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Preparation of Si/C/Al/N Ceramics by Pyrolysis of Polyaluminasilazanes

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Polyaluminasilazanes were prepared quantitatively by reaction of oligosilazanes (RSi(H)NH)$_n$ (R = Me, Et) with various amounts of either trimethylaluminum, $(CH_3)_3Al$, or dimethylaluminum amide, $(CH_3)_2AlNH_2$. The products were characterized by ^1H, ^{29}Si and ^{27}Al NMR and IR spectroscopy. Alkylation of the Si—H groups was observed when trimethylaluminum was used. Their pyrolysis was carried out under argon or ammonia. Ceramic residues were obtained in high yield and were characterized by elemental analysis and X-ray powder diffraction. Formation of mixed ceramics containing silicon nitride, silicon carbide and/or aluminum nitride was observed depending on the precursor and the experimental procedure that was used. The thermal decomposition of the polyaluminasilazane between 50 and 700 °C was investigated by IR analysis of the gas evolved during the pyrolysis. Molecular aluminasilazanes were studied as model compounds. Copyright © 1999 John Wiley & Sons, Ltd.

Keywords: polyaluminasilazanes; pyrolysis; ceramic meterial

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INTRODUCTION

Aluminum nitride is an attractive ceramic with useful properties such as thermal and chemical stability and high thermal conductivity, and its thermal expansion matches closely that of silicon.[1] Recent interests focus on the alloying of AlN with other covalent refractory materials such as Si_3N_4 or SiC. For example, densification of silicon nitride is promoted by addition of aluminum nitride,[2] and films of AlN/Si_3N_4 have been produced and were found to be superior to AlN, BN, Si_3N_4 or TiN as protective coating.[3] It was also shown that AlN is a good candidate for solid-solution formation with SiC.[4] Sputtering, hot-pressing and sintering methods were used to prepare and characterize both mixtures and solid solutions of these ceramics. However, the preparation of ceramic fibers or films is possible only through the pyrolytic transformation of suitable organometallic precursor fibers or films.

Paciorek *et al.* prepared $\{[(Me_3Si)_2N]_2AlNH_2\}_2$ and $\{[(Me_3Si)_2N]_2Al(NH_2)_2\}_3$.[5] Pyrolysis of the dimer yielded $\{Me_3Si)_2NAlNH\}_4$ at 225 °C, and further heating to 900 °C resulted in an AlN-based ceramic together with differing amounts of SiC, Si_3N_4 and/or carbon, depending on the gas used during the pyrolysis. In both cases the ceramic yields were poor. Paine and co-workers investigated the preparation of AlN/SiC ceramics below 900 °C by pyrolysis of the adduct formed between $(Me_3Si)_3Al$ and ammonia.[6] The final product was described as a solid solution of AlN and SiC, since SiC and AlN are known to have the same wurtzite crystal structure with nearly identical lattice constants. Interrante *et al.* prepared aluminum nitride/silicon carbide ceramics using a precursor mixture of polycarbosilanes and $(Et_2AlNH_2)_3$.[7] Slow pyrolysis yielded a mixture of SiC and AlN, while an SiC/AlN solid/solution was obtained by fast-pyrolysis, 'hot-drop' process.

Processing of oligomeric polysilazanes has been widely used for the preparation of ceramic precursors. In our laboratories the volatile oligosilazane obtained by ammonolysis of CH_3SiHCl_2 was converted into a useful ceramic precursor of higher molecular weight by treatment with KH,[8] $H_3B{\cdot}S(CH_3)_2$[9] or urea.[10] Recently, we reported briefly the preparation of a polyaluminasilazane by reaction of such oligomeric silazanes, $(CH_3SiHNH)_n$, with $Al(CH_3)_3$ or AlH_3,[11] and similar work was patented by Bolt.[12]

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We report here our further work on polyaluminasilazanes and present details of our studies directed toward an understanding of the mechanism of formation of the polyaluminasilazanes and their constitution. Also, we describe their thermal behavior and our investigation to delineate the mechanism of their pyrolysis. The preparation and characterization of some ceramic materials are described.

