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Raising pyrolysis yield of preceramic polymers of silicon carbonitride

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Polymeric precursors for silicon carbonitrides are prepared by three synthetic routes starting with ammonolysis of dichloromethylsilane (CH_3SiHCl_2). Two methods for raising pyrolysis yield are investigated. One method is to enhance the degree of crosslinking by copolymerizing with trichlorosilane ($SiHCl_3$) consecutively. The other is to leach out the less soluble macromolecules in the polymer precursor by organic solvents. A 92% pyrolysis yield can be reached through combining these two methods. Those precursors with higher yields are characterized with weight losses and heat events during pyrolysis shifting towards higher temperatures.

1. Introduction

Polymeric precursors of silicon nitrides and carbides provide processing routes that are difficult for traditional powder processing. Various ceramic precursors were developed and applied to fabrications of ceramic fibres, coatings and near net-shape engineering [1, 2]. In the synthesis of precursors for silicon carbonitrides, most polymerization reactions started with ammonolysis or aminolysis of chlorosilicon compounds, which were inexpensive raw materials of high purity [3, 4]. Precursors were subsequently pyrolysed into mixed compounds of Si_3N_4, SiC, residual carbon and silica (if oxygen was present). The ratio of Si_3N_4/SiC and residual carbon could be adjusted by conditions during pyrolysis or through proper design of the molecular structure of the polymer [5–10].

Pyrolysis yield is one important criteria in evaluating a ceramic precursor. Raising pyrolysis yield can be achieved by introducing backbone branching and/or crosslinking into the macromolecular structure. Branching and crosslinking of the backbone can retard back reactions, which result in the production of volatile fragments during pyrolysis. Therefore chemical design of a preceramic polymer often involves bringing in appropriate reactive or potentially reactive functional groups so that crosslinking and branching can be done before pyrolysis [11, 12]. Functional groups of desired latent reactivity can also enhance crosslinking of macromolecules in the thermal pretreatment of pyrolysis [13, 14].

Although crosslinking was demonstrated to be very effective in raising pyrolysis yield, a near theoretical yield ($> 95\%$) was reported [15]. Understanding of the relationship between yield and synthesis (crosslinking or branching) is still limited. As-prepared silazane products often possess a considerable range of molecular weight and degree of crosslinking. Each macromolecule pyrolyses slightly differently and interacts with each other differently during pyrolysis. Systematic alteration of the molecular structure and appropriate separation of the precursor can shed more light on this relationship.

In this paper, the structure of the polymeric precursor is modified by branching and crosslinking its Si–N backbone with a trifunctional agent. The trifunctional crosslinking agent, $HSiCl_3$, was consecutively added into the synthetic route. Also, the prepared macromolecular mixture is separated by leaching out its lighter portion with organic solvents. The separated precursors allow one to analyse its individual contribution to the yield. The pyrolysis behaviour and other properties of the precursors after these chemical and physical treatments are investigated and discussed.

2. Experimental procedure

The starting chemical is dichloromethylsilane, CH_3SiHCl_2, (Aldrich, $> 97\%$), which has two active Si–Cl bonds, a relatively inert Si–H bond, and an inert Si–CH_3 bond. The basic synthetic procedure was ammonolysis of CH_3SiHCl_2 by NH_3, removal of NH_4Cl, deprotonation by potassium hydride and removal of potassium. The product was labelled as LPK. The involved chemistry details are well documented by Seyferth [12].

The ammonolysis product (LP) consisted of linear and cyclic oligomers with many basic amino groups. Therefore, the synthesis route could be altered by reacting LP with trichlorosilane, $HSiCl_3$ (ICI, $> 98\%$), whose Si–Cl bonds would undergo nucleophilic attack on those amino groups. Consequently, these oligomers were crosslinked or branched by this

