APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2006; **20**: 527–534

(www.interscience.wiley.com) DOI:10.1002/aoc.1079

Pyrolytic conversion of an Al–Si–N–C precursor prepared via hydrosilylation between $[Me(H)SiNH]_4$ and $[HAlN(allyl)]_m[HAlN(ethyl)]_n$

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Received 23 February 2006; Revised 7 March 2006; Accepted 20 March 2006

An iminoalane-silazane polymer (ISP), an Al–Si–N–C precursor, has been synthesized via Pt-catalyzed hydrosilylation between poly(allyl iminoalane-*co*-ethyl iminoalane) {$[HAlN(allyl)]_m[HAlN(ethyl)]_n$, AE-alane} and 1,3,5,7-tetrahydro-1,3,5,7-tetramethylcyclotetrasilazane {$[Me(H)SiNH]_4$, TCS}. The IR and ^1H NMR spectra of ISP indicate that the relative amounts of the allyl groups decrease slightly in comparison with those of AE-alane, suggesting that hydrosilylation occurs partially. TG analysis up to 900 °C reveals that the ceramic yield of ISP is 83.1 mass%. It is suggested that the high ceramic yield can be ascribed to cross-linking reactions occurring during pyrolysis. Possible reactions during pyrolysis are hydrosilylation, polymerization of the C=C bonds in the allyl groups and dehydrocoupling among the SiH groups, NH groups and AlH groups in ISP. The pyrolyzed residue at 1700 °C contains crystalline AlN, *2H*-SiC, β-SiC and β-Si_3N_4 and amorphous carbon, as revealed by solid-state nuclear magnetic resonance (NMR) spectroscopy, Raman spectroscopy and X-ray diffraction (XRD) analysis. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: precursor; pyrolysis; hydrosilylation; silicon carbide; aluminum nitride; ceramic-based composites; solid-state nuclear magnetic resonance (NMR)

INTRODUCTION

Ceramic-based composites have proven attractive materials, since they provide a unique combination of characteristics and therefore permit tailoring and improvement of their properties.[1] An aluminum nitride (AlN)-silicon carbide (SiC) composite has been a promising material for high-temperature and electrical applications, because AlN possesses high thermal conductively, high electrical resistance and low thermal expansion,[2–4] whereas SiC has excellent resistance to oxidation and corrosion[5,6] and greater hardness, toughness and creep compared with AlN.[7]

Pyrolytic conversion of precursors involving inorganic and organometallic polymers provides a novel route to non-oxide ceramics and ceramic-based composites.[8–11] This process can offer significant advantages for fabrications into ceramics and ceramic-based composites with desirable shapes, including coatings and fibers. Since desired elements can be introduced easily into precursors, the chemical compositions of the resulting materials can be controlled. This process could lead to a high degree of homogeneity of the resulting materials on a micro- or nano-meter scale, moreover, in comparison with the conventional powder process.[11]

Pyrolytic conversion of the precursors for Al–Si–N–C ceramic composites has previously been extensively reported.[12–28] We have prepared precursors for Al–Si–N–C ceramic composites derived from a cage-type oligomer $(HAlN^iPr)_n$ and cyclosilazane $[Me(H)SiNH]_m$ by means of a 'molecular building block approach'.[29,30] This approach has been applied to chemical processing of ceramic-based composites to achieve better control of the conversion processes of precursors.[31] Since particle sizes in ceramic-based composites (1–20 nm[1]) are similar to or larger than those of molecular building blocks, this approach is an extremely attractive route to designing precursors for ceramic-based composites.

Poly(alkyliminoalane)s [$(HAlNR)_n$; PIAs] are well-known cage-type oligomers possessing Al–N backbones.[32] We have prepared AlN from cage-type PIAs $[(HAlNEt)_8$

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and $(HAlN^iPr)_6$], and revealed their pyrolytic behavior at lower temperatures.[33–38] The ceramic yields of the PIAs are, however, relatively low. The PIAs can also be regarded as candidates for molecular building blocks for AlN-based composites. We have prepared a novel AlN precursor, poly(allyl iminoalane-*co*-ethyl iminoalane) {$[HAlN(allyl)]_m[HAlN(ethyl)]_n$, AE-alane}, which contains mainly *octamers* from $LiAlH_4$, allylamine hydrochloride and ethylamine hydrochloride.[39] Since C=C bonds in allyl groups are generally capable of addition reactions, such as hydrosilylation, it appears possible to tailor AE-alanes with appropriate compounds possessing SiH groups.

Here we report the preparation of an iminoalane–silazane polymer (ISP) as an Al–Si–N–C precursor via Pt-catalyzed hydrosilylation between two building blocks: AE-alane and 1,3,5,7-tetrahydro-1,3,5,7-tetramethylcyclotetrasilazane {$[Me(H)SiNH]_4$, TCS}. Since C=C bonds in allyl groups can undergo hydrosilylation with SiH groups, it is expected that Si–C bonds are formed between these precursors. We also report the pyrolysis process of ISP and the characterization of the pyrolyzed residues.

