



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Journal of Organometallic Chemistry 687 (2003) 27–32

Journal
of Organo
metallic
Chemistrywww.elsevier.com/locate/jorganchem

Effect of polyborazine additive on thermolysis of polyphenylsilane and polyvinylsilane

Lan-Young Hong^a, Feng Cao^b, Dong-Jin Kim^a, Hee-Gweon Woo^{c,*}, Bo-Hye Kim^c,
Myong-Shik Cho^c, Xiao-Dong Li^b, Dong-Pyo Kim^{a,*}

^a Department of Fine Chemical Engineering and Chemistry, Chungnam National University, Taejon 305-764, Republic of Korea

^b Key Lab of C.F.C., National University of Defense Technology, Changsha 410073, PR China

^c Department of Chemistry and Nano Technology Research Center, Chonnam National University, Yong-Bong Dong, Kwangju 500-757, Republic of Korea

Received 7 May 2003; received in revised form 5 August 2003; accepted 6 August 2003

Abstract

To improve the ceramic residue yields and processabilities of polyphenylsilane (PPS) and polyvinylsilane (PVS), polyborazine (PBN) was employed as an additive. The ceramic residue yield of PPS increased from an original 39wt% to 65wt%, and of PVS from an original 26wt% to 64wt% by simply heating with 1wt% PBN at 70 °C. Furthermore, low viscous PPS and PVS were transformed into highly viscous polymers, which were found to be suitable for hand drawing into green fibers. The enhanced properties were attributed to an increased molecular weight, as analyzed by GPC. ¹H-NMR and ²⁹Si-NMR spectra suggested that dehydrocoupling of SiH₃ in PVS and Si–H in PPS by PBN was responsible for the improved ceramic yields.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Polyphenylsilane; Polyvinylsilane; Polyborazine; Dehydrocoupling; Cross-linking; Ceramic residue yield; Curing; Additive; SiC ceramic

1. Introduction

SiC ceramic is an excellent candidate for non-oxide ceramics with high-temperature stability and suitable mechanical properties. Since silicon-containing polymers are generally used for preparing the non-oxide ceramic, various polymeric precursors with different structures have been designed to synthesize. Preceramic polycarbosilane (PCS), used for preparing commercial Nicalon fibers, is synthesized by the low efficient thermolysis of polydimethylsilane (PDMS) [1]. As an alternative precursor for SiC ceramics, we studied polyphenylsilane (PPS, [SiH(Ph)]_n) [2] and polyvinylsilane (PVS, [CH₂CH(SiH₃)]_n) [3]. An ideal preceramic precursor for SiC ceramics should exhibit (1) high ceramic residue yield, to minimize the cost and volume changes associated with pyrolytic conversion to cera-

mics and consequently to maximize the control of porosity and densification, and (2) a suitable processability (i.e. viscosity) allowing it to be shaped into the needed forms prior to pyrolysis. In this context, it is disadvantageous that too low viscous PPS and PVS to shape undergoes drastic mass loss during pyrolysis, which leads to low ceramic residue yields (20–40wt%) [4]. There have been various attempts to resolve such drawbacks of SiC precursors. Toreki et al. enhanced the ceramic residue yield of PCS to 78wt% by synthesizing high molecular weight PCS by a rather crude procedure, which involved the thermolysis of PDMS at 435 °C and 7 atm pressure for 22 h [5]. Baney and coworkers explored an alternative way of improving the ceramic yield of PCS, using hydrosilylation reaction between PCS and unsaturated compounds such as polyolefin, vinylsilane or vinylsiloxane, but an additional amount of carbon was introduced to the already carbon-rich PCS [6]. A few studies for improving the ceramic residue yield of PCS have been undertaken on cross-linking reactions of PCS using organoborate additives at relatively high temperatures [7,8]. Several boron compounds were

* Corresponding authors. Tel.: +82-62-530-3378; fax: +82-62-530-3389.