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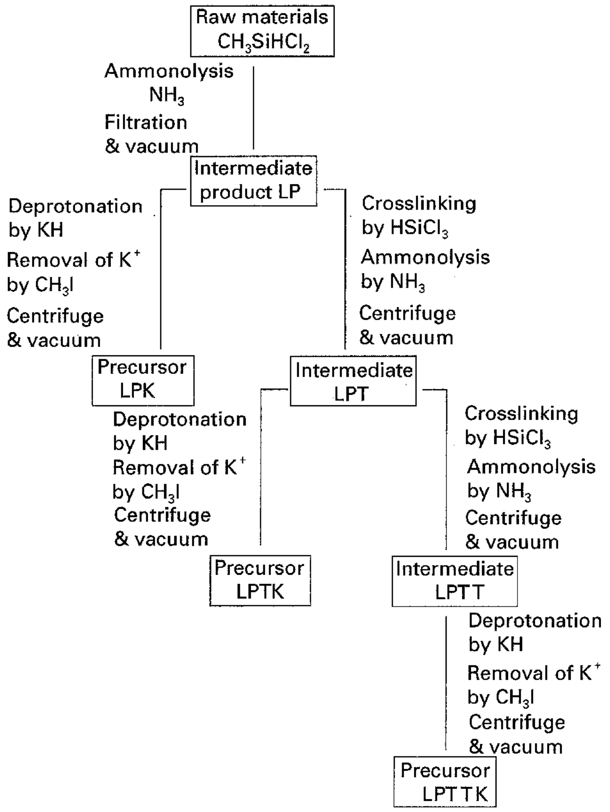


Figure 1 Consecutive synthesis procedures for precursors LPK, LPTK and LPTTK.

trifunctional $HSiCl_3$. The crosslinked polymer was then treated with ammonia again, to remove chlorine in Si–Cl and replace it with an NH_2 group. An intermediate product LPT was obtained. After deprotonation and removal of potassium, LPT was converted into precursor LPTK, which was $HSiCl_3$ and NH_3 treated once. Similarly, precursor LPTTK was made by consecutively crosslinking with $HSiCl_3$ and ammonolysis twice. The synthetic routes of LPK, LPTK and LPTTK are illustrated in Fig. 1. The molar ratio of $HSiCl_3 : CH_3SiHCl_2$ was 6 : 100 in the first addition of $HSiCl_3$. This molar ratio was reduced to 3 : 100 in the second addition of $HSiCl_3$.

Separation of the polymeric precursor was carried out by leaching a precursor with sufficient tetrahydrofuran (THF, C_4H_8O) or chloroform ($CHCl_3$). The insoluble polymer was filtered, dried and weighed. The soluble portion of one batch was crosslinked with $HSiCl_3$, and treated with ammonia and KH again to increase its molecular weight and degree of crosslinking further.

Thermogravimetric analysis (RIKO TGD-7000 HD) was performed under a flowing nitrogen atmosphere, at a heating rate 10 °C min^{-1}. Differential thermal analysis (DTA, DuPont 9900) was executed to 1000 °C, at a ramping rate of 10 °C min^{-1} under flowing N_2. Infrared analysis was performed on LPK, LPTK, LPTTK and their pyrolysed residues after 500, 700 and 1000 °C thermal treatment (ramping rate 5 °C min^{-1}) under flowing N_2. The conventional KBr method was utilized.

Molecular weight distributions of THF soluble silazanes were determined by gel permeation chromatograph (GPC) (Shodex RI61). The GPC analysis was calibrated with polystyrene of molecular weight 9000, 4000, 2900 and 700. The soluble portion of precursor was dissolved in $CDCl_3$ and analysed by ^1H nuclear magnetic resonance (NMR) spectrometer under 60 MHz (EM-360). The crystalline phase of the pyrolysed product was analysed by an X-ray diffractometer (D/Max-RC Rigaku). The pyrolysed residues were observed under a scanning electron microscope (Cambridge S- 360).

TABLE I The insoluble portions (wt%) of typical preceramic polymers LPK, LPTK and LPTTK in tetrahydrofuran (THF) and chloroform

	THF (wt%)	Chloroform (wt%)
LPK18	46.1	59.0
LPTK18	65.5	71.9
LPTTK18	76.9	77.2

3. Results and discussion

LPK is an oil-like slurry that contains viscous oil and a small amount of polymeric colloids. LPTK and LPTTK are yellow-tinted waxy solids. After the addition of $HSiCl_3$, the viscosity of the intermediate product LPT becomes significantly higher than that of LP. The viscosity of LPTT is even higher than that of LPT. The increasing viscosity is an indication of the effectiveness of $HSiCl_3$ as a crosslinking agent.

