-3$  ppm is left representing the nitrogen-substituted environments. In the FT/IR spectra of the same sample significant bands at 1170  $\text{cm}^{-1}$  ( $\nu_{\text{N—H}}$  in  $\text{Si—NH—Si—}$  structures<sup>27</sup>) and 905  $\text{cm}^{-1}$  ( $\nu_{\text{as}}$   $\text{SiNSi}$ ) are observed. They suggest that the broad  $^{29}\text{Si}$  NMR signal should be attributed to  $\text{SiN}_2\text{CSi—}$  and  $\text{SiNCSi}_2$ — environments in cross-linked structures.



**Figure 3.** REM picture of an example of a hollow fiber.



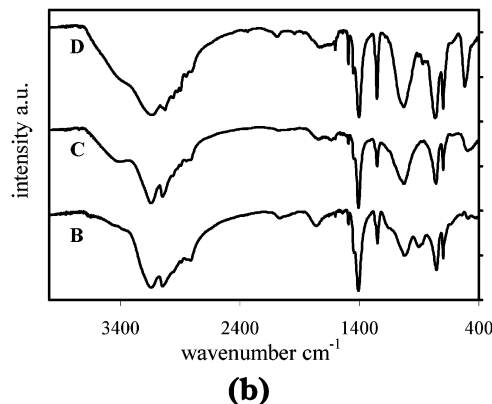
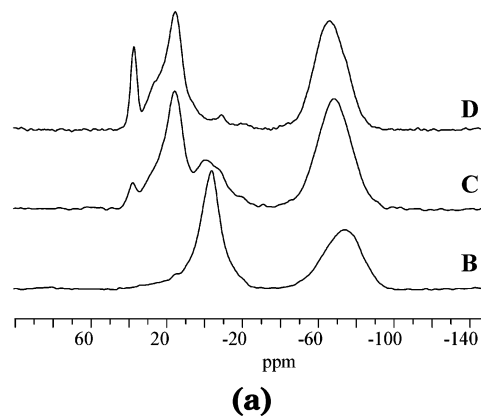
**Figure 4.** <sup>15</sup>N CP/MAS NMR spectrum of sample B, NH<sub>4</sub>Cl-signal cut at 30%, contact time  $t = 1$  ms (CP for  $\text{NSi}_3$  and NH<sub>4</sub>Cl less efficient than for  $\text{NSi}_2\text{H}$ - and  $\text{NSiH}_2$ - groups).

The <sup>29</sup>Si NMR signal of the polysilane backbone is further broadened and shifted to  $-73.7$  ppm. Chemical analysis of the total chlorine content (23 wt %) together with the XRD analysis of chlorine fixed in NH<sub>4</sub>Cl (20 wt %) showed that nearly all chlorine in the PCMS has been substituted by amino groups. The difference of 3% is in the order of magnitude of the experimental error.

<sup>15</sup>N CP/MAS measurements show that the nitrogen environment is dominated by  $\text{NSi}_3$ - and  $\text{NSi}_2\text{H}$ - units and that  $\text{NSiH}_2$ - moieties are still present to a minor content (see Figure 4).

*(b) Annealing under Streaming Argon.* To study the temperature influence on the cross-linking progress, sample B was annealed in an argon atmosphere for 30 min at 150 and 200 °C, yielding samples C and D, respectively. The resulting <sup>29</sup>Si CP/MAS spectra and FT/IR spectra are given in Figures 5a and 5b, respectively.

Both pictures indicate that the cross-linking was not intensified by this annealing but back reactions took place. In the <sup>29</sup>Si NMR spectra again signals of the different chlorosilyl groups are observed. The signal at  $-3$  ppm representing cross-linked amino-substituted silyl groups is strongly reduced at 150 °C and nearly disappears at 200 °C. In contrast, the signal of the dichloromethylsilyl groups **1** increases with temperature. The broadening of the polysilane backbone signal is reduced, and the signal is shifted back to lower field.



