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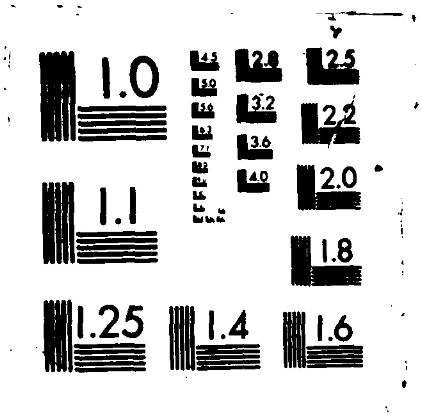

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19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

The program objectives are to develop: (1) Transition metal catalyzed synthetic routes to designed, tractable silicon nitride (Si_3N_4) preceramic polymers (polysilazanes) based on SRI developed technology; (2) Methods of spinning the resultant polysilazanes into continuous preceramic fibers; and, (3) Pyrolysis techniques for transforming the preceramic fibers into high strength Si_3N_4 and silicon carbide nitride (SiCN) fibers. In the past year, we have learned to prepare polysilazanes drived from precursors of the type-$[H_2SiNMe]_x$-, whose viscoelastic properties can be carefully controlled by type of catalyst and/or reaction conditions. This control has permitted us to draw preceramic fibers of diameters as small as 10 μm as seen in the attached photographs. Furthermore, we have developed pyrolysis methodology that permits us to obtain ceramic yields of 50-70% with Si_3N_4 purities ranging from 80-99%. We have discovered that polymer molecular weight greatly influences the ceramic yield but only monomer design or pyrolysis under a reactive atmosphere seems to influence selectivity to specific ceramic products as shown in the attached Table.

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SILICON NITRIDE CERAMIC FIBERS FROM PRECERAMIC POLYMERS

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POLYMER PRECURSORS TO SILICON NITRIDE COATINGS, BINDERS AND FIBERS

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Hamlin, A. Chow, and P. L. Lundquist

<u>Inorganic and Organometallic Chemistry,
Physical Polymer Program,
and Ceramics Program</u>

SRI INTERNATIONAL
Menlo Park, CA

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Of Naval Research

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PROGRAM OBJECTIVES

- Synthesize tractable polymer precursors to silicon nitride, using SRI's catalytic dehydrocoupling process nitride that can be spun and that give high ceramic yields of high purity Si_3N_4.

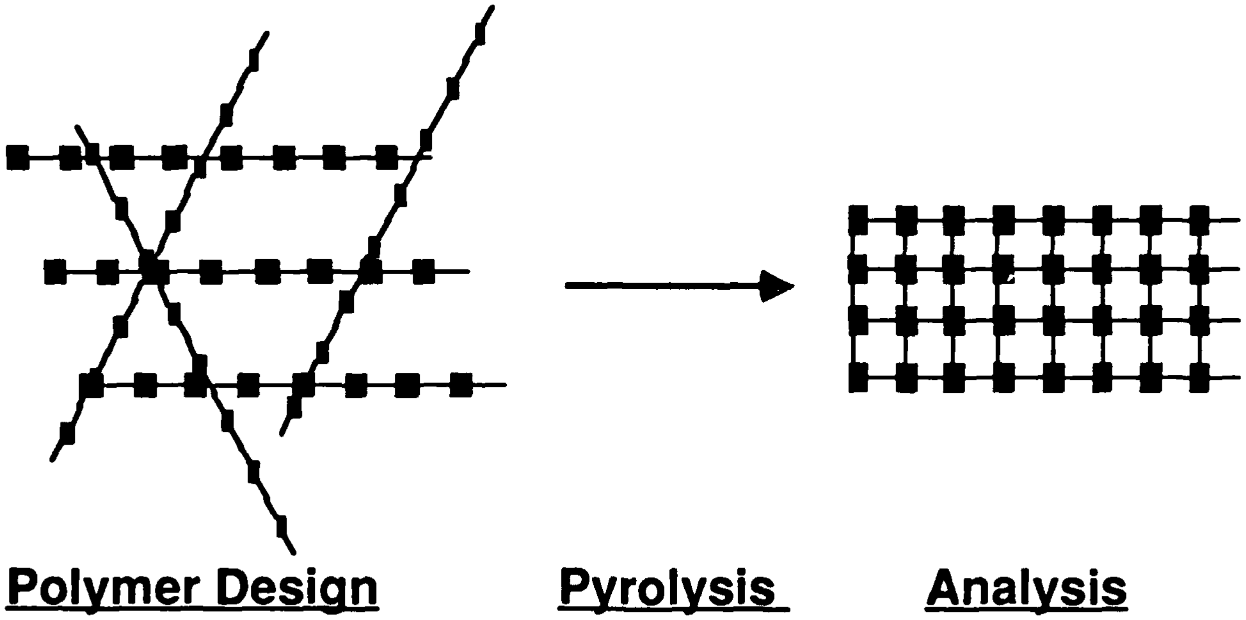
- Develop an understanding of the kinetics and mechanisms of the catalytic process.

