

Synthesis and Polymer-to-Ceramic Conversion of Tailorable Copolysilazanes

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ABSTRACT: Tailorable copolysilazanes (CPSZs) with variable chemical structure and molecular weights were prepared by coammonolysis of dichloromethylsilane, dichloromethylvinylsilane, and trichloromethylsilane. The as-synthesized CPSZ was characterized by gel permeation chromatography, Fourier transformed infrared (FTIR) spectroscopy, and nuclear magnetic resonance spectroscopy. The CPSZ could be cured in an inert atmosphere at 180°C for 24 h. Pyrolysis behavior and structure evolution of the cured CPSZ were studied by means of thermal gravimetric analysis and FTIR. Hydro-silylation, transamination, dehydrogenation, and demethanation reactions were involved in the polymer-to-

ceramic conversion of CPSZ. The ceramization process was complete at 900°C with a ceramic yield of 81–84%. Elemental analysis indicated that the compositions of final ceramics can be tailored by controlling the feed ratios of the starting chlorosilanes. Moreover, the microstructural evolution of the resultant Si—C—N ceramics was further investigated by X-ray diffraction, Raman spectroscopy, and transmission electron microscopy. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1286–1292, 2011

Key words: precursors-organic; crosslinking; thermal properties; SiC; Si₃N₄

INTRODUCTION

Synthesis of silicon-based nonoxide ceramics via polymer pyrolysis offers attractive advantages in terms of processing temperatures, chemical purity, structure homogeneity, and achievable chemical and phase composition.^{1,2} Among these polymer-derived ceramics, silicon carbonitride (Si—C—N) ceramics derived from silicon-containing polymers are candidate materials for high-temperature applications.^{3,4} As is well known, polysilazanes (PSZs) have been investigated as precursors to Si—C—N ceramics for over 30 years.^{5–8} Ammonolysis reactions have been explored extensively and have become the major synthesis methods for PSZ. Of the wide variety of PSZs, copolysilazanes (CPSZs) have found wide applications as precursors to Si—C—N ceramics,

which is due to the simplicity in controlling the properties of the ammonolysis products (polymer structure, viscosity, thermal stability, etc.) by varying the chlorosilazane monomers.^{9–11}

CPSZ was originally synthesized by Seyferth through ammonolysis of a mixture of trichlorosilane and methylchlorosilane.^{12,13} By design of the chlorosilanes mixture, well-defined CPSZ can be achieved, which are useful to study precursor chemistry and the polymer-to-ceramic conversion. Commercially available CPSZs were gradually explored, such as HVNG (average formula $-\text{[CH}_3\text{HSiNH]}_n-\text{[(CH}_2=\text{CH)Si(NH)}_{1.5}\text{]}_n-$), HPS (average formula $-\text{[CH}_3\text{HSiNH]}_n-\text{[CH}_3(\text{CH}_2=\text{CH)SiNH]}_n-$), CERASETTM, etc.^{14,15} CERASET has drawn great attention for its high ceramic yield and tailorable viscosity.^{16–18} The precursor is prepared by a two-step reaction (1): reacting ammonia with dichloromethylsilane ($\text{CH}_3\text{SiHCl}_2$) and dichloromethylvinylsilane ($\text{CH}_3\text{Si}(\text{CH}=\text{CH}_2)\text{Cl}_2$) (2); reacting ammonolysis product with isocyanate.¹⁵ However, the introduction of oxygen element from isocyanate is detrimental to the control of elemental and phase composition of the final ceramic.⁷ It is still a challenge to realize the various demands, such as tailorable molecular weights and chemical composition, shaping capabilities, high ceramic yields, and desired microstructure of final ceramics in one precursor molecule.

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It was reported that trichlorosilanes can be varied to introduce branching, thus control the viscosity.^{7,10} In this work, a series of liquid CPSZs with tailorable molecular weights and chemical structure were prepared by ammonolysis of $\text{CH}_3\text{SiHCl}_2$, $\text{CH}_3\text{Si}(\text{CH}=\text{CH}_2)\text{Cl}_2$ and trichloromethylsilane (CH_3SiCl_3). CH_3SiCl_3 , a relatively cheap and commercially available monomer, was incorporated to adjust the average molecular weight and chemical composition of the resultant CPSZ. In the present work, the preparation of the CPSZ becomes more simple and controllable via the one-step synthesis route. Compared to CERASET synthesis, the following reaction with isocyanate is not necessary. The precursor's characterization, properties, and pyrolytic conversion to Si—C—N ceramics are investigated.

