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Precursors for Silicon Carbide Synthesised from Dichloromethylsilane Derivatives

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Abstract

Several polysilanes, including two groups of co-polymers and a group of ter-polymers, with overall functionalities ranging between 2 and 3 were prepared using the alkali metal dechlorination reaction. The yields of the soluble solid fractions of these polymers (the potential ceramic precursor) were in the range 40–70% wt and decreased with increasing overall functionalities in both cases of co- and ter-polymers. The molecular weights and FT-IR spectra of the precursors have been determined and the ceramic in the residue after pyrolysis has been identified as silicon carbide. The pyrolytic yield can be increased by using a polymeric precursor of higher overall functionality. The reasons for this are discussed with reference to pyrolysis mechanisms. In particular, some of the ter-polymeric precursors synthesised with a high yield also give a high yield on pyrolysis due to the presence of branched structures and potential cross-linking sites. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

The conversion of polymeric precursors to ceramics enables the use of new processing techniques in fibre and film production.[1–4] Polymeric precursors are also being used in plastic forming techniques applicable to ceramics and in the development of fibre-reinforced ceramic matrix composites.[5–8]

The pioneering effort in converting polymeric precursors to silicon carbide (SiC) is attributed to Yajima and his co-workers.[9,10] They converted an intractable polydimethylsilane by a two-stage reaction to produce mainly SiC fibres. West et al.[11] synthesised phenylmethyl-dimethylsilane co-polymers and converted these into SiC directly after ultra-violet light-induced cross-linking. However, on pyrolysis, the ceramic yield was only about 30% wt because of incomplete cross-linking and this was regarded as too low for a potential SiC precursor. In an attempt to improve the ceramic yield, Schilling[12] has shown that polycarbosilanes, when branched at backbone Si atoms, and vinylic polysilanes can be more effective SiC precursors. The vinylic polysilanes can be thermally cross-linked in an inert atmosphere due to a combination of hydrosilation and vinyl polymerization. Carlsson et al.[13] studied the products of homo-,co-, and ter-polymerization of Si backbone polymers. The ceramic yield was found to increase as the polydimethylsilane structure was substituted with hexyl and especially, phenyl groups. Recently, Cranstone et al.[14] and Shieh and Sawan[15] have synthesised polymeric precursors with higher functionalities based on combinations of a di-functional and a tri-functional monomer, giving an overall functionality of $> 2{\cdot}0$. Thus, branched structures of the polymers have been obtained resulting in higher ceramic yields after pyrolysis.

The aim of the research reported here was to synthesise a range of processable co- and ter-polymers with a higher overall functionality and reactive side-groups. It was anticipated that a better compromise between the yield of the polymeric precursor and its yield of residue after pyrolysis could be achieved by the combination of three monomers, i.e. dichloromethylphenylsilane, trichloromethylsilane and dichloromethylvinylsilane. Accordingly, several polymeric systems have been synthesised. The resulting polysilanes have been characterised and pyrolysed to produce SiC. The role of the polysilane composition on the SiC yield attainable is examined as well as the possible mechanisms of the pyrolysis process.

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2 Experimental Details

2.1 Monomers and solvents

The di- and tri-chlorosilane monomers used (Table 1) were obtained from Aldrich Chemicals Ltd., Poole, Dorset, UK and were purified by distillation in a nitrogen atmosphere. Dry toluene and tetrahydrofuran (THF) were obtained by refluxing over sodium hydride and distilling under a nitrogen atmosphere immediately before starting the reactions. In Table 1, the functionality of MP (f = 2) and TCM (f = 3) are directly dependent on the number of Cl atoms present. In the case of MV (f = 4) the functionality takes into account the two Cl atoms present and the double bond associated with the vinyl group.

2.2 Synthesis of polymers

The alkali metal dechlorination reaction was used to prepare the polymers. A method described by Zhang and West[16] was used with some modifications. A typical polymerisation procedure is described below.