- Detail the conditions necessary to shape the polymer precursor into a finished, infusible preceramic form.

- Detail the *pyrolysis conditions necessary to* transfrom the infusible shape into a finished, high density ceramic product.

- Develop analytical methods of characterizing the final ceramic product.

Polymer precursor design, synthesis and pyrolytic transformation make up the three steps in the development of preceramics useful for the preparation of coatings and fibers or for binder applications.

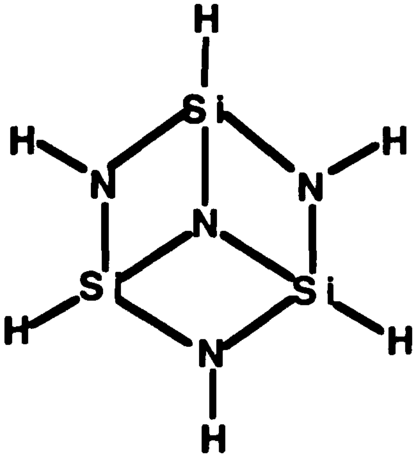


BASIC CONCEPTS IN MATERIALS CHEMISTRY

MOLECULAR ANALOGS OF MATERIALS

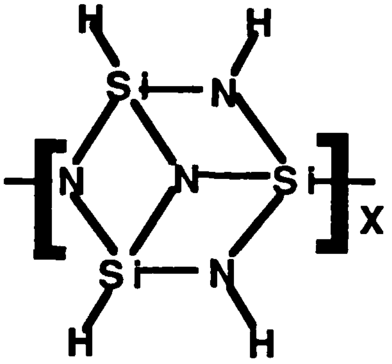
IN THEORY, Given the Empirical Formula for a Material, It Should be Possible to Prepare a Chemical Analog

