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Pyrolytic conversion of methyl- and vinylsilane polymers to Si–C ceramics

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Poly(methylsilane) and poly(vinylsilane) were synthesized using a titanocene catalyst, and their pyrolytic conversion to ceramics was followed using a combination of thermal analysis and infrared spectroscopy. The two polymers have distinctly different backbone structures, as determined by ^{29}Si NMR; methylsilane polymerizes to a polysilane, while vinylsilane polymers have a predominately polycarbosilane backbone, with some polysilane structure as well. The pyrolysis path and char yield were dependent primarily on backbone structure, with little influence of polymer molecular weight. The majority of the weight loss on conversion occurs below 650 °C, although bond rearrangement continues to 1400 °C. Poly(vinylsilane) produced a carbon-rich Si–C ceramic in which the carbon was dispersed on a sufficiently fine level to show resistance to oxidation on heating in air to 1400 °C. Copolymerization of methyl- and vinylsilane produced stoichiometric SiC; however, polymers of methylsilane were sensitive to oxygen incorporation and sometimes pyrophoric. Polymerization of vinylsilane with disilylethane permitted control of rheology and imparted thermoset behaviour.

1. Introduction

The conversion of organometallic precursors to ceramics enables processing techniques not attainable with more traditional powder sintering approaches, particularly in the areas of fibre and film formation and in the development of fibre-reinforced ceramic matrix composites having complex shapes. The composition and structure of the precursor polymer, as well as the pyrolysis cycle and atmosphere, determine the composition and morphology of the final ceramic, as well as its physical and mechanical properties. Control of polymer structure, molecular weight and curing mechanism permits tailoring of the polymer rheology for fibre spinning or composite matrix fabrication, and can decide ceramic yield and ultimate properties.

One of the most often cited examples of this approach is the work by Yajima and coworkers on the pyrolytic conversion of polydimethylsilane to a polycarbosilane, and finally to silicon carbide [1, 2]. This work has become the foundation for the production of Nicalon fibre (Nippon Carbon). Typically, crosslinking of the polycarbosilane is accomplished by the intentional introduction of several per cent oxygen, which ultimately leads to the formation of an amorphous Si–C–O ceramic that exhibits a loss in strength at temperatures above 1200 °C, accompanied by evolution of SiO and CO [3, 4].

More recently, a variety of other approaches to silicon carbide have been proposed which avert the deliberate introduction of oxygen to achieve crosslinking. Polymer systems under investigation include polysilanes [5], other polycarbosilanes [6], and polysilazanes [7–11].

We previously [12–14] have reported the synthesis and characterization of a number of polymers of alkyl and alkenylsilanes. The present work was concerned with characterizing the pyrolytic conversion of these polymers to Si–C ceramics, with the objective of understanding the relationship between polymer structure and the conversion process, as well as ceramic stoichiometry. The intent of the work was the development of a series of polymers having tailorable rheological behaviour that are suitable precursors to ceramic composite matrices and ceramic coatings.

2. Experimental procedure

Poly(methylsilane), poly(vinylsilane) and copolymers of methyl and vinylsilane, and of vinylsilane and 1,2-disilylethane (BSE) were synthesized using a titanocene catalyst [12, 14–17].

Two types of synthesis conditions were employed: a room-temperature synthesis, for periods of nominally 30 days (condition A), and a protocol in which polymerization was started at room temperature for a period of 7 days, and then continued at a temperature of 50 °C for an additional 7 days (condition B). One of two solvents, tetrahydrofuran (THF) or cyclohexene, was used for polymerization.

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^{29}Si, ^{13}C and ^{1}H nuclear magnetic resonance (NMR) spectra were collected using a Bruker AC-300 NMR spectrometer. Chloroform-d was used as the solvent. Tetramethylsilane was used as a reference for ^{29}Si spectra, and chloroform was the reference for the ^{13}C and ^{1}H spectra.

Fourier transform–infrared (FT–IR) spectra of as-synthesized polymer samples were obtained using a Perkin–Elmer Model 1750 (Perkin–Elmer, Norwalk, CT) Fourier transform–infrared spectrometer at a resolution of 2 cm^{-1}. Infrared studies of the early stages of polymer conversion, from 25–300 °C, were conducted on liquid films held between two KBr crystals and heated at a rate of 5 °C min^{-1} within the spectrometer under an atmosphere of flowing nitrogen. Characterization of partially pyrolysed materials was performed using standard diffuse reflectance techniques (DRIFTS).

