Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 28 (2008) 887–891
www.elsevier.com/locate/jeurceramsoc

Effect of the polycarbosilane structure on its final ceramic yield

Houbu Li[a], Litong Zhang[a], Laifei Cheng[a], Yiguang Wang[a,*], Zhaoju Yu[b,*], Muhe Huang[b], Huibin Tu[b], Haiping Xia[b]

[a] National Key Laboratory of Thermostructure Composite Materials, Northwestern Polytechnical University, Xi'an 710072, China
[b] Advanced Materials Laboratory and Department of Materials Science & Engineering, College of Chemistry & Chemical Engineering, Xiamen University, Xiamen 361005, China

Received 17 April 2007; received in revised form 7 July 2007; accepted 27 July 2007
Available online 23 October 2007

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 pyrolysized at 1400 °C has a composition close to 1.1:1 Si:C with a ceramic yield of about 70%.

Keywords: Polycarbosilane structure; Ceramic yield; Cross-linking; Precursors-organic; SiC

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.[1,2] Furthermore, polymer derived ceramics have high thermal stability,[3] thermal mechanical properties,[4,5] and oxidation resistance both in dry and wet environments.[6–9] 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,[10,11] as well as review articles[12,13] were published concerning preceramic precursors. Several researchers have set forth a series of empirical rules for designing a proper ceramic precursor.[14,15] 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.[16] Lücke et al.[17] 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.[16,18] The results showed that the vinyl group will allow a high ceramic yield. The study of Bahloul et al.[19] 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 (Y. Wang), zhaojuyu@163.com (Z. Yu).

0955-2219/$ – see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2007.07.020

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 chloromethylmethyldichlorosilane ($Cl_2MeSiCH_2Cl$), chloromethyltrichlorosilane (Cl_3SiCH_2Cl) and allyl chloride ($ClCH_2CH{=}CH_2$), followed by the reduction with lithium aluminum hydride ($LiAlH_4$).[20] The structures of as-received liquid polymers were characterized by ^1H NMR and FTIR. The FTIR spectra were obtained by placing the liquid on NaCl plates using the Nicolet Avator 360 Spectrometer (Wisconsin, USA). The ^1H NMR experiments were carried out on a Bruker AV300MHz spectrometer (Germany) operating at 300.13 MHz in $CDCl_3$ 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 °C/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 cm^{-1} (Si–CH_3 stretching) and the stretching band at 2950 cm^{-1} (C–H stretching in Si–CH_3) indicate the existence of Si–CH_3. The strong band at 2120 cm^{-1} is assigned to Si–H. The bands attributed to vinylsilyl group ($CH_2{=}CH{-}Si$) are C–H vibration in $CH{=}CH_2$ at 3073 cm^{-1} and C=C stretching at 1630 cm^{-1}. The CH_2 bending in Si–CH_2–Si at 1000 cm^{-1} and the C–H stretching in Si–CH_2 at 2920 cm^{-1} indicate that Si–CH_2–Si chain, the backbone of polymer, exists in this LPCS. Peaks at around 820 cm^{-1} are assigned to Si–CH_3 rocking and Si–C stretching.[21–23] The stretching vibration band at around 3400 cm^{-1} is due to the water that was adsorbed in KBr during FTIR testing. The structure of liquid polycarbosilane is further confirmed by ^1H NMR spectrum (Fig. 2). The peaks in ^1H NMR spectrum of the LPCS are overlapped and broadened, which confirms that the structure is highly branched.[24] The two groups of peaks centered at −0.2 and 0.15 ppm are attributed to the various $SiCH_2Si$ environments and the $SiCH_2$– functionalities. Si–CH_3 functionality in the polymer from reduced CH_2Cl end groups would also appear in these regions.[25,26] The $SiCH_2Si$ and $SiCH_2$– 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 $LiAlH_4$ treatment, and the methylene protons derived from THF.[26] The three peaks ranged from 3.3 to 4.5 ppm match the values for the SiH, SiH_2, and SiH_3 groups.[27] The two multiplets at 4.77 and 5.76 ppm are assigned to the protons in $-CH{=}CH_2^*$ and $-CH^*{=}CH_2$, respectively.[24] From the above analysis, it is generally believed that the polymer precursor has a highly branched structure with a Si–CH_2–Si chain (the structure is shown below).

