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Modification of SiC precursors with an amine–borane complex

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Two methods for preparing precursors of Si/C/B-based thermostructural materials have been developed. The first consists of a thermal treatment of a mixture of polydimethylsilane (PDMS), $(Me_2Si)_n$, and triethylamine–borane adduct, $Et_3N:BH_3$ at atmospheric pressure. The second involves two steps: (i) transformation of PDMS into a polymer displaying Si–CH_2–Si and Si–Si linkages in its backbone, and (ii) heating this product at atmospheric pressure, in the presence of $Et_3N:BH_3$. The ceramic material obtained from the second approach contains 2.2 at% boron and 1.5 at% oxygen.

1. Introduction

In 1977, Yajima *et al.* [1] showed that the addition of a few per cent of polyborodiphenylsiloxane to polydimethylsilane (PDMS) allowed its transformation into a polycarbosilane (PCS) at 350 °C, under atmospheric pressure. This PCS precursor, referred to as Mark III, contained a significant amount of oxygen and 30 p.p.m. boron.

Recently, it has been reported that the curing of a fibre prepared from a commercial PCS (Nippon Carbon, Japan) with NO_2/BCl_3 induced beneficial effects at high temperatures [2–4]. After pyrolysis at 1800 °C under argon, a dense ($d > 3.1$), nearly stoichiometric fibre was obtained, containing a very low proportion of oxygen (< 0.1 wt%), and possessing good mechanical properties at room temperature (Young's modulus, $E = 450$ GPa and strength, $\sigma_R = 2600$ MPa). The mechanism of the conversion by NO_2/BCl_3 has not been reported. Moreover, the reactions occurring at high temperature have not been described. Curing the same PCS fibre with BCl_3/NH_3, NO/B_2H_6, or NO/BCl_3 did not give satisfactory results. Indeed, the fibres obtained from pyrolysis at 1800 °C under argon were nearly pure SiC, with a low oxygen content and $\sim 0.2\%$ boron, but they did not exhibit mechanical properties as good as those of the fibres treated with NO_2/BCl_3 [5] (Table I).

On the other hand, only a few methods have been developed to synthesize Si/C/B-based ceramic precursors: (i) the sodium co-condensation of compounds possessing Si–Cl and B–Cl bonds [6, 7], (ii) hydroboration of unsaturated organopolysilane derivatives with borane adducts [8], or (iii) condensation of halogenosilylborane $B(C_2H_4SiCl_2X)_3$ ($X = Cl$ or alkyl) [9]. The condensation in the presence of sodium of di- and (or) trihaloboranes and dimethyldichlorosilane affords soluble, fusible polymers (softening temperature < 150 °C) with fairly low average molecular weights ($\bar{M}_n \approx 1000$). Their ceramic residue at 1100 °C under nitrogen is greater than 64%, and the materials are constituted with silicon carbide and boride [10].

The aim of the present work was to introduce boron into organosilicon precursors before spinning. We chose the triethylamine–borane adduct, $Et_3N:BH_3$, as the source of boron because it is far less toxic than B_2H_6, much easier to handle, and does not decompose below 230–240 °C. The first approach is a thermal treatment of PDMS in the presence of $Et_3N:BH_3$ adduct at atmospheric pressure. The second approach involves two steps: (i) the partial conversion of PDMS into a polysilacarbosilane (PSCS) under pressure (an earlier work in our Laboratory [11] had shown that heating a commercial PCS in the presence of an amine–borane adduct at 250 °C, led to an infusible, insoluble material), and (ii) the thermolysis at atmospheric pressure of a PSCS/$Et_3N:BH_3$ mixture.

2. Experimental procedure

2.1. Characterizations

2.1.1. Infrared spectroscopy (IR)

The IR spectra were recorded between 4000 and 400 cm^{-1} on a Nicolet FT 20 SXC spectrometer. Solid samples were analysed as KBr pellets.

