Chem. Mater. 1992, *4*, 141-146

Silicon Carbonitride from Polymeric Precursors: Thermal Cross-Linking and Pyrolysis of Oligosilazane Model Compounds

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Received July 23, 1991. Revised Manuscript Received September 25, 1991

The thermal cross-linking and the pyrolysis under argon of various oligosilazanes were investigated using a thermobalance coupled with a mass spectrometer. The ceramic yield, the ceramic composition, and the gaseous evolutions strongly depend on the number and the nature of the functional groups borne by the silicon atom. The presence of vinyl and Si-H groups allows a fast and efficient thermal cross-linking through hydrosilation: the carbosilane bridges formed in this way are not affected by the main depolymerization reactions, transamination and exchange of Si-N bonds, which lower the ceramic yields.

Introduction

Polysilazanes of general formula $-(SiR^1R^2-NR^3)_n-$, which have found application as precursors to silicon carbonitride,[1,2] are usually prepared by ammonolysis of the corresponding dichlorosilanes $SiCl_2R^1R^2$ (Scheme I). However, this synthesis leads to a mixture of low molecular weight cyclic oligomers (mainly trimer and tetramer) which usually distill during the pyrolysis step thus leading to low ceramic yields.

The ceramic yield may be increased to 85% by cross-linking the oligomers prior to pyrolysis.[3] This cross-linking may be performed either chemically, in the presence of a catalyst, or thermally if the silazane is reactive enough.[4-9] In a previous publication,[10] we reported the synthesis of oligovinylsilazane $-(SiViH-NH)_n-$ (OVS), which led to excellent ceramic yields (85%) after a short thermal treatment under atmospheric pressure (typically 2 h at 120 °C) without any catalyst. This behavior may be ascribed to the high thermal reactivity of OVS, which allows efficient cross-linking below the distillation temperature. Such thermally curable precursors offer a great simplicity of processing in the absence of catalyst or solvent. They are particularly attractive in the formulation of composite, the impregnation of matrices or as pore fillers.

In the case of OVS, numerous reactions are possible during the thermal cross-linking, as well as the first step of the pyrolysis (Scheme II), due to the unusually high functionality of this oligomer. To have a better understanding of the importance of each reaction, we have prepared a series of oligosilazane and co-oligosilazane model compounds in which each function (vinyl, Si–H, or N–H) was successively replaced by a nonreactive methyl group (Table I). The possible cross-linking reactions for each model compound are detailed in Table II. In this paper, we discuss the influence of these structural changes on the thermal reactivity of the polysilazanes, during the curing step at low temperature (120 °C) and during the subsequent pyrolysis.

Scheme I. Preparation of Oligosilazanes

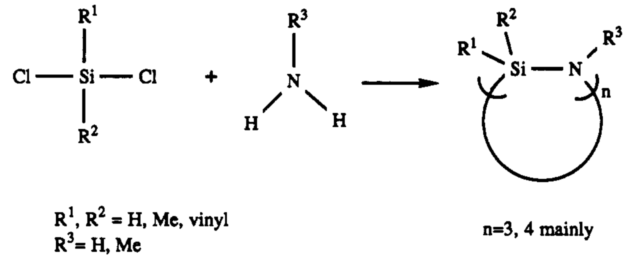

Table I. Synthesis of the Oligosilazanes

sample	idealized formula	synthesis[a]
OVS	$(-SiViH-NH-)_n$	$SiViHCl_2 + NH_3$, toluene
OVNMS	$(-SiViH-NMe-)_n$	$SiViHCl_2 + NMeH_2$, toluene
OMS	$(-SiMeH-NH-)_n$	$SiMeHCl_2 + NH_3$, toluene
OVMS	$(-SiViMe-NH-)_n$	$SiViMeCl_2 + NH_3$, toluene
OMNMS	$(-SiMeH-NMe-)_n$	$SiMeHCl_2 + NMeH_2$, toluene
O(VS/MMS)	$(-SiViH-NH-)_x$-$(-SiMe_2-NH-)_y$	$0.5\ SiViHCl_2 + 0.5\ SiMe_2Cl_2 + NH_3$, toluene
O(VS/MS)	$(-SiViH-NH-)_x$-$(-SiMeH-NH-)_y$	$0.5\ SiViHCl_2 + 0.5\ SiMeHCl_2 + NH_3$, toluene

[a] All at 0 °C.

Table II. Curing of the Oligosilazanes

sample	F^a	possible cross-linking reactions	gel time[b]
OVS	3	hydrosilation, vinyl polymerization, dehydrocoupling (SiH/NH and SiH/SiH), transamination	2 h
OVNMS	2	hydrosilation, vinyl polymerization, dehydrocoupling (SiH/SiH)	1 day
OMS	2	dehydrocoupling (SiH/NH and SiH/SiH), transamination	5 days
OVMS	2	vinyl polymerization, transamination	>8 days
OMNMS	1	dehydrocoupling (SiH/SiH)	>8 days
O(VS/MMS)	2	same as for OVS	1 day
O(VS/MS)	2.5	same as for OVS	15 h

[a] Mean number of reactive function (vinyl, Si–H, or N–H) per silazane unit. [b] At 120 °C under argon, without solvent.

