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Effect of processing variables on the properties of polysilane ceramic precursors

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The Wurtz synthesis of polysilanes is a useful route in the production of polymeric precursors for silicon carbide ceramics and especially fibres. Copolymers have been synthesized by the dechlorination of methylphenyldichlorosilane and phenyltrichlorosilane in a 1 : 1 molar ratio using sodium metal dispersed in xylene. Changes have been made to the work-up procedure, leading to the separation of the various reaction products, in an attempt to improve the processing of ceramic fibres via polymeric precursors. It has been found that variation in the solvent used to separate the reaction products modified their yields and characteristic properties. Gel permeation chromatography (g.p.c.) showed that the molecular weight distribution of the soluble solid fraction, of importance as a potential precursor for ceramic fibres, had changed, which altered the softening temperature range observed. Thermomechanical analysis demonstrated that these changes could be as much as 70°C, which has important consequences for the processing of ceramic fibres from these precursors. Although some small variations in the ceramic yield were observed by thermogravimetry, these did not correlate with the g.p.c. data, suggesting that their chemical structure is at least as important as their molecular weight distribution in determining this yield. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polysilane precursors; silicon carbide fibres; thermal characterization)

INTRODUCTION

The synthesis of polysilane precursors for silicon carbide ceramics by an alkali metal dechlorination of chlorosilane monomers is now a well established procedure. The precursor can be spun, using conventional melt-spinning techniques, into a fibre which is then pyrolysed into a ceramic material. This method allows the production of thin, flexible ceramic fibres with good mechanical properties[1]. This procedure requires the precursor to meet certain criteria; for example, it must soften sufficiently for the spinning process and also must have an adequate yield on pyrolysis to enable a coherent fibre to be maintained.

The literature reports many variations for the production of polysilanes for use as ceramic precursors by the alkali metal dechlorination route, e.g. the use of different chlorosilanes, reaction conditions and 'work-up' procedures. For example, solvent/alkali metal combinations include tetrahydrofuran (THF) and potassium[2], benzene and sodium[3], toluene and sodium[4–7] and benzene or toluene with a sodium/potassium alloy of varying composition[8]. The subsequent treatments of the product to produce a usable polysilane are varied, with each group having a different method of quenching the reaction and then separating out the three fractions of polysilane which form, i.e. insoluble solid, soluble solid and soluble liquid. As an example of the variations reported, a brief summary of the preparation routes described by four of these authors is detailed in *Table 1*.

This study was undertaken to assess whether or not these different treatments could be considered largely responsible for the differences observed in the final properties. The experimental method used for these syntheses was developed from initial work by Emsley[9] and was selected to avoid both filtration and the addition of water and methanol in large amounts. The former stage was removed as it is a time-consuming process and the latter because of the possibility of causing hydrolysis of the polysilane[10]. A description of the method is given in *Table 1*, as previously described, and is detailed fully in the Experimental section. When comparing all the data in *Table 1*, the possibility arises that had our standard procedure been different (e.g. in the choice of solvents), different yields, molecular weights and properties of the polysilanes might have resulted. For example, our results for the synthesis of copolymers in the poly(dimethylsilylene-*co*-diphenylsilylene) system[11] were mostly very similar to those of Sartoratto and Yoshida[7], but they differed in some important respects, such as the relative amounts of soluble solid and liquid fractions observed. These differences may be due in part to variation in the work-up procedures. The aim of this study was to determine if changing some of these variables would significantly alter the physical properties of the polysilane product. The variations were employed only at the final precipitation stages and were effected by altering the solvent/non-solvent combinations.

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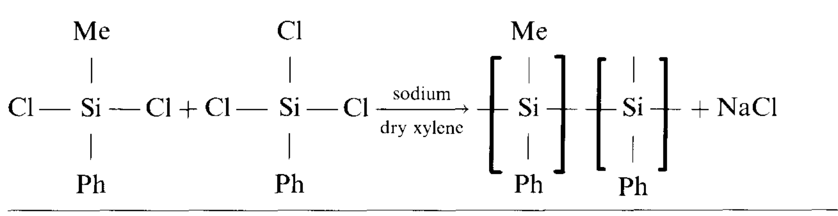
Table 1 Brief summary of processing procedures used by selected authors

Schilling *et al.*[2]	West *et al.*[4]	Gauthier & Worsfold[5]	Sartoratto & Yoshida[7]	Sheffield Group
Heat THF & K in Ar	Heat toluene & Na in Ar, (+ dispersing agent)	Heat toluene in N_2, add Na to refluxing solvent	Heat toluene & Na in Ar	Heat xylene & Na in Ar
Stir → metal dispersion	Stir → metal dispersion	Stir → metal dispersion	Stir → metal dispersion	Stir → metal dispersion
Turn off heat	Remove heating mantle	Add catalyst; remove heating mantle	Remove heating mantle	Turn off heat
Add chlorosilanes (over 3 h)	Add chlorosilanes	Add chlorosilanes	Add toluene solution of chlorosilanes	Add chlorosilanes
Heating resumed, reflux for further 2 h	Heating resumed, reflux for 7 h	Heating resumed, reflux for 2 or 3 h	Reflux for 6 h (chain terminator after 4 h)	Heating resumed, reflux for 7 h
Cool in wet ice bath	Cool	Cool in ice bath		Cool
Stand overnight	Quench by adding methanol then water		Distil → remove solvent & unreacted monomers. Add toluene & methanol	Centrifuge, pour off liquid, add more xylene & repeat at least twice
Collect solids by filtration, triturate with THF, recollect by filtration	Organic layer separated and solvent stripped off	Water added to destroy excess sodium	Hydrolyse mixture with HCl, separate organic layer & wash with water to neutral pH	Add propan-2-ol to solids to destroy excess sodium; wash in distilled water
Add solids to water, insoluble solid precipitates; wash with water & acetone	Dissolve in THF and separate THF-insoluble solid by centrifuging		Centrifuge to separate toluene-insoluble solid	Separate xylene-insoluble solids by filtration, wash in water & vacuum dry
Dry combined THF solutions & strip to smaller volume		Wash reaction mixture three times	Strip off remaining solvent	Distil xylene solution to remove solvent
Add solution dropwise to stirred acetone/MeOH	Add excess methanol to the THF solution	Add the toluene solution to isopropanol	Dissolve the residue in THF & add excess methanol	Dissolve the product in dry THF & add dropwise to stirred methanol
Collect soluble solid precipitate	Soluble solid precipitates	Polymer precipitates	Polymer precipitates	Soluble solid precipitates, collect by filtration & vacuum dry
Strip solvent/non-solvent mix to oil, vacuum distil to give soluble liquid				Rotary evaporate solvent/non-solvent mixture to give soluble liquid product

EXPERIMENTAL

The polysilanes discussed in this work were prepared via the sodium dechlorination, in xylene, of methylphenyldichlorosilane (MPDCS) and phenyltrichlorosilane (PTCS) at a 1 : 1 ratio, as described by equation (1):



$$\mathrm{Cl-\underset{Ph}{\overset{Me}{Si}}-Cl + Cl-\underset{Ph}{\overset{Cl}{Si}}-Cl} \xrightarrow[\text{dry xylene}]{\text{sodium}} \left[\underset{Ph}{\overset{Me}{Si}}\right]\left[\underset{Ph}{\overset{|}{Si}}\right] + \mathrm{NaCl} \qquad (1)$$

The reaction procedure adopted was as follows.

