APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 11, 833–841 (1997)

Synthesis and Thermally Induced Ceramization of a Non-oxidic Poly(methylsilsesquicarbodi-imide) Gel

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A novel polymeric organosilicon gel with the composition $[\mathrm{MeSi(NCN)_{1.5}}]_n$ synthesized by the reaction of $\mathrm{MeSiCl_3}$ with $\mathrm{Me_3Si{-}N{=}C{=}N{-}SiMe_3}$ is reported. The reaction is performed without any solvent and with catalytic amounts of pyridine and provides highly cross-linked poly(methylsilsesquicarbodi-imide) in the form of a stable non-oxidic gel with unusual low open porosity ($<1\ \mathrm{m^2\,g^{-1}}$). The Si–C–N gel transforms to an amorphous silicon carbonitride ceramic, $\mathrm{SiC_{1.1}N_{1.6}}$, by the thermally induced ceramization at 1200 °C in inert atmosphere (argon). The gel-derived silicon carbonitride is thermally stable up to 1450 °C. The synthesis, characterization and pyrolysis behavior of the new polyorganosilicon gel is discussed. © 1997 John Wiley & Sons, Ltd.

Appl. Organometal. Chem. **11**, 833–841 (1997)

No. of Figures: 8 No. of Tables: 1 No. of Refs: 17

Keywords: silylcarbodi-imide; bis(trimethylsilyl)carbodi-imide; poly(methylsilsesquicarbodi-imide); sol–gel; pyrolysis; thermal analysis; mass spectra; silicon carbonitride; argon physisorption; high-resolution transmission electron microscopy (HR TEM)

Received 4 November 1996; accepted 17 March 1997

INTRODUCTION

Dense silicon carbonitride ceramics, $\mathrm{Si}_x\mathrm{C}_y\mathrm{N}_z$, are produced by the thermal decomposition of compacted organo-substituted polysilazanes.[1] The materials formed at 1000–1200 °C in 0.1 MPa argon are completely amorphous and provide polycrystalline α-$\mathrm{Si_3N_4}/\alpha(\beta)$-SiC composites after crystallization at $T>1400$ °C.[2] A novel class of organosilicon polymers denoted as polysilylcarbodi-imides, of the form $[\mathrm{R}_x\mathrm{Si(N{=}C{=}N)}_{(4-x)/2}]_n$ with $x=0$, 1 or 2 and with R = H, $\mathrm{CH_3}$ or $\mathrm{HC{=}CH_2}$, were developed in the course of our work concerning the synthesis of Si–C–N ceramics.[3–6] The first stoichiometric crystalline phases in the ternary Si–C–N system, $[\mathrm{Si(NCN)_2}]_n=\mathrm{SiC_2N_4}$ (**1**) and $\mathrm{Si_2N_2(NCN)}=\mathrm{Si_2CN_4}$ (**2**), were obtained by the reaction of silicon tetrachloride with bis(trimethylsilyl)carbodi-imide according to Eqns [1] and [2].[5]

$$n\mathrm{SiCl_4}+2n\mathrm{Me_3Si{-}N{=}C{=}N{-}SiMe_3} \xrightarrow{\text{pyridine}} [\mathrm{Si(NCN)_2}]_n+4n\mathrm{Me_3SiCl} \qquad [1]$$

$$[\mathrm{Si(NCN)_2}]_n \xrightarrow{400\ ^\circ C} \underset{\mathbf{1}}{\beta\text{-}\mathrm{SiC_2N_4}} \xrightarrow[-\mathrm{N_2/C_2N_2}]{960\ ^\circ\mathrm{C}} \underset{\mathbf{2}}{\mathrm{Si_2CN_4}} \qquad [2]$$

Recently, we reported on the formation of a non-oxidic gel by the reaction of methyltrichlorosilane with bis(trimethylsilyl)carbodi-imide.[6] The conventional sol–gel technique is widely used for the preparation of oxidic glasses and ceramics. The variety of technological applications reflects the important position of the sol–gel process in applied inorganic chemistry.[7] With the exception of results from Bocarsly and co-workers[8] based on coordinate covalent cyanogels in aqueous solutions, sol–gel chemistry was still limited to oxidic systems. The present

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Contract grant sponsor: Deutsche Forschungsgemeinschaft, Bonn, Germany.
Contract grant sponsor: Fonds der Chemischen Industrie, Frankfurt, Germany.

CCC 0268–2605/97/100833–09 $17.50

study focuses on the preparation, characterization and thermal decomposition of the as-synthesized poly(methylsilsesquicarbodi-imide) gel, $[MeSi(NCN)_{1,5}]_n$.