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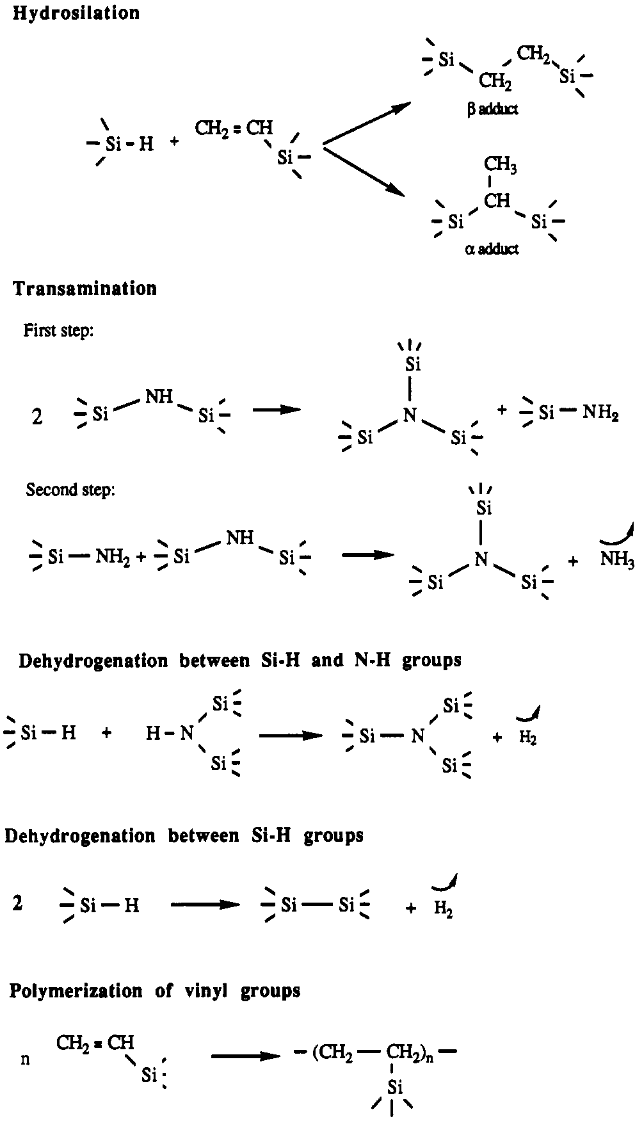
Scheme II. Possible Thermal Cross-Linking Reactions in the Case of Oligovinylsilazane (OVS)



Experimental Section

Syntheses. Oligosilazanes (or oligo-*N*-methylsilazanes) were obtained by bubbling ammonia (or methylamine) through a molar solution of the appropriate dichlorosilanes in toluene at 0 °C (Table I). After 5 h, the ammonium chloride produced was filtered off and the solvent evaporated under vaccum. The yields of silazane were in excess of 80%. Each oligomer was characterized by elemental analysis, gel permeation chromatography (GPC), and infrared and ^{1}H NMR spectroscopies.

Characterization. ^{1}H NMR spectra were recorded on a Bruker AW 60 instrument. Chemical shifts, relative to TMS (ppm), are as follows: OVS δ 5.9 (m, 3, Vi), 4.7 (br s, 1, SiH), 0.7 (v br, 1, NH); OVNMS δ 5.9 (m, 3, Vi), 4.6 (br s, 1, SiH), 2.5 (m, 3, NCH_3); OMS δ 4.6 (br, 1, SiH), 0.7 (v br, 1, NH), 0.35 (m, 3, $SiCH_3$); OVMS δ 5.9 (m, 3, Vi), 0.7 (v br, 1, NH), 0.17 (s, 3, $SiCH_3$); OMNMS δ 4.56 (br, 1, SiH), 2.47 (s, 3, NCH_3), 0.18 (d, 3, $SiCH_3$); O(VS/MMS) δ 5.9 (m, 3, Vi), 4.6 (br s, 1, SiH), 0.7 (v br, 2, NH), 0.15 (m, 6, $SiCH_3$); O(VS/MS) δ 5.9 (m, 3, Vi), 4.6 (br s, 2, SiH), 0.7 (v br, 2, NH), 0.15 (m, 3, $SiCH_3$).

