

# Synthesis and Pyrolysis of Polysilazane Precursors Containing Linear–Cyclic Structures for Si/N/C-Based Ceramics

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**ABSTRACTS:** A new kind of polysilazane precursor containing linear–cyclic structure was synthesized from the de-lithium chloride condensation reaction of hexamethylcyclotrisilazane lithium salts ( $D_3^{NLi}$ ) and 1,3-dichlorotetraorganodisilazanes  $[(ClR_1R_2Si)_2NH]$ . Pyrolyses of these precursors and some comparable linear polysilazanes were carried out at 900 °C in nitrogen. The results indicated that the existence of linear–cyclic structure in precursors provided relatively crosslinked or branched structures, which were helpful for improving ceramic yields. The precursor containing a linear–cyclic structure as well as reactive vinyl groups gave the highest pyrolytic yields. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2827–2831, 2001

**Key words:** polysilazane precursors; Si/C/N-based ceramics; pyrolysis

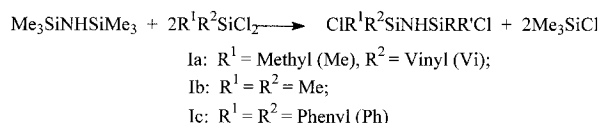
## INTRODUCTION

Silicon-based nonoxide ceramics, such as silicon nitride ( $Si_3N_4$ ) and silicon carbide (SiC), have attracted continuous interest for many years.<sup>1–3</sup> Their chemical durability, low density, great hardness, and high mechanical strength at high temperature make them uniquely applicable to extreme conditions. Since the pioneering work of Verbeek<sup>4</sup> and Yajima<sup>5</sup> in the 1970s, intense research over the past 25 years has focused on the elaboration of SiC-,  $Si_3N_4$ -, or Si/C/N-based materials from organosilicon precursors.<sup>6–8</sup> Compared with more traditional powder-forming methods, the precursor method has attractive characteristics, such as lower processing temperature and the ability to prepare ceramic fibers,

films, and other fiber-reinforced ceramic matrix composites having complex shapes, which is difficult with conventional technologies. The properties of the final ceramic materials strongly depend on the structures and the chemical composition of precursors. Many experiments have shown that polysilazanes containing Si-alkyl or aryl groups can be pyrolyzed under an inert atmosphere to produce Si/C/N-based ceramics, and the ceramic composition can be varied by changing the polymer composition.<sup>9–11</sup> According to the literature, the ideal precursors should (a) have a branched, ring, or cage structure to decrease the polymer skeleton degradation, and (b) contain latent chemical reactivity to form a networked structure during pyrolysis to obtain a high ceramic yield.<sup>12,13</sup> In an attempt to prepare precursors that accord with these rules, we designed a new route to synthesize polysilazanes containing linear–cyclic structures as well as reactive groups via the condensation of hexamethylcyclotrisilazane lithium salts ( $D_3^{NHi}$ ) and 1,3-dichlo-

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Scheme 1

rotetraorganodisilazanes. These precursors were pyrolyzed under nitrogen environment. Ceramic yields depended on the composition and molecular structure of the precursors.

## EXPERIMENTAL

### Materials

All liquid organosilicon compounds were purchased from Beijing Chemical Works or from Kaihua Organosilicon Factory and were purified by distillation. Tetrahydrofuran (THF) and *n*-hexane were commercially available. They were dried by refluxing over sodium and distilled under a nitrogen atmosphere. Reactions were carried out in glass equipment, which was oven dried and flushed with dry nitrogen just before use.

