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Synthesis of poly(dimethylsilylene-co-diphenylsilylene) polymers as precursors for SiC ceramics

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ABSTRACT

Silicon carbide ceramics, especially fibres, are being fabricated via polymeric precursors. Although such fibres are commercially available, there is a demand for improved performance particularly at elevated temperatures. A range of copolymers has been synthesized from the monomers, dimethyldichlorosilane and diphenyldichlorosilane, by a Wurtz reaction involving dechlorination using sodium metal in xylene. The products of reaction were characterised by a range of techniques, including gel permeation chromatography (GPC), infra-red spectroscopy (IR), X-ray powder diffraction (XRD) and thermogravimetry (TG).

INTRODUCTION

As silicon carbide fibres cannot be manufactured by conventional ceramic processing, an alternative method must be found. There are two commercial alternatives: either chemical vapour deposition or a polymeric precursor route. This paper discusses some results obtained from an on-going study involving the latter route.

Precursors have been prepared by a Wurtz reaction involving the dechlorination of chlorosilane monomers using sodium in dry xylene. Three types of polymeric product were formed during these reactions; insoluble solid, soluble solid and soluble liquid. It is the soluble solid fraction which is of potential use as a ceramic fibre precursor as this can often be spun successfully. However, the insoluble solid may be of interest as a matrix material and so is still characterised. The overall functionality of the product, F , is given by

$$F = \frac{x_1 f_1 + x_2 f_2 + \dots + x_n f_n}{x_1 + x_2 + \dots + x_n},$$

where f is the functionality of each individual monomer and x is the number of moles of that monomer. Values of $F=2$ give a linear polymer and higher values give a more networked product. It is generally observed that linear polymers can be spun readily but tend to give relatively low ceramic yields on pyrolysis, whereas cross-linked polymers usually give good ceramic yields but can be spun only with difficulty.

Much of our work has involved changing the overall F value, using a variety of starting monomers, in an attempt to optimise soluble solid and ceramic yields. To try to differentiate between the effect of varying the starting materials and the effect of varying F , a series of reactions were carried out in which two monomers of $f=2$ were used. The monomers chosen were diphenyldichlorosilane (DPDCS) and dimethyldichlorosilane (DMDCS), as the respective organic side groups are very different in size and shape and should illustrate any differences most readily. Using these two monomers the overall functionality cannot be changed from 2.0 but a series of reactions can be carried out with varying proportions of each monomer. The products were characterised by various methods and their suitability as precursors assessed. During the course of this work we became aware of a paper by Sartoratto and Yoshida¹, discussing the copolymers formed from these two monomers and our results are compared with their findings.

EXPERIMENTAL

The copolymers investigated in this study were prepared by an alkali dechlorination route. Reactions were carried out in either an argon atmosphere or in a nitrogen filled glove box. The reaction is illustrated in Figure 1.

Figure 1: Synthesis of poly(dimethylsilylene-co-diphenylsilylene)

The reactions carried out are listed in Table 1 below.

Synthesis	Starting Composition	Conditions
S1	% DMDCS 0:100 % DPDCS	7 hours under argon
S2	25:75	7 hours under argon
S3	50:50	7 hours under argon
S4	50:50	7 hours in nitrogen glove box
S5	50:50	6 hours in nitrogen glove box, TMCS added*
S6	50:50	3 hours in nitrogen glove box
S7	75:25	7 hours under argon
S8	100:0	7 hours under argon

* TMCS, trimethylchlorosilane, added as a chain terminator after four hours.

Table 1: Experimental details of syntheses carried out.

Syntheses S1, S2, S3, S7 and S8 were carried out to allow comparisons to be made when the proportions of the starting monomers were varied and S3, S4, S5 and S6 to investigate the effect of different experimental conditions on the same starting mixture. The product of the syntheses was worked up to give up to three different fractions, referred to as insoluble solid, soluble solid and soluble liquid. The appropriate fractions have been characterised by X-ray diffraction (XRD), infra-red spectroscopy (IR), gel permeation chromatography (GPC) and thermogravimetry (TG).

RESULTS AND DISCUSSION

Copolymer Yields:

The effect of varying the starting monomers on the yields of the various fractions is illustrated in Figures (2a) and (2b). The results obtained by Sartoratto and Yoshida are also included although their "work-up" procedure was different. To allow comparison between the data all the yields have been calculated in relation to 100% monomer conversion.