Infrared spectroscopy was performed using a Perkin-Elmer Series 1600 FTIR using KBr pellets. ν (cm^{-1}) values are as follows: OVS 3375 (NH stretching), 3050, 3010, 2977, 2944 (CH stretching), 2132 (SiH stretching), 1592 (C=C stretching), 1403, 1269 (vinyl CH_2 and CH deformation), 1174 (NH deformation), 1007 (CH deformation), 940 (SiNSi stretching); OVNMS 3050, 3010 (CH stretching), 2110 (SiH stretching), 1590 (C=C stretching), 1465 (NCH_3 deformation), 1075 (NCH_3 stretching); OMS 3380 (NH stretching), 2960, 2900 (CH_3, CH stretching), 2130 (SiH stretching), 1250 (Si–CH_3 deformation), 1170 (NH deformation); OVMS 3400 (NH stretching), 3050, 3005 (vinyl CH stretching), 1590 (C=C stretching), 1400, 1269 (vinyl CH_2 and CH deformation), 1250 (Si–CH_3 deformation), 1174 (NH deformation); OMNMS 2110 (SiH stretching), 1470 (NCH_3 deformation), 1250 (Si–CH_3 deformation), 1180 (NCH_3 stretching); O(VS/MMS) 3380 (NH stretching), 3050, 3010 (vinyl CH stretching), 2120 (SiH stretching), 1592 (C=C stretching), 1402, 1267 (vinyl CH_2 and CH deformation), 1250 (Si–CH_3 deformation), 1174 (NH deformation); O(VS/MS) 3370 (NH stretching), 3050, 3010 (vinyl CH stretching), 2130 (SiH stretching), 1590 (C=C stretching), 1400, 1267 (vinyl CH_2 and CH deformation), 1250 (Si–CH_3 deformation), 1174 (NH deformation).

Table III

	OVS	OVNMS	OMS	OVMS	OMNMS	O(VS/MMS)	O(VS/MS)
M_n	390	300	295	310	250	320	300
M_w	450	310	335	350	260	380	470

Gel permeation chromatography (GPC) was performed using Waters Ultrastyragel columns (100, 500 and 1000 Å), calibrated with polystyrene standards, in tetrahydrofuran (flow rate 1 mL/min). All the samples consisted in a mixture of very low molecular weight oligomers, mainly trimers and tetramers according to the mass spectrometry. Number average molecular weight (M_n) and weight average molecular weight (Mw) are reported in Table III.

Pyrolysis of cured samples was done in a Carbolite oven for 5 h at 1000 °C under an argon flow in alumina crucibles.

Elemental analyses were performed by the Service Central d'Analyses du CNRS.

Thermogravimetric analysis (TGA) was performed using a Netzsch STA409 thermobalance. About 30 mg of the sample in an alumina crucible was heated from room temperature to 1200 °C at 10 °C min^{-1} in an argon flow (50 mL min^{-1}).

TG/MS analysis: the thermogravimetric analyzer was interfaced to a Kenos KSM88 quadrupole mass spectrometer (MS). The volatiles evolved during the pyrolysis were captured by a stainless steel capillary (0.25-mm i.d.) heated at 150 °C. This capillary was placed in the furnace above the sample and was connected to the MS through a molecular leak. The ionization energy was 75 eV. During the pyrolysis one scan from 2 to 150 amu was collected every 30 s and stored. In this way, the different gases evolved during the pyrolysis may be identified; it is possible either to plot mass spectra obtained at selected temperatures or to plot the evolution of the signal of characteristic ions as a function of the temperature. In the absence of standardization only qualitative information may be drawn from these curves. It is noteworthy that due to the limited range of the MS and because of condensation in the capillary only low molecular weight compounds such as gases or volatile liquids are detected by TG/MS. Thus loss of heavy, condensable compounds such as oligomers may not be detected by MS although it will lead to a weight loss apparent on the TGA curve.

Results

Each oligosilazane was first cross-linked by heating neat at 120 °C; if a solid was obtained, its pyrolysis under argon was then investigated by coupled TG/MS analysis and by elemental analysis.

(1) Curing at 120 °C. Thermogravimetric analysis (TGA) of un-cross-linked oligosilazanes under an inert atmosphere revealed that distillation occurred above 150–200 °C, depending on the sample. To avoid distillation, we chose to cure our models at 120 °C until a solid was obtained. The time needed for the solidification (gel time) is reported in Table II. The main cross-linking reactions which may occur in each case are also reported in Table II; these reactions are described in Scheme II. From Table II, it can be seen that even a slight decrease in the mean number of reactive functions (Si–H, N–H, or vinyl) per monomeric unit leads to a significant increase in the gel time. Furthermore, oligo(*N*-methyl,methylsilazane) (OMNMS) and oligo(vinylmethylsilazane) (OVMS) did not

Table IV. Ceramic Yield, Elemental Analysis, and Loss of Silicon for the Cured Oligosilazanes Pyrolyzed 5 h at 1000 °C under Argon

		ceramic analysis, wt %						
starting silazane	ceramic yield, %	Si	C	N	O	H	$\Delta Si/Si_0$,[a] %	1st wt loss,[b] %
OVS	83	47.3	29.9	21.8	1.1	0.2	0.5	3.5
OVNMS	66	43.5	29.5	21.8	3.5	0.15	13	13.5
OMS	46	56.3	15.4	22.8	1.5	0.2	46	47
O(VS/MMS)	63	51.4	22.9	20.1	1.2	0.15	17	21
O(VS/MS)	77	51.1	22.2	20.8	4.7	0.5	8	10.5