3.1. Solubilities in organic solvents

Solubilities of preceramic polymers in THF and chloroform are listed in Table I. Incorporation of $HSiCl_3$ in the synthesis procedure enhances weight fractions of insoluble products, i.e. it reduces the solubilities of polymers in both solvents. The insoluble weight fraction in THF is 46.1% (LPK18) $<$ 65.5% (LPTK18) $<$ 76.9% (LPTTK18). The insoluble weight fraction in chloroform is 59.0% (LPK18) $<$ 71.9% (LPTK18) $<$ 77.2% (LPTTK18). The increase of the insoluble portion implies the degree of crosslinking is raised by $HSiCl_3$. Increase of the insoluble portion in the precursor by the first addition of $HSiCl_3$ (LPTK) is more significant than that by the second addition (LPTTK). Also, the solubility of a precursor in THF is always higher than that in chloroform. Higher solubility means THF is a better solvent for these silazanes. Exact quantities of solubilities may vary somewhat from batch to batch, but the trend described above remains unchanged.

Only the soluble part in the precursor can be subjected to molecular weight analysis by GPC. Typical molecular weight distributions, Mn are: LPK(17) 170–10 600; LPTK(17) 2410–4610; LPTTK(17) 120–6640. Although, $HSiCl_3$ is expected to crosslink small oligomers into less soluble, larger molecules. The result that very small molecules exist in LPTTK17 indicates that not all $HSiCl_3$ reacts with LPT. Unreacted $HSiCl_3$ might undergo ammonolysis later and produce small oligomers.

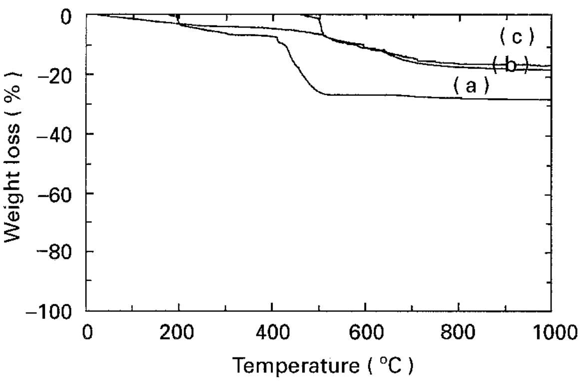


Figure 2 Thermogravimetric curves of (a) LPK18 (72%), (b) LPTK18 (82%) and (c) LPTTK18 (84%). Pyrolysis conditions: heating rate of 10 °C min^{-1} under flowing N_2.

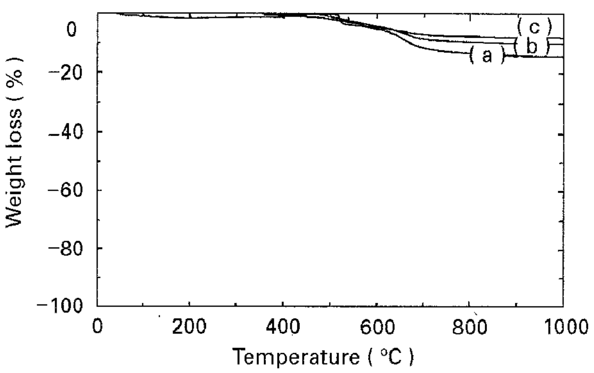


Figure 4 Thermogravimetric curves of (a) LPK18N (86%), (b) LPTK18N (90%) and (c) LPTTK18N (92%). Pyrolysis conditions: heating rate 10 °C min^{-1} under flowing N_2.

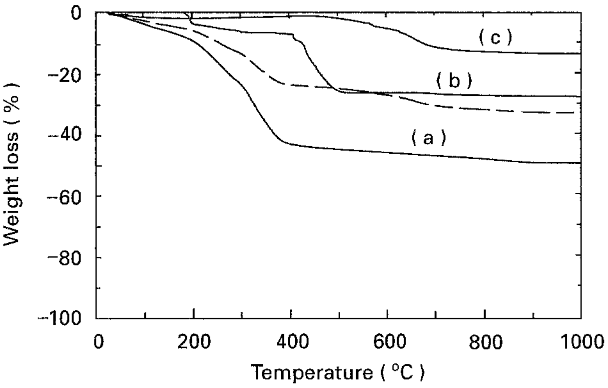


Figure 3 Thermogravimetric curves of (a) soluble (LPK18S, 50%), (b) LPK18S (72%) and (c) insoluble LPK (LPK18N, 86%). Pyrolysis conditions: heating rate 10 °C min^{-1} under flowing N_2.

