

Synthesis and Pyrolysis of Ti-Containing Precursors for Advanced Si/C/N/Ti-Based Ceramics

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ABSTRACT: A new kind of polytitanosilazane (PTSZ) precursor for Si/C/N/Ti-based ceramic was synthesized from the condensation reaction of silazane lithium salts and titanium tetrachloride (TiCl_4). Titanium in the precursors was bonded to silazane compounds in the Si—N—Ti bond. The obtained PTSZs were characterized by Fourier transform infrared (FTIR), nuclear magnetic resonance (NMR), and elemental analyses. The PTSZs were pyrolyzed at 900 to 1300°C under nitrogen, argon, and ammonia atmosphere, respectively, to give amorphous inorganic products. The

results indicated that ceramic yields of PTSZs were much higher than that of their corresponding silazane oligomers and ceramic yields increased with the increase in Ti content in PTSZs. Precursors containing reactive vinyl groups gave higher pyrolytic yields. The pyrolytic yield under ammonia is lower than that under nitrogen and argon. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2733–2739, 2004

Key words: polytitanosilazane; ceramic precursor; inorganic materials; pyrolysis; composite

INTRODUCTION

Multicomponent ceramic composites often exhibit improved properties compared with the single component ceramics.¹ Therefore, researchers have paid much attention on the preparation of multicomponent ceramics. For example, to improve the mechanical properties of monolithic silicon nitride (Si_3N_4) ceramic, various types of silicon carbide (SiC),^{2,3} zirconium dioxide (ZrO_2),⁴ and titanium nitride (TiN)^{5,6} powders were used as toughening agents. Among these, TiN particles were found to be particularly useful because of the microcracking mechanism when optimum amounts of TiN particles are dispersed in Si_3N_4 matrix. TiN/ Si_3N_4 composites were suggested as structural materials because of their superior properties.⁷

On the other hand, increasing attention has been directed to the use of polymeric precursors for the manufacture of Si_3N_4 -, SiC-, or Si/C/N-based ceramics.^{8–12} Compared with the more traditional powder metallurgical process, the precursor method has attractive characteristics, such as lower processing temperature and the ability to prepare ceramics fibers, films, and other fiber-reinforced ceramic composites

having complex shapes. Another significant advantage of this route for the preparation of ceramics is the ability of the synthesis of silicon-based multicomponent ceramics through chemical modification of silicon-based polymeric precursors. In this process, desired elements for reinforcement can be introduced to the precursors and the chemical composition of the resulting multicomponent ceramic systems can be regulated at the molecular or atomic level, which is expected to produce new types of high-performance silicon-based ceramic composites.^{12,13}

In this article, we have introduced titanium to polysilazanes from the condensation reaction of silazane lithium salts and titanium tetrachloride (TiCl_4) to obtain polytitanosilazane precursors for Si/C/N/Ti-based ceramics. These precursors were pyrolyzed under argon (Ar), nitrogen (N_2), and ammonia (NH_3) atmosphere. The results showed that ceramic yields depended on the composition and molecular structure of the precursors.

EXPERIMENTAL

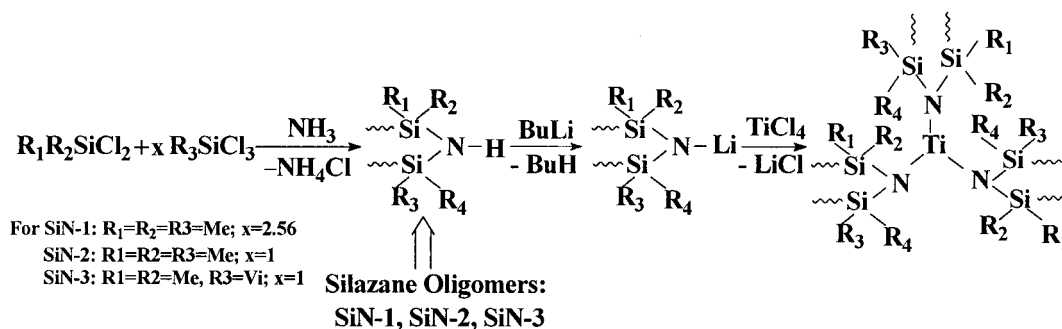
Materials

All liquid chlorosilanes were purchased from Kaihua Organosilicon Factory (Zhejiang, China) and purified by distillation. Tetrahydrofuran (THF), *n*-hexane, and toluene were commercially available and dried by refluxing over sodium and distilled under nitrogen. *n*-Butyllithium (1.6M in hexane) was purchased from Aldrich. TiCl_4 was purchased from Beijing Jinlong Reagents Co. Ltd. (Beijing, China).