[a] $\Delta Si/Si_0(\%) = (Si_0 - Y(Si_c))/Si_0 \times 100\%$, where Si_0 is the theoretical silicon content of the starting oligosilazane, Si_c is the silicon content of the ceramic, and Y the ceramic yield. [b] TGA weight loss (%) from 20 to 450 °C.

gel even after 8 days at 120 °C. Gel permeation chromatography (GPC) and ^1H NMR and IR spectroscopies showed that OMNMS was unchanged, indicating that dehydrocoupling between SiH bonds did not occur at 120 °C. In the case of OVMS, GPC indicated the occurrence of some cross-linking reactions. No new ^{13}C NMR resonances arising from saturated aliphatic carbons were visible; this indicates that polymerization of the vinyl groups is negligible at 120 °C. Chemical analysis showed a slight decrease in the nitrogen content of the sample, from 14.6% to 13% (w/w) after 3 days at 120 °C, which indicated the occurrence of some transamination reaction.

Oligo(*N*-methyl,vinylsilazane) (OVNMS) and oligomethylsilazane (OMS) gave cross-linked solids after 1 and 5 days at 120 °C, respectively. Thus the cross-linking of OVNMS may be attributed to hydrosilation, whereas the cross-linking of OMS involves dehydrogenation between SiH and NH functions and transamination reactions.

From these results, a rough order of reactivity at 120 °C may be drawn up: hydrosilation > dehydrogenation SiH/NH ~ transamination > polyaddition of vinyl groups ~ dehydrocoupling between SiH bonds. However, even when solids were obtained, infrared spectroscopy showed a substantial presence of unreacted SiH, vinyl, or NH functions, which indicates that cross-linking is far from complete.

(2) Pyrolysis. Ceramic Yields and Elemental Analysis of the Ceramics. Oligo(vinylmethylsilazane) and oligo(*N*-methylmethylsilazane), which did not solidify during the curing step at 120 °C, gave negligible ceramic yields and were not further studied. The pyrolysis under argon of the cross-linked solids obtained after the curing step was investigated by thermogravimetric analysis combined with mass spectrometry (TG/MS analysis) which allows the continuous analysis of the gases evolved during pyrolysis. The ceramic yields and the elemental analyses of the pyrolyzates are reported in Table IV.

The aim of the cross-linking step is to avoid the loss of organosilicon species during the pyrolysis, which is detrimental to the ceramic yield. Acutally it can be seen from Table IV that even a slight decrease in the mean number of reactive functions per silazane units leads to a significant decrease in the ceramic yield. Moreover the absence of vinyl groups in OMS leads to a particularly low ceramic yield (46%).

TG/MS Analysis. The TG/MS analyses of the cured samples of OVS, OVNMS, and OMS are given in Figures 1–3. In the case of cured oligovinylsilazane (Figure 1), three stages may be distinguished:

From 150 to 220 °C a small weight loss (3%) is observed, which corresponds to the distillation of low molecular weight oligomers (not detected) and residual solvent. This low weight loss well demonstrates the efficiency of the thermal cross-linking in that case.

From 220 to 400 °C the weight loss is negligible (0.5%). A slight escape of ammonia is detected, which indicates a low degree of transamination. Hydrogen is detected as low as 310 °C, indicating the occurrence of dehydrogenation reactions.

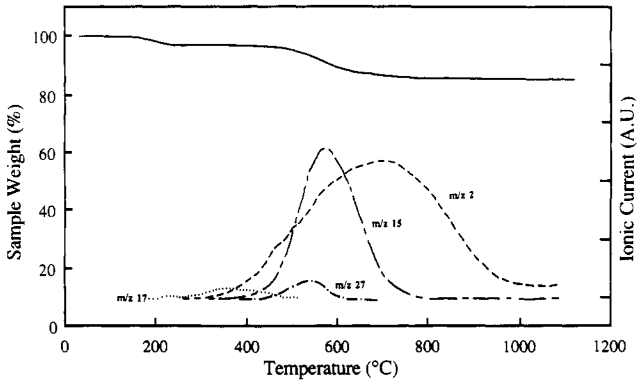


Figure 1. TG/MS analysis under argon of OVS cured at 120 °C. (—) TGA curve; the ion signal at m/z 2 (- - -) arises from hydrogen; *m/z* 15 (— —) arises from methane; *m/z* 17 (···) arises from ammonia; *m/z* 27 (—·—) arises from ethylene and ethane.

