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# The thermal behaviour of potential polymeric precursors for silicon carbide fibres

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## Abstract

As silicon carbide fibres cannot be manufactured by conventional methods, alternative fabrication routes must be found. One such is the polymeric precursor route. The production of polysilanes via the alkali dechlorination route is described, as is the effect of varying the functionality $f$ of the starting monomers on the overall functionality $F$ of the product. To produce a silicon carbide fibre, the polysilane must be separated into suitable fractions, the soluble solid fraction has to be spun into a fibre and the product eventually pyrolysed to a ceramic material. In this paper the advantageous use of thermomechanical analysis (TMA) to determine a spinning temperature is described and also the use of derivative thermomechanical analysis (dTMA). The determination of the potential ceramic yield by the use of thermogravimetry (TG) is also discussed.

## INTRODUCTION

Silicon carbide fibres, used in metal matrix and ceramic matrix composites, cannot be manufactured by conventional methods and so alternative processing routes must be found. Chemical vapour deposition (CVD) can be used or, as will be discussed here, a polymeric precursor can be formed into a fibre and then pyrolysed to give the ceramic fibre product [1–8]. A potential precursor must meet several requirements as described briefly below.

Firstly, it must be possible to spin the polymer into a fibre which can be readily handled for further processing. The fibre shape must then be fixed by curing to prevent softening on further heating. The final stage is to pyrolyse the cured fibre, at which stage the ceramic yield must be high enough for a continuous fibre of the required diameter to be maintained. It is also important that the desired product, i.e. SiC, rather than a mixture containing graphite and silica, is obtained.

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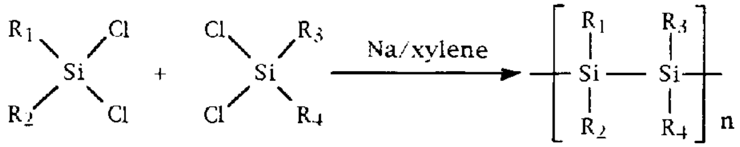


Fig. 1. Alkali dechlorination of chlorosilanes.

Therefore, the fabrication of a silicon carbide fibre via this route involves various heat treatments and it is important to be able to characterise the behaviour of a potential precursor at these different stages. This study describes some of the work carried out on certain polysilanes to determine their suitability as polymeric precursors. In particular, the use of thermomechanical analysis (TMA) and thermogravimetry (TG), to determine spinning temperature and ceramic yield, are discussed.

Polymeric precursors can be prepared by various methods [1, 4, 5, 7]: the polysilanes discussed in this paper were prepared by the alkali metal dechlorination of chlorosilanes as illustrated in Fig. 1.

This reaction usually produces three types of polymer: insoluble solid, soluble solid and soluble liquid. The following discussion refers only to the solid fractions as the liquid form is not suitable for conversion into a ceramic material.

Monomers of different functionalities can be used to vary the degree of crosslinking occurring in the polymer. In the example given in Fig. 1, both monomers have a functionality $f$ of 2, but starting materials where $1 \leq f \leq 5$ are possible, e.g. trimethylchlorosilane ($f = 1$), phenyltrichlorosilane ($f = 3$) and vinyltrichlorosilane ($f = 5$). The overall functionality of the reaction $F$ is calculated as shown below, where $x$ is the number of moles of each monomer [4]

$$F = \frac{x_1 n_1 + x_2 n_2 + \cdots + x_n f_n}{x_1 + x_2 + \cdots + x_n}$$

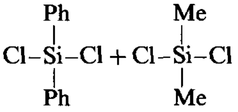
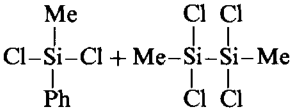
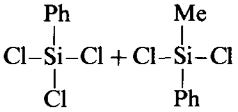
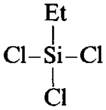
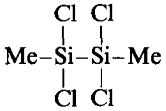
Values of $F = 2$ give a linear polymer and higher values give a more networked product. It is generally observed that linear polymers can be spun readily but tend to give relatively low ceramic yields, whereas crosslinked polymers usually give good ceramic yields and can be spun only with difficulty.