All glass devices were oven and flame dried prior to use. Polymerisation was carried out in dry nitrogen. 50 ml and 8 ml of freshly dried toluene and THF, respectively, were charged into a 100 ml three-necked round-bottomed flask equipped with a reflux condenser, nitrogen inlet and addition funnel. Freshly cut sodium ($[Na]_0/[Si-Cl]_0 = 1.1$) was placed in the flask and the mixture was heated to reflux and stirred for 30 min, producing a fine dispersion. Then, a mixture of 1.26 g (8.4×10^{-4} mol) of freshly distilled TCM and 3.31 g (0.0156 mol) of MP in 6 ml of toluene were added dropwise (with stirring) to the dispersion. The heating was turned off during the monomer addition to maintain the reaction in gentle boiling. Depending on the reaction conditions, an exotherm occurred after 5–15 min and continued for a further 10–30 min. During addition, the colour of the reaction mixture turned from grey to dark blue. After addition, the mixture was stirred and refluxed for 4 h and then 0.26 g (0.0024 mol) of the quenching monomer, Me_3SiCl, was added to the reaction flask and refluxed for another 2 h. The solvent and possible unreacted monomers were removed by vacuum distillation. Seventy millilitres of toluene and 15 ml of ethanol were added to the blue solid obtained. The mixture was

then hydrolyzed with 50 ml of a 10^{-3}M HCl solution, the organic layer was separated and immediately washed with 100 ml portions of water until a neutral pH was reached. The toluene-insoluble polymer fraction (IS) was separated by centrifugation. The remaining solvent was then stripped off and the greasy residue was dissolved in 10 ml of tetrahydrofuran (THF) and then precipitated in excess methanol (150 ml) to obtain the soluble solid polymer (SS). Most of the oligomers and some cyclic compounds (SL) remain in solution. Both soluble and insoluble products were dried under vacuum at 70°C for 8 h.

In all the other similar experiments carried out to synthesize the other polymers, parameters such as stirring speeds, time of monomer addition and total reaction time were kept approximately constant.

In one set of experiments the solvents were changed from a mixture of toluene and THF (volume of toluene/THF = 7/1) to toluene alone while the monomers were added into the reaction flask as a mixture (as in previous experiments). The 7/1 toluene/THF blend ratio was selected to provide a solvent medium which had a reflux temperature above the melting point of sodium.[12,17] In another set of experiments, the addition sequence was changed from the three monomers being added together to first adding TCM/MP and then adding MV, in order to optimise the reaction conditions with the intention of attaining a better yield of the SS polymer fraction. The 7/1 toluene/THF solvent blend was used in these experiments.

2.3 Characterisation

The SS fractions of the polymers synthesized were characterised as described below.

Molecular weights were determined at RAPRA Technology Ltd., Shrewsbury, Shropshire, UK, by gel permeation chromatography (GPC) calibrated by polystyrene standards and with chloroform ($CHCl_3$) as the eluent. The flow rate was 1.0 ml min^{-1}. For comparison, THF was used as the eluent for some of the polymers but this did not make a significant difference to the results.

Fourier transform-infrared (FT-IR) spectra of the polymers and selected as-synthesized samples heated from 100 to 800°C (in steps of 100°C) for 30 min in nitrogen were obtained using a Nicolet

Table 1. Details of monomers used in this study. Me, Ph and Vin refer to methyl,phenyl and vinyl groups, respectively

Monomers	Formula	Abbreviation	Functionality (f)
Dichloromethylphenylsilane	MePhSiCl$_2$	MP	2
Trichloromethylsilane	MeSiCl$_3$	TCM	3
Dichloromethylvinylsilane	MeVinSiCl$_2$	MV	4

710 FT-IR spectrometer. One milligramme of polymer was ground and mixed with 150 mg of dried KBr powder before pressing small pellets. Scanning was carried out at a resolution of 4cm^{-1} in the wavenumber range of $4000-400 \text{cm}^{-1}$. The spectrum was analysed using a computer program called OMNIC. A Perkin-Elmer DSC7 machine was used for the thermal analysis of both the as-synthesized polymers and specimens heated to 280°C (just before the onset of thermal degradation) for 4 h. A few milligrams of material were placed in the sample pan of the machine and heated from the ambient temperature to 300°C at $5°C \text{min}^{-1}$ in a flowing nitrogen atmosphere (flow rate of 20ml min^{-1}).

Thermogravimetric analysis was used to investigate the conversion of the polymers to ceramic. A small quantity of material was placed in the sample pan of a TGA7 Perkin-Elmer thermogravimetric balance. A heating ramp of $10°C \text{min}^{-1}$ from the ambient temperature to 900°C was used. During each experiment nitrogen gas was passed through the heating column to maintain an inert atmosphere (flow rate of 0.5ml min^{-1}).