2.1.2. Size exclusion chromatography (SEC)

SEC profiles were obtained with a Waters chromatograph with four TSK (Toyo Soda) columns (porosity range 4–10^6 nm), calibrated with narrow polystyrene standards, connected to ultraviolet and refractometer detectors. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1 ml min^{-1}.

2.1.3. *Thermogravimetric analysis (TGA)*

TGA curves from 40–950 °C were recorded on a Perkin–Elmer model TGS2 thermobalance, then processed with a model 3600 data station (conditions: argon N56, flow rate 40 ml min^{-1}; heating rate 5 °C min^{-1}; sample mass 10–20 mg).

2.1.4. *Differential scanning calorimetry (DSC)*

DSC thermograms under argon were recorded with a Perkin–Elmer DSC 7 microcalorimeter at a heating rate of 20 °C min^{-1} (high pressure, gold-plated sealed pans).

2.1.5. *Pyrolysis*

The pyrolyses of the precursors were carried out in a tubular furnace under an argon (N56) flow. The samples were put in an alumina boat. The heating rate was 1 °C min^{-1} with a final isothermal plateau of 1 h.

2.1.6. *Chemical analysis*

Elemental analyses of the ceramics were obtained from an electron probe microanalyser (EPMA) data (Camebax from CAMECA). A pentaerythritol (PET) crystal was used for silicon (Si K_α) and a multilayered pseudo crystal (PCI) for carbon (C K_α) and oxygen (O K_α), the references, being SiC, SiO_2, and B.

2.2. Solvents and reagents

Pentane (from "Solvents, Documentation, Synthèses" Company, SDS) was distilled over Na/benzophenone, then over $LiAlH_4$. It was kept on molecular sieves (0.4 nm) and stored in the dark under argon. Triethylamine–borane adduct (Aldrich) and polydimethylsilane (Hüls) were used as-received.

TABLE I Mechanical properties of PCS fibres cross-linked with various gas mixtures and heat treated at high temperatures [5]

	Cross-linking agent		
	BCl_3/NH_3	NO/B_2H_6	NO/BCl_3
σ_R (MPa)	1650	1150	1700
E (GPa)	220	180	270

2.3. Apparatus

All filtrations and manipulations were carried out in a dry glove-box under a nitrogen atmosphere or with an argon line, to prevent pollution by oxygen or moisture. Glassware was carefully dried and purged with argon before use. Gases were dried through potassium hydroxide columns.

2.4. Preparation of homogeneous reaction mixtures

Weighed quantities of PDMS (or PSCS) and $Et_3N:BH_3$ complex were introduced in a 100 ml round-bottomed flask. Pentane (25 ml) was added, and the mixture was manually homogeneized. After evaporation of the solvent under vacuum, the obtained mixtures were subsequently tested in DSC experiments or thermolysed to various precursors.

2.5. Thermolysis of PDMS: synthesis of precursors 1–4

The silica vessel consists of a 250 ml, three-necked flask fitted to an argon inlet, a thermometric well, and a reflux condenser connected to a safety bottle and a gasmeter. The PDMS/$Et_3N:BH_3$ mixtures were introduced into the flask and the vessel was carefully purged with argon U, then heated to 350 °C with a fluidized sand-bath at 400 °C for 5 h. During the reaction, the internal temperature and the gaseous volume were noted every 10–15 min. Beyond 200–250 °C, an important reflux and increasing gas evolution were observed. After 5 h, the internal temperature reached 300–350 °C, and the mixture was allowed to cool under an argon flow. The solid materials were dissolved in dry pentane, then filtered in the dry glove-box. The solutions were evaporated under vacuum, then the soluble, fusible polymers were devolatilized for 2 h at 100 °C under vacuum (0.1 torr), yielding precursors P1–P4. Results are collected in Table II.

TABLE II Thermolysis of PDMS in the presence of $Et_3N:BH_3$; SEC and TGA results for precursors P1–P4

Precursor	PDMS (g)	Complex (g)	R = PDMS/complex (mol %)	T (°C)	t (h)	Yield[a] (%)	$\bar{M}_n$	I_p^b	TGA residue (%)
P1	11.6	5.75	4	480	5	14.2	690	1.5	22
P2	11.6	3.8	6	470	4	9.5	700	1.5	40
P3	11.6	2.9	8	350	5	16.1	1065	2.2	47
P4	11.6	2.3	10	425	4	14.2	780	2.5	43

[a] Overall yield in soluble fraction after devolatilization.