## EXPERIMENTAL

The polysilanes discussed in this paper were produced by the alkali dechlorination of various combinations of chlorinated silane monomers. The monomers were selected to allow the functionality $F$ of the reaction to be changed according to the mole fractions used, as described in the

TABLE 1

Variations of *F* used

| *F* value (Reaction number) | Reaction | Polymer type discussed |
|---|---|---|
| 2.0 (R11) |  $\mathrm{Cl{-}\overset{Ph}{\underset{Ph}{Si}}{-}Cl + Cl{-}\overset{Me}{\underset{Me}{Si}}{-}Cl}$ | Soluble and insoluble |
| 2.2 (R6) |  $\mathrm{Cl{-}\overset{Me}{\underset{Ph}{Si}}{-}Cl + Me{-}\overset{Cl}{\underset{Cl}{Si}}{-}\overset{Cl}{\underset{Cl}{Si}}{-}Me}$ | Soluble only |
| 2.5 (R1) |  $\mathrm{Cl{-}\overset{Ph}{\underset{Cl}{Si}}{-}Cl + Cl{-}\overset{Me}{\underset{Ph}{Si}}{-}Cl}$ | Soluble only |
| 3.0 (R10) |  $\mathrm{Cl{-}\overset{Et}{\underset{Cl}{Si}}{-}Cl}$ | Soluble and insoluble |
| 4.0 (R3) |  $\mathrm{Me{-}\overset{Cl}{\underset{Cl}{Si}}{-}\overset{Cl}{\underset{Cl}{Si}}{-}Me}$ | Soluble and insoluble |

introduction. Syntheses were carried out in an argon atmosphere using dry xylene as the solvent and sodium as the alkali metal source [6].

The thermal characterisation of a number of polymer products from these reactions, i.e. at five different values of *F*, is described. The syntheses and corresponding values of *F* are shown in Table 1. Where appropriate, both soluble and insoluble solid fractions were studied but in two cases insufficient insoluble polymer product was obtained to allow characterisation to be carried out.

TG was carried out on a Stanton Redcroft TG 672 using a sample mass of 10 mg and a heating rate of 20°C $\mathrm{min}^{-1}$ in a flowing nitrogen atmosphere. TMA was observed on a Du Pont 943 TMA and was carried out in air (as spinning was not in a controlled atmosphere) using the separated powder fraction at a heating rate of 5°C $\mathrm{min}^{-1}$.

Fibre spinning was carried out on a small-scale spinning rig supplied by Bradford University Research Ltd. A schematic diagram of the spinning rig is shown in Fig. 2 from which it is seen that the polymer is forced onto a heater block. As the polymer softens it is forced through the heater block

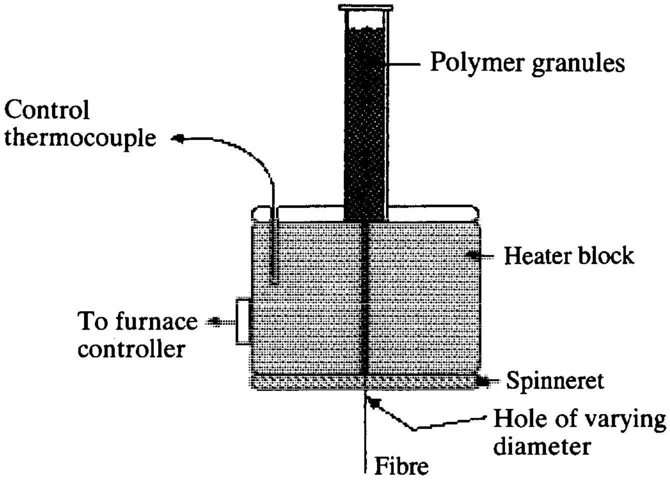


Fig. 2. Fibre spinning rig.

and then through a spinneret. The diameter and number of the spinneret holes can be altered but typically one hold of 250 μm is used.

