

# Synthesis of silicon oxynitride from a polymeric precursor

## Part I *Hydrolysis of dichloromethylsilane*

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Previous studies suggest that silicon oxynitride can be synthesized by pyrolysing polymers which are produced by the copolymerization of cyclic polysiloxanes and cyclic polysilazanes. The cyclic polysiloxanes required are  $[\text{CH}_3\text{Si}(\text{H})\text{O}]_m$  with  $m = 4, 5$  and  $6$ , and these can be produced by the hydrolysis of dichloromethylsilane. In the present work, a significantly improved combined yield of these cyclic polysiloxanes is reported. Three main reasons are attributed to this achievement: an improved hydrolysis procedure; optimization of the initial acidity of the reaction medium; and changes in the total reaction time. Thus a mixture containing  $> 95$  mol% cyclic tetramer, pentamer and hexamer has been prepared and this represents a  $\sim 20$  mol% improvement over previously reported results. Investigations of the preparation and characterization of the cyclic polysilazanes, copolymers and silicon oxynitride will be described in Parts II–IV, respectively.

### 1. Introduction

Silicon oxynitride is a ceramic material with very attractive properties. Its thermal and mechanical properties are similar to those of silicon nitride [1–3] whilst its oxidation resistance is superior to that of silicon nitride [1]. This combination of properties make it an ideal candidate for ceramic engine components such as nozzles and turbine blades. Further, the high resistance of silicon oxynitride to damage and major dimensional changes during fast-neutron irradiation makes it a desirable material for nuclear engineering applications [4]. It is also very useful as a protective thermal barrier coating for porous refractories [5]. These excellent properties have not been fully exploited because of difficulties in the synthesis of silicon oxynitride. Conventional methods for the preparation of silicon oxynitride involve a well-established high-temperature nitridation reaction between silicon and silicon dioxide, with metal oxides acting as catalysts [6]. However, the product usually contains silicon nitride and unreacted silicon dioxide which have a detrimental effect on the properties of the ceramic.

It has been shown that high-purity silicon oxynitride can be produced by the pyrolysis of a polymeric precursor synthesized from dichloromethylsilane [7]. Separate hydrolysis and ammonolysis of dichloromethylsilane produces cyclic polysiloxanes and cyclic polysilazanes, respectively. Copolymerization of the siloxanes and silazanes gives a product which can be pyrolysed to silicon oxynitride. However, a key feature of this process is the hydrolysis

reaction where the combined yield of cyclo-polysiloxanes,  $[\text{CH}_3\text{Si}(\text{H})\text{O}]_m$  with  $m = 4, 5$  and  $6$ , has to be maximized in order to produce a suitable copolymer which on pyrolysis gives a high yield of silicon oxynitride [7].

Hydrolysis of diorganodichlorosilanes has been extensively investigated and several reviews on this subject are available (e.g. [8–10]). It is well established that the hydrolysis products contain a mixture of both linear and cyclic polysiloxanes with a wide distribution of molecular size [11–14]. However, this distribution depends on the method of hydrolysis [8] and the acidity of the reaction medium [10, 15]. The hydrolysis of dichloromethylsilane has been investigated to a lesser extent (e.g. [16, 17]) but similar factors might be expected to influence significantly the distribution of the products. Recently, Seyferth *et al.* have compared the reactivities of dichlorosilane, dichloromethylsilane and dichlorodimethylsilane under similar reaction conditions [18]. The reactivity of dichloromethylsilane was found to be between dichlorosilane and dichlorodimethylsilane. Dichloromethylsilane, dissolved in dichloromethane, was completely hydrolysed at room temperature by the addition of controlled amounts of water to produce a combined yield of 77 mol% cyclic tetramer, pentamer and hexamer based on the total yield of the cyclic polysiloxane produced [19].

In the present work, we have improved the hydrolysis procedure mainly by careful control of the initial acidity of the reaction medium and the total reaction time to give a combined yield of the three cyclics

required to > 95 mol% based on the total yield of the polysiloxanes produced. In Part II [20] we will report investigations on the ammonolysis of dichloromethylsilane to produce the cyclic polysilazanes required. Synthesis and characterization of various copolymers produced by reacting these polysiloxanes and polysilazanes will be described in part III [21]. The conversion of these copolymers to ceramic products and their characterization will be reported in part IV [22].

## 2. Experimental procedure

### 2.1. Starting material

Dichloromethylsilane (DMS) was obtained from Aldrich Chemicals Ltd, Poole, UK and distilled over mercury under dry nitrogen. The middle cut (at 41 °C) was collected and used in the experiments described below.