[b] Polydispersity index.

2.6. Synthesis of precursor P5

The reaction was carried out in the same vessel. Oligomer P3 (1.5 g) was introduced in the flask and heated at 380 °C for 2.5 h. After cooling under argon (N56), the solid material was washed with dry pentane, giving an infusible polymer P5 (1 g, 67%). SEC results, $\bar{M}_n = 2400$, $I_p = 1.8$; TGA residue 60%.

2.7. Synthesis of PSCS

PDMS (37.5 g) was introduced in a 150 ml autoclave under argon. Then, the autoclave was heated to 470 °C for 4 h, the thermal treatment was stopped when the internal pressure reached 3 MPa (30 bar). After cooling, the residue was dissolved in pentane, then filtered. The solution was concentrated to yield a viscous PSCS polymer (22.5 g, 60%). SEC results, $\bar{M}_n \approx 680$, $I_p \approx 1.5$. Its infrared spectrum shows the characteristic absorption bands of the Si–CH$_2$–Si fragment at 1350 cm^{-1} (δ_{CH_2}) and 1023 cm^{-1} (W_{CH_2}), and the Si–H valence band at 2105 cm^{-1}.

2.8. Thermolysis of PSCS: synthesis of precursor P6

The previously described apparatus was modified to improve its airtightness. The three-necked flask, the thermometric well, the argon inlet, and the condenser were equipped with silica glass–metal connections and copper seals. Moreover, N56 grade argon was used for purging.

PSCS (11 g) and $Et_3N:BH_3$ adduct (2 g) were introduced into the 250 ml, three-necked round-bottomed flask. Then the flask was fitted to the argon inlet, the thermometric well, and the reflux condenser connected to the gasmeter. The vessel was carefully purged with argon N56, then heated to 350 °C with a fluidized sand-bath at 400 °C for 3 h. During the reaction, the internal temperature and the gaseous volume were measured every 10–15 min. At 200–250 °C, a substantial reflux was observed and the gas evolution increased significantly. After 3 h, the internal temperature reached 300–350 °C, and the mixture was allowed to cool under an argon flow. The solid material was dissolved in dry pentane, then filtered in a dry glove-box. The solution was evaporated under vacuum, then the soluble polymer (8.8 g) was devolatilized for 2 h at 100 °C under vacuum (0.1 torr), yielding the precursor P6 (8.4 g, 76%) which decomposes upon heating. SEC results, $\bar{M}_n = 3140$, $I_p = 2.1$; TGA residue 60%.

2.9. Preparation of precursor P7

Polymer P6 (6 g) was partially dissolved in 100 ml ethyl acetate, and filtered to separate the high molecular mass fraction. The solution was evaporated under vacuum, then heated at 100 °C for 1 h under vacuum (0.1 torr) to eliminate traces of solvent and oligomers, yielding precursor P7 (4.5 g, 75%). Softening temperature, 120 °C; SEC results, $\bar{M}_n = 1640$ and $I_p = 1.8$.

3. Results and discussion

3.1. First method of thermal treatment of PDMS with amine–borane complex at atmospheric pressure

3.1.1. Preliminary study by DSC

To obtain better information about the thermolysis conditions, a preliminary study by DSC was carried out on PDMS/$Et_3N:BH_3$ mixtures in various molar proportions, R (Table II).

Fig. 1a and b show that pure $Et_3N:BH_3$ adduct is stable up to 230–240 °C, and that PDMS becomes a liquid towards 370 °C, while DSC diagrams (Fig. 2a–d) clearly demonstrate a reaction between PDMS and $Et_3N:BH_3$. When $R = 4$, two peaks were observed: an exotherm near 282 °C, and an endotherm near 343 °C. When $R = 6$, the peak at 343 °C completely disappeared. These results show that the temperature of conversion of PDMS substantially decreased in the presence of the amine–borane adduct.