## RESULTS AND DISCUSSION

### *Determination of spinning temperature by use of thermomechanical analysis (TMA)*

Once the co-polymer has been prepared, it is necessary to assess the suitability of the product as a precursor for a ceramic fibre. It is obviously important that it is possible to process the precursor material into a fibre and therefore it is necessary to determine a temperature at which to attempt to spin the polymer. Previously a conventional melting point apparatus had been used but this is a rather subjective test, usually only giving an approximate range of temperature over which softening occurs. In an attempt to define a spinning temperature more clearly, thermomechanical analysis (TMA) was carried out to determine the softening behaviour of the sample [9]. Initially a TMA run was carried out on polypropylene, as considerable experience of spinning has been gained using this material. A "melt flow index" of 230°C is quoted for this material and this has proved to be a suitable temperature for spinning. The TMA curve obtained for polypropylene (Fig. 3) shows that softening first starts to occur at ≈160°C and that softening is complete at 230°C, i.e. at the previously established spinning temperature.

TMA runs were also carried out on other conventional polymers, i.e. polystyrene and nylon 66 as shown in Fig. 3. By comparison with the polypropylene data, spinning temperatures of 275 and 265°C were chosen for the polystyrene and nylon 66, respectively. However, in practice, temper-

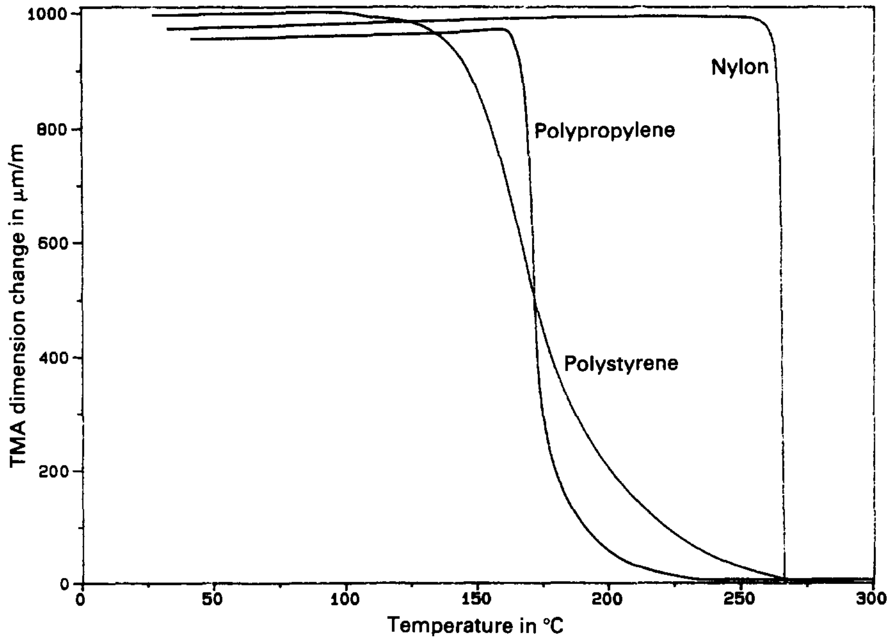


Fig. 3. TMA data for various polymers.

atures of 280 and 285°C are actually required to allow the polymers to be spun. Further work showed that the difference in these temperatures, especially for the nylon where a very specific melting temperature had to be exceeded by ≈20°C, could be explained by measuring the actual temperature of the heater block. This has been the subject of a thorough investigation [9] which showed that there is a temperature difference across the block, e.g. at a set temperature of 300°C, the top of the block is only at 271°C. Therefore, under certain conditions, the temperature at which spinning is attempted, as determined by TMA, must be increased by an appropriate amount. If the temperature range over which softening occurs is wide then this effect is less important, as a difference of a few degrees between the set and the actual temperature has less effect on the state of the polymer, because it is still virtually molten despite the lower temperature. For example, polypropylene softens over a 65°C range with the greatest change in the first 10°C, polystyrene over a range of about 150°C but the change is very gradual, whereas nylon melts at a very specific temperature.