Pyrolysis of polymer samples was carried out in tube furnaces in a flowing nitrogen and nitrogen—5% hydrogen atmosphere (flow rate of 0·4 1min^{-1}). Specimens were heated from the ambient temperature at a rate of $2°C \text{min}^{-1}$ to various final temperatures in the range 900–1700°C. The final temperature was maintained for 120 min after which a cooling ramp of $10°C \text{min}^{-1}$ to the ambient temperature was applied.

The residues produced from thermogravimetric studies and pyrolysis experiments were subjected to X-ray diffractometry. Specimens were prepared by grinding the residues using a boron carbide mortar and pestle. A small amount of industrial methylated spirits (IMS) was added during grinding to aid preparation and a small sample of the resulting

paste was placed on a single crystal silicon plate which was attached to a 20 mm diameter stainless steel stub. The IMS was allowed to evaporate before X-ray analysis. X-ray studies were conducted using a Philips X-ray diffractometer, CuKα radiation of wavelength 0·15406 nm and a Ni filter. The X-ray diffractometer was operated at 35 kV and 20 mA. The scan range was from 10° to 90° with a step size of 0·021° and a scan speed of $0.02° \text{s}^{-1}$.

3 Results and Discussion

3.1 Polymers prepared
As described in Section 2.2, the polymers were synthesized by the most common and easy preparative technique for polysilanes. Here Wurtz-type coupling of chlorosilanes was carried out by a molten sodium dispersion in a mixture of toluene/THF (or toluene) and the generalized equation for this reaction is given below. A series of reactions were carried out using the monomers listed in Table 1 and the proportion of each was altered to give different values of the overall functionality, F, defined in eqn (1).
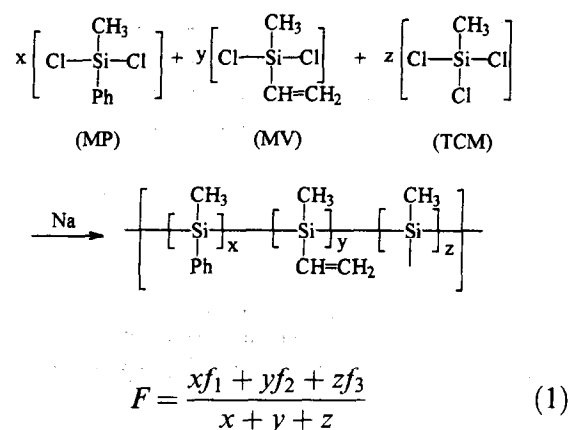
$$F = \frac{xf_1 + yf_2 + zf_3}{x + y + z} \quad (1)$$

Table 2. Details of polymers prepared in this study and percentage yields (based on the theoretical yield) of the various polymer fractions obtained. Abbreviations used in column 2 are defined in Table 1 and values in parentheses represent yields of repeat preparations

Polymer	Molar ratios of monomer(s)	F	SS (%wt)	IS (%wt)	SL (%wt)
p1	MP = 100	2·00	43	2	46
p2	MP/MV = 80/20	2·40	52	3	43
p3	MP/MV = 65/35	2·70	37(34)	25(48)	21(16)
p4	MP/MV = 50/50	3·00	20	56	15
p5	MP/TCM = 80/20	2·20	73	5	18
p6	MP/TCM = 65/35	2·35	65(69)	10(8)	26(31)
p7	MP/TCM = 50/50	2·50	48	35	15
p8	MP/MV/TCM = 68/15/15	2·51	57	14	21
p9	MP/MV/TCM = 55/15/30	2·60	52(45)	21(25)	20(27)
p10	MP/MV/TCM = 55/30/15	2·75	44(30)	35(41)	18(22)
p11	MP/MV/TCM = 50/25/25	2·75	47	25	20
p12	MP/MV/TCM = 40/20/40	2·80	42	39	12
p13	MP/MV/TCM = 40/40/20	3·00	27	55	11

where f_1 f_2 and f_3 are the respective molar functionalities of the monomers reacted (see Table 1) in the molar ratio $x : y : z$.