EXPERIMENTAL

Synthesis

All manipulations were carried out in an inert gas atmosphere. Hexane was dried with a sodium benzophenone mixture under reflux; the chlorosilanes were distilled; ammonia (>99.999%) was used as received.

A series of experiments of synthesizing liquid CPSZs were designed with different molar ratios of $\text{CH}_3\text{SiHCl}_2/\text{CH}_3\text{Si}(\text{CH}=\text{CH}_2)\text{Cl}_2/\text{CH}_3\text{SiCl}_3$ as 3/1/1, 3/1/2, and 3/1/4. One typical synthesis of CPSZ was described as the following procedure. Dry hexane (500 mL), $\text{CH}_3\text{SiHCl}_2$ (0.2 mol and 23 g), $\text{CH}_3\text{Si}(\text{CH}=\text{CH}_2)\text{Cl}_2$ (0.067 mol and 9.4 g), and CH_3SiCl_3 (0.13 mol and 20 g) were introduced into a 2 L, three-necked flask equipped with a reflux condenser, mechanical stirrer, and an ammonia/nitrogen inlet tube. The ammonia was gradually added to the mixed solution while being stirred. After 2 h, the ammonia flow was stopped, and the reaction mixture was cooled to room temperature (RT). This mixture was kept in a 60°C oil bath for 2 h and then separated by a glass-fritted funnel to remove the precipitated ammonium chloride. The solvent was removed at 60°C under vacuum to give 15.5 g of viscous transparent oil with a yield of about 60%.

Curing and pyrolysis

Thermal curing of the CPSZ was carried out in an argon atmosphere, using 2 g samples in a Schlenk flask placed in a 180°C oil bath. The liquid transformed into a compact, pale, rubbery solid after kept at this temperature for 24 h. For $T_p < 900^\circ\text{C}$ (T_p being the highest temperature during pyrolysis), the cured sample was put in a graphite crucible and heated in a glass silica tube under an argon flow. The temperature was progressively raised up to T_p at a rate of 5°C/min and kept at this value for 1 h. For $T_p > 900^\circ\text{C}$, the sample (prepyrolyzed at 900°C)

was put in a graphite crucible, heated rapidly to T_p at a rate of 40°C/min, and kept at this temperature for 10 min under an argon flow. After pyrolysis, the resulting ceramic was furnace-cooled to RT.

Characterization

Fourier transformed infrared (FTIR) spectroscopy (transmission mode) was used by a Nicolet Avator 360 apparatus (Nicolet, Madison, WI) with KBr plates for liquid samples and KBr disks for solid samples. NMR experiments were carried out on a Bruker AV300 MHz spectrometer (Bruker, Germany) operating at 300.13 MHz for ^1H , 75.46 MHz for ^{13}C (^1H decoupling), and 59.63 MHz for ^{29}Si (^1H decoupling), and the delay time was 30 s. The specimen used for NMR was dissolved in CDCl_3 solution. Gel permeation chromatography (GPC) was performed using an Agilent 1100 system (Agilent, Palo Alto, CA) at 35°C in THF as the eluant (1.0 mL/min). Average molecular weights were obtained from narrow polystyrene standards. Thermal analysis for the pyrolytic conversion of the cured CPSZ was performed on a thermal gravimetric analysis (TGA; Netzsch STA 409C, Netzsch, Germany) in argon gas with a heating rate of 10°C/min ranging from RT to 1400°C. Elemental analyses were carried out by a Horiba Carbon/Sulfur Analyzer EMIA-320V (Horiba, Japan) for the carbon element, a Horiba Oxygen Nitrogen Analyzer EMGA-620W for the oxygen, and nitrogen element. The silicon content was calculated as the difference of the sum of the measured carbon, nitrogen, and oxygen content to 100%. X-ray diffraction (XRD) studies were executed on a PANalytical X'Pert PRO diffractometer (PANalytical, the Netherlands) with $\text{Cu K}\alpha$ radiation. The specimens were continuously scanned from 10° to 90° (2 θ) at a speed of 0.0167°/s. Raman spectra were recorded on a Raman spectrometer (LabRam I, Dilor, France). Transmission electron microscopy observations and high resolution image were performed using a JEM 2100 (JEOL, Japan) operated at 200 kV.

RESULTS AND DISCUSSION

Synthesis and characterization of CPSZ

A series of CPSZs with various molecular weights were synthesized by controlling the molar ratio of starting materials in feed. The GPC result (Fig. 1) reveals that the CPSZ has wide molecular distribution, which might be due to the branching when CH_3SiCl_3 is used as the monomer.

