Transition Metal Catalysed Synthesis of Oligo- and Polysilazanes

THEIR USE AS PRECURSORS TO SILICON NITRIDE CONTAINING CERAMIC MATERIALS

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Organometallic polymer research offers many potential academic and industrial rewards because of the number of elemental variations possible. Unfortunately, there are no general synthetic methods as found for carbon based polymers. Transition metal catalysed dehydrocoupling reactions may prove to be generally applicable to the synthesis of silicon based organometallic polymers. We report here our efforts to synthesise organometallic polymers with a silicon-nitrogen backbone, polysilazanes, using the dehydrocoupling reaction. We also describe the synthesis of polysilazanes for use as precursors to silicon nitride.

The design and synthesis of organometallic polymers is currently receiving considerable attention because of their potential utility in a wide variety of applications ranging from precursors to ceramic materials—for example for high T_c superconductors—to substrates for pharmaceutically active materials (1). Despite the fact that general methods exist for the synthesis of an extensive variety of carbon based polymers, no simple, general synthetic methods exist for the preparation of organometallic polymers, except for polysiloxanes and polyphosphazenes. Moreover, in contrast to the industrially important carbon based polymerisation methods, where transition metal catalysis plays a major role, transition metal catalysed syntheses of organometallic polymers are limited to the production of several specific types of polysiloxane polymers.

Given the exceptional number of elements available for the synthesis of organometallic polymers, it seems likely that many more industrially useful organometallic polymers will be developed in the forthcoming years. The question is, "Can transition metal catalysis play a role in the development of general routes to organometallic polymers?" It is the intention of this paper to illustrate a potentially general method of synthesis, transition metal catalysed dehydrocoupling, and show how it can be applied to the development of organometallic polymers, polysilazanes, that are precursors to silicon nitride containing ceramics.

Polymer syntheses based on catalytic processes are attractive because they can provide thermodynamic advantages, greater control of product stereoregularity and, especially, improved control of product selectivity/purity over non-catalytic processes. It is assumed that catalyst removal is facile or not necessary, the impurity level resulting from the presence of catalyst being extremely low. Unfortunately, catalytic approaches to the synthesis of organometallic polymers require the development of bond forming reactions that are not likely to have analogies in organic chemistry. The general types of catalytic reactions employed in the synthesis of carbon based polymers often rely on the reactions of unsaturated molecules such as in the production

Table I
Catalytic Promotion of Silylamination of Benzaldehyde Using N-Silylaniline

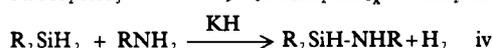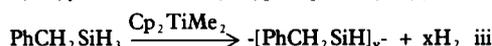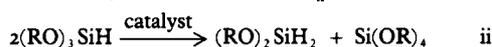| Catalyst precursor	Conversion,[a] per cent	Turnover frequency[b]
$Fe(CO)_5$	95	134
$Fe_3(CO)_{12}$	90	121
$Ru_3(CO)_{12}$	24	34
$Os_3(CO)_{12}$	4	4
$Co_2(CO)_8$	85	117
$Rh_6(CO)_{16}$	87	120
$(Ph_3P)_4Pd$	5	6

(a) Mole per cent of products formed
(b) Turnover frequency = moles product/moles catalyst precursor/hour

of polyethylene and polypropylene. Unsaturation in organometallic molecules is relatively rare and cannot be expected to provide access to general catalytic methods for the synthesis of organometallic polymers.
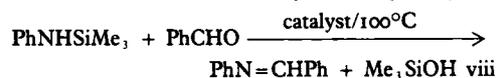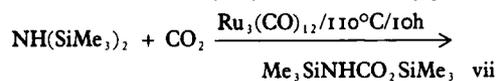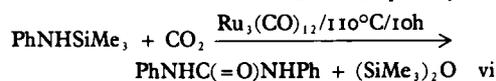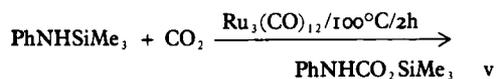
General synthesis methods must take into account the fact that organometallic polymers are often air and moisture sensitive. Thus, purification and characterisation in the presence of co-products are extremely difficult. One approach that appears to be general in nature and which should resolve the co-product problem requires that the bond forming reactions which occur during polymerisation lead to the loss of small, innocuous gaseous molecules.