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Scheme 1 Reaction routes.

Measurements

Fourier transform infrared (FTIR) spectra were obtained with a Perkin–Elmer 2000 IR spectrometer in the wavenumber range 4000–370 cm⁻¹ by using standard procedures. ¹H- and ²⁹Si-nuclear magnetic resonance (NMR) spectra of samples were recorded in CDCl₃ solution with a Bruker WM 300 spectrometer. Thermogravimetric analysis (TGA) was performed on a Perkin–Elmer Pyris 1 TGA in 30 mL/min nitrogen flow up to 1000°C, at a heating rate of 10°C/min. Elemental analyses for C and H in precursors were determined with a Carlo Erba 1106 analyzer; N content in precursors was obtained by Coulomb titration method.¹⁴ Analyses of Ti content were performed on the polymeric and the pyrolyzed samples on inductively coupled plasma (ICP) spectroscopy. X-ray diffraction (XRD) measurements were performed on the pyrolyzed samples with a powder diffractometer (Rigaku D/M4X 2500) by using Cu/Kα radiation.

Pyrolysis

Pyrolysis under Ar, N₂, or NH₃ was performed in a quartz tube furnace. Ceramic boats were used to contain the precursors in the quartz tube under flowing Ar, N₂, or NH₃ (40 mL/min). The temperature program used was as follows: ambient temperature to 200°C at 2°C/min, hold at 200°C for 1 h; 1°C/min to 350°C, hold at 350°C for 1 h; 5°C/min to 600°C, hold at 600°C for 1 h; then, 1°C/min to 900°C, hold at 900°C for 2 h.

Synthesis

Synthesis of silazane oligomers

Silazane oligomers were synthesized from coammonolysis of dichlorosilanes and trichlorosilanes. The typical synthetic procedure is described as follows: Into a 5000-mL three-necked flask with a reflux condenser, a gas inlet tube, and a mechanical stir under N₂ were added 3000 mL of toluene, 1.8 mol (237 g) of Me₂SiCl₂ (Me: methyl group CH₃), and 4.6 mol (686 g)

of MeSiCl₃. Ammonolysis was carried out at room temperature under high-speed stirring until no NH₃ was absorbed. The reaction mixture was filtered, and 1000 mL toluene was added to wash the slurry two to three times; ammonium chloride was removed and transparent solution was obtained. The solution was concentrated and dried below 80°C under vacuum to a constant weight. SiN-1 (380 g) was obtained in 63% yield. The result of elemental analysis for SiN-1 was C, 22.84; H: 7.70; N: 25.81.

The silazane oligomers SiN-2 and SiN-3 were obtained from coammonolysis of Me₂SiCl₂/MeSiCl₃ = 1:1 and Me₂SiCl₂/ViSiCl₃ (Vi: vinyl group CH₂=CH-) = 1:1 in mole ratio, respectively. Their preparation followed the same procedure as that of SiN-1. Elemental analysis for SiN-2 was C, 27.00; H: 8.34, N: 22.07; for SiN-3: C, 31.46; H: 7.50; N: 21.15.