EXPERIMENTAL

All the manipulations were performed under a protective nitrogen atmosphere using the standard Schlenk technique or a nitrogen-filled glove box.[40] Toluene was distilled over sodium and benzophenone under a nitrogen atmosphere. The preparation procedures for TCS[41,42] and AE-alane[39] were described elsewhere.

Preparation of ISP via hydrosilylation

ISP was synthesized via Pt-catalyzed hydrosilylation between TCS and AE-alane with a molar Si : Al ratio of 1 : 1. The allyl : ethyl ratio of AE-alane was 1 : 3, which exhibited the highest ceramic yield among the AE-alanes, as described in the previous report.[39]

The reaction was conducted in a three-necked round-bottomed flask equipped with a gas inlet tube and a glass stopper. The apparatus was charged with TCS (7.2 g, 0.122 mol) and toluene. AE-alane (9.0 g, 0.122 mol) and (1,5-cyclooctadiene)dimethylplatinum (II) [$Pt(CH_3)_2(C_8H_{12})$, 0.013 g, 0.039 mmol] in toluene were added to this solution slowly using a dropping funnel. After the solution was stirred at room temperature for 3 days, toluene was removed from the resulting yellowish transparent solution by trap-to-trap distillation under reduced pressure to yield a yellow-colored soluble solid.

Pyrolysis of ISP

For pyrolysis at 200–400 °C, ISP was placed on a BN boat in a quartz tube under an argon atmosphere and pyrolyzed at the desired temperature with no holding time. The heating and cooling rate was 5 °C/min. For pyrolysis at 1700 °C, ISP was placed on a BN boat in an alumina tube under an argon atmosphere. The heating rate was 10 °C/min from room temperature to 200 °C and 5 °C/min from 200 to 1700 °C. The temperature was maintained at 1700 °C for 2 h, and the pyrolyzed residue was then cooled to room temperature at 5 °C/min.

Characterization of ISP and the pyrolyzed residues

ISP was characterized by infrared (IR) spectroscopy (JASCO, FT/IR-460) and nuclear magnetic resonance (NMR) spectroscopy (JEOL, JNM-Lambda 500). The IR spectrum of ISP was recorded using the hexachloro-1,3-butadiene (C_4Cl_6; hcb) technique. The ^1H NMR spectrum of the precursor was recorded as a benzene-d_6 solution using tetramethylsilane [$(CH_3)_4Si$, TMS, 0 ppm] as an external standard. The ^{27}Al NMR (130.20 MHz) spectrum of the precursor was recorded on the same apparatus using $[Al(H_2O)_6]^{3+}$ (0 ppm) as an external standard. Thermogravimetry (TG, Perkin-Elmer, TGA-7) was carried out at a heating rate of 10 °C/min under flowing argon up to 900 °C.

The pyrolyzed residues were characterized by IR spectroscopy, solid-state NMR spectroscopy (JEOL, NM-GSX 400), Raman spectroscopy (Thermo Electron, Nicolet Almega XR) and X-ray diffraction (XRD, Rigaku, Rint-2500) analysis. For the residues pyrolyzed at 200–400 °C, the IR spectra of the pyrolyzed residues were recorded using the hcb technique. The solid-state NMR spectra of the pyrolyzed residues were obtained at 100.54 MHz (^{13}C) and 79.43 MHz (^{29}Si) with cross polarization and magic angle spinning (CP/MAS) techniques. The solid-state ^{27}Al NMR (104.17 MHz) spectra were recorded with the MAS technique only. The residues were packed in sample tubes in a nitrogen-filled glove box and kept under nitrogen flow during the measurements. Five hundred scans were accumulated with a pulse delay of 5 s (^{13}C and ^{29}Si) or 1 s (^{27}Al) and a spinning rate of 7 kHz (^{13}C and ^{29}Si) or 9 kHz (^{27}Al).

For the residue pyrolyzed at 1700 °C, the solid-state ^{27}Al and ^{29}Si NMR spectra of the pyrolyzed residue were recorded on the same instrument with the MAS technique only. Five hundred scans were accumulated with a pulse delay of 100 s (^{29}Si) or 1 s (^{27}Al) employing the spinning rate described above. The XRD pattern of the pyrolyzed residue was obtained using monochromated Cu Kα radiation.

The amounts of silicon and aluminum in ISP were determined using inductively coupled plasma (ICP) emission spectrometry (Variant, Vista-MPX), and those in the residue pyrolyzed at 1700 °C were determined using X-ray fluorescence (XRF, Rigaku, RIX2100) analysis. The amounts of carbon, nitrogen and hydrogen in ISP were determined with a Perkin-Elmer PE 2400-II instrument. The amounts of carbon, nitrogen and oxygen in the pyrolyzed residue were determined with LECO CS-444LS and TC-436 instruments.