EXPERIMENTAL

Commercially pure trimethylaluminum, $(CH_3)_3Al$, and triethylaluminum, $(CH_3CH_2)_3Al$ (Ventron), and 2 M $(CH_3)_3Al$ solutions in toluene (Aldrich), were used as received. Dimethylaluminum amide, $(CH_3)_2AlNH_2$, was prepared according to previous literature,[13] for simplicity's sake we write it as $(CH_3)_2AlNH_2$, although it is a nitrogen-bridged trimer by reference to the known Et_2AlNH_2 trimer.[14,15] The oligomethylhydridosilazane $(CH_3Si(H)NH)_n$ was prepared as described in the literature;[16] oligoethylhydridosilazane, $(EtSi(H)NH)_n$ and oligodimethylsilazane, $(Me_2SiNH)_n$, were prepared by the same procedure using the corresponding ethyldichlorosilane, $Et(H)SiCl_2$ and dimethyldichlorosilane, Me_2SiCl_2, respectively. All solvents were purified and dried by standard methods.[17] Ammonia was dried by passing it through a column filled with pellets of anhydrous KOH. Due to the pyrophoric nature of aluminum alkyls and the sensitivity of the oligosilazanes to hydrolysis, all manipulations were carried out with exclusion of air. Elemental analyses were performed by Galbraith Laboratories Inc. (sensitivity ± 1%). ^1H, ^{29}Si and ^{27}Al NMR spectra were obtained on a Varian 300XL or a Varian Gemini 300 NMR spectrometer. $(Al(H_2O)_6)^{3+}$ was used as external reference for the ^{27}Al NMR spectra and Me_4Si as external reference for ^{29}Si NMR spectra. Fourier transform IR (FTIR) spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrometer, those of solids on KBr pellets of the sample. Qualitative analyses of the pyrolysis gases were performed using a gas IR cell with AgCl windows. Identification of the gases was effected with reference to standard compounds analyzed under the same conditions or by reference to the literature. 18 x-ray diffraction (XRD) spectra were taken using a Rigaku (RU 300, with CuK_α radiation. Yields of preparations, NMR data and elemental analyses of the polyaluminasilazanes are summarized in Tables 1–6. The pyrolyses were carried out under the specified gas in a Lindberg Model 59545 single-zone tube furnace equipped with a mullite tube, a Eurotherm Model ES controller and a graphite or boron nitride sample boat.

Table 1. Quantities of reagents used for the preparation of the polyaluminasilazanes 1–4

	$(CH_3Si(H)NH)_n$		2 M solution of $(CH_3)_3Al$		Polyaluminasilazane	
	(g)	(mmol)	(ml)	(mmol)	Mass (g)	Yield[a] (%)
1	1.6	27.1	2.3	4.5	1.8	98
2	1.5	26.4	4.3	8.6	1.9	94
3	1.5	26.5	6.6	13.2	2.2	95
4	1.6	27.9	13.9	27.9	3.0	94

[a] Yields are based on Eqn [1].

Table 2. Quantities of reagents used for the preparation of the polyaluminasilazanes 7–10

	$(CH_3Si(H)NH)_n$		$(CH_3)_2Al(NH_2)$		polyaluminasilazane	
	(g)	(mmol)	(g)	(mmol)	Mass (g)	Yield[a] (%)
7	1.8	30.4	2.22	30.0	3.7	99
8	2.8	48.9	1.85	25.0	4.4	101
9	3.6	60.9	1.48	20.2	4.6	99
10	3.5	60.5	0.74	10.1	4.1	92

[a] Yields are based on Eqn [5].

Table 3. ^{1}H NMR data for 1–4 (C_6D_6 solution) (δ, ppm)

	1	**2**	**3**	**4**
Si—H	4.5 to 5.4; 1 H	4.5 to 5.5; 1 H	4.5 to 5.5; 1 H	4.5 to 5.5; 1 H
N—H	0.7 to 0.9; 0.35 H			
		0 to 0.8; 4.2 H	0 to 0.8; 4.2 H	0 to 0.7; 5.2 H
Si—CH_3	0 to 0.7; 3.1 H			
Al—CH_3	−0.7 to 0; 0.6 H	−0.6 to 0; 2 H	−0.7 to 0; 4.2 H	−0.8 to 0; 5.6 H

Table 4. ^{1}H NMR data for 7–10 (C_6D_6 solution) (δ, ppm)

	7	**8**	**9**	**10**
Si—H	4.1 to 5.4; 1 H	4.4 to 5.5; 1 H	4.5 to 5.5; 1 H	4.5.to 5.5; 1 H
N—H + Si—CH_3	−0.1 to 0.9; 5.2 H	−0.2 to 1.5; 5.0 H	−0.2 to 1.4; 4.9 H	−0.3 to 1.4; 4.3 H
Al—CH_3	−1.0 to −0.1; 0.7 H	−1.1 to −0.2; 1.1 H	−1.1 to −0.2; 1.6 H	−1.3 to −0.3; 3.5 H

Table 5. Elemental analyses (%) of 1–4 and 7–10

Compd	C	H	N	Si	Al
1	22.8	7.18	20.76	38.86	7.17
2	27.01	7.56	17.86	31.57	11.67
3	30.67	8.00	13.47	21.14	20.77
4	33.09	8.58	11.35	18.76	22.80
7	20.64	7.52	25.14	33.06	13.94
8	20.54	7.39	24.94	32.53	12.48
9	19.15	7.33	24.15	30.96	15.67
10	21.36	7.92	22.69	20.51	21.44

Table 6. ^{27}Al NMR data for 1–4 and 7–10 (C_6D_6 solution)

	1	**2**	**3**	**4**	**7**	**8**	**9**	**10**
δ (ppm)	63	61	66	63	63	61	66	63
δ ($h_{1/2}$) (Hz)[a]	4100	3800	4500	6600	4100	3800	4500	6600

[a] Signal width at half height.