The pyrolysis process was studied by thermogravimetry (TG) up to 1400 °C, thermogravimetric analysis coupled with infrared spectroscopy of evolved gases (TG–IR) up to 1000 °C, and X-ray diffraction (XRD) of polymers pyrolysed to various final temperatures under an argon atmosphere in a tube furnace.

Thermogravimetric analysis was conducted in flowing argon (60 cm^3 min^{-1}) and in air at a heating rate of 10 °C min^{-1} using a Perkin-Elmer TGA 7. Analyses of gases evolved during the early stages of pyrolysis were determined using a Bio-Rad FTS 40 interfaced with a Stanton Redcroft TGA 1000 (Bio-Rad, Cambridge, MA). Spectra were collected at 8 cm^{-1} resolution co-adding 16 scans per spectrum. Samples were heated from 35–1000 °C at a rate of 10 °C min^{-1}.

Samples for X-ray diffractometry were crushed using a boron carbide mortar and pestle. X-ray diffraction patterns were recorded with a Scintag X-ray diffractometer utilizing CuK_α radiation.

Elemental analysis of the pyrolysed materials was performed by Galbraith Laboratories (Knoxville, TN). Carbon was determined by combustion in oxygen using an induction furnace technique. Silicon was measured by sodium fusion and inductively coupled plasma (ICP) analysis.

3. Polymer characterization

Poly(methylsilane) was determined by NMR analysis to have a polysilane backbone structure as synthesized, in which each internal silicon is attached to one hydrogen and one methyl substituent, and to two other silicon atoms. The chains would terminate in $-SiH_2CH_3$ groups, although cyclic structures are not excluded based on NMR. Vinylsilane polymerization produced a mixture of a polycarbosilanes, including $-C-SiH_2-CH(CH_3)-Si-$ and $-C-SiH_2-CH_2-CH_2-Si-$ linkages (nominally 80%), the remainder consisting of a polysilane backbone ($-Si-SiH(CH_2CH_3)-Si-$) arising predominantly from dehydrogenative coupling and reduction of the double bond. No saturation was present in the polymer. The polymer chains, if linear, should terminate with $-SiH_2C_2H_5$ groups.

Typical i.r. spectra are shown in Fig. 1. Both polymers exhibit characteristic C–H stretching between 3000 and 2700 cm^{-1} and Si–H stretching near 2100 cm^{-1}. In the methylsilane polymer, methyl group stretching is observed at 2956 and 2894 cm^{-1}. The Si–H stretching peak is asymmetric, with a maximum at 2079 cm^{-1}, indicative of a mixture of SiH and terminal SiH_2 groups. Additional peaks at 1409 and 1248 cm^{-1} are characteristic, respectively, of the asymmetric and symmetric bending modes of CH_3 bonded to silicon. A series of four bands at 931, 867, 686 and 648 cm^{-1} (Si–H_2 deformations of terminal groups) and a band at 766 min^{-1} (Si–C stretching) are typical [18]. The broad band at 1048 cm^{-1} is attributed to Si–O–Si groups introduced by reaction of the polymer with air during handling. The spectrum is similar to that reported by Zhang *et al.* [5] for poly(methylsilane) prepared under somewhat different conditions.

The i.r. spectrum for poly(vinylsilane), Fig. 1b, exhibits C–H stretching at 2950 and 2898 cm^{-1} (CH_3), as well as 2928 and 2867 cm^{-1} (CH_2), and a sharp Si–H stretching peak at 2119 cm^{-1}. Three characteristic bands are observed at 1457 ($CHCH_3$ [19]), 1410 ($SiCH_3$ asymmetric bending plus possible scissoring of CH_2 groups attached to silicon [18]) and 1377 cm^{-1} (likely symmetric bending of CH_3 groups not attached to silicon). Also characteristic are a pair of bands at 941 and 837 cm^{-1} (SiH_2 bending modes). A small 1136 cm^{-1} ($Si-CH_2-CH_2-Si$) peak [19] is also observed. Peaks in the 1615–1590 cm^{-1} range, where vinyl groups occur, were notably absent, supporting the NMR findings of no saturation (see above).