3.2. Thermogravimetric analysis

Typical weight loss curves during pyrolysis of LPK, LPTK and LPTTK are illustrated in Fig. 2. The incorporation of $HSiCl_3$ into a consecutive polymerization route can effectively raise the pyrolysis yield of the precursor. The yield of LPTK18 (82%) is 10% higher than that of LPK18 (72%). Further addition of $HSiCl_3$ is less effective, the yield of LPTTK18 (84%) is only 2% higher than that of LPTK18 (82%).

The pyrolysis behaviour of LPK can be divided into two distinct temperature ranges, i.e. a low and a high temperature range. The low temperature loss of LPK18 is located between 200–400 °C; the high temperature loss is located between 400–500 °C. Major weight loss occurs in the high temperature region. LPTK has a little loss at low temperatures; almost all weight loss is in the high temperature range, 500–800 °C. It is difficult to distinguish the low and the high temperature loss regions of LPTTK18. They seem to merge into one region. Although LPTTK18 loses more weight than LPTK18 before 500 °C, its overall weight loss is less. The effects of $HSiCl_3$ are (a) to shift high temperature loss of the precursor into a higher temperature range, and (b) to reduce weight loss in high temperatures.

The soluble and the insoluble portion of silazane (in THF) have quite different pyrolysis behaviours. Their weight losses versus temperature are plotted in Fig. 3. The soluble portion of LPK18 (LPK18S) has a great deal of weight loss below 400 °C. Weight loss above 400 °C is comparatively small. This high temperature loss occurs in a wide temperature range, it stops near 900 °C. The pyrolysis yield of LPK18S is only 50%. On the other hand, the insoluble portion of LPK18 (LPK18N) has most of its weight loss above 500 °C. Only a little weight loss of LPK18N occurs before 500 °C. The pyrolysis yield of LPK18N is much higher, 86%.

The dashed curve in Fig. 3 is an arithmetic sum of the insoluble (LPK18N) and the soluble (LPK18S) weight loss multiplied with their own weight fractions, respectively. Although, the dashed curve is, like the weight loss curve of LPK18, located between weight loss curves of the insoluble and the soluble. The dashed curve is very different from the weight loss curve of LPK18. Since LPK18N and LPK18S are physically separated from LPK18, the difference indicates molecules in the precursor interact with each other during pyrolysis. Neighbours of a macromolecule might be degraded and evolve reactive fragments which affect subsequent pyrolysis reactions. Possible reaction mechanisms were discussed by Blum *et al.* [14]. Nevertheless, it is still reasonable to conclude that early weight loss of LPK18 results from those short-chain, soluble molecules of LPK18S; since, those crosslinked, insoluble molecules of LPK18N pyrolyse only a little at low temperatures.

Since the weight loss of the insoluble portion is significantly lower than that of the soluble portion, $HSiCl_3$ can reduce weight loss in pyrolysis. It can be inferred that the insoluble portion of the polymer precursors synthesized by crosslinking with $HSiCl_3$ should have an even higher pyrolysis yield. Typical thermogravimetric curves of insoluble portions of LPK, LPTK and LPTTK are illustrated in Fig. 4. These precursors are LPK18, LPTK18 and LPTTK18 leached by THF to remove their soluble short-chain molecules. There are small but detectable differences in pyrolysis yield among these three insoluble polymers. Pyrolysis yields are 92% (LPTTK18N) > 90% (LPTK18N) > 86% (LPK18N) . One common pyrolysis characteristic among these three polymers is that they have small low temperature weight loss. Most of their weight losses occur at temperatures higher than 500 °C.

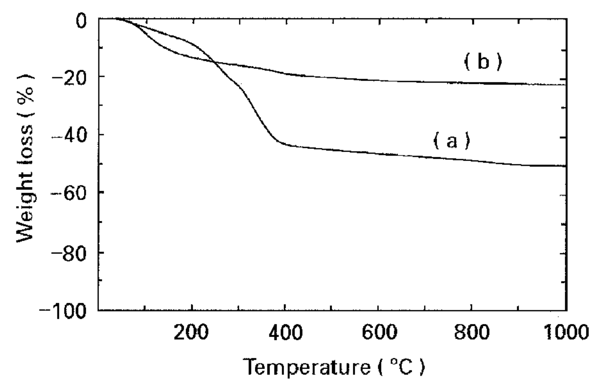


Figure 5 Thermogravimetric curves of (a) LPK18S (50%) and (b) LPK18ST (78%). Pyrolysis conditions: heating rate 10 °C min^{-1} under flowing N_2.