DOI: 10.1002/aoc

RESULTS AND DISCUSSION

Preparation of ISP via hydrosilylation

The ^{1}H NMR spectra of ISP and AE-alane are shown in Fig. 1. In the spectrum of AE-alane, the integral ratio of the $CH_2 = C\underline{H}-$ signal at 6.5–5.9 ppm (b) to the $C\underline{H}_3$-CH_2- signal at 1.9–1.0 ppm is 1 : 9, reflecting the nominal allyl : ethyl ratio in AE-alane (1 : 3).[39] The spectrum of ISP reveals that the allyl : ethyl ratio is 0.7 : 9. The ^{27}Al NMR spectrum of ISP demonstrates one broad signal centered at 135 ppm, which is assignable to the $H\underline{Al}N_3$ environment,[32] and the chemical shift of ISP in the ^{27}Al NMR spectrum is similar to that of AE-alane.[39]

Since the SiH and NH groups in TCS, the C=C bonds in the allyl groups and the AlH groups in AE-alane are reactive groups, hydrosilylation between the SiH groups and C=C bonds[43] and dehydrocoupling between the NH and AlH groups[24] could occur. (No dehydrocoupling between SiH and NH groups should occur below 200 °C.[44]) As shown in the ^{1}H NMR spectra of ISP and AE-alane, the integral ratio of the $CH_2 = C\underline{H}-$ signal to the $C\underline{H}_3$-CH_2- signal decreases from 1 : 9 in AE-alane to 0.7 : 9 in ISP. This result indicates that the relative amounts of the allyl groups in ISP are slightly lower than those in AE-alane, and it consequently suggests that hydrosilylation occurs partially.

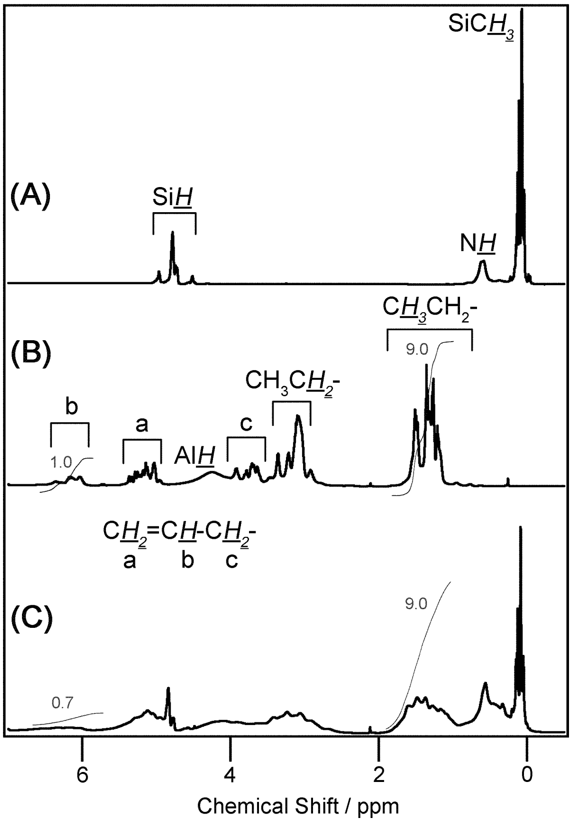


Figure 1. ^{1}H NMR spectra of (A) TCS, (B) AE-alane and (C) ISP.

As for dehydrocoupling, our previous paper showed that the ^{27}Al NMR spectrum of the precursor derived from $(HAlN^{i}Pr)_n$ and $[Me(H)SiNH]_m$ exhibited a broad signal assignable to the $\underline{Al}N_4$ environment[27] at 100 ppm, suggesting the occurrence of dehydrocoupling between the AlH groups in $(HAlN^{i}Pr)_n$ and the NH groups in $[Me(H)SiNH]_m$.[29,30] Since the signal at 100 ppm is not observed in the ^{27}Al NMR spectrum of ISP, however, essentially no dehydrocoupling occurs during the preparation of ISP. These observations suggest that only hydrosilylation occurs.

Pyrolytic process of ISP

Figure 2 shows the TG curves of ISP, AE-alane and TCS. TG analysis shows that the ceramic yield of ISP up to 900 °C under an Ar atmosphere is 83.1 mass%, which exceeds those of AE-alane (73.1 mass%) and TCS (4.3 mass%). Since hydrosilylation occurs partially, and since essentially no dehydrocoupling occurs between the AlH groups in AE-alane and the NH groups in TCS during the preparation of ISP, only a limited amount of TCS reacts with AE-alane. The ceramic yield of ISP is, however, higher than that of AE-alane. It is therefore supposed that cross-linking reactions occur mainly during pyrolysis.

In order to investigate the pyrolytic process of ISP in detail, spectroscopic characterizations of the residues pyrolyzed at 200–400 °C were conducted and the results are described below.