### Measurements

Fourier-transform infrared (FT-IR) spectra were obtained with a Perkin-Elmer 2000 IR spectrometer in the wave number range 4000–370  $\text{cm}^{-1}$  using standard procedures. Number-average molecular weights were determined with a Knauer vapor pressure osmometer (VPO) in  $\text{CHCl}_3$  solution.  $^1\text{H}$  and  $^{29}\text{Si}$  nuclear magnetic resonance (NMR) spectra of samples were recorded with a Unity 200 MHz spectrometer, with deuterated chloroform as a solvent and hexamethyldisiloxane (MM,  $\delta^{29}\text{Si}$  6.90) as an external reference in  $^{29}\text{Si}$  NMR. Thermogravimetric analysis (TGA) curves of samples were obtained by a Perkin-Elmer 7 thermal balance in 40  $\text{cm}^3/\text{min}$  nitrogen flow up to 800  $^\circ\text{C}$ , at a heating rate of 10  $^\circ\text{C}/\text{min}$ .

### Pyrolysis

Pyrolyses to 900  $^\circ\text{C}$  (under  $\text{N}_2$ ) were performed using a SK2-1-10 tube furnace equipped with a KSW-2-11 controller and a quartz tube. Fused silica boats were used to contain the precursor in the quartz tube. After the samples were introduced into the furnace, an initial furnace purge of 200  $\text{cm}^3/\text{min}$  was run for 15 min to remove oxygen before heating. Then the gas flow was decreased,

and a flow of 80  $\text{cm}^3/\text{min}$  was used during the pyrolysis. The temperature program used was as following: ambient temperature to 350  $^\circ\text{C}$  at 10  $^\circ\text{C}/\text{min}$ , hold at 350  $^\circ\text{C}$  for 0.5 h, 350–900  $^\circ\text{C}$  at 10  $^\circ\text{C}/\text{min}$ , and hold at 900  $^\circ\text{C}$  for 1 h. Every sample was pre-heat treated (190  $^\circ\text{C}/2$  h) under nitrogen before pyrolysis.

## Synthesis

### 1,3-Dichlorotetraorganodisilazanes Synthesis (Ia–Ic)

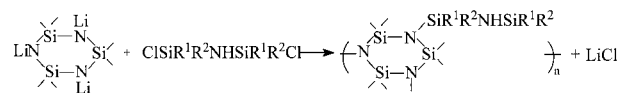
The syntheses of 1,3-dichlorodisilazanes **Ia–Ic** were according to our previous work<sup>14</sup> as shown in Scheme 1.

### Hexamethylcyclotrisilazane Lithium Salts ( $\text{D}_3^{\text{NLi}}$ ) Synthesis

Hexamethylcyclotrisilazane lithium salts ( $\text{D}_3^{\text{NLi}}$ ) were prepared by using a method of Fink<sup>15–17</sup> with some modification. For example, in a 100-mL three-necked, round-bottomed flask equipped with a dropping funnel and a gas inlet tube, 30 mL of freshly distilled *n*-hexane and 36.88 mmol *n*-BuLi (solution in hexane) were charged by syringe after the air in the flask was replaced by dry nitrogen. To the solution, a mixture of 36.50 mmol hexamethylcyclotrisilazane ( $(\text{Me}_2\text{SiNH})_3$ ,  $\text{D}_3^{\text{N}}$ ) and 10 mL of hexane was added in a dropwise manner while stirring. An immediate white precipitate formed. The reaction mixture was stirred for 3 h at room temperature (25  $^\circ\text{C}$ ). Then the solvent was removed by filtration under nitrogen. The white precipitate was washed with hexane and dried under vacuum to give 8.47 g of  $\text{D}_3^{\text{NLi}}$  (98%).  $\text{D}_3^{\text{NLi}}$  is very sensitive to air and moisture, so it must be kept under an inert atmosphere.

### Precursors Synthesis

Polysilazane precursors (PSZ) were prepared from the reaction of  $\text{D}_3^{\text{NLi}}$  and 1,3-dichlorotetraorganodisilazanes **I**. The synthesis is described in Scheme 2. As an example, PSZ-1 was synthesized as follows: 21.70 mmol  $\text{D}_3^{\text{NLi}}$ , 10 mL of THF, and 60 mL of hexane were added into a 100-mL three-necked flask equipped with a dropping funnel and a gas inlet. To the solution, a mixture of 32.55



Scheme 2

mmol **1c** and 10 mL of THF was added in a dropwise manner at 25 °C. The mixture was stirred for a further 8 h at room temperature. Then, high-purity NH<sub>3</sub> was bubbled through the mixture for 4 h to eliminate any unreacted Si—Cl bonds. Precipitated LiCl and NH<sub>4</sub>Cl were removed by filtration, and the resulting clear solution distilled to give 14.53 g of PSZ-1 as a pale yellow resinous solid.