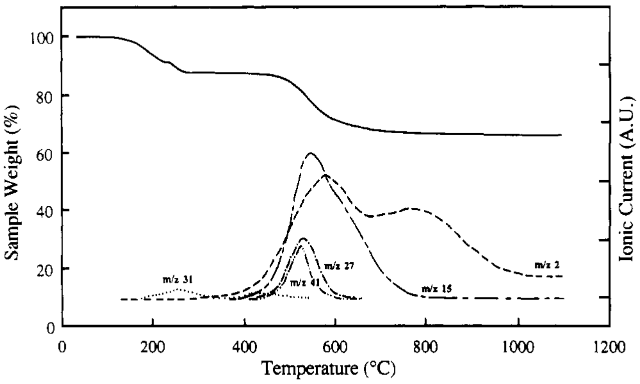


Figure 2. TG/MS analysis under argon of OVNMS cured at 120 °C. (—) TGA curve; the ion signal at *m/z* 2 (- - -) arises from hydrogen; *m/z* 15 (— —) arises from methane; *m/z* 31 (···) arises from *N*-methylamine; *m/z* 27 (—·—) arises from ethylene and ethane; *m/z* 41 (—···—) arises from propene.

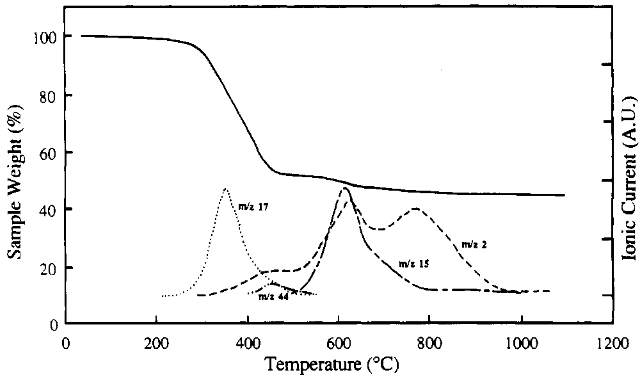


Figure 3. TG/MS analysis under argon of OMS cured at 120 °C. (—) TGA curve; the ion signal at *m/z* 2 (- - -) arises from hydrogen; *m/z* 15 (— —) arises from methane; *m/z* 17 (···) arises from ammonia; *m/z* 44 (—···—) arises from methylsilane, $MeSiH_3$.

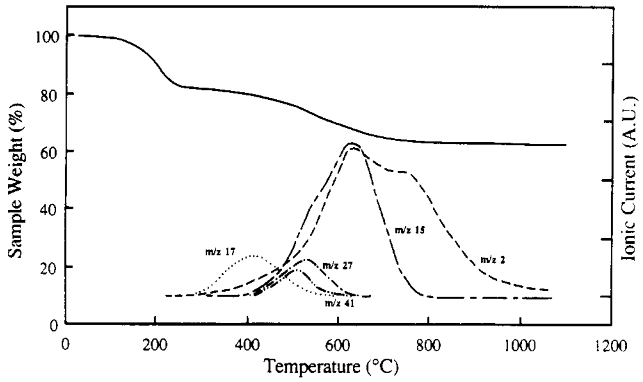


Figure 4. TG/MS analysis under argon of O(VS/MMS) cured at 120 °C. (—) TGA curve; the ion signal at m/z 2 (- - -) arises from hydrogen; m/z 15 (– –) arises from methane; m/z 17 (···) arises from ammonia; m/z 27 (–·–) arises from ethylene and ethane; m/z 41 (–··–) arises from propene.

Above 400 °C a second weight loss (12%) corresponds to the mineralization step. During this step C–C and C–H bonds are cleaved, and the main gases detected are methane and hydrogen. Ethylene, ethane, and propylene are also detected from 400 to 600 °C. It is noteworthy that the escape of hydrogen is not completed even at 1100 °C; the total weight loss at this temperature is 15.5%.

The thermal decomposition of cross-linked OVNMS follows the same pattern. However the weight loss corresponding to the loss of oligomers during the first stage is much larger, 20% instead of 3%, indicating less efficient cross-linking. Small amounts of methylamine are detected, arising from transamination of the –Si–NMeH groups corresponding to the ends of the chains of linear oligomers present in that sample. An additional experiment was carried out at a higher sensitivity and with the capillary near the crucible in order to identify the organosilicon species evolved from 100 to 260 °C; the spectra obtained were similar to those of the starting oligosilazane, except for two peaks at m/z 85 and 86, which were attributed to $(SiVi–NHMe)^+$ and $(SiViH–NHMe)^+$, respectively, arising from $SiViH_2–NHMe$. Above 400 °C the mineralization process appears to be similar to that of cured OVS. The larger weight loss observed arises from a larger escape of hydrocarbons. Indeed, although no quantitative inferences may be drawn from our MS experiments, the loss of ethylene and propene appeared to be more extensive than for cured OVS. The total weight loss amounted to 34.8% at 1100 °C.

In the case of cured OMS the first weight loss (48%), which mainly corresponds to the loss of organosilicon species, takes place from 200 to 500 °C, contrary to the previously descirbed precursors where this loss is complete at 260 °C. Simultaneously a large escape of ammonia indicates extensive transamination. In addition a small escape of methylsilane $MeSiH_3$ (m/z 44) was detected at about 450 °C. Above 500 °C the only gases detected are methane and hydrogen; neither ethylene nor propene were observed; the total weight loss reaches 54.9% at 1100 °C.