Figure 3 shows the IR spectra of ISP and the pyrolyzed residues. The IR spectrum of ISP exhibits adsorption bands at 3386 cm^{-1} (ν_{NH}),[45] 3235 cm^{-1} (ν_{NH_2}),[45] 3078 cm^{-1} ($\nu_{CH_2=CH}$),[45] 3000–2760 cm^{-1} (ν_{CH}),[45] 2124 cm^{-1} (ν_{SiH})[45] and 1860–1820 cm^{-1} (ν_{AlH}).[32] The $\nu_{CH_2=CH}$ band at 3078 cm^{-1} is

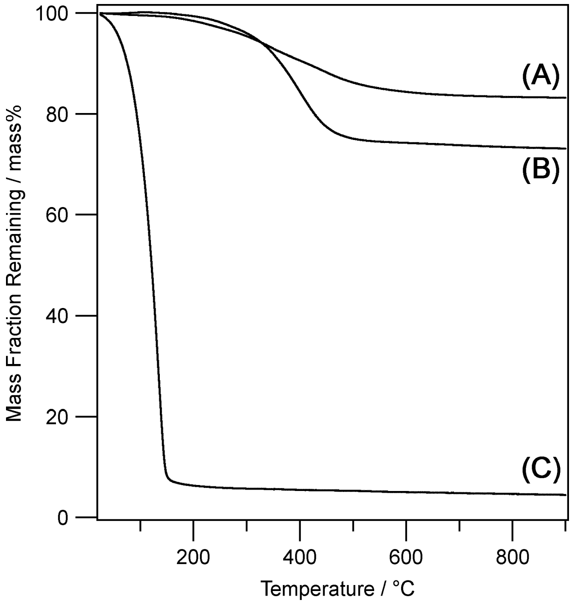


Figure 2. TG curves of (A) ISP, (B) AE-alane and (C) TCS under Ar flow.

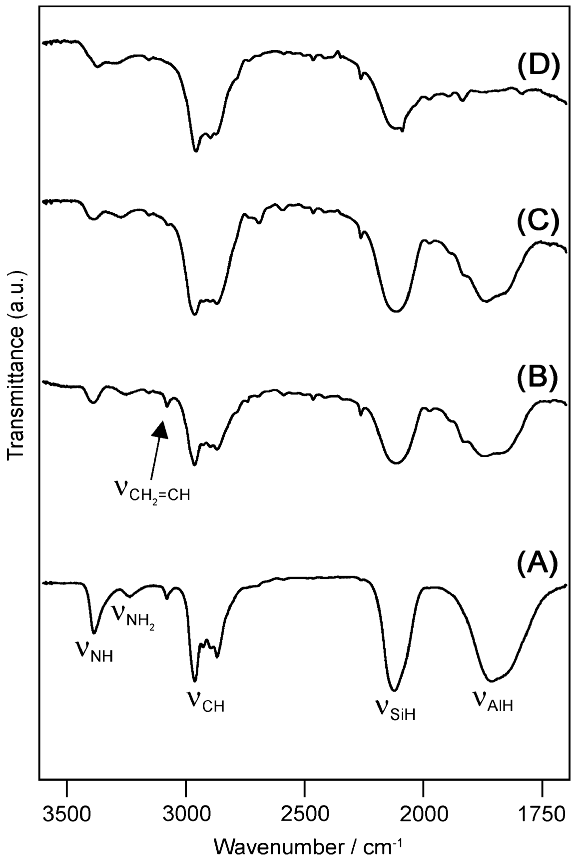


Figure 3. IR spectra of (A) ISP and the residue pyrolyzed at (B) 200 °C, (C) 300 °C and (D) 400 °C.

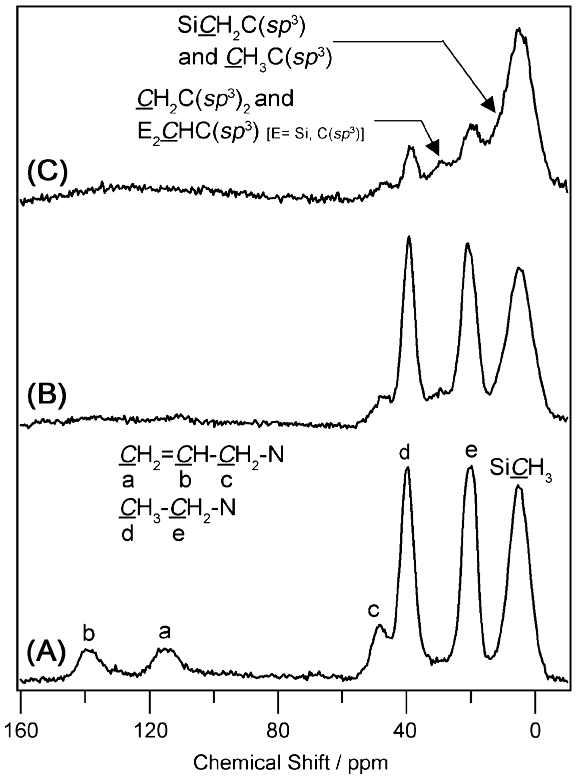


Figure 4. Solid-state ^{13}C NMR spectra of the residue pyrolyzed at (A) 200 °C, (B) 300 °C and (C) 400 °C.