3.1.2. Results

When a mixture PDMS/$Et_3N:BH_3$ was allowed to react at 350 °C for 5 h, two fractions were obtained (cf. Section 2), a soluble, fusible compound, and an insoluble, infusible part. Only the soluble, fusible fractions have been characterized by infrared (IR) spectroscopy,

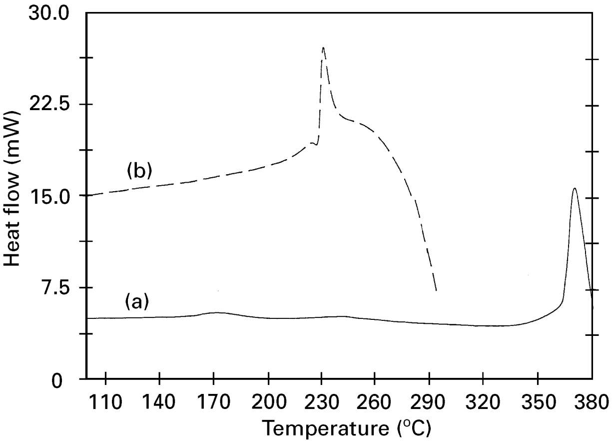

Figure 1 DSC curves of (a) PDMS and (b) $Et_3N:BH_3$ adduct.

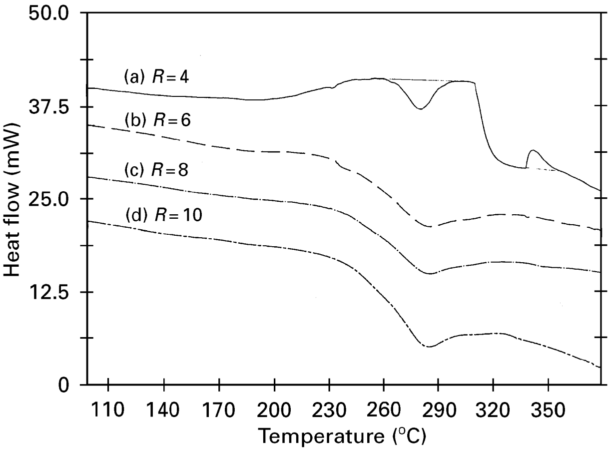

Figure 2 DSC curves of PDMS/$Et_3N:BH_3$ mixtures.

SEC, and TGA. As indicated in Table II, P1, P2, P3, and P4 corresponds to $R = 4, 6, 8$ and 10, respectively.

3.1.2.1. Infrared spectroscopy. The IR spectra of polymers P1–P4 are all similar (see Fig. 3a, corresponding to P4). Bands were assigned from literature data [12, 13]. A broad absorption between 2800 and 3000 cm^{-1} corresponds to the symmetrical and antisymmetrical stretching vibrations of CH_2 and CH_3. The Si–H valence band is observed near 2100 cm^{-1}. Bands at 1406, 1250, and 830 cm^{-1} are assigned to δ_aCH_3, δ_sCH_3, and ρCH_3, respectively. The two absorptions at 1350 (δ_{CH_2}) and 1027 cm^{-1} (W_{CH_2}) support the occurrence of the Kumada rearrangement (methylene insertion between two silicon atoms) [14].

The IR spectra of the insoluble, infusible fractions (Fig. 3b) are similar to that of the commercial PCS (Fig. 3c): this suggests that the transformation of polysilane into polycarbosilane is effective. In this case, $Et_3N:BH_3$ would act essentially as a cross-linking agent.

3.1.2.2. SEC and TGA. SEC and TGA data are given in Table II. These results show that the compounds are poorly cross-linked oligomers with moderate char yields. Owing to the presence of Si–H bonds that can induce thermal cross-linking, suitable precursors of Si/C/B materials can be obtained via a subsequent thermal treatment.