E-mail addresses: hwoo@chonnam.ac.kr (H.-G. Woo), dpkim@cnu.ac.kr (D.-P. Kim).

reported to catalyze the disproportionation reaction between Si–Si and Si–H or the elimination of hydrogen between two Si–H containing intermediates, creating new Si–Si bonds [9–11]. In our previous work we first reported that the simple addition of 1wt% polyborazine (PBN, $[B_3N_3H_4]_n$) to polymethylsilane (PMS) dramatically improved the ceramic residue yield from 30% to 78% [12]. Here we wish to report our study on the modification of two different types of preceramic polymers PPS and PVS using PBN additive at mild conditions, resulting in improved ceramic residue yield and processability, in order to generalize the novel curing method. An additional benefit is that this system does not introduce molecularly bound oxygen or carbon which could adversely affect the high temperature stability of the final products.

2. Results and discussion

2.1. Curing of PPS and PVS using PBN additive

Figs. 1 and 2 showed TGA and DSC curves of modified PVS and PPS versus their feedstocks.

It is evident that the ceramic residue yields of both preceramic polymers were efficiently improved by simply treating with a small amount of PBN. The ceramic residue yield of PPS was enhanced to 65wt% from 39wt% after treating with 1wt% PBN at 70 °C for 10 h. When PPS was treated with 1wt% PBN at 200 °C for 4 h, its ceramic residue yield reached 71wt%. The ceramic residue yield of PVS was improved from 26wt% to 64wt% after treatment at 70 °C for 10 h with 1wt% PBN, to 71wt% with 1wt% PBN at 200 °C for 1 h. On the other hand, both polymers treated at 70 °C for 10 h in

the absence of PBN gave no improvement in ceramic residue yield and showed significant weight loss between room temperature and 350 °C. These behaviors are attributed to exothermic peaks at 200–300 °C, which caused drastic weight loss due to the lack of cured network structure. When the polymers were treated after the addition of 1wt% of PBN, the exothermic peaks were shifted to higher temperatures (250–400 °C) with significantly reduced weight loss. These results indicate that the presence of PBN highly stabilizes the polymeric structure of PPS and PVS against early stage thermal decomposition by promoting the curing reaction at a low temperature.

The existence of a modified reaction between the SiC precursors by PBN was further proven by determining molecular weights. As shown in Fig. 3, the GPC curve of the modified PPS gradually shifted to shorter retention due to increased molecular weight.

As summarized in Table 1, after treatment with 1wt% PBN at 70 °C for 10 h, the M_n and M_w of PPS were enhanced from 1640 and 1670 to 1880 and 2100, and the M_n and M_w of PVS also increased from 1300 and 1330 to 1450 and 3580.

By comparison, both polymers treated without PBN under the same conditions did not change appreciably in molecular weights. Furthermore, we demonstrated the processability of the modified polymers by simple hand-drawing in a glove-bag filled with N_2 gas. As shown in Fig. 4, green fibers of 30–35 μm diameter and length exceeding 10 cm were obtained from both highly viscous modified polymers.

However, the polymer feedstocks were not appropriate for fiber drawing due to their low viscosity. The spinnability of modified PVS was lower than that of modified PPS probably because of its high polydisper-

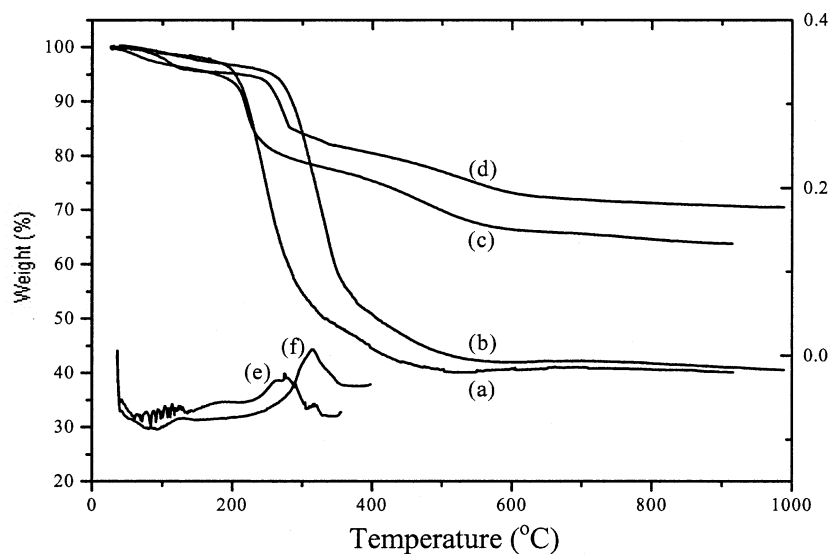


Fig. 1. TGA curves for (a) PPS feed stock, (b) non-enhanced PPS treated at 70 °C for 10 h, (c) enhanced PPS treated with 1wt% PBN at 70 °C for 10 h and (d) at 200 °C for 4 h. Also shown are DSC curves for (e) PPS feed stock, and (f) enhanced PPS treated with 1wt% PBN at 200 °C for 4 h.