**Figure 5.** (a) <sup>29</sup>Si CP/MAS NMR spectra of samples B, C, and D. (b) FT/IR spectra of samples B, C, and D.

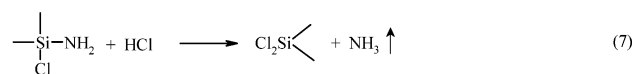
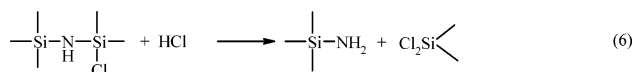
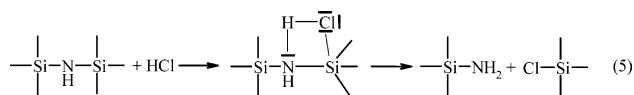
This reversibility demonstrates that the silicone backbone is not yet significantly changed at the reaction conditions applied until then, even at pressures up to 3.8 bar.

The FT/IR spectra show that the asymmetric valence vibration Si–N–Si (at 906 cm<sup>-1</sup>) nearly disappears already in the sample annealed at 150 °C. Even the Si–Cl– stretching vibration at 520 cm<sup>-1</sup> can be observed again, very weak after annealing at 150 °C but strong after annealing at 200 °C. This conversion process, which implies back reactions restoring silicon–chlorine bonds (reactions (3) and (4)) can only be explained with the participation of the NH<sub>4</sub>Cl precipitated in the fiber during the ammonia treatment.

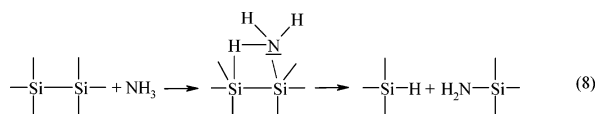
Equilibria between chlorosilanes and ammonium halogenides have already been investigated by Krüger and Rochow.<sup>22</sup> They observed the cleaving of Si–N– bonds as well as the introduction of chlorine from the salt into the silane. Cleavage of Si–N– bonds by HCl has been described by other authors,<sup>23</sup> too. In our system the presence of a streaming argon atmosphere should force the ammonium chloride to dissociate partially into HCl and NH<sub>3</sub> with increasing temperature. HCl might be able to split the Si–N– bonds, whereas ammonia is removed from the reaction site by the argon stream. Interaction of HCl with the polymer should yield reaction steps similar to reactions (5)–(7).

An argon atmosphere combined with elevated temperatures causes a re-equilibration of the system. The precipitated NH<sub>4</sub>Cl is not only a byproduct, but rather the driving force to rebuild Si–Cl– bonds.

A very weak Si–H– vibration at about 2100 cm<sup>-1</sup> in sample B indicates a partial scission of Si–Si– bonds;



see reaction (8). We attribute this reaction to the presence of  $\text{NH}_3$  formed by dissociation of  $\text{NH}_4\text{Cl}$ .

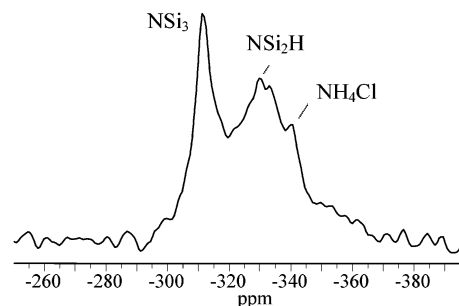


Nevertheless, both the NMR and IR spectra indicate that for sample B a process according to (8) does not disintegrate the polysilane backbone to a significant extent.