As shown in Table I, the number-average molecular weights (M_n), weight-average molecular weights (M_w) as well as the polydispersity index (D) increase with the increase of CH_3SiCl_3 in feed, suggesting

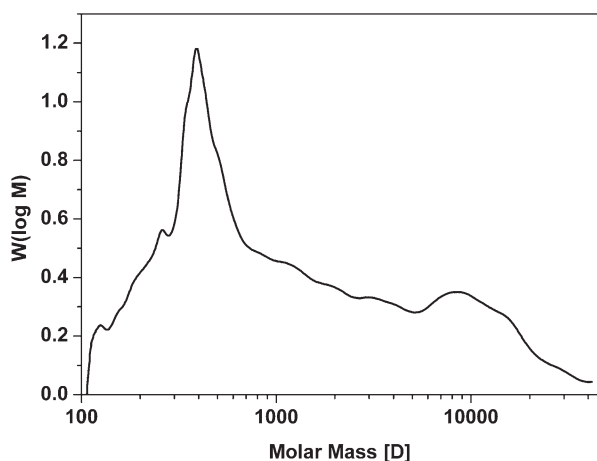


Figure 1 Typical GPC curve of CPSZ in THF.

that the branching degree of the CPSZ enhanced. The synthesized CPSZs were not sensitive to air and moisture and could be kept in air for several days without obvious viscosity increasing, which would be convenient for later processing.

The as-synthesized CPSZs were characterized by FTIR and NMR. The functional groups of the resulting polymer were identified by FTIR (Fig. 2). The Si–NH–Si stretching at 1175 cm^{-1} and the N–H stretching in Si–NH at 3385 cm^{-1} indicate that the Si–NH–Si chain, the backbone of polymer, exists in this polymer. The bands at around 1250 cm^{-1} (Si–CH₃ stretching) and 1400 cm^{-1} (Si–CH₃ deformation), and at 2955 and 2900 cm^{-1} (C–H stretching in Si–CH₃) show the existence of Si–CH₃. The bands at around 1590 cm^{-1} (C=C stretching) and at 3050 and 3005 cm^{-1} (C–H stretching in CH=CH₂) show the existence of Si–CH=CH₂. The strong band at 2120 cm^{-1} is assigned to the Si–H group.¹⁰ The FTIR results confirm the existence of functional groups in CPSZ including Si–NH–Si, Si–CH₃, –CH=CH₂, and Si–H.

The structure of CPSZ was further confirmed by NMR spectra (Fig. 3). ¹H signals [Fig. 3(a)] are detected at 0–0.5 ppm (Si–CH₃), 0.5–1.3 ppm (Si–NH–Si), 4.2–5.0 ppm (Si–H), 5.6–6.0 ppm (Si–CH=CH₂), 6.0–6.3 ppm (Si–CH=CH₂).¹⁰ Calculated from ¹H-NMR, the relative content of each structural unit can be determined and shown in Table I. The structural units of [CH₃HSiNH],

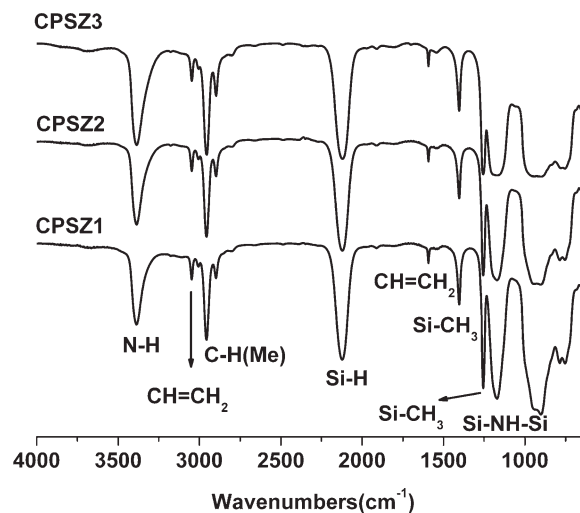


Figure 2 FTIR spectra of the synthesized CPSZs.