not observed in the spectrum of the residue at 400 °C. In the spectrum of the residue at 200 °C, the relative intensity of the ν_{NH} band at 3386 cm^{-1} to the ν_{CH} bands at 3000–2760 cm^{-1} decreases in comparison with that in the spectrum of ISP. (Since mass loss is scarcely observed up to 200 °C, as shown in Fig. 2, and the CH$_x$ groups hardly react below 200 °C, the ν_{CH} bands are regarded as standard bands.)

Figure 4 shows the solid-state ^{13}C NMR spectra of the pyrolyzed residues. As the temperature increases, the two broad signals centered at 137 and 115 ppm, which can be assigned to the allyl groups, decrease gradually in comparison with the signals centered at 40 and 20 ppm that are assignable to the ethyl groups. These ethyl signals dramatically decrease at 400 °C in comparison with the $\mathrm{Si\underline{C}H_3}$ signal at ~0 ppm. The shoulder at ~10 ppm is observed in the solid-state ^{13}C NMR spectra of the residues at 300–400 °C, and the chemical shifts in the range from 5 to 15 ppm can be assigned to the $\mathrm{Si\underline{C}H_2C}(sp^3)$ and $\mathrm{\underline{C}H_3C}(sp^3)$ environments.[44] A new signal at 27 ppm, which can be assigned to the $\mathrm{\underline{C}H_2C}(sp^3)_2$ and $\mathrm{E_2\underline{C}HC}(sp^3)$ [E = Si, C(sp^3)] environments,[44] is observed above 300 °C.

Figure 5 shows the solid-state ^{29}Si NMR spectra of the pyrolyzed residues. The residues pyrolyzed at 200–400 °C exhibit a broad signal centered at −21 ppm, which is assignable to the $\mathrm{N_2\underline{\mathit{Si}}(H)C}(sp^3)$ environment.[46–49] An additional shoulder is observed at approximately −8 ppm and the chemical shifts in the range from 0 to −10 ppm are assignable to the $\mathrm{N_2\underline{\mathit{Si}}C}(sp^3)_2$ environment.[46,47,49] In the spectrum of the residue at 400 °C, a shoulder, which is assignable to the $\mathrm{N_3\underline{\mathit{Si}}C}(sp^3)$ environment, is observed at −37 ppm.[28,50]

The solid-state ^{27}Al NMR spectrum (*not shown*) of the residue pyrolyzed at 200 °C exhibits a new broad signal at ~100 ppm, which is assignable to the $\underline{\mathit{Al}}\mathrm{N_4}$ environment.[27] The profiles of the solid-state ^{27}Al NMR spectra of the residues pyrolyzed at 300–400 °C are similar to that of the residue pyrolyzed at 200 °C.

Based on these observations, the pyrolysis mechanism can be described as follows. In the IR spectrum of the residue pyrolyzed at 200 °C, the intensity of the ν_{NH} band decreases slightly in comparison with that of the ν_{CH} bands, suggesting that the NH groups in ISP can react below 200 °C. In the pyrolysis of polysilazanes, no reaction between the SiH groups the NH groups occurs below 200 °C.[42] In addition, dehydrocoupling between the AlH groups in $(\mathrm{HAlN}^i\mathrm{Pr})_n$ and the NH groups in $[\mathrm{Me(H)SiNH}]_m$ occurred at low temperatures (above ~100 °C) to form new Al–N bonds.[27,28] A signal assignable to the $\underline{\mathit{Al}}\mathrm{N_4}$ environment is actually observed in the solid-state ^{27}Al NMR spectrum of the residue pyrolyzed at 200 °C, suggesting the presence of new Al–N bonds in the residue. (Please note that the ^{27}Al NMR