Stage 1. The xylene was first dried by boiling with sodium (using benzophenone as an indicator) and then collected. The volume of xylene was six times the yield of expected product, i.e. for a 50 g size reaction, 300 ml would be used. A minimum quantity of 150 ml had to be used or the stirrer paddle could not create a sodium dispersion. A reaction vessel was flushed with argon and xylene added. Sodium (including a 3% excess over the stoichiometric amount) was added to the xylene and heating applied by a heating mantle. Stirring was carried out, using an overhead stirrer of variable speed, to form a sodium dispersion.

Stage 2. The monomers (MPDCS from Fluka Chemie and PTCS from Aldrich Chemical Company Ltd) were then added dropwise in a 1 : 1 ratio, leading to a molar functionality of 2.5. The heating mantle was switched off before the monomer addition began as the reaction was strongly exothermic. When all the monomer had been added, a gentle heat was applied during the reaction time, which was usually 7 h. The heating mantle was then switched off and the products allowed to cool.

Stage 3. The contents of the vessel were then centrifuged and the solid material separated from the liquid.

Stage 4. This solid fraction was first treated with propan-2-ol to remove the excess sodium and then with water to dissolve the sodium chloride formed during the reaction. The whole was then filtered to isolate any insoluble solid product which was then dried.

Stage 5. The liquid separated at stage 3 was then distilled to remove the xylene and left a thick, often greasy, deposit. The deposit was dissolved in THF (which had been dried and distilled) and then added dropwise to stirred methanol. A white precipitate of 'soluble solid' polysilane was formed, which was recovered by filtration and dried under vacuum.

Stage 6. The THF–methanol mixture from stage 5 contained any soluble liquid oligomers which had been produced and these were isolated by rotary evaporation.

The procedure is depicted in the flow chart shown in *Figure 1*. During this study, stages 1–4 were not varied, but alterations to the procedure were made at stage 5 giving stages 5i and 5ii.

First synthesis

A polysilane was synthesized exactly as described in the previous section. The soluble solid polysilane was isolated in the stated manner (stage 5), i.e. after distillation the residue was dissolved in THF and then added to methanol to precipitate the copolymer (sample R1S-A). To determine the effect of further treatments upon this polysilane, a sample of this already prepared soluble solid was redissolved in THF and precipitated into propan-2-ol (sample R1S-B); i.e. an extra stage, 5i, was introduced. Both samples were then characterized and it is shown below that the reprecipitation altered the properties of the polysilane.

Reprecipitation series (samples R2S-A to R2S-H)

A second series of samples was prepared from the original soluble solid R1S-A via stage 5i using various solvent/non-solvent combinations, as detailed in *Table 2*. In each case 0.5 g of the parent material was used and the yield of the new soluble solid fraction determined. This series includes a repeat of the previous reprecipitation, i.e. sample R2S-B was produced by the same fractionation procedure as R1S-B.

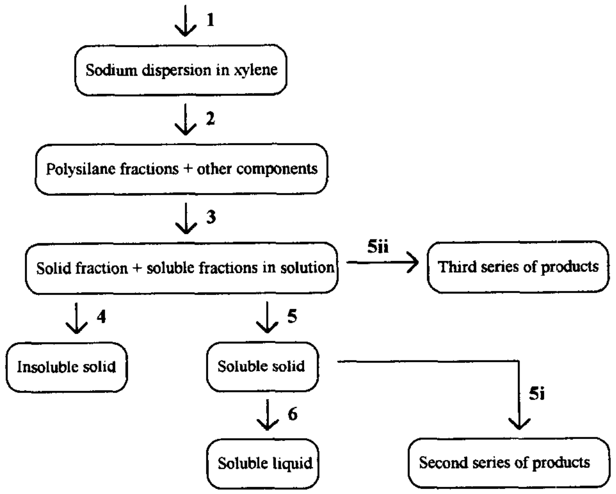


Figure 1 Flow chart depicting reaction procedure

Table 2 Solvent/non-solvent combinations used for samples R2S-A to R2S-H

Sample	Dissolved in	Precipitated in
R2S-A	THF	Methanol
R2S-B	THF	Propan-2-ol
R2S-C	THF	Butanol
R2S-D	THF	Acetone then methanol
R2S-E	THF	Water
R2S-F	Acetone	Methanol
R2S-G	Acetone	Propan-2-ol
R2S-H	Acetone	Butanol

Table 3 Solvent/non-solvent combinations used for synthesis R3S

Sample	Dissolved in:	Precipitated in:
R3S-A	THF	Methanol
R3S-B	THF	Propan-2-ol
R2S-F	Acetone	Methanol
R3S-G	Acetone	Propan-2-ol
R3S-IS	Acetone insoluble	–

Details of third synthesis (R3S)

A third synthesis was carried out using the same starting monomers in the same ratio, but in this case the xylene containing the soluble polysilane mixture, obtained after centrifuging at stage 3, was divided into two aliquots. Each was distilled to remove the xylene, after which one fraction was dissolved in THF and the other in acetone (both solvents were of dried and distilled grade). In the latter case, some solid material precipitated, i.e. some acetone-insoluble solid was formed. Each solution was then divided again to allow precipitation into either methanol or propan-2-ol (both of dried, distilled grade). The scheme, referred to as stage 5ii above, is summarized in *Table 3*.

Characterization

After drying under vacuum all the polymer products were thoroughly characterized. Thermogravimetry (t.g.) was carried out on a Stanton Redcroft TG 672 thermobalance using a sample mass of 10 mg at a heating rate of 20°C min^{-1} in a flowing nitrogen atmosphere. Thermomechanical analysis (t.m.a.) was obtained on a Du Pont 943 TMA and was carried out in air using the separated powder fraction, at a heating rate of 5°C min^{-1}. Gel permeation chromatography (g.p.c.) was carried out by RAPRA Technology, the results being expressed as the 'polystyrene equivalent' molecular masses.