[CH₃(CH₂=CH)SiNH] and [CH₃Si(NH)_{1.5}] are derived from the corresponding monomers of CH₃HSiCl₂, CH₃(CH₂=CH)SiCl₂, and CH₃SiCl₃. Careful examination shows that the molar ratio of [CH₃HSiNH]/[CH₃(CH₂=CH)SiNH] is lower than the theoretical value while that of [CH₃Si(NH)_{1.5}]/[CH₃(CH₂=CH)SiNH] is higher than the theoretical one. It seems that CH₃SiCl₃ is more active than CH₃SiHCl₂. The ratio of three structural units varies in proportion with the feed ratio of comonomers. As expected, CPSZs with tailorable chemical structure were synthesized by adjusting the amount of starting materials.

The ¹³C-NMR spectra [Fig. 3(b)] show three groups of peaks, which are assigned to CH=CH₂ (141 ppm), CH=CH₂ (132 ppm), and Si–CH₃ groups (–3 – 10 ppm).¹⁰ A broad peak appears in the ²⁹Si-NMR spectrum [Fig. 3(c)], which comprises superposed –14 to –17 ppm (N₂Si(CH₃)CH=CH₂), –22 ppm (N₂Si(H)CH₃), and –22 ppm (N₃SiCH₃) resonances.^{10,14,19} The minor peak at –32 ppm is assigned to NSi(H₂)CH₃, which is the functionality of the ammonolysis byproduct of CH₃SiHCl₂.²⁰

The broad signals detected in the ²⁹Si-NMR and ¹H-NMR spectra indicate that CPSZ may have both different substitution patterns and different numbers of monomeric [≡Si–NH–] units. According to the

TABLE I
Synthesis and Molecular Weights of CPSZs with Different Amount of CH₃SiCl₃

Polymer	Feed molar ratio ^a	Structural unit molar ratio ^b	M_n (g mol ⁻¹)	M_w (g mol ⁻¹)	D
CPSZ1	3/1/1	2.8/1/1.2	400	1700	4.2
CPSZ2	3/1/2	2.7/1/2.2	500	2300	4.6
CPSZ3	3/1/4	2.7/1/3.5	600	4500	7.5

^a Feed molar ratio denotes CH₃SiHCl₂/CH₃Si(CH=CH₂)Cl₂/CH₃SiCl₃.

^b Structural unit molar ratio denotes [CH₃HSiNH]/[CH₃(CH₂=CH)SiNH]/[CH₃Si(NH)_{1.5}], which is calculated from ¹H-NMR.

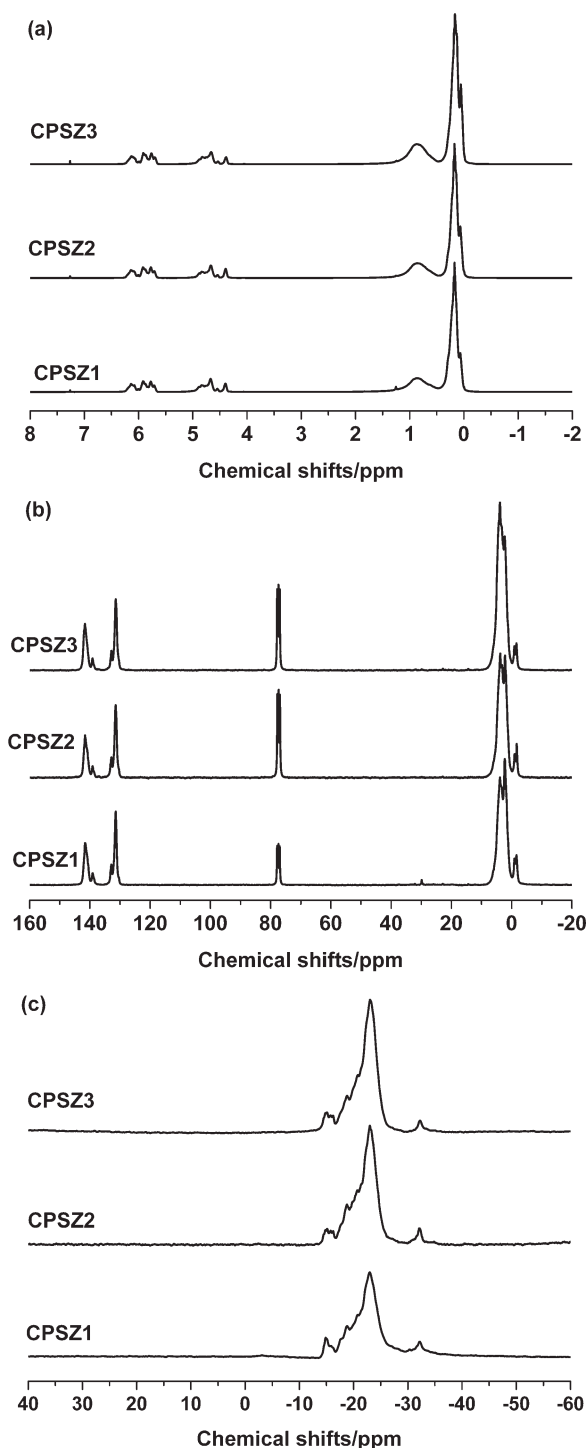
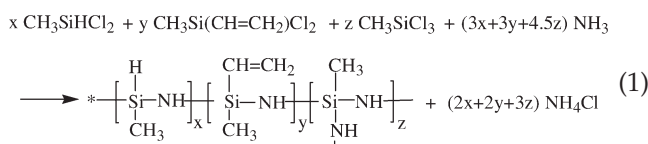