Four groups of polymers were prepared (Table 2); p1 is a homopolymer and has the lowest functionality. Polymers p2 to p4 and p5 to p7 are two groups of co-polymers and p8 to p13 are ter-polymers with higher overall functionalities (F) as given in Table 2. These are compared with reference to p1, which gave similar experimental results (stated in the ensuing text of this paper) to that reported previously.[13]

The reactions can lead to the production of three different polymer fractions as indicated in Section 2.2. Thus, SS, IS and SL fractions of the polymers synthesized were calculated as a percentage of the theoretical yield (Table 2). In some cases the total yield obtained was less than 100%, showing that all the expected products were not formed. This could be because some of the monomers have not reacted fully, resulting in a lower overall yield than that expected.[14]

It can be seen from Table 2 that both in the case of the two groups of co-polymer synthesized, the soluble solid yield of the polymers (SS) decreased and the insoluble solid content (IS) increased with the increase of dichloromethylvinylsilane (MV) or trichloromethylsilane (TCM) used, i.e. the increase of overall functionality F. The increase of insoluble solids is probably due to cross-linking caused by vinyl groups in the case of MP/MV co-polymers and trifunctional TCM in the case of MP/TCM co-polymers. Ter-polymers show the same trend (Table 2) shown by the co-polymers due to similar reasons.

The change in the reaction conditions investigated was two-fold. First, the effect of the solvent change from a mixture of toluene/THF (Table 2) to only toluene (Table 3, those denoted by s) resulted in a lower SS yield. The better SS yields in the toluene/THF solvent blend is probably due to the fact that the chlorosilane reactivities are dependent on the presence or absence of THF.[18] Second, the addition sequence of monomers also influenced the polymer yields (compare Table 2 and Table 3). When the monomers were added separately, i.e. MP and TCM were added first,

followed by MV, the yield of the SS fraction obtained was much higher (Table 3, those denoted by a) than in instances when the monomers were added together (refer to corresponding yields given in Table 2), probably due to less cross-linking occurring during polymerisation in the former case. Cross-linking during polymerisation increases the IS fraction of the polymer yield.

Some of the reactions were repeated to check the reproducibility of the various fractions of the polymer yields (see Tables 2 and 3). The reproducibility of alkali metal dechlorination reactions used in this work is generally poor[15,19-21] and in some instances there is appreciable variation in the yields of supposedly identical reactions.

As SS is the fraction that is the potential precursor for the ceramic, the yields obtained in this study (Tables 2 and 3) show that successful combinations of reactant monomers and suitable reaction conditions were selected. The yields of SS obtained in the systems investigated here were mostly in the range 40–70% wt and represent the higher range of values reported in the literature.[12-15,22,23] The characterisation results in Section 3.2 refer to the SS fraction of the polymers prepared unless otherwise stated.

3.2 Polymer characteristics

3.2.1 Molecular weight

Molecular weight distributions determined by GPC of all the polymers showed typical polymodal characteristics expected of products of the alkali metal dechlorination reaction (Fig. 1). Values of $\bar{M}_n$, $\bar{M}_w$ and the polydispersity ($\bar{M}_w/\bar{M}_n$) of all the polymers deduced from GPC results are given in Table 4. Repeat preparations show that some variation of the molecular weight resulted (Table 4) and is characteristic of the preparation method used as discussed in Section 3.1.
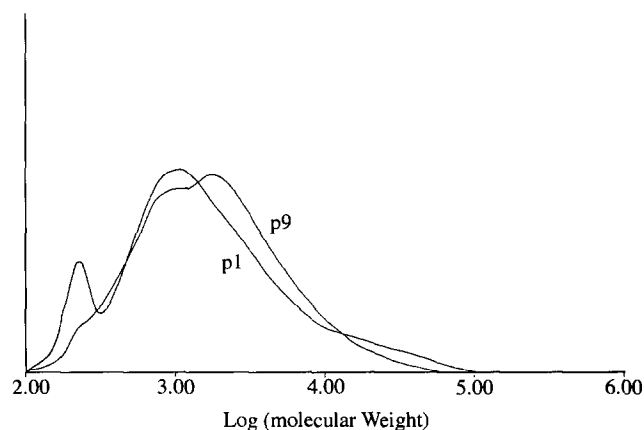
Table 3. The influence of the solvent used (denoted by s) and the addition sequence (denoted by a) on the various fractions of the polymer yields. Values in parentheses represent yields of repeat experiments

Polymer	Solvent(s)	SS(%wt)	IS(%wt)	SL(%wt)
p10s	Toluene	32(22)	50(63)	13(14)
p10a	Toluene/THF	57(53)	15(21)	25(24)
p13s	Toluene	19	68	10
p13a	Toluene/THF	48	34	26

Fig. 1. Molecular weight distribution of polymers p1 and p9.