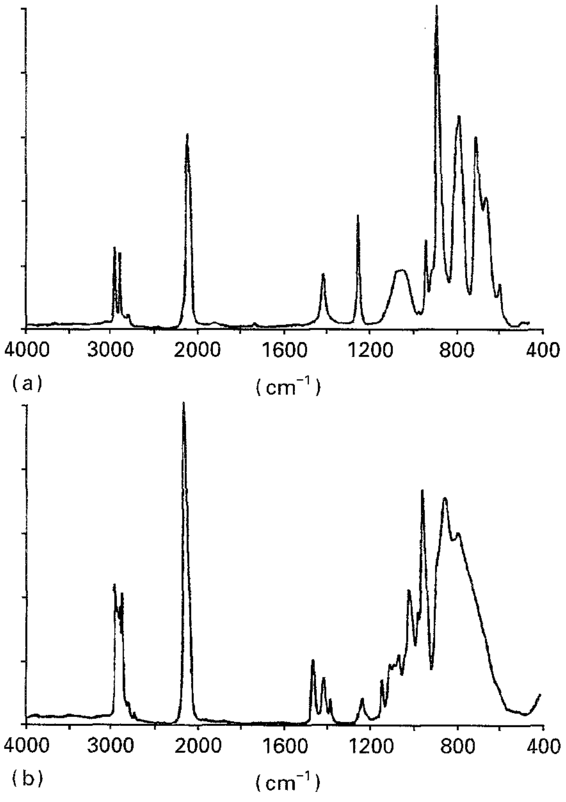

Figure 1 Typical infrared spectra of (a) poly(methylsilane) and (b) poly(vinylsilane).

TABLE I Influence of polymerization conditions on molecular weight (Daltons)

Polymer	Polymerization condition	Solvent	M_n	M_w
Methylsilane	A	THF or cyclohexene	200–800	950–2230
	B	THF	365–760	765–1500
	B	Cyclohexene	1236, 1503[a]	5800, 9800[a]
Vinylsilane	A	THF or cyclohexene	250–670	1170–3030
	B	THF	260–510	1080–1300
	B	Cyclohexene	370–980	1700–3900
95 vinylsilane: 5 BSE	B	THF	411–655	1203–1630
	B	Cyclohexene	930–1150	4100–5800

[a] Two experiments only.

Synthesis from either THF or cyclohexene produced similar spectra, except that the relative intensities of the 1457 (CH_3 bend, CH_3 not attached to silicon) and 1410 cm^{-1} (CH_2 scissoring) bands varied with the solvent. The 1457 cm^{-1} was comparatively more intense from cyclohexene, suggesting increased hydrosilation, or decreased metathesis, in this solvent. The relative ratios of the Si–H and C–H stretching peaks varied as well. There were relatively fewer Si–H groups when cylohexene was the solvent, as observed by infrared spectroscopy, as well as by integration of the SiH region of the ^1H NMR spectra. ^1H and ^{29}Si NMR revealed subtle differences between polymers in the two different solvents, although the overall constitution of the backbone remained fairly constant.

The influence of polymerization conditions on molecular weight is summarized in Table 1. Methylsilane polymers formed at room temperature (condition A) exhibited molecular weights of $M_n = 200–800$, and $M_w = 950–2230$ Daltons, based on polystyrene standards; these were independent of solvent. For polymerization under condition B, M_w values of 765–1500 Daltons were obtained in THF (four experiments), whereas weight average molecular weights of 5800 and 9800 were obtained in two experiments using cyclohexene.

Vinylsilane polymers formed under condition A showed a similar molecular weight range: $M_n = 250–670$; $M_w = 1170–3030$ Daltons. Condition B polymerization produced values of $M_n = 260–510$; $M_w = 1080–1300$ Daltons in THF, and $M_n = 370–980$, $M_w = 1700–3900$ Daltons in cyclohexene, demonstrating some influence of solvent on the vinylsilane polymerization (the difference in M_w was significant at $p = 0.012$), though not as large an influence as was noted in the polymerization of methylsilane. The addition of 5 wt% BSE to vinylsilane produced a small increase in molecular weight when the polymerization was carried out in THF. However, in cyclohexene, M_w increased to 4100–5800 Daltons, and indicated a significant interaction between BSE and solvent. The addition of larger amounts of BSE (15–25%) did produce increases in molecular weight, but also led to gelation, which was considered to be undesirable.

The increase in molecular weight of alkylsilane polymers in the presence of cyclohexene can be explained by reaction of hydrogen generated during polymerization with the unsaturated solvent, which furthers the extent of the reaction. In the polymerization of vinyl(silane), the unsaturated vinyl group is able to react with the hydrogen generated during polymerization, which may explain the reduced influence of cyclohexene on molecular weight. The highest molecular weights were obtained when BSE, an alkylsilane, was copolymerized with vinylsilane.