From Figure 2, it can be seen that for both sets of data the amount of insoluble solid formed shows a minimum value at about a 50% mix of the two monomers. As the proportion of either is increased, the amount of insoluble material increases. Both sets of data show similar amounts of insoluble material. The proportions of soluble solid and soluble liquid are however quite different, with the soluble liquid quantities formed in this work being more comparable to the soluble solid amounts described by Sartoratto and Yoshida¹. This difference is presumably accounted for in the different processing procedure in preparing the various fractions. The amount of this major fraction varies in the opposite way to the insoluble material, i.e. it is at a minimum for the end members of the sequence and at a maximum for the 50:50 copolymer.

The results for the homopolymerisation of DMDCS are in keeping with early work by Burkhard², who reported the formation of insoluble $(\text{SiMe}_2)_n$ plus a minor amount of soluble $(\text{SiMe}_2)_6$, and the pioneering work by Yajima³. In the latter case the intractable polydimethylsilane produced was converted in an

autoclave to a polycarbosilane which could then be melt-spun into fibres. The addition of a small amount of DPDCS was later incorporated as this was found to give a polymer which had improved spinning properties. The results obtained from the homopolymerisation of DPDCS are also in keeping with results in the literature^{4,5}.

The results obtained for syntheses S3-6, that is the reactions all with a 1:1 starting ratio of DPDCS:DMDCS, are given in Table 2. For synthesis S5, the molar ratio of TMCS:DMDCS:DPDCS was 1:10:10.

Yield %	Total	Insoluble solid	Soluble solid	Soluble liquid
S3	98 (100)	16 (16)	19 (19)	63 (64)
S4	97 (100)	2 (2)	35 (36)	60 (62)
S5	94 (100)	2 (2)	46 (49)	46 (49)
S6	77 (100)	4 (5)	41 (53)	32 (42)

Figures in brackets show yields in relation to 100% conversion.

Table 2: Variation of polymer yields with experimental conditions

Altering the experimental conditions is therefore seen to affect the proportions of the various fractions formed. The much better atmosphere control of a nitrogen recirculating glove box decreased the yield of insoluble solid and increased that of the soluble solid. Further alterations, either the addition of TMCS or a decrease in the reaction time, improved the yield again, this time at the expense of the soluble liquid. The use of a shorter reaction time (3 hours rather than 7) produced a better yield of usable product (soluble solid), although the reaction did not reach completion, i.e. only 77% of the expected yield of copolymer.

Thermogravimetry:

As these copolymers are being prepared as potential precursors to silicon carbide fibres they must be characterised to determine their suitability. One of the most important requirements of a precursor is that upon pyrolysis a sufficiently high ceramic yield is obtained. Each fraction from syntheses S2-S7 was subjected to TG analysis and the results are shown in Figures 3-6. Data from the insoluble solid from S8 and the soluble solid from S1 are also included.

Figure 3 illustrates the TG data for all three polymer fractions of synthesis S4. The data are fairly typical of those obtained for all the copolymers, i.e. the soluble solid shows a better ceramic yield than the insoluble which is an unexpected observation. The yield for the liquid is about the same as for the insoluble solid. For the other samples, there is only one case (S3) where the insoluble solid has the best yield and one case (S2) where the insoluble solid has a poorer yield than the liquid.

Comparing the particular polymer fractions across the whole range of syntheses allows the effect (if any) of the variation in the starting monomers or the experimental conditions. Figure 4 shows the data obtained for all the soluble liquids and from this it is seen that as expected the overall yields are poor (12-18% at 900°C) and that there is little difference between the yields of the various samples.

For the soluble solids, again all the samples are similar with the exception of S2 which gives a slightly higher yield. It was thought that this synthesis would give the lowest ceramic yield as there are more of the heavier phenyl side groups which would be lost during the pyrolysis. Unfortunately none of these samples shows a sufficiently high ceramic yield (~30%) to be eligible as a precursor, since a value of 40% is considered to be the practical minimum at which a coherent fibre can be maintained. The low ceramic yield of this fraction is not unexpected as the use of an F value of 2.0 is known to produce a copolymer which is linear in nature and upon pyrolysis easily undergoes reversion to cyclic volatile species giving a large weight loss⁶.