CERAMIC MONOMERIC UNIT	CHEMICAL MONOMERIC UNIT
Si_3N_4	$H_6Si_3N_4$

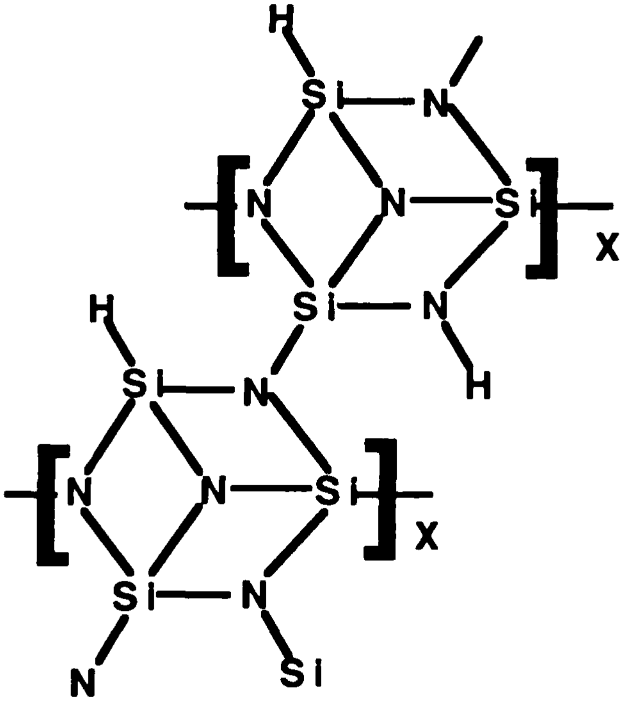


THIS ANALOG REPRESENTS A POTENTIAL PRECURSOR TO THAT MATERIAL

MONOMERS ARE OFTEN VOLATILE and Therefore not Suitable as Precursors to Ceramics--One Needs Oligomeric or Polymeric Species



LINEAR OLIGOMERS AND POLYMERS MUST RETAIN LATENT REACTIVITY--So They Can Be Made Infusible By Crosslinking:



POLYSILAZANE PRECURSORS TO Si_3N_4

IN PRACTICE:

It is Difficult to Synthesize Even Simple, High Molecular Weight Preceramic Polysilazanes That Are Tractable; Yet Retain Latent Reactivity.

The Polysilazane, $H\text{-}[Me_2SiNH]_x\text{-}H$, a Nitrogen Analog of Polysiloxane Exhibits no Latent Reactivity and Therefore Depolymerizes when Pyrolyzed --Giving No Ceramic Product

Polysilazane Syntheses by Catalytic Dehydrocoupling

SRI has recently developed a catalytic method of forming Si-N bonds from Si-H and N-H bonds that can be used to form polysilazanes:

$$Et_2SiH_2 + NH_3 \xrightarrow{Ru_3(CO)_{12}/60°C} H_2 + \text{-}[Et_2Si\text{-}NH]_x\text{-} \qquad M_n \approx 500$$

The products obtained by this reaction are mostly cyclomeric. However, by performing modeling studies on this type of reaction, we been able to obtain sufficient kinetic information to establish a preliminary picture of the reaction mechanism and use this to develop better approaches to preceramic polymers as shown in the next slides:

MODELING THE DEHYDROCOUPLING REACTION

$$Et_3SiH + RNH_2 \xrightarrow{Ru_3(CO)_{12}/THF/70°C} H_2 + Et_3SiNHR$$

Rate = $k[Et_3SiH][RNH_2]^{-1.X}$ for R = n-Pr, n-Bu

Rate = $k[Et_3SiH][RNH_2]^{0.X}$ for R = s-Bu

Rate = $k[Et_3SiH]^{0.Y}[RNH_2]^{0.X}$ for R = t-Bu

Rate = 0 for piperidine

Rate = $k[Ru_3(CO)_{12}]^{-0.X}$

PROPOSED DEHYDROCOUPLING MECHANISM

$$RNH_2 + M \longleftrightarrow (RNH_2)M + RNH_2 \longleftrightarrow (RNH_2)_2M$$

$$(RNH_2)M + Et_3SiH \longleftrightarrow Et_3SiM(H)(RNH_2)$$

$$Et_3SiM(H)(RNH_2) + RNH_2 \longrightarrow Et_3SiNHR + (RNH_2)MH_2$$

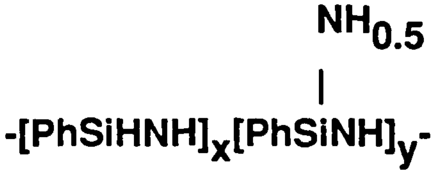
$$(RNH_2)MH_2 \longrightarrow (RNH_2)M + H_2$$

The above results indicate that transition metal catalyzed dehydrocoupling is extremely susceptible to steric inhibition. This is supported by the phenyl silane coupling reactions wherein, the 60°C reaction leads exclusively to linear oligomers and only at 90°C does crosslinking occur by formation of imino bridges. This latter observation suggests that imino bridge formation could be the mechanism whereby linear preceramic polysilazanes can be made infusible.