### 2.2. Hydrolysis

#### 2.2.1. Method 1

A three-necked round-bottomed flask (500 cm<sup>3</sup>) equipped with a mechanical stirrer and a water-cooled condenser, was charged with DMS and dichloromethane as the solvent. Deionized water (~ 1.1 mol per mol DMS) was slowly dropped into the stirred mixture over 2.5 h. Stirring was continued for a further period (Table I). Subsequently, the aqueous phase was removed and the organic phase was washed several times until it was neutral. The products were concentrated by distillation of the solvent through a 600 mm Vigreux column at atmospheric pressure.

#### 2.2.2. Method 2

The DMS in dichloromethane was dropped into a mixture of hydrochloric acid (60 cm<sup>3</sup>), or in experi-

ment B, only into 60 cm<sup>3</sup> water, and dichloromethane. The reaction time was varied between 2 and 20 h in separate experiments (Table II) before the aqueous and organic phases were separated. A mechanical stirrer was used in all these experiments. Other details are identical to Method 1.

### 2.3. Gas chromatography (GC)

Samples were taken from the final organic phase in order to analyse the yield of the individual cyclic oligomers formed by gas-liquid chromatography (Pye type 6 analyser system) using 5% SE30 on diatomite in a 600 mm column with the temperature programmed to change from 40 °C (or 60 °C) to 300 °C at 10 °C min<sup>-1</sup>.

### 2.4. GC/mass spectroscopy (MS)

GC/MS experiments were performed on the concentrated organic phase (after most of the solvent was removed by distillation using a vacuum line). A Perkin-Elmer Chromatograph 8700 linked to a Q-Mass 910 mass spectrometer was used. The capillary column, which contained SGE BP-20, was 25 m long. The column temperature was programmed to increase from 60 °C to 250 °C at 10 °C min<sup>-1</sup>. The injection temperature was set at 250 °C.

### 2.5. Nuclear magnetic resonance spectroscopy (NMR)

A 2%–10% solution of a sample of the concentrated organic phase in deuteriochloroform was used to obtain the <sup>1</sup>H NMR spectra on a Jeol FX200 spectrometer. Tetramethylsilane was used as an internal standard.

### 2.6. Fourier transform infrared spectroscopy (FTIR)

A Nicolet 710 FTIR spectrometer was used. A sample was dropped on to a potassium bromide plate and left in air for about 1 min to evaporate the solvent before a second potassium bromide plate was placed on it. Subsequently, the sample was placed in the spectrometer and scanned in the wave number range 4000–400 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>.

TABLE I Details of Experiment A conducted using the hydrolysis Method 1. In the case of reaction time, *x* denotes the time taken for the initial addition of water into the stirred system, whilst *y* is the time the mixture was stirred after the addition was complete

DMS (g)	40.3
Dichloromethane (cm <sup>3</sup> )	250
Water (g)	7.0
Reaction time, <i>x</i> + <i>y</i> (h)	2.5 + 2.5

TABLE II Details of experiments conducted using the hydrolysis Method 2. In the case of the volume of dichloromethane used, *V*<sub>1</sub> is the volume of dichloromethane mixed initially with DMS. The mixture was dripped from a funnel under nitrogen into the reaction system which contained a mixture of *V*<sub>2</sub> cm<sup>3</sup> dichloromethane and hydrochloric acid (or water). In the case of reaction time, *x* denotes the time taken for the initial addition of dichloromethylsilane into the stirred system, whilst *y* is the time the mixture was stirred after the addition was complete

	Experiment									
	B	C	D	E	F	G	H	I	J	
DMS (g)	35.9	32.2	34.3	25.7	30.9	35.7	35.7	34.8	33.0	
Dichloromethane, <i>V</i> <sub>1</sub> + <i>V</i> <sub>2</sub> (cm <sup>3</sup> )	200 + 50	200 + 50	200 + 50	200 + 50	200 + 50	200 + 50	200 + 500	200 + 50	200 + 50	
Initial molar concentration of HCl	–	0.1	1	3	3	3	3	5	5	
Reaction time, <i>x</i> + <i>y</i> (h)	4 + 1	4 + 1	1.7 + 2	1.5 + 1.3	1.3 + 3	1.8 + 2	1.8 + 15	5 + 1	1 + 1	

### 3. Results and discussion

#### 3.1. Products

GC, GC/MS, NMR and FTIR characterization showed that the products of each experiment were cyclic polysiloxanes. Fig. 1 shows the GC trace of a typical product before dichloromethane was removed. It shows that the major components present are the cyclic tetramer, pentamer and hexamer. The  $^1\text{H}$  NMR spectrum of this product (Fig. 2) shows  $^1\text{H}$  resonances from Si-H ( $\delta = 4.7$  p.p.m.) and Si-CH<sub>3</sub> ( $\delta = 0.21$  p.p.m.) with a ratio of 1:3. Resonances from the end group -HSi(CH<sub>3</sub>)OH were not observed. Therefore, the NMR results show that the product contains cyclics. GC/MS analysis confirmed that cyclic polysiloxanes were present in the product.