The TMA data obtained from the various soluble and insoluble polysilanes investigated in this study are shown in Fig. 4. There are two distinct sets of behaviour illustrated in this plot. The first applies to the soluble solid obtained from reactions 1, 6 and 11 (R1 S, R6 S and R11 S respectively) when the polymer is seen to soften completely, as would be expected. Complete softening of R11 S occurs at a much higher temperature than the two other soluble polymers and this plot also shows three different stages.

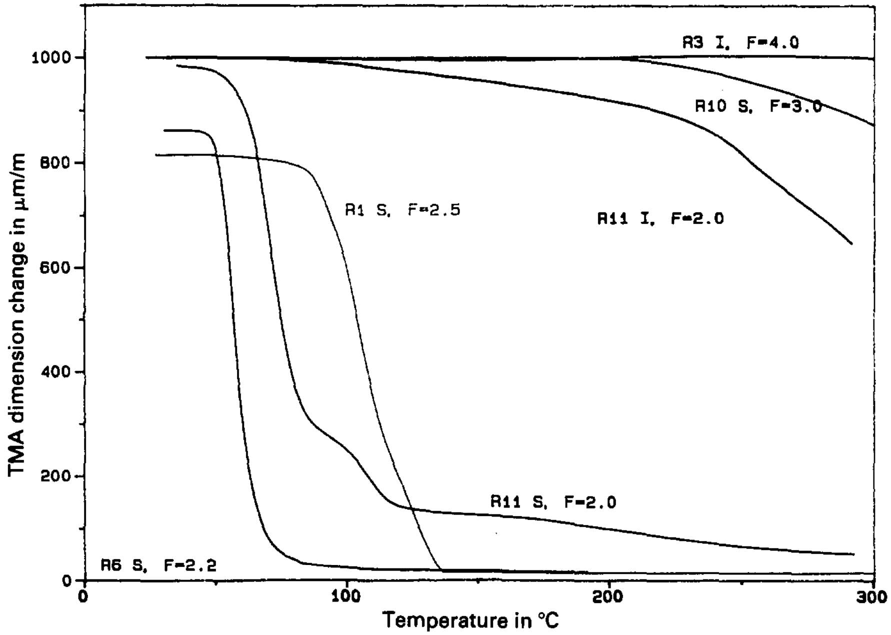


Fig. 4. TMA data for polysilanes of different *F* values.

These data can be compared with that of the insoluble solid fraction obtained from the same synthesis, i.e. R11 I. The other soluble solid polymer included in this study (R10 S) is different in that it only partially softens and in fact shows a plot similar to the insoluble solid fractions from reactions R3 and R11. This observatioin seemed unusual until further investigation showed that, although polymer R10 S was soluble at some stages of preparation, after the final precipitation procedure it was no longer soluble in common solvents. Again the plot for R11 appears to show more than one stage of softening.

These data show which polymers are suitable for spinning into polymer fibres, because a sample which will soften is required. In this case, the soluble solid fractions obtained from R1, R6, and R11 all appear suitable for spinning and using the example of the "conventional" polymers discussed previously, spinning temperatures of 135, 105 and 300°C were chosen.

From R1 S, at 135°C, several metres of fibre were readily spun but this was somewhat brittle and although collected onto a reel, it was difficult to unravel. Subsequent work carried out on these fibres indicated that after curing and pyrolysis a black material, bearing some of the original fibre texture, was obtained.