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

viscous oil, $M_n = 1000$

$$\mathrm{H\text{-}[PhSiHNH]_x\text{-}H + NH_3 \xrightarrow{Ru_3(CO)_{12}/90^{\circ}C} H_2 +}$$



$$\begin{array}{c} \mathrm{NH_{0.5}} \\ | \\ \mathrm{\text{-}[PhSiHNH]_x[PhSiNH]_y\text{-}} \end{array}$$

solid, $M_n = 1400$

Preceramic Polysilazanes

The ammonolysis of H_2SiCl_2 gives oligomers, $-[H_2SiNMe]_x-$, where $x \approx 10$:

$$H_2SiCl_2 + 3MeNH_2 \longrightarrow -[H_2SiNMe]_x- + 2xMeNH_3Cl$$

Pyrolysis of these oligomers gives a 38-39 wt % yield of ceramic product that is reported to be mostly silicon nitride. Considerable precursor volatilization occurs during pyrolysis.

Seyferth and Wiseman, 1984

Because the Polysilazane $HNMe-[H_2SiNMe]_x-H$ has N-H caps that can react, when heated at 60-90°C, with the internal H_2Si groups. The Dehydrocoupling Reaction can be used to form tractable higher molecular weight (less volatile) polymers and then to crosslink (thermoset) these polymers to render them infusible:

$$HNMe-[H_2SiNMe]_x-H \xrightarrow{Ru_3(CO)_{12}/60^\circ C} \text{polymers}$$

polymers ——> gels——>rubbers——>plastics

Figure 1, following, illustrates the changes in molecular weight and dispersion that occur as polymerization proceeds.