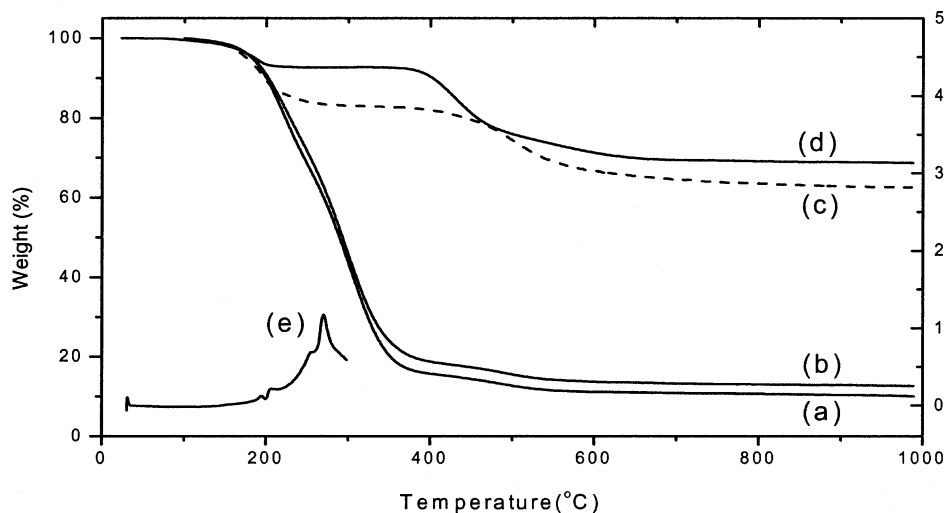


Fig. 2. TGA curves for (a) PVS feed stock, (b) non-enhanced PVS treated at 70 °C for 10 h, (c) enhanced PVS treated with 1wt% PBN at 70 °C for 10 h, and (d) enhanced PVS treated with 1wt% PBN at 200 °C for 1 h. DSC curve for (e) enhanced PVS treated with 1wt% PBN at 70 °C for 10 h.

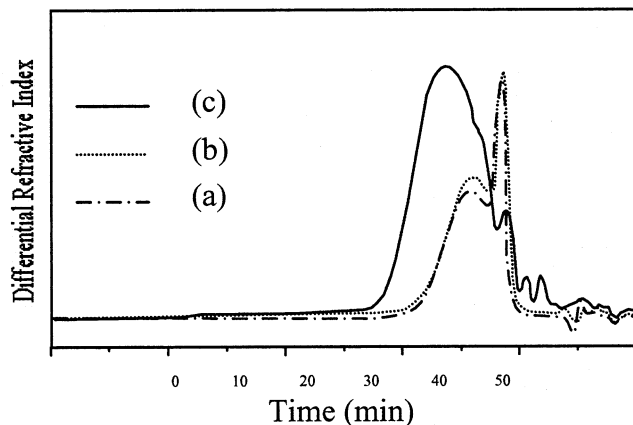


Fig. 3. Molecular weight distributions of (a) PPS feed stock, (b) non-enhanced PPS treated at 70 °C for 10 h and (c) enhanced PPS treated with 1wt% PBN at 70 °C for 10 h.

Table 1
GPC data of PPS and PVS samples produced in different conditions

Samples	M_n	M_w	PDI (M_w/M_n)
PPS feed stock	1640	1670	1.02
PPS, 70 °C, 10 h	1640	1670	1.02
PPS + 1wt%PBN, 70 °C, 10 h	1880	2100	1.12
PVS feed stock	1300	1330	1.02
PVS, 70 °C, 10 h	1300	1330	1.02
PVS + 1wt%PBN, 70 °C, 10 h	1450	3580	2.47

sity. We are further investigating the development of an economic process of producing oxygen-free SiC fiber using a dry-spinning process and subsequent pyrolysis at high temperatures with no extra-curing step in air.