The spinning of R6 S at 105°C was not so successful: a fibre was produced but was very different to fibres previously produced from polysilanes. As the fibre emerged it was very viscous and much fatter than normal, i.e. it was swelling. There was a tendency for the fibre to fold back on itself and the heater rather than fall with gravity although it could be pulled straight. After cooling, the resultant fibre was very stiff and very brittle. Raising the temperature at which spinning was carried out did not alter the nature of the fibre, indicating that the use of the TMA data had allowed the selection of the optimum temperature.

### *Use of derivative thermomechanical analysis*

As has already been mentioned, there is a difference between the shapes of the plots for R11 when compared to the other results, because there appears to be more than one stage of softening. Careful examination of the other plots also reveals a discontinuity and this effect can be made much more obvious by plotting the derivative dimensional change against temperature. Because DTMA might be construed to mean dynamic thermomechanical analysis, which is a quite distinct technique, the abbreviation dTMA is used below to indicate the derivative thermomechanical analysis curve. Figure 5 compares the dTMA and the TMA plots of copolymers R1 S and R11 S and shows that the different effects are more clearly illustrated. It is also of interest to compare this plot with the molecular weight distributions of the two polymers as obtained by gel permeation chromatography (GPC) (Fig. 6). R11 shows two distinct groups of molecular weight distribution, has a higher overall molecular weight and a wider range of molecular weight, when compared to R1. This is reflected in the TMA and dTMA plots where the former shows various stages of softening and completely softens at a higher temperature, i.e. there appears to be some correlation between the appearance of thermal analysis plots and the GPC data. This point is further illustrated in Fig. 7 which compares the dTMA and GPC data for samples R1SS-B and R1SS-E. These two samples were obtained by dissolving R1 S in THF and reprecipitating into propan-2-ol and water respectively. There is a clear difference in the resulting dTMA plots and the GPC data, and a pronounced similarity in the shape of the two sets of data.

The different stages in the softening behaviour of the polysilanes would therefore appear to be due to the different molecular weight species of the polymer softening in different temperature ranges.

### *Determination of ceramic yield*

As already described, a potential precursor must have a sufficiently high ceramic yield to maintain a continuous fibre on pyrolysis; a minimum value of 40% [4] is generally quoted. As has been illustrated elsewhere [9], polysilane and polycarbosilane precursors prepared by different synthesis