The TG/MS analysis of O(VS/MMS) is displayed in Figure 4. The TGA curve exhibits a large weight loss (17.5%) from 100 to 260 °C, corresponding mainly to the loss of oligomers, followed by a continuous weight loss from 260 to about 500 °C. The escape of ammonia, between 200 and 500 °C, is much greater than in the case of OVS. After 400 °C the mineralization process resembles that of cured OVS; the total weight loss reaches 37.2% at 1100 °C.

It is interesting to compare the TG/MS analysis of OMS (Figure 3) with that of O(VS/MS) displayed in Figure 5. The presence of the vinylsilazane units (–Si(ViH)–NH–) limits the first weight loss to 10.8% at 480 °C; as mentioned above for O(VS/MMS), the escape of ammonia, between 200 and 500 °C, is larger than in the case of OVS. After 400 °C the mineralization process is similar to that of cured OVS; the total weight loss reaches 23.4% at 1100 °C.

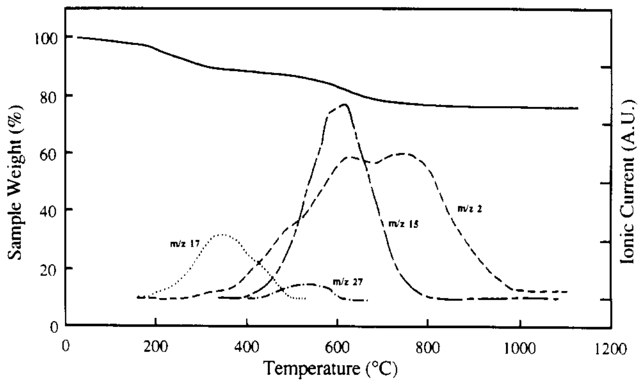


Figure 5. TG/MS analysis under argon of O(VS/MS) cured at 120 °C. (—) TGA curve; the ion signal at m/z 2 (- - -) arises from hydrogen; m/z 15 (– –) arises from methane; m/z 17 (···) arises from ammonia; m/z 27 (–·–) arises from ethylene and ethane.

Discussion

Ceramic Yields and Loss of Silicon. The design of an oligosilazane precursor which could be cured thermally without any catalyst may be tentatively drawn from Table IV. Actually, an exceedingly high functionality as well as low-temperature reactivity are required to obtain reasonable gel times and high ceramic yields.

Low ceramic yields are directly related to the loss of organosilicon species during pyrolysis. Unfortunately, the oligomers evolved during the pyrolysis condense in the cold parts of the apparatus and are therefore not detected by the mass spectrometer. However the amount of silicon lost during the pyrolysis, ΔSi, is easily calculated from the ceramic yield (Y) and the silicon contents of the starting oligomer (Si_0) and of the final ceramic (Si_c), according to

$$\Delta Si = Si_0 - Y(Si_c)$$

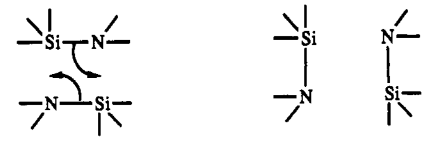
The relative loss of silicon, $\Delta Si/Si_0$, calculated for each oligosilazane is reported in Table IV. These values provide an estimate of the weight percentage W of organosilicon species lost during the pyrolysis: actually $\Delta Si/Si_0$ is equal to W in so far as the volatile organosilicon species have the same composition as the starting silazane.

Inspection of Table IV shows that $\Delta Si/Si_0$ varies as a function of the gel time. Thus, the faster cross-linking takes place during the curing step, the higher are the ceramic yields in the subsequent pyrolysis. It is noteworthy that a slight decrease in the mean functionality F of the oligosilazane leads to a significant increase in the loss of organosilicon species during pyrolysis: thus ΔSi is negligible for OVS ($F = 3$); and reaches 8% for O(VS/MS) ($F = 2.5$). The nature of the functions is also important: $\Delta Si/Si_0$ is equal to 13%, 17%, and 46% for OVNMS, O(VS/MMS), and OMS, respectively, although they have the same functionality value ($F = 2$).

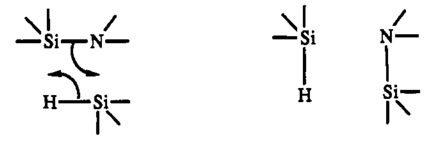
Depolymerization Reactions. The escape of organosilicon species may have two sources: (i) distillation of low molecular weight oligomers when cross-linking is inadequate; (ii) thermal depolymerization with the release of low molecular weight organosilicon species.

In our case the former phenomenon may be neglected, as all the cured samples were highly cross-linked, insoluble solids. In the temperature range 150–450 °C (before the

Scheme III



Schematic representation of a redistribution involving the exchange of Si-N bonds.



Schematic representation of a redistribution involving the exchange of Si-N and Si-H bonds.

mineralization step), two kinds of reactions may account for depolymerization: transamination reactions; bond redistribution around the silicon atoms.