To understand the chemistry behind the promoting effect of PBN, $^1\text{H-NMR}$ spectral data were compared as summarized in Table 2.

The $^1\text{H NMR}$ of PPS displayed discrete peaks at δ 3.6–4.6 and δ 6.4–7.8, attributed to Si–H and Si–C₆H₅ resonances, respectively [2]. Integration ratios of Si–C₆H₅/Si–H increased from an initial δ 5.0 to δ 5.2, as shown in Table 2, indicating that some of the Si–H groups are consumed by the dehydrocoupling reaction. In PVS, peaks at δ 0.6–1.8 and δ 3.4–3.6 were assigned to Si–CH₂CH₂ and Si–H, respectively [3]. Integration ratios of Si–CH₂CH₂/Si–H increased from an initial δ 2.82 to δ 3.05. FTIR analysis confirmed the conclusions drawn from the results of $^1\text{H-NMR}$ analyses, as the intensity of the Si–H peak at 2145 cm⁻¹ was significantly reduced versus to other peaks in the non-enhanced spectrum.

In Fig. 5, the $^{29}\text{Si-NMR}$ spectrum of non-enhanced PPS showed only the broad and poorly defined spectrum in which the $-\text{[PhSiH]}_n-$ region ranged between δ -55 and δ -66 [15], while that of enhanced PPS, produced by 10wt% PBN at 200 °C for 4 h, showed extra resonance at δ -21, which was assigned to Si NSi₂(Ph) units [16–20].

In Fig. 6, the $^{29}\text{Si-NMR}$ spectrum of PVS showed resonances in the region between δ -50 and δ -60, which were assigned to $-\text{[CH}_2\text{CH(SiH}_3\text{)]}_n-$ [3].

Both $^{29}\text{Si-NMR}$ spectra of enhanced PVS, produced by 1wt% PBN at 70 °C for 10 h and 300 °C for 1 h, showed additional resonances at δ -22, a characteristic peak of Si(N)₂CH units [16–20]. Moreover, this peak at δ -22 was significantly increased in intensity as the treatment temperature approached 200 °C. It is most likely that the dehydrocoupling reaction between Si–H in PVS and N–H in the presence of 1wt% PBN was more significant than that of PPS with 1wt% PBN due

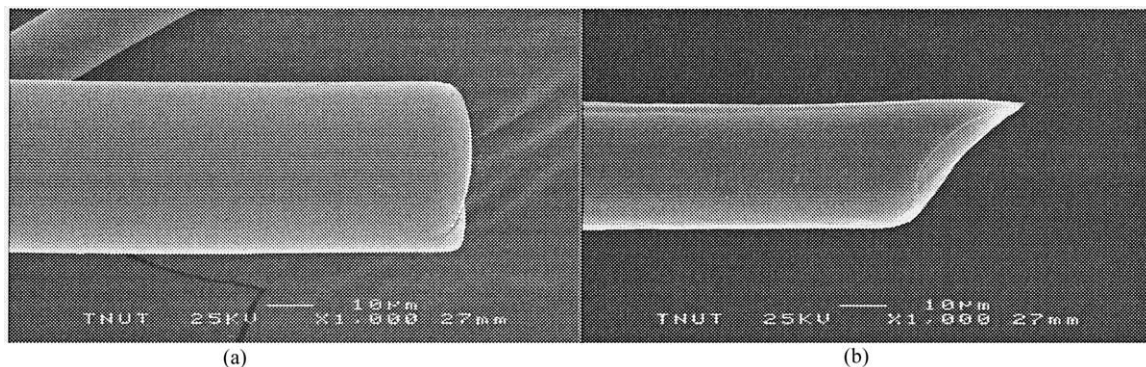


Fig. 4. SEM micrographs of (a) PBN-modified PPS green fiber, and (b) PBN-modified PVS green fiber, treated with 1wt% PBN at 70 °C for 10 h, respectively.