Synthesis of silazane lithium salts and polytitanosilazanes

A series of polytitanosilazane (PTSZ) precursors was synthesized as described in Scheme 1. N—H bonds in silazane oligomers were partially lithiated in the first step of the reaction to prepare silazane lithium salts by a method of Fink.¹⁵ The mole ratio of *n*-BuLi/N—H is defined by us as lithiation degree. In the second step, TiCl₄ reacted with silazane lithium salts to produce PTSZs. As an example, PTSZ 1b was synthesized as follows: Into a 250-mL three-necked flask equipped with a dropping funnel and a gas inlet tube, 120 mL freshly distilled *n*-hexane and 11.7 g SiN-1 (containing 0.24 mol N—H) were added, and 30 mL 1.6M *n*-BuLi (0.048 mol) was charged into the dropping funnel by syringe after air was replaced by dry nitrogen. *n*-BuLi was added dropwise while stirring, and a white precipitate formed. The reaction mixture was stirred for 8 h at room temperature, and then the solvent was removed by distillation at room temperature under reduced pressure to obtain white silazane lithium salts. In the protection of nitrogen, 120 mL toluene was added into the flask while stirring. Charged

TABLE I
Detail Information of PTSZ Precursors

Starting silazane oligomers	Obtained PTSZs	Lithiation degree of silazane oligomers	PTSZ yields
SiN-1	PTSZ-1a	1/10	>90%
	PTSZ-1b	1/5	
	PTSZ-1c	1/4	
	PTSZ-1d	1/3	
SiN-2	PTSZ-2b	1 : 5	>90%
SiN-3	PTSZ-3b	1 : 5	

into the dropping funnel were 1.3 mL (0.0094 mol) TiCl_4 and 10 mL toluene and then the mixture was added dropwise into the silazane lithium salts/toluene system. The temperature was raised to 110°C and held for 24 h and then the mixture was cooled to room temperature. THF (40 mL) was added to the mixture. Precipitated LiCl was removed by filtration, and the resulting solution was distilled to give 12.0 g of PTSZ 1b as yellow solid powders. The result of elemental analysis for PTSZ 1b was C, 22.47; H, 6.91; N, 24.63; Ti, 4.8.

Detailed information of PTSZ precursors was listed in Table I.

RESULTS AND DISCUSSION

Synthesis and characterization of the polytitanosilazane precursors

As shown in Scheme 1, silazane lithium salts were first synthesized from the reaction of different starting silazane oligomers with *n*-BuLi; then PTSZs were obtained from the reaction of silazane lithium salts with TiCl_4 , and LiCl was removed from the system as the byproduct. It is obvious that higher content of Ti can be introduced to the final products with higher lithiation degree of silazane oligomers in the first step. However, too high a degree of lithiation will lead to producing insoluble PTSZs, which cannot be isolated from LiCl because the second step of the above reaction is the condensation reaction between multifunctional silazane lithium salts and TiCl_4 . Therefore, in our experiments, the lithiation degree of silazane oligomers varied from 1/10 to 1/2. The condensation reaction could take place smoothly in toluene at more than 80°C , and easy isolation could be achieved. The obtained PTSZs are soluble in THF and toluene and partially soluble in hexane. Therefore, thin ceramic films are expected to be obtained by dipping or spin-coating from the PTSZ solution and the subsequent pyrolysis.

Although the structure of the final PTSZs was very complex because of the multifunctional polyconden-

sation between silazane lithium salts and TiCl_4 , the PTSZs were characterized by NMR, FTIR, and elemental analyses.

For SiN-1 as the starting reactant, the Ti content of the obtained PTSZ 1a, 1b, 1c, and 1d are 2.2, 4.8, 5.3, and 5.0%, respectively. It can be seen that Ti content increased with the lithiation degree increasing from 1/10 to 1/4, and the PTSZs could be easily isolated from LiCl. However, when the lithiation degree reached 1/3, the yield of isolated PTSZ became much lower, as shown in Table I, and the Ti content of the product was also lower than that of PTSZ 1c.