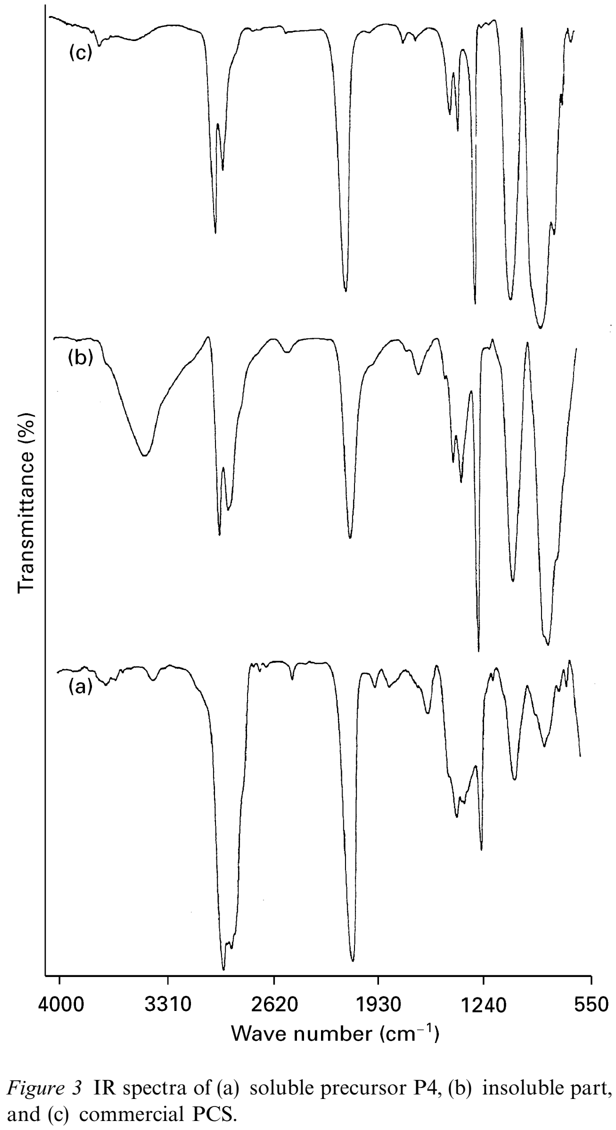

Figure 3 IR spectra of (a) soluble precursor P4, (b) insoluble part, and (c) commercial PCS.

3.1.2.3. Second thermolysis. This was carried out with oligomer P3 which was heated at 380 °C for 2.5 h, providing a soluble, but infusible precursor P5 in 67% yield. SEC calculation gave an average molecular weight $\bar{M}_n = 2400$, and a polydispersity index $I_p = 1.8$ (Fig. 4). Its TGA char yield at 95 °C under argon was ≈60% (Fig. 5a).

3.2. Second route to Si/C/B-based ceramic precursors

The yields of the thermolysis of $PDMS/Et_3N:BH_3$ mixtures at atmospheric pressure are rather low. Consequently, a second strategy has been envisaged. It consists in preparing a PSCS from PDMS, upon controlled heating under pressure. Then, like PDMS, the resulting PSCS was reacted with $Et_3N:BH_3$ at atmospheric pressure to provide a ceramic precursor.

3.2.1. Conversion of PDMS into PSCS in an autoclave

This conversion was performed under pressure. It produced a few Si–CH_2–Si sequencies and Si–H bonds in the polysilane backbone, according to the Kumada rearrangement. The resulting PSCS exhibits a low viscosity and has been characterized by IR

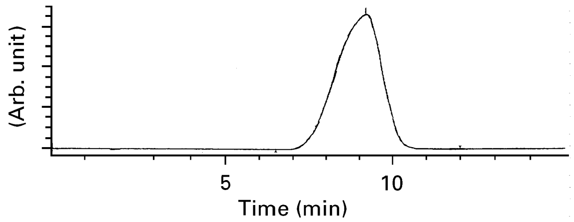

Figure 4 SEC profile of precursor P5.