Since $HSiCl_3$ has crosslinking capability, the pyrolysis yield of the soluble portion is low because of small molecular weight with less crosslinking. Can the pyrolysis yield of soluble silazane be raised by reacting with $HSiCl_3$ again? The answer is positive. Fig. 5 depicts the weight loss of soluble polymer LPK18S and that of LPK18ST, which is the soluble LPK18S subjected to further polymerization with $HSiCl_3$. The pyrolysis yield increases from 50 to 78%. It is interesting to note that there is a crossover between LPK18ST and LPK18S in the low temperature region. LPK18ST has more weight loss than LPK18S at the beginning of the pyrolysis. More weight loss at low temperatures implies LPK18ST has more small molecules. Those small molecules are the result of a high weight ratio of reactants, $HSiCl_3$: soluble LPK18 equals 1 : 1.9. The ammonolysis of unreacted $HSiCl_3$ after polymerization produces small oligomers, which cause more weight loss at the beginning.

3.3. Differential thermal analysis

DTA curves of LPK18, LPTK18 and LPTTK18 are plotted in Fig. 6. Most of the thermal events in pyrolysis are exothermic. The addition of $HSiCl_3$ shifts these thermal events towards higher temperatures. Therefore exothermic events of LPK18 occur between 232 and 558 °C. On the other hand, major thermal events of LPTK18 and LPTTK18 occur between 400 and 725 °C.

The DTA curve of LPK has two sharp exothermic peaks; one at 232 °C and another at 558 °C. Between these two peaks, there is a hump located near the 558 °C peak. This hump consists of a number of smaller exothermic peaks. These peaks occur within the high temperature range, in which LPK loses most of its weight in pyrolysis. These overlapping, exothermic peaks reflect the complex nature of the pyrolysis reactions in the high temperature region. Further, broadened exothermic peaks appear in the pyrolysis of LPTK and LPTTK, which were synthesized with the addition of $HSiCl_3$. These broad peaks of LPTK and LPTTK are located in higher temperature regions. The widths of peak temperature of LPTK and LPTTK imply the complexity of pyrolysis is enhanced by $HSiCl_3$.

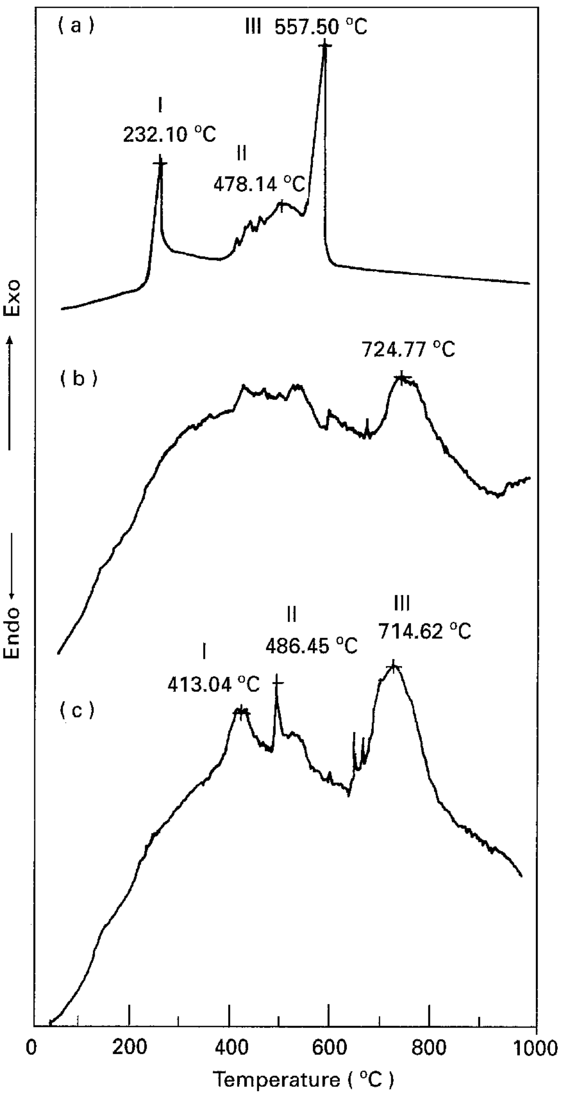


Figure 6 DTA thermograms of (a) LPK18, (b) LPTK18 and (c) LPTTK18. Pyrolysis conditions: 10 °C min^{-1} and N_2 atmosphere.

