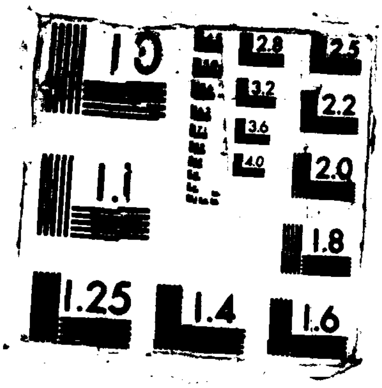
AD-A183 441 SYNTHETIC ROUTES TO OLIGO- AND POLYSILAZANES 1/1
POLYSILAZANE PRECURSORS TO SILICON NITRIDE(U) SRI
INTERNATIONAL MENLO PARK CA R M LAINE ET AL. 1987 TR-6
UNCLASSIFIED N00014-84-C-0392 F/G 7/6 NL


1.0
2.8
2.5
3.2
2.2
3.6
4.0
2.0
1.1
1.8
1.25
1.4
1.6

DTIC FILE COPY

(12)

SECURITY CL

REPORT DOCUMENTATION PAGE

1a. REPORT AD-A183 441

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE

3 DISTRIBUTION / AVAILABILITY OF REPORT
Approved for public release.
Distribution unlimited.

DTIC
ELECTE
AUG 05 1987
S D

4 PERFORMING ORGANIZATION REPORT NUMBER(S)
Technical Report No. 6

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
SRI International

6b. OFFICE SYMBOL (If applicable)

7a. NAME OF MONITORING ORGANIZATION
ONR

6c. ADDRESS (City, State, and ZIP Code)
Organometallic Chemistry Program
333 Ravenswood Avenue
Menlo Park, CA 94025

7b. ADDRESS (City, State, and ZIP Code)
Department of the Navy
Arlington, VA 22217

8a. NAME OF FUNDING / SPONSORING ORGANIZATION
Office of Naval Research

8b OFFICE SYMBOL (If applicable)
ONR

9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
N00014-84-C0392
N00014-85-C0668

8c. ADDRESS (City, State, and ZIP Code)
Department of the Navy
Arlington, VA 22217

10 SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO	TASK NO	WORK UNIT ACCESSION NO

11 TITLE (Include Security Classification)
Synthetic Routes to Oligo- and Polysilazanes. Polysilazane Precursors to Silicon Nitride

12 PERSONAL AUTHOR(S)
R. Laine, Y. Blum, D. Tse, R. Glaser

13a TYPE OF REPORT
Publication

13b TIME COVERED
FROM ______ TO ______

14 DATE OF REPORT (Year, Month, Day)

15 PAGE COUNT

16 SUPPLEMENTARY NOTATION
Accepted for publication in ACS Symp. Series: Inorganic and Organometallic Polym.

17 COSATI CODES

FIELD	GROUP	SUB-GROUP

18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
Polysilazanes; preceramic polymers; ~~Si-H~~ bond activation catalysis; ~~Si_3N_4~~; silanes, ammonia; amines; silicon ⇐

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

Organometallic polymer precursors offer the potential to manufacture shaped forms of advanced ceramic materials using low temperature processing. Polysilazanes, compounds containing Si-N bonds in the polymer backbone, can be used as precursors to silicon nitride containing ceramic materials. This chapter provides an overview of the general synthetic approaches to polysilazanes with particular emphasis on the synthesis of preceramic polysilazanes. The latter part of the chapter focusses on catalyzed dehydrocoupling reactions as a route to polysilazanes. (Keywords: ——

20 DISTRIBUTION / AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS

21 ABSTRACT SECURITY CLASSIFICATION
Unclassified

22a NAME OF RESPONSIBLE INDIVIDUAL
Kenneth Wynne

22b TELEPHONE (Include Area Code)
(202) 696-4410

22c OFFICE SYMBOL
NC

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted.
All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

87 8 4 030

OFFICE OF NAVAL RESEARCH

Contract No. N00014-84-C-0392
Contract No. N00014-85-C-0668

Technical Report No. 6

SYNTHETIC ROUTES TO OLIGO- AND POLYSILAZANES. POLYSILAZANE PRECURSORS TO SILICON NITRIDE

Richard M. Laine, Yigal D. Blum,
Doris Tse, and Robert Glaser
Inorganic and Organometallic Chemistry
SRI International, Menlo Park, CA 94025

Accepted for Publication
in
American Chemical Society Symposium Series:
Inorganic and Organometallic Polymers

1987

Synthetic Routes to Oligo- and Polysilazanes. Polysilazane Precursors to Silicon Nitride

Richard M. Laine,* Yigal D. Blum, Doris Tse, and Robert Glaser†
Contribution from the Inorganic and Organometallic Chemistry
Programs, SRI International, Menlo Park, CA 94025

Organometallic polymer precursors offer the potential to manufacture shaped forms of advanced ceramic materials using low temperature processing. Polysilazanes, compounds containing Si-N bonds in the polymer backbone, can be used as precursors to silicon nitride containing ceramic materials. This chapter provides an overview of the general synthetic approaches to polysilazanes with particular emphasis on the synthesis of preceramic polysilazanes. The latter part of the chapter focusses on catalyzed dehydrocoupling reactions as a route to polysilazanes.

Introduction

Non-oxide ceramics such as silicon carbide (SiC), silicon nitride (Si_3N_4), and boron nitride (BN) offer a wide variety of unique physical properties such as high hardness and high structural stability under environmental extremes, as well as varied electronic and optical properties. These advantageous properties provide the driving force for intense research efforts directed toward developing new practical applications for these materials. These efforts occur despite the considerable expense often associated with their initial preparation and subsequent transformation into finished products.

The expense in preparation derives from the need for high purity products. The cost in fabricating three-dimensional shapes of SiC, Si_3N_4 or BN arises from the need to sinter powders of these materials at high temperatures (>1500°C) and often under high pressure. Coatings of these materials are at present produced by chemical or

---

*Address all correspondence to this author at the Dept. of Materials Science and Engineering, Roberts Hall, FB-10, The University of Washington, Seattle, WA 98195.

†On leave from the Dept. of Chemistry, Ben Gurion University Beer Sheva, Israel.

physical vapor deposition (CVD or PVD). In each instance, the process is equipment and energy intensive and, has numerous limitations. If inexpensive methods for the synthesis and fabrication of non-oxide ceramics can be developed, then the number of useful applications could be enormous.

One potential solution to these problems, suggested some 20 years ago by Chantrell and Popper (1), involves the use of inorganic or organometallic polymers as precursors to the desired ceramic material. The concept (2) centers on the use of a tractable (soluble, meltable or malleable) inorganic precursor polymer that can be shaped at low temperature (as one shapes organic polymers) into a coating, a fiber or as a matrix (binder) for a ceramic powder. Once the final shape is obtained, the precursor polymer can be pyrolytically transformed into the desired ceramic material. With careful control of the pyrolysis conditions, the final piece will have the appropriate physical and/or electronic properties.