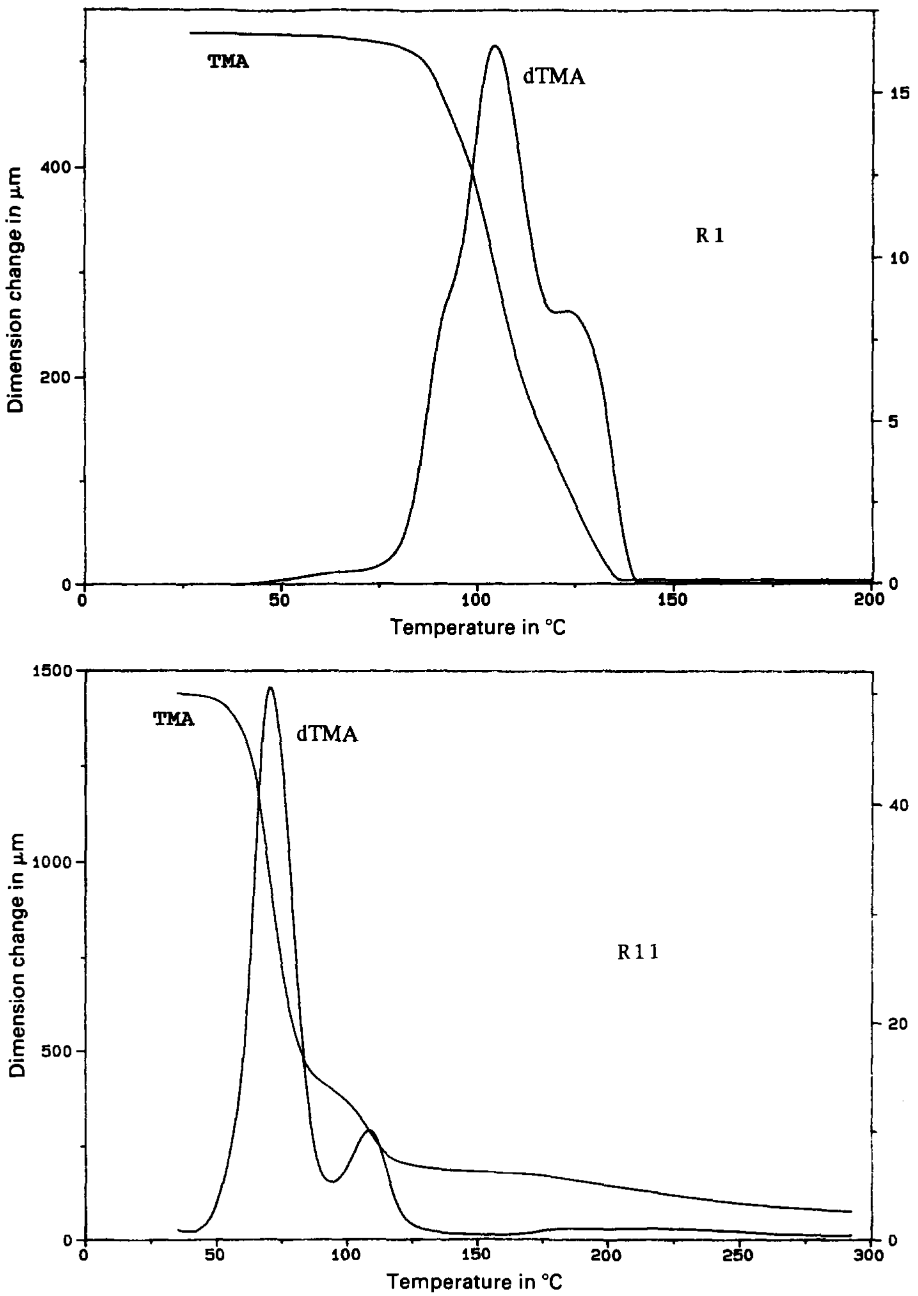


Fig. 5. TMA and dTMA data for polysilanes R1 and R11.

methods can exhibit very different ceramic yields on pyrolysis. In this paper, the effect of varying $F$ on polysilanes prepared only by the dechlorination reaction has been studied and some thermogravimetric analyses obtained from the various polysilanes are shown in Fig. 8.