Preparation of polyaluminasilazanes 1–4

Compounds **1–4** were prepared using the experimental procedure described below for **1**. A 200-ml Schlenk flask, equipped with a rubber septum, a magnetic stir-bar and a gas inlet/outlet tube connected to the Schlenk line, was charged by syringe with 1.6 g (27.1 mmol) of $[CH_3Si(H)NH]_n$ oligomer mixture dissolved in 50 ml of toluene. The resulting solution was stirred at room temperature while 2.3 ml of a 2 M solution of trimethylaluminum in toluene (0.33 g, 4.5 mmol of $(CH_3)_3Al$; hence the Si/Al ratio was 3:1) was added during 30 min via syringe. After the first drops had been added, gas evolution commenced. A slightly exothermic reaction occurred during the addition, raising the temperature to 30–35 °C. After the addition was complete the reaction mixture was stirred for 18 h at room temperature. The solvent was then removed at reduced pressure (0.1–1 mmHg) during 12 h at 40–45 °C, leaving 1.8 g of **1** as a white solid.

Preparation of polyaluminasilazanes 5 and 6

Compounds **5** and **6** were prepared using the experimental procedure described for **1**.

Using 2.0 g (34.0 mmol) of $(CH_3Si(H)NH)_n$ oligomer mixture dissolved in 50 ml of toluene and 0.50 ml (0.38 g, 5.3 mmol) of neat triethylaluminum, 2.03 g of **5** was recovered as a viscous oil. 1H NMR (C_6D_6): δ(ppm) = 4.4 to 5.5 (broad multiplet, 1 H, SiH), 1.3 (broad multiplet, 0.9 H, $C\underline{H}_3CH_2Al$), 0.4 (broad multiplet, 5.5 H, $SiC\underline{H}_3 + AlC\underline{H}_2CH_3 + NH$).

Using 3.0 g (41.0 mmol) of $[EtSi(H)NH]_n$ oligomer mixture in 50 ml of toluene and 3.4 ml of a 2 M solution (0.48 g, 6.8 mmol) of trimethlyaluminum in toluene 3.5 g of 6 was isolated as a waxy solid. 1H NMR (C_6D_6): δ(ppm) = 4.5 (broad multiplet, 1 H, SiH), 0.9–0.5 (broad multiplet, 6.5 H, $NH + SiC\underline{H}_2C\underline{H}_3$), 0.5 to −0.4 (broad multiplet, 1 H, $AlC\underline{H}_3 + SiC\underline{H}_3$).

Infrared study of the decomposition of 1,4,5 and 6

The corresponding compound (2–2.5 g in an Al_2O_3 boat) was introduced in a furnace tube connected to a Schlenk line and purged with a continuous flow of nitrogen (50 ml min^{-1}). The product was progressively heated (2 °C min^{-1}) and an aliquot of the gas phase was taken every 5 minutes and analyzed with the gas IR cell. The following gases were identified by reference to analyzed pure compounds: CH_4, CH_2CH_2, $MeSiH_3$ and CH_3CH_3.[18,19]

Preparation of compounds 7–10

Compounds **7–10** were prepared using the experimental procedure described below for 7. A 200-ml Schlenk flask, equipped with a rubber septum, a magnetic stir-bar and a gas inlet/outlet tube connected to a Schlenk line, was charged under argon with 1.80 g (30.4 mmol) of $[CH_3Si(H)NH]_n$ oligomer mixture dissolved in 40 ml of toluene. The resulting solution was stirred at room temperature while 2.22 g (30.0 mmol) of dimethylaluminum amide, $(CH_3)_2AlNH_2$, dissolved in 50 ml of toluene was added under argon via syringe. No reaction was observed at room temperature. The flask was then placed in an oil bath at 85–90 °C. Gas evolution started rapidly. The reaction mixture was kept for 5 h at this temperature and was subsequently stirred for 18 h at room temperature. The solvent was removed at reduced pressure (0.1–1 mmHg) for 12 h at 40–45 °C, leaving 3.72 g of **7** as a white solid.

Preparation and thermal treatment of polyaluminasilazane 11

The reaction was carried out using the experimental procedure described for **1** with 6.5 ml (37.0 mmol) of 1,1,3,3-tetramethyldisilazane, $(Me_2HSi)_2NH$, dissolved in 50 ml of toluene and 3.5 ml (2.63 g, 37.0 mmol) of pure trimethylaluminum. After removal of the solvent, 6.7 g of **11** was isolated as a white solid. ^1H NMR (C_6D_6): δ(ppm) = 5.0 (broad multiplet, 1 H, SiH), 0.20 (broad multiplet, 6.8 H, $SiCH_3$), −0.12 (broad multiplet, 3.5 H, $AlCH_3$). Thermolysis of this product was effected at atmospheric pressure in a Schlenk tube connected to a vacuum line via two traps kept at 0 °C and −80 °C, respectively. Compound **11** (6.50 g) was placed in the Schlenk tube and heated to 170–190 °C with an oil bath. After 1.5 h, the thermal treatment was stopped, leaving 4.5 g of a clear solid (m.p. 140–150 °C). ^1H NMR (C_6D_6): δ(ppm) = 4.6–4.8 (broad multiplet, 1 H, SiH), 0.25 (broad multiplet, 57 H, $SiCH_3$), −0.25 (broad multiplet, 21 H, $AlCH_3$). No liquid was trapped at 0 °C and 1.8 g of a volatile compound (b.p. −20 to −22 °C) was condensed at −80 °C) A solution of this compound at 0 °C was examined by ^1H NMR ($CDCl_3$): δ(ppm) = 3.3 (1 H, SiH), 0.2 (3.2 H, $SiCH_3$)[20] and the IR spectrum of the gas indicated the presence of dimethylsilane.[18]