EXPERIMENTAL

General methods

The liquid starting materials were distilled before use and stored under dry argon gas. The solvent, tetrahydrofuran (THF), was distilled from a sodium/benzophenone mixture. All chemical reactions and spectroscopic investigations were performed under inert atmospheres (argon or nitrogen). The synthesized samples were manipulated in a glove box (Braun MB 150G-I SPS; $O_2 < 1$ ppm; $H_2O < 1$ ppm). Infrared and Raman spectra were measured on a Perkin-Elmer FT-IR 1750 (KBr pellets) and a Bruker IFS 55 (1.5 mm glass tubes), respectively. Simultaneous thermal analysis (STA) of the poly(methylsilsesquicarbodi-imide) xerogel was conducted in combination with mass spectrometry (Netzsch STA 429 and Balzers QMG 420) in the temperature range 20–1500 °C with a heating rate of 2 °C min^{-1} under flowing helium (75 cm^3 min^{-1}). The solid-state ^{29}Si-NMR measurements of the $[MeSi(NCN)]_{1.5}]_n$ gel were obtained on a Bruker MSL 300 with a resonance frequency of 59.6 MHz using magic-angle spinning (MAS) with a rotation frequency of 4500 Hz and with a cross-polarization (CP) sequence. The chemical shift value is referenced to tetramethylsilane (TMS).

The argon adsorption isotherms were taken at liquid argon temperature (87 K) with an Omnisorp 360 using the static-dosage mode. The $[MeSi(NCN)_{1.5}]_n$ gel dried at 140 °C was degassed at 80 °C, 1×10^{-4} mbar for 2 h prior to the measurement. The $[MeSi(NCN)_{1.5}]_n$ polymers, pyrolyzed at 700 or 1200 °C, were treated for 12 h at 250 °C, 1×10^{-4} mbar. Specific surface areas were calculated using the BET model with the ADP Software, Version 3.0.2 (Porotec GmbH, Frankfurt/Main, Germany).

High-resolution transmission electron microscopy (HR TEM) was performed with a Hitachi HF-2000 (200 kV) equipped with a Noran Voyager EDX system. The samples were prepared in a glove box (Braun MB 150B-G SPS: $O_2 < 1$ ppm; $H_2O < 1$ ppm). The $[MeSi(NCN)_{1.5}]_n$ gels, pyrolyzed at 700 °C and 1200 °C, were ground to fine powders and suspended in dry THF. The particles were mounted on holey carbon grids (copper, 400-mesh, 3 mm diameter).

The chemical analysis data were determined at the Mikroanalytisches Labor Pascher, 53424 Remagen, Germany.

Synthesis of N,N′-bis(trimethylsilyl)carbodi-imide (4)

Method A

Cyanamide, $H_2N–CN$ (105 g; 2.5 mol) was dissolved in 150 cm^3 of THF. The solution was added dropwise to 403 g (2.5 mol) of hexamethyldisilazane (HMDS), $Me_3Si–NH–SiMe_3$, in a 1-dm^3 three-necked, round-bottomed flask. The reaction mixture was heated to reflux until ammonia evolution was complete (*ca* 1.5 h). Solid by-products were separated by filtration, and the filtrate was distilled using a 30-cm Vigreux column. Bis(trimethylsilyl)carbodi-imide (**4**) was obtained at 164 °C in 81% yield (377 g).

Method B[9]

A mixture of dicyandiamide (42 g, 500 mmol), HMDS (177 g, 1.098 mol) and ammonium sulfate (0.2 g, 151 mmol) was heated in a round-bottomed flask with a reflux condenser. The vapor temperature gradually rose to 160 °C. In the course of the reaction, the solid disappeared. Final fractionation of the reaction mixture through a 30-cm Vigreux column gave 71% bis(trimethylsilyl)carbodi-imide (**4**) (132 g, 709 mmol) at 164 °C.

The spectroscopic data for **4** corresponded to those given in Ref. 10.

$[MeSi(NCN)_{1.5}]_n$ gel (5 + 6)

In a 100-cm^3 round-bottomed flask, methyltrichlorosilane (**3**) (10.7 g, 71.6 mmol), was mixed with **4** (20.0 g, 107 mmol) and a catalytic amount of pyridine (1.70 g, 21.5 mmol). The reaction mixture was heated to 90 °C with stirring. The time until gelation depended strongly on the amount of pyridine. In the case of 0.3 equiv pyridine relative to **3**, the time until gelation took about 4 h. After it had been cooled to room temperature, the gel was aged by annealing at 45 °C. The three-dimensional shrinkage of the gel was complete after about 50 days under these conditions. The xerogel **5** was obtained in 89% yield after evaporation of the liquid phases,

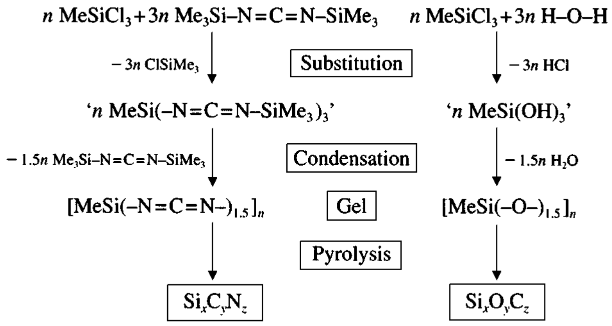


Figure 1 Comparison of the non-oxidic sol–gel process (left-hand side) with the aqueous counterpart (right-hand side) and the final products obtained after pyrolysis of the dried gels.