The FTIR spectrum (Fig. 3) of the same product referred to above shows the typical characteristics of a mixture of cyclic polysiloxanes described in the literature (e.g. [23–25]). The stretching vibration of C-H in -CH<sub>3</sub> occurs at about 2968 cm<sup>-1</sup>. The absorptions at 2100–2200 and 768 cm<sup>-1</sup> are due to stretching and bending of the Si-H bond, respectively. The peaks in the spectrum at about 1400 and 1260 cm<sup>-1</sup> involve the -CH<sub>3</sub> group with the former representing -CH<sub>3</sub> deformation vibration. Strong absorption in the region 1000–1200 cm<sup>-1</sup> refers to the Si-O-Si asymmetric stretch vibration. Vibration of Si-C bonds results in the strong absorption at 874 cm<sup>-1</sup>.

The area under each peak in the GC traces was used to calculate the weight percentages of the cyclics produced. In these calculations it was assumed that each cyclic oligomer has a similar detector response factor. The weight percentages were converted to the mole percentages and are reported in Table III.

#### 3.2. Hydrolysis reaction

The hydrolysis of DMS is a two-phase reaction. DMS molecules react with water at the interface between water and the solvent. The hydroxy compounds produced then condense to form cyclic compounds according to the overall reaction

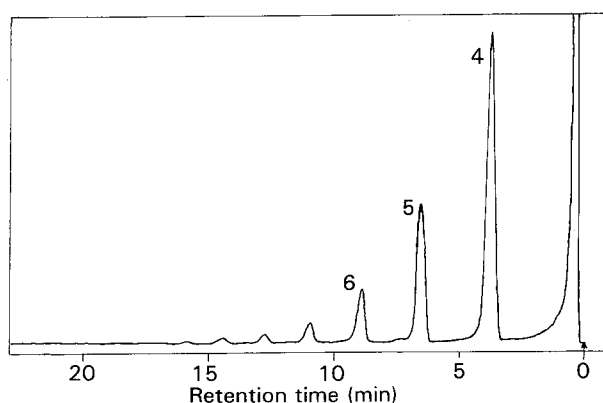
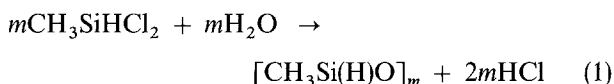


Figure 1 GC trace of the product of Experiment E before removal of dichloromethane. 4, 5 and 6 denote the peaks of the cyclic tetramer, pentamer and hexamer, respectively.

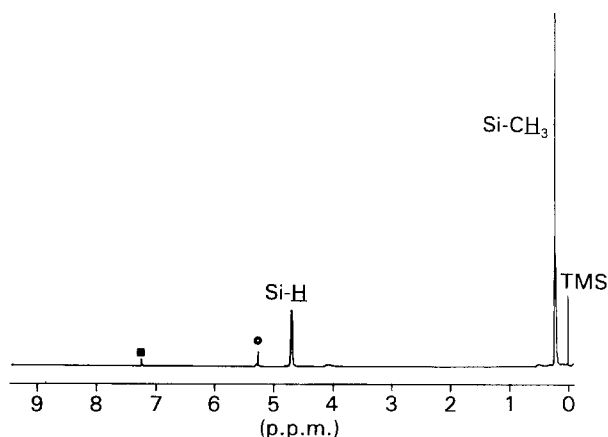


Figure 2  $^1\text{H}$  NMR spectrum of the product of Experiment E after removal of dichloromethane. TMS refers to the peak shown by tetramethylsilane. (■) Residual  $\text{CHCl}_3$ , (○) residual  $\text{CH}_2\text{Cl}_2$ .

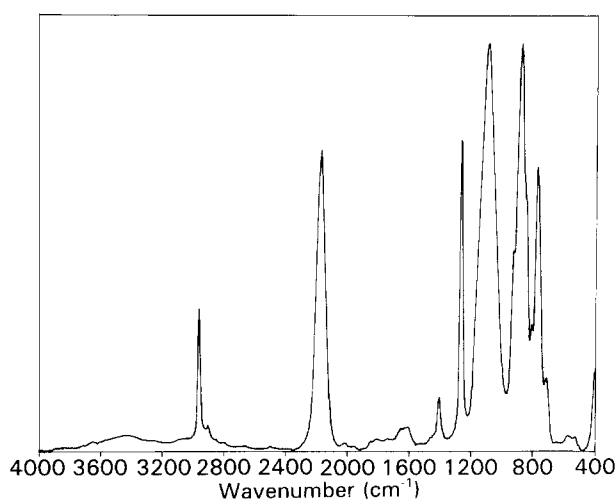


Figure 3 FTIR spectrum of the product of Experiment E after removal of dichloromethane.