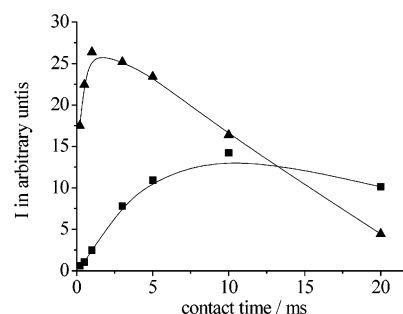
(c) *Annealing under Ammonia and Increased Pressures.* The above-described annealing procedure did not significantly affect the polysilane backbone structure. Further investigations included annealing under ammonia at increased pressure and temperatures (samples E and F, see Table 2). We observed a decreasing intensity of the  $^{29}\text{Si}$  NMR high-field signal at  $-71$  ppm. This indicates a conversion of the PCMS backbone, being very slow as long as the temperature is below  $240^\circ\text{C}$ . The higher the temperature, the faster the conversion proceeds, as can be seen from the spectrum of sample F. At  $290^\circ\text{C}$  the polysilane signals disappeared already after 2 h of reaction time. Only one signal at about  $-22$  ppm is left, which is much narrower than those of the polysilane backbone observed before. Comparing the spectrum of the starting material with the one of sample F, it seems that the polysilane, exhibiting several different structure units, is transformed into a chemically very homogeneous product!

$^{15}\text{N}$  CP/MAS NMR spectroscopy in natural abundance was carried out to investigate the nitrogen environment in sample F. Figure 6 shows the obtained spectrum for a contact time of 5 ms. Three different environments emerge at  $-311$ ,  $-330$ , and  $-355$  ppm. An additional narrow signal of small intensity at  $-341$  ppm is due to remaining small amounts of crystalline  $\text{NH}_4\text{Cl}$ .<sup>34</sup>

Own investigations<sup>35</sup> and the comparison with literature data<sup>26,34,36,37</sup> lead to the conclusion that the  $^{15}\text{N}$  chemical shift is often strongly influenced by the next nearest neighbors. Thus, the values cannot simply be transferred from one system to another. The signals were therefore assigned by means of variable contact time measurements. There the time for magnetization transfer from protons to the insensitive nucleus (=contact time) is varied between the experiments. The dependence of the signal intensity on the contact time is given in Figure 7 for the two main components of the  $^{15}\text{N}$  spectrum. The steep rise in the signal intensity at short contact times is typical for hydrogen-containing groups in bridging positions such as  $\text{NH-}$  bridges between two silicon atoms. Thus, the signal at  $-330$  ppm was assigned to  $\text{NSi}_2\text{H-}$  structures, the minor component at  $-355$  ppm to  $\text{NSiH}_2$ . In contrast,  $\text{NSi}_3$ -



**Figure 6.**  $^{15}\text{N}$  CP/MAS NMR spectrum of sample F,  $\tau_{\text{CP}} = 5$  ms, spinning speed  $\nu_{\text{R}} = 3$  kHz.



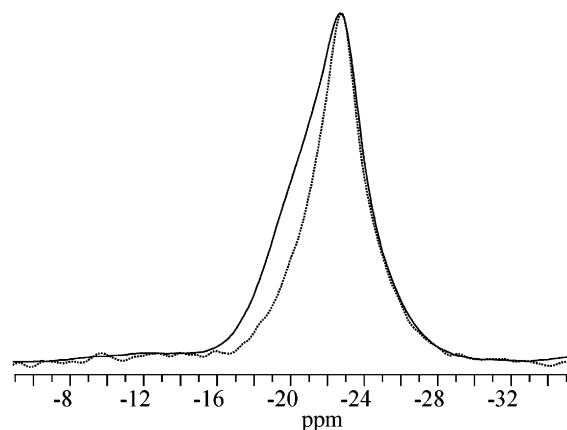
**Figure 7.** Intensity dependence of the two  $^{15}\text{N}$  CP/MAS NMR main signals in the spectra of sample F. (■)  $\text{NSi}_3$ - groups at  $-311$  ppm; (▲)  $\text{NSi}_2\text{H-}$  groups at  $-330$  ppm.

groups ( $-311$  ppm), having no directly bonded hydrogen atoms, show only a slow increase of signal intensity with contact time.