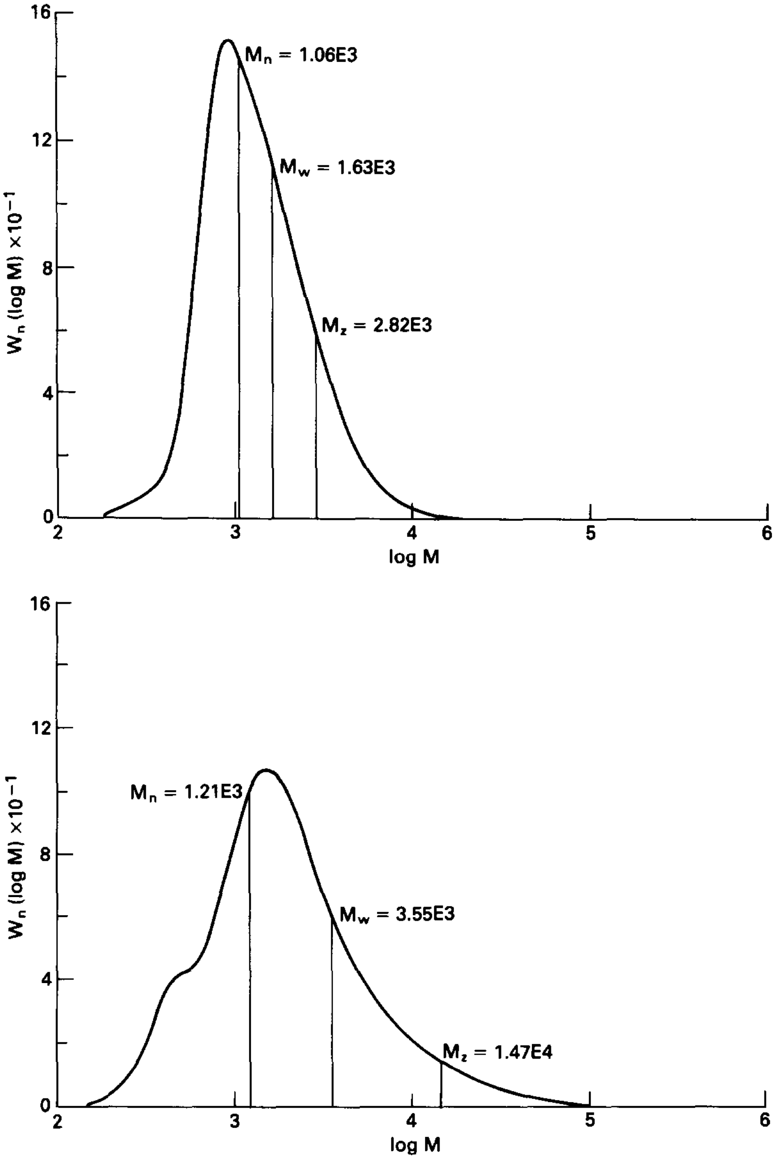


Fig. 6. Molecular weight distributions for R1 and R11.

Figure 8a shows the data obtained for the soluble products obtained. As expected, the reaction where $F = 2.0$ gave the poorest yield upon pyrolysis and that where $F = 3.0$ showed the highest yield. When $F = 2.2$ or 2.5, the data are very similar and show an intermediate ceramic yield. This plot therefore illustrates the effect of increasing $F$ upon the expected ceramic yield of a potential precursor material, i.e. the higher values of $F$ give a much improved ceramic yield.

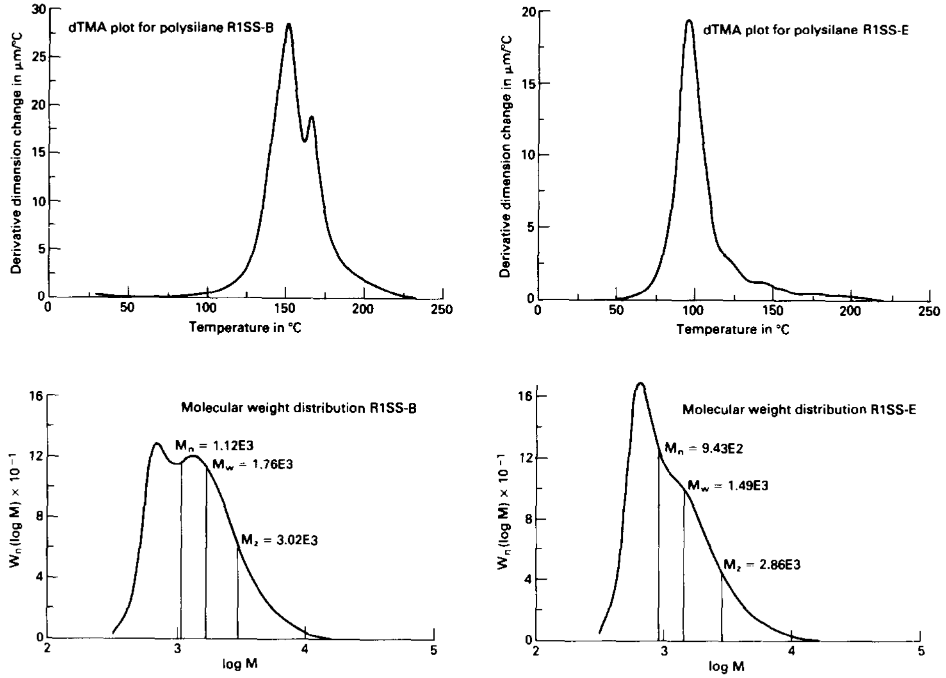


Fig. 7. Comparison of molecular weight distributions and dTMA data for R1SS-B and R1SS-E.