Figure 3 NMR spectra of CPSZs: (a) ^1H -NMR; (b) ^{13}C -NMR; (c) ^{29}Si -NMR.

FTIR and NMR results, the CPSZs with expected structure were prepared. Equation (1) represents the overall reaction:



Ceramic conversion of CPSZ

It was reported by Seyferth that a previous cross-linking treatment before pyrolysis could improve the final ceramic yield.²¹ In the present work, the as-synthesized CPSZ was thus treated at 180°C for 24 h to gain a pale solid. And then, the structure changes and thermal behavior of the cured CPSZ during the ceramic conversion were measured. After curing at 180°C, the absorption intensities of the active groups (vinyl at 3050 cm^{-1} , Si-H at 2120 cm^{-1} , and N-H at 3385 cm^{-1}) obviously decrease as shown in Figure 4.

The vinyl reaction degree (P_{vinyl}) of the polymer is measured through the characteristic peak's ratio of vinyl to Si-CH₃ in FTIR spectra.²² The Si-H and N-H reaction degree ($P_{\text{Si-H}}$ and $P_{\text{N-H}}$) are determined similarly. The P_{vinyl} , $P_{\text{Si-H}}$, and $P_{\text{N-H}}$ are calculated according to the following eqs. (2)–(4):

$$P_{\text{vinyl}} = \frac{(A_{3050}/A_{1250})_{\text{uncured}} - (A_{3050}/A_{1250})_{\text{cured}}}{(A_{3050}/A_{1250})_{\text{uncured}}} \quad (2)$$

$$P_{\text{N-H}} = \frac{(A_{3385}/A_{1250})_{\text{uncured}} - (A_{3385}/A_{1250})_{\text{cured}}}{(A_{3385}/A_{1250})_{\text{uncured}}} \quad (3)$$

$$P_{\text{Si-H}} = \frac{(A_{2120}/A_{1250})_{\text{uncured}} - (A_{2120}/A_{1250})_{\text{cured}}}{(A_{2120}/A_{1250})_{\text{uncured}}} \quad (4)$$

At 180°C, the calculated P_{vinyl} , $P_{\text{Si-H}}$, and $P_{\text{N-H}}$ are 34%, 10%, and 9%, respectively. As shown in Table I, the factual $M_{\text{vinyl}}/M_{\text{Si-H}}$ (overall molar ratio of vinyl to Si-H groups) of CPSZ2 is 1/2.7. The reacting molar ratio of vinyl to Si-H is close to stoichiometric because of $P_{\text{vinyl}} \cdot (M_{\text{vinyl}}/M_{\text{Si-H}}) / P_{\text{Si-H}} = 1.2$. The results indicated that the hydrosilylation reaction [eq. (5)] occurred via consumption of vinyl and Si-H bonds. In addition, transamination reaction

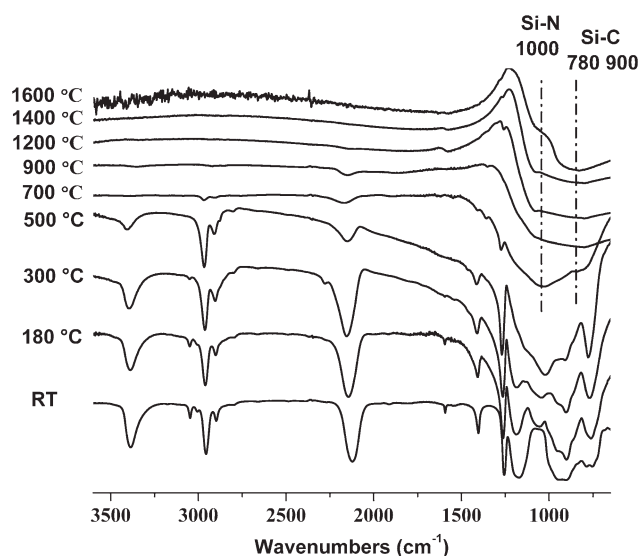


Figure 4 FTIR spectra of CPSZ2 heat-treated at different temperatures.