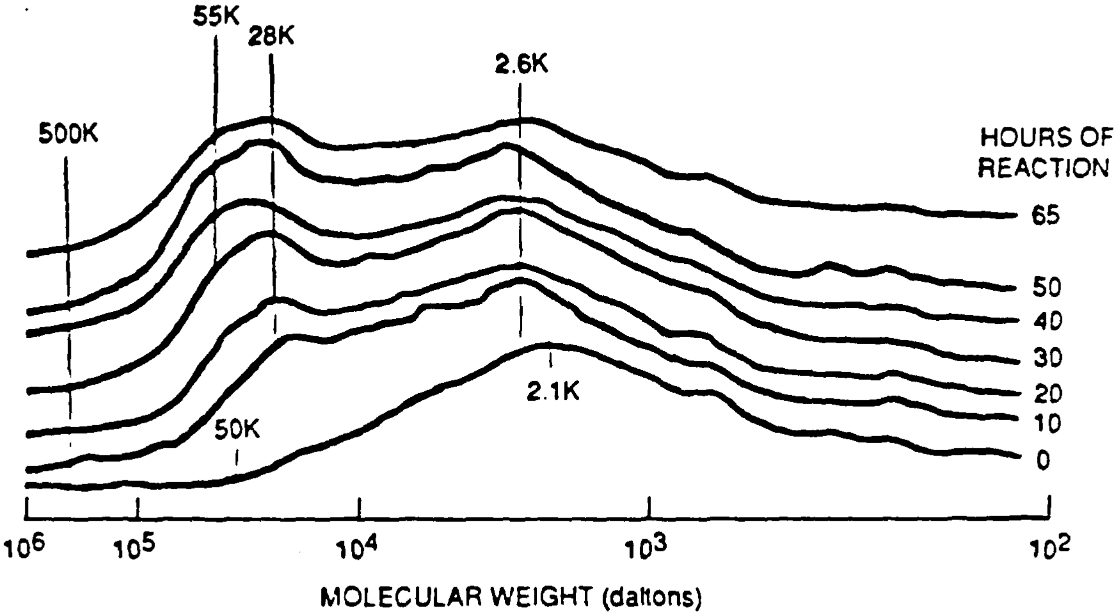


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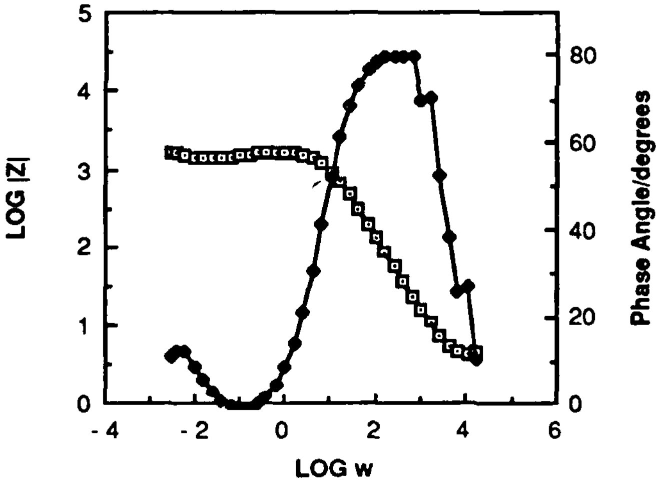
FIGURE 1 GPC RESULTS OF $[H_2SiNMe]_x$ POLYMERIZATION CATALYZED BY $Ru_3(CO)_{12}$

The tractable polymers shown in the last slide have been used to make 2000 Å coatings of silicon nitride on stainless steel, aluminum, silica and graphite/graphite composites. The coatings on stainless steel were featureless in the SEM at the highest magnification. Electrochemical corrosion studies were conducted on coated aluminum 6061 coupons to establish the microporosity of these coatings and their ability to protect the surface from corrosive environments over extended periods. The results of these electrochemical corrosion studies (shown on the following slides) reveal that the coatings contained some flaws but were unchanged upon exposure to 3.5% NaCl solution for as long as 21 days. These results suggest that silicon nitride coatings prepared by simple dipcoating techniques may be useful in a variety of composite applications [e.g. as protective coatings on graphite fibers during the fabrication of aluminum/graphite fiber composites.

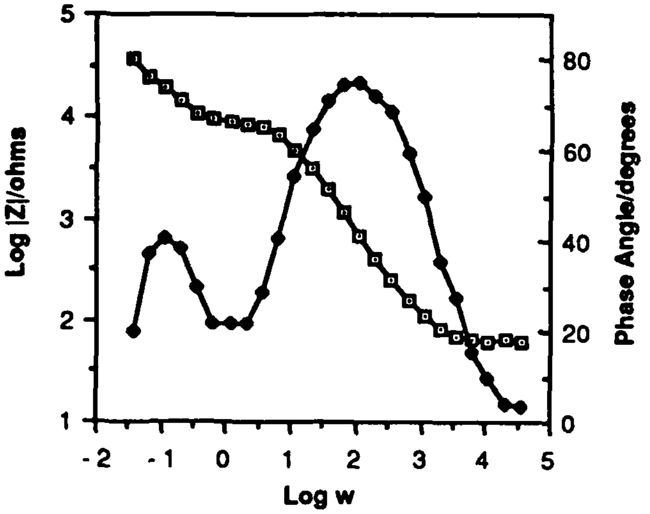
6061 Aluminum Alloy in 3.5% NaCl for 3 hours



AC Impedance Spectrum

<u>Observation</u>: The Polarization Resistance R_p is at least 10^3 which is relatively low.

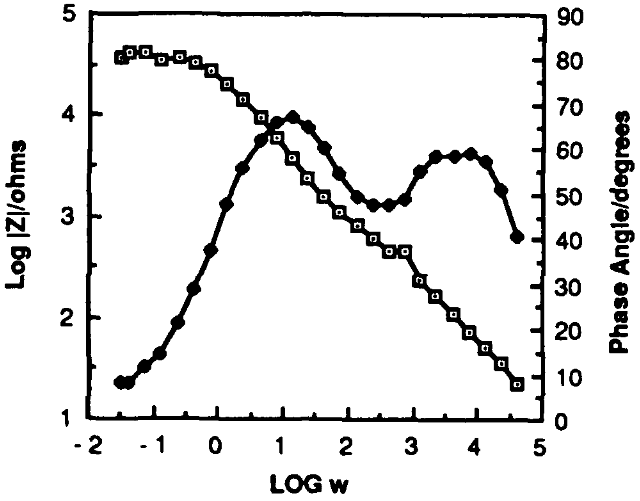
Coated 6061 Alloy in 3.5% NaCl for 5 hours