RESULTS

First polysilanes prepared (samples R1S-A and R1S-B)

The first results obtained were those from the soluble solid fraction of the polysilane produced by the initial synthesis, i.e. from R1S-A and from the sample which had been redissolved in THF and precipitated in propan-2-ol (sample R1S-B), via routes 5 and 5i. The data obtained by t.m.a., g.p.c. and t.g. were compared and the results are illustrated in *Figures 2*, *3* and *4*, respectively.

T.m.a. gives information about the softening behaviour of the polymers[12,13] and the data obtained for samples R1S-A and R1S-B are illustrated in *Figure 2*. The molecular weight distribution data obtained from g.p.c. for both these polysilane samples are shown in *Figure 3*. The potential ceramic yield of the polysilane precursors was determined by t.g. and the different data obtained for these samples are plotted in *Figure 4*.

The polysilanes prepared in this synthesis and those described below were also characterized by infra-red (i.r.) spectroscopy. As expected, the spectra obtained were all similar and contained bands indicating the presence of phenyl and methyl groups. A broad absorption peak due to Si–O–Si and Si–O–C was also observed in all cases.

X-ray diffraction studies showed these soluble solid polysilanes to be amorphous, although it has been shown that the insoluble solid fractions of similar polysilanes produced in this manner can be crystalline[11]. Negligible amounts of insoluble solid were formed in the syntheses performed in this study, which may be due to the unsymmetrical nature of the starting monomers, in contrast to the regular monomers of the system reported previously[11].

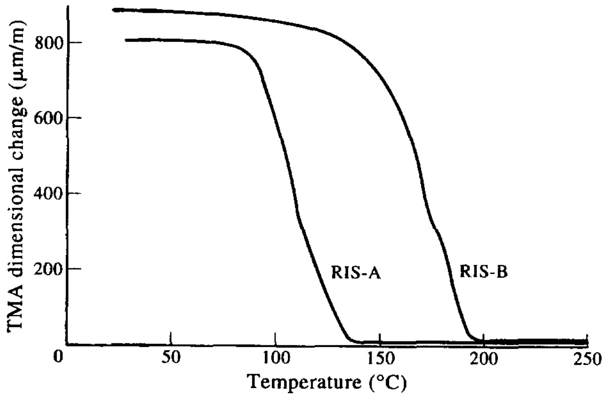


Figure 2 T.m.a. dimensional change of R1S-A (parent material) and R1S-B (reprecipitated THF/propan-2-ol)

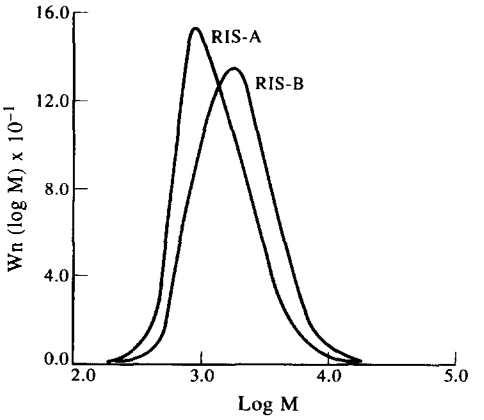


Figure 3 Molecular weight distribution of R1S-A (parent material) and R1S-B (reprecipitated THF/propan-2-ol)

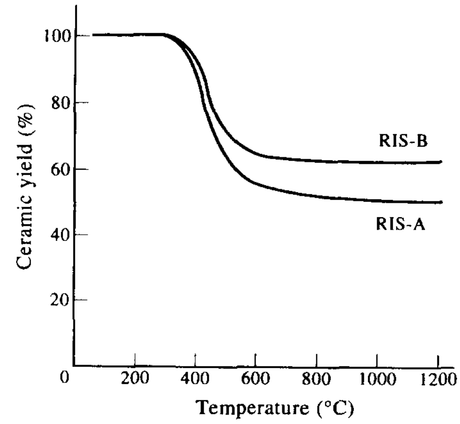


Figure 4 Thermogravimetry curves of R1S-A (parent material) and R1S-B (reprecipitated THF/propan-2-ol)

Table 4 Yields of polysilane obtained from the parent R1S-A by using various solvent/non-solvent combinations

Sample	Dissolved/precipitated	Yield (%)
R2S-A	THF/methanol	62
R2S-B	THF/propan-2-ol	62
R2S-C	THF-butanol	38
R2S-D	THF/acetone/methanol	40
R2S-E	THF/water	65
R2S-F	Acetone/methanol	74
R2S-G	Acetone/propan-2-ol	67
R2S-H	Acetone/butanol	51

Reprecipitation series (samples R2S-A to R2S-H)

As the initial experiment showed clear differences between the parent and the reprecipitated samples, a further study using a wider variety of solvents than that previously described was carried out; i.e. route 5i using a variety of solvent/non-solvent combinations. The yield of polysilane obtained from the original 0.5 g is given in *Table 4*.

The samples were characterized by t.m.a., g.p.c. and t.g. as illustrated in *Figures 5–8*. I.r. spectra were also obtained but they are not shown since there were no obvious differences between them and they showed the expected peaks.

The t.m.a. data, which have been split into groups to show the results more clearly, are shown in *Figure 5*. In *Figure 5a* the data for the five samples dissolved in THF before reprecipitation are compared with R1S-A′, which is a further sample of the parent material. The samples dissolved in acetone are also compared with the parent sample, R1S-A′, in *Figure 5b*. *Figure 5c* is included to illustrate the reproducibility of the results for repeat runs involving samples R1S-A′, R2S-C and R2S-F.

The g.p.c. data obtained for samples R2S-A to R2S-H are shown in *Figures 6a, 6b* and *6c*. Each plot also contains a trace for R1S-A′, the parent material, for reference.

In addition to the t.m.a. data, derivative traces (referred to as d.t.m.a. plots[13]) can also be obtained. It is interesting to compare the shape of these with the shape of the relevant g.p.c. curves, as illustrated by two examples in *Figure 7*.

T.g. data obtained for all nine samples are shown in *Figure 8*. In three cases the experimental curves were so close together that, for clarity, only one line has been drawn to illustrate two experiments.