The TG data for the insoluble fractions show much more variation in the final yields (5-35% at 900°C), suggesting a difference in the composition of the various products which was not obvious in the soluble fractions. However, the overall yields are much lower than would generally be expected for insoluble copolymer fractions suggesting that the products are not of a highly crystalline nature.

X-Ray Diffraction:

All the soluble and insoluble solid samples from syntheses S2-S7 were characterised by XRD analysis apart from the insoluble fraction of S6. For all the soluble solids there was no structure to be seen. The traces all showed an amorphous "halo" and peaks due to the mounting plate. However, the traces for the insoluble solids all showed evidence of crystalline material. Some peaks due to the plate could be seen and also there was slight evidence of sodium chloride remaining from the original reaction. S3 (1:1 ratio in Ar) showed slight evidence of peaks corresponding to the data for polydimethylsilylene quoted in the literature^{7,8}. S7 (3:1 DMDCS:DPDCS) showed clearer evidence of this phase. The synthesis in which an excess of DPDCS

was used (S2) yielded an insoluble product which gave many clear, strong XRD peaks, the pattern of which is very similar to that shown in reference (1) for $(\text{SiPh}_2)_4$. These results are in agreement with those of Sartoratto and Yoshida who also show that if the starting composition contains only a small amount of DPDCS then the insoluble solid contains $(\text{SiMe}_2)_n$. Using a larger amount of DPDCS results in the formation of insoluble $(\text{SiPh}_2)_m$ compounds. However, when the experimental conditions were changed (S4 and S5) a different XRD trace was obtained. It is clearly different from that of S3, i.e. a different insoluble phase is forming which is similar to but not the same as for S2. This phase is still to be identified but the difference is of interest. The results under discussion show good agreement with Sartoratto and Yoshida when comparing the effect of compositional variables, but our work also shows that a change in experimental conditions can alter the product obtained.

Infra-red Spectroscopy:

All the insoluble and soluble solids were characterised by infra red spectroscopy. The spectra obtained for the soluble solid fractions were very similar and showed all the expected absorptions, e.g. Si-Ph and Si-Me. There were however differences to be seen in the spectra of the insoluble solids. The syntheses S2 and S7 had the most variation in the starting composition, i.e. 3:1 and 1:3 DPDCS:DMDCS respectively. The IR spectra for these samples showed clear differences. The trace for S2 is comparable to that shown by Sartoratto and Yoshida for $(\text{SiPh}_2)_4$ which is in agreement with both their findings and our XRD data. S7 again agrees with the observations in reference (1) and the XRD data as the spectrum is similar to that of $(\text{SiMe}_2)_n$. The spectra of S3 (1:1) and S8 (100% DMDCS) were similar to S7 whilst S4, S5 and S6 were more comparable with S2.

Both XRD and IR data confirm that there are differences in the insoluble solid fractions produced from the various syntheses. There is not the same evidence for the soluble solid, i.e. the IR spectra are very similar and the XRD traces only show that these samples are amorphous in nature. Since the insoluble fractions contain the excesses of Me or Ph groups, the soluble fractions must be more similar than the starting compositions suggest, hence the similarity of the TG curves shown in Figure 5.

Gel Permeation Chromatography:

The soluble solid samples were all characterised by Gel Permeation Chromatography (GPC) so their relative molecular weight distributions could be assessed. To date one liquid sample has been assessed and is included for comparison.

Sample	Mw	Mn	Polydispersity
S2	1,860 ; 1,890	1,080 ; 1,100	1.7 ; 1.7
S2 (soluble liquid)	760 ; 770	610 ; 620	1.2 ; 1.2
S3	3,550 ; 3,200	1,210 ; 1,180	2.9 ; 2.7
S4	2,410 ; 2,400 ; 2,610	1,120 ; 1,120 ; 1,140	2.1 ; 2.1 ; 2.3
S5	2,850 ; 2,810 ; 3,480	1,180 ; 1,200 ; 1,290	2.4 ; 2.3 ; 2.7
S6	2,460 ; 2,380 ; 2,850	1,100 ; 1,060 ; 1,140	2.2 ; 2.2 ; 2.5
S7	4,400 ; 4,220	1,480 ; 1,470	3.0 ; 2.9

Table 3: GPC data for the soluble solid fractions.

For samples S4, S5 and S6 a third figure is given in italics. This value is from the initial run carried out on the sample and the other two figures are values obtained consecutively on a later date. This confirms that deterioration of the sample in solution occurs with time⁹. All the molecular weights are rather low.