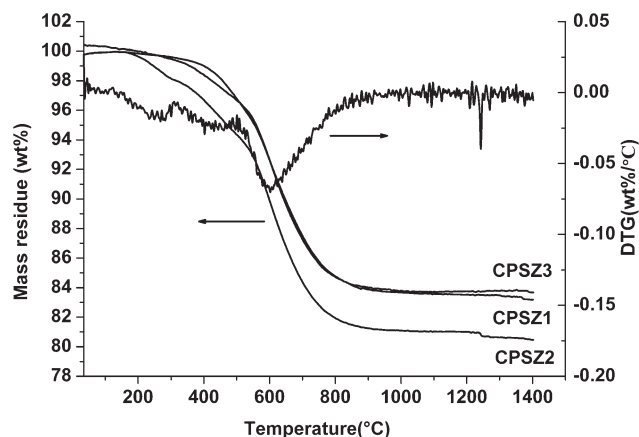
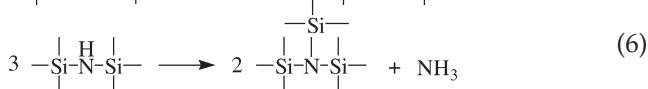
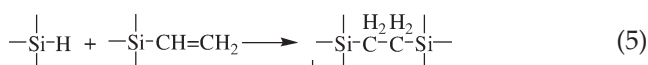


Figure 5 TGA curves of cured CPSZs at 180°C for 24 h.

[eq. (6)] was involved in the solidification of CPSZ at a relatively low temperature of 180°C, which is supported by the fact that 9% N—H bonds were consumed. It was reported by Kroke that the hydrosilylation reaction and transamination reaction contributed to the crosslinking of PSZ.⁷ In the present study, the hydrosilylation and transamination reactions are responsible for the solidification at 180°C by means of FTIR.

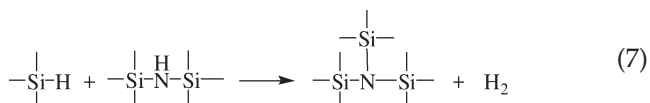


Between 180 and 300°C, further hydrosilylation and transamination reaction occurred during this process, as the absorption of vinyl groups at 3050 and 1590 cm^{-1} almost disappeared and the N—H absorption band at 3385 cm^{-1} decreased in the FTIR spectra at 300°C.

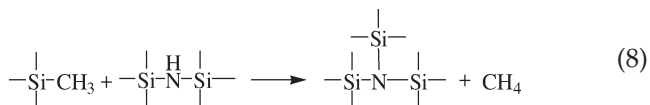
To investigate the thermal behavior of the CPSZ accompanied by its structure evolution, TGA curves of CPSZs are shown in Figure 5. With the aid of the first derivative, three main regions can be identified in the weight loss curves. The corresponding weight losses are 0.5–2 wt % (180–300°C), 3 wt % (300–500°C), and 13 wt % (500–900°C). The first weight loss occurred between 180 and 300°C and was caused by the evolution of ammonia derived from the transamination reaction [eq. (6)] and/or

distillation of low-molecular weight oligomers.⁹ The low weight loss well demonstrates the efficiency of the crosslinking process.

The second weight loss occurred between 300 and 500°C and was associated with the evolution of ammonia and hydrogen.^{9,16} As mentioned earlier, the ammonia is produced by transamination reaction [eq. (6)]. The hydrogen was attributed to the dehydrogenation reaction [eq. (7)],^{7,23} which is supported by that the bands at 3385 and 1175 cm^{-1} from N—H and 2120 cm^{-1} from Si—H decrease dramatically in the FTIR spectra between 300 and 500°C.