The commercialization of Nicalon (Nippon Carbon Co.), a SiC based ceramic fiber fabricated by pyrolysis of fibers of polycarbosilane (3), has sparked intensive efforts to synthesize polymer precursors of use in the fabrication of Si_3N_4 and BN fibers, coatings and binders. In this regard, oligo- and polysilazanes have recently been shown to offer considerable potential as precursors to Si_3N_4. The objective of this chapter is to provide an overview of the general methods for synthesizing oligo- and polysilazanes and to show how some of these routes have been used to synthesize oligo- and polysilazane preceramic polymers. In the latter part of the chapter, we will emphasize our own work on transition metal catalyzed dehydrocoupling reactions.

General Synthetic Approaches

Historically, oligo- and polysilazane synthetic chemistry has passed through three stages of development with quite differing goals. Initial efforts, beginning with the work of Stock and Somieski in 1921, were directed simply towards the preparation and classification of the general properties of polysilazanes (4,5). The commercial success of polysiloxanes or silicones in the fifties and sixties prompted studies on the synthesis of polysilazanes as potential analogs (without much success). As mentioned above, current interest derives from their use as silicon nitride preceramic polymers.

Reactions (1)-(5) illustrate known methods for forming silicon-nitrogen bonds of potential use in the formation of oligo- and polysilazanes. The most common method of forming silazanes is via ammonolysis or aminolysis as shown in reaction (1) (4,5):

$$R_3SiCl + 2R'_2NH \longrightarrow R_3SiNR'_2 + R'_2NH_2{}^+Cl^- \qquad (1)$$

Si-N bonds can also be formed by a dehydrocoupling reaction catalyzed by alkali (6-11) or transition metals (12):

$$R_3SiH + R'_2NH \xrightarrow{\text{catalyst}} R_3SiNR'_2 + H_2 \qquad (2)$$

In rare instances, one can also obtain displacement of oxygen by nitrogen as illustrated by reaction (3) (13). Reaction (3) proceeds despite the fact that the Si-O bond is 25-30 kcal/mole stronger than the Si-N bond (14).

$$R_3Si\text{-}OH + R'_2NH \longrightarrow R_3SiNR'_2 + H_2O \qquad (3)$$

Si-N bond (14).

Verbeek and Winter have used a deamination/condensation reaction to form new Si-N bonds as exemplified by reaction (4) (15,16).

$$2R_2Si(NHR')_2 \xrightarrow{\Delta} (R'NH)R_2SiN(R')SiR_2(NHR') + R'NH_2 \qquad (4)$$

It has been suggested that reaction (4) passes through an $R_2Si{=}NR'$ intermediate; although, no substantiation exists (17,18).

Van Wazer (19) has described the use of a redistribution reaction, illustrated in (5), to form linear oligomers from cyclic species:

$$2R_2SiCl_2 + \boxed{[R_2SiNH]_3} \longrightarrow ClR_2SiNHSiR_2Cl + Cl\text{-}[R_2SiNH]_2\text{-}SiR_2Cl \qquad (5)$$

With the exception of reaction (3), the utility of all of the above reactions for the synthesis of oligo- and polysilazanes has been examined in varying detail. In the following paragraphs, we attempt to examine the pertinent studies in each area especially as it relates to the synthesis of preceramic polymers.

Polymerization by Ammonolysis and Aminolysis

The simplicity of the ammonolysis/aminolysis of dihalohalosilanes, reactions (6) and (7), made them the original method of choice for the synthesis of oligo- and polysilazanes, especially because of the analogy to the hydrolytic synthesis of polysiloxanes. The ammonolysis of dihalosilanes, reaction (6), has been found to be extremely sensitive to steric factors (6).

$$R^1RSiCl_2 + 3xNH_3 \longrightarrow -[R^1RSiNH]_x- + 2xNH_4^+Cl^- \qquad (6)$$

For example, with $R^1 = R = H$, reaction (6) gives only oligosilazanes; with $R^1 = CH_3$ and $R = H$, both cyclic and oligosilazanes are formed; and with $R^1 > CH_3$ and $R = H$ then one obtains mostly cyclotri- and cyclotetrasilazanes as the products.

Aminolysis of dihalosilanes, reaction (7), is also extremely sensitive to the steric bulk of the amine (20). For $R^1 = CH_3$,

$$xR^1RSiCl_2 + 3xR'NH_2 \longrightarrow -[R^1RSiNR']_x- + 2xR'NH_3^+Cl^- \qquad (7)$$

$R = CH_3$ and $R' > Et$, the products are predominantly the cyclotri- and cyclotetrasilazanes and/or simple disilazanes, e.g., $R^1RSi(NHR')_2$. For reactions where $R^1 = H$ or CH_3, $R = H$ and $R' = CH_3$, the products can be mostly linear oligosilazanes depending on conditions (see below) (21-23). The preference for cyclotri- and cyclotetrasilazanes, in these reactions, is not surprising given that the hydrolysis of dihalosilanes also leads to cyclotri- and cyclotetrasiloxanes.

The search for silicon nitride precursors has renewed interest in ammonolysis as a route to polysilazanes. In our own work, we have followed up on early studies by Seyferth and Wiseman (20,21) on the preparation of $-[H_2SiNMe]_x-$ from $MeNH_2$ and H_2SiCl_2. We find that the molecular weight of this oligomer is greatly affected by the reaction conditions. Originally, Seyferth and Wiseman were able to produce mixtures of oligomers of $-[H_2SiNMe]_x-$ and the cyclotetramer (22). Removal of the cyclotetramer by distillation gave a polymer with Mn ≈ 600 Daltons ($x = 10$). We have now succeeded in preparing quantities of $-[H_2SiNMe]_x-$ with Mn ≈ 1000-1200 ($x = 18-20$) with less than 10% cyclomers (23). The resulting oligosilazane can be used directly as a precursor for transition metal catalyzed dehydrocoupling polymerization (see below).

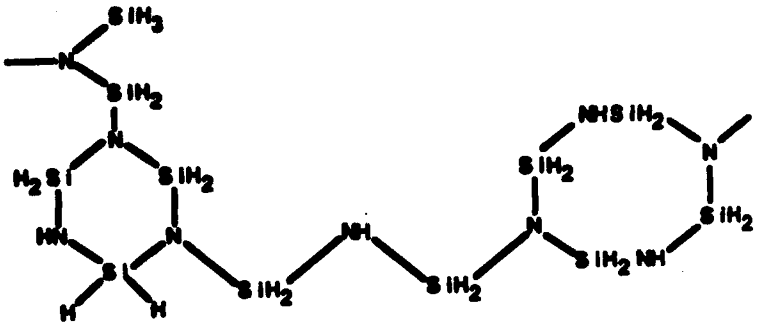
Arai et al. (24) have devised a novel approach to ammonolysis wherein the silyl halide is modified by complexation to pyridine (py) prior to ammonolysis:

$$RHSiCl_2 + 2py \longrightarrow RHSiCl_2 \cdot 2py \qquad (8)$$

$$RHSiCl_2 \cdot 2py + NH_3 \longrightarrow NH_4Cl \text{ (or py.HCl)} + -[RHSiNH]_x- \qquad (9)$$

$R = Me$ or H

The oligosilazanes formed via this approach give higher molecular weights than obtainable by direct ammonolysis. When $R = H$, the product is a polydispersed polymer with a weight average molecular weight (M_w) of ≈ 1300 D. The polymer is not stable and crosslinks to form an intractable product in a short time in the absence of solvent. Pyrolysis of this material gives an 80% ceramic yield of silicon nitride mixed with silicon. Silicon is found even when pyrolysis is conducted under an ammonia atmosphere. The tentatively proposed oligomer structure is (25):



Of interest is the fact that IR and NMR evidence point to the presence of SiH_3 groups in the oligosilazane. The SiH_3 groups must arise as a consequence of a redistribution process; although, further study remains to verify these results. When R = Me, the resulting polymer, $-[MeHSiNH]_x-$, can have molecular weights of 1700 D. Pyrolysis of this material gives high ceramic yields. The composition of the ceramic product was not reported.