3.2.2 FT-IR spectra

Typical FT-IR spectra of the polymers prepared are shown in Fig. 2(a) and (b). They showed characteristic C-H stretching between 3100 and $2700 \, cm^{-1}$. The appearance of a Si-H stretching band around $2100 \, cm^{-1}$ implies that there were some hydrosilane groups formed in the polymers during polymerisation.[24] Methyl group stretching was observed at 2956 and $2894 \, cm^{-1}$. Additional

Table 4. Relative molecular weights of polymers p1-p13 (see Table 2), p10s and p10a (see Table 3). Values in parentheses represent data of repeat preparations

Polymers	$\overline{M}_w$	$\overline{M}_n$	Polydispersity
p1	7680	1520	5·1
p2	6610	1500	4·4
p3	6470 (7940)	1540 (1680)	4·2 (4·7)
p4	5340	1110	4·8
p5	3450	1440	2·4
p6	1930 (3740)	1110 (1530)	1·7 (2·4)
p7	7470	2070	3·6
p8	5400	1430	3·8
p9	4240 (5590)	1510 (1600)	2·8 (3·5)
p10	5860 (7080)	1740 (1830)	3·4 (3·9)
p11	5020	2030	2·5
p12	8280	2220	3·7
p13	3000	1360	1·9
p10s	3000 (4000)	1360 (1250)	2·2 (3·2)
p10a	5400 (5240)	1430 (1600)	3·8 (3·3)

peaks at 1406 and $1248 \, cm^{-1}$ are characteristic of the asymmetric and symmetric bending modes of CH_3 bonded to silicon, respectively. Three peaks at 1949, 1887 and $1815 \, cm^{-1}$ are attributed to phenyl-Si vibration. The peaks at low wave-numbers of $697 \, cm^{-1}$ for Si-C stretching and $464 \, cm^{-1}$ for Si–Si are typical of these polymers.[13,16,25–29]

The FT-IR spectrum of co-polymer p3 [Fig. 2(b)] with an unsaturated side group exhibits stretching at $2946 \, cm^{-1}$ (CH), $2827 \, cm^{-1}$ (CH_2) and $2893 \, cm^{-1}$ (CH_3). The peak at $1589 \, cm^{-1}$ indicates the presence of the vinyl group (C = C stretch). It also shows a $1247 \, cm^{-1}$ absorption with a shoulder or weak peak at $1255 \, cm^{-1}$. The latter relates to cross-linking in these reactive co-polymers.[13] The FT-IR spectra of ter-polymers showed similar characteristics to that of the co-polymers.

3.3 Conversion to ceramic

XRD patterns [Fig. 3(a) and (b)] of the residues obtained from pyrolysis of the SS fractions in nitrogen and nitrogen—5% vol hydrogen atmospheres to different maximum temperatures showed that up to 900°C the products are largely amorphous. Partial crystallisation was observed at 1700°C in both atmospheres. Three peaks observed at $2\theta = 36°$, 61° and 72° in samples pyrolysed to
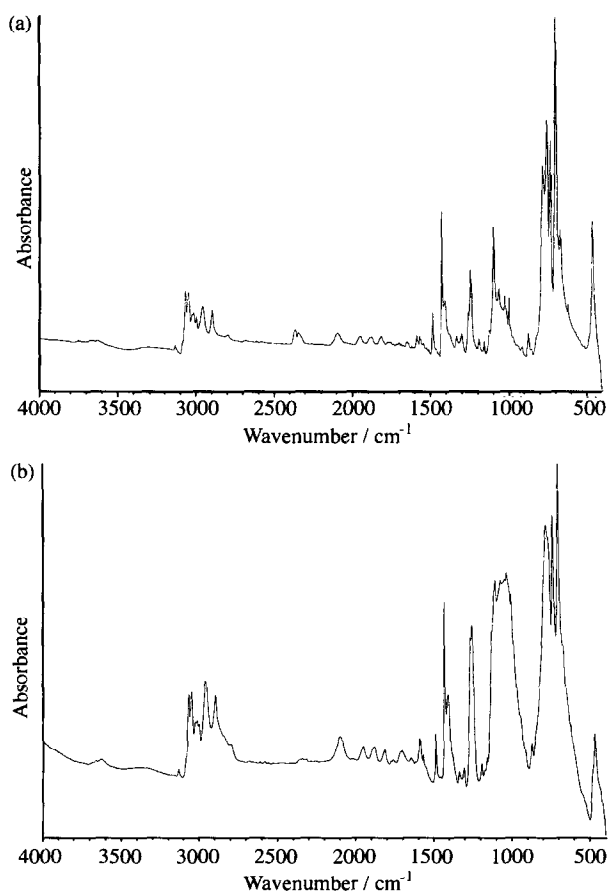