## RESULTS AND DISCUSSION

### Synthesis and Characterization of the Polysilazane Precursors

Polysilazane precursors were prepared from the reaction of D<sub>3</sub><sup>NLi</sup> and different starting 1,3-dichlorodisilazanes as shown in Table I.

It is well known in the art that a Si—N bond can be formed from the elimination of lithium chloride between Si—Cl and N—Li.<sup>18</sup> Compared with another reaction, hydrogen chloride elimination between ≡Si—NH—Si≡ and ≡Si—Cl, which also results in the formation of a Si—N bond, the reaction of Si—Cl and N—Li is carried out under milder conditions. The produced LiCl precipitated from organic solvents and the Si—N bonds in cyclodisilazane were not cleaved. Thus, the silazane precursors containing cyclic and linear units can be obtained. However, the products were very complicated because of the complication of 3–2 functional polycondensation between D<sub>3</sub><sup>NLi</sup> and 1,3-dichlorodisilazane. The complication was demonstrated by their NMR and FT-IR spectra. For example, the <sup>29</sup>Si NMR spectra of sample PSZ-1 consist of two-group resonance peaks. The signals in the range δ -0.5 to -5.8 are assigned to N—SiMe<sub>2</sub>—N in the cyclic, and the signals in the range δ -18.3 to -31.6 are assigned to N—SiPh<sub>2</sub>—N. The FT-IR spectrum of PSZ-1 is shown in Figure 1. The spectrum exhibits C—H stretching in the phenyl group at 3068, 3053, and 3005 cm<sup>-1</sup>. A strong peak at 1428 cm<sup>-1</sup> and four

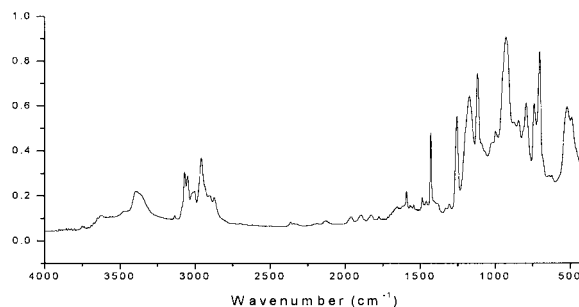


Figure 1 FT-IR spectrum of PSZ-1.

weak peaks at 1959, 1892, 1827, and 1773 cm<sup>-1</sup> are attributed to the Si-phenyl vibration. The peak at 925 cm<sup>-1</sup> is typical of asymmetric stretching of Si—N—Si. The peak at 700 cm<sup>-1</sup> is Si—C symmetric stretching. The peaks at 3392 and 1170 cm<sup>-1</sup> are assigned to the N—H bond. All PSZ samples are tractable and can be dissolved in common solvents, such as toluene, THF, and hexane.

### Pyrolytic Yields

To evaluate PSZ as ceramic precursor, we performed a series of bulk pyrolysis and TGA experiments on these samples and compared the results with those of similar experiments on the linear silazane oligomers PDMSZ and PVMSZ prepared according to Laine<sup>19</sup> and Duguet,<sup>20</sup> respectively. The results are shown in Table II. The pyrolytic behavior of polysilazane is affected by its structure. From the data of II, it can be shown that the ceramic yields are very dependent on the structures of the polymer precursors. The proposed structures of samples in Table 2 are shown in Scheme 3.