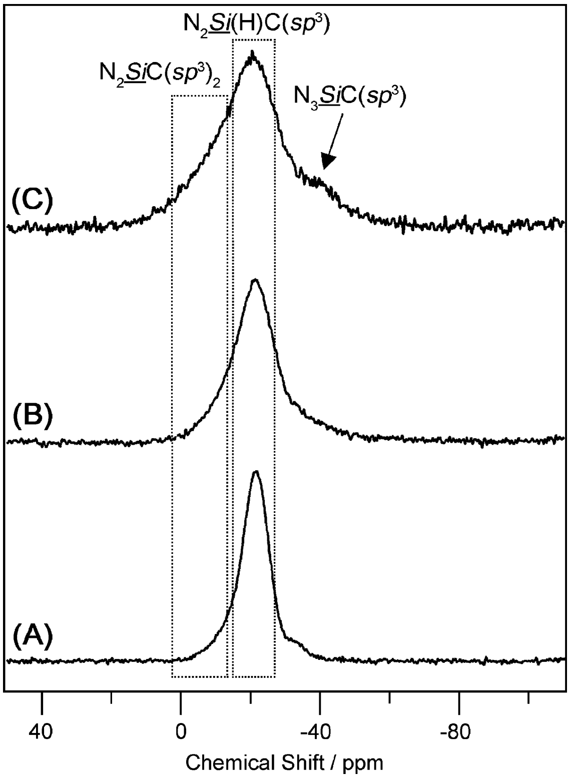
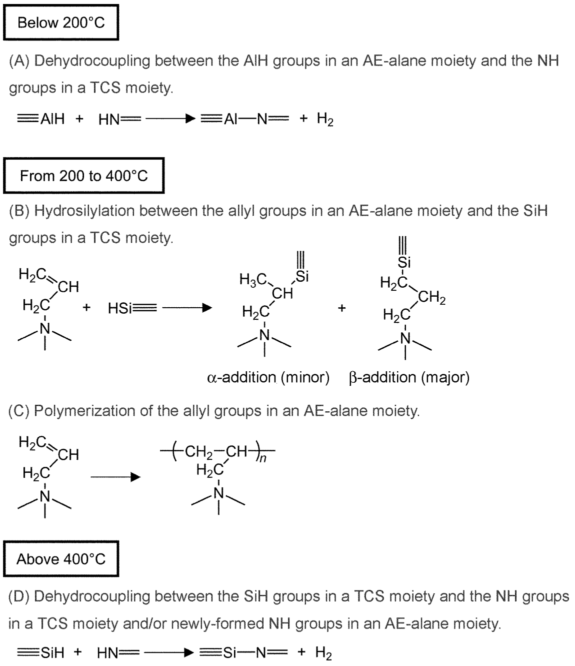


Figure 5. Solid-state ^{29}Si NMR spectra of the residue pyrolyzed at (A) 200 °C, (B) 300 °C and (C) 400 °C.



Scheme 1. Possible reactions during pyrolysis.

spectrum of ISP exhibits only the H$\underline{Al}$N$_3$ resonance.) Thus, it is suggested that dehydrocoupling between the AlH groups in an AE-alane moiety and the NH groups in a TCS moiety could occur to form new Al–N bonds below 200 °C [Scheme 1(A)]. Since the profiles of the solid-state ^{27}Al NMR spectra of the residues pyrolyzed at 300–400 °C are unchanged compared with that of the residue pyrolyzed at 200 °C, essentially no further dehydrocoupling between the AlH and NH groups occurs above 200 °C.

In the temperature range from 200 to 400 °C, most of the allyl groups in ISP are reacted, as observed in the solid-state ^{13}C NMR spectra. Possible reactions involving the allyl groups are hydrosilylation and polymerization of the allyl groups. Hydrosilylation between SiH groups and C=C bonds forms new Si–C bonds.[43] In the solid-state ^{29}Si NMR spectra of the pyrolyzed residue, the N$_2\underline{Si}$C(sp^3)$_2$ resonance at approximately −8 ppm is observed in the temperature range from 200 to 400 °C. This observation indicates that new Si–C bonds are formed, and thus suggests that hydrosilylation occurs in this temperature range. In the solid-state ^{13}C NMR spectra, a shoulder attributable to the Si$\underline{C}$H$_2$C(sp^3) and $\underline{C}$H$_3$C(sp^3) environments[44] is observed at ∼10 ppm. The solid-state ^{13}C NMR spectra also exhibit a new signal at 27 ppm, which is attributable to the $\underline{C}$H$_2$C(sp^3)$_2$ and E$_2\underline{C}$HC(sp^3) [E = Si, C(sp^3)] environments.[44] The Si$\underline{C}$H$_2$C(sp^3) (∼10 ppm) and $\underline{C}$H$_2$C(sp^3)$_2$ (27 ppm) environments can be formed via the β-addition on hydrosilylation, and the $\underline{C}$H$_3$C(sp^3) (∼10 ppm) and Si$\underline{C}$HC(sp^3)$_2$ (27 ppm) environments can arise from the α-addition on hydrosilylation. Several studies on the regioselectivity of hydrosilylation reported that β-addition occurred mainly rather than α-addition[51–53] and that, in the case of allylhydrosilanes, β-addition occurred only, leading to the formation of SiCH$_2$CH$_2$CH$_2$ groups.[54,55] It is therefore assumed that the β-addition on hydrosilylation between the SiH groups in a TCS moiety and the C=C bonds in the allyl groups in an AE-alane moiety can occur mainly in this temperature range [Scheme 1(B)]. The $\underline{C}$H$_2$C(sp^3)$_2$ and $\underline{C}$HC(sp^3)$_3$ environments,[44] whose presence is shown by the signal at 27 ppm in the solid-state ^{13}C NMR spectra, can also form via polymerization of the allyl groups. Thus, this type of polymerization could also occur above 300 °C [Scheme 1(C)].