Another feature common to these three curves is that they have no endothermic peak. It indicates that LPK, LPTK and LPTTK are infusible. Infusible LPK, LPTK and LPTTK were also confirmed in the attempt to measure their melting points. Temperatures of these silazanes were slowly raised up to 400 °C, and no melting phenomena was observed.

3.4. Infrared analysis

Infrared spectra of LPK18, LPTK18 and LPTTK18 are compared in Fig. 7. A single absorption band at 3400 cm^{-1} indicates the N–H (not NH_2) group. Absorptions at 2840–2960 cm^{-1} result from C–H_3 stretching vibrations. The Si–H stretching vibration leads to absorption at 2150 cm^{-1}. Si–CH_3 deformation and a rocking absorption band occur at 1260 and 950–870 cm^{-1}, individually. Broad absorptions in 1080–980 and 1160–1080 cm^{-1}, are due to stretching vibrations of Si–N–Si and Si–N, respectively. Since the functional group $SiCH_3$ is considered to be inert in the consecutive synthesis procedure, the intensity ratio $NH/SiCH_3$ could be used to indicate variation (approximately) in the number of functional NH groups

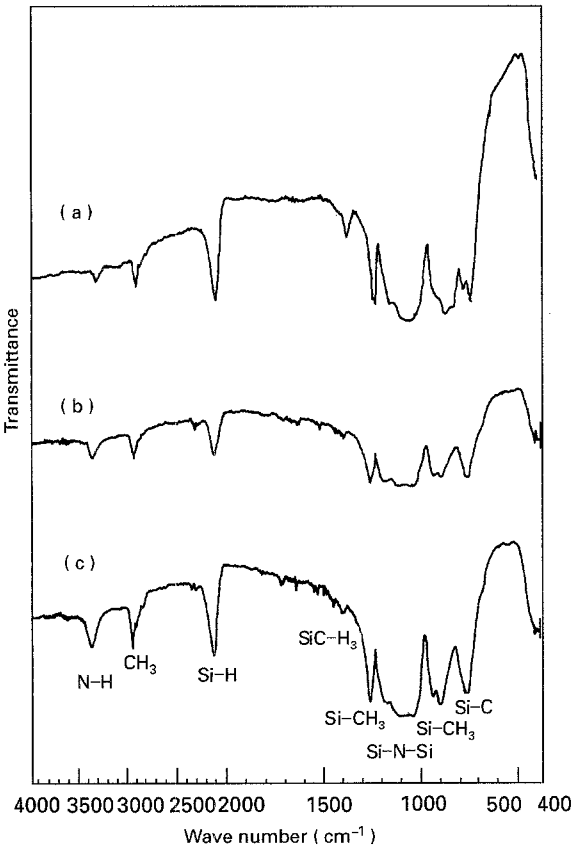
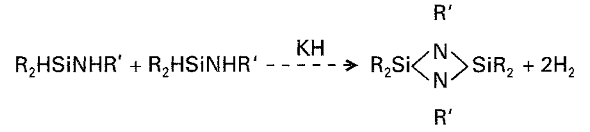


Figure 7 Infrared spectra of LPK18 (a), LPTK18 (b) and LPTTK18 (c).

during synthesis. The increasing intensity ratio of NH/SiCH$_3$ in the sequence of adding HSiCl$_3$ (LPTTK > LPTK > LPK) implies that the addition of HSiCl$_3$ followed by ammonolysis will increase the number of NH groups in the precursors. On the other hand, the intensity ratio SiH/SiCH$_3$ decreases with the addition of HSiCl$_3$ (LPK > LPTK ≅ LPTTK). The reduction of a number of SiH groups is caused by more NH available for dehydrogenation catalysed by KH. The dehydrogenation reaction between NH and SiH is believed to enhance crosslinking, consequently the pyrolysis yield of silazane [4,12]



