

## Effect of the polycarbosilane structure on its final ceramic yield

Houbu Li<sup>a</sup>, Litong Zhang<sup>a</sup>, Laifei Cheng<sup>a</sup>, Yiguang Wang<sup>a,\*</sup>, Zhaoju Yu<sup>b,\*</sup>,  
Muhe Huang<sup>b</sup>, Huibin Tu<sup>b</sup>, Haiping Xia<sup>b</sup>

<sup>a</sup> National Key Laboratory of Thermostructure Composite Materials, Northwestern Polytechnical University, Xi'an 710072, China

<sup>b</sup> Advanced Materials Laboratory and Department of Materials Science & Engineering,  
College of Chemistry & Chemical Engineering, Xiamen University, Xiamen 361005, China

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### Abstract

The ceramic yield of a new polycarbosilane is discussed based on its structure, including vinyl functionality, branched structure, as well as polymer molecular weight. The cross-linking behavior of this polymer is studied up to 400 °C. According to the cross-linking mechanism, the optimized heat-treatment conditions can be obtained for a high ceramic yield. The product pyrolyzed at 1400 °C has a composition close to 1.1:1 Si:C with a ceramic yield of about 70%.

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### 1. Introduction

The technique for the fabrication of non-oxide ceramics by the pyrolysis of polymer precursors has attracted a great deal of interest due to its advantages over the powder-based ceramic processing such as fabricating unconventional structures and getting ceramics at relatively low temperatures.<sup>1,2</sup> Furthermore, polymer derived ceramics have high thermal stability,<sup>3</sup> thermal mechanical properties,<sup>4,5</sup> and oxidation resistance both in dry and wet environments.<sup>6–9</sup> These unique properties of polymer derived ceramics render them as potential materials for high temperature structural applications.

The silazane-based polymer precursors are necessary for the preparation of polymer derived silicon-based ceramics. In the past decades, many books,<sup>10,11</sup> as well as review articles<sup>12,13</sup> were published concerning preceramic precursors. Several researchers have set forth a series of empirical rules for designing a proper ceramic precursor.<sup>14,15</sup> They stated that a general requirement for the polymer precursor is a high ceramic yield and good processing characteristics. Hence, a useful polymer

precursor should be liquid, fusible and/or soluble for processing, and should possess high molecular weight, presence of latent reactivity, and cages or ring structure for high ceramic yield.

The ceramic yield of polymer precursors strongly depends on their chemistry, backbone structure, the functionalities, and the degree of cross-linking. The cross-linked polysilazanes can give a ceramic yield of 80 wt% or higher while the uncross-linked silazanes give only 20% ceramic residue.<sup>16</sup> Lücke et al.<sup>17</sup> systematically investigated the effect of branched and unbranched structure of polysilazanes on their ceramic yield. It was found that the branched precursor had a much higher ceramic yield than that of the unbranched one due to its lower evaporation of oligomers. The functionality such as vinyl group is also widely studied in PHMS system and PVS system.<sup>16,18</sup> The results showed that the vinyl group will allow a high ceramic yield. The study of Bahloul et al.<sup>19</sup> indicated that the pyrolysis conditions also greatly affected the final ceramic residue.

Polycarbosilanes are the precursors for SiC ceramics. The ideal structure of the polymer should present alternating silicon and carbon atoms in the main chain with branching nodes. The type of branching nodes can be designed to control the free carbon in the final ceramic composition. In this study, liquid polycarbosilanes with a highly branched structure are used. A systematic investigation on the effect of functional groups existed in the polycarbosilane structure has been carried out to

\* Corresponding authors.

E-mail addresses: [wangyiguang@nwpu.edu.cn](mailto:wangyiguang@nwpu.edu.cn) (Y. Wang),  
[zhaojuyu@163.com](mailto:zhaojuyu@163.com) (Z. Yu).

maximize its conversion to the ceramic. The influence of the heat treatment prior to pyrolysis is also studied in order to optimize the ceramic yield of this polymer.

## 2. Experimental procedure

A liquid polycarbosilane (LPCS) with highly branched structure was synthesized in the Laboratory of Advanced Materials at Xiamen University. Briefly, LPCS was synthesized by Grignard coupling of chloromethylmethylchlorosilane ( $\text{Cl}_2\text{MeSiCH}_2\text{Cl}$ ), chloromethyltrichlorosilane ( $\text{Cl}_3\text{SiCH}_2\text{Cl}$ ) and allyl chloride ( $\text{ClCH}_2\text{CH}=\text{CH}_2$ ), followed by the reduction with lithium aluminum hydride ( $\text{LiAlH}_4$ ).<sup>20</sup> The structures of as-received liquid polymers were characterized by  $^1\text{H}$  NMR and FTIR. The FTIR spectra were obtained by placing the liquid on NaCl plates using the Nicolet Avator 360 Spectrometer (Wisconsin, USA). The  $^1\text{H}$  NMR experiments were carried out on a Bruker AV300MHz spectrometer (Germany) operating at 300.13 MHz in  $\text{CDCl}_3$  solution, using (trimethylsilyl)silane (TMS) as the internal standard.

The polymers were cross-linked at different temperatures with argon gas protection for 6 h. The structures of resultant solids were also characterized by FTIR by using pellets made from the mixture of the solid powders and dried KBr powders. The thermal analysis for the cross-linking process was carried out on thermal gravimetric analysis–differential scanning calorimetry (TGA–DSC) (Netzsch STA 409C) in argon gas with a ramping rate of  $10^\circ\text{C}/\text{min}$ . The average molecular weight of LPCS was measured by gel permeation chromatography (GPC) using Angilent 1100 (Angilent Co., USA) with tetrahydrofuran (THF) as a solvent.