AC Impedance Spectrum

Observation: R_p is at least $10^{4.5} = 31600$ ohms which is relatively high.

Coated 6061 Alloy in 3.5% NaCl for 21 days



AC Impedance Spectrum

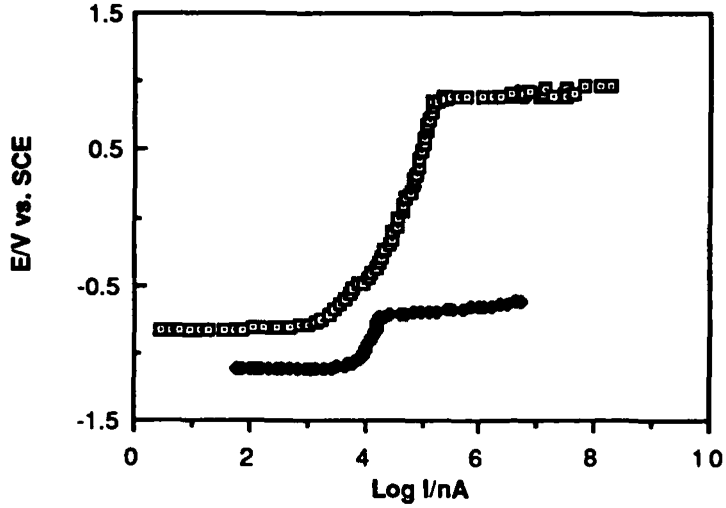
Observation: R_p is still at least $10^{4.5}$ or 31600 ohms after 21 days in solution.

$i_{corr} \leq 22.6 \mu A/cm^2$ Uncoated 6061 T6

$i_{corr} \leq 2.6 \mu A/cm^2$ Coated 6061 T6

Significance: The Corrosion Protection Afforded by Si_3N_4 Coatings Does not Degrade with Time over 21 Days

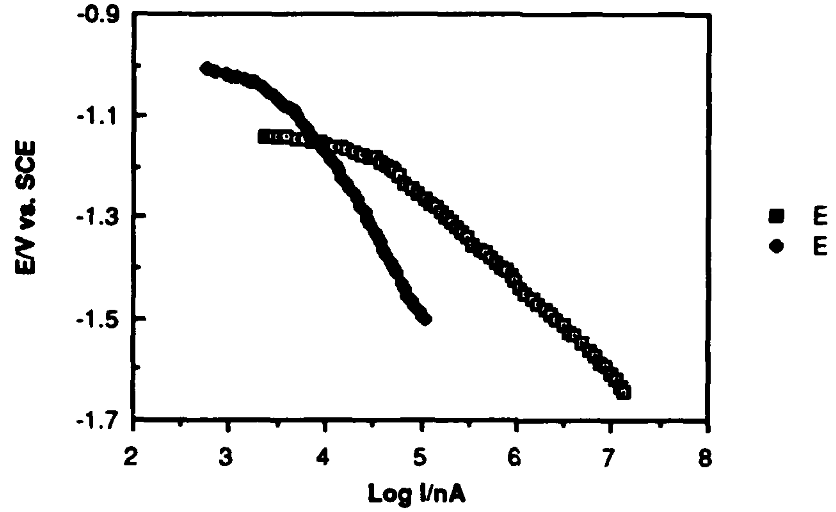
ANODIC POLARIZATION DIAGRAM



Observation: Si_3N_4 Coated Al 6061 T6 Alloy has a Pitting Potential about 1.75 Volts Higher than Uncoated alloy.