Results from synthesis R3S

In the third series, the original reaction was repeated but the different precipitations were carried out during

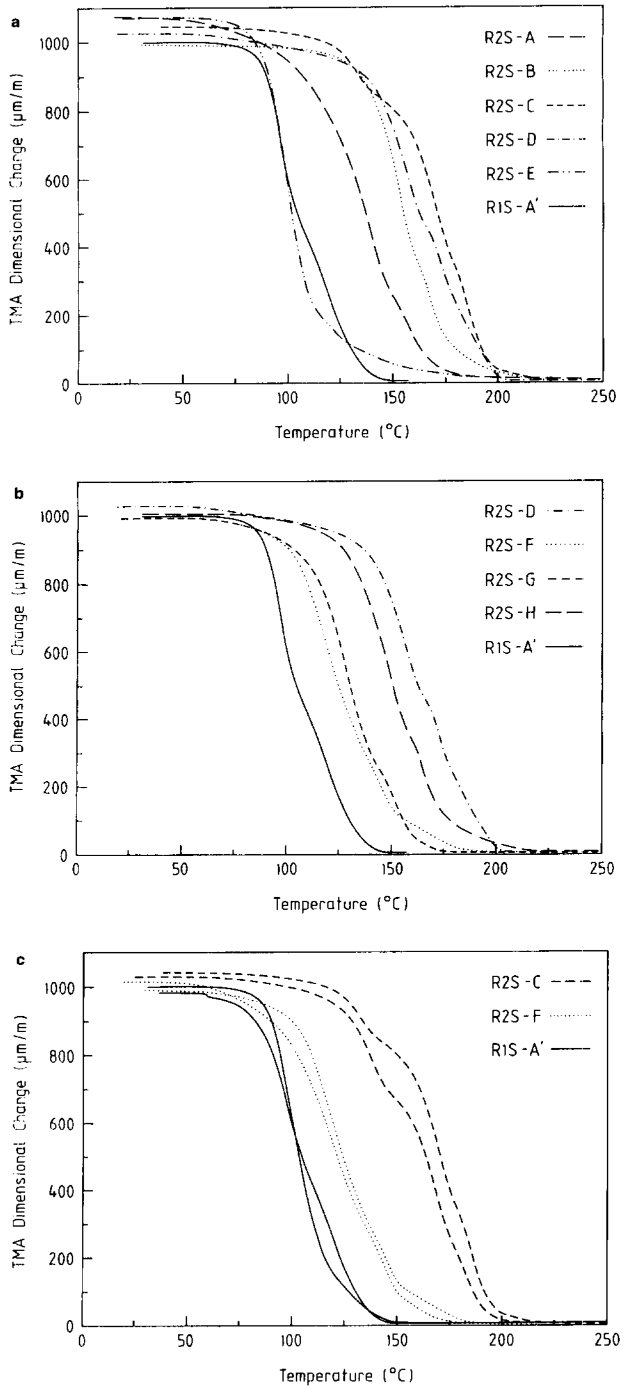


Figure 5 T.m.a. dimensional change of (a) R1S-A' (parent material), R2S-A (THF/methanol), R2S-B (THF/propan-2-ol), R2S-C (THF/butanol), R2S-D (THF/acetone/methanol) and R2S-E (THF/water), and (b) R1S-A' (parent material), R2S-D (THF/acetone/methanol), R2S-F (acetone/methanol), R2S-G (acetone/propan-2-ol) and R2S-H (acetone/butanol). (c) Reproducibility of the t.m.a. dimensional change of R1S-A', R2S-C and R2S-F

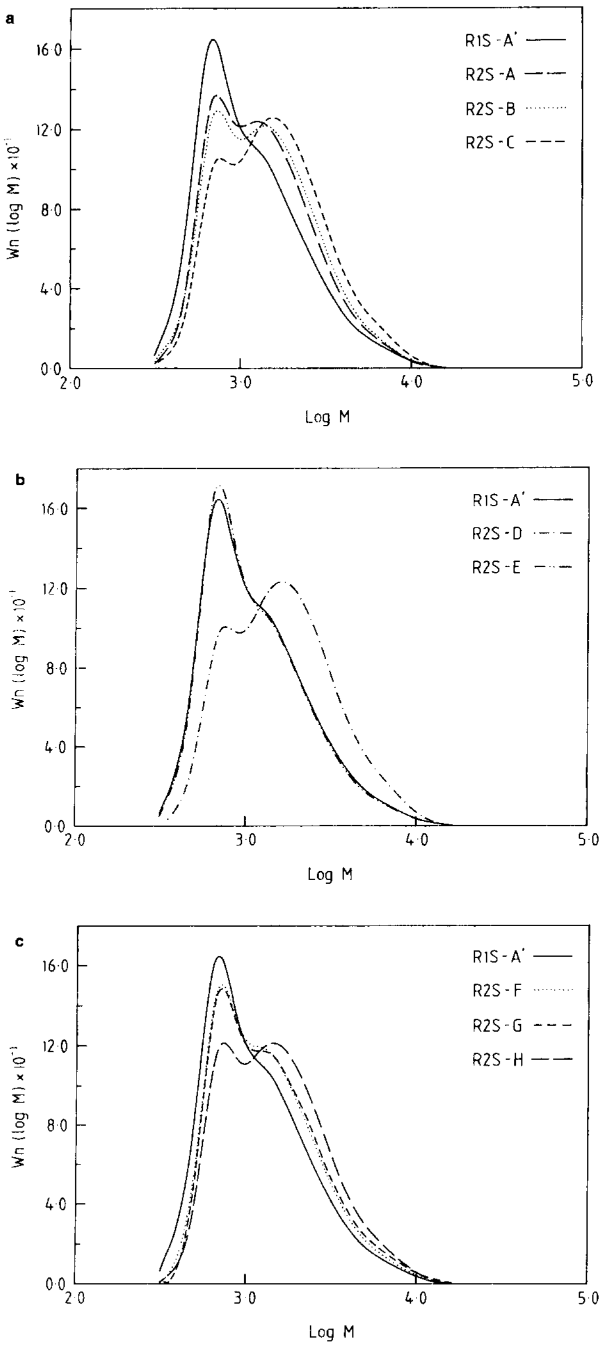


Figure 6 Molecular weight distribution of (a) R1S-A' (parent material), R2S-A (THF/methanol), R2S-B (THF/propan-2-ol) and R2S-C (THF/butanol), (b) R1S-A' (parent material), R2S-D (THF/acetone/methanol) and R2S-E (THF/water), and (c) R1S-A' (parent material), R2S-F (acetone/methanol), R2S-G (acetone/propan-2-ol) and R2S-H (acetone/butanol)

the 'work-up' procedure, rather than on previously prepared soluble solid material as described above. In this case all the solvents used were of dried, distilled grade. In this synthesis, route 5ii was followed in which the soluble polysilane fractions produced in the normal manner up to stage 4 were dissolved in THF or acetone (whereas the original samples were only dissolved in THF), although when acetone was used a small amount of insoluble material was obtained. Precipitation of the soluble solid was achieved by adding each solution dropwise to either methanol or propan-2-ol (the original samples were only precipitated into methanol), so giving four different soluble polysilanes in total. Soluble liquid fractions were also produced and collected during these experiments and, as they were of a very thick consistency, it was possible to characterize them by t.m.a. in addition to the soluble solid fractions. The various polysilane yields obtained are shown in *Table 5*, where the actual mass of each product collected is given. If the calculated yield of the synthesis was achieved, then the sum of all the fractions should be 20 g.