Transamination is equivalent to an exchange of N–Si and N–H bonds and thus involves the breaking and formation of Si–N bonds. In other words, Si–N bonds are liable to be cleaved in the presence of N–H bonds. Such cleavages may lead to the formation of volatile fragments, which would be distill out under the conditions of the pyrolysis (atmospheric pressure and high temperature).

Redistribution reactions (also called ligand-exchange reactions) at the silicon atom are well documented.[11,12] Roughly speaking, halogen, oxy, amino, and thio ligands are regarded as labile ligands, hydrogen and silicon as semilabile ligands, and alkyl and aryl as nonlabile ligands. Thus, in the case of oligosilazanes the most likely reaction would be the exchange between Si–N bonds and, to a lesser extent, exchange between Si–N and Si–H bonds (Scheme III). Exchange involving Si–C bonds are much less probable, although it might occur at high temperature.

Exchange of Si–N bonds would lead to the formation of oligomers built up from the same silazane units as the precursor. On the other hand, redistribution involving Si–H and Si–N bonds may lead to volatile silanes. Thus the small amount of methylsilane ($MeSiH_3$) detected at 480 °C in the case of OMS (Figure 3), as well as the release of vinylsilylamine suspected in the case of OVNMS, probably originate from such reactions. However these reactions appear to be of minor importance. In the case of OVNMS, the methyl groups on the nitrogen atoms prevent transamination; thus, the loss of oligomers during the pyrolysis may be ascribed mainly to redistribution of Si–N bonds.

It is worth noting that, since transamination and redistribution of Si–N bonds appear to be the main mechanisms of depolymerization of oligosilazane precursors, the oligomers evolved during pyrolysis have approximately the same composition as the starting oligosilazane. As mentioned above, in that case $\Delta Si/Si_0$ is roughly equal to the weight loss (%) corresponding to the escape of these oligomers. The values reported in Table IV show that $\Delta Si/Si_0$ and the first weight loss detected on the TGA curve are in good agreement, which confirms that the weight loss below 450 °C arises mainly from the escape of organosilicon species.

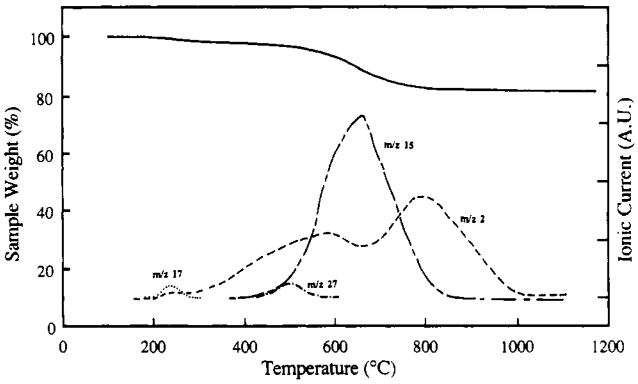


Figure 6. TG/MS analysis under argon of OMS cross-linked in the presence of KH. (—) TGA curve; the ion signal at m/z 2 (- - -) arises from hydrogen; m/z 15 (— —) arises from methane; m/z 17 (···) arises from ammonia; m/z 27 (–·–) arises from ethylene and ethane.

Table V. Atomic Composition of the Oligosilazanes (Theoretical) and Ceramic Composition (Pyrolysis under Argon, 5 h at 1000 °C)

starting oligosilazane	at. compn. of starting oligosilazane (theor)	at. compn of the final ceramic
OVS	SiC_2NH_5	$SiC_{1.48}N_{0.92}H_{0.06}O_{0.04}$
OVNMS	SiC_3NH_7	$SiC_{1.58}N_{1.00}H_{0.05}O_{0.14}$
OMS	$SiCNH_5$	$SiC_{0.64}N_{0.81}H_{0.05}O_{0.05}$
O(VS/MMS)	SiC_2NH_6	$SiC_{1.04}N_{0.78}H_{0.04}O_{0.03}$
O(VS/MS)	$SiC_{1.5}NH_5$	$SiC_{1.01}N_{0.81}H_{0.13}O_{0.16}$

Avoiding Depolymerization. The nature of the crosslinking bridges has a large influence on the ceramic yields; for instance the yield is only 46% in the case of OMS whereas it increases to 77% for O(VS/MS) which contains 50% of vinylsilazane units. The cross-linking processes involved in the curing of OMS are transamination and dehydrogenation between N–H and Si–H bonds; thus the preceramic network is built of Si–N bonds only, and therefore it may easily be damaged by transamination and exchange of Si–N bonds. Actually, TG/MS analysis (Figure 3) shows that in the case of OMS the loss of oligomers occurs exactly in the same temperature range as the escape of ammonia arising from transamination, which very likely indicates that these two processes are connected. On the other hand, the curing of O(VS/MS) leads by hydrosilation to Si–CH_2CH_2–Si and Si–CH(CH_3)–Si bridges, which are much more stable toward redistribution than Si–N bonds, and therefore maintain the network although transamination remains significant, as indicated by the large escape of ammonia.