Ring Opening Polymerization

Base and acid catalyzed ring opening polymerization of cyclotrisiloxane, $-[Me_2SiO]_3-$ [e.g. reaction (10)], is a well-known method of generating high molecular weight polysiloxanes.

$$RO- + x \left\lfloor [Me_2SiO]_3 \right\rfloor \xrightarrow{\hspace{6em}} RO-[Me_2SiO]_{3x}- \qquad (10)$$

RO− = alkoxide or hydroxide

A number of groups have attempted to develop the analogous reaction for cyclotri- and cyclotetrasilazanes. Ring opening polymerization represents an alternative to direct ammonolysis even though the cyclomer precursors are normally made by ammonolysis or aminolysis.

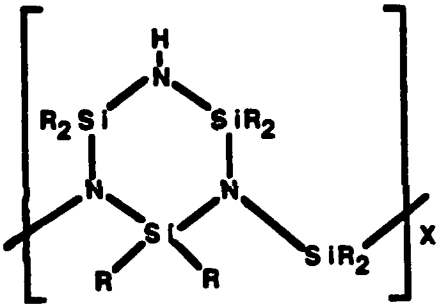
Thus, Andrianov et al. (26) attempted to catalyze polymerization of a number of alkyl and alkyl/aryl cyclosilazanes using catalytic amounts of KOH or other strong bases at temperatures of up to 300°C. In general, the reactions proceed with evolution of NH_3, hydrocarbons and the formation of intractable, crosslinked, brittle products even at low temperatures. Contrary to what is observed with cyclotrisiloxanes, no evidence was found for the formation of linear polysilazanes. Copolymerization of mixtures of cyclosilazanes and cyclosiloxanes gave somewhat more tractable polymers with less evolution of hydrocarbons or ammonia; however, very little was done to characterize the resulting materials.

An explanation for the lack of formation of linear polysilazanes in base catalyzed ring opening is suggested by one of Fink's publications (7). Fink observes that oligosilazane amides will undergo fragmentation to simple amides under the conditions employed by Andrianov:

$$R_3SiN(Li)SiR_2N(SiR_3)_2 \longrightarrow LiN(SiR_3)_2 + 0.5(R_3SiNSiR_3)_2 \qquad (11)$$

Presumably, any type of strong base will react with cyclosilazanes to form amido species. If amido species are extremely susceptible to fragmentation then reactions such as reaction (11) would promote depolymerization rather than polymerization. Consequently, the only way polymeric species can form would be through a condensation process that leads to trisubstituted nitrogens and fused rings.

Rochow et al. (27-28) have examined acid catalyzed ring opening polymerization as an approach to the formation of polysilazanes. They find that heating cyclotri- and cyclotetrasilazanes with ammonium halide catalysts at temperatures of 160°C for 6-8 h results in a condensation polymerization process that evolves ammonia and leads to the formation of waxy polysilazanes. Analytical results suggest that these polysilazanes consist of rings linked by silyl bridges as illustrated by the following structure:



Polymers of this type were found to have the highest molecular weight, $M_n \approx 10K$ D, of any polysilazanes produced to date. Unfortunately, no one has examined the utility of these compounds as preceramic polymers.

Rochow et al. (29) also report that heating tri- and cyclotetrasilazanes under ammonia leads to the formation of linear oligodimethylsilazanes, reaction (12); however, they were never able

$$NH_3 + \overline{\lfloor [Me_2SiNH]_3 \rfloor} \longrightarrow NH_2\text{-}[Me_2SiNH]_x\text{-}H \qquad (12)$$

to obtain conversions much greater than 10% and molecular weights were always on the order of $M_n \approx 1200$ D.

Ring opening polymerization can also be catalyzed by transition metals as shown in reaction (13) (12,30). The process appears to involve hydrogenolysis of the Si-N bond, given that reaction (13)

$$(Me_3Si)_2NH + \overline{\lfloor [Me_2SiNH]_4 \rfloor} \xrightarrow{Ru_3(CO)_{12}/135^\circ C/1h/H_2} Me_3Si\text{-}[Me_2SiNH]_x\text{-}SiMe_3 \qquad (13)$$

requires only 1h to equilibrate in the presence of as little as 1 atm of H_2, and more than 30h without a source of hydrogen. The value of x in $Me_3Si-[Me_2SiNH]_x-SiMe_3$ varies depending on the relative proportions of the capping agent, $(Me_3Si)_2NH$, to the tetracyclomer. Because the catalyst indiscriminantly cleaves Si-N bonds in both the tetracyclomer and the product oligomers in reaction (13), equilibration prevents the growth of high molecular weight species.

If reaction (13) is carried out under H_2 in the absence of capping agent then oligomers with $M_n \approx 2000$ D can be isolated following distillation of the volatile cyclomers. We believe that in this case the product polymers are both condensed ring systems and hydrogen capped linear oligomers.

None of the above described ring opening polymerization methods has, as yet, proved useful for the formation of polysilazane preceramic polymers. However, Si-N bond cleavage and reformation, as it occurs in reaction (13), is probably responsible in part for the curing or thermoset step in transition metal catalyzed dehydrocoupling polymerization of hydridosilazanes (31), as described below.

Deamination/Condensation Polymerization Reactions

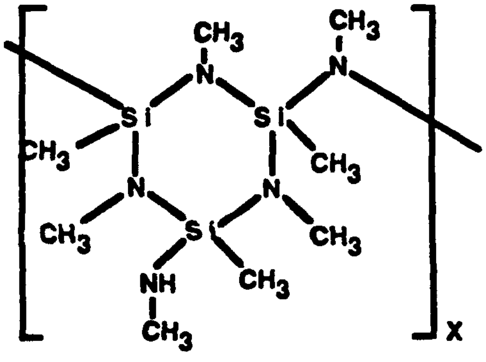
Reaction (4) was the first reaction successfully used to synthesize preceramic polysilazanes. Verbeek et al. found that fusible polysilazane resins could be produced by pyrolysis of bis- or trisalkylaminosilazanes (or mixtures) (15,16):

$$R_2Si(NHMe)_2 \xrightarrow{\Delta\ 200\text{-}800^{o}C} MeNH_2 + \overline{(R_2SiNMe)_3} + \text{polymer} \qquad (14)$$

$$RSi(NHMe)_3 \xrightarrow[R\ =\ Me\ or\ Phenyl]{\Delta\ 520^{o}C/3h} MeNH_2 + \text{polymer} \qquad (15)$$

The cyclotrisilazane (R = Me) produced in reaction (14) is recycled at 650°C [by reaction with $MeNH_2$, the reverse of reaction (14)] to increase the yield of processible polymer. Physicochemical characterization of this material shows it to have a softening point at 190°C and a C:Si ratio of 1:1.18. Filaments 5-18 μm in diameter can be spun at 315°C. The precursor fiber is then rendered infusible by exposure to air and transformed into a ceramic fiber by heating to 1200°C under N_2. The ceramic yield is on the order of 54%; although, the composition of the resulting amorphous product is not reported. The approach used by Verbeek is quite similar to that employed by Yajima et al. (13) in the pyrolytic preparation of polycarbosilane and its transformation into SiC fibers.