4. Pyrolysis studies

4.1. Poly(methylsilane)

The thermogravimetry trace of poly(methylsilane) pyrolysed in flowing argon was characterized by a major weight loss centred at 310–325 °C with a shoulder, or sometimes a resolved derivative peak at 350–360 °C and a smaller, broad weight loss at nominally 500 °C, as shown in Fig. 2a. In some instances, a low-temperature weight loss region was seen at 135–195 °C (Fig. 2b). This lowest temperature reaction seemed to correlate with lower molecular weight polymers, and may correspond to the elimination of small cyclics.

The major loss region is shown by TG–IR to be related to evolution of mixed silanes, with several overlapping Si–H peaks in the region from 2172–2135 cm^{-1}, and additional peaks at 954, 920 cm^{-1}, suggesting formation of SiH_2 species, as well as bands at 1276 and 882 cm^{-1} (Si–CH_3). This would be consistent with cleavage of the Si–Si backbone ($D_{Si-Si} = 42$ kcal mol^{-1}, 25 °C) [20]. Some methane production was observed beginning at 395 °C. The poly(methylsilane) was extremely air sensitive and siloxanes were generated in this temperature range as well, as evinced by an Si–O–Si peak at 1078 cm^{-1} and Si–OH at 920 cm^{-1}. At 525 °C, methane was the primary volatile species. Hydrogen evolution also might occur in this range [19], but is not observable by i.r.

Infrared studies of poly(methylsilane) heated between two KBr crystals show that Si–H groups disappear more rapidly than C–H species (Fig. 3), suggesting the formation of Si–Si cross-link formation beginning below 100 °C. Between 250 and 300 °C a new infrared peak is observed at 1268 cm^{-1} as a shoulder on the 1250 cm^{-1} peak, and may be the result of a change in symmetry of the Si–CH_3 stretching as Si–Si bonds are cleaved (Fig. 4).

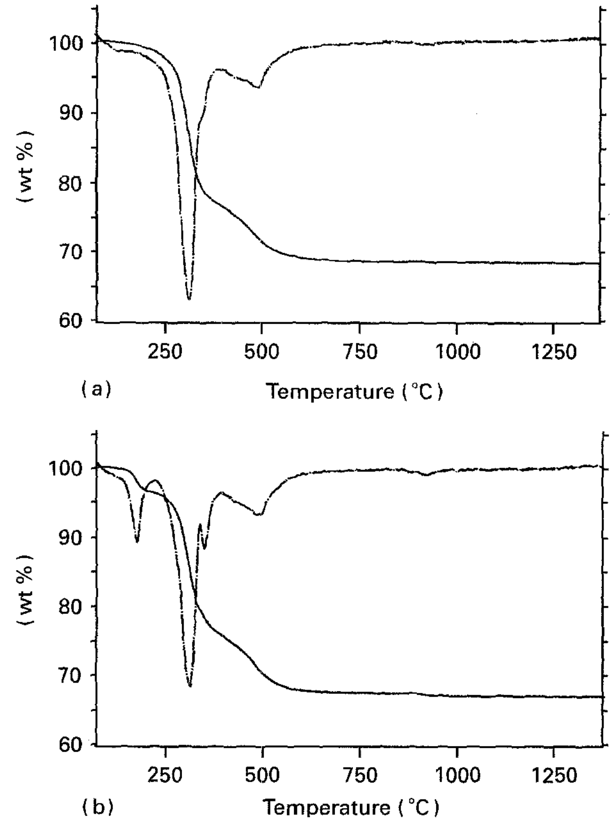

Figure 2(a) Typical TG trace of poly(methylsilane) heated in flowing argon at 10 °C min^{-1}. (b) Poly(methylsilane) sample representative of polymers exhibiting an additional weight loss at 135–195 °C: (——) weight per cent; (—·—) first derivative.

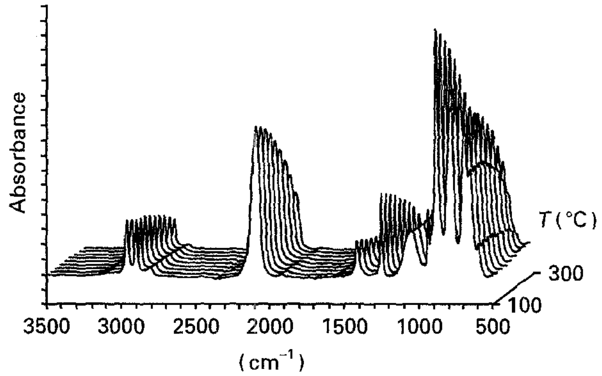

Figure 3 Infrared spectra of poly(methylsilane) heated in the spectrometer between two KBr discs plotted as a function of temperature. Spectra are plotted at 25 °C intervals.