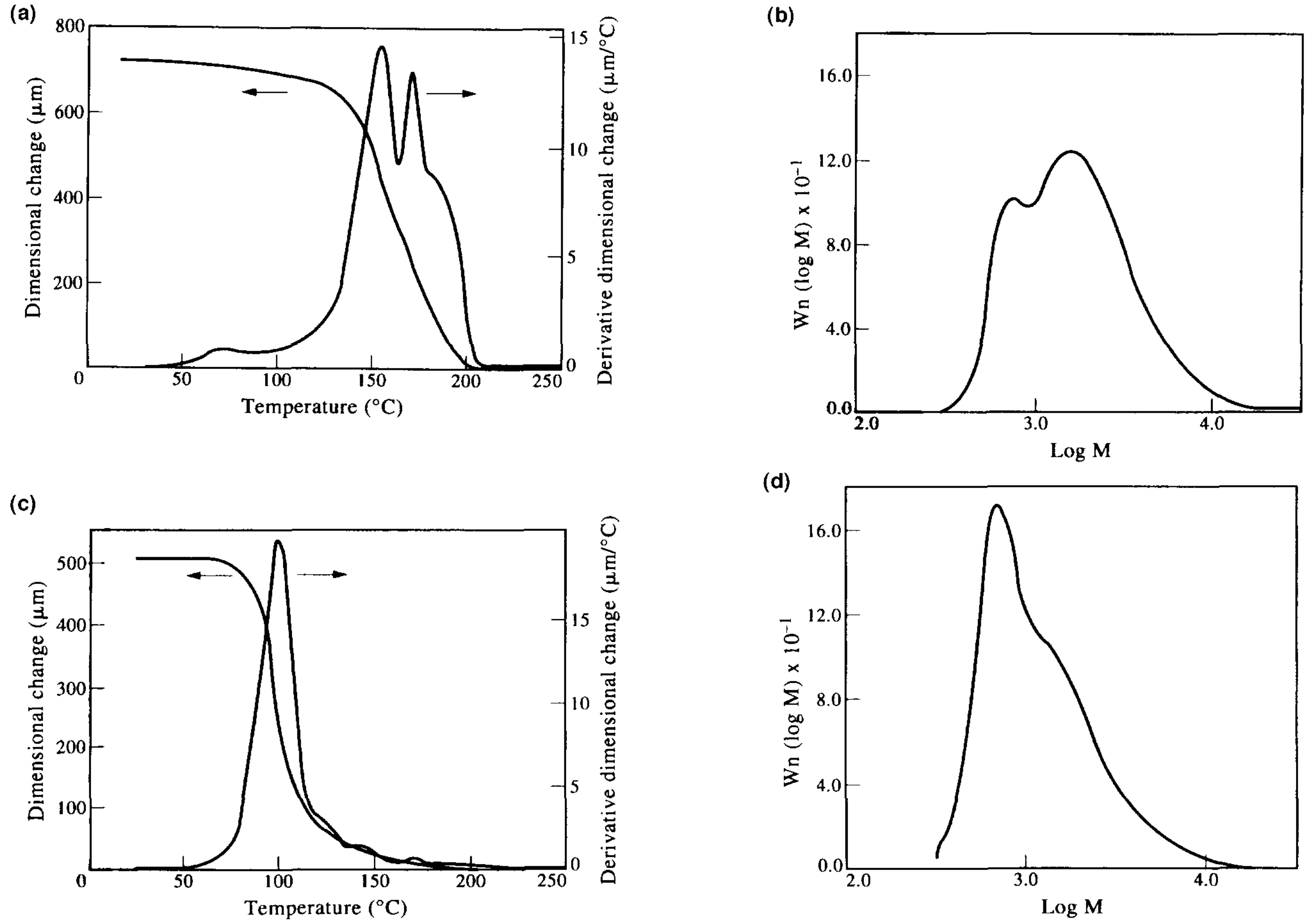


Figure 7 Comparison of (a) the t.m.a. derivative dimensional change plot and (b) the molecular weight distribution for R2S-D (THF/acetone/methanol); and (c) the t.m.a. derivative dimensional change plot and (d) the molecular weight distribution for R2S-E (THF/water)

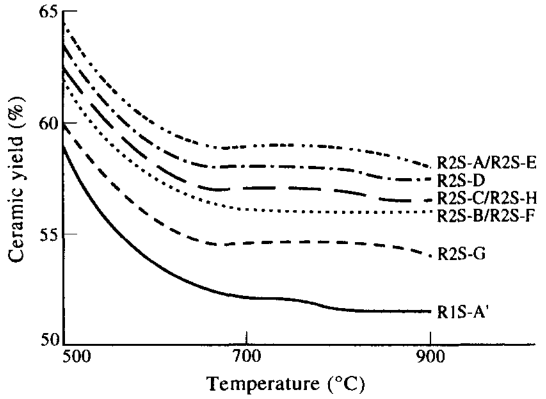


Figure 8 Thermogravimetry curves of R2S-A (THF/methanol), R2S-B (THF/propan-2-ol), R2S-C (THF/butanol), R2S-D (THF/acetone/methanol), R2S-E (THF/water), R2S-F (acetone/methanol), R2S-G (acetone/propan-2-ol), R2S-H (acetone/butanol) and R1S-A' (parent material)

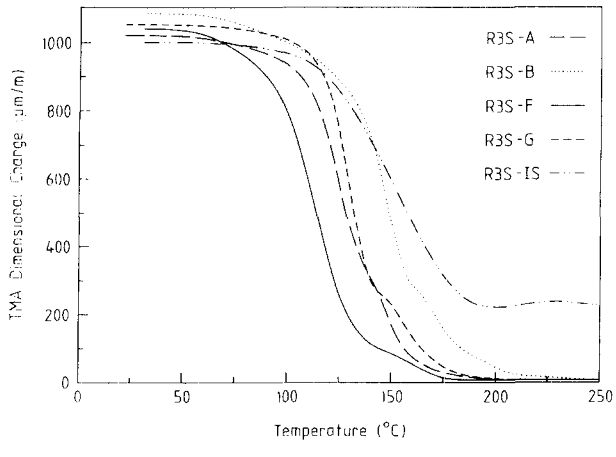


Figure 9 T.m.a. dimensional change of the soluble solid fractions of R3S-A (THF/methanol), R3S-B (THF/propan-2-ol), R3S-F (acetone/methanol), R3S-G (acetone/propan-2-ol) and R3S-IS (acetone insoluble)

T.m.a. data for the soluble solid and acetone-insoluble fractions are shown in *Figure 9*. The t.m.a. curve for sample R3S-B was recorded twice and gave excellent reproducibility.