Reaction (15) has recently been studied in greater detail by a group at Marshal Space Flight Center (31-33). Wynne and Rice propose (2) the following structure for the polysilazane produced when R = Me:



The Marshall group has optimized reaction (14) to obtain a polysilazane with $M_w \approx 4000$ Daltons which can be hand drawn to give 10-20 μm preceramic fibers. These fibers are then rendered infusible by exposure to humid air and pyrolyzed to give fibers with the same ceramic yields, $55^{+}\%$, as found by Verbeek et al. The ceramic products are mainly amorphous SiC and Si_3N_4 with some SiO_2 (a consequence of the humidity treatments).

Unfortunately, the chemistry of the deamination/condensation process is poorly understood; thus, little can be said about the mechanisms and kinetics of the amine elimination step, the nature of the "silaimine" (7,8) intermediate or the condensation step. It seems reasonable to predict that if one could learn to control the relative rates for these two steps, more control could be exerted over the condensation process and the properties of the precursor polymer.

Si-Cl/Si-N Redistribution Polymerization Reactions

In the past five years, researchers at Dow Corning have made a concentrated effort to explore and develop the use of Si-Cl/Si-N redistribution reactions as a means of preparing tractable, polysilazane precursors to Si_3N_4 (34-42). Initial work focussed on the reaction of chlorosilanes and chlorodisilanes with hexamethyldisilazane:

$$MeSiCl_3 + (Me_3Si)_2NH \longrightarrow Me_3SiCl + \text{Polymer} \qquad (16)$$

$$MeCl_2SiSiMeCl_2 + (Me_3Si)_2NH \longrightarrow Me_3SiCl + \text{Polymer} \qquad (17)$$

Surprisingly, pyrolysis of these polysilazane polymers gave mostly SiC rather than the expected Si_3N_4. It was later found that the use of $HSiCl_3$ in place of $MeSiCl_3$ provides useful precursors to Si_3N_4 (42):

$$\begin{aligned} HN(SiMe_3)_2 + HSiCl_3 \longrightarrow{}& Me_3SiCl + \\ & -[HSi(NH)_{1.5}]_x[HSiNH(NHSiMe_3)]_y- \qquad (18) \\ & M_n \approx 3{,}500 \text{ Daltons} \\ & M_w \approx 15{,}000 \text{ Daltons} \end{aligned}$$

The sequence of redistribution reactions leading to the polymer shown in reaction (18) is illustrated by the following:

$$HSiCl_3 + (Me_3Si)_2NH \longrightarrow Me_3SiCl + Me_3SiNHSiHCl_2 \qquad (19)$$

$$Me_3SiNHSiHCl_2 + (Me_3Si)_2NH \longrightarrow Me_3SiCl + (Me_3SiNH)_2SiHCl \qquad (20)$$

$$(Me_3SiNH)_2SiHCl + (Me_3Si)_2NH \rightleftharpoons Me_3SiCl + (Me_3SiNH)_3SiH \qquad (21)$$

$$2(Me_3SiNH)SiHCl \longrightarrow (Me_3Si)_2NH + Me_3SiNHSiHClNHClHSiNHSiMe \qquad (22)$$

The polymer produced in reaction (18) can be spun to give 15-20 μm fibers. These fibers must then be made infusible prior to being pyrolyzed in order to obtain high quality ceramic fibers. The curing process involves vapor phase reaction of the spun precursor with $HSiCl_3$. This final redistribution reaction removes residual Me_3Si-groups, reduces carbon content and crosslinks the precursor polysilazane. After appropriate processing the resulting amorphous ceramic fiber consists of 96% Si_3N_4, 2% C and 2% O and the overall ceramic yield is approximately 45-55%.

Catalytic Dehydrocoupling--Dehydrocyclization Reactions

Catalytic dehydrocoupling, as shown in reaction (3), was pioneered by Fink (6-10) and later studied by Andrianov et al (43). Although Fink described the synthesis of the first polysilazanes, (9) reaction (23), this route to oligo- and polysilazanes remained unexplored

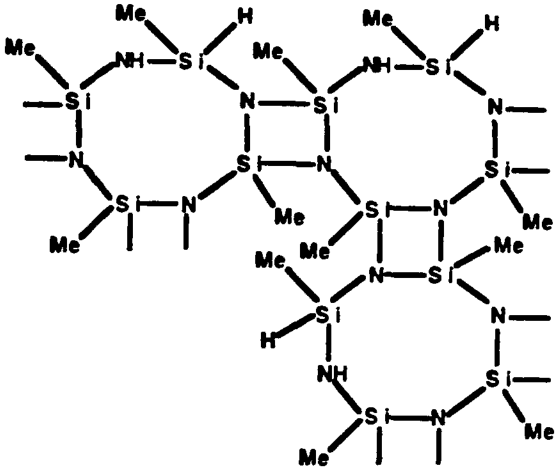
$$H_2NRNH_2 + 2R_2SiH_2 \xrightarrow{\text{strong base}} H_2 + -[RN(\mu\text{-}R_2Si)_2N]_x- \qquad (23)$$

until the work of Seyferth and Wiseman, (11,20-22,44,45) twenty years later.

Seyferth and Wiseman find that cyclomers and oligomers of the type $-[MeSiHNH]_x-$, produced by ammonolysis of $MeSiHCl_2$, will react with a strong base, eg KH, to undergo "dehydrocyclization", reaction (24), akin to reaction (23). The resulting products are soluble, tractable, sheetlike polymers that can be spun into fibers and give extremely high ceramic yields upon pyrolysis.

$$-[MeSiHNH]_x- \xrightarrow{1\%KH}$$

$x \approx 4.9$



(24)

This structure derives from the formula, $(MeSiHNH)_{0.39}(MeSiHNMe)_{0.04}(MeSiN)_{0.57}$, established by both NMR and combustion analysis.

Pyrolysis of a typical polysilazane produced according to reaction (24), under N_2, gives ceramic yields of 85%. Based on chemical analysis the ceramic composition appears to be a mixture of Si_3N_4, SiC, carbon and possibly some SiO_2 in a 0.88:1.27:0.75:0.09 ratio. If the pyrolysis is carried out under NH_3 then carbon can be eliminated from the ceramic product giving essentially pure Si_3N4. Seyferth suggests that NH_3 displaces the Me-Si groups via nucleophilic attack.