Upon pyrolysis above 400 °C, the ethyl signals at 40 and 20 ppm in the solid-state ^{13}C NMR spectra dramatically decrease in comparison with the Si$\underline{C}$H$_3$ signal at ∼0 ppm. In the pyrolysis process of (HAlNEt)$_n$ below ∼300 °C, nitrogen terminals (=N:) generated by the heterolytic Al–N bond cleavage attacked the ethyl groups to form new NH groups in an AE-alane moiety and ethylene (CH$_2$ = CH$_2$) with regeneration of nitrogen terminals.[38] In addition, from ∼300 to ∼560 °C, new NH groups can be generated in an AE-alane moiety by the concerted β–elimination mechanism.[38,56] The formation of NH groups in an AE-alane moiety also appears to be possible via hydrogen abstraction of nitrogen radicals (=N$^\cdot$), which forms via the homolytic cleavage of C–N bonds in the NCH$_2$CH$_3$ groups.[57] Since a shoulder at −37 ppm, which is assignable to the N$_3\underline{Si}$C(sp^3) environment,[28,50] is observed in the solid-state ^{29}Si NMR spectrum of the residue

DOI: 10.1002/aoc

pyrolyzed at 400 °C, it is suggested that the residue forms new Si–N bonds. In the pyrolysis of aluminum- or boron-modified polysilazane, dehydrocoupling between the SiH and NH groups occurred to form new Si–N bonds in this temperature range.[28,50] It is therefore suggested that dehydrocoupling between the SiH groups in a TCS moiety and the NH groups in a TCS moiety and/or newly-formed NH groups in an AE-alane moiety occurs above 400 °C [Scheme 1(D)].

Based on these results, possible reactions during pyrolysis are hydrosilylation, polymerization of the C=C bonds in the allyl groups, and dehydrocoupling among the SiH, NH and AlH groups, as summarized in Scheme 1.

Characterizations of the residue pyrolyzed at 1700 °C

The residue pyrolyzed at 1700 °C was characterized by solid-state NMR spectroscopy, Raman spectroscopy and XRD analysis. Figure 6 shows the solid-state ^{27}Al and ^{29}Si NMR spectra of the residue. The solid-state ^{27}Al NMR spectrum exhibits one signal assignable to the $\underline{Al}N_4$ environment at 110 ppm, indicating the presence of AlN in the residue.[58] The residue pyrolyzed at 1700 °C demonstrates three signals at approximately −48, −20 and −16 ppm in the solid-state ^{29}Si NMR spectrum. The signal at approximately −48 ppm corresponds to the reported chemical shift for Si_3N_4 (−48.5 ppm).[59] The signal at −16 ppm and the shoulder at −20 ppm appear to be similar to the chemical shifts for β-SiC (−16.3 ppm)[60] and 2*H*-SiC (−20.0 ppm).[61] In the Raman spectrum of the residue, two bands are observed at 1337 and 1595 cm^{-1}, which are consistent with the Raman spectrum of amorphous carbon.[62,63]

The XRD pattern of the pyrolyzed residue is shown in Fig. 7. The XRD pattern of the residue pyrolyzed at 1700 °C is consistent with overlapping patterns of a 2*H* wurtzite-type compound and β-Si_3N_4. In addition, the reflection of β-SiC possibly overlaps with those of a 2*H* wurtzite-type compound and β-Si_3N_4, because it is suggested by the solid-state ^{29}Si NMR spectrum that β-SiC is present in the residue. The XRD peaks of the 2*H* wurtzite-type compound are too broad to determine whether this phase is an SiC–AlN solid solution or a mixture of AlN and 2*H*-SiC. Since the solid-state NMR spectra of the residue at 1700 °C indicate the presence of AlN and 2*H*-SiC in the residue, it is reasonable to assume that the 2*H* wurtzite-type compound is a mixture of AlN and 2*H*-SiC. Based on these observations, it is assumed that the residue pyrolyzed at 1700 °C contains crystalline AlN, 2*H*-SiC, β-SiC and β-Si_3N_4 and amorphous carbon.

Table 1 shows the compositions of ISP and the residue pyrolyzed at 1700 °C. The loss of aluminum or silicon during pyrolysis can be calculated by the following equation, based on the aluminum or silicon in the ceramic residue (C_M), the aluminum or silicon in ISP (P_M) and the ceramic yield (Y), as shown in Table 1:

$$\text{Loss (M)(\%)} = [(P_M - Y \times C_M)/P_M] \times 100$$

During the pyrolysis of ISP at 1700 °C, the loss of aluminum [Loss (Al)] during the pyrolysis is about 4.5% and that of silicon [Loss (Si)] is about 6.8%. In our previous study, during

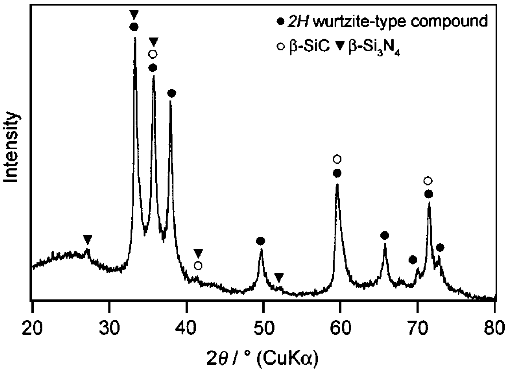


Figure 7. XRD pattern of the residue pyrolyzed at 1700 °C.