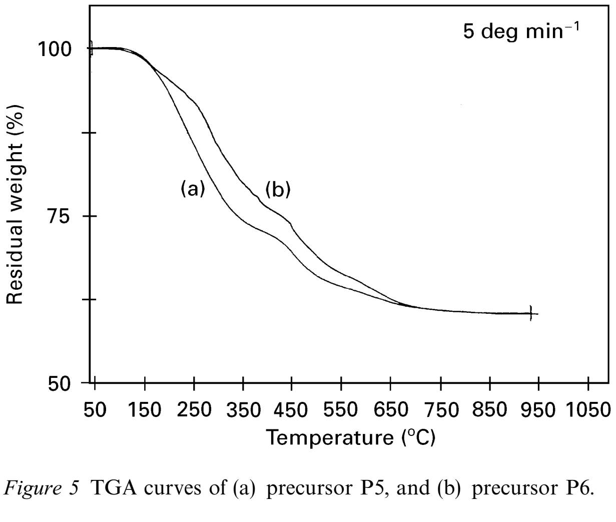

Figure 5 TGA curves of (a) precursor P5, and (b) precursor P6.

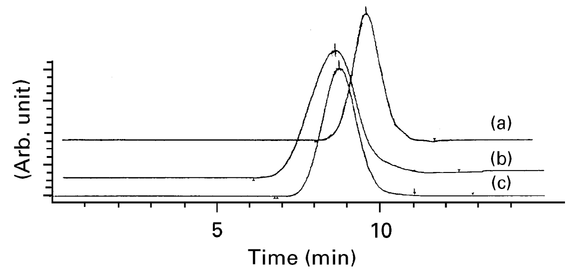

Figure 6 SEC profiles of (a) PSCS, (b) precursor P6, and (c) precursor P7.

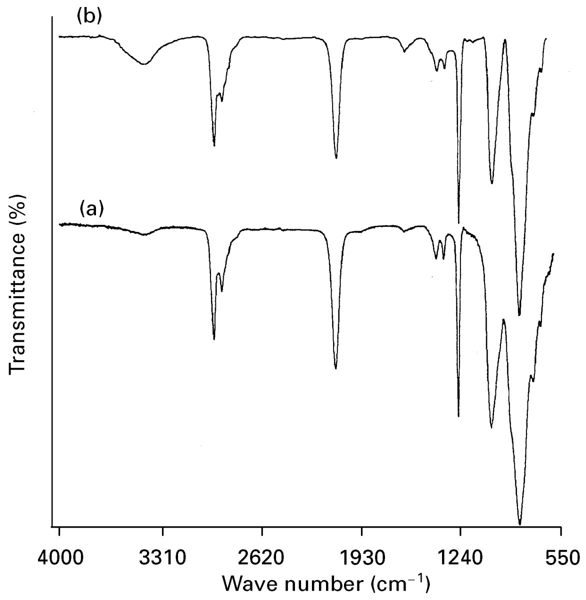

Figure 7 IR spectra of (a) PSCS, and (b) precursor P6.

spectroscopy and SEC. It displays a low molecular weight, $\bar{M}_n \approx 680$ with $I_p = 1.5$ (Fig. 6a). Characteristic infrared bands are observed for Si–CH$_2$–Si sequencies at 1350 cm^{-1} (δ_{CH_2}) and 1023 cm^{-1} (W_{CH_2}), as well as the Si–H valence band at 2105 cm^{-1} (Fig. 7a).

3.2.2. Thermolysis of PSCS in the presence of Et$_3$N : BH$_3$ at atmospheric pressure

The PSCS/Et$_3$N : BH$_3$ mixture (10 mol % adduct) was heated to 350 °C for 3 h, resulting in an important gas release. In this case, the yield of soluble, solid polymer is ≈ 80%. The precursor P6 was characterized by IR spectroscopy, SEC ($\bar{M}_n = 3140$, $I_p = 2.1$, Fig. 6b), and TGA. The 1020 cm^{-1} IR band, assigned to (W_{CH_2}) vibrations, is sharp, without a shoulder at high frequency (Fig. 7b). This suggests that oxygen in the polymer should be hardly present. The TGA residue of P6 under argon reaches 60% at 950 °C (Fig. 5b).