The mechanism of the dehydrocyclization reaction is not completely understood. Two alternatives were proposed (11), one which proceeds via a silaimine mechanism, exemplified by reaction (25), and one wherein ring closure occurs by nucleophilic displacement of hydrogen, reaction (26).

$$2R_2Si(H)\text{-}NR'(Li) \xrightarrow{-LiH} 2[R_2Si{=}NR'] \dashrightarrow R_2Si(\mu\text{-}NR')_2SiR_2 \qquad (25)$$

$$2R_2Si(H)\text{-}NR'(Li) \xrightarrow{-LiH} [R_2Si\text{-}NR'\text{-}SiR_2\text{-}NR'(Li)]$$

$$\xrightarrow{-LiH} R_2Si(\mu\text{-}NR')_2SiR_2 \qquad (26)$$

Modeling studies where R = R' = Me provide evidence in favor of a silaimine intermediate; however, efforts to trap the silaimine species were unsuccessful. Thus, the support for a specific ring closure mechanism remains inconclusive.

Transition Metal Catalyzed Dehydrocoupling Polymerization Reactions

Transition metal catalyzed dehydrocoupling, reaction (27), offers an alternative to the alkali metal dehydrocyclization process

$$R_2SiH_2 + R'NH_2 \xrightarrow{\text{catalyst}} H_2 + -[R_2SiNR']_x- \qquad (27)$$

and provides routes to different types of oligo- and polysilazanes (12,46-50). We have examined, in a preliminary fashion, the kinetics and mechanisms involved in reaction (27) using reaction (28) (50):

$$Et_3SiH + R'NH_2 \xrightarrow{Ru_3(CO)_{12}/70^\circ C/THF} H_2 + Et_3SiHNR' \qquad (28)$$

We find that the rates of reaction for the various amines examined in (28) are governed by an extremely complex set of equilibria. For example, when R' = n-Pr, n-Bu or s-Bu, the rate of reaction exhibit first order dependence on $[Et_3SiH]$ at constant amine concentration. However, the rate of reaction exhibits inverse non-linear dependence on $[n\text{-}PrNH_2]$ and $[n\text{-}BuNH_2]$, but positive non-linear dependence on $[s\text{-}BuNH_2]$ at constant $[Et_3SiH]$. Furthermore, if R' = t-Bu, then the rate of reaction is almost independent of both $[t\text{-}BuNH_2]$ and $[Et_3SiH]$. Studies of the rate dependence on catalyst concentration for reaction (28) where $R'NH_2$ is $n\text{-}BuNH_2$ reveal relative catalyst activities that are inversely dependent on $[Ru_3(CO)_{12}]$. Similar studies with $R'NH_2$ = $t\text{-}BuNH_2$ reveal that the rate of reaction is linearly dependent on $[Ru_3(CO)_{12}]$. Piperidine is unreactive under the reaction conditions studied.

Based on our previous work with $Ru_3(CO)_{12}$/amine catalytic systems, we can propose mechanisms that account for these observations; although, additional work will have to performed to validate some of our assumptions. The rate vs reactant concentration studies suggest that there are three different rate determining steps in the catalytic cycle for reaction (28), depending on the steric demands of the amine. In the cases where the rate of reaction is inversely dependent on $[RNH_2]$, one can assume that the amine is not participating in the rate determining step or there are competing reactions where the dominant reaction is inhibition. The conclusion then is that the rate determining step is probably oxidative addition of Et_3SiH to the active catalyst. The inverse dependence can be interpreted in light of Kasez et al's work (51) on the low temperature reactions of primary amines with $Ru_3(CO)_{12}$, and our work on amine/$Ru_3(CO)_{12}$ interactions (52,53).

Kaesz et al. have shown that simple, primary amines (e.g. $MeNH_2$) will react with $Ru_3(CO)_{12}$ to form μ-acetamido ligands at temperatures as low as -15°C. We find that simple primary, secondary and tertiary alkyl amines will react with $Ru_3(CO)_{12}$ at temperatures of 70-150°C to undergo catalytic deuterium for hydrogen exchange reactions on the hydrocarbon groups and transalkylation (52). We have found that a variety of aliphatic and aromatic amines will react with $M_3(CO)_{12}$ (M = Ru or Os) by binding through the nitrogen coincident with oxidative addition of an alpha C-H bond to form (μ^2-iminium)$HM_3(CO)_{10}$ and (μ^2-iminium)$_2H_2M_3(CO)_9$ complexes (53). We suggest that with n-$PrNH_2$ and n-$BuNH_2$ there is successful competition between amine and silane for sites of coordinative unsaturation on the active catalyst species.

With regard to the s-$BuNH_2$ results, it is likely that steric bulk, especially at the tertiary C-H alpha to the NH_2- group, limits its ability to bind to the active catalyst site and therefore it cannot compete with Et_3SiH, although it can still function as a reactant. If this logic is correct, then we can also suggest that Si-N bond formation probably occurs by nucleophilic attack directly on the silicon moiety bound to metal rather than through initial ligation at the metal followed by reaction. Because the rate of silazane formation is dependent on both [Et_3SiH] and [s-$BuNH_2$] we suggest that the rate limiting step in this instance is the formation of the Si-N bond. On changing amine from s-$BuNH_2$ to t-$BuNH_2$, there is a significant reduction in the reaction rate. As discussed above, the fact that this rate is almost completely independent of changes in both [Et_3SiH] and [t-$BuNH_2$] suggests that catalyst activation must become the rate determining step.

An alternate rationale to the above cycle can be proposed if the amine serves as both a spectator ligand and reactant in the catalytic cycle. In the case of n-$PrNH_2$ and n-$BuNH_2$, the complex containing the spectator ligand can add a second amine (causing inhibition) or it can react with silane. Inhibition may include stabilization of the cluster towards fragmentation given the stability of the (μ^2-iminium)$HM_3(CO)_{10}$ and (μ^2-iminium)$_2H_2M_3(CO)_9$ complexes (53). In this regard, we find that piperidine will react with $Ru_3(CO)_{12}$ to form very stable bis(piperidino)cluster complexes (53). If we attempt to carry out reaction (28) using piperidine, a sterically undemanding secondary amine, we observe no reaction. If piperidine is acting as a ligand to totally deactivate by inhibition, then addition of piperidine to reaction (28) run with n-$BuNH_2$ should inhibit or totally poison the reaction. In fact, the addition of more than one equivalent of piperidine per equivalent of catalyst served only to slightly accelerate the reaction rather than inhibit it. Thus, we must conclude that the spectator ligand concept does not appear to be valid. These results support the following very general mechanism for dehyrocoupling as catalyzed by M = $Ru_3(CO)_{12}$:

$$M + RNH_2 \rightleftharpoons M(RNH_2)$$

$$M + Et_3SiH \longrightarrow Et_3SiMH$$

$$Et_3SiMH + RNH_2 \longrightarrow Et_3SiNHR + MH_2$$

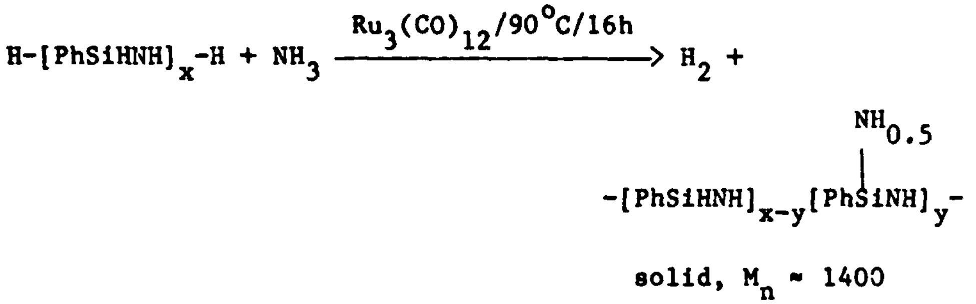
$$MH_2 \rightleftharpoons M + H_2$$

There appear to be considerable steric demands involved in formation of the Si-N bond in reaction (28). Support for the importance of steric constraints in dehydrocoupling comes from studies on the synthesis of oligosilazanes from $PhSiH_3$ and NH_3. When reaction (29) is run at 60°C, NMR and elemental analysis

$$PhSiH_3 + NH_3 \xrightarrow{Ru_3(CO)_{12}/60^{o}C/THF} H_2 + H\text{-}[PhSiHNH]_x\text{-}H \qquad (29)$$

$$\text{viscous oil, } M_n \approx 1000$$

confirm that the resulting oligomer is essentially linear (49). In order for this to occur, chain growth must occur by stepwise addition at the $PhSiH_2$ end caps without competition from reaction at the interior Si-H bonds. This implies that steric selectivity affects the facility of the oxidative addition step. If the oligomer produced in reaction (29) is treated with additional NH_3, but at 90°C, higher molecular weight oligomers can be formed but, NMR and elemental analysis now indicate the formation of pendant NH_2 groups and imino crosslinks as shown in reaction (30).



$$H\text{-}[PhSiHNH]_x\text{-}H + NH_3 \xrightarrow{Ru_3(CO)_{12}/90^{o}C/16h} H_2 + -[PhSiHNH]_{x-y}[Ph\overset{\overset{NH_{0.5}}{|}}{S}iNH]_y- \qquad (30)$$

$$\text{solid, } M_n \approx 1400$$

The structural changes that occur at 90°C are again indicative of steric constraints. We find no evidence that the N-H bonds in the $-[PhSiHNH]_x-$ backbone participate in the crosslinking process observed in (30) which is in keeping with our observation concerning piperidine's lack of reactivity. We also observe similar behavior for reactions of n-hexylsilane with NH_3 (23).

The following reactions were performed to demonstrate the utility of transition metal dehydrocoupling for the synthesis of different types of polysilazanes and a novel polysiloxazane:

$$HMe_2SiNHSiMe_2H + NH_3 \xrightarrow{Ru_3(C)_{12}/60^{o}C/THF} H_2 + -[Me_2SiHN]_x- \qquad (31)$$

$$Mn \approx 2000$$

$$\text{(volatiles distilled off)}$$

$$xHMe_2SiNHSiMe_2H + NH_3 + yPhSiH_3 \xrightarrow{Ru_3(CO)_{12}/60^{o}/THF}$$

$$H_2 + [HMe_2SiNHSiMe_2H]_x[PhSiHNH]_y \qquad (32)$$

$$HMe_2SiOSiMe_2H + NH_3 \xrightarrow{Ru_3(CO)_{12}/60^{o}/THF} H_2 + -[Me_2SiHNMe_2SiO]_x- \quad (33)$$

$$Mn \approx 5000\text{-}7000$$

Preceramic Polymers by Dehydrocoupling

We have also explored the use of the dehydrocoupling reaction for the synthesis of preceramic polysilazanes starting from the precursor $MeNH\text{-}[H_2SiNMe]_x\text{-}H$. As described above, $MeNH\text{-}[H_2SiNMe]_x\text{-}H$ is produced by aminolysis of H_2SiCl_2 with $MeNH_2$ under conditions where $x \approx 18\text{-}20$ ($Mn \approx 1150$).

Seyferth and Wiseman reported that oligomers of $MeNH\text{-}[H_2SiNMe]_x\text{-}H$ where $x \approx 10$ gave a 38% ceramic yield when pyrolyzed to 900°C (21,22). The ceramic product appeared to be mostly silicon nitride. Because $MeNH\text{-}[H_2SiNMe]_x\text{-}H$ has N-H bonds as end caps and internal Si-H bonds, the possibility of forming chain extended and/or branched polymers using the dehydrocoupling reaction exists. We find that treatment of this precursor, as in reaction (34), does lead to species with higher

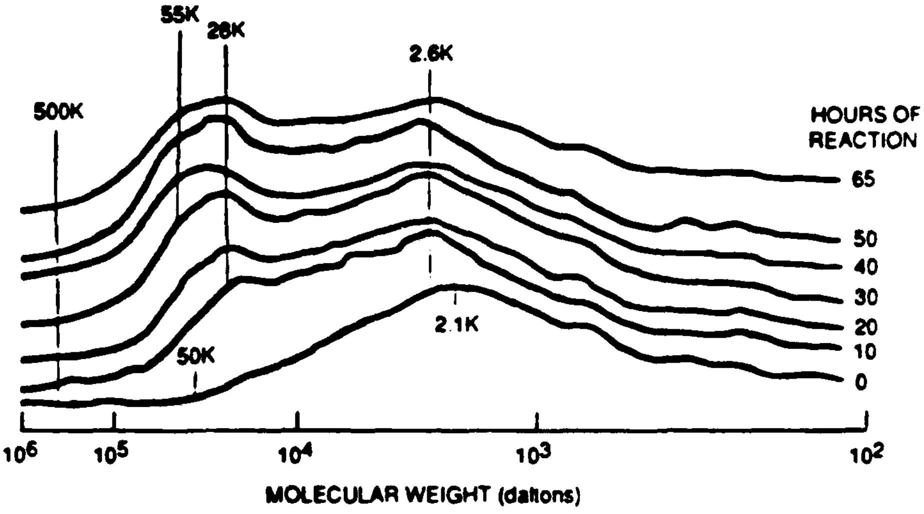
$$MeNH\text{-}[H_2SiNMe]_x\text{-}H \xrightarrow{Ru_3(CO)_{12}/90^{o}C/THF} H_2 +$$

$$\text{polymer} \dashrightarrow \text{gel} \dashrightarrow \text{resin} \quad (34)$$

molecular weights. Depending on the reaction conditions and time, it is possible to produce tractable, processable polymers with viscoelastic properties useful for making ceramic coatings, fibers and three dimensional objects (when used as a binder for silicon nitride powder). With increased reaction times or higher temperatures more crosslinking occurs in reaction (34), and the resulting product first turns into a gel and then into an intractable resin.