PSZ-1, PSZ-2 and PSZ-3 have similar structures, all containing the same cyclic segment, but different substituents are attached on Si atoms in the linear parts. PSZ-3, which contains a linear-cyclic structure and also the reactive group,

Table I Details of Polysilazane Precursors PSZ

Sample	(ClSiR <sup>1</sup> R <sup>2</sup> ) <sub>2</sub> NH	Si-Cl/NLi <sup>+</sup> (mol)	M <sub>n</sub>
PSZ-1	(ClPh <sub>2</sub> Si) <sub>2</sub> NH	1:1	2167
PSZ-2	(ClMe <sub>2</sub> Si) <sub>2</sub> NH	1:1	1765
PSZ-3	(ClMeViSi) <sub>2</sub> NH	1:1	1572

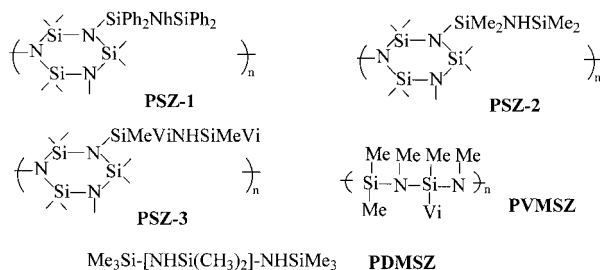
Table II Pyrolytic Yields of PSZ

Sample	Appearance	Pyrolytic Yields (%)
PSZ-1	Resinous solid	18.0
PSZ-2	Viscous liquid	10.2
PSZ-3	Viscous liquid	75.4
PDMSZ	Viscous liquid	negligable
PVMSZ	Viscous liquid	40.0

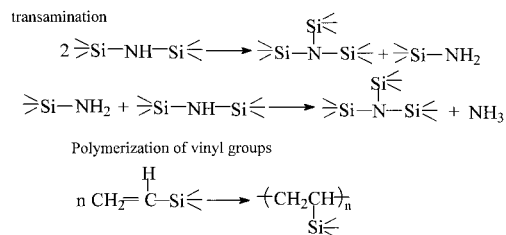
—CH=CH<sub>2</sub>, gave the highest ceramic yield. For PSZ-3, there were two reactions (Scheme 4) during pyrolysis that can make it more crosslinked, which were opposite to a thermolytic degradation reaction that caused the splitting out of volatile small molecules or cyclomers. During the pre-heat treatment, the polymerization of vinyl groups occurred, which further crosslinked PSZ-3. The crosslink not only retards the thermolytic degradation reaction that causes the splitting out of volatile small molecules, but also restrains the transamination because of bulk effects. However, for PSZ-1 and PSZ-2, which lack reactive groups that can be thermally crosslinked and for which the crosslink caused by transamination cannot counteract the weight loss by evolution of ammonia and small molecules, lower ceramic yields were obtained than with PSZ-3.

Between PSZ-1 and PSZ-2, neither of which contains reactive hydrocarbon substituents, PSZ-1 gave higher pyrolytic yields. The possible reasons for this result are that thermal degradation reactions were inhibited by bulky phenyl groups and the splitting of small molecules was decreased.

For PDMSZ and PSZ-2, both of which contain —SiMe<sub>2</sub>—NH— units, the former yielded negligible amounts of ceramic products but the latter gave 10.2% ceramic residue. The explanation for this result is suggested by their different molecular structures. The linear polysilazanes tend towards cyclization and, during pyrolysis, volatile cyclomers were split out from the polymer skeleton, leading to continuous weight loss. However, PSZ-2 contains a cyclic-linear structure, with the existence of the cyclic providing relatively high branching or cross linking that can decrease the thermolytic degradation reaction and cyclization. The results in Table II are similar for PSZ-3 and PVMSZ, both of which contain reactive vinyl groups. This phenomenon confirms the general empirical rule that the existence of cages or rings



**Scheme 3**



in polymer precursors is helpful to decrease the polymer degradation and to give higher ceramic residues.

## CONCLUSIONS

A new kind of polysilazane precursors containing a linear-cyclic structure was synthesized. Investigation on pyrolysis of these new precursors and some linear silazane precursors indicated that cyclic structures introduced into precursors could provide branching or cross linking, which are helpful for increasing ceramic yields. Precursors containing linear-cyclic structures as well as reactive functional groups can give better ceramic yields.

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