Several catalytic reactions of this genre have proved to be useful in the synthesis of organometallic polymers, as illustrated below. The types of reactions include condensation [Reaction i](2), redistribution [Reaction ii](3), and dehydrocoupling reactions, [Reactions iii and iv](4,5).

$$xM(HNR)_2 \xrightarrow{\text{catalyst}} \text{-[N(R)-M]}_x\text{-} + xRNH_2 \quad \text{i}$$

$$2(RO)_3SiH \xrightarrow{\text{catalyst}} (RO)_2SiH_2 + Si(OR)_4 \quad \text{ii}$$

$$PhCH_2SiH_3 \xrightarrow{Cp_2TiMe_2} \text{-[PhCH}_2SiH]_x\text{-} + xH_2 \quad \text{iii}$$

$$R_2SiH_2 + RNH_2 \xrightarrow{KH} R_2SiH\text{-}NHR + H_2 \quad \text{iv}$$

Our own work in this area has been directed towards the synthesis of polysilazane, $\text{-[R}_2SiNR']_x\text{-}$ ($R = R' = H$, alkyl, aryl, etc), precursors to silicon nitride and silicon carbonitride using dehydrocoupling reactions. We became interested in the possibility of using transition metal catalysed reactions to prepare polysilazanes based on our discovery (6) that transition metals will promote the activation of the silicon-nitrogen bond, as illustrated by Reactions v to viii:

$$PhNHSiMe_3 + CO_2 \xrightarrow{Ru_3(CO)_{12}/100°C/2h} PhNHCO_2SiMe_3 \quad \text{v}$$

$$PhNHSiMe_3 + CO_2 \xrightarrow{Ru_3(CO)_{12}/110°C/10h} PhNHC(=O)NHPh + (SiMe_3)_2O \quad \text{vi}$$

$$NH(SiMe_3)_2 + CO_2 \xrightarrow{Ru_3(CO)_{12}/110°C/10h} Me_3SiNHCO_2SiMe_3 \quad \text{vii}$$

$$PhNHSiMe_3 + PhCHO \xrightarrow{\text{catalyst}/100°C} PhN=CHPh + Me_3SiOH \quad \text{viii}$$

Reaction viii was used to survey a group of transition metal catalyst precursors to identify the most active catalyst systems. This survey is shown in Table I. Surprisingly, the $Fe(CO)_5$ catalyst proved to be the most effective of all the catalyst precursors examined.

However, as is shown below, the silylamination catalyst studies do not correlate with a similar survey designed to identify the most active catalysts for activation of the silicon-nitrogen bond during the production of oligosilazanes.

Given that we could promote the catalytic activation of Si-N bonds as exemplified by Reactions v to viii and Table I, the thought occurred to us that it might be possible to catalyse the formation of polysilazanes using a ring opening polymerisation reaction of the type shown in Reaction ix (7):

$$[Me_2SiNH]_4 + (Me_3Si)_2NH \xrightarrow{\text{catalyst}}$$
$$Me_3SiNH\text{-}[Me_2SiNH]_x\text{-}SiMe_3 \ + [Me_2SiNH]_y$$
$$y = 3\text{-}8 \qquad \text{ix}$$
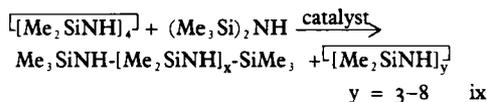
The basic idea in Reaction ix is to catalytically cleave a Si-N bond in the cyclotetramer, $[Me_2SiNH]_4$, and couple this ring-opened species with an already existing linear chain or with another ring-opened species. To prevent ring closure, $(Me_3Si)_2NH$ is added to cap one end of the Si-N bond, while permitting chain extension to occur at the other end. In principle the relative ratio of the chain capping agent to the cyclotetramer will control the ultimate chain length of the resultant polysilazane.

In two sets of experiments, with $Ru_3(CO)_{12}$ as catalyst, the molar ratio of capping agent to cyclotetramer was first set at 2.5 : 1 and then at 1 : 2.5. In the first experiment, an envelope of oligomers was observed with x = 1 to 6 together with cyclomeric species containing from 3 to 6 silazane units ($Me_2Si\text{-}NH$). The second experiment provided an envelope of oligomers with x = 1 to 12 and the corresponding cyclomers. Further decreases in the relative amount of capping agent lead to increased production of the various other cyclomers rather than to higher molecular weight oligomers.