From the FTIR in Figure 1 and ^{29}Si -NMR in Figure 2 of the silazane oligomers and PTSZs, we found that the basic silazane skeleton changed little after the introduction of Ti. The ^{29}Si -NMR spectra of the starting silazane oligomers and the obtained polytitanosilazanes consisted of two groups of broad resonance peaks. For SiN-1 and SiN-2, the signals in the range $\delta -3.8$ to -12 are assigned to $\text{N}-\text{SiMe}_2-\text{N}$ (D^{N}), and $\delta -18$ to -26 are assigned to N_3-SiMe (T^{N}). It can be seen from ^{29}Si -NMR spectra Figure 2(i, iii) that there

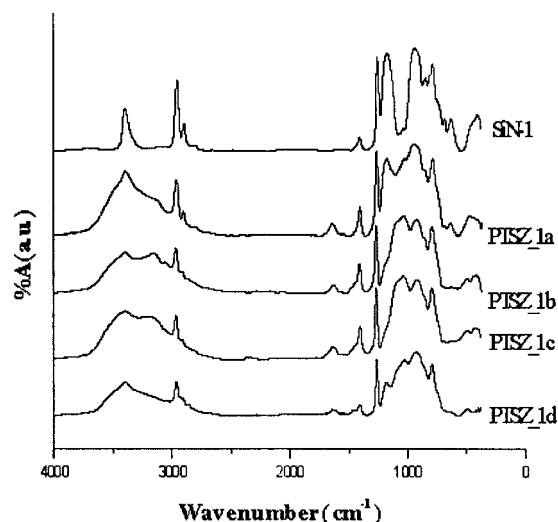


Figure 1 FTIR spectra of SiN-1 and its PTSZ derivatives.