The results show that, depending on the reaction conditions, only part of the silicon chlorine bonds is substituted for amino groups, including subsequent cross-linking reactions between  $\text{Si-NH}_2$  and  $\text{Si-Cl}$  moieties. With increasing temperature and ammonia pressure the polysilane backbone is converted into a new structure. Therefore, we focused on clarifying the structure of the obtained product and the related reaction steps.

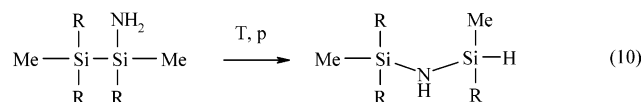
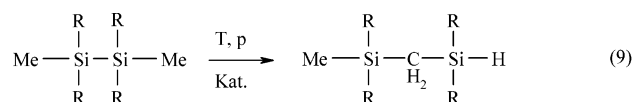
$^{29}\text{Si}$  NMR signals at about  $-22$  ppm have been assigned to different environments of silazane structures in  $\text{Si-C-N-}$  systems:  $\text{SiCN}_3$  and  $\text{SiCN}_2\text{H}$ .<sup>24-32</sup> Several authors<sup>24-27</sup> observed that both these environments gave overlapping signals in the same chemical shift region, which is supported by our own FT/IR measurements. The FT/IR spectra of the samples E and F (see Figure 2b) exhibit a strong vibration at about  $2100\text{ cm}^{-1}$ , which is significant for  $\text{Si-H-}$  moieties. A detailed analysis of the  $^{29}\text{Si}$  NMR signal at  $-22$  ppm proved that it consists of more than one component. To assign signal components to the environments,  $^{29}\text{Si}$  CP/MAS NMR investigations combined with dipolar dephasing before acquisition<sup>33</sup> (see Figure 8) and variable contact time CP/MAS NMR investigations were carried out. Both experiments showed that the signal stems from two components at about  $-22$  and  $-20$  ppm. The one at  $-20$  ppm has a higher intensity at shorter contact times and gives a faster decay of the signal during the dipolar dephasing experiment. This behavior is typical for environments with silicon-bonded hydrogen atoms. The signal could therefore be assigned to  $\text{SiCN}_2\text{H}$  and the component at  $-22$  ppm to the  $\text{SiCN}_3$ - environment.

Two possible pathways have to be considered for the rearrangement of the silicon-silicon bonds of the poly-



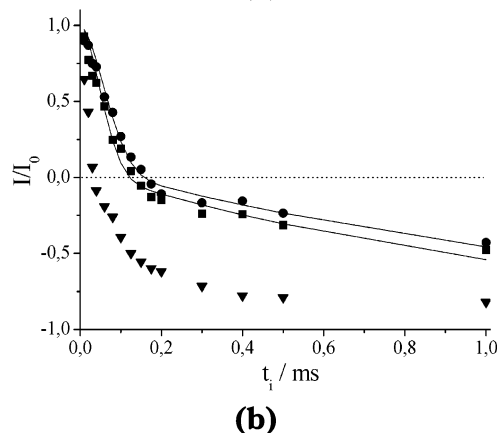
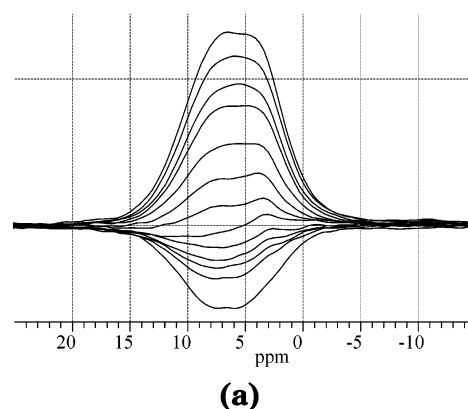
**Figure 8.** Part of the  $^{29}\text{Si}$  CP/MAS NMR spectra of a sample similar to F, contact time 5 ms. (···) 3 ms dipolar dephasing before acquisition; (—) without dipolar dephasing before acquisition. For better comparability the spectra have been normalized to equal intensity.