The flaw with the ring-opening polymerisation reaction is that the same catalyst species that promotes ring-opening via Si-N bond cleavage will also catalyse Si-N bond cleavage in the linear oligomers, to reform cyclomers and capping agent. However, a catalyst survey carried out to identify the most active catalyst for Reaction ix provided an escape from this dead-end.

As illustrated in Table II, a variety of catalyst precursors were found to promote Reaction ix. The most important finding of this study was

the fact that small amounts of hydrogen greatly improve the rate of oligomerisation and lower the reaction temperature required to obtain effective catalysis. Moreover, the use of metal hydride containing precursors eliminates the need for hydrogen, which indicates that metal hydrides are the true active catalysts (7).

If metal hydrides are required to promote Si-N bond cleavage, we can suggest a mechanism for cleavage that involves partial or total hydrogenation of the Si-N bond:

$$MH_2 + R_ySi\text{-}NR'_x \longrightarrow R_ySi\text{-}MH + NHR'_x$$
$$\longrightarrow M + R_ySiH + NHR'_x \qquad x$$
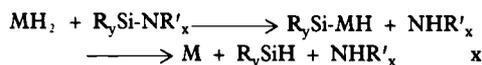
We can then suggest that the reverse reaction, Si-N bond formation, must occur by the reaction of the amine N-H bond with the $R_ySi\text{-}MH$ species:

$$R_ySi\text{-}MH + NHR'_x \longrightarrow MH_2 + R_ySi\text{-}NR'_x \quad xi$$
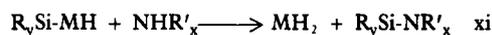
If reaction xi is indeed responsible for the formation of Si-N bonds, and given that species similar to $R_ySi\text{-}MH$ are proposed to be intermediates in hydrosilylation, Reaction xii,

$$R_xSiH + M \longrightarrow R_xSi\text{-}MH + R'CH=CH_2$$
$$\longrightarrow M + R'CH_2CH_2SiR_x \qquad xii$$
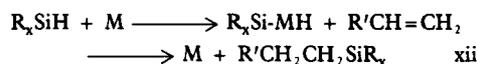
then it should be possible to test the validity of Reaction xi by direct reaction of a silane, for example Et_2SiH_2, with ammonia. As shown in Reaction xiii, it is possible to form oligosilazanes in this manner.

$$Et_2SiH_2 + NH_3 \xrightarrow{Ru_3(CO)_{12}/60°C/THF}$$
$$H_2 + [Et_2SiNH]_y + H\text{-}[Et_2SiNH]_x\text{-}H \quad xiii$$
$$y = 3\text{-}5 \qquad x = 3\text{-}5$$
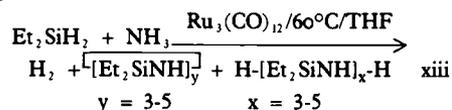
More important is the fact that in Reaction xiii, Si-N bonds are formed under conditions (60°C) where Si-N bond cleavage does not occur. Thus, Si-N bond breaking reactions should not interfere with the formation of higher molecular weight polysilazanes. Furthermore, the by-product, hydrogen, will not contaminate the product polysilazanes.

In practice, it has not been possible to prepare high molecular weight polysilazanes using reactions analogous to xiii for a variety of reasons (8,9). In particular, these reactions are

| Catalyst	Temperature, °C	Time, hours	Conversion of cyclotetramer,[a] per cent	Remarks
$Ru_3(CO)_{12}$	135	6	22	
$Ru_3(CO)_{12}$	180	15	80	
$Ru_3(CO)_{12}$	135	1	80	1 atm hydrogen
$H_4Ru_4(CO)_{12}$	135	1	77	
$Fe_3(CO)_{12}$	135	6	80	1 atm hydrogen catalyst decomposes
$Os_3(CO)_{12}$	180	20	80	
$Os_3(CO)_{12}$	135	6	75	1 atm hydrogen
$H_2Os_3(CO)_{10}$	135	3	78	
$Ir_4(CO)_{12}$	180	15	70	
$Ir_4(CO)_{12}$	135	3	78	1 atm hydrogen