P6 decomposes before melting, needing appropriate modification. A treatment with ethyl acetate eliminated the high molecular weight fraction, whereas oligomers were distilled under vacuum. After this treatment, the resulting precursor P7 exhibited a narrower mass distribution: $\bar{M}_n = 1640$ and $I_p = 1.8$ (Fig. 6c). P7 is fusible, with a softening temperature ≈ 120 °C, and can be eventually melt-spun.

TABLE III Elemental composition of the ceramic materials (hydrogen was not taken into account)

Precursor	Pyrolysis atmosphere	At% in the ceramics Si	C	O	B
P4	Hydrogen	46.0	49.0	4.0	1.0
P5	Argon	35.1	54	7.2	3.6
P6	Argon	33.4	61.9	1.5	2.2

4. Study of the obtained ceramics

The precursors were pyrolysed at 1000 °C under an argon or an hydrogen flow. The elemental compositions of the residues are given in Table III. Nitrogen was not detected: Et$_3$N would not react in our operative conditions. These results show that the pyrolysis under hydrogen affords a quasi stoichiometric SiC ceramic. On the other hand, oxidation of the precursor can be largely reduced when appropriate reaction conditions are used.

5. Conclusion

We propose a cheap, easy route to Si/C/B-based ceramic precursors, which requires only small amounts of solvent. The Et$_3$N : BH$_3$ adduct has been used as a cross-linking agent for polysilanes and polycarbosilanes, and allowed introduction of variable amounts of boron in SiC-based ceramic precursors. Thermal treatment of a polysilacarbosilane at atmospheric pressure in the presence of Et$_3$N : BH$_3$ gave an infusible, but soluble polymer in good yields, then a Si/C/B ceramic with a low oxygen content. The elimination of the high molecular weight fraction of this polymer led to a soluble, fusible precursor, which could be melt-spun. The results of curing, pyrolysis, and physicochemical properties of monofilaments, will be reported in a forthcoming paper.

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References

1. S. YAJIMA, J. HAYASHI and K. OKAMURA, *Nature* **266** (1977) 521.
2. J. A. RABE, J. LIPOWITZ and P. P. LU, US Pat. 5051 215 (1991).
3. J. LIPOWITZ, J. A. RABE and G. A. ZANK, “5th International Conference on Ultrastructure Processing”, edited by L.L. Hench, J.K. West and D. R. Ulrich (Wiley, New York, 1992) p. 767.
4. R. M. LAINE and F. BABONNEAU, *Chem. Mater.* **5** (1993) 260.
5. D. C. DELEEUW, J. LIPOWITZ and P. P. LU, Eur. Pat. Appl. 438 117 (1991).
6. M. T. HSU, T. S. CHEN and S. R. RICCITIELLO, *J. Appl. Polym. Sci.* **42** (1991) 851.
7. P. VON GUTENBERGER, W. HABEL, C. NOVER and P. SARTORI, *J. Organomet. Chem.* **453** (1993) 1.

8. R. RIEDEL, A. KIENZLE, V. SZABO and J. MAYER, *J. Mater. Sci.* **28** (1993) 3931.
9. R. RIEDEL, A. KIENZLE, G. PETZOW, M. BRUECK and T. VAAHS, Ger. Pat. 4320 782-7 (1994).
10. M. T. S. HSU, T. S. CHEN and S. R. RICCITIELLO, *Polym. Prepr.* **27** (1986) 261.
11. P. ROUX, Thesis, Bordeaux (1993).
12. L. J. BELLAMY, "The Infrared Spectra of Complex Molecules" (Wiley, New York, 1962).
13. G. SOCRATES, "Infrared Characteristic Group Frequencies" (Wiley, New York, 1980).
14. T. ISHIKAWA, M. SHIBUYA and T. YAMAMURA, *J. Mater. Sci.* **25** (1990) 2809.

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