Table 2
¹H-NMR integration ratio for various PPS and PVS samples

	C–H (δ 6.4–7.8)	Si–H (δ 3.6–4.6)	C–H/Si–H
PPS feed stock	20.0	4.00	5.00
PPS, 70 °C, 10 h	20.0	3.98	5.02
PPS+1wt% PBN, 70 °C, 10 h	20.0	3.85	5.20
	C–H (δ 0.6–1.8)	Si–H (δ 3.4–3.6)	C–H/Si–H
PVS feed stock	6.00	2.13	2.82
PVS, 70 °C, 10 h	6.00	2.07	2.90
PVS+1wt% PBN, 70 °C, 10 h	6.00	1.97	3.05

to the reactivity difference of Si–H units in PPS backbone and SiH₃ units as a substituent of PVS. We propose that the dehydrocoupled curing reaction between Si–H in polysilane and N–H in PBN occurs as shown in Scheme 1.

Similarly, it has been reported that the desirable cross-linking reactions are the dehydrocoupling of Si–H and N–H units in boron-modified polysilazane with the formation of Si–N bonds [21]. Alternatively, this mechanism may be supported by considering bond polarities, since the positively charged hydrogen atoms of the N–H groups tend to react with the negatively charged hydrogen atoms of the Si–H groups [22]. Moreover, the formation of Si–N bonds is more favored thermodynamically than the generation of weak Si–Si or Si–C bonds [22]. Finally, this work suggests that organosilicon polymers containing a multiplicity of Si–H bonds can be converted to useful ceramic precursors by simple chemical modification, which triggers the dehydrocoupling reactions of Si–H bonds by the addition of a small quantity of PBN.

2.2. Conclusions

We have developed an efficient procedure, which improves the ceramic residue yields and processabilities

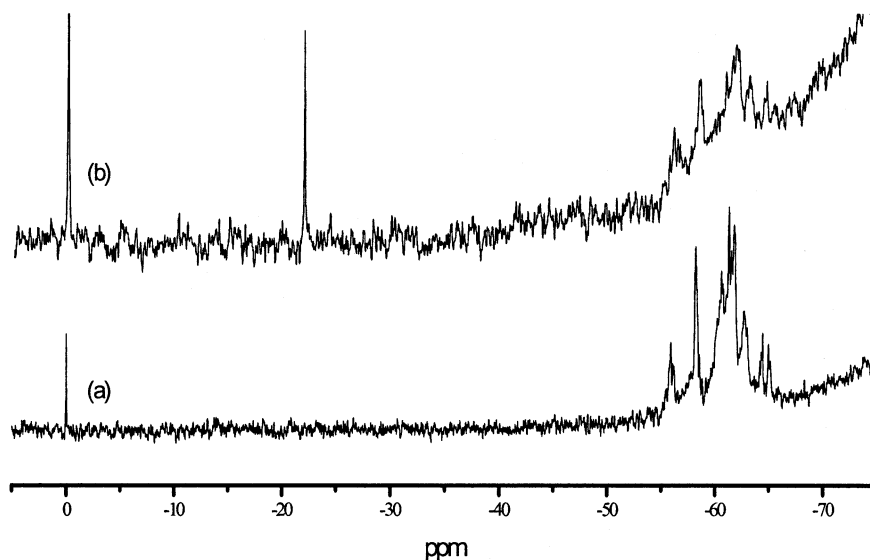


Fig. 5. ²⁹Si-NMR spectra of (a) PPS feed stock and (b) enhanced PPS treated with 10 wt% PBN at 200 °C for 4 h.