(a) Molar ratio of cyclomer to capping agent to catalyst is 250 : 84 : 1

extremely susceptible to the steric environment about both silicon and nitrogen. We are currently modelling the dehydrocoupling reaction using Reaction xiv,

$$Et_3SiH + RNH_2 \xrightarrow{Ru_3(CO)_{12}/THF/70°C} H_2 + Et_3SiNHR \qquad xiv$$
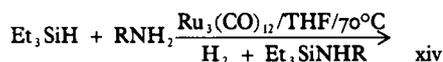
where R = n-Pr, n-Bu, s-Bu, and t-Bu (10). The kinetics and the catalytic cycle(s) for this reaction turn out to be extremely complex.

In the absence of amine, the silane reacts with the catalyst to produce $(Et_3Si)_2Ru_2(CO)_8$, Reaction xv, which can be isolated and used as the catalyst in place of $Ru_3(CO)_{12}$.

$$6Et_3SiH + 2Ru_3(CO)_{12} \xrightarrow{110°C/10 min.} 3H_2 + 3(Et_3Si)_2Ru_2(CO)_8 \qquad xv$$
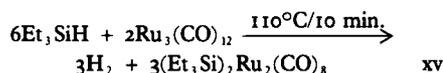
Catalyst concentration studies demonstrate that the rate of Reaction xiv is non-linearly and inversely dependent on both $[Ru_3(CO)_{12}]$ and $[(Et_3Si)_2Ru_2(CO)_8]$. On a molar basis, the $(Et_3Si)_2Ru_2(CO)_8$ catalyst is more active than the trimeric carbonyl. These results suggest that catalyst formation occurs as a result of cluster fragmentation. Indeed, the true active species may be monomeric.

With regard to the amines, we find from rate versus $[RNH_2]$ studies that the steric bulk of R controls both reaction rate and reaction mechanism. The simple primary amines n-$PrNH_2$ and n-$BuNH_2$ show an inverse, non-linear rate dependence on $[RNH_2]$, despite the fact that they are reactants; whereas, the $[s-BuNH_2]$ studies reveal a non-linear positive dependence. On moving to the most bulky amine, t-$BuNH_2$, the rate shows almost no dependence on either $[t-BuNH_2]$ or $[Et_3SiH]$.

Our previous work on the reaction of $Ru_3(CO)_{12}$ with amines provides reasonable explanations for many of the above observations. We have already shown that simple primary and secondary amines will react with $Ru_3(CO)_{12}$ to form rather stable complexes similar to the type shown in Reaction xvi (11).

$$Ru_3(CO)_{12} + EtCH_2NH_2 \longleftrightarrow (\mu^2-EtCH=NH)HRu_3(CO)_{10} \qquad xvi$$

If these species are sufficiently stable to resist fragmentation to the active catalyst species under the reaction conditions then we would expect an inverse dependence on $[n-RNH_2]$, which we observe. With s-$BuNH_2$ the steric bulk at the amine may reduce the role that a

reaction analogous to Reaction xvi plays in the global reaction rate. With t-BuNH$_2$, there is no alpha hydrogen and Reaction xvi need not be considered. However, the apparent simultaneous independence on [Et$_3$SiH] is more difficult to explain and suggests that catalyst activation becomes the slow step in the reaction mechanism. The relative global rates of reaction are qualitatively

n-PrNH$_2 \geq$ n-BuNH$_2$ > s-BuNH$_2$ $\gg$ t-BuNH$_2$

The potential product, (Et$_3$Si)$_2$NR, is never observed.

The severe steric effects observed in Reaction xiv are also observed when the dehydrocoupling reaction is used to synthesise oligosilazanes (9). For example, in Reaction xiii, we attempted to prepare linear, high molecular weight diethylpolysilazanes. The only products from this reaction are mixtures of the cyclotrimer and cyclotetramer with low molecular weight linear species (M$_n \approx$ 500 D). In contrast, the use of monosubstituted silane precursors provides access to true oligosilazanes, as illustrated by Reactions xvii and xviii:

$$PhSiH_3 + NH_3 \xrightarrow{Ru_3(CO)_{12}/60°C}$$
$$H_2 + \text{-}[PhSiHNH]_x\text{-} \qquad xvii$$
$$M_n = 800\text{-}1000 \text{ D}$$

$$n\text{-}C_6H_{13}SiH_3 + NH_3 \xrightarrow{Ru_3(CO)_{12}/60°C}$$
$$H_2 + \text{-}[n\text{-}C_6H_{13}SiHNH]_x\text{-} \qquad xviii$$
$$M_n \approx 2700 \text{ D}$$