Preparation and thermal treatment of polyaluminasilazane 12

The reaction was carried out using the experimental procedure described for **1** with 6.5 ml (37.0 mmol) of 1,1,3,3-tetramethyldisilazane, $(Me_2HSi)_2NH$, dissolved in 50 ml of toluene with 5.0 ml (4.2 g, 37.0 mmol) of neat triethylaluminum. After removal of the solvent, 8.3 g of **12** was recovered as a white solid. ^1H NMR (C_6D_6): δ(ppm) = 4.8 (broad multiplet, 1 H, SiH), 1.05 (triplet, 2.2 H, $AlCH_2C\underline{H}_3$), 0.26–0.0 (broad multiplet, 8 H, $AlC\underline{H}_2CH_3 + SiCH_3$). Thermolysis of 2.9 g of **12** was performed using the procedure described for thermolysis of **11**. After 2 h at 150 °C, 2.2 g of a white, pasty solid remained. ^1H NMR (C_6D_6): δ(ppm) = 4.5–5.0 (broad multiplet, 1 H, SiH), 1.3 (broad multiplet, 10.3 H, $AlCH_2C\underline{H}_3$), 0.95–0.0 (broad multiplet, 50 H, $AlC\underline{H}_2CH_3 + SiCH_3$). In the trap kept at −80 °C, 0.75 g of a volatile compound (b.p. −20 to −22 °C) was condensed whose identity as Me_2SiH_2 was confirmed by its ^1H NMR and by comparison with the IR spectra of pure Me_2SiH_2.

Treatment of polyaluminasilazane 4 with NH_3

A 100-ml Schlenk tube equipped with a rubber septum was charged with 3.0 g of **4** and a stream of NH_3 was introduced through an 18-gauge steel needle. After a few seconds, the foamy solid polymer liquefied and the temperature of the reaction mixture increased to 40–50 °C. After 2 h, the stream of ammonia was stopped, leaving 2.9 g of a sticky, slightly yellow polymer. ^1H NMR (C_6D_6): δ(ppm) = 4.4–5.1 (broad multiplet, 1 H, SiH), 0.8 (broad multiplet, 2.5 H, NH), 0.4–0.0 (broad multiplet, 6.5 H, $SiCH_3$), −0.8 (broad multiplet, 7.5 H $AlCH_3$). ^{27}Al NMR (C_6D_6): δ(ppm) = 155 (broad singlet, $\delta(h_{1/2})$ = 1500 Hz). Analysis: C, 28.27; H, 9.26; N, 19.88; Si 16.52; Al 19.24%.

Thermolysis of polyaluminasilazanes 1–4

Thermolysis of 5.0 g of **4** was performed under the conditions described for the thermolysis of **11**. The product was heated rapidly with an oil bath kept at 180 °C. It melted with formation of a foam and then transformed into a viscous oil. The temperature was then increased slowly to 250 °C and kept at this temperature for 0.5 h. After the flask had cooled to room temperature, 3.9 g of a hard, clear solid remained. ^1H NMR (C_6D_6): δ(ppm) = 4.7–5.5 (broad multiplet, 1 H, SiH), 0–0.8 (broad multiplet, 17 H, $SiCH_3$), −0.2 to 0.0 (broad multiplet, 7.6 H, $AlCH_3$).

Pyrolysis

The following temperature program was used.

Pyrolysis A: to 1000 °C, Al_2O_3 boat; NH_3 flow rate of 50 ml min^{-1}; from room temperature to 250 °C at 5 °C $min^{-1} + 1$ h at 250 °C + from 250 °C to 1000 °C at 5 °C $min^{-1} + 2$ h at 1000 °C.

Pyrolysis B: to 1500 °C; after pyrolysis A, BN or C boat; argon flow rate of 100 ml min^{-1}; from room temperature to 1500 °C at 10 °C $min^{-1} + 4$ h at 1500 °C.

Pyrolysis C: to 1000 °C then to 1500 °C; Al_2O_3 and BN boats; argon flow rate of 100 ml min^{-1}; from room temperature to 1000 °C at 5 °C $min^{-1} + 2$ h at 1000 °C, then from room temperature to 1500 °C at 10 °C $min^{-1} + 4$ h at 1500 °C.