Me_3SiCl (**6**) and residual **4**, at room temperature and 50 °C under reduced pressure (3×10^{-2} mbar).

IR (KBr pellets): 2965, 2152, 1270 cm^{-1}; Raman (powder): 2974, 2906, 1533 cm^{-1}; ^{29}Si CP/MAS NMR: $\delta = -62.3$ ppm. Analysis: $C_{2.5}H_3N_3Si$ (**5**) (103.16): Calcd: C, 29.11; N, 40.73; O, 0.00; Si, 27.23; Found: C, 28.75; N, 38.3; O, 0.28; Si, 26.9%. Xerogel (**5**) pyrolyzed at 700 °C: C, 19.0; N, 44.8; O, 0.26% ($SiC_{1.2}N_{2.5}$). Xerogel (**5**) pyrolyzed at 1200 °C: C, 21.1; N, 34.4; O, 0.32% ($SiC_{1.1}N_{1.6}$).

RESULTS AND DISCUSSION

Comparison with aqueous sol–gel processes

The novel organosilicon polymer **5** is formed by the reaction of methyltrichlorosilane (**3**) with bis(trimethylsilyl)carbodi-imide (**4**) without any solvent (Eqn [3]):

$$\underset{\substack{\text{liquid}\\ \mathbf{3}}}{n\mathrm{MeSiCl_3}} + 1.5n\ \underset{\substack{\text{liquid}\\ \mathbf{4}}}{\mathrm{Me_3Si{-}N{=}C{=}N{-}SiMe_3}} \xrightarrow{\text{pyridine}} \underbrace{\underset{\text{solid}}{[\mathrm{MeSi(NCN)_{1.5}}]_n} + \underset{\text{liquid}}{3n\mathrm{Me_3SiCl}}}_{\substack{\text{gel}\\ \mathbf{5}\qquad\qquad \mathbf{6}}} \qquad [3]$$

Product **5** was obtained as a colorless, jellylike gel. The time until gelation could be adjusted by changing the temperature and the amount of pyridine added to the reaction mixture. Accordingly, the reaction time decreased with increasing pyridine content.[6] However, gelation did occur in the absence of pyridine. At room temperature the reaction mixture gelled after five days with a pyridine content of 1 equiv relative to the chlorosilane (**3**). If 0.1 equiv was used instead, the gelation time increased to 30 days. Under reflux conditions, gelation occurred in 30 min ([pyridine] = 1 equiv) or 14 h ([pyridine] = 0.1 equiv). Furthermore, the stirring rate also influenced the onset of gelation. Strong agitation significantly delayed the gelation time.

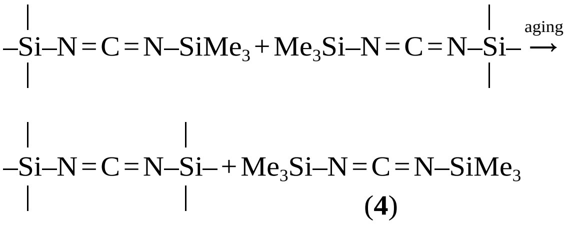
The reaction sequence is closely related to that of chlorosilanes, R_xSiCl_{4-x} (R = H, alkyl or aryl; $x = 0$, 1 or 2), with water-forming silica gels, silicones or organically modified silicon oxides denoted as ORMOSILs.[11] In the novel sol–gel processes described here, bis(trimethylsilyl)carbodi-imide (**4**) adopts the role of H_2O applied in the conventional oxidic sol–gel route as indicated in Fig. 1. The first reaction step involves the substitution of the silicon-bonded chlorine atoms by hydroxy groups in the oxidic sol–gel path while chlorine is replaced by the silylcarbodi-imide unit in the non-oxidic counterpart. Subsequent polycondensation results in the formation of polymeric gels. Finally, calcination and/or pyrolysis of the gels up to 1000–1200 °C in argon or nitrogen yields silicon oxycarbide ($Si_xO_yC_z$) glasses[12, 13] and silicon carbonitride ($Si_xC_yN_z$) ceramics, respectively.

Characterization of the gel

Figure 2(a) shows the as-prepared highly transparent poly(methylsilsesquicarbodi-imide) gel. After an aging period of five days at 45 °C, the gel becomes cloudy (Fig. 2b) without change in gel volume. Further annealing at 45 °C induces irreversible shrinkage (Fig. 2c). Careful evaporation of the liquid fraction, mainly Me_3SiCl, provides the transparent xerogel (**5**) (Fig. 2d). The corresponding length and volume shrinkage values of the $[MeSi(NCN)_{1.5}]_n$ gel are summarized in Table 1.

The rate of gel shrinkage is mainly determined by two parameters. Increased pyridine content (0.0–1.5 equiv) and prolonged annealing temperature (20–45 °C) accelerate aging and consequently enhance the degree of crosslinking of the gel network. During tempering at 45 °C, the gel remains completely amorphous to x-rays.