Infrared spectra of LPTK after pyrolysis at various temperatures are illustrated in Fig. 8. When the pyrolysis temperature reaches 500 °C, Si–H and N–H bonds in LPTK silazane diminish first; and C–H, Si–N, Si–CH$_3$ and Si–C (760 cm^{-1}, stretch) bonds persist. When the temperature reaches 700 °C, absorptions of the C–H$_3$ stretching band and Si–CH$_3$ band become very small, the stretch bands of Si–C, Si–N and Si–N–Si become even broader. When the temperature reaches 1000 °C, C–H$_3$ and Si–C absorption disappear and the Si–N–Si absorption band becomes so broad that it is almost indistinguishable from the background.

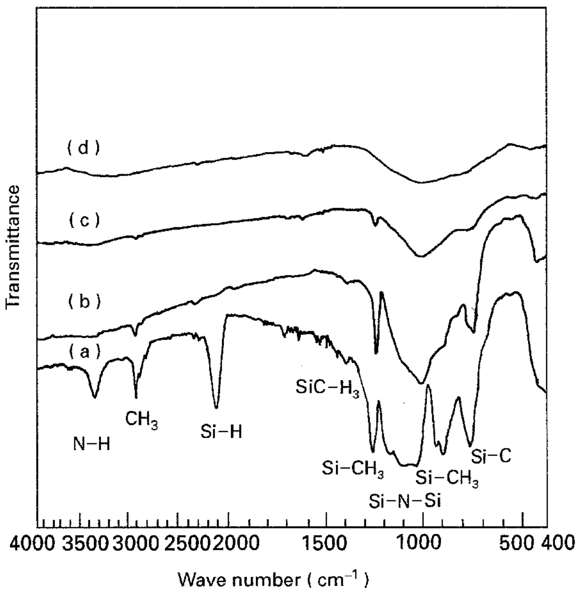
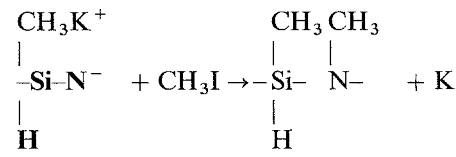


Figure 8 Infrared spectra of LPTK18 (a) without heat treatment, and pyrolysed at 500 (b), 700 (c) and 1000 °C (d) in N$_2$.

3.5 ^{1}H-NMR analysis

The portion of precursor soluble in CDCl$_3$ was subjected to ^{1}H NMR analysis. The chemical shift of each type of proton and its corresponding integration intensity is listed in Table II for LPK, LPTK and LPTTK. The NCH$_3$ intensities of LPTK and LPTTK are higher than that of LPK. Higher NCH$_3$ intensity is due to using CH$_3$I to remove the K$^+$ ion. The following reaction is assumed



$$\begin{array}{ccccc} CH_3K^+ & & CH_3 & CH_3 & \\ | & & | & | & \\ -Si-N^- & + CH_3I \rightarrow & -Si- & N- & + KI \\ | & & | & & \\ H & & H & & \end{array}$$

The ^{1}H NMR result of soluble LPK18 allows one to determine its composition as [(CH$_3$SiHNH)$_a$(CH$_3$SiN)$_b$(CH$_3$SiHNCH$_3$)$_c$] with $a = 0.48$, $b = 0.48$ and $c = 0.04$. There is 50% (CH$_3$SiHNH) in soluble LPK18 not involved in the dehydrogenation reaction.

TABLE II Chemical shifts of various types of protons in polymeric precursors LPK, LPTK and LPTTK (soluble in CDCl$_3$) and their associated integration intensities

Precursor	Chemical shift
LPK18	δ 0.15–0.55 (3H SiCH$_3$)
	δ 1.13–1.48 (0.19H NH)
	δ 1.51–1.62 (0.33H NH)
	δ 2.20–2.40 (0.09H NCH$_3$)
	δ 4.80–5.00 (0.9H SiH)
LPTK18	δ 0.30–0.60 (1.09H SiCH$_3$)
	δ 1.45–1.65 (0.82H N–H)
	δ 1.85–2.00 (1.09H N–H)
	δ 2.40–2.65 (3.0H NCH$_3$)
	δ 4.00–4.30 (0.54H SiH)
LPTTK18	δ 0.30–0.60 (0.65H SiCH$_3$)
	δ 1.35–1.60 (0.75H NH)
	δ 1.75–1.90 (0.79H NH)
	δ 2.40–2.60 (3.0H NCH$_3$)