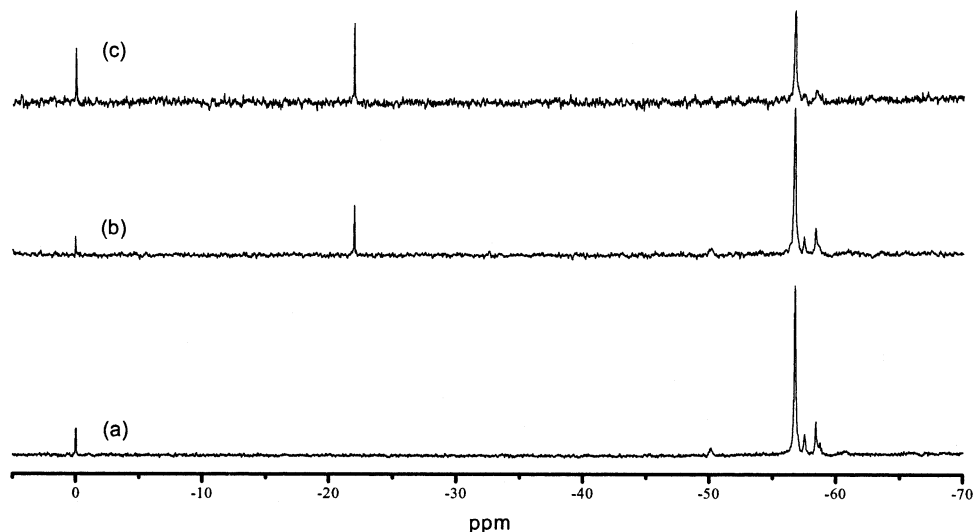
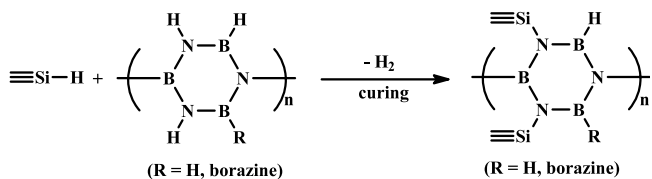


Fig. 6. ^{29}Si -NMR spectra of (a) PVS feed stock, (b) enhanced PVS treated with 1 wt% PBN at 70 °C for 10 h, and (c) enhanced PVS treated with 1wt% PBN at 300 °C for 1 h.



Scheme 1. Cross-linking of polysilanes by dehydrocoupling of Si–H with N–H units of PBN.

of polyphenylsilane (PPS) and polyvinylsilane (PVS) by heating with 1wt% polyborazine (PBN) at mild temperature. In the present study, the ceramic yield of PPS was increased from 39wt% to 65wt%, and of PVS from 26wt% to 64wt%. The thermal properties of polyphenylsilane (PPS) and polyvinylsilane (PVS) were improved due to the increased molecular weight (judged by GPC analysis) achieved by the dehydrocoupling of the Si–H groups in the PPS and PVS polymers with the N–H groups in PBN, as assessed by ^1H -NMR and ^{29}Si -NMR spectroscopic investigations. It is believed that the technique has the general ability to promote the dehydrocoupled curing of Si–H containing polymers, and that it will allow the production of varied dense ceramics from a range of Si–H containing preceramic polymers.

3. Experimental

All samples described in this investigation were manipulated in a prepurified nitrogen atmosphere or in a vacuum system. THF was dried by distillation over sodium. PPS was prepared by the dehydropolymerization of PhSiH_3 with $\text{Cp}_2\text{TiCl}_2/\text{Red-Al}$ catalyst, followed by flash chromatography (packed with Florisil[®]) with toluene as eluent [2]. PVS was prepared by polymeriza-

tion of $\text{CH}_2=\text{CH}-\text{Si}(\text{OEt})_3$ in the presence of $t\text{Bu}_2\text{O}$ initiator at 130 °C for 6 h followed by reaction of resulting polymer with LiAlH_4 [3]. PBN was synthesized according to the method described in our previous work [9]. The modifications of PPS and PVS were carried out by adding 1wt% PBN, followed by dissolving in THF, stirring for 2 h, and then removing the THF in vacuum. The low viscous PPS or PVS mixture was then heated in an oil bath at 70 °C or 200 °C for several hours, which was transformed into highly viscous polymers. Viscous polymer solutions for the fiber-spinning process were obtained by dissolving 2 g of the modified PPS or PVS precursor, treated with 1wt% PBN at 70 °C for 10 h, in about 0.5 ml of THF, and by aging the mixture overnight to remove bubbles. Green fibers of modified PPS or PVS were prepared with lengths exceeding 20 cm by hand drawing in a nitrogen atmosphere in a glove-bag, as described by Yajima [13,14]. To investigate the reaction between preceramic polymers and PBN by NMR spectroscopy, 10wt% PBN was mixed with PPS.