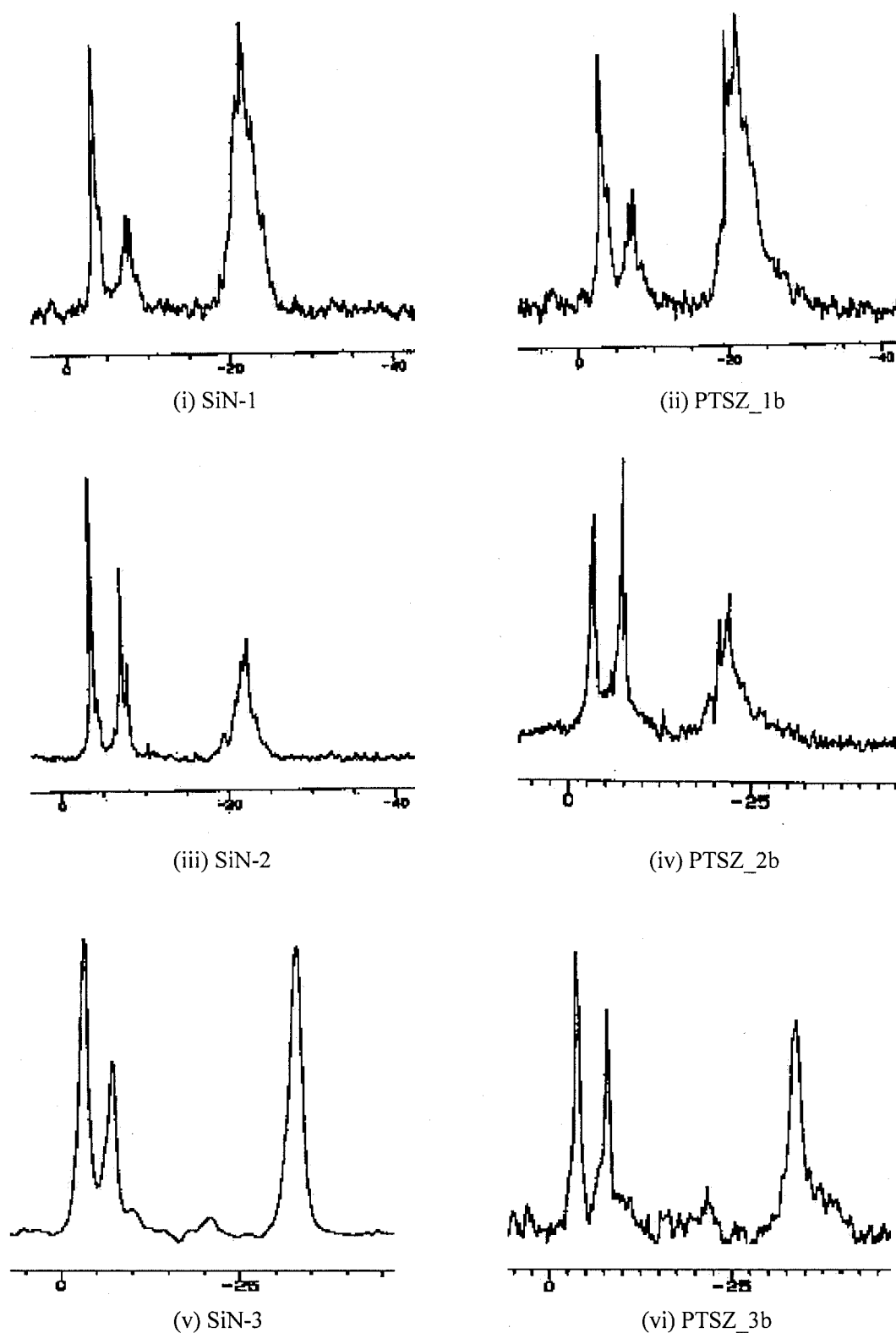


Figure 2 ^{29}Si -NMR of silazane oligomers and their PTSZ counterparts.

are more crosslinkage structure (T^{N}) units in SiN-1 than in SiN-2. So are their counterparts PTSZ 1b and PTSZ 2b. In the ^{29}Si -NMR spectra of SiN-3 and PTSZ 3b, the signals in the range δ -3 to -7 are

assigned to $\text{N}-\text{SiMe}_2-\text{N}$ (D^{N}), and the broad peak around δ -33 are assigned to N_3-SiVi (T^{NVi}). The ^1H -NMR spectra of SiN-3 and PTSZ 3b are shown in Figure 3. It can be observed that the vinyl group was

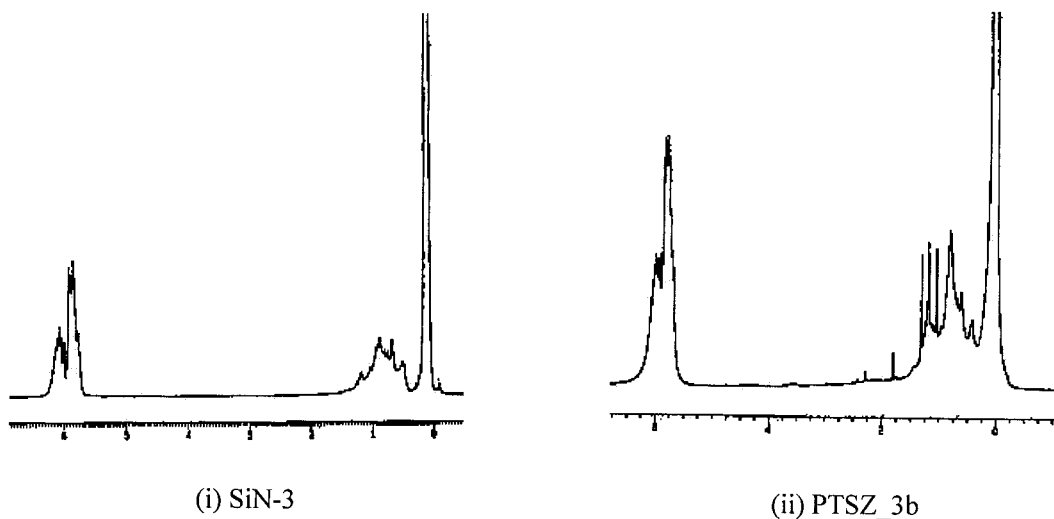


Figure 3 $^1\text{H-NMR}$ of (i) SiN-3 and (ii) PTSZ 3b.

retained in PTSZ 3b after the reaction of SiN-3 with *n*-BuLi and TiCl_4 .