The Figure shown below illustrates the changes in molecular weight and dispersion as reaction (34) proceeds (49). The bimodal distribution suggests that there is more than one mechanism for polymer growth. At least one mechanism, if not more, leads to gelation as evidenced by the disparity between $M_n \approx 2300$ and $M_w \approx 25K$ at 65 h. This disparity is typical of a gelation via branching process (54).

The following Table lists the molecular weights and viscoelastic properties for the precursors and selected polymers produced in reaction (34). It also contains the ceramic yields obtained on pyrolysis to 900°C and the composition of the ceramic product.



JA-m-8997-13

FIGURE 1. SIZE EXCLUSION CHROMATOGRAPHY OF $Ru_3(CO)_{12}$ CATALYZED POLYMERIZATION OF $MeNH-[H_2SiNMe]_x-H$ AS A FUNCTION OF TIME
Polystyrene standards used for calibration

<u>Table.</u> Pyrolysis Studies on $MeNH-[H_2SiNMe]_x-H$ Oligomers and Polymers.

Oligomer	Mn (GPC)	Viscosity (poise)	Ceramic Yield (% at 900°C)	Si_3N_4 (Percent)
$-[H_2SiNMe]_x-$ $x = 10$	600-700	1	40	80-85
$-[H_2SiNMe]_x-$ $x = 19$	1150	5	45-50	80-85
$-[H_2SiNMe]_x-$ $Ru_3(CO)_{12}$/90 C/THF or 30h	1560	18	60-65	80-85
$-[H_2SiNMe]_x-$ $Ru_3(CO)_{12}$/90°C/THF for 65h	1620	100	65-70	80-85

The salient features of the results summarized in the Table are: (1) The molecular weight and the structure (extent of branching and/or crosslinking) of the oligo- or polysilazane play a role in the total ceramic yield; (2) Catalytic dehydrocoupling can be used to increase the overall ceramic yield and modify the viscoelastic properties of the precursor polymer; and, (3) The composition of the ceramic product (83% Si_3N_4 and 17%C for all precursors) appears to be defined by the monomer unit and appears to be independent of molecular weight or viscoelastic properties. This latter point is extremely important to synthetic chemists in that it strongly suggests that one can use custom-designed "molecular building blocks" to synthesize precursors to a wide range of known materials and possibly to some that are unknown.

Concluding Remarks

It is intriguing to note that good synthetic routes to tractable, high molecular weight (>20K) polysilazanes are still not available despite the extensive efforts and progress made in the last five years and the facility with which the analogous polysiloxanes are prepared. Part of the problem may be that the reaction mechanisms for the above discussed approaches are still poorly understood. We would like to suggest here some additional reasons for this lack of success.

Consider the effects of the N-R group on the structure and reactivity of polysilazanes as susceptible to hydrogen bonding effects. These effects alone should favor ring closure over the respective siloxane analogs. Moreover, for R = H, a new type of depolymerization reaction, analogous to reaction (4), is available as illustrated in reaction (35). Thus, reaction (35) could also contribute to the

$$H\text{-}[R_2SiNH]_{x-y}[R_2SiNH]_y\text{-} \xleftrightarrow{\Delta} \text{-}[R_2SiNH]_{x-y}\text{-}H + [R_2Si{=}N][R_2SiNH]_{y-1}\text{-}H \qquad (35)$$

instability of oligosilazanes. In fact, the polysiloxazane produced in reaction (33) cannot rearrange via reaction (35) which may explain why we are able to produce this polymer with such high M_n (5000-7000 D). For the case where R > Me, it has already been shown that steric effects work in favor of ring closure (21-23).

Another likely but heretofore unrecognized problem with the common ammonlysis/aminolysis method of polysilazane synthesis is that the byproduct will always contain Cl^- salts. Walsh finds that the Si-Cl and Si-N bond strengths are equivalent (about 100 kcal/mole) (14). Given the well known ability of F^- to promote cleavage and rearrangement of bonds at silicon, it may be that Cl^- exhibits similar properties with the relatively weak Si-N bonds (compared to Si-O bonds); albeit, to a lesser degree than F^-. Support for this idea comes from the identification of SiH_3 oligomer caps formed during the ammonolysis of $H_2SiCl_2{\cdot}2py$, see reaction (9) above (24). The redistribution reaction necessary to obtain the SiH_3 groups could readily be promoted by Cl^- and represents another mechanism whereby growth of high molecular weight polysilazanes is prevented. If redistribution reactions to form chain capping species are promoted by Cl^-, then processes which avoid ammonolysis may provide the key to making high molecular weight polysilazanes. The results shown in the Figure suggest that catalytic dehydrocoupling may offer the opportunity to surmount this problem if appropriately selective catalysts can be developed.

In the area of preceramic polysilazanes, sufficient progress has been made to produce precursors for silicon nitride fibers, coatings and as binders for silicon nitride powder. However, particular problems still remain to be solved particularly with regard to reducing impurity levels and improving densification during pyrolysis.

Acknowledgments

We would like to thank Dr. Andrea Chow and Mr. Richard Hamlin for their contributions in the characterization of the polymer species and for discussions concerning the implications of these results. We gratefully acknowledge support for this research from the Strategic Defense Sciences Office through Office of Naval Research Contracts N00014-84-C-0392 and N00014-85-C-0668.

Literature Cited

1. Chantrell, P. G. and Popper, E. P.; "Special Ceramics", E. P. Popper Ed.; New York; Academic (1964) pp. 87-102.
2. For recent reviews see a. Wynne, K. J. and Rice, R. W.; Ann. Rev. Mater. Sci. (1984) 14, 297. b. Wills, R. R.; Mark, R. A.; Mukherjee, S. A.; Am. Ceram. Soc. Bull. (1983) 62, 904-915. c. Rice, R. R.; Cer. Bull. (1983) 62, 889-892.
3. Yajima, S.; Shishido, T.; Kayano, H.; Nature (London) (1976), 264, 237.
4. Stock, A. and Somieski, K.; Ber. Dtsch. Chem. Ges.(1921) 54, 740 see also ref 5.
5. a. Brewer, S. D. and Haber, C. P.; J. Am. Chem. Soc. (1948) 70, 361. b. Osthoff, R. C. and Kantor, S. W.; Inorg. Synth. (1957) 5, 61.
6. Fink, W.; Angew. Chem. Inter. Nat. Ed. (1966) 5, 760-776.
7. Fink, W.; Chem. Ber. (1963) 96, 1071-1079.
8. Fink, W.; Helv.Chim. Acta. (1964) 47, 498-508.
9. Fink, W.; Helv. Chim. Acta. (1964) 49, 1408-1415.
10. Fink, W.; Helv. Chim. Acta. (1964) 51, 954.
11. Wiseman, G. H.; Wheeler, D. R.; and Seyferth, D.; Organomet. (1986) 5, 146-152.
12. Blum, Y. D. and Laine, R. M.; Organomet. (1986) 5, 2081.
13. Gilman, H.; Hofferth, B.; Melvin, H. W. and Dunn, G. E.; J. Am. Chem. Soc.(1950) 72, 5767-5768.
14. Walsh, R.; Acc. Chem. Res. (1981) 14, 246-252.
15. Verbeek, W.; U. S. Patent No. 3,853,567 Dec 1974.
16. Winter, G. and Verbeek, W.; and Mansmann, M.; U. S. Patent No. 3,892,583 Jul 1975.
17. a. Parker, D. R. and Sommer, L. H.; J. Am. Chem. Soc. (1976) 98, 618-620. b. Parker, D. R. and Sommer, L. H.; J. Organomet. Chem. (1976) 110, C1-C4. For other studies on the Si-N bond see the following ref. and ref 7.