The third weight loss corresponded to the ceramization step between 500 and 900°C. During this step, N—H, C—H, Si—H, and Si—CH₃ were cleaved. The FTIR spectra reveal a significant decrease of bands at 3385, 2955, 2120, and 1250 cm^{-1} respectively. The possible dehydrogenation and demethylation reactions can be demonstrated as [eqs. (7) and (8)] for their lower reaction enthalpy.²³ The polymer-to-ceramic conversion is complete at 900°C as the organic groups almost disappear in the FTIR spectra. The 900°C spectrum shows a broad absorption band in the range of 750–1100 cm^{-1} , comprising superposed Si—N (1000 cm^{-1}) and Si—C (780 and 900 cm^{-1}) bond vibration.^{24–26}



Subsequently, the spectra of samples at 1200 and 1400°C are similar to that of the one at 900°C. At 1600°C, an increase in intensity and sharpening of the Si—C (780 and 900 cm^{-1}) bands relative to the Si—N (1000 cm^{-1}) bands is observed, suggesting the formation of crystalline SiC.^{25,26}

To investigate the influence of the feed ratios of the starting materials on the composition of the final ceramics, elemental analysis was performed, and the results are given in Table II. Generally, the structural unit derived from CH₃SiCl₃ contains more nitrogen than that from dichlorosilanes. With the increase of CH₃SiCl₃ in feed, more nitrogen and less carbon are

TABLE II
Average Formulas for Polymers and Ceramics

Polymer	Feed molar ratio ^a	Average formula for polymer	Average formula for 900°C ceramic	Average formula for 1400°C ceramic
CPSZ1	3/1/1	SiC _{1.19} N _{0.74} O _{0.03}	SiC _{0.69} N _{0.86} O _{0.09}	SiC _{0.71} N _{0.86} O _{0.08}
CPSZ2	3/1/2	SiC _{1.15} N _{0.80} O _{0.03}	SiC _{0.66} N _{0.88} O _{0.12}	SiC _{0.70} N _{0.93} O _{0.09}
CPSZ3	3/1/4	SiC _{1.12} N _{0.89} O _{0.03}	SiC _{0.60} N _{1.01} O _{0.15}	SiC _{0.68} N _{1.04} O _{0.16}

^a Feed molar ratio denotes CH₃SiHCl₂/CH₃Si(CH=CH₂)Cl₂/CH₃SiCl₃.

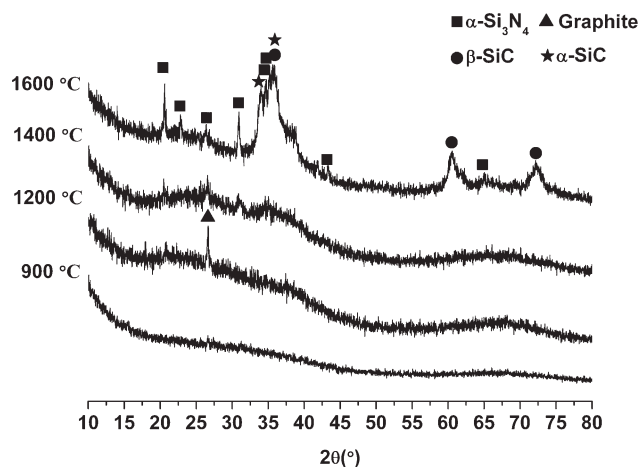


Figure 6 XRD patterns of CPSZ2-derived Si-C-N ceramics pyrolyzed at different temperatures.

expected in the precursor. The chemical analysis of the ceramics pyrolyzed at 900 and 1400 °C follows the same trend. So, the compositions of final ceramics can be tailored by controlling the feed ratios of the starting chlorosilanes. In summary, the ceramic yields of CPSZs range from 81 to 84% at 900 °C, together with its tailorable molecular weight and chemical composition, which make CPSZ a promising precursor to Si-C-N ceramics.

Crystallization

The evolution of the crystalline phases was studied by XRD as shown in Figure 6. It shows that the 900 °C ceramic is amorphous and highly disordered. Further heating at 1200 °C leads to the formation of graphite. At 1400 °C, a very small amount of α - Si_3N_4 can be detected. The intensity of the α - Si_3N_4 peaks increases rapidly above 1400 °C. The crystallization of SiC has started at 1600 °C. The crystallized SiC is a mixture of β -phase and the α -phase.