Infrared spectroscopic investigations also revealed that polycondensation continues after gelation according to Eqn [4]:



$$-\overset{|}{\underset{|}{Si}}-N{=}C{=}N-SiMe_3 + Me_3Si-N{=}C{=}N-\overset{|}{\underset{|}{Si}}- \xrightarrow{\text{aging}}$$

$$-\overset{|}{\underset{|}{Si}}-N{=}C{=}N-\overset{|}{\underset{|}{Si}}- + \underset{(\mathbf{4})}{Me_3Si-N{=}C{=}N-SiMe_3}$$

[4]

In the FT-IR spectra of the as-synthesized and dried-gel absorption bands at $\nu = 2850$–$2930\ cm^{-1}$ can be assigned to C–H bonds of $Si(CH_3)_3$ end groups ($\nu_s(CH_3) = 2922\ cm^{-1}$ and $\nu_{as}(CH_3) = 2852\ cm^{-1}$). In contrast, after aging for 30 days the relative intensity of the characteristic C–H vibration bands of $Si(CH_3)_3$ cannot be detected, while the rest of the spectrum corresponds to that of the starting material (Fig. 3).

The presence of the carbodi-imide group in the aged gel (**5**) is supported by FT-IR [$\nu_{as}(N{=}C{=}N) = 2152\ cm^{-1}$] and Raman [$\nu_s(N{=}C{=}N) = 1533\ cm^{-1}$] spectroscopy. In contrast to IR spectroscopy, the symmetrical vibration band ν_s of the carbodi-imide group is not forbidden in Raman spectroscopy. The absorption bands of the Me groups are located at $2974\ cm^{-1}$ and $2906\ cm^{-1}$, respectively, in the Raman spectrum shown in Fig. 4. Furthermore, the deformation vibrations of $Si–CH_3$ bonds at $\nu = 1270\ cm^{-1}$ can also be analyzed in the FT-IR spectrum in both samples (Fig. 3).

The ^{29}Si solid-state NMR measurement shown in Fig. 5 revealed a single peak at $\delta = -62.3$ ppm. The chemical shift corresponds to that found in poly(organosilsesquioxanes) and

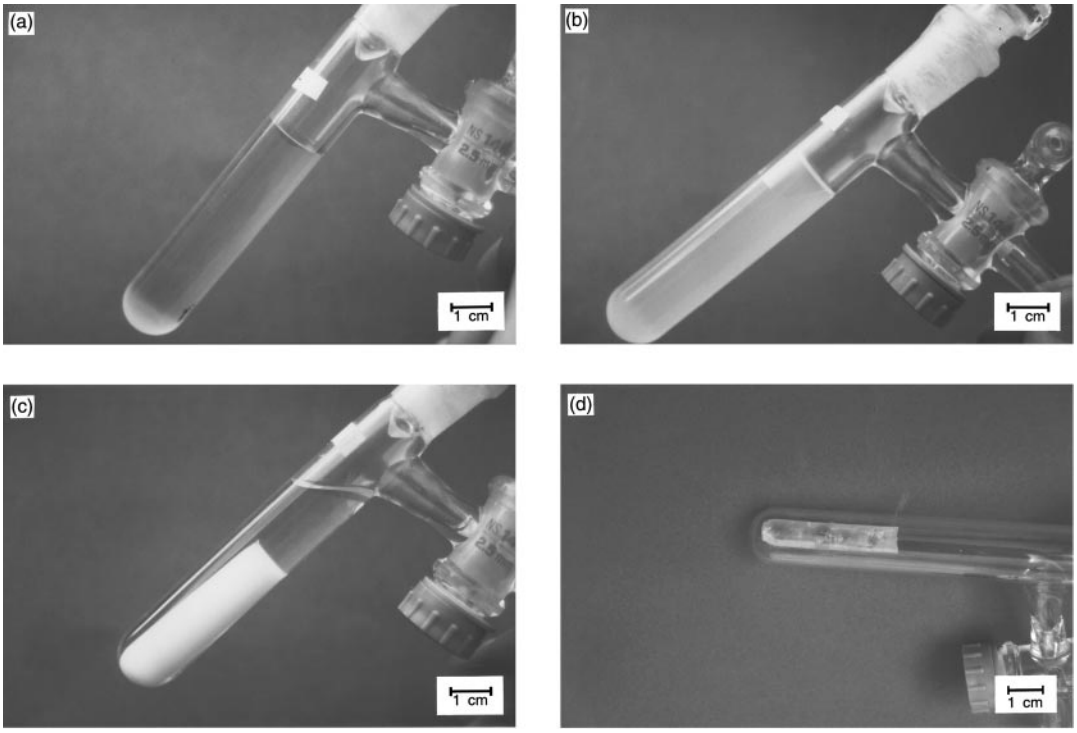


Figure 2 Different stages of the $[MeSi(NCN)_{1.5}]_n$ gel after synthesis (a) and aging at 45 °C for 5 days (b) and 50 days (c). Evaporation of the liquid phases gives the transparent xerogel **5** (d).