silane structure to give Si–H– bonds. The so-called Kumada rearrangement is based on a  $\text{CH}_2$ – insertion into the silicon–silicon bond (reaction (9)). Combined with cross-linking reactions of Si–H and  $\text{HNSi}$ – groups, this rearrangement would lead to a carbosilazane network. Alternatively, the insertion of NH– groups into the silicon–silicon bond would give  $\text{NSi}_2\text{H}$ – and  $\text{NSi}_3$ – moieties (reaction (10)). Both ways result in the formation of Si–H– bonds in the polymer, but only the Kumada-type reaction would also give significant amounts of methylene groups. Therefore, sample F was investigated using  $^{13}\text{C}$  NMR to search for methylene groups.



Because it is difficult to distinguish between methyl and methylene groups bound to silicon only by their chemical shifts, techniques taking advantage of differences in the cross-polarization (CP) dynamics of these groups had to be employed. The Inversion Recovery Cross Polarization (IRCP) method used here has been developed by Wu and Zilm<sup>38</sup> for spectral editing in organic structures and applied for polysilane applications by Babonneau and co-workers.<sup>39,40</sup> The basic idea behind the editing techniques is that the dynamics of CP and polarization inversion (PI) depends on the strength of dipolar interaction within the groups. For  $\text{CH}_3$ – groups dipolar interaction is reduced by its rotation compared to that of the more rigid methylene bridges between silicone atoms. Thus, CP and PI of methylene groups are much faster than those for methyl groups due to their stronger dipolar interactions.

Figure 9a gives a section of the IRCP/MAS spectra of sample F. The spectrum at  $t_i = 0.01$  ms is nearly consistent with the  $^{13}\text{C}$  CP/MAS spectrum of the sample. A broad signal can be observed within a chemical shift region from 15 to –5 ppm.



**Figure 9.** (a)  $^{13}\text{C}$  IRCP spectra of sample F at inversion times of  $t_i = 0.01, 0.02, 0.03, 0.04, 0.06, 0.08, 0.1, 0.125, 0.15, 0.3, 0.4, 0.5$ , and 1 ms (from top to bottom) (b) Inversion behavior of signals in the  $^{13}\text{C}$  CP/MAS spectra of sample F: (●) signal at 3.6 ppm and fitted function to eq 1; (■) signal at 7.9 ppm and fit to eq 1; (▼)  $\text{CH}_2$ – groups of polystyrene.

**Table 3. Values Obtained for the Variables of Eq 1, Sample F**

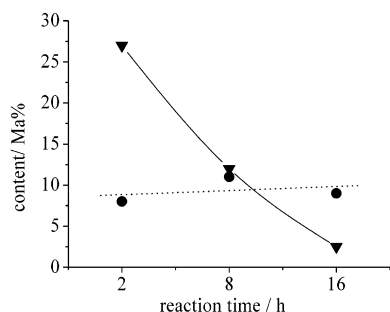
chemical shift/ppm	$n$	$T_{\text{CH}}/\text{ms}$	$\tau_{\text{D}}/\text{ms}$
3.6	$0.95 \pm 0.07$	$0.073 \pm 0.004$	$2.1 \pm 0.4$
7.9	$1.17 \pm 0.09$	$0.075 \pm 0.003$	$1.5 \pm 0.2$