Si–Si bonds are not expected to persist above 380 °C [19], however, insertion of carbon into the backbone would be anticipated [5, 19, 21, 22]. Such rearrangement to form –Si–C– backbone units would explain the small weight loss peak observed at approximately 350–360 °C in some poly(methylsilane) samples, and the larger peak at 490 °C. Both coincide in temperature with peaks seen in the pyrolysis of poly(vinylsilane), which is known to contain considerable polycarbosilane structure (see below).

Char yields at 1400 °C (30 min) averaged 66.9% (s.d. = 2.16). There was no correlation between char yield and molecular weight. XRD showed evidence of excess silicon.

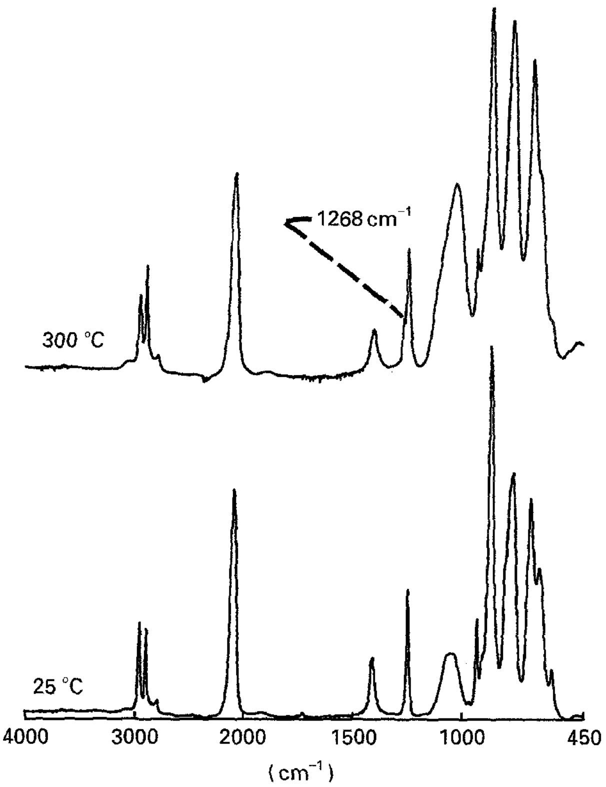

Figure 4 Infrared spectra of poly(methylsilane) at ambient temperature and after heating between KBr discs to 300 °C.

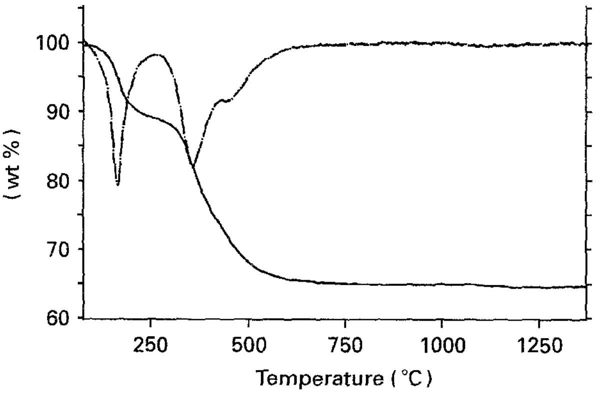

Figure 5 Representative TG trace of poly(vinylsilane) heated in flowing argon at 10 °C min^{-1}: (——) weight per cent; (—·—) first derivative.

4.2. Poly(vinylsilane)

In contrast to the single major weight loss at 310–320 °C observed in the pyrolysis of poly(methylsilane), the TG trace for poly(vinylsilane) was characterized by two primary weight loss regions centred at 160–200 °C and 350–375 °C, and a third region overlapping the second at nominally 435–480 °C (Fig. 5). Considerable variation in the relative magnitude of the 160–200 °C weight loss was observed (cf. Fig. 7). A very small weight loss is also observed just above 1000 °C, which is outside the range of the coupled TG–IR instrumentation. This probably corresponds with elimination of hydrogen.