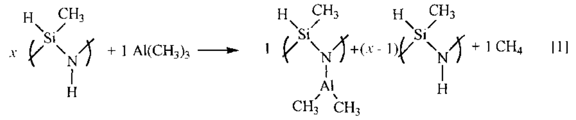
X-ray diffraction data

For ceramics prepared from 1, 4, 7 and 10 the crystalline phases were identified by reference to the JCPS files: AIN (no. 25-1133), β-Si_3N_4 (no. 33-1160), α-Si_3N_4 (no. 41-360).[21] AIN–SiC solid/solution was identified by reference to the previously reported results.[22,23]

RESULTS AND DISCUSSION

Synthesis of the polyaluminasilazanes

The oligo-$[CH_3Si(H)NH]_n$ is a mixture of cyclic oligomers (mainly $n = 3, 4, 5$). Our reactions are based on the simple chemistry that takes place when a hexa-alkyldisilazane reacts with trimethylaluminum.[24–27] Both the evolution of methane during the reaction of $[CH_3Si(H)NH]$ with $(CH_3)_3Al$ and the loss of the N—H function as determined by the NMR spectrum of the residual material confirmed that the silazane had reacted with $(CH_3)_3Al$ following Eqn 1.



1 $(x = 6)$

2 $(x = 3)$

3 $(x = 2)$

4 $(x = 1)$

The formation of the polyaluminasilazanes was quantitative, assuming that each $(CH_3)_3Al$ reacts with an N—H function with loss of CH_4. The number of N–Al bonds formed depends on the ratio polysilazane/$(CH_3)_3Al$ used. In the products, unreacted Al—CH_3 and N—H were characterized by ^1H NMR analysis. Using ^{27}Al NMR spectroscopy (Fig. 1), a very broad signal at 64 ppm [$\delta(h_{1/2})$ = 4000 Hz] was observed which we attribute to tetra- or possibly penta-coordinated aluminum. Similar very broad signals were reported for dimeric species such as $(Et_2AlNHtBu)_2$ or $(Me_2AlNHMe)_2$.[28]

The formation of Lewis acid/Lewis base adducts is well known in aluminum–nitrogen chemistry.[14,29,30] In the case of our polyaluminasilazanes,

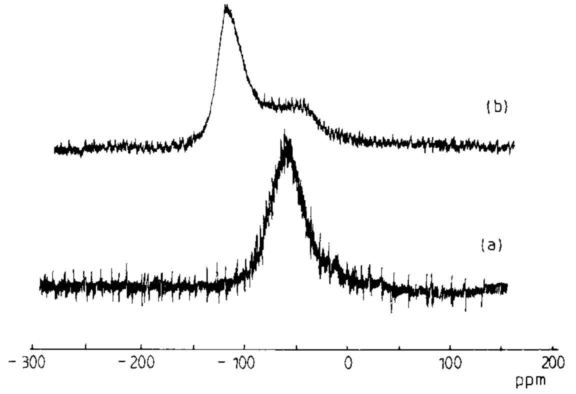


Figure 1 ^{27}Al NMR spectra of polyaluminasilazanes (a) **1** and (b) **10**.

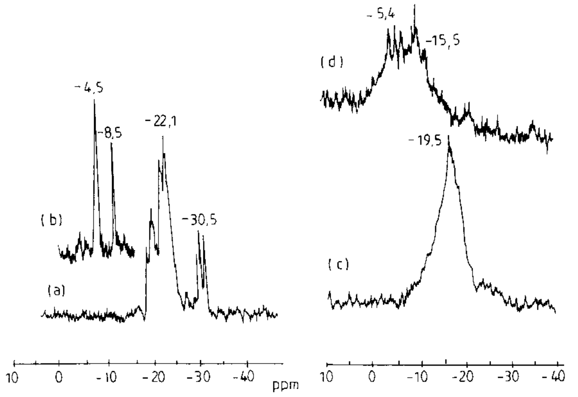
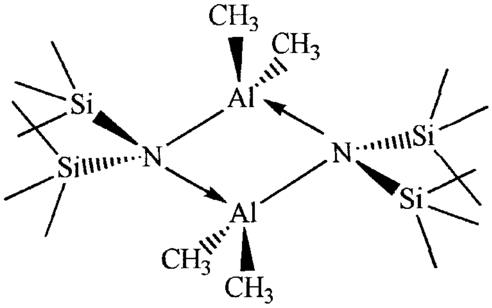


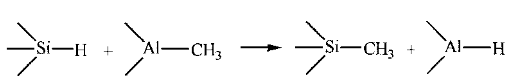
Figure 2 ^{29}Si NMR spectra of: (a) oligodimethylsilazane $[(CH_3)_2SiNH]_n$, (b) oligomethylsilazane $[CH_3Si(H)NH]_n$, (c) **1** and (d) **4**.

intramolecular association can lead to species with Al_2N_2 rings as depicted in Formula **A**.