At 60°C both oligosilazanes are essentially linear. We find no evidence for dehydrocoupling at the tertiary Si-H bond nor do we see any reaction at the internal N-H bonds. At 90°C, we observe activation of the internal Si-H bonds and crosslinking of the polysilazanes is obtained as shown for the phenylpolysilazane in Reaction xix.

$$H\text{-}[PhSiHNH]_x\text{-}H + NH_3 \xrightarrow{Ru_3(CO)_{12}/90°C} H_2 +$$
$$\begin{array}{c} NH_{0.5} \\ | \end{array}$$
$$\text{-}[PhSiHNH]_x[PhSiNH]_y\text{-}$$
$$\text{solid, } M_n = 1400D \qquad xix$$

However, we have recently found that PhSiH$_3$ will disproportionate by itself in the presence of the ruthenium catalyst, probably as in Reaction xx (12).

$$PhSiH_3 \xrightarrow{Ru_3(CO)_{12}/90°C/THF} SiH_4 + Ph_2SiH_2$$
$$xx$$

The redistribution reaction illustrated by Reaction xx represents an additional mechanism whereby crosslinking could occur in polysilazanes; although we have no evidence for its participation in Reaction xix. In contrast to PhSiH$_3$ and n-hexylSiH$_3$, EtSiH$_3$ reacts indiscriminately to give a crosslinked polysilazane that is sufficiently intractable to resist effective characterisation (11).

Preceramic Polysilazanes

Having established the basic mechanisms involved in catalytic dehydrocoupling and shown that they are useful in the synthesis of oligo- and polysilazanes, we can now consider their application to the synthesis of useful preceramic polysilazanes. To be useful, a preceramic polymer must have several properties including tractability, latent reactivity and high ceramic yield. The exact nature of the individual properties is developed in the following paragraphs.

Because the objective of using a preceramic polymer is to form a ceramic shape that is difficult or impossible to obtain by normal ceramics processing techniques, a preceramic polymer must be tractable (soluble, meltable or malleable). Moreover, because different applications, for example coatings and fibres, will require different viscoelastic properties, some mechanism to control viscoelasticity must be available. Linear or lightly branched polymers such as produced in Reactions xviii and xix are tractable.

Once the finished preceramic shape is obtained, the shape must be rendered infusible to avoid further changes during pyrolytic transformation to ceramic product. In order to achieve this, the preceramic piece must be susceptible to some form of manipulation that does not distort its shape. It must have latent reactivity.

One common method of making a tractable polymer intractable/infusible is to crosslink it.

If crosslinking can be controlled, it also represents a method of controlling polymer viscoelasticity. For example, Reactions i–iv and xix are useful forms of crosslinking that can be used to control viscoelasticity in polysilazanes and to render them infusible. Once crosslinking is sufficient to ensure infusibility, the shaped piece can be pyrolysed.

Typical preceramic polymers will have densities that are as little as 20 per cent of the density of the ceramic product. Consequently, tremendous volume changes occur during pyrolysis. If a portion of the precursor is volatilised during pyrolysis, then the ceramic yield (on a weight per cent basis) will be diminished and the volume changes will be magnified. For example, typical polysilazanes have densities of the order of 1.1 g/cc, while that for silicon nitride (Si_3N_4) is 3.2 g/cc. A 100 per cent ceramic yield will result in a volume change—assuming a fully dense ceramic is obtained—of approximately 70 per cent. A 50 per cent ceramic yield results in a volume change of 85 per cent. Therefore, high ceramic yields are extremely desirable. More important is the fact that these volume changes limit applications for preceramics. It is almost impossible to obtain a fully dense three dimensional ceramic piece with near-net-shape using preceramic polymers. However, preceramic polymers are still quite useful for binder, coating and fibres applications where volume change is less important.