It is seen that the highest molecular weights occur in the sample with the most DMDCS in the starting mixture (S7) and also that these samples showed the highest polydispersity, i.e. the largest range of molecular weights. Sample S3 also has a relatively high molecular weight but this is not the case for S4, S5 and S6 which contained the same ratio of starting monomers.

Addition of a small amount of TMCS as a chain terminator (as carried out by Sartoratto and Yoshida) (S5) appeared to increase the molecular weight a little, especially in the first run and increased the polydispersity. Reducing the reaction time from 7 to 3 hours had little effect on the molecular weight, i.e. the polymer chains are not degrading with time of reaction but indeed are not growing either.

CONCLUSIONS

A series of copolymers can be produced by varying the ratio of the DPDCS:DMDCS monomers. The yields of the three fractions formed; insoluble solid, soluble solid and soluble liquid are seen to vary with the

starting composition. The homopolymers produce large amounts of crystalline, insoluble products. The mixed systems produce much less insoluble material and more of the amorphous, soluble material. The soluble solid fraction is the required form for spinning into a fibre and the TG data obtained show little difference in ceramic yield over the range of copolymers studied, with the exception of S2 showing a slight improvement. It was initially thought that sample S2 would show the poorest yield upon pyrolysis as the phenyl groups would be lost and therefore a dramatic weight loss seen. The XRD data showed all the soluble polymer fractions to be amorphous and the IR data showed very similar spectra. GPC data showed a variety of molecular weight distributions but these differences were not reflected elsewhere.

At the present time we are establishing a technique^{10, 11}, using thermomechanical analysis (TMA) to assess the expected spinning behaviour and to determine a suitable spinning temperature. It is intended to apply this technique to the various copolymers and spin fibres and so assess if any differences are seen with varying composition.

The characterisations carried out on the insoluble solids showed that these samples are different in their composition. S2 (75% DPDCS) was shown by XRD and IR to contain $(\text{SiPh}_2)_4$ whilst S7 (75% DMDCS) was seen to contain $(\text{SiMe}_2)_n$ and presumably similar behaviour occurred in the homopolymers. S7 and S8 showed the lowest ceramic yield on pyrolysis which can be explained by the occurrence of the rapid reversion reaction forming $(\text{SiMe}_2)_6$ ⁶. The change from 25-50% DPDCS, i.e. an increase in the number of phenyl groups improved the yield. It is thought that the presence of the phenyl rings slows the reversion reaction as the liberation of the relatively large, volatile molecular fragments is sterically hindered⁶. However, the copolymers prepared from a 50:50 blend showed different products, depending on the experimental conditions. S3 (under Ar for 7 hours) is similar to S7 by both IR and XRD although by the latter techniques the peaks are not strong. The insoluble solids from S4 and S5 contain a crystalline material but this is not $(\text{SiMe}_2)_n$ or $(\text{SiPh}_2)_4$. The XRD traces from both products are identical and a similar ceramic yield is obtained. Further increasing the amount of DPDCS to 75% did not improve the ceramic yield of the insoluble solid although a slight increase in that for the soluble solid was observed.

As the insoluble solids were shown to contain Si-Ph or Si-Me crystalline phases, depending on which monomer was in excess in the starting mixture, the soluble fractions must be deficient in the relevant group. This then explains why the soluble phases are all similar in their pyrolysis behaviour. S2 is a possible exception as there is a slight improvement in ceramic yield (~5%) perhaps due to more phenyl groups remaining in the soluble solid fraction than in the samples with a lower starting DPDCS content.

With regard to the overall aim of this project, i.e. to produce a silicon carbide fibre, there are certain observations which can be made. Syntheses S5 and S6 produced the required soluble solid fraction at the greatest yield. However, S2 showed the best ceramic yield and so it must be considered whether an increase in polymer yield could be effected by a change in experimental conditions as was the case for S3. An improvement in ceramic yield would also be beneficial as the current values are below the recommended minimum.

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Figure 2a:
Variation in polymer yield with composition

Figure 2b:
Data from Sartaratto & Yoshida

Figure 3:
TG data for all S4 fractions

Figure 4:
Comparison of all soluble liquids.

Figure 5:
Comparison of all soluble solids.

Figure 6:
Comparison of all insoluble solids.