A

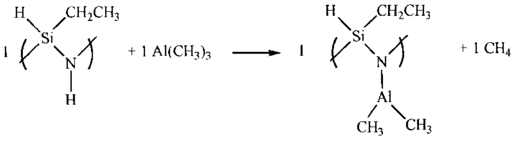
The ^{1}H NMR spectra of the polyaluminasilazanes show that some of the Si–H links of the starting oligosilazane were consumed in the reaction with $(CH_3)_3Al$. Methylation of the Si—H function by reactive metal alkyls is a known reaction Eqn 2.[31,32]



$$\equiv\text{Si—H} + {>}\text{Al—CH}_3 \longrightarrow \equiv\text{Si—CH}_3 + {>}\text{Al—H} \quad [2]$$

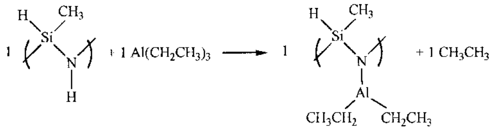
In the present case this results in the formation of Al–H bonds, which were observed by IR analysis of **4** ($\nu_{Al\text{–}H} = 1764\ cm^{-1}$). This side reaction became particularly important when increasing amounts of trimethylaluminum were used. For example, the Si—CH_3/Si—H ratio was 1.2:1 in the starting oligomethylsilazane in **1** but it was 1.7:1 in **4**. More evidence for the occurrence of Si—H methylation was provided by ^{29}Si NMR spectroscopy. A signal corresponding to dimethylsilyl groups, implying the presence of $[Me_2Si—NH]$ units, was observed for **4**, but was not detected in **1** (Fig. 2).

Model compounds **5** and **6** were prepared according to Eqns 3 and 4 in order to study the reactions that occur during the thermal decomposition. The IR and NMR data of these compounds were similar to those reported for **1–4** except for the EtSi and EtAl resonances in the ^{1}H NMR spectra of **5** and **6**.



[3]

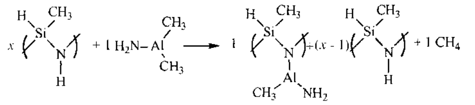
5



[4]

6

A reaction using dimethylaluminum amide, $(CH_3)_2AlNH_2$, was carried out in order to prepare another type of polyaluminasilazane. Following Eqn 5, compounds **7–10** were obtained using different $[CH_3Si(H)NH]_n/(CH_3)_2AlNH_2$ ratios. This organoaluminum reagent was easier to handle than trimethylaluminum and its reactivity toward N—H functions is lower. For example, $(CH_3)_2AlNH_2$ is known to form a polymer $(CH_3AlNH)_n$ but only upon heating to 200 °C.[29] This lower reactivity allows better control of the reaction with $[CH_3Si(H)NH]_n$. When $(CH_3)_2AlNH_2$ was mixed with different amounts of the oligomethylsilazane, no reaction was observed at room temperature. However, gas evolution started when the temperature reached 70–80 °C,



[5]

7 $(x = 6)$

8 $(x = 3)$

9 $(x = 2)$

10 $(x = 1)$

Analysis of the ^1H NMR spectra of **7–10** suggests that formation of Al–N bonds was effected without alkylation of Si—H groups because no change in the Si—H/Si—CH_3 ratio was observed. In addition, the ^{29}Si NMR resonance due to the $[CH_3Si(H)NH]$ unit of the starting oligosilazane remained unchanged in **7** and **10** (Fig. 3). Finally, bands due to Al–H bonds were not observed in the IR spectra of **7–10**. The broad signals at 65–67 ppm observed in the ^{27}Al NMR spectra were similar to those in the spectra of compounds **1–4** (Fig. 1). Accordingly, we conclude that the aluminum atoms are in an environment similar to that in these compounds. In the ^{27}Al NMR spectrum of **10**, a second signal at 154 ppm indicated the presence of some unreacted $(CH_3)_2AlNH_2$ by reference to the pure reagent (Fig. 1).

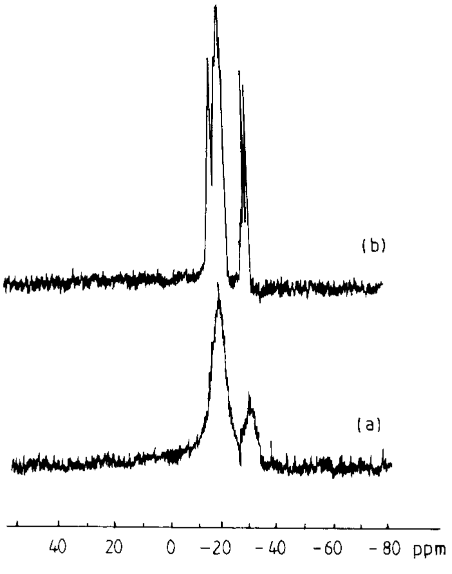


Figure 3 ^{29}Si NMR spectra of (a) polyaluminasilazanes **7–10** and (b) oligomethylsilazane $[CH_3Si(H)NH]_n$.

Pre-pyrolysis thermal transformations of polyaluminasilazanes 1–4

We investigated the thermal decomposition of compounds **1–4** by qualitative IR analysis of the gases evolved at different temperatures. During the first stage, between 50 and 300 °C, a gaseous alkane was evolved which corresponded to the alkyl group attached to aluminum. Therefore, it can be assumed that polycondensation between residual Al—CH_3 and N—H groups is the main reaction that occurs in this temperature range. Methane was formed in the case of **1**, **4** and **5**, while ethane was detected using **6** (Fig. 4). As long as the temperature was kept below 300 °C the alkyl group attached to the silicon atom was not lost, such a loss occurring only at higher temperature. Between 300 and 450 °C the alkane originating from R—Si was detected: methane for **1**, **4** and **5**, ethane and ethylene for compound **6**.