Because of the slightly different inversion behavior of the environments contributing to the signal, two components with nearly the same intensity could be distinguished at 3.6 and 7.9 ppm. Their signal intensities obtained by peak deconvolution are given in Figure 9b. The intensity was analyzed by fitting the experimental data to eq 1<sup>39,40</sup>

$$\begin{aligned} I/I_0 = & [2/(n+1) \exp(-t_i/\tau_{\text{D}}) + \\ & 2n/(n+1) \exp(-3t_i/2\tau_{\text{D}}) \exp(-t_i^2/T_{\text{CH}}^2) - 1] \quad (1) \end{aligned}$$

with  $T_{\text{CH}}$  = cross polarization rate,  $\tau_{\text{D}}$  = spin diffusion time,  $t_i$  = polarization inversion time (all in ms), and  $n$  = effective number of protons. The results are given in Table 3. The values for both signals are typical for methyl groups and are consistent with the results for the polysilane system,<sup>39,40</sup> where  $T_{\text{CH}} = 0.07$  ms,  $\tau_{\text{D}} = 2$ –2.4 ms, and  $n = 1.1$  were determined for methyl groups and  $T_{\text{CH}} = 0.01$  ms and  $n \approx 2$  for methylene groups. The difference in the behavior of methyl and methylene moieties becomes obvious by comparing the inversion behavior of the  $\text{CH}_2$ – groups of the polystyrene part of the blend, given in Figure 9b, for same sample F.





**Figure 10.** Nitrogen distribution in samples treated with ammonia at 240 °C and  $p = 3.8$  bar. NH<sub>4</sub>Cl = ▼; total nitrogen = ●. The NH<sub>4</sub>Cl content was determined by X-ray analysis and the total nitrogen amount by chemical analysis.

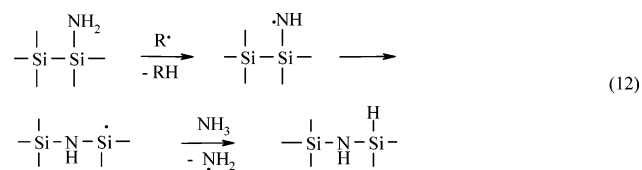
Hence, we conclude that the insertion of amino groups is responsible for the transformation of the polysilane backbone into a silazane structure and the formation of Si–H– groups. The two different carbon environments can therefore be attributed to methyl groups situated in SiN<sub>3</sub>(CH<sub>3</sub>)– (7.9 ppm) and SiN<sub>2</sub>H(CH<sub>3</sub>)– environments (3.6 ppm).

Figure 10 gives the content of NH<sub>4</sub>Cl and total nitrogen in samples treated in ammonia at 240 °C for 2, 8, and 16 h. Whereas the concentration of NH<sub>4</sub>Cl decreases with increasing reaction time, the total nitrogen content (nitrogen in NH<sub>4</sub>Cl and polymer) stays constant within the experimental error! The nitrogen must be transferred from the ammonium chloride into the polymer via insertion reactions. So it has to be concluded that besides the amino substituents in the polymer another source of the nitrogen insertion must be ammonium chloride.

A similar rearrangement was observed by Schmidt et al.<sup>9</sup> for a vinylic polysilane during pyrolysis in ammonia at temperatures from 300 to 650 °C. There the incorporation of nitrogen into the polymer network is discussed in two ways. One is the reaction of ammonia with the polysilane network to displace alkane, silane, hydrogen (reaction (11)) and the other the reaction of •NH<sub>2</sub>– radicals produced via radical quenching reactions of NH<sub>3</sub> with free radical sites formed during the pyrolytic conversion of the material (reaction (12)).

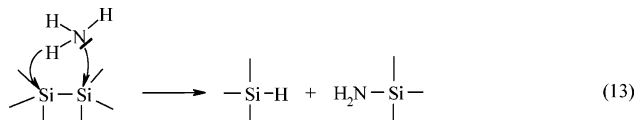


This nitrogen introduction reaction is followed by the insertion of the amino group (see eq 10), leading to a cleavage of Si–Si– bonds and a transformation to a silazane network. Analogous to the Kumada rearrangement, the process is discussed to proceed radicalic too:



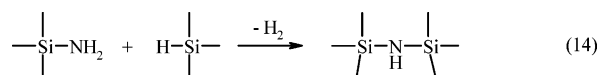
The occurrence of these reactions is supported by the large intensity of the Si–H infrared stretching vibration for the pyrolyzed samples. The formed silane groups might undergo cross-linking with amino groups under elimination of hydrogen. Because of the experimental conditions applied, the occurrence of radicalic species

is unlikely for our system. And, as stated above, the presence of ammonium chloride is one of the driving forces of the rearrangement. The gas phase above the polymer consists of mainly ammonia, the concentration of which will increase with rising temperature due to dissociation of NH<sub>4</sub>Cl. Obviously, ammonia is able to cleave Si–Si– bonds at the chosen temperatures and pressures according to (13):



As ammonia is consumed by the reaction, further dissociation of ammonium chloride will provide it again.

The nitrogen-introducing step can be followed by an insertion reaction according to reaction (10) or by cross-linking reactions as outlined above (reactions (1)–(4)). In addition, the formed silane groups can undergo dehydrocoupling with amino groups (reaction (14)).



Considering the carbon balance obtained from <sup>13</sup>C CP/MAS spectra and the vibration spectra, it can be derived that the percentage of methyl groups decreases relative to that of polystyrene during the rearrangement. As can be shown by integration of the NMR spectra, about 50% of the carbon in the PCMS/polystyrene fibers is bound in methyl groups of the PCMS. In sample F only about 35% of the carbon is left in the silazane, indicating a decrease of the amount of organosilicon component in the blend. This fact supports the elimination of methane or low molecular weight silanes formed via reaction (13).

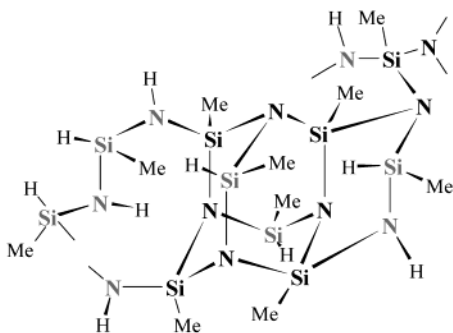
Unfortunately, the experimental design of the curing apparatus did not allow for the investigation of the gaseous reaction products. It would have been valuable additional information with respect to the silanes eliminated and products of the cross-linking process (HCl, NH<sub>3</sub>, H<sub>2</sub>, and CH<sub>4</sub>).

<sup>13</sup>C MAS NMR was used to estimate the amount of polystyrene contributing to the carbon content in the PCMS/PS blend. Combined with chemical analysis, it gave an average composition of the polysilazane part of Si:N:C:H = 1:1.0.9–1.3:3.5.

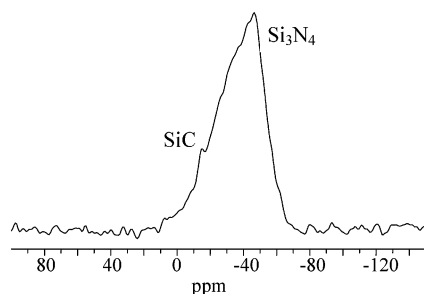
From the information of the <sup>29</sup>Si, <sup>13</sup>C, and <sup>15</sup>N NMR investigations it turns out that the formed polysilazane must consist of a three-dimensional network formed by SiN<sub>3</sub>(CH<sub>3</sub>)– and SiN<sub>2</sub>H(CH<sub>3</sub>)– environments in approximately equal amounts. The nitrogen links either three silicon atoms giving NSi<sub>3</sub>– groups or two silicon atoms giving NSi<sub>2</sub>H– groups. They occur in equal amounts too. The approximately equal amounts of the different structure elements were estimated by the <sup>29</sup>Si and <sup>15</sup>N CP/MAS NMR investigations at different contact times. A section of the proposed resulting polysilazane structure is given in Figure 11.