The FTIR absorption peaks of silazane oligomers and PTSZs are at 2954–2960, 2897–2905, and 1403–1408 cm^{-1} (C—H); 1253–1260, 790, and 839 cm^{-1} (Si— CH_3); 3390 and 1170–1180 cm^{-1} (N—H). For SiN-3 and PTSZ 3b, the absorption peaks at 3048, 3007, 1600 cm^{-1} (—CH=CH₂) are observed. The strong peak at 940 cm^{-1} in the spectra of silazane oligomers is the typical asymmetric stretching vibration of Si—N—Si, which shifted to 925 cm^{-1} in the PTSZs' spectra. The intensity of N—H absorption peak decreased in the PTSZs' spectra compared with that in their corresponding silazane oligomers. A new strong absorption peak at 1030 cm^{-1} appeared in the spectra of PTSZs. The reason is that Si—N—H bonds have been partially replaced by Si—N—Ti bonds. This can be verified from Figure 1 that the intensity of the absorption peak at 1030 cm^{-1} increased with the lithiation degree increasing from 1/10 to 1/4 (PTSZ 1a to PTSZ 1c).

Pyrolysis behavior and ceramic yields

To evaluate PTSZ as ceramic precursor, we performed a series of pyrolysis in tube furnace and TGA experiments on these samples. The results showed that the ceramic yields are very dependent on the structure and composition of the polymer precursors. The TGA curves of silazane oligomers and PTSZs are shown in Figures 4 and 5, and the bulk pyrolysis results are shown in Table II. From the above $^{29}\text{Si-NMR}$ spectra (Fig. 2), it can be seen that SiN-1 and SiN-2 have similar structure units, but in SiN-1 there are more T^{N} (crosslinkage structure) portions in SiN-1, so the ceramic yield of SiN-1 is larger than that of SiN-2. In

SiN-3, T^{NVi} replaced the T^{N} in SiN-2. The polymerization of the reactive group —CH=CH₂ occurred during the heating process, which further crosslinked SiN-3. So, the ceramic yield of SiN-3 is larger than that of SiN-2 and even larger than that of SiN-1. For the same reason, the order of ceramic yields for the PTSZs is PTSZ-3b > PTSZ-1b > PTSZ-2b. This agrees with the literature¹⁶ that the presence of a crosslinked structure or the capability of a polymer to further crosslink at low temperature retards the thermolytic degradation reaction frequently encountered in organosilicon compounds.

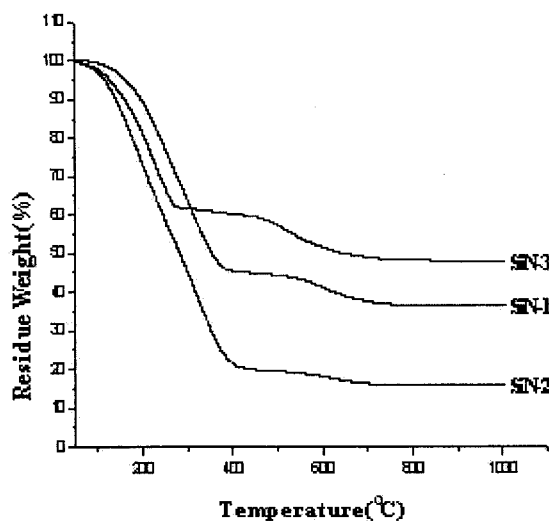
As shown in Table III, the ceramic yields of PTSZs are higher than their corresponding silazane oligomers, which indicated that there are more crosslinkage structure units in PTSZs. It was indicated in Table IV and Figure 5 that the ceramic yields increased with the increasing Ti content, also because of the existence of increasing crosslinkage structure units.

From Table II, we can observe that the pyrolysis atmosphere also plays an important role in the ceramic yield. Under ammonia, the pyrolysis yield is lower than that under nitrogen and argon. This agrees with previously reported literature¹⁷ that at high temperature (400–600°C) carbon can be eliminated with NH_3 .

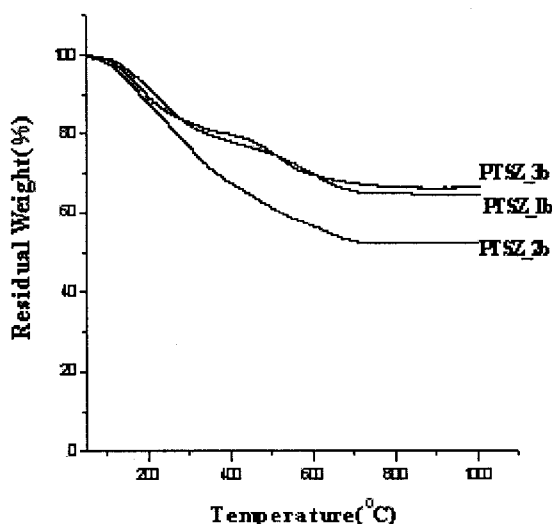
Table V showed that the Ti content in the pyrolyzed products was higher than that in their respective counterpart PTSZ precursors.