The g.p.c. data for the soluble solids and the acetone-insoluble fraction are shown in *Figure 10*. T.g. data for these fractions are shown in *Figure 11*, in which solid curves are used to represent data obtained from the solid fractions and dashed curves from the liquid fractions. Once again, for clarity, on two occasions one curve is

Table 5 Yields obtained from the different fractions of R3S

Sample	Dissolved/precipitated	Soluble solid yield (g)	Soluble liquid yield (g)
R3S-A	THF/methanol	2.7	1.8
R3S-B	THF/propan-2-ol	2.9	1.4
R3S-F	Acetone/methanol	3.1	1.0
R3S-G	Acetone/propan-2-ol	4.2	2.4
R3S-IS	Acetone-insoluble	0.3	–

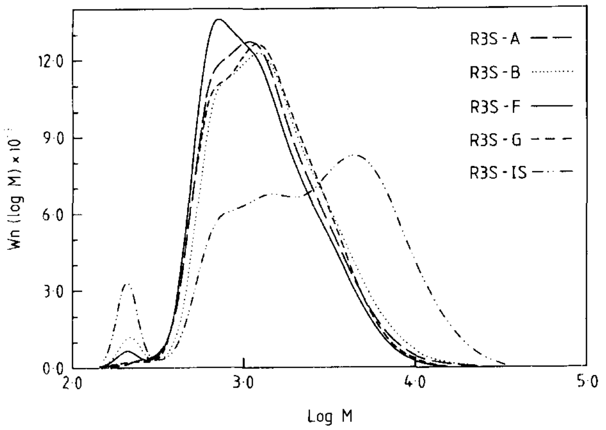


Figure 10 Molecular weight distribution of the soluble solid fractions of R3S-A (THF/methanol). R3S-B (THF/propan-2-ol), R3S-F (acetone/methanol), R3S-G (acetone/propan-2-ol) and R3S-IS (acetone insoluble)

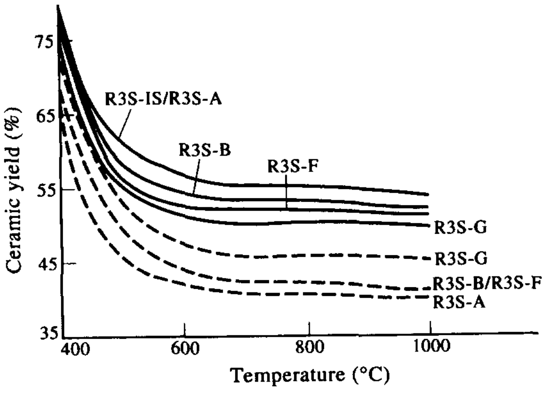


Figure 11 Thermogravimetry curves of the soluble solid fractions (—) of R3S-A (THF/methanol), R3S-B (THF/propan-2-ol), R3S-F (acetone/methanol), R3S-G (acetone/propan-2-ol) and R3S-IS (acetone insoluble) and of the soluble liquid fractions (- - -) of R3S-A (THF/methanol), R3S-B (THF/propan-2-ol), R3S-F (acetone/methanol) and R3S-G (acetone/propan-2-ol)

used to represent two sets of closely similar experimental data.

DISCUSSION

It was anticipated that varying the processing of the polysilanes would alter certain properties, e.g. molecular weight, as this is well documented. The aim of this study was to show how these changes affected the suitability of the polysilane as a precursor material. If the processing and pyrolysis behaviour of the polymeric precursor is affected, it may be improved by simple changes to the work-up procedure of the products from the chemical synthesis.

In the initial experiment, when a simple comparison was made between the soluble solid fraction produced by the standard route and the reprecipitated sample, it was shown by t.m.a. (*Figure 2*) that the softening behaviour of the latter fraction was significantly different from that of the original material. (Duplicate runs of the same material gave good reproducibility as shown in *Figure 5c*.) The reprecipitated fraction began to soften at about 60°C higher than the original and also showed a similarly higher 'end point'. It has been shown elsewhere[12,13] that the t.m.a. curve gives a good indication of the temperature required to achieve spinning of the polymer into a continuous fibre. Therefore, this reprecipitated material required a substantially higher spinning temperature, which is crucially important to know if the polymer is to be converted into ceramic fibres.

The gel permeation chromatography data shown in *Figure 3* also indicated a difference between the two samples. Not surprisingly, in view of its different t.m.a. curve, it was seen that the reprecipitated sample had less of the low-molecular-weight species and consequently there was a shift in the distribution to higher molecular weights.

The t.g. data shown in *Figure 4* indicated that the ceramic yield of the reprecipitated sample (R1S-B) was higher than that of the parent material (R1S-A). The ceramic yield obtained from this original material had been determined from t.g. data on several occasions over a period of three years and found to vary within the range 45–55%. Although some differences must occur in the experimental conditions, the nature of the polysilane alters with time, because crosslinking can occur and also degradation due to exposure to ultraviolet radiation. Therefore caution should be exercised in interpreting small changes in ceramic yield as significant. It was seen from *Figure 4*, however, that in this case the reprecipitated material showed at least a 10% increase in ceramic yield when compared with the parent material, which was clearly a significant difference. Since a good polymer precursor for ceramic fibres must give a high ceramic yield, a processing step that increased this yield was considered to be worthy of further investigation.

Reprecipitation series (samples R2S-A to R2S-H)

The reprecipitation series, R2S-A to R2S-H, provided more data for comparison. The samples were observed by t.m.a. to soften at slightly different temperatures. Data for all those samples which were dissolved in THF prior to precipitation in the various solvents are shown in *Figure 5a*. All the polysilanes produced by precipitation into organic solvents showed an increase in softening temperature when compared with R1S-A′, the original material. The greatest increases in the final softening temperature were observed for samples R2S-C (THF + butanol) and R2S-D (THF + acetone + methanol). The same behaviour was seen when the original polysilane was dissolved in acetone (*Figure 5b*). *Figure 5c* is included to show the reproducibility of these t.m.a. results. Although slight differences were observed when a run was repeated, this experimental error was much less than the increases in softening temperature observed after precipitation from the various solvents. However, within experimental error, the t.m.a. curve for sample R2S-E, reprecipitated in water, was the same as that for R1S-A′ (*Figure 5a*).