The infrared spectra of the evolved gases were identical in the first two areas of weight loss, and indicated silane evolution, with peaks at 3000–2700 (C–H stretch), 2143 (Si–H), 946 and 873 cm^{-1}. The first of these weight loss regions is in the same temperature regime as the lowest temperature weight loss seen in poly(methylsilane), and may correspond with the evolution of cyclic silanes or small oligomers. It previously has been shown [12] that poly(vinylsilane) comprises a mixture of polysilane and polycarbosilane backbone structures, as determined by ^{29}Si NMR of the polymer. The absence of a substantial weight change at 310–320 °C, combined with the presence of a weight loss at 160–200 °C, suggest that Si–Si backbone structures seen in the ^{29}Si NMR of the polymer coincide primarily with small cyclics which have been volatilized in the lower temperature range.

The second weight loss region centred at 350–375 °C (Fig. 5) probably arises from cleavage of the Si–C backbone ($D_{\mathrm{Si-C}} = 69$ kcal mol^{-1} [20]). The third weight loss region centred between 400 and 500 °C corresponded with evolution of silanes and ethylene as observed by TG–IR, and occurs at the same temperature range as was reported for the pyrolysis of poly(silylethylene) as reported by Corriu *et al.* [19], who used TG–MS analysis to assign this broad weight loss region to evolution of hydrogen and ethylene, as well as several silane species. Production of ethylene is consistent with the presence of –Si–C–C– sequences observed in the ^{13}C NMR spectra of the polymer [12]. Pyrolysis of the Yajima poly (carbosilane) [23] produces a similar TG trace to that shown here; however, methane is the primary species seen by TG–MS in the 500–800 °C range [19].

DRIFTS spectra of sample pyrolysed in a tube furnace under an argon atmosphere to final temperatures of 600, 800, 1000, 1200 and 1400 °C and held at the final temperature for 30 min are shown in Fig. 6. Si–H groups (2091 cm^{-1}) are seen to persist to 1000 °C. The Si–C peak is seen to shift from 818 cm^{-1} at 600 °C to 883 cm^{-1} at 1400 °C, and at the same time to narrow considerably. This corresponds with formation of small SiC crystallites observed by XRD. The average Si/C ratio in these materials is 0.82, as determined by elemental analysis. (The sum of analysed silicon, carbon, hydrogen and titanium was approximately 90%, therefore, some incorporation of oxygen might have occurred in this sample on transfer to or within the pyrolysis furnace). This ratio increases only slightly over the temperature regime (600–1400 °C), and the TG trace is fairly flat in this region, so that the infrared spectral changes are attributed predominantly to bond rearrangement and structural ordering [24].

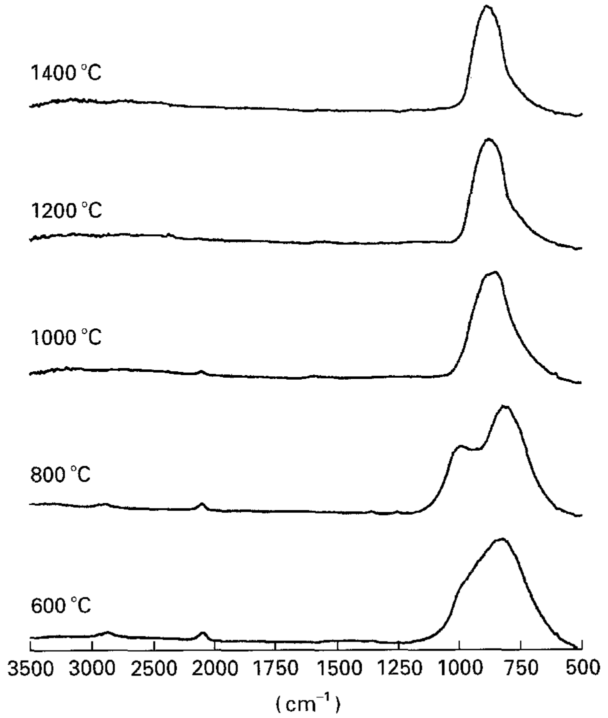

Figure 6 DRIFTS spectra of poly(vinylsilane) pyrolysed in a tube furnace under flowing argon to final temperatures of 600, 800, 1000, 1200 and 1400 °C.

Although the ceramic product contains excess carbon, the material pyrolysed in argon to 1400 °C was extremely resistant to oxidation. Reheating the sample in the TGA in the presence of oxygen produced no change in weight (Fig. 7). The presence of some excess carbon might actually be of benefit in the final material by inhibiting grain growth.