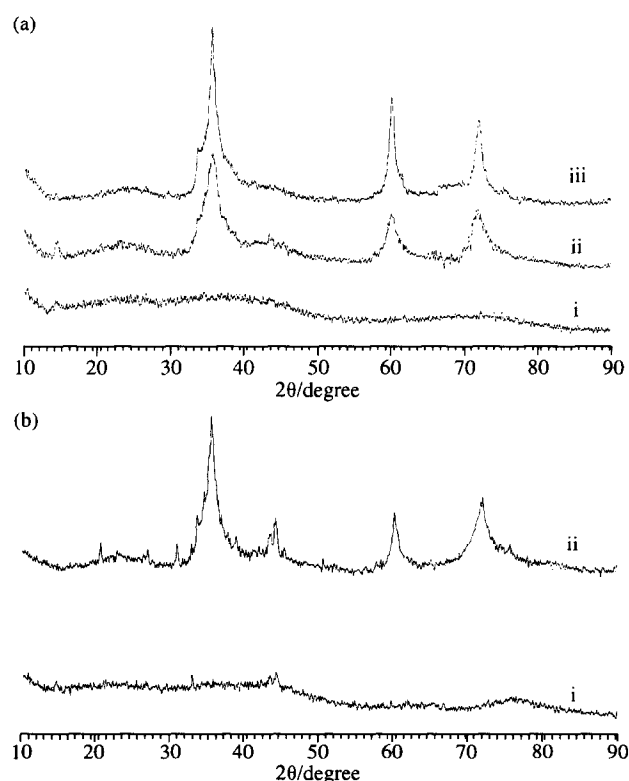**Fig. 2.** FT-IR spectra of (a) p1 and (b) p3.

Fig. 3. (a) X-ray diffraction patterns of polymer p4 after heat treatments; (i) at 900°C for 2 h in nitrogen; (ii) at 1700°C for 2 h in nitrogen; and (iii) at 1700°C for 2 h in nitrogen/hydrogen: (b) X-ray diffraction patterns of polymer p9; (i) at 900°C for 2 h in nitrogen; and (ii) at 1700°C for 2 h in nitrogen.

1700°C correspond to the (111), (220), and (311) planes of silicon carbide (β-SiC), respectively.[12,14,30] The yields obtained from the thermogravimetric experiments carried out on the SS fractions of the polymers (Table 5) are very dependent on the composition of the polymers. Co- and ter-polymers gave a better yield, compared with the homopolymer (p1). Some IS and SL fractions were also subjected to thermogravimetry and results obtained are given in Table 5 for comparison. Generally, the ceramic yield from IS is higher than that from SS due to the higher level of cross-linking formed in the latter during polymerisation. It is well established that cross-linking helps to increase ceramic yield.[12,31] The residues were black in all cases, indicating that some free C was present[13] and this is the reason that some ceramic yields exceed the theoretical maximum of SiC attainable from each polymer calculated on the basis that all the Si atoms are retained. However, it is well known that the presence of some C in SiC is helpful for the post-forming sintering stage.

Onset of thermal degradation of the polymeric precursors takes place soon after 300°C and the pyrolytic yield can be increased significantly with the increase of the overall functionality as shown in Fig. 4(a)–(c). However, there are different mechanisms of pyrolysis operating in each instance and these can be used to explain the possible increases in SiC yield as discussed below.

It is generally believed that a polysilane must go through a carbosilane intermediate prior to formation of the SiC network.[9,10] A competition between depolymerisation and the carbosilane rearrangement could occur as the temperature increased as shown below.[13] High yields of SiC can be expected when branched structures are formed in precursors containing TCM so that the loss of silane fragments can be minimised by the competing chain-scission process.
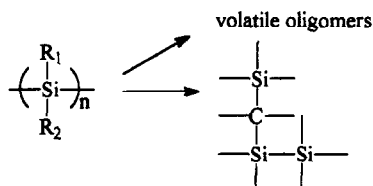
The increase of SiC yields from polysilane precursors with unsaturated side groups, such as those synthesized using MV, can be attributed directly to the thermal cross-linking capability of reactive vinyl side-groups. This can result from a combination of hydrosilation and vinyl polymerisation

Table 5. Yields obtained after pyrolysis and theoretical SiC yields of the polymers investigated. Values in parentheses represent data of repeat experiments