Methylsilane, CH_3SiH_3, was also detected in the

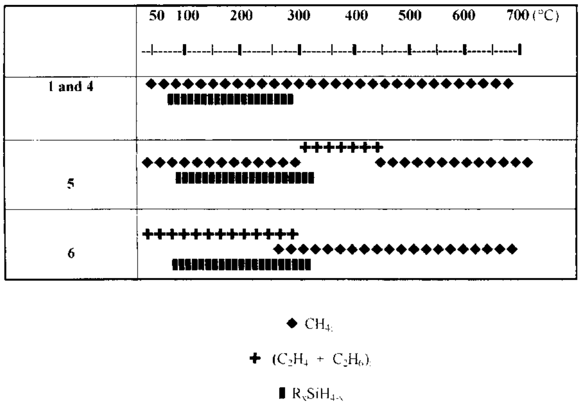
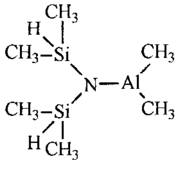
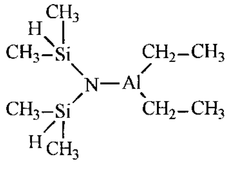


Figure 4 Qualitative IR analysis of gases evolved during the pyrolysis of **1, 4, 5** and **6**.

first stage of the pyrolysis. This gas was characterized during pyrolysis of **1** and **4**, between 100 and 300 °C. Neither dimethylsilane, $(CH_3)_2SiH_2$, nor trimethylsilane, $(CH_3)_3SiH$, was observed. To explain the formation of CH_3SiH_3, the same type of thermolysis experiment was carried out using $(CH_3)_2AlN[SiH(CH_3)_2]_2$ (**11**) and $(CH_3CH_2)_2AlN[SiH(CH_3)_2]_2$ (**12**) as model aluminasilazanes. They were prepared by reaction of 1,1,3,3,-tetramethylsilazane with a stoichiometric amount of trimethyl- or triethyl-aluminum.[25]

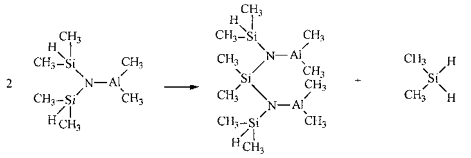


11



12

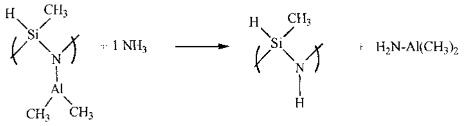
Thermolysis of **11** and **12** at 210 °C was performed under argon and the evolved gases were trapped at −80 °C. In both cases, $(CH_3)_2SiH_2$, identified by NMR and IR spectroscopy, was the only gas trapped. The amount of trapped dimethylsilane was close to 1 mol per mole of the starting silazane. By ^1H NMR analysis of the residues of the thermolyses, we found that 90% of the Si—H functions had been consumed during the thermal treatment. To account for the formation of dimethylsilane, the exchange reaction between Si—N and Si—H shown in Eqn 6 may be proposed. Such disproportionation reactions are well documented in organosilicon chemistry and are known to be catalyzed by Lewis acids.[33] We conclude that the formation of CH_3SiH_3 observed during the pyrolysis of **1** and **4** can be explained by such exchange reactions between the Si–N and Si–H bonds of the polysilazane structure (Eqn 6).



[6]

Reaction of 1 and 4 with ammonia

When polyaluminasilazanes **1** and **4** were treated with ammonia between 50 and 300 °C, the materials foamed and partially melted. Needles of $(CH_3)_2AlNH_2$ were isolated in the cold part of the reactor. The cleavage of the N–Al link in the starting polyaluminasilazane (Eqn 7) is in good agreement with previous literature that has shown that exchange of an Al–NR_2 bond with a stronger base can occur.[29,34] In the present case, the nonvolatile $(CH_3)_2AlNH_2$ is formed but remains in the reaction mixture and probably reacts at higher temperature with the N—H function of the silazane or with itself.



[7]

Preparation of ceramics

The ceramic residue yields at 950 and 1500 °C for the polyaluminasilazanes **1–4** and **7–10** are reported in Table 7. The polyaluminasilazanes prepared using $(CH_3)_2AlNH_2$ gave higher ceramic yields than those **(1–4)** prepared with trimethylaluminum. In the case of **1–4**, we also found a decrease in the ceramic yield with increasing proportion of aluminum reagent used. Rationalization of these results is possible if we assume that the ceramic yields are closely related to the possibility of

Table 7. Ceramic residue yields (%) of polyaluminasilazanes after pyrolysis

Pyrolysis conditions	**1**	**2**	**3**	**4**	**7**	**8**	**9**	**10**
1500 °C, under N_2	80	75	53	40	74	71	75	72
1500 °C, under NH_3	74	74	65	62	78	77	79	73