The g.p.c. data for the various polysilanes shown in *Figures 6a*, *b* and *c* also show differences between the products and the parent material. The molecular weight distribution of the polysilane was found to affect the spinning behaviour of the material[14,15]; if it was too high the polysilane tended to be infusible and if too low the polysilane melted readily on subsequent heat treatment. The original sample (R1S-A′) clearly consisted of two main components and the various fractionation procedures removed varying proportions of the lower molecular weight material. The products, therefore, contained a higher proportion of the higher molecular mass component with the exception of the sample R2S-E (precipitated into water) which had a very similar molecular weight distribution to the reference sample R1S-A′. While polysilanes R2S-F and R2S-G still contained a large proportion of the lower molecular weight species, samples R2S-A and R2S-B showed a more marked decrease in the amount of the lower molecular weight species and a subsequent increase in the higher molecular weight species, but samples R2S-H and especially R2S-C and R2S-D contained a large proportion of the higher molecular weight fraction. The results can be tabulated (*Table 6*) to demonstrate these differences; each determination was repeated, sometimes twice, and the reproducibility of the results was excellent.

These molecular weight data can be correlated with the yields obtained when producing the different polysilanes which are listed in *Table 4*. In general terms, the samples showing the poorer yields on fractionation had the higher molecular weight distributions, e.g. R2S-C, R2S-D and R2S-H. The reprecipitation procedure resulted in a polysilane containing a larger proportion of the higher molecular weight fraction than the parent material, because the lower molecular weight fraction of the original remained in the solvent. The yield of polysilane must therefore be reduced. When the product contained more of the original low molecular-weight fraction there was less material remaining in solution and the yields were higher.

These data correlate well with the t.m.a. data shown in *Figure 5*. Samples R2S-C and R2S-D, followed by R2S-H and R2S-B, showed the greatest increase in softening temperature and had the highest proportions of the greater molecular weight species. In contrast, samples R2S-E and the parent material R1S-A′ showed the lowest softening temperatures and the lowest molecular weight values. The other samples showed values between these extremes.

Further correlation is observed between the g.p.c. data and d.t.m.a. data as illustrated in *Figure 7*, which contrasts data for samples R2S-D and R2S-E. The shape of the two plots is seen to be similar; thus, as the proportion of the higher molecular weight species increased, so the second, higher temperature d.t.m.a. peak became more prominent.

This relationship between molecular weight and softening temperature range was not, however, reflected in the t.g. data, although it has been reported by Schilling *et al.*[2] that, 'yields increase with polycarbosilane molecular weight for each preparation, but only to a point'. As shown in *Figure 8*, in all cases the ceramic yield was improved slightly by the fractionation procedure, i.e. all gave a higher value than sample R1S-A′. However, samples R2S-C and R2S-D, which had the highest molecular weight distributions and softening temperatures, did not give the best ceramic yields. These were obtained from samples R2S-A (THF + methanol) and R2S-E (THF + water), the former polysilane giving intermediate values for t.m.a. and g.p.c. and the latter giving the poorest. The ceramic yield seems, therefore, to be dependent upon the chemical structure of the product. If the polysilane can easily undergo a reversion reaction producing volatile cyclic species, it gives a greater loss in mass on pyrolysis. The actual molecular weight of the species seems to be less important; indeed, if long, high-molecular-weight chains are formed rather than a more crosslinked species, reversion reactions are more likely. These observations are of great relevance to the conversion of these copolymers into ceramic products.

Table 6 G.p.c. data for samples R2S-A to R2S-H (R1S-A′ included for reference)

Sample	M_w	M_n
R1S-A′	1510; 1470; 1570	940; 940; 1030
R2S-A	1700; 1700	1090; 1090
R2S-B	1760; 1750	1120; 1110
R2S-C	2000; 1990	1250; 1220
R2S-D	2070; 2060	1280; 1250
R2S-E	1490; 1470	940; 950
R2S-F	1650; 1620	1060; 1040
R2S-G	1740; 1720	1090; 1090
R2S-H	1890; 1900; 1910	1180; 1180; 1200

Synthesis R3S

The t.m.a. data for the solid fractions of R3S (*Figure 9*) also showed a difference in softening behaviour with the different precipitation procedure. The samples obtained by precipitation into methanol or propanol showed similar behaviour; once again the samples were observed to soften completely. Sample R3S-IS, which was produced as an acetone-insoluble fraction, exhibited rather different behaviour. The early stages of softening were comparable with those of the other samples but only a degree of softening was observed. At 300°C this sample did not completely soften, as confirmed by direct observation of the sample after the analysis had finished. The other four samples showed similar softening temperatures, with the sequence being as follows: R3S-F < R3S-A < R3S-G < R3S-B.

The data obtained from the liquid samples showed a different pattern of behaviour. Samples R3S-B and R3S-F, which were the end members of the previous series, showed softening at very similar temperatures. The softening temperatures were in the sequence R3S-F < R3S-B < R3S-A < R3S-G.

When all the t.m.a. data for R3S were compared, it was seen that, as expected, the soluble solid fractions softened at considerably higher temperatures than the corresponding liquid fractions.

Examination of the g.p.c. data for the soluble solid fractions (*Figure 10*) indicates that sample R3S-IS had a markedly different molecular weight distribution from the other members of the group, with this polysilane containing much more of a higher molecular weight species. The plots for the other soluble solids are very similar, although sample R3S-F can be seen to contain rather more of the low-molecular-weight species.

The g.p.c. data obtained for the soluble liquids all had very similar molecular weight distributions. The variation observed in the soluble liquid samples was less than in the case of the soluble solids, suggesting that the liquids remaining as a consequence of the different precipitations were of a more regular composition than these solids. The similarity of the g.p.c. data is not reflected in the t.m.a. data, as a significant variation in softening temperature of the liquids has been demonstrated. This observation may be due to the nature of the soluble liquid samples which, although very viscous, probably behaved differently under the load than the usual soluble solid samples investigated. Some of the viscous liquid may even have been squeezed out from under the probe.

When the t.m.a. and g.p.c. data are compared, as for the previous examples, a correlation is seen but only for the soluble solid samples. Polysilane R3S-IS was shown to soften only partially in contrast to the other samples and the corresponding g.p.c. data showed a larger proportion of higher molecular weight material. It seemed that the lower molecular weight material softened as the sample was heated (in a similar manner to that of the other polysilanes in the series) but the remainder, i.e. the higher molecular weight material, did not, presumably because of crosslinking. Of the other samples, R3S-F had the largest amount of the lower molecular weight fraction and exhibited the lowest softening temperature. Polysilanes R3S-A and R3S-G were very similar ($M_w = 1749$ and 1723, respectively) and showed related softening temperatures. Sample R3S-B had a slightly higher molecular weight distribution and a correspondingly higher softening temperature.