## 3. Results and discussion

The functionalities in as-received liquid polycarbosilanes (1#, see in Table 1) were identified by FTIR (Fig. 1). The deformation band at around  $1250\text{ cm}^{-1}$  ( $\text{Si}-\text{CH}_3$  stretching) and the stretching band at  $2950\text{ cm}^{-1}$  ( $\text{C}-\text{H}$  stretching in  $\text{Si}-\text{CH}_3$ ) indicate the existence of  $\text{Si}-\text{CH}_3$ . The strong band at  $2120\text{ cm}^{-1}$  is assigned to  $\text{Si}-\text{H}$ . The bands attributed to vinylsilyl group ( $\text{CH}_2=\text{CH}-\text{Si}$ ) are  $\text{C}-\text{H}$  vibration in  $\text{CH}=\text{CH}_2$  at  $3073\text{ cm}^{-1}$  and  $\text{C}=\text{C}$  stretching at  $1630\text{ cm}^{-1}$ . The  $\text{CH}_2$  bending in  $\text{Si}-\text{CH}_2-\text{Si}$  at  $1000\text{ cm}^{-1}$  and the  $\text{C}-\text{H}$  stretching in  $\text{Si}-\text{CH}_2$  at  $2920\text{ cm}^{-1}$  indicate that  $\text{Si}-\text{CH}_2-\text{Si}$  chain, the backbone of polymer, exists in this LPCS. Peaks at around  $820\text{ cm}^{-1}$  are assigned to  $\text{Si}-\text{CH}_3$  rocking and  $\text{Si}-\text{C}$  stretching.<sup>21–23</sup> The stretching vibration band at around  $3400\text{ cm}^{-1}$  is due to the water that was adsorbed in

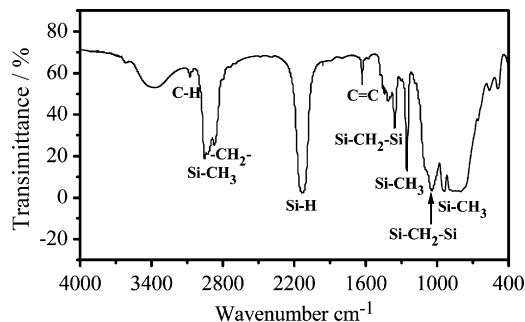


Fig. 1. FTIR analysis of synthesized liquid polycarbosilanes.

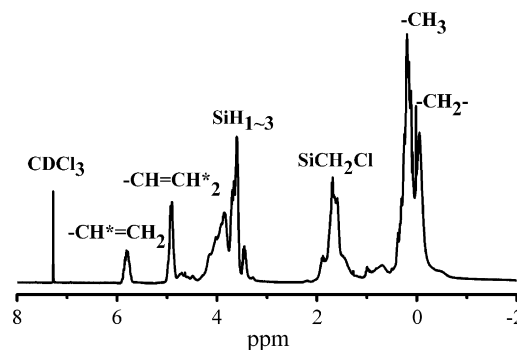


Fig. 2.  $^1\text{H}$  NMR analysis of synthesized liquid polycarbosilanes.

KBr during FTIR testing. The structure of liquid polycarbosilane is further confirmed by  $^1\text{H}$  NMR spectrum (Fig. 2). The peaks in  $^1\text{H}$  NMR spectrum of the LPCS are overlapped and broadened, which confirms that the structure is highly branched.<sup>24</sup> The two groups of peaks centered at  $-0.2$  and  $0.15$  ppm are attributed to the various  $\text{SiCH}_2\text{Si}$  environments and the  $\text{SiCH}_2-$  functionalities.  $\text{Si}-\text{CH}_3$  functionality in the polymer from reduced  $\text{CH}_2\text{Cl}$  end groups would also appear in these regions.<sup>25,26</sup> The  $\text{SiCH}_2\text{Si}$  and  $\text{SiCH}_2-$  are likely to be generated by Grignard reaction to form the backbone of the polymer. The multiplet between 1.5 and 2 ppm is due to the absorption of methylene protons of the residual chloromethyl functionalities not reduced by  $\text{LiAlH}_4$  treatment, and the methylene protons derived from THF.<sup>26</sup> The three peaks ranged from 3.3 to 4.5 ppm match the values for the  $\text{SiH}$ ,  $\text{SiH}_2$ , and  $\text{SiH}_3$  groups.<sup>27</sup> The two multiplets at 4.77 and 5.76 ppm are assigned to the protons in  $-\text{CH}=\text{CH}_2^*$  and  $-\text{CH}^*=\text{CH}_2$ , respectively.<sup>24</sup> From the above analysis, it is generally believed that the polymer precursor has a highly branched structure with a  $\text{Si}-\text{CH}_2-\text{Si}$  chain (the structure is shown below).

Table 1  
Contents of functional groups and ceramic yield of polycarbosilanes

Types of LPCS	Si-H content (%)	Si-CH <sub>2</sub> -CH=CH <sub>2</sub> content (%)	Si-CH <sub>3</sub> content (%)	Ceramic yield (%)
1#	31	3	54	60.22
2#	25	9	46	71.07
3#	37	7	48	63.58
4#	12	8	72	29.79

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