Table 1 Relative shrinkages in length and volume ($\Delta L/L$ and $\Delta V/V$) during aging and drying of the $[MeSi(NCN)_{1.5}]_n$ gel **5**

Dimensions	Gel as prepared (Fig. 2a)	Aged gel[a] (Fig. 2c)	Xerogel **5**[b] (Fig. 2d)
$\Delta L/L$ (%)	0	37	44
$\Delta V/V$ (%)	0	75	82

[a] Aging conditions: 30 days at 45 °C, pyridine content 0.6 equiv.

[b] Drying conditions: evaporation of the liquid phase at 50 °C during 24 h.

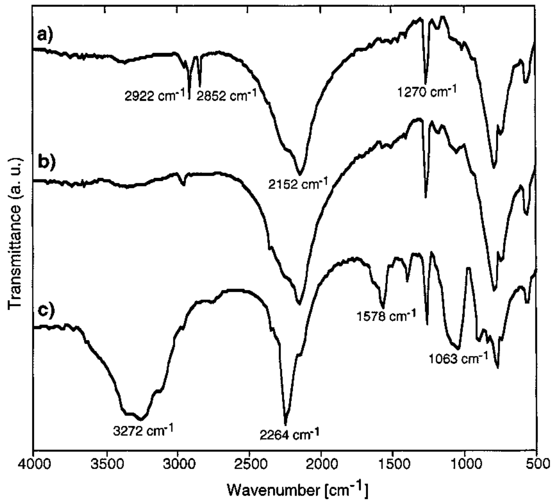


Figure 3 FT-IR spectra of $[MeSi(NCN)_{1.5}]_n$ gel (a) as-synthesized, (b) aged and (c) hydrolyzed in air.

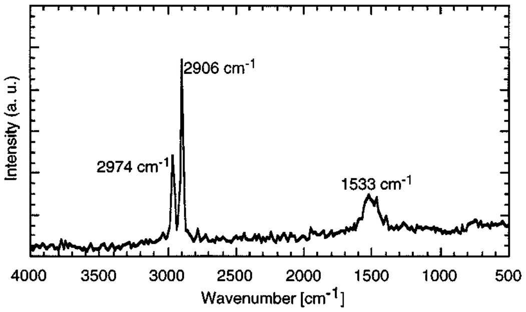


Figure 4 Raman spectrum of aged $[MeSi(NCN)_{1.5}]_n$.

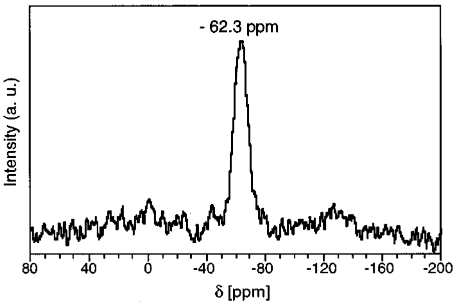
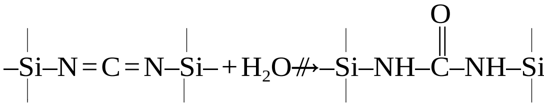


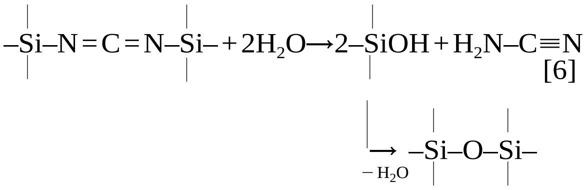
Figure 5 Solid-state ^{29}Si NMR (CP MAS) spectrum of $[MeSi(NCN)_{1.5}]_n$.

can be clearly assigned to $[MeSi(NCN)_{1.5}]_n$. This analogy is explained by the pseudochalcogenic character of the carbodi-imide group.[14] The absence of NMR signals at about 0 ppm is a further indication that no $SiMe_3$ end groups remain in the aged gel (**5**). These findings agree very well with the polysilylcarbodi-imides synthesized via the reaction of bis(trimethylsilyl)carbodi-imide (**4**) with dimethyldichlorosilanes[3,4] and tetrachlorosilane.[5]

The poly(methylsilsesquicarbodi-imide) xerogel (**5**) is very sensitive to moisture. According to Pump and Wannagat, hydrolysis of silylcarbodi-imides proceeds by attack of H_2O at the silicon atom, forming silanol groups and cyanamide.[15] Subsequent condensation of the silanol species gives Si–O–Si bonds. This behavior is in contrast to that of organic di-imides which react with H_2O to give urea derivatives (Eqns [5] and [6]).