Pyrolysis of these polysilazane/ polystyrene blends leads to materials strongly dominated by silicon nitride, as can be seen by the <sup>29</sup>Si MAS NMR spectrum in Figure 12.





**Figure 11.** Proposed structure for polysilazane formed during ammonia treatment at high pressures and temperatures above 200 °C. Gray: Si-H and N-H moieties. Black: Si and N environments possessing *three* links to the silazane network.



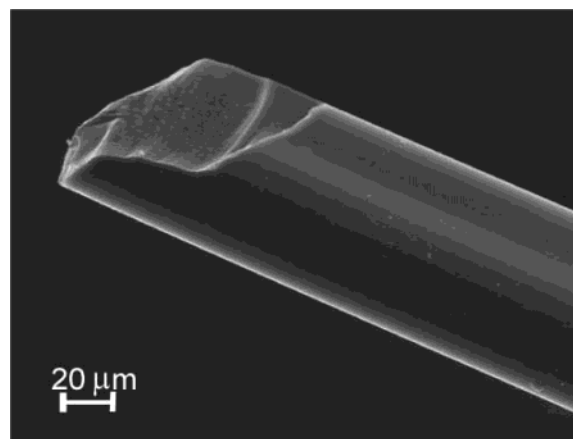
**Figure 12.**  $^{29}\text{Si}$  MAS NMR spectrum of a sample prepared according to F after pyrolysis in Ar at 1200 °C.

#### 4. Conclusions

The investigations showed that the reaction with ammonia at mild reaction conditions leads to a Si-Cl substitution by amino groups and cross-linking within the polymer. Increasing the temperature and pressure causes a breaking of the polysilane structure and transformation into a polysilazane due to the reactivity of ammonium chloride precipitated in the polymer by the  $\text{NH}_3$  treatment.

Despite of the complex intercombination steps process conditions could be found to stabilize the shape of the polysilane green fibers prior to pyrolysis.<sup>41,42</sup> An example of a SiC(N) fiber obtained from polychloromethylsilanes after curing with ammonia and pyrolysis in argon is given in Figure 13.

The investigation of the structural changes prove that, as long as  $\text{NH}_4\text{Cl}$ -precipitation is not prevented within the fiber, it will not be possible to obtain SiC-fibers with low nitrogen content. The formed ammonium chloride at lower pressures and temperatures suppresses the formation of sufficient Si-N-Si linkages but



**Figure 13.** REM picture of a SiC(N) fiber obtained from polychloromethylsilanes after curing with ammonia and pyrolysis in argon.

supports the cleavage of Si-Si bonds at pressures up to 4 bar and temperatures  $>200$  °C. The nitrogen of  $\text{NH}_4\text{Cl}$  is incorporated into the polymer, which either directly leads to a cleavage of Si-Si bonds or in a subsequent oxidative addition step of introduced amino groups transforms the polysilane structure into a silazane network. Thus, at higher pressures and temperatures the desired shape stabilization is achieved at the cost of the conversion of the polysilane into a polysilazane network. The structural diversity of the PCMS is changed into a structurally homogeneous material, the composition of which can only be explained assuming the cage-like structure (see Figure 11) often reported for highly cross-linked organosilicon polymers.

The problem of the  $\text{NH}_4\text{Cl}$  precipitation could be avoided or reduced by dissolving the polychloromethylsilane in an inert organic solvent, partly cross-linking the polymer with ammonia or alkylamines and filtration of the formed ammonium chloride. Fibers can then be obtained by either spinning of the solution or melt-spinning after removing the solvent. Further exposition to higher temperatures should lead to cross-linking reactions and give the wanted stabilization of the fiber.

**Acknowledgment.** The Deutsche Forschungsgemeinschaft is acknowledged for financial support under the Major Task Program "Neue Precursorkeramik aus kondensierten molekularen Vorstufen" and "Höchsttemperaturbeständige Leichtbauwerkstoffe".

CM030619A