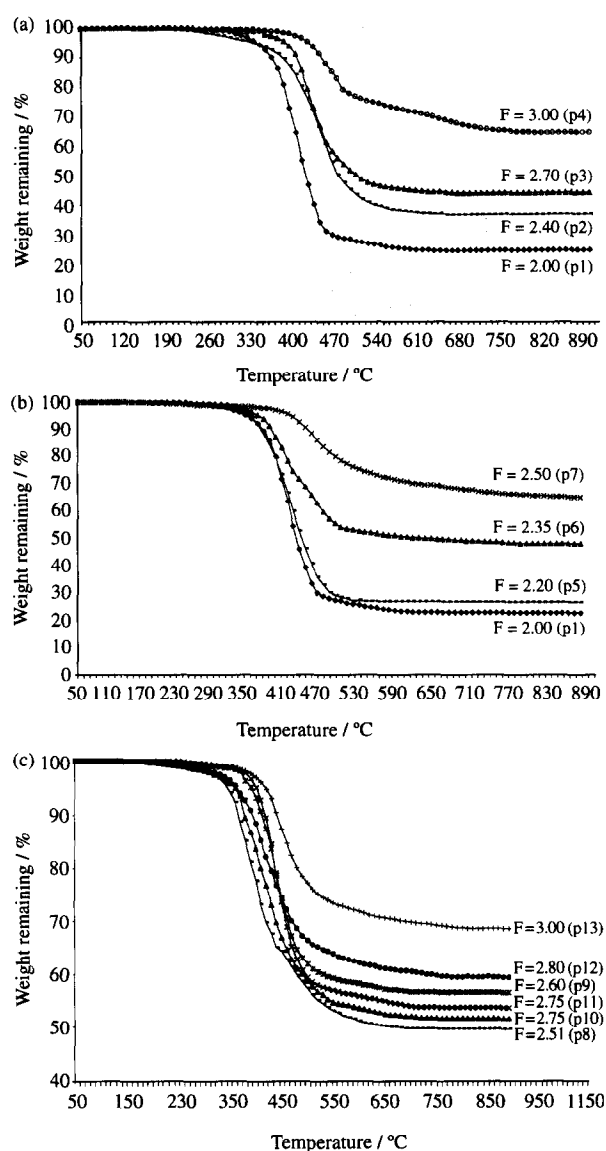| Polymers	SS (%wt)	IS (%wt)	SL (%wt)	Theoretical yield of SiC (%wt)
p1	23·6			33·3
p2	36·6			38·1
p3	44·5	77·4	21·5	41·6
p4	63·1 (61·8)	74·0	32·5	45·2
p5	27·1			45·2
p6	49·0 (40·3)	79·0	15·8	54·2
p7	66·3			63·2
p8	50·7			46·7
p9	56·8			54·8
p10	52·0 (62·5)	82·3	22·6	49·4
p11	54·1			54·2
p12	60·9			61·9
p13	69·0			54·8

Fig. 4. (a) The influence of the trichloromethylsilane (TCM) on the ceramic yield. F is the overall functionality of each polymer p1, p2, p3 and p4 considered: (b) the influence of the addition of dichloromethylvinylsilane (MV) on the ceramic yield. F is the overall functionality of each polymer p1, p5, p6 and p7 considered: (c) the influence of the use of the monomers dichloromethylvinylsilane (MV)/trichloromethylsilane (TCM) on the ceramic yield. F is the overall functionality of each polymer p8, p9, p10, p11, p12 and p13 considered.
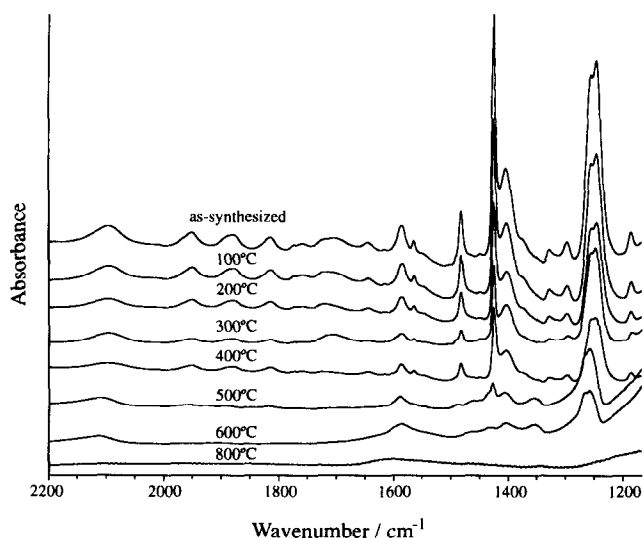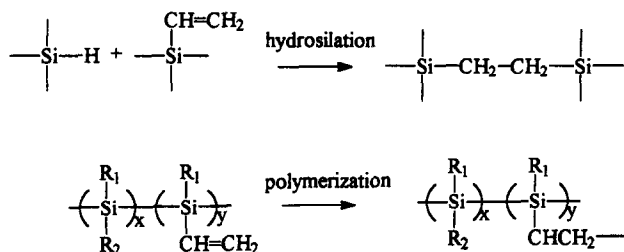
Fig. 5. FT-IR spectrum changes caused by heat treatment of polymer p3 to different temperatures.