XRD results showed that pyrolytic products at 900 to 1300°C are amorphous powders. This indicated that the obtained Si/C/N/Ti powders have good high-temperature performance.

Further work on the high-temperature behavior of the pyrolyzed Si/Ti/C/N solids, the formation of hy-



(i) silazane oligomers



(ii) PTSZs

Figure 4 TGA curves of (i) silazane oligomers and (ii) PTSZs.

brid composites, and their high-temperature characteristics is still in progress.

CONCLUSION

Titanium can be introduced into polysilazanes by the condensation reaction of silazane lithium salts and TiCl_4 to give PTSZ precursors for Si/C/N/Ti-based ceramics. The PTSZs can be dissolved in common solvents such as toluene and THF. Investiga-

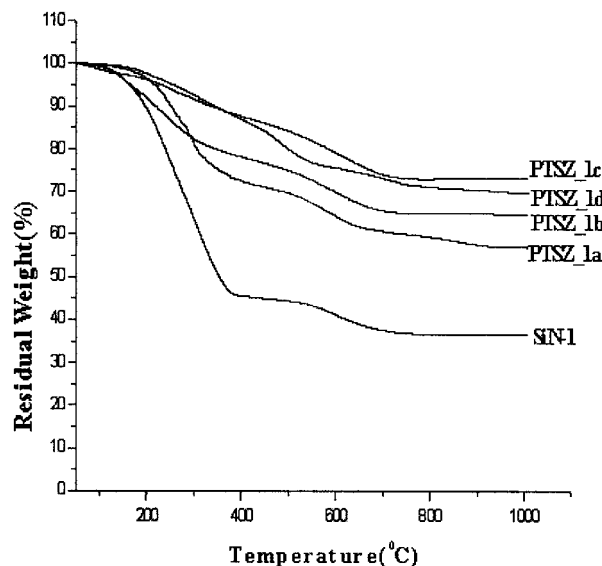


Figure 5 TGA curves of SiN-1 and PTSZs derived from SiN-1.

tions on pyrolysis of these precursors indicated that the existence of crosslinkage structure units and reactive vinyl groups is favorable for improving ceramic yields. Amorphous inorganic powders are obtained from the pyrolysis of PTSZs at 900 to 1300°C under nitrogen, argon, and ammonia atmo-

TABLE II
Ceramic Yields of PTSZs Pyrolyzed in Tube Furnace at 900°C under N_2 and NH_3

Sample	Ceramic Yield (%)	
	Under N_2	Under NH_3
PTSZ-1a	66.0	54.4
PTSZ-1b	71.0	58.7
PTSZ-1c	72.6	66.4

TABLE III
TGA Ceramic Yields of Silazane Oligomers and PTSZs

Silazane oligomers	Ceramic yield (%)	Ceramic yield (%)	
		PTSZ	
SiN-1	36.5	PTSZ_1b	64.7
SiN-2	15.9	PTSZ_2b	52.2
SiN-3	48.0	PTSZ_3b	66.5

TABLE IV
TGA Ceramic Yields of PTSZs Derived from SiN-1

Sample	Ceramic yield (%)
PTSZ_1a	56.9
PTSZ_1b	64.7
PTSZ_1c	73.3
PTSZ_1d	69.5

TABLE V
Comparison of Ti Content Before and
After Pyrolysis Under N₂

Sample	Ti (%)	
	Before pyrolysis	After pyrolysis
PTSZ-1b	4.8	6.9
PTSZ-1c	5.3	7.6

sphere, respectively. The pyrolysis atmosphere also plays an important role in the ceramic yield.

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