Molecular weight distributions were determined by GPC (gel permeation chromatography, Waters) equipped with s-Styragel columns calibrated using polystyrene standards and eluted using THF at a flow rate of 0.5 ml min^{-1} . Thermogravimetric analysis (TGA; TA Instrument 2950) was carried out at a heating rate of 10 °C min^{-1} to 1000 °C in nitrogen atmosphere. Differential scanning calorimetry (DSC; TA Instrument DSC 2010) was carried out at a heating rate of 5 °C min^{-1} to 350 °C under N_2 atmosphere. ^1H -NMR spectra were acquired using a Bruker DMX 600 spectrometer with a $\text{CDCl}_3-\text{CHCl}_3$ reference at δ 7.24 downfield from TMS. ^{29}Si -NMR spectra were obtained on a Bruker DMX 600 spectrometer (operating at 119.19 MHz) using TMS (δ 0.00) as a standard. Infrared spectra were obtained using a Mattson Instru-

ment Genesis II FT-IR spectrophotometer. The morphology of the fibers was studied by scanning electron microscopy (SEM) using a JSM-6300 (JEOL).

Acknowledgements

This work was supported by the Korea Research Foundation Grant (KRF-2001-005-E00033), by the ADD Research Grant (ADD-03-09-02), and by the Chinese Natural Science Fund (Grant No. 59972042). H.-G.W. is grateful to the Korea Science and Engineering Foundation for financial support (KOSEF Project No. R01-2001-000-00053-0; 2003). Additionally we thank the Korean Basic Science Institute (KBSI) for carrying out the $^1\text{H-NMR}$ and $^{29}\text{Si-NMR}$ investigations.

References

- [1] R.M. Laine, F. Babonneau, *Chem. Mater.* 5 (1993) 260.
- [2] H.-G. Woo, S.-J. Song, *Chem. Lett.* (1999) 457.
- [3] D. Seyferth, M. Tasi, H.-G. Woo, *Chem. Mater.* 7 (1995) 236.
- [4] H.-G. Woo, Research report, M.I.T. (1991).
- [5] W.C. Toreki, D. Batich, G. Choi, *Polym. Prepr.* 32 (1991) 584.
- [6] R.H. Baney, G.T. Burns, European Patent 0,251,67s (1987).
- [7] B. Boury, *Chem. Mater.* 10 (1998) 297.
- [8] T. Iseki, M. Narisawa, K. Okamura, *J. Mater. Sci. Lett.* 18 (1999) 185.
- [9] J.G. Kho, D.S. Min, D.P. Kim, *J. Mater. Sci. Lett.* 19 (2000) 303.
- [10] H. Ishikawa, F. Machino, S. Mitsuno, T. Ishikawa, K. Okamura, Y. Hasegawa, *J. Mater. Sci.* 24 (1989) 1177.
- [11] S. Yajima, Y. Hasegawa, K. Okamura, T. Shishido, *Nature* 273 (1987) 525.
- [12] T. Ishikawa, M. Shibura, T. Yamamura, *J. Mater. Sci.* 25 (1990) 2809.
- [13] S. Yajima, J. Hayashi, M. Otori, *Chem. Lett.* (1975) 931.
- [14] S. Yajima, K. Okamura, J. Hayashi, *Chem. Lett.* (1975) 1209.
- [15] G.J. Frimmond, J.Y. Corey, *Organometallics* 18 (1999) 2223.
- [16] K. Tamao, G.R. Sun, A. Kawachi, S. Yamaguchi, *Organometallics* 16 (1997) 780.
- [17] J. Seitz, J. Bill, N. Egger, F. Aldinger, *J. Eur. Ceram. Soc.* 16 (1996) 885.
- [18] M. Suzuki, U. Hasegawa, M. Aizawa, Y. Nakata, T. Okutani, *J. Am. Ceram. Soc.* 78 (1995) 83.
- [19] Y. Kortobi, H. Sfihi, A.P. Legrand, E. Musset, N. Herlin, M. Cauchetier, *Colloid Surface A* 115 (1996) 319.
- [20] G. Ziegler, H.-J. Kleebe, G. Motz, H. Müller, S. Traßl, W. Weibelzahl, *Mater. Chem. Phys.* 61 (1999) 55.
- [21] M. Weinmann, J. Schuhmacher, H. Kummer, S. Prinz, J. Peng, H.J. Seifert, M. Christ, K. Müller, J. Bill, F. Aldinger, *Chem. Mater.* 12 (2000) 623.
- [22] Y.L. Li, E. Kroke, R. Riedel, C. Fasel, C. Gervais, F. Babonneau, *Appl. Organomet. Chem.* 15 (2001) 820.