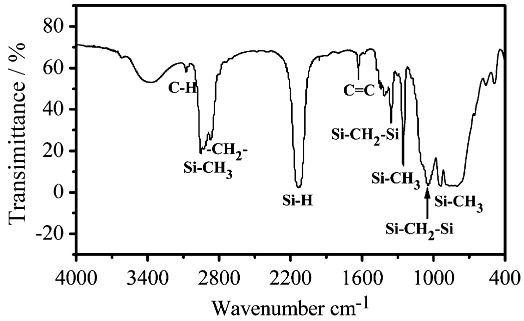


Fig. 1. FTIR analysis of synthesized liquid polycarbosilanes.

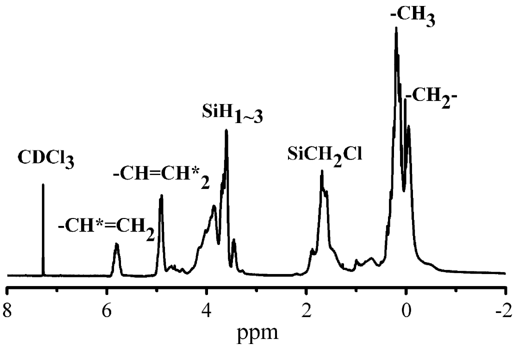


Fig. 2. ^1H NMR analysis of synthesized liquid polycarbosilanes.

Table 1
Contents of functional groups and ceramic yield of polycarbosilanes

Types of LPCS	Si—H content (%)	Si—CH_2—CH=CH_2 content (%)	Si—CH_3 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

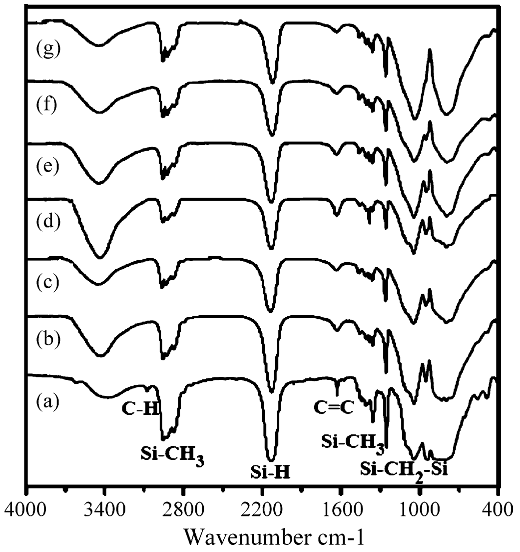
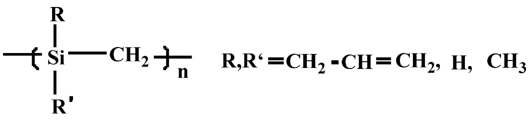


Fig. 3. FTIR spectra of polycarbosilanes heat-treated at (a) un-cured, (b) 170 °C, (c) 200 °C, (d) 250 °C, (e) 300 °C, (f) 350 °C, (g) 400 °C.



$$-\!\!\left[\mathrm{Si}(R)(R')-\mathrm{CH_2}\right]_n- \quad \mathrm{R,R' = CH_2\text{-}CH{=}CH_2,\ H,\ CH_3}$$

The cross-linking behavior of the LPCS is studied by FTIR (Fig. 3). At the temperatures of 200 °C, the intensity of Si–CH_3 (1250, 2950, 2900, 1400 and 1355 cm^{-1}) does not change too much while the absorption peaks related to Si–H (2130, 900 cm^{-1}) and –CH=CH_2 (1630 cm^{-1}) decrease in intensity after curing. It is believed that hydrosilylation and dehydrocoupling reactions occurred during the cross-linking process, as shown below:

$$\equiv\mathrm{Si{-}CH{=}CH_2} + \equiv\mathrm{Si{-}H} \rightarrow \mathrm{Si{-}CH_2CH_2{-}Si} \tag{1}$$

$$\equiv\mathrm{Si{-}H} + \mathrm{H{-}Si}\equiv \rightarrow \equiv\mathrm{Si{-}Si}\equiv + \mathrm{H_2} \tag{2}$$