Table 8. Elemental analysis and XRD data of residues after pyrolysis at 1500 °C under argon

	Elemental composition (%)						
Compd	*C*	*H*	*N*	*Si*	*Al*	*Formulation*	*Crystalline phases by XRD*
1	13.1	<0.5	26.7	48.6	9.5	$Al_1 Si_{4.84} N_{4.32} C_{3.11}$	Si_3N_4, SiC, AlN
7	11.5	<0.5	29.3	47.5	9.9	$Al_1 Si_{4.66} N_{4.88} C_{2.63}$	Amorphous
4	16.1	<0.5	18.6	32.5	33.7	$Al_1 Si_{0.84} N_{0.4} C_{0.99}$	$(AlN + AlN–SiC)_{SS}$
10	9.0	<0.5	29.0	29.3	30.4	$Al_1 Si_{0.91} N_{0.84} C_{0.66}$	$(AlN + AlN–SiC)_{SS}$

Table 9. Elemental analysis and XRD data of residues after pyrolysis at 1000 °C under ammonia followed by pyrolysis up to 1500 °C under argon

	Elemental composition (%)						
Compd	*C*	*H*	*N*	*Si*	*Al*	*Formulation*	*XRD data*
1	0.95	<0.5	38.3	49.1	10.6	$Al_1 Si_{4.47} N_{5.96} C_{0.01}$	α-Si_3N_4 + AlN
7	0.2	<0.5	36.2	46.6	9.7	$Al_1 Si_{4.58} N_{6.08} C_{0.02}$	α-Si_3N_4 + AlN
4	0.3	<0.5	33.9	27.9	37.0	$Al_1 Si_{0.66} N_{0.72} C_{0.19}$	α- and β-Si_3N_4 + AlN
10	0.5	<0.5	31.3	28.0	30.1	$Al_1 Si_{0.88} N_{1.00} C_{0.03}$	β-Si_3N_4 + AlN

crosslinking of the material during the heating process, prior to its decomposition. In **1** there is residual N—H and Al—CH_3 functionality and these species can further condense upon heating, resulting in crosslinking and thus in a high ceramic yield. However, when a stoichiometric amount of $(CH_3)_3Al$ is used, as for compound **4**, no N—H functionality is left. Thus there is no possibility of further crosslinking in the early stages of the pyrolysis. On the other hand, **7–10** contain Al—NH_2 groups, whatever the amount of $(CH_3)_2AlNH_2$ used. The thermal reaction with CH_3—Al groups can result in crosslinking via CH_4 loss, and thus high ceramic residue yields are obtained in all cases.

The elemental analyses of the materials obtained in pyrolyses in a stream of argon are presented in Table 8; these ceramics were black powders. The possible presence of oxygen as a contaminant cannot be excluded, but its determination was not possible. For all polyaluminasilazanes, the use of ammonia as the pyrolysis gas served to remove almost all of the carbon and enriched the sample in nitrogen (Table 9).[35] As a consequence, all the ceramic products in this case were white. The use of $(CH_3)_2AlNH_2$ instead of $(CH_3)_3Al$ for the preparation of the polyaluminasilazanes resulted in the lowest carbon retention on pyrolysis in an ammonia stream.

The pyrolysis products were examined by XRD. Depending on the compound used and the conditions of pyrolysis, it is possible to form completely different mixtures of ceramics. All ceramics obtained in pyrolyses up to 1000 °C were amorphous. Crystalline products were detectable only in the residues which had been pyrolyzed up to 1500 °C. α- and β-Si_3N_4 and AlN were present in the sample obtained by pyrolysis under ammonia.

When the precursor contained a high Al/Si ratio, upon pyrolysis under argon it was possible to obtain a ceramic that exhibits a crystallized AlN–SiC solid solution. Similar materials were reported as products of the pyrolysis of aluminum amide/polycarbosilane systems.[7] This phase was also prepared by sintering at 1950 or 2300 °C under pressure, or in vacuum, of an SiC/AlN powder mixture.[36–38] At the present time, we have not found peak splitting of the (110) peak, which has been reported elsewhere to be representative of a Si-rich (at 59.95 °) or Al-rich phase (at 59.40 °) in SiC–AlN solid solution.[22,23] Other single phases, such as Si_3N_4–Al_4C_3 have been prepared by the latter method,[39] but were not detected in our ceramics.

CONCLUSION

Polyaluminasilazanes were prepared in high yield by reacting $[CH_3Si(H)NH]_n$ oligomethylsilazane with either $(CH_3)_3Al$ or $(CH_3)_2AlNH_2$. In both cases the polymeric materials obtained can be transformed with high yields into ceramics. The nature and composition of the ceramics can be tuned by adjusting the composition of the starting polyaluminasilazane, the gas used during the pyrolysis and the final temperature of pyrolysis. The use of $(CH_3)_2AlNH_2$ instead of $(CH_3)_3Al$ for the preparation of the polyaluminasilazane offers some advantages due to its lower alkylating activity and the presence of crosslinkable Al—NH_2 groups.

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