In the case of OMS, a well-known way to increase the ceramic yield is to cross-link the silazane in the presence of a dehydrogenation catalyst, such as potassium hydride,[5] which promotes the formation of trisilylated nitrogen atoms. The much higher degree of cross-linking of the precursor reduces the segment mobility, which significantly hinders depolymerization reactions.[4] Furthermore, the TG/MS analysis of OMS cross-linked in the presence of KH (Figure 6) shows that the evolution of gases is somewhat different of that of thermally cross-linked OMS (Figure 3); the release of hydrogen starts at a temperature about 150 °C lower, indicating that some catalyst still remains in the sample and promotes further dehydrogenation reactions.

Composition of the Final Ceramic. The atomic composition of the final ceramics are reported in Table V and compared to the theoretical composition of the starting silazanes. All the starting oligosilazanes have the same nitrogen to silicon ratios, N/Si = 1. On the other hand,

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the N/Si ratios of the ceramics obtained from OVS or from copolymers O(VS/MMS) and O(VS/MS) are significantly lower than 1. The only cause of a loss of nitrogen is the transamination reaction (see Scheme II). Other reactions should not decrease the nitrogen content. It is noteworthy that a complete transamination would lead to a ratio N/Si = 0.67, according to

$$3{\equiv}Si{-}NH{-}Si \rightarrow 2N(Si{\equiv})_3 + NH_3$$

Thus a ratio N/Si = 0.80 corresponds to 60% transamination, a ratio N/Si = 0.92 to 24% transamination. The comparison of the N/Si ratios of O(VS/MMS) and OVS indicates that the rate of transamination is lower in the case of OVS; this is probably related to the higher degree of cross-linking of OVS, which hinders such exchange reactions. Note that the escape of ammonia detected by TG/MS analysis indicates that transamination occurs between 200 and 500 °C whatever the precursor.

Comparisons of the compositions of the starting silazane and the ceramic shows that the final carbon content depends on the nature of the aliphatic groups: methyl groups lead to a lower final carbon content than do vinyl groups. For instance, the carbon to silicon ratio of the copolymer O(VS/MMS) is identical to that of OVS (C/Si = 2), whereas the final C/Si ratios are quite different: 1.04 instead of 1.48. This behavior reflects the thermal lability of the $Si{-}CH_3$ groups compared to that of the $Si{-}C_x{-}Si$ bridges, arising from the vinyl groups through hydrosilation or polymerization reactions. It is also noteworthy that the presence of a methyl group on the nitrogen atom in OVNMS does not significantly increase the carbon content of the ceramic: C/Si = 1.58 compared to C/Si = 1.48 for pyrolyzed OVS.

Conclusion

The hydrosilation reaction appears to be an efficient thermal cross-linking reaction for the preparation of silicon carbonitride precursors: it is fast even at relatively low temperature (120 °C), before the distillation of the lightest oligomers. In addition, hydrosilation leads to the formation of carbosilane bridges, Si–C–Si or Si–C–C–Si, which are not affected by the main depolymerization reactions (transamination and exchange of Si–N bonds) which are responsible for low ceramic yields. On the other hand, these carbosilane bridges lead, after pyrolysis, to a high carbon content in the final ceramic. Co-oligosilazanes containing vinyl and Si–H groups might provide a good compromise between ceramic yield and final carbon content.

Registry No. Silicon carbonitrile, 64477-28-7.

Graded Spatial Distribution in Conducting Copolymers of Pyrrole and Thiophene

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Received August 9, 1991. Revised Manuscript Received October 22, 1991

Random and spatially graded copolymers of pyrrole and thiophene formed at fixed concentrations of monomer under potentiostatic control are characterized by X-ray photoelectron spectroscopy and electroanalytical techniques. Unlike previously described copolymers composed of discrete bilayers of polypyrrole and polythiophene, neither the random nor spatially graded copolymers exhibited appreciable long-term charge rectification.

Introduction

Our interest in conducting polymers as components for electronic devices has led us to the sequential electrochemical synthesis of discrete layered polymeric structures (based on polybithiophene and polypyrrole) with charge-rectifying properties.[1,2] For practical purposes, it would be very convenient to prepare a polymeric device with similar rectifying properties in a single polymerization step. Despite the assumed quasi-one-dimensional structure of conducting organic polymers, spatial control of electron transfer in homopolymers synthesized by conventional electrochemical methods has not yet been achieved because three-dimensional effects render the resulting films isotropic. Attainment of directional control of charge transfer across a conducting organic polymeric film could be expected, in principle, in a material in which the redox potential changed in a graduated staircase fashion with film thickness. In such an array, electrons might be expected to move preferentially in one direction down the potential gradient. This concept of "staircase potential"[3] is employed in the construction of inorganic semiconductor materials for high-speed devices such as graded gap avalanche photodiodes[4] and the repeated velocity overshoot device.[5] An example of a polymeric material with such graded properties is a copolymer film in which the concentration of the monomer units changes gradually as a function of film thickness.

Copolymerization, the incorporation of two or more structurally different monomers into the same polymer chain, is commonly used to control the properties of a composite polymer. Structural modification of organic

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