$$-\underset{|}{\overset{|}{Si}}-N=C=N-\underset{|}{\overset{|}{Si}}- + H_2O \not\rightarrow -\underset{|}{\overset{|}{Si}}-NH-\overset{\overset{O}{\|}}{C}-NH-\underset{|}{\overset{|}{Si}}- \qquad [5]$$



$$-\underset{|}{\overset{|}{Si}}-N=C=N-\underset{|}{\overset{|}{Si}}- + 2H_2O \rightarrow 2-\underset{|}{\overset{|}{Si}}OH + H_2N-C\equiv N \qquad [6]$$

$$\xrightarrow[-H_2O]{} -\underset{|}{\overset{|}{Si}}-O-\underset{|}{\overset{|}{Si}}-$$

The infrared spectrum of the hydrolyzed polymer **5** is shown in Fig. 3. Vibration bands located at 1063 cm^{-1} (Si–O stretching vibration) and at 1578 cm^{-1} [ν(C–N)] unambiguously illustrate the postulated hydrolysis mechanism. In addition, the shift of the asymmetric carbodi-imide vibration band [ν_{as}(N=C=N)] from 2152 cm^{-1} to the typical cyanamide absorption frequency [ν(N–CN)] at 2264 cm^{-1} and the broad signals of the SiO–H and N–H stretching

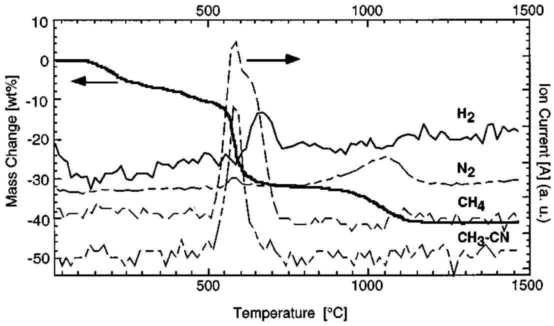


Figure 6 Thermal gravimetric analysis (TGA) of **5** in flowing helium at a heating rate of 2 °C min^{-1}. The gas species H_2, N_2, CH_4 and MeCN with $m/z=2$, 28, 16 and 41, respectively, evolved during the thermally induced ceramization were detected by a coupled mass spectrometer.

vibrations at 3272 cm^{-1} also support the above reaction path.

Thermally induced ceramization

The quantitative analysis of the thermally induced ceramization of $[MeSi(NCN)_{1.5}]_n$ up to 1450 °C gives a total ceramic yield of 60 wt% (Fig. 6). A weight loss of 10% is observed in the 20–550 °C range and is attributed to evaporation of residual Me_3SiCl (**6**) and **4**. At about 570 °C, a 20% decrease in mass takes place. According to mass-spectrometry analyses, the first ceramization step is due to the evolution of MeCN or MeNC ($m/z=41$) and CH_4 ($m/z=16$). Hydrogen is also detected (Fig. 6). In a second step, nitrogen is produced between 850 and 1100 °C and the corresponding weight loss amounts to about 10%. At higher temperatures, no mass change is analyzed up to 1450 °C. In addition, the evolved organic species were identified by their characteristic fragmentation patterns (not shown in Fig. 6).

To obtain more detailed information about the thermally induced ceramization, FT-IR spectra of xerogels (**5**) annealed at different temperatures were recorded (Fig. 7). Up to 400 °C, no significant change in the infrared absorptions is found, while a new vibration band at 1564 cm^{-1} is assigned to C–N single bonds formed after the first ceramization step is complete at $T>600$ °C (Fig. 7). Simultaneously, the intensity of the Si–CH_3 vibration (1270 cm^{-1}) decreases. This finding coincides with the loss of CH_4 and MeCN at this temperature analyzed by TGA. The relative intensity of the asymmetric carbodiimide vibration at 2152 cm^{-1} remains nearly unchanged after annealing of the gel **5** at $T=800$ °C. The Si–CH_3 vibration bands at 1270 cm^{-1} are no longer detected in samples heat-treated at 800 °C. After heating the $[MeSi(NCN)_{1.5}]_n$ gel between 800 and 1200 °C, the relative intensity of the carbodi-imide and the ν(C–N) vibrations decrease with evolution of nitrogen. However, the (N=C=N) absorption band is still found in samples annealed at 1200 °C.

The temperature-dependent *in-situ* X-ray powder diffraction measurements of the $[MeSi(NCN)_{1.5}]_n$ gel between room temperature and 850 °C give no indication of the formation of crystalline phases; the material remains completely amorphous.

Pyrolysis mechanism

The ceramization of the xerogel **5** occurs in two temperature ranges. Taking into account the thermal analysis and the infrared spectroscopic results, the following pyrolysis mechanism can be discussed:

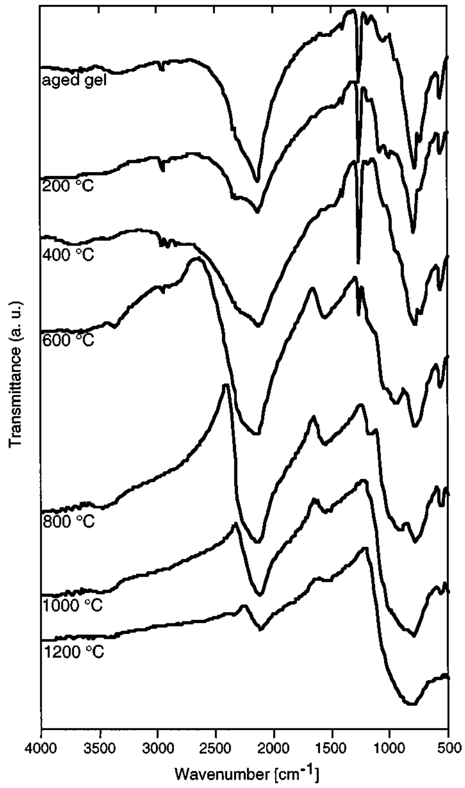


Figure 7 FT-IR spectra of $[MeSi(NCN)_{1.5}]_n$ gel after annealing at different temperatures under argon and cooling to room temperature. The holding time at the final temperature was 1 h.

(1) Between 550 and 600 °C, the cleavage of the Si–CH_3 bonds is responsible for the evolution of CH_4. In addition, some of the methyl groups originally bonded to silicon migrate to carbon or nitrogen of the polysilylcarbodi-imide backbone and CH_3CN or CH_3NC evolves, respectively. Due to this reaction sequence, the Si–N–C–N units are cracked. The appearance of C–N single bonds at $T > 600$ °C (Fig. 7) indicates a severe rearrangement of the $[MeSi(NCN)_{1.5}]_n$ structure during pyrolysis. Since the methyl/carbodi-imide ratio is 1:1.5, some of the carbodi-imide groups remain unchanged in the polymer after the first ceramization step. The characteristic strong $\nu_{as}(N=C=N)$ vibration frequency at 2152 cm^{-1} is clearly present in samples heated to $T > 600$ °C.

(2) In the second ceramization step between 850 and 1100 °C, nitrogen is formed, exclusively, indicating decomposition of the carbodi-imide units. However, according to elemental bulk analysis, most of the nitrogen remains in the ceramic. The nitrogen content decreases from 44.8 wt% in **5** heat-treated at 700 °C to 34.4 wt% after annealing the gel at 1200 °C and coincides with the measured 10% weight loss between 800 and 1200 °C (Fig. 6).

Materials microstructure

The release of equimolar amounts of Me_3SiCl, during the gelation of the initial sol and formation of the Si–C–N materials, is analogous to release of alcohol during classic sol–gel processes, which leads to the formation of silica or other metal oxides (Eqn [7]):[7]

$$(RO)_4Si + 2H_2O \rightarrow SiO_2 + 4ROH \qquad [7]$$

These metal oxides, which form by hydrolysis and polycondensation, are highly porous. The pores formed as a result of transport of the alcohols released. If the classic sol–gel process is carried out properly, microporous metal oxides with a narrow pore size distribution can be obtained.[16] It was therefore expected that our novel Si–C–N materials would be highly porous, even microporous. Changes in the porosity were expected in materials treated at 700 °C due to the additional release of CH_4, and further changes were expected in the material treated at 1200 °C due to the observed release of nitrogen.

Argon adsorption experiments were performed on these materials to investigate the surface area and the pore structure. The gels dried and pyrolyzed at 140, 700 and 1200 °C have only type III adsorption isotherms, corresponding to external adsorption. According to the BET model, specific surface areas < 1 m^2 g^{-1} were found for the samples treated at 400 and 700 °C, while the $[MeSi(NCN)_{1.5}]_n$ polymer pyrolyzed at 1200 °C exhibits a low surface area of 16 m^2 g^{-1}.

To exclude preparation errors or hydrolysis effects, the adsorption experiments were repeated with exclusion of air in all preparation and adsorption steps; they reproduced the initial results. This indicates that the materials formed are essentially nonporous. From classic sol–gel processes it is well known that basic reaction conditions, as used in the preparation of the Si–C–N materials, lead to particle growth during the polycondensation, while acidic conditions result in linear polymerization. It was shown in rheological studies of classical sol–gel processes that an acidic pH gives preferentially linear polymers forming three-dimensional networks and continuous glasses as the final material, whereas basic sol–gel conditions show particle growth which results in a powder of low porosity and particle sizes below 10 nm.[17] From the low porosity and the basic preparation conditions it was expected that the gel-derived silicon carbonitride product may also show a particle morphology. The Si–C–N gel (**5**) pretreated at 700 and 1200 °C, respectively, was therefore studied by high-resolution transmission electron microscopy (HR TEM). Figure 8 shows a representative micrograph of the materials. The Si–C–N ceramics obtained proved to be completely amorphous, even at atomic resolution. They appear to be continuous glasses with no indication of domains. The elemental distributions of selected areas obtained by energy dispersive x-ray analysis (EDX) analysis confirm its homogeneous nature. Clearly, there is little analogy between the classic sol–gel process and the formation of the organosilicon gel-derived Si–C–N materials.