The thermal analysis indicates that there is an exothermic peak at about 230 °C. It is believed that this peak arises from the hydrosilylation and dehydrocoupling reactions.[28] At this temperature, the evaporation of hydrogen gas and small oligomers should be the main reason for weight loss. Hence, the weight change in TGA (Fig. 4) is small. With the temperature increasing, the absorption bands attributed to Si–CH_3 greatly decreased in intensity. At the temperature of 400 °C, the C–H stretching in –CH=CH_2 (3073 cm^{-1}) almost disappears and the intensity of the absorption band attributed to C=C (1630 cm^{-1}) is reduced markedly, which indicates that the CH_2=CH– functionality evolves in the cross-linking reaction. The following reactions should happen during the cross-linking process

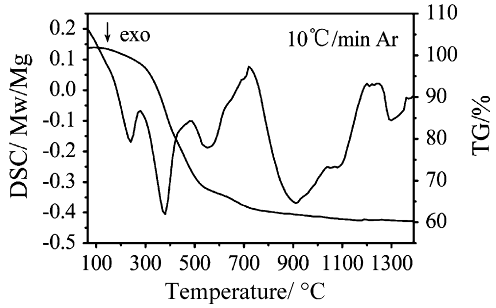


Fig. 4. TGA–DSC analysis of cured polycarbosilanes in argon gas with a ramping rate of 10 °C/min.

$$\equiv\mathrm{Si{-}H} + \mathrm{CH_3{-}Si}\equiv \rightarrow \equiv\mathrm{Si{-}Si}\equiv + \mathrm{CH_4} \tag{3}$$

$$\mathrm{CH_2{=}CH{-}Si}\equiv \rightarrow -\mathrm{CH_2{-}CH(-Si}\equiv)- \tag{4}$$

The exothermic peak at about 380 °C should account for the reactions above. Gaseous products such as CH_4 and H_2 will evaporate out, contributing to the weight loss in this stage. The low weight molecules that require further cross-linking will escape out at high temperatures, which should also accounts for the weight loss in this stage.

Previous study[17] indicated that the unbranched precursors had a very low ceramic yield (no more than 11 wt%) due to the evaporation of oligomers around 300 °C. Hence, highly branched polycarbosilane is preferred at the beginning of structural design in order to avoid great oligomers loss. Structural analysis of our obtained LPCSs shows that they are highly branched structure. No obvious weight loss below 300 °C is observed in TGA for our LPCSs, which indicates that the highly branched structure is beneficial to ceramic yield.

The content of functionalities can be calculated from ^1H NMR. The calculation results and the final ceramic yield are listed in Table 1. It can be seen that the ceramic yield increase from 60 to 71% with the vinyl content from 3 to 9%; and that the pyrolysis residue decreases to around 30% with the content of –CH_3 up to 72%. The Si–CH_3 bonds will be broken at temperatures higher than 300 °C and evaporate out in the form of methane gas. The loss of –CH_3 is the main reason for weight loss during pyrolysis. However, it has a beneficial effect by reducing the free carbon residue. An introduction of a vinyl group into the polymer as a side chain will increase the ceramic yield. With the vinyl, a hydrosilylation cross-linking happens at around 230 °C. The degree of cross-linking at low temperature was enhanced to greatly reduce the oligomers evaporation.

In order to get a composition of close to 1:1 Si:C from the highly branched LPCS, side chains such as allyl, butyl, and hexyl should be avoided. Although these functionalities could increase the ceramic yield, the free carbon residual will be high. An ideal structure has only –H and –CH_3 as the side chains. However, the presence of pendent methyl groups in the polymer generally leads to a major loss of carbon as methane. Thus, a suitable amount of vinyl groups are welcomed as side chains. The ceramic yield can be greatly enhanced due to improvement of cross-linking, though its pyrolysis leads to a little free-carbon-richness because of the preliminary polymerization of vinyl moieties and subsequent formation of carbon during the pyrolysis step.