With these directives in mind, we can discuss the design and synthesis of a useful preceramic polysilazane. The tremendous importance of ceramic yield limits the types of extraneous moieties that can be added to the polymer chain to aid in tractability, enhance stability or provide latent reactivity. In polysilazane synthesis the objective is to obtain pure silicon nitride following pyrolysis; thus, -[H_2SiNH]$_x$-, -[$H_2SiNHNH$]$_x$-, -[$MeHSiNH$]$_x$-, and -[H_2SiNMe]$_x$- represent optimal silicon nitride precursors because they only need to lose hydrogen and/or methane to form silicon nitride upon pyrolysis.

Oligomers of most of these potential precur-

sors have been synthesised by ammonolysis of H_2SiCl_2 or $MeSiHCl_2$ as in Reaction xxi.

$$H_2SiCl_2 + NH_3 \xrightarrow{o°C/Et_2O} \text{-[H_2SiNH]_x- + [H_2SiNH]_y^{-}} \quad \text{xxi}$$
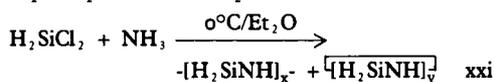
Unfortunately, these types of oligosilazanes tend to be unstable or the ammonolysis product has too low a molecular weight to be directly useful as a preceramic. For example, -[H_2SiNH]$_x$- crosslinks rapidly, even at 0°C, and therefore cannot be easily handled. By comparison, -[H_2SiNMe]$_x$-, synthesised in analogy to Reaction xxi, is stable for long periods of time in the absence of oxygen or moisture but the ceramic yield upon pyrolysis under nitrogen is only 38 to 40 per cent because of the low molecular weight (x = 10, M_n = 600 D) (5).
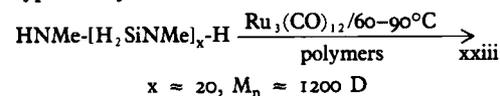
A surprising problem associated with all reported methods of synthesising polysilazanes (13) is their inability to provide products with molecular weights much greater than $M_n \approx$ 2000 D; although oxygen analogs with molecular weights of millions can be prepared readily.

In theory, the dehydrocoupling reaction could be used to make any type of polysilazane, as illustrated by Reaction xxii.
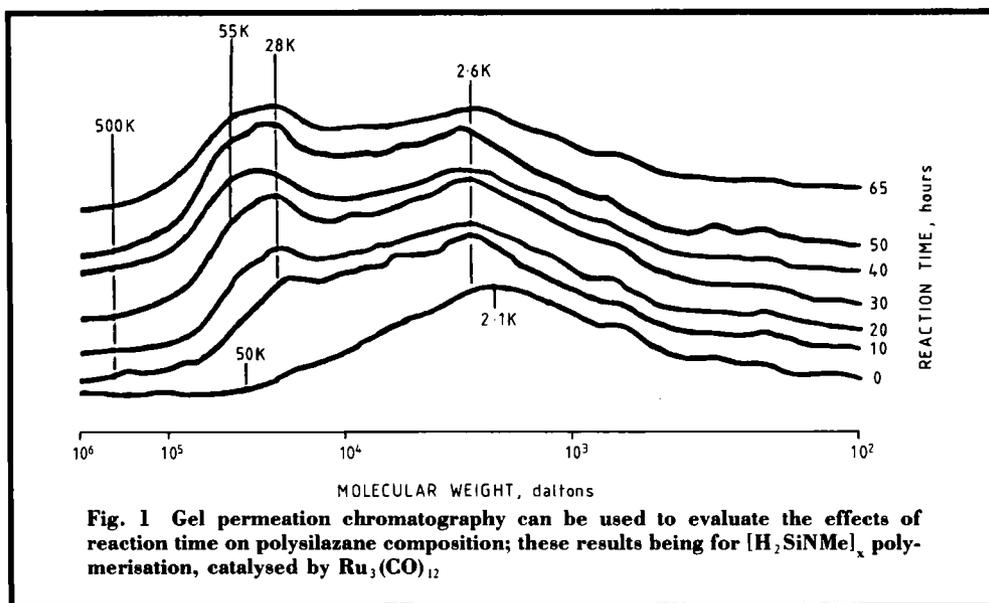
$$MeSiH_3 + NH_3 \xrightarrow{\text{catalyst}} H_2 + \text{-[MeHSiNH]_x-} \quad \text{xxii}$$
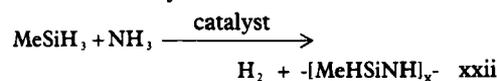
In practice, because of the dangers of handling $MeSiH_3$ or SiH_4, it is easier to prepare an oligomer via ammonolysis and modify it catalytically to a useful ceramic precursor.