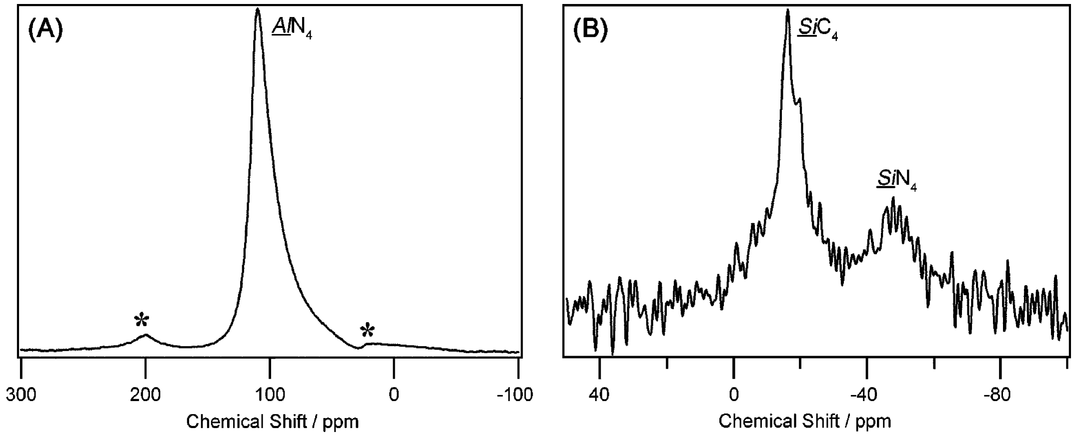


Figure 6. Solid-state (A) ^{27}Al and (B) ^{29}Si NMR spectra of the residue pyrolyzed at 1700 °C. The signals marked by asterisks are spinning side bands.

Table 1. The compositional characteristics of ISP and the residue pyrolyzed at 1700 °C

Sample ID	Elemental analysis/mass% Al	Si	N	C	H	O	Total	Compositional formula
ISP	22.3	21.7	20.7	29.8	7.9	—	102.3	$AlSi_{0.94}N_{1.79}C_{3.00}H_{9.46}$
1700 °C	31.8	30.2	20.4	16.3	—	1.2	99.9	$AlSi_{0.91}N_{1.24}C_{1.15}O_{0.06}$

the pyrolysis of the Al–Si–N–C precursor derived from $(HAlN^{i}Pr)_n$ and $[Me(H)SiNH]_m$, the loss of aluminum and silicon at 1600 °C was about 46 and 18%, respectively.[29,30] One possible reason for the suppression of the loss of aluminum and silicon is that TCS reacts with AE-alane via hydrosilylation, and relatively stable Si–C bonds are therefore formed at low temperatures. Thus, the allyl groups in ISP appear to play a significant role in the suppression of volatile aluminum- and silicon-containing compounds during pyrolysis, leading to an increase in ceramic yields.

CONCLUSIONS

ISP has been prepared via Pt-catalyzed hydrosilylation between $[Me(H)SiNH]_4$ and $[HAlN(allyl)]_m[HAlN(ethyl)]_n$. As determined TG analysis, the ceramic yield of ISP up to 900 °C under an Ar atmosphere is 83.1 mass%. The high ceramic yield and the suppression of the evolution of aluminum and silicon compounds during pyrolysis can be ascribed to cross-linking reactions, possibly involving dehydrocoupling between the AlH and NH groups (below 200 °C), hydrosilylation and polymerization of the C=C bonds in the allyl groups (200–400 °C), and dehydrocoupling between the SiH and NH groups (above 400 °C). The results of solid-state NMR, Raman and XRD indicate that the residue pyrolyzed at 1700 °C is composed of crystalline AlN, *2H*-SiC, β-SiC and β-Si_3N_4 and amorphous carbon. These results indicate that hydrosilylation at low temperatures can be highly effective in suppressing the evolution of aluminum and silicon compounds, and that AE-alane, which possesses the C=C bonds in the allyl groups, can be considered as an excellent candidate for building blocks.

Acknowledgements

The authors gratefully thank Prof. Kazuyuki Kuroda, Department of Applied Chemistry at Waseda University, for valuable discussion. This work was supported by 21COE 'Practical Nano-Chemistry' from MEXT, Japan.

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