Char yield (1400 °C, 30 min) for poly(vinylsilane) averaged 59.57% (S.D. = 0.90), and is significantly lower than 67% (char yield for poly(methylsilane) ($p < 0.001$). The differences are attributed to differences in polymer structure, and not to molecular weight.

4.3. Poly(vinylsilane)/BSE copolymers

Copolymerization of vinylsilane with difunctional BSE was explored as a means of increasing cross-linking, and possibly char yield [25]. Additions of 5–8 wt % BSE did improve thermosetting behaviour, but did not significantly increase char yield. Char yield was found to increase with larger amounts of BSE (15%–20%), but produced sufficient cross-linking at this level to lead to gelation.

During the early stages of heating poly(vinylsilane), between 25 and 300 °C, the intensity of the Si–H infrared stretching peak increases, reaching a maximum at 150 °C, then decreases on further heating (Fig. 8). The peak at 830 (Si–H bending) also shows an increase in intensity between 125 and 150 °C, which

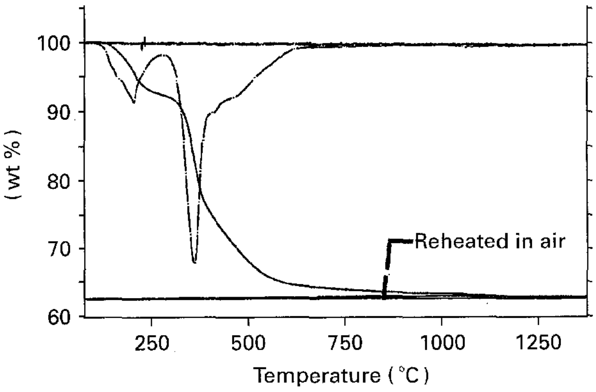

Figure 7 TG trace of poly(vinylsilane) heated in flowing argon to 1400 °C min^{-1}, held at the final temperature for 30 min, cooled to ambient temperature and reheated in air at 1400 °C: (——) weight per cent; (—·—) first derivative.

coincides with the onset of weight loss. Such an increase in Si–H groups is not observed in the methylsilane polymers. As small amounts of BSE were added to the polymerization (2.5–8 wt %), the increase in Si–H groups during early heating diminished with BSE concentration, and at 8% BSE was not observed at all (Fig. 9), suggesting that BSE incorporation occurs as the polymer is heated, rather than during the original synthesis, at least for the case in which THF is the polymerization solvent. (Where cyclohexene acts as the solvent, higher molecular weight polymers are obtained, as discussed in the section on polymer synthesis, above). At this level of BSE addition, no significant change in the Si/C ratio of the resulting ceramic is observed.

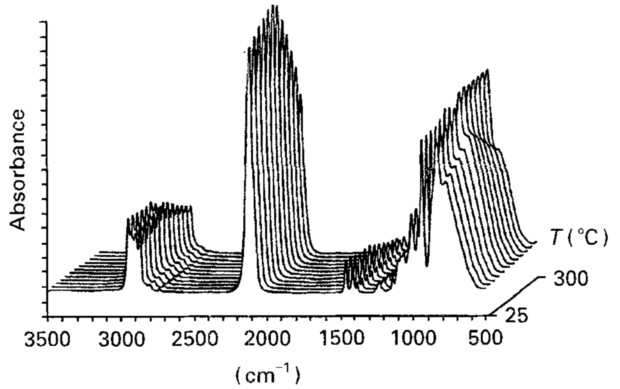

Figure 8 Infrared absorbance spectra of poly(vinylsilane) heated in the spectrometer between two KBr discs plotted as a function of temperature. Spectra are plotted at 25 °C intervals over the temperature range 25–300 °C.

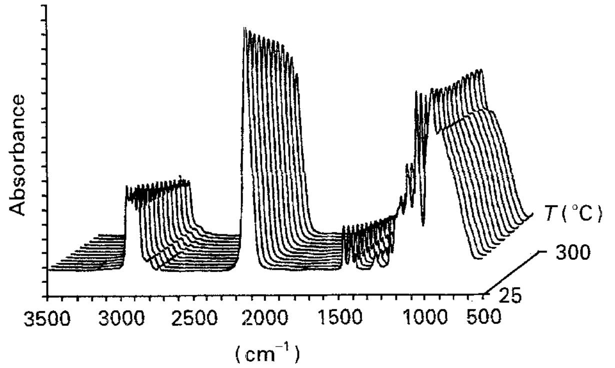

Figure 9 Infrared absorbance spectra of poly(vinylsilane) copolymerized with 8% BSE, heated in the spectrometer between two KBr discs, plotted as a function of temperature. Spectra are plotted at 25 °C intervals over the temperature range 25–300 °C.