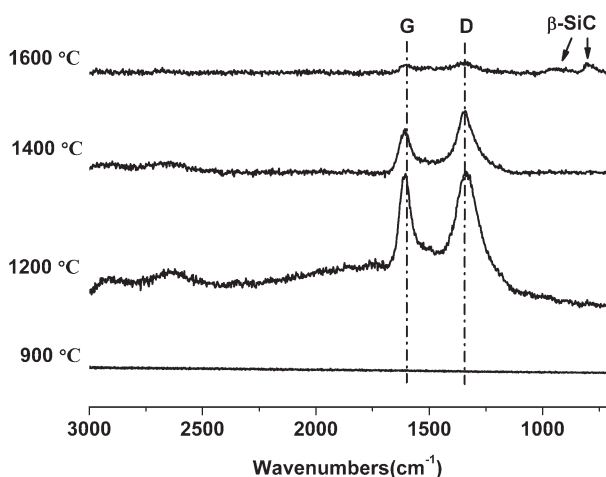


Figure 7 Raman spectra of CPSZ2-derived Si-C-N ceramics pyrolyzed at different temperatures.

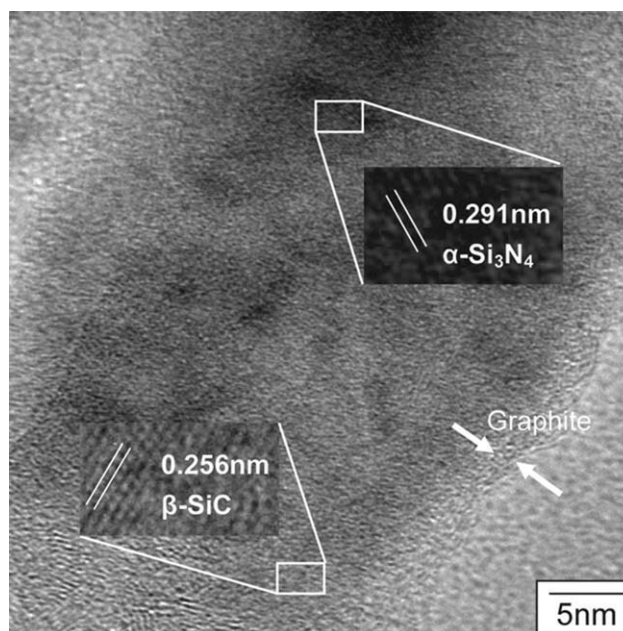


Figure 8 HRTEM imaging of CPSZ2-derived Si-C-N ceramics pyrolyzed at 1600 °C.

Raman spectroscopy is one of the most sensitive methods for the characterization of the different modifications of carbon. Raman investigations (Fig. 7) were thus carried out to get insight into the correlation between the evolution of free carbon and the crystallization of SiC.

In the spectrum of the CPSZ2-derived ceramic at 900 °C, no signals are observed. For $T_p = 1200$ °C, two peaks centered around 1330 and 1600 cm^{-1} are discernable, which correspond to the D and G peaks observed in free carbon.^{27,28} The Raman spectrum indicates the carbon network interconnects at long distance to form free carbon at 1200 °C. At 1600 °C, two new bands centered at 790 and 960 cm^{-1} attributed to β -SiC appeared, accompanied by the decrease of free carbon absorption band.^{28,29} It might be due to the reactions of free carbon with Si_3N_4 above 1500 °C [eq. (9)].^{11,16,23}



Microstructural evolution in the Si-C-N ceramic treated at 1600 °C was analyzed using high-resolution transmission electron microscopy (HRTEM). The HRTEM imaging of CPSZ2-derived Si-C-N ceramics pyrolyzed at 1600 °C is shown in Figure 8. It is observed that amorphous Si-C-N phase is surrounded by cages of free carbon. Nanocrystals (2–3 nm) are found embedded in the amorphous phase. The interplanar spacing of the layers at 0.291 and 0.256 nm correspond to the $(2\ 0\ 1)_{\alpha\text{-Si}_3\text{N}_4}$ and $(1\ 1\ 1)_{\beta\text{-SiC}}$ planes. As expected, α - Si_3N_4 and β -SiC were detected in grains as shown in Figure 8, which is consistent with the XRD results.

CONCLUSIONS

In this work, a series of tailorable CPSZs were successfully prepared. The as-synthesized CPSZs were characterized by means of GPC, FTIR, and NMR. The CPSZ could be cured at a low temperature (180°C) in an inert atmosphere. Hydrosilylation, transamination, dehydrogenation, and demethanation reactions were involved in the polymer-to-ceramic conversion of CPSZ. Silicon nitride nucleated above 1400°C while silicon carbide formed from the reaction of free carbon with silicon carbonitride upon annealing at 1600°C. The ceramic yield of CPSZ ranging from 81 to 84% at 900°C, together with its tailorable chemical composition and final ceramic composition, makes CPSZ a promising precursor to Si—C—N ceramics.

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