Given that the polymer -[H_2SiNMe]$_x$- is actually $HNMe$-[H_2SiNMe]$_x$-H, and has both N-H bonds and Si-H bonds in the same oligomer, we sought to increase the molecular weight, and thereby the ceramic yield, of this polymer using the dehydrocoupling reaction. We find that it is indeed possible to catalyse the formation of high molecular weight species as typified by Reaction xxiii.

$$HNMe\text{-[H_2SiNMe]_x-H} \xrightarrow[\text{polymers}]{Ru_3(CO)_{12}/60-90°C} \quad \text{xxiii}$$

$$x \approx 20, M_n \approx 1200 \text{ D}$$

The effects of reaction time on the

Fig. 1 **Gel permeation chromatography can be used to evaluate the effects of reaction time on polysilazane composition; these results being for [H₂SiNMe]ₓ polymerisation, catalysed by Ru₃(CO)₁₂**

polysilazane composition can be evaluated by gel permeation chromatography as shown in Figure 1 (14). Over a 65 hour period the M_n changes from approximately 1200 D to only 2300 D, with $M_w \approx 25,000$ D. The viscosity of the polysilazane changes from approximately 1 to 3 poise to 100 poise in the same time period. These results are typical of a gelation process. The presence of several maxima in

Figure 1 suggests that more than one mechanism is responsible for the polymerisation process. We have confirmed that in addition to the dehydrocoupling reaction, Reaction i also plays a role in the crosslinking process.

If we continue to heat the reaction solution, the polymer eventually gels and then turns into a plastic. The same process occurs more rapidly at higher temperatures. Control of the extent of

Table III

Chemical Analyses of the 900°C Pyrolysis Products of Polysilazanes of the Type MeNH-[H₂SiNMe]ₓ[HSi(NHMe)NMe]ᵧ-H

Polysilazane (Mₙ)	Ceramic product analyses					
		C	H	N	Si	O
Mₙ = 800 pyrolysed	found:	18.89	0.88	35.44	45.18	<0.5
Mₙ = 1200 pyrolysed	found:	18.46	1.03	33.97	44.91	1.07
Mₙ = 1700 pyrolysed	found:	19.09	0.83	35.87	43.64	0.71
Mₙ = 2300 pyrolysed	found:	17.99	1.12	33.60	46.62	1.10

gelation permits us to control viscoelasticity. In this way, we have tailored the N-methylpolysilazane (NMPS) precursor, -[H$_2$SiNMe]$_x$-, so that it can be used successfully for coating and binder applications; and we have been able to draw fibres under appropriate conditions.

As mentioned above, the use of the dehydrocoupling reaction permits us to synthesise an organometallic polymer without the formation of a contaminating by-product, hydrogen. It is important to note that the catalyst concentration is at the hundred ppm level and should not interfere with the utility of the ceramic product, although this remains to be determined.

Pyrolysis Studies

Perhaps the most important findings are those of the pyrolyses tabulated in Table III.

The pyrolysis of NMPS at temperatures of 800 to 900°C permits conversion to ceramic product (15). We find that there is a direct correlation between molecular weight and ceramic yield. As noted previously, with molecular weights of the order of 600 D, the ceramic yield is ≈ 38 to 40 per cent. The M_n ≈ 2300 D case

gives ceramic yields of 60 to 65 per cent. The theoretical ceramic yield for NMPS should be just above 70 per cent, assuming that the polymer is converted to silicon nitride alone.

The evidence shows that within the error limits of the method, the chemical analyses of the ceramic products obtained by pyrolysis of several NMPS derivatives are identical (16). This is despite the significant differences in both molecular weight and viscosity. We conclude that it is the chemical composition of the monomer unit, -[H$_2$SiNMe]$_x$-, that defines the type of ceramic product, rather than the macromolecular properties.

If this conclusion is correct, and if it can be shown to be general in nature, then it demonstrates the feasibility of manufacturing ceramic materials by chemical means.

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