CONCLUSIONS AND OUTLOOK

The organosilicon polymer $[MeSi(NCN)_{1.5}]_n$ is synthesized by the reaction of $MeSiCl_3$ with $Me_3Si–N=C=N–SiMe_3$ and is characterized by various spectroscopic methods. The thermally induced ceramization of **5** involves the loss of CH_4 as well as migration of methyl groups to

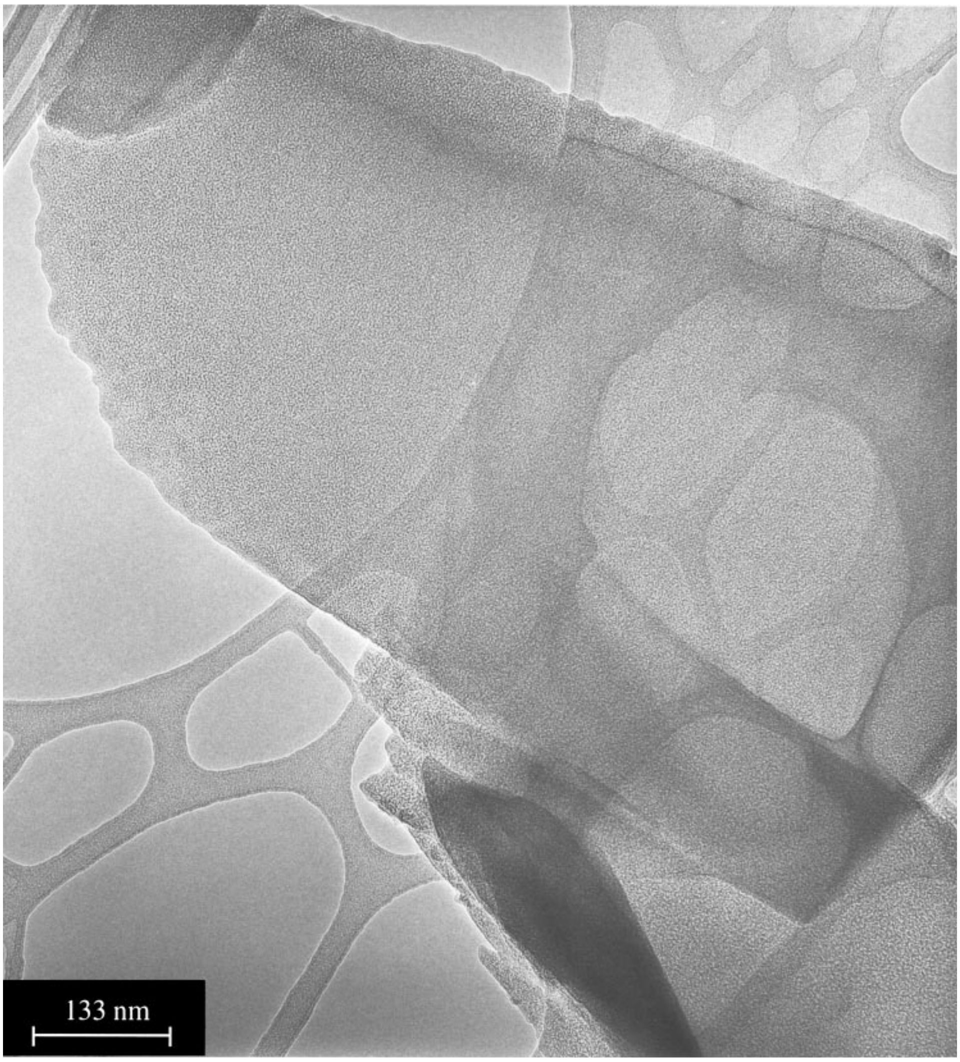


Figure 8 HR TEM of the $[\mathrm{MeSi(NCN)_{1.5}}]_n$ xerogel (**5**) heat-treated at 1200 °C under argon.

carbon or nitrogen, forming MeCN or MeNC in the course of the successive thermal degradation of the polymer at $T > 400$ °C.

The pyridine-catalyzed reaction to poly(methylsilsesquicarbodi-imide) can be controlled to follow a completely non-aqueous sol–gel process. The resulting Si–C–N gel (**5** + **6**) is transformed at $T = 1200$ °C to amorphous silicon carbonitride with the composition $\mathrm{SiC_{1.1}N_{1.6}}$ by the polymer-to-ceramic transformation. The novel non-oxide sol–gel chemistry opens a new path to a broad range of technological applications such as ceramic Si–C–N coatings, membranes, fibers, bulk materials or spherical Si–C–N powders.

Acknowledgements The authors gratefully appreciate the financial support the Deutsche Forschungsgemeinschaft, Bonn, Germany, and by the Fonds der Chemischen Industrie, Frankfurt, Germany. We also thank S. Reichert for the STA (Simultaneous Thermal Analysis–Mass Spectrometry) investigations, Dr N. Egger, Hoechst AG, Frankfurt, Germany, for the solid-state NMR measurements and M. Dinges, TH Darmstadt, for the x-ray diffraction investigations.

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