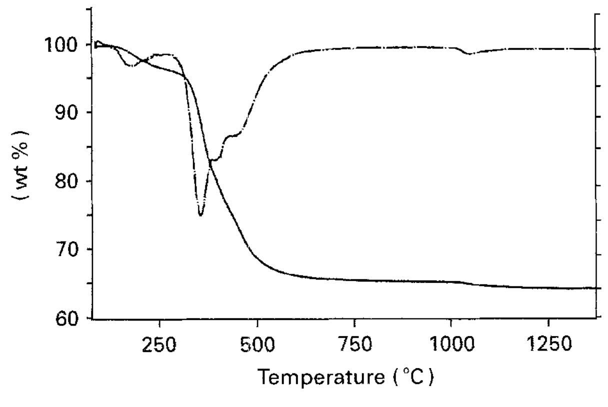

Figure 10 Representative TG trace of poly(vinylsilane) copolymer with 5% BSE, heated in flowing argon to 10 °C min^{-1}: (——) weight per cent; (—·—) first derivative.

The presence of BSE increases the relative magnitude of the weight loss at 435–480 °C (Fig. 10), and thus may suggest enhanced formation of –Si–C–C– linkages as the copolymer is heated [19]. Heating the polymer at 50 °C for 60–70 h without solvent leads to the formation of higher molecular weight species, as confirmed by gel permeation chromatography (GPC), and further increases the weight loss in the 435–480 °C region. Staging at higher temperatures readily leads to thermosetting within a shorter time frame.

4.4. Methyl- or vinylsilane copolymers

Stoichiometric SiC was obtained by copolymerization of methyl- and vinylsilane at a ratio of nominally 7:3. This material formed small crystallites of SiC on pyrolysis to 1400 °C in flowing argon, with the final temperature maintained for 30 min. BSE also was incorporated at the 5% level as a third comonomer to control rheology. The copolymers produced exhited char yields as high as 77%. However, these copolymers are pyrophoric, as are the methylsilane polymers, and therefore are a problem for use as ceramic precursors on any scale.

5. Conclusion

Homo- and copolymers of methyl- and vinylsilane have been prepared using a titanocene catalyst. While methylsilane polymerizes with a Si–Si backbone, vinylsilane produces predominantly polycarbosilanes of mixed –Si–C– and –Si–C–C– backbone structures. The products are primarily oligomers, having a M_w range of 1000–10 000, depending on solvent and polymerization conditions. The highest molecular weights for methylsilane polymers were attained in cyclohexene by polymerization for 7 days at room temperature followed by 7 days at 50 °C. Vinylsilane yielded M_w values of nominally 6000 in cyclohexene when 5% difunctional BSE was added as a reactant.

BSE appeared to enhance formation of –Si–C–C– linkages, and impart thermosetting behaviour to the polymers.

Pyrolytic fragmentation was dependent upon the backbone structure, rather than molecular weight. In both types of polymer, evolution of fragments having structures identical to one another and similar to that of the parent polymer occurred over two separate temperature ranges, suggesting the possibility that the species evolved at the lower temperatures comes from cyclic material, while that occurring at higher temperature is due to the cleavage of a linear, extended backbone. In both the methyl and vinylsilane polymers weight loss is mostly completed by 650 °C; however, significant bond rearrangement continues to occur to 1400 °C.

Pyrolysis of the methylsilane homopolymer produces a silicon-rich ceramic. Copolymerization with vinylsilane yields stoichiometric SiC. However, methylsilane polymers and copolymers are extremely sensitive to oxygen incorporation and are pyrophoric, which introduces limitations to working with them on a large scale.

Vinylsilane polymers can be used to produce a carbon-rich Si–C ceramic in which the carbon is sufficiently well dispersed to produce oxidation-resistant materials, making poly(vinylsilanes) the preferred system for further investigation. Introduction of multifunctional groups as cross-linking sites can be used to tailor polymer rheology, imparting thermoset behaviour to the system. The vinylsilane polymers have low viscosity as synthesized, making them suitable candidates for transfer moulding or for use as coatings.

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