Significance: The coated material is significantly more resistant to pitting corrosion.

CATHODIC POLARIZATION DIAGRAM



Observation: i_{corr} = 7.4 µA/cm^2 Uncoated 6061 T6 Alloy
i_{corr} = 1.4 µA/cm^2 Coated 6061 T6 Alloy
by Tafel Extrapolation

Observation: b_c = 175 mv/decade Uncoated 6061 T6 Alloy
= 340 mv/decade Coated 6061 T6 Alloy

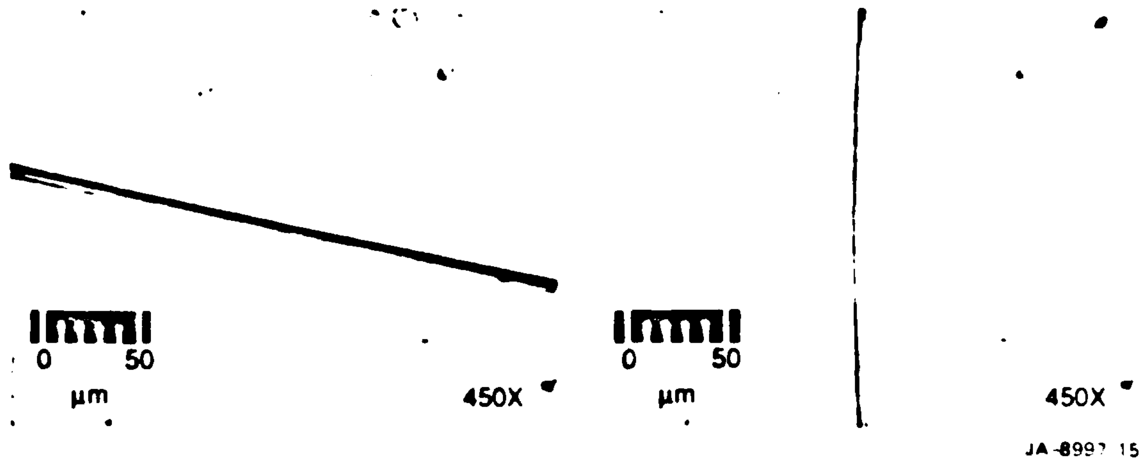
Interpretation: Based on Geometric Surface Area, the Substrate Corrosion Rates and Hydrogen Evolution Rates are Significantly Lower on the Coated Specimen.

These precursor polysilazane polymers have proved extremely useful as binders in the fabrication of fully dense silicon nitride bodies by pressureless sintering of compression molded silicon nitride powder. We find that pyrolysis of shapes compression molded with polysilazane at 800°C leads to densification and observable intrinsic strength in the green body. Densities of up to 75% have been obtained. Further heating at 1725°C for 20h under N_2 leads to full densification if sintering aids are present.

By comparsion, 800°C pyrolysis of shapes molded with a standard organic binder does not result in densification and the resulting product is similar to chalk.

The more viscous polymer can be extruded to give fibers of 100-300μm and hand drawn, as shown in the following Figure, to give smooth precursor fibers of approximately 10 μm.

HAND DRAWN 10 μm FIBERS USING POLYMER DERIVED FROM $-[H_2SiNMe]_x$:



Pyrolysis of -$[H_2SiNMe]_x$- Oligomers and Polymers

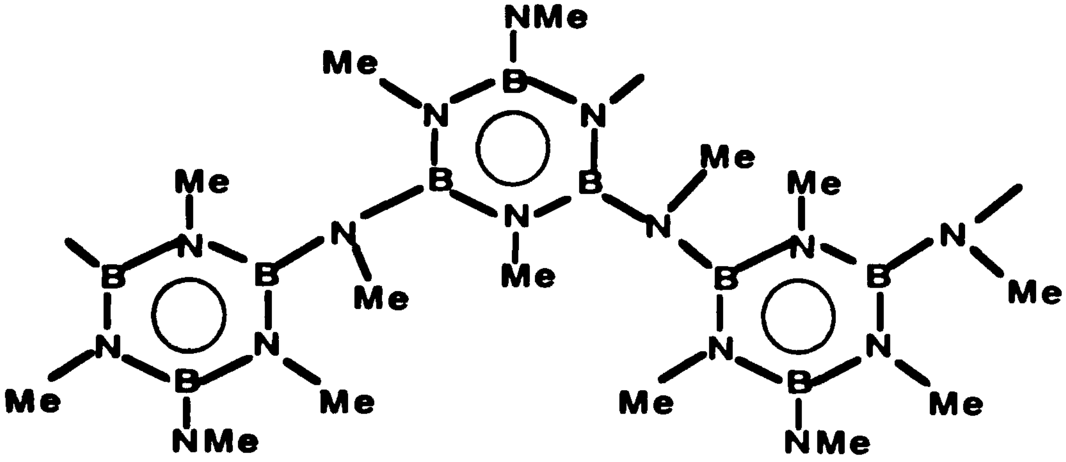
Oligomer	M_n (GPC)	Viscosity (poise)	Ceramic Yield (900°C)	Si_3N_4 %
$[H_2SiNMe]_x$ x = 10	650	1	40	80-85
$[H_2SiNMe]_x$ x = 19	1150	5	45-50	80-85
$[H_2SiNMe]_x$ $Ru_3(CO)_{12}$/90°C 30h	2100	18	60-65	80-85
$[H_2SiNMe]_x$ $Ru_3(CO)_{12}$/90°C 65h	2300	100	65-70	80-85

The salient features seen in the above table are that there is a direct correlation between the molecular weight M_n of the precursor and the ceramic yield. This is to be expected if precursor volatilization results in physical loss of precursor. Also of importance is the fact that the viscosity of the polymer changes from 1 to 100 poises while the M_n changes from only

650 to 2300 D. These observations indicate that the polymerization process is most likely a gelation process. The mostly linear macromolecular structure of the 650 D material is therefor quite different from the highly branched species present in the 2300 D polymer. Of considerable importance is that the selectivity to ceramic products (83% Si_3N_4 and 17% amorphous carbon) remains unchanged despite the considerable change in polymer molecular weight and macroscopic structure. These results suggest that it is the monomer unit $-H_2SiNMe-$, at the molecular level, that determines the selectivity to ceramic products.

This last conclusion, if valid, supports the concept that it is indeed feasible to design materials at the molecular level. Finally, transition metal catalyzed dehydrocoupling has now been domonstrated for the formation of oligo-borazines from BH_3 and $MeNH_2$. In addition, we have found a simple condensation process that leads to polyiminotitanides which can be used as perceramic precursors to titanium nitride.

BN OLIGOMER PRECURSORS BY CATALYTIC DEHYDROCOUPLING



Pyrolysis at 800°C: Ceramic Yield 60 Wt %

Pyrolysis at 1600°C: Ceramic Yield 49 Wt %

TITANIUM NITRIDE PRECURSORS

$Ti(NMe_2)_4 + PrNH_2 \longrightarrow Me_2NH +$

$-[Ti(NMe_2)_3(\mu\text{-}NPr)]_x-$

or

$-[Ti(NMe_2)_2(\mu\text{-}NPr)_2]_x-$

Pyrolysis at 800°C under NH_3 gives TiN

PROGRESS

- Developed an understanding of the mechanism(s) of the dehydrocoupling reaction.
- Learned how to polymerize oligomers of -$[H_2SiNMe]_x$- and to control product rheological properties.
- Demonstrated the feasibility of preparing thin, corrosion resistant coatings on metals and silica using a preceramic polymer.
- Demonstrated the utility of using preceramic polymers as binders for compression molded Si_3N_4.
- Prepared 10-100 μm preceramic fibers from preceramic polymers.
- 6 publications in press or in preparation. 2 patent applications. One major spin-off project to improve the strength of glass bottles.

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