The combined yield of cyclic tetramer, pentamer and hexamer obtained by the hydrolysis Method 1 (Experiment A, Table III) is about 12 mol% greater than that obtained by Seyferth *et al.* [18, 19]. Furthermore, the total reaction time was also reduced from 24 h to 5 h. The major reason for this is the method of stirring used. Seyferth *et al.* [18] used magnetic stirring. Mechanical stirring used in the present work helps to create a larger interface for reactions and so allows a higher yield in a shorter total reaction time.

The concentration of acid in the aqueous phase increases very rapidly as the addition of DMS occurs. It is noteworthy that, compared with our results of hydrolysis Method 1 (Experiment A, Table III), a wider distribution of cyclic oligomers was produced by Seyferth *et al.* [18, 19]. This is possibly caused by prolonged exposure of the products to the concentrated hydrochloric acid. Assuming all the HCl is in the aqueous phase, it can be shown that the final concentration of HCl may be > 50 M. Therefore, ring opening polymerization could occur according to the cationic mechanism to give linear polymers or large cyclics [10].

TABLE III Composition (mol%) of cyclo-[CH<sub>3</sub>Si(H)O]<sub>m</sub> formed from hydrolysis of DMS

m	Experiment									
	A	B	C	D	E	F	G	H	I	J
3	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	6.2	4.9
4	42.9	53.5	54.0	68.0	68.9	67.4	68.4	60.9	46.4	55.7
5	30.7	28.6	30.9	21.7	21.2	23.2	23.2	23.4	25.7	24.0
6	15.3	11.0	9.9	6.6	6.6	6.8	7.0	8.5	12.1	10.7
7	6.4	3.5	4.0	2.2	2.1	2.0	1.5	4.8	4.6	2.9
8	2.5	1.5	0.8	0.8	0.7	0.5	Trace	1.2	1.9	1.1
9	1.3	0.9	0.4	0.3	0.3	0.1		0.6	1.2	0.5
10	0.7	0.6	Trace	0.1	0.1	Trace		0.3	0.7	0.1
11	0.3	0.5		Trace	Trace			0.2	0.6	Trace
12	0.1	Trace						Trace	0.4	
13	Trace								0.2	
14									Trace	
15										
16										
17										
18										
Combined yield of 4, 5 and 6	88.9	93.1	94.8	96.3	96.7	97.4	98.6	92.8	84.2	90.4

The combined yield of the cyclic tetramer, pentamer and the hexamer was further increased to ~93 mol% by using a larger volume of aqueous phase in the second hydrolysis method (compare Table I and Experiment B, Table II). The use of excess of water dilutes the HCl formed and the yield of small cyclics such as the tetramer is appreciably increased.

### 3.3. HCl concentration and reaction time

Results shown in Table III (Experiments C–J) clearly indicate that the combined yield of the cyclic polysiloxanes required depends on the contact of the hydrolysis products with hydrochloric acid. Contact can be minimized by controlling the initial concentration of hydrochloric acid and the total reaction time.

An initial hydrochloric acid concentration of 0.1–3M HCl and a total reaction time of up to 5 h (Table II) gave a very high combined yield (~95–99 mol%) of the cyclic tetramer, pentamer and hexamer (Experiments C–G, Table III). A significant reduction in this yield, (to ~84 mol%), is shown when the initial HCl concentration changed to 5 M (Experiment I, Table III). However, at an initial HCl concentration of 5 M, reduction of the total reaction time from 6 h to 2 h allowed some recovery in the combined yield of the cyclics required (Experiment J, Table III). Also in both of these experiments, with an initial HCl concentration of 5 M, an appreciable amount of the cyclic trimer was produced. The effect of total reaction time is again clearly shown in the experiments where the optimum initial HCl concentration of 3 M was used. A four-fold increase in total reaction time reduced the combined yield of the required oligomers from 98.6 mol% to 92.8 mol% (comparing experiments G and H, Table III) with a wider distribution of products. These results show that although the concentration of acid is of primary importance in maximizing the combined yield of the cyclic

oligomers required, it can be further improved by careful control of the total reaction time.

In each of these experiments, the total yield of polysiloxanes obtained was > 90% of the theoretical value predicted by Equation 1. For example, in Experiment B, 20 g product with a small amount of dichloromethane was obtained from 32.3 g DMS.

## 4. Conclusions

The hydrolysis of DMS, which is a key reaction in the preparation of a polymeric precursor suitable for conversion to the ceramic silicon oxynitride, has been optimized to increase the combined yield of the required cyclic polysiloxanes to > 95 mol%. This has been achieved by modifying the hydrolysis procedure and optimizing the initial acidity of the reaction system and the total reaction time.

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