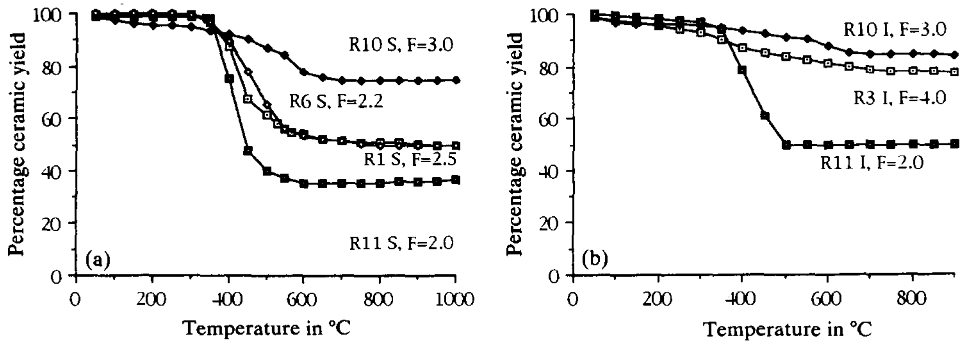


Fig. 8. a. TG data for soluble polysilanes. b. TG data for insoluble polysilanes.

Figure 8b illustrates the ceramic yields obtained for the insoluble solid products. The reaction R11, where $F = 2.0$, shows a yield significantly lower than that when $F = 3.0$ or 4.0. The yields for the latter two $F$ values are about 80% at 900°C, i.e. very high, as expected.

There are two reactions where the TG data for soluble and insoluble solid can be compared. These are R11 where $F = 2.0$ and R10 where $F = 3.0$. For the former, the ceramic yield obtained for the soluble solid at 900°C was

36% and for the insoluble solid it was 50%, i.e. the insoluble solid gave a higher ceramic yield than the soluble solid, as predicted. However, the yield from the insoluble solid is only of the same order as the soluble fractions of R6 and R1 (Figs. 8a and 8b), where the *F* value is higher. A lower value for a reaction where $F = 2.0$ might be expected and it has also been shown [10] that the insoluble solid formed in this instance was actually a crystalline product based on volatile $(SiMe_2)_n$ cyclics which are readily lost during heating.

For reaction R10, ceramic yields of 75% and 84% were obtained from the soluble and insoluble solids, respectively. These are particularly high compared with literature data, especially that obtained from the soluble solid. As discussed previously, the soluble fraction of R10 did actually become insoluble after the final treatment but a higher ceramic yield was still obtained from the sample which was truly insoluble at all stages.

## CONCLUSIONS

This study shows that thermomechanical analysis and its derivative can be used to obtain a temperature at which to spin a polysilane into a fibre. The shape of the curve is also important in the determination of this temperature. A sharp melting point means that more account must be taken of any temperature gradient across the spinning rig apparatus than if a more gradual softening is observed.

The use of thermogravimetric analysis allows the potential ceramic yield of a precursor to be assessed. In general, the higher the *F* value of the initial reaction, the better the ceramic yield of the potential precursor will be. As would be expected, the insoluble solid fractions show a better yield than the soluble products.

The comparison of the TMA and TG data shows one of the problems in determining a suitable precursor reaction. To obtain a product which will soften to allow spinning, a low *F* value is required, while a good ceramic yield is favoured by a high *F* value and the use of insoluble (and therefore infusible) material. It is also seen that the softening behaviour of the polysilane does not relate to the TG data: R11 S started to soften at a temperature between that of R1 and R6 and finished at a significantly higher value, although this sample had the poorest ceramic yield due to the use of a low *F* value.

## ACKNOWLEDGEMENTS

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