According to TGA results (Fig. 4), the weight loss mainly happens in the temperature range of 300–500 °C. In this stage, the polymerization of C=C, hydrosilylation and dehydrocoupling reactions occur to increase the degree of cross-linking, accompanying the process of the depolymerization and evapora-

Table 2
Molecular weight and ceramic yield of polycarbosilanes

Types of LPCS	M_n	M_w	Polydispersity	Viscosity (cP)	Ceramic yield (%)
5#	756	2319	3.06	100	51.47
6#	904	3629	4.01	450	59.27

tion of low molecular weight molecules. Sufficient cross-linking at the beginning of this period is critical to reduce the weight loss and to get a high final ceramic yield. From the analysis of the cross-linking process, it is believed that 300 °C is a good temperature for heat treatment of PCS because the cross-linking reactions such as polymerization, hydrosilylation and dehydrocoupling occur and the temperature is not high enough for violent evaporation of oligomers. By this treatment, the final ceramic yield can be increased by 10 wt% or more. However, the ceramic residual for LPCS with high $-CH_3$ content have no obvious increase even after heat treatment at 300 °C for a long time. This indicates that the type of side chain is critical for ceramic yield as well.

Molecular weight also has an important effect on the ceramic yield. Two precursors having the same structure with different molecular weight were investigated in this study. As summarized in Table 2, the M_n and M_w of LPCS were enhanced from 756 and 2319 to 904 and 3629, while the ceramic residue was increased from 51.47 to 59.27 wt%. It is easy to understand that higher molecular weight leads to less weight loss during cross-linking and pyrolysis. However, a high molecular weight also means a high viscosity, which will reduce the processability of the liquid polymer. Therefore, a suitable of molecular weight is required for optimizing the process.

4. Conclusion

In conclusion, the effect of structure factors such as branched structure, side chains, vinyl functionality, and molecular weight on the final ceramic yield, combined with the cross-linking mechanism is discussed. By optimizing the structure and cross-linking process, a liquid polycarbosilane is obtained with a ceramic yield of 70 wt% and a composition of close to 1.1:1 Si:C.