18. Elseikh; M. and Sommer, L. H.; J. Organomet. Chem. (1980) 186, 301-308.
19. a. Van Wazer, J. R.; Moedritzer, L.; Moedritzer, K. and Groves, W.; U. S. Patent No. 3,393,218 July, 1968. b. see also Wannagat, U.; Pure and Appl. Chem. (1966) 13, 263-279.
20. Seyferth, D. and Wiseman, G. H.; "Ultrastructure Processing of Ceramics, Glasses and Composites", L. L. Hench and D. R. Ulrich, Eds. (1984) pp. 265-275.
21. Wiseman, G. H.; Ph.D. Dissertation, M. I. T., Aug. 1984.
22. a. Seyferth, D.; Wiseman, G. H. and C. Prud'homme, J. Am. Ceram. Soc.(1983) 66, C13-C14. b. Seyferth, D. and Wiseman, G. H.; Am. Chem. Soc. Poly. Div. Prprt. (1984) 25, 10-12.
23. Laine, R. M.; Blum, Y. D.; Dodge, A. unpublished results.
24. Arai, M. and Isoda, T.; Japan Kokai Tokkyo Koho JP. 61 89,230.
25. Arai, M.; Sakurada, S.; Isoda, T. and Tomizawa, T.; Am. Chem. Soc. Polymer Div. Polym. Prpts. (1987) 27, 407.
26. a. Zhdanov, A. A.; Kotrelev, G. V.; Kazakova, V. V. and Redkozubova, Ye. P.; Polym. Sci., U.S.S.R. (1985) 27, 1593-1600. b. Andrianov, K. A.; Ismailov, B. A.; Konov, A. M. and Kotrelev, G. V. ; J. Organomet. Chem. (1965) 3, 129-137. c. Andrianov, K. A.; Kotrelev, G. V.; Kamaritski, B. A.; Unitski, I. H. and Sidorova, N. I.; J. Organomet. Chem. (1969) 16, 51-62.
27. Rochow, E. G.; Mon. Chem. (1964) 95, 750-765.
28. Kruger, C. R. and Rochow, E.; J. Poly. Sci. A, (1964) 2, 3179-3189.
29. Redl, G. and Rochow, E. G; Angew. Chem. (1964) 76, 650.
30. Zoeckler, M. T. and Laine, R. M.; J. Org. Chem. (1983) 48, 2539.
31. Chow, A. W.; Hamlin, R. D.; Blum, Y. and Laine, R. M.; submitted to J. Pol. Sci.
32. a. Penn, B. G.; Daniels, J. G.; Ledbetter, III, F. E.; and Clemons, J. M.; Poly. Eng. and Sci. (1986) 26, 1191-1194. b. Penn, B. G.; Ledbetter III, F. E.; Clemons, J. M. and Daniels, J. G.; J. Appl. Polym. Sci.(1982) 27, 3751-3761.
33. Penn, B. G.; Ledbetter III, F. E. and Clemons, J. M.; Ind. Eng. Chem. Process. Des. Dev. (1984) 23, 217-220.
34. Gaul Jr, J. H.; U. S. Patent No. 4,340,619 Jul 1982.
35. Baney, R. H.; Gaul, J. H.; U. S. Patent 4,310,651 1982.
36. Gaul Jr, J. H.; U. S. Patent No. 4,395,460 Jul 1983.
37. Gaul Jr, J. H.; U. S. Patent No. 4,312,970 Jan 1985.
38. Cannady, J. P.; U. S. Patent No. 4,535,007 Aug 1985.
39. Cannady, J. P.; U. S. Patent No. 4,543,344 Sep 1985.
40. Bujalski, D. R.; Eur. Patent Appl. EP 175,382 Mar 1986.
41. Baney, R. H.; Bujalski, D. R.; Eur. Patent Appl. EP 175,383 Mar 1986.
42. Legrow, G. E.; Lim, T. F.; Lipowitz, J. and Reaoch, R. S.; "Better Ceramics Through Chemistry II", Mat. Res. Symp. Proc. Vol. 73, Brinker, C. J.; Clark, D. E.; and Ulrich, D. R.; Eds. (1986) pp 553-558.
43. Andrianov, K. A.; Shkol'nik, M. I.; Syrtsova, Zh. S.; Petrov, K. I.; Kopylov, V. M.; Zaitseva, M. G. and Koroleva, E. Z.; Dokl. Akad. Nauk. SSSR (1975) 223, 347-350.
44. Seyferth, D.; Prud'Homme, C. C.; Wiseman, G. H.; U. S. Patent 4,397,828 Aug 1984.
45. Seyferth, D. and Wiseman, G. H.; U. S. Patent 4,482,669 Nov. 1984.

46. Blum, Y. D.; Laine, R. M.; Schwartz, K. B.; Rowcliffe, D. J.; Bening, R. C.; and Cotts, D. B. "Better Ceramics Through Chemistry II" Mat. Res. Soc. Symp. Proc., Brinker, C. J.; Clark, D. E. and Ulrich, D. R. Eds. (1986) 73, pp 389-393.
47. Schwartz, K. B.; Rowecliffe, D. J.; Blum, Y. D. and Laine, R. M.; "Better Ceramics Through Chemistry II" Mat. Res. Soc. Symp. Proc., Brinker, C. J.; Clark, D. E. and Ulrich, D. R. Eds. (1986) 73 pp 407-412.
48. Laine, R. M. and Blum, Y. D.;U. S. Patent 4,612,383 Sept 1986.
49. Laine, R. M.; Blum, Y. D.; Hamlin, R. D.; Chow, A.; in "Ultrastructure Processing of Glass, Ceramics and Composites II" D. D. Mackenzie and D. R. Ulrich, Eds., J. Wiley and Sons, (1987) in press.
50. Biran, C.; Blum, Y. D., Laine, R. M.; Glaser, R. and Tse, D. S.; manuscript submitted for publication.
51. Lin, Y. C.; Knobler, C. B. and Kaesz, H. D.; J. Am. Chem. Soc. (1981) 103, 1216-1218 and references therein.
52. Wilson, Jr., W. B. and Laine, R. M.; J. Am. Chem. Soc. (1985) 107, 361-368.
53. Eisenstadt, A.; Giandomenico, C.; Fredericks, M. F.; and Laine, R. M.; Organomet. (1985) 4, 2033.
54. Billmeyer, Jr., F. W.; "Textbook of Polymer Science" 2nd Ed. John Wiley and Sons, N. Y., N. Y., 1971 pp. 272-278.

END
9-87
DTIC