chemistries starting above 200°C,[12,32] as illustrated below. Si-H groups required for hydrosilation can also be formed during pyrolysis[13] in addition to these being present initially, as discussed earlier in Section 3.2.

Taking p3 as an example, evidence for cross-linking[13,32] during heating is shown in Fig. 5 because as heating progressed to higher temperatures, there
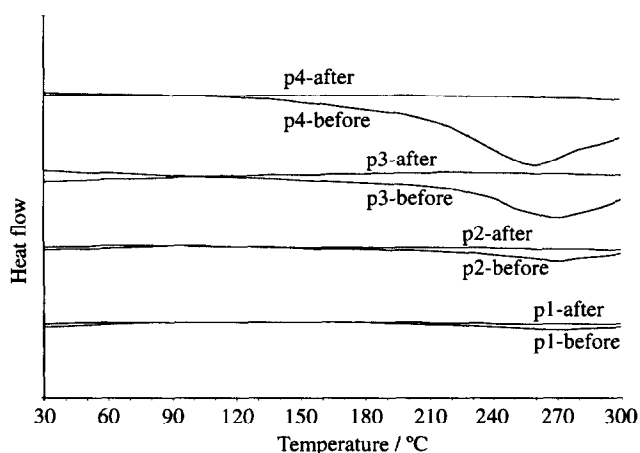

Fig. 6. DSC traces of polymers p1, p2, p3 and p4 before and after heat treatment.

was a decrease in the intensity of the C=C stretch (1590 cm^{-1}) and the Si-H band (2100 cm^{-1}), while there was an increase in the intensity of the 1255 cm^{-1} absorption.

DSC studies were also used to confirm the cross-linking process of these polysilanes with unsaturated side groups (Fig. 6). If cross-linking occurs in these polymers on heating, an exothermic peak will be present in the DSC trace. The results show that on heating there were exothermic peaks observed in unsaturated polysilanes p2, p3 and p4, while no significant peak was present in the saturated polysilane p1. The peaks were reduced dramatically after the samples were heated at 280°C for 4 h. This proves that the cross-linking occurred during heating. The branched and cross-linked structures formed during pyrolysis of the co- and ter-polymers helped to achieve good SiC yields.

4 Conclusions

Co- and ter-polymers prepared from three monomers—dichloromethylphenylsilane, trichloromethylsilane and dichloromethylvinylsilane—consisted of three fractions: soluble solid, insoluble solid and soluble liquid and their yields were dependent on the composition of reactant monomers which determined the overall functionality. The yields of the soluble solid which is the potential precursor for the ceramic, decreased with increasing overall functionality both in the case of co-polymers and ter-polymers and in this investigation ranged from 40–70% wt.

The ceramic residue obtained by pyrolysis of the precursors was β-silicon carbide and the total yield was dependent on the type and the composition of the reactant monomers used. Therefore, the overall yield could be increased significantly by increasing the overall functionality. Thus, the pyrolytic ceramic yields have been greatly improved from 23% wt for the homopolymer, poly(methylphenylsilane), to between 40–70% wt for co- and ter-polymers. The polymers prepared by adding trichloromethylsilane to dichloromethylphenylsilane produced high yields on pyrolysis mainly because of the branched structures present in them. The addition of dichloromethylvinylsilane with reactive vinyl side groups provided cross-linking sites in the co-polymers prepared and this led to improved yields after pyrolysis.

Some of the ter-polymers, in particular, with both branched structures and potential cross-linking sites give appreciable yields of both the polymeric precursor and SiC containing residue after pyrolysis.

Acknowledgements

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