The t.g. data obtained for all the R3S samples are shown in *Figure 11*. The five soluble solid products all showed very similar ceramic yields, in the range 50–54%. The ceramic yields obtained for the soluble liquid fraction were in the range 40–46% which is lower than that for the soluble solids, as expected. Where there are both solid and liquid fractions to compare, the better the ceramic yield of the solid, the poorer that of the liquid; e.g. R3S-A showed the best yield for the solid and the poorest for the liquid. The fractionation therefore isolated different amounts of the higher ceramic yield material in the solid and the balance was made up in the liquid. As also observed in the previous series, there does not appear to be any correlation of the ceramic yield with either g.p.c. or t.m.a. data.

Polysilanes produced from starting monomers of functionalities of 2.0 and 3.0 are also discussed elsewhere[15]. It is concluded in this work that the combination of methylphenyldichlorosilane and phenyltrichlorosilane gave the best overall properties of those studied with regard to the spinning of precursors for ceramic fibres. The characteristic properties of these polysilane systems are thoroughly compared with those of related systems described in the literature.

Comparison of like samples

The discussion so far has concentrated on each set of experiments individually. It is of interest finally to compare related samples from each set since Wurtz syntheses are notorious for the difficulty in achieving a product of reproducible quality[5,8,16].

Polysilanes of similar type are listed in *Table 7*. Samples R1S-A and R1S-A′ were from the same stock material, i.e. they should show reproducibility, while R1S-B and R2S-B were repeats of the same experiment. In the other examples, there are some differences due to the R2S-A to R2S-H series being reprecipitated from an initial starting material and the R3S series being individually prepared.

The ceramic yield, softening temperature and molecular weight of each group of samples are listed in *Table 8*. These values suggest that the results obtained are reproducible within the limits that can be expected based on an inhomogeneous starting material, produced by a method which is noted for the variability of products[5,8,16].

Samples R1S-A and R1S-A′ gave very similar t.m.a. plots and g.p.c. data, especially considering that the data were obtained some months apart and these polysilanes are known to age. The ceramic yield of sample R1S-A′ was 52% which is within the range 45–55% reported for sample R1S-A in *Table 8*, the softening temperature of the second sample was 140°C compared with 135°C, and the molecular weight averages were comparable. All of these characteristics indicate that these two samples from the same batch provided a good test confirming that the reproducibility of the methods used was very satisfactory.

Samples R1S-B and R2S-B were obtained by repeating the same procedure, i.e. the stock material was dissolved in THF and reprecipitated in propan-2-ol. The ceramic yields (*Table 8*) obtained for both polysilanes were within the same range, the softening temperature of R2S-B was 15°C higher and the average molecular weight was significantly different. Although these polysilanes are similar, they display more variation than the repeat tests carried out on the same material.

Reprecipitating polysilane R1S-A, even into the same solvent (sample R2S-A), altered the product significantly. The most noticeable change was a large increase in the softening temperature. The ceramic yield and the average molecular weight also varied but these were smaller changes. Where the different precipitations were carried out directly (R3S), polysilanes of similar softening behaviour to the reprecipitated samples were obtained. G.p.c. data and ceramic yields were also comparable.

This pattern of behaviour was also observed in the properties of the other related samples based on the use of acetone in place of THF (series F and G). The repre-

Table 7 Summary of samples produced by similar solvent/non-solvent routes

Sample	Preparation	Comments
R1S-A	THF/methanol	Original polysilane
R1S-A′	THF/methanol	Original polysilane
R2S-A	2 × THF/methanol	Dissolved/reprecipitated from original
R3S-A	THF/methanol	New sample, dried distilled solvents
R1S-B	THF/methanol + THF/propanol	Dissolved/reprecipitated from original
R2S-B	As above	Dissolved/reprecipitated from original
R3S-B	THF/propanol	New sample, dried distilled solvents
R2S-F	THF/methanol + acetone/methanol	Dissolved/reprecipitated from original
R3S-F	Acetone/methanol	New sample, dried distilled solvents
R2S-G	THF/methanol + acetone/propanol	Dissolved/reprecipitated from original
R3S-G	Acetone/propanol	New sample, dried distilled solvents

Table 8 Comparison of properties obtained from samples prepared in a similar manner

Sample	Ceramic yield (%)	Softening temperature (°C)	M_n	M_w
R1S-A	45–55[a]	135	1058; 1062	1629; 1614
R1S-A′	52	140	944; 936	1513; 1470
R2S-A	58	180	1088; 1085	1699; 1698
R3S-A	54	190	1055; 1042	1775; 1723
R1S-B	64/52	195	1458; 1376	2293; 2184
R2S-B	56	210	1117; 1114	1761; 1746
R3S-B	53	225	1083; 1068	1939; 1869
R2S-F	56	180	1055; 1035	1652; 1624
R3S-F	52	175	968; 951	1592; 1589
R2S-G	54	170	1089; 1092	1741; 1723
R3S-G	50	190	1080; 1100	1738; 1708

[a] Several determinations made over a three-year period

cipitation using the same solvent/non-solvent combination produced a polysilane with similar properties (series R2S and R3S).

The ceramic yields obtained from these polysilanes ranged from 45 to 64% with an average value of 54%. These yields compare favourably with those in the published literature; for example, Schilling *et al.*[2] reported yields of 18–44%. West *et al.*[4] quoted a best value of 30% and Carlsson *et al.*[17] quoted 39%. Molecular weight data reported in the literature are very varied. Jones *et al.*[16] described a typical distribution consisting of at least three molecular weight fractions. The molecular weight averages for the polysilanes reported in this study are at the lowest end of these fractions, since the use of THF and propan-2-ol resulted in a polysilane which showed the highest molecular weight average, M_w, of only around 2200. Experience reported elsewhere[12,15] has demonstrated that polysilanes of similar molecular weights and softening behaviour can be spun successfully into fibres.

CONCLUSIONS

This study has shown that varying the work-up procedure used to separate the fractions formed in the chemical synthesis modified the properties and the yield of the soluble solid polysilane product. The molecular weight distribution changed as greater proportions of a higher molecular weight species were detected by g.p.c. Although this observation was expected, it is highly significant in the further processing of fibres from these polymer precursors. Increases in the final softening point of up to 70°C have been observed by t.m.a. and d.t.m.a., and a good correlation between such data and the spinning behaviour of the polysilane has been demonstrated previously[12,13]. Hence altering the details of the chemical synthesis modified the temperature at which the polysilane could be spun into a fibre, with consequent effects on the production of the precursor fibre itself. As the spinning temperature is a rather subjective property and spinning fibres from these polysilane precursors can be extremely difficult, the ability to tailor the softening point is of great value. Although some small variations in the ceramic yield, as determined by t.g. were also observed, these changes did not correlate with the g.p.c. and t.m.a. data. If the ceramic yield could be controlled by a variation in the precipitation procedure, it would be very advantageous, as a high ceramic yield is desirable at the next production stage when the fibre is pyrolysed to silicon carbide.

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