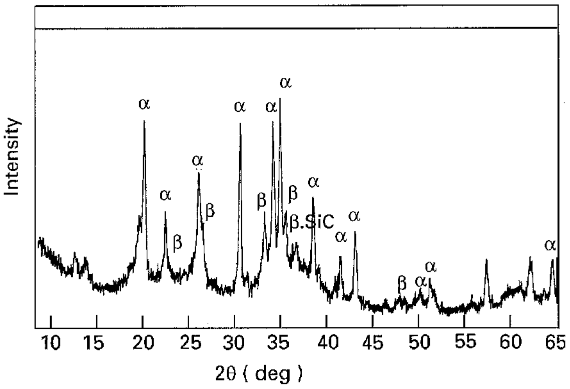


Figure 9 X-ray powder diffraction of LPTK16 residues pyrolysed in N_2 at 1550 °C for 12h.

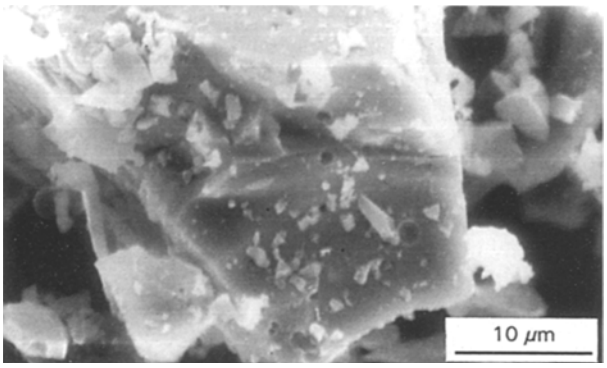


Figure 10 A micrograph for residues pyrolysed in N_2.

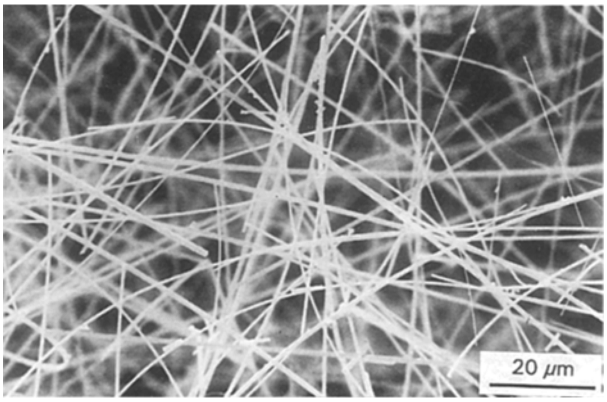


Figure 11 A micrograph of silicon carbonitride whiskers grown from the pyrolysed residues.

3.6. Pyrolysis residues

Fig. 9 demonstrates a typical X-ray powder diffraction pattern of residues pyrolysed at 1550 °C in nitrogen for 12h. The major phases are α- and β-Si_3N_4. Fig. 10 is a micrograph of pyrolysis residues. One large particle has several round and shallow holes on its surface which are generated by volatile fragments in pyrolysis. Fig. 11 indicates Si_3N_4 whiskers that can be produced from pyrolysis under the appropriate conditions. These whiskers, with an appearance of glass wool, were grown at the bottom of a cover of a half-open alumina crucible. Whiskers have a rectangular cross-section and a length of over 100 μm. X-ray analysis indicates that these whiskers have a preferred crystalline face (2 1 0) of α-Si_3N_4. These results are similar to those reported by Wang and Wada who synthesized whiskers by carbothermal reduction of silica [16].

4. Conclusions

The degree of crosslinking and branching of backbone in polymeric precursors for silicon cabonitrides is systematically enhanced through consecutive copolymerization with trifunctional $HSiCl_3$. The pyrolysis yields of the precursor and the insoluble portion in the precursor increase with crosslinking and branching. Those insoluble macromolecules of a precursor play a major role in raising the pyrolysis yield. Therefore leaching out the soluble portion enhances the pyrolysis yield of the precursor. Further, crosslinking the soluble precursor with $HSiCl_3$ also enhances the pyrolysis yield.

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