References

1. Yajima, S., Hasegawa, Y., Okamura, K. and Matsuzawa, T., Development of high tensile strength silicon carbide fiber using an organosilicon polymer precursor. *Nature*, 1978, **273**, 525–527.
2. Riedel, R., Passing, G., SchoÈnfelder, H. and Brook, R. J., Synthesis of dense silicon-based ceramics at low temperatures. *Nature*, 1992, **355**, 714–717.
3. Riedel, R., Kienzle, A., Dressler, W., Ruwisch, L., Bill, J. and Aldinger, F., A silicoboron carbonitride ceramic stable to 2000 °C. *Nature*, 1996, **382**, 796–798.
4. An, L., Riedel, R., Konetachny, C., Kleebe, H. J. and Raj, R., Newtonian viscosity of amorphous silicon carbo-nitride at 1280 °C. *J. Am. Ceram. Soc.*, 1998, **81**, 1349–1352.
5. Riedel, R., Ruwisch, L. M., An, L. and Raj, R., Amorphous silicoboron carbonitride ceramic with very high viscosity at temperatures above 1500 °C. *J. Am. Ceram. Soc.*, 1998, **81**, 3341–3344.
6. Wang, Y., Fan, Y., Zhang, L., Burton, S., Gan, Z. and An, L., Oxidation of polymer-derived SiAlCN ceramics. *J. Am. Ceram. Soc.*, 2005, **88**, 3075–3080.
7. Wang, Y., Fan, Y., Zhang, L., Zhang, W. and An, L., Polymer-derived SiAlCN ceramics resist oxidation at 1400 °C. *Scripta Mater.*, 2006, **55**, 295–297.
8. Wang, Y., Fei, W. and An, L., Oxidation/corrosion of polymer-derived SiAlCN ceramics in water vapor. *J. Am. Ceram. Soc.*, 2006, **89**, 1079–1082.
9. Wang, Y., Fei, W., Fan, Y., Zhang, L., Zhang, W. and An, L., Silicoaluminum carbonitride ceramic resist to oxidation/corrosion in water vapor. *J. Mater. Res.*, 2006, **21**, 1625–1628.
10. Eigen, P., Keller-Rudek, H., Kurtz, W., Merlet, P., Schaefer, H. and Schroeder, F., *Gmelin handbook of inorganic chemistry* (*8th ed.*). Silicon Suppl., Berlin, 1989.
11. Pawlenko, S, In *Methoden der organischen Chemie (Houben-Weyl), Vol 13, part 5*, ed. O. Bayer and E. MuÈller. 4th ed. Georg Thieme, Stuttgart, 1980.
12. Birot, M., Pillot, J. P. and Dunogues, J., Comprehensive chemistry of polycarbosilanes, polysilazane, and polycarbosilazanes as precursors of ceramics. *Chem. Rev.*, 1995, **95**, 1443–1447.
13. Kroke, E., Li, Y., Konetschny, C., Lecomte, E., Fasel, C. and Riedel, R., Silazane derived ceramics and related materials. *Mater. Sci. Eng. R*, 2000, **26**, 97–199.
14. Wynne, K. J. and Rice, R. W., Ceramics via polymer pyrolysis. *Annu. Rev. Mater. Sci.*, 1984, **14**, 297–334.
15. Seyferth, D., In *Inorganic and organometallic polymers, ACS Symposium Series 360*, ed. M. Zeldin, K. J. Wynne and H. R. Allcock. American Chemical Society, Washington, DC, 1988.
16. Seyferth, D. and Wiseman, G. H., High-yield synthesis of Si_3N_4/SiC ceramic materials by pyrolysis of a novel polyorganosilazane. *J. Am. Ceram. Soc.*, 1984, **67**, C132–C133.
17. Lücke, J., Hacker, J., Suttor, D. and Ziegler, G., Synthesis and characterization of silazane-based polymers as precursors for ceramic matrix composites. *Appl. Organomet. Chem.*, 1997, **11**, 181–194.
18. Lavedrine, A., Bahloul, D., Goursat, P., Choong Kwet Yive, N., Corriu, R., Leclerq, D. *et al.*, Pyrolysis of polyvinylsilazane precursors to silicon carbonitride. *J. Eur. Ceram. Soc.*, 1991, **8**, 221–227.
19. Bahloul, D., Pereira, M., Goursat, P., Choong Kwet Yive, N. S. and Corriu, R. J. P., Preparation of silicon carbonitrides from an organosilicon polymer. I. Thermal decomposition of the cross-linked polysilazane. *J. Am. Ceram. Soc.*, 1993, **76**, 1156–1162.
20. Huang, T. H., Yu, Z. J., He, X. M., Huang, M. H., Chen, L. F., Xia, H. P. *et al.*, One-pot synthesis and characterization of a new, branched polycarbosilane bearing allyl groups. *Chin. Chem. Lett.*, 2007, **18**, 754–757.
21. Bouillon, E., Langlais, F., Pailler, R., Naslain, R., Cruege, F., Huong, P. V. *et al.*, Conversion mechanisms of a polycarbosilane precursor into an SiC-based ceramic material. *J. Mater. Sci.*, 1991, **26**, 1333–1345.
22. Hasegawa, Y. and Okamura, K., Synthesis of continuous silicon carbide fiber. IV. The structure of polycarbosilane as the precursor. *J. Mater. Sci.*, 1986, **21**, 321–328.
23. LY, H. Q., Taylor, R., Day, R. J. and Heatley, F., Conversion of polycarbosilane (PCS) to SiC-based ceramic. Part 1. Characterization of PCS and curing products. *J. Mater. Sci.*, 2001, **36**, 4037–4043.
24. Rushkin, I. L., Shen, Q., Lehman, S. E. and Interrante, L. V., Modification of a hyperbranched hydridopolycarboxysilanes as a route to new polycarbosilanes. *Macromolecules*, 1997, **30**, 3141–3146.
25. Peter, E. F., Synthesis and properties of a new, branched polyhydridocarbosilane as a precursor for silicon carbide. *J. Inorg. Organomet. Polym.*, 1993, **3**(3), 251–258.

26. Whitmarsh, C. K. and Interrante, L. V., Synthesis and Structure of a highly branched polycarbosilane derived from (chloromethy1)trichiorosilane. *Organometallics*, 1991, **10**, 1336–1344.
27. Matthews, S., Edirisinghe, M. J. and Folkes, M. J., Effect of pre-pyrolysis heat treatment on the preparation of silicon carbide from a polycarbosilane precursor. *Ceram. Int.*, 1999, **25**, 49–60.
28. Mocaer, D., Pailler, R., Naslain, R., Richard, C., Pillot, J. P., Dunogues, J. *et al.*, Si-C-N ceramics with a high microstructural stability elaborated from the pyrolysis of new polycarbosilazane precursors. Part I. The organic/inorganic transition. *J. Mater. Sci.*, 2001, **28**, 2615–2631.