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Structure/Reactivity Relationships
of Polysilazane Preceramics

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and fabrication of non-oxide ceramic coatings is needed. Fibers are also of interest because of their potential utility in ceramic and metal matrix composites.

Polysilazanes have received renewed interest since their discovery [1] in the 1920's as precursors to Si_3N_4 . However, little is known about their high temperature reaction chemistry. In order for polysilazanes to become useful precursors, questions need to be addressed and answers provided concerning the types of catalysts needed to provide controlled polymer structures. Also, one must determine what chemical and microstructural changes occur in the precursor during pyrolysis in the 200 to 900 °C range and at what temperature intermediate (e.g. 400-600 °C) products begin to resemble the target ceramic products.

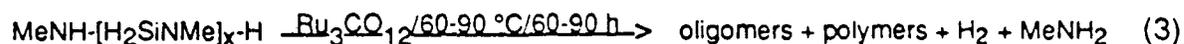
This paper will concentrate on the pyrolysis studies of the precursor polysilazanes, $-\text{[H}_2\text{SiNMe]}_x-$ and $-\text{[MeHSiNH]}_x-$, and will show how ceramic product selectivity is controlled by molecular structure. The experimental details of the work reported here will be described in detail elsewhere [2].

2. Results and Discussion

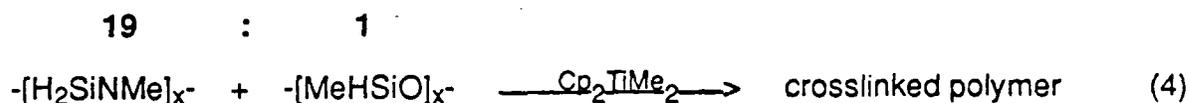
The two polysilazane oligomers, $-\text{[H}_2\text{SiNMe]}_x-$ and $-\text{[MeHSiNH]}_x-$, are prepared by ammonolysis or aminolysis, reactions (1) and (2). The termini are MeNH- and NH_2- respectively.



As we have previously shown [3-5], it is possible to treat these oligomers with a ruthenium catalyst derived from $\text{Ru}_3(\text{CO})_{12}$, to form higher molecular weight oligomers and polymers, reaction (3). However, we would like to reduce or even



eliminate the dependence on ruthenium catalysts, as well as find catalysts that will increase the rate of the current catalytic process and improve control of the polysilazane rheology. As reported elsewhere in this volume, we have succeeded in eliminating the need for ruthenium as shown in reaction (4):



TGA and bulk pyrolysis studies on $\text{---}[\text{H}_2\text{SiNMe}]_x\text{---}$ and $\text{---}[\text{MeHSiNH}]_x\text{---}$ prepared via reaction (3) give the same results under nitrogen or argon. Likewise, ceramic yields and products do not change even when heating schedules are varied between 1 and 10 °C/min. The apparent ceramic products obtained from pyrolysis of $\text{---}[\text{H}_2\text{SiNMe}]_x\text{---}$ are silicon nitride and carbon, whereas pyrolysis of $\text{---}[\text{MeHSiNH}]_x\text{---}$ leads to the formation of SiC in addition to Si_3N_4 and carbon.

Figures 1 and 2 provide information about pyrolytic weight losses (TGA

Insert Figures 1 and 2.

curves) for $\text{---}[\text{H}_2\text{SiNMe}]_x\text{---}$ and $\text{---}[\text{MeHSiNH}]_x\text{---}$ and the chemical compositions of the intermediate materials at selected temperatures. If considered together with Figures 3 and 4, one obtains a reasonable picture of the chemical changes that

Insert Figures 3 and 4.

occur as each precursor first undergoes extensive crosslinking followed by decomposition into an amorphous ceramic product.

At temperatures up to 400 °C, the chemical compositions of the two polymers evolve slowly; however, the DRIFT spectra (Figures 3 and 4) show that significant changes occur in the chemical structure. The bands due to Si-H bonds (~2200 cm^{-1}) in both polymers decrease relative to the bands of the fingerprint region (< 1300 cm^{-1}) and broadening is observed in both the C-H (~3000 cm^{-1}) and N-H (3450 cm^{-1}) regions. These changes are most likely a result of crosslinking which restricts the movement of the polymer chains, causing the IR bands to broaden as various polymer segments are frozen in different conformations.

There is significant weight loss in both polymers over the temperature range from 200-400 °C with little change in composition. Examination of the DRIFT spectra shows that the N-H band increases in intensity relative to C-H and Si-H bands, which suggests that either Si-N or C-N bonds are being broken and subsequent hydrogen abstraction is leading to formation of new N-H bonds. We suggest that this cleavage takes place during polymer fragmentation resulting in the observed weight loss.

At 400 °C, both intermediates still retain structural and compositional features resembling the precursors. However, by 600 °C, the composition of both intermediates resembles the end product even though the hydrogen content is high. This temperature region is important in that the product obtained has qualities associated with the initial polymer (e.g. flexibility) as well as properties associated with the ceramic product (e.g. oxidation resistance).

4. Conclusions

Transition metal catalysts may be used to polymerize $-(\text{H}_2\text{SiNMe})_x-$ and $[\text{MeHSiNH}]_x-$ oligomeric silazanes, thereby increasing the molecular weight. The ceramic yield of the product is a function of the precursor molecular weight, whereas the ceramic composition of the product is influenced by the precursor structure.

The transformation into ceramic products can be monitored by FTIR, TGA, and chemical analysis. The 400-600 °C temperature region may prove to be very important since the intermediates produced at this stage have properties befitting both a polymer and a ceramic.

Acknowledgements

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References

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- [2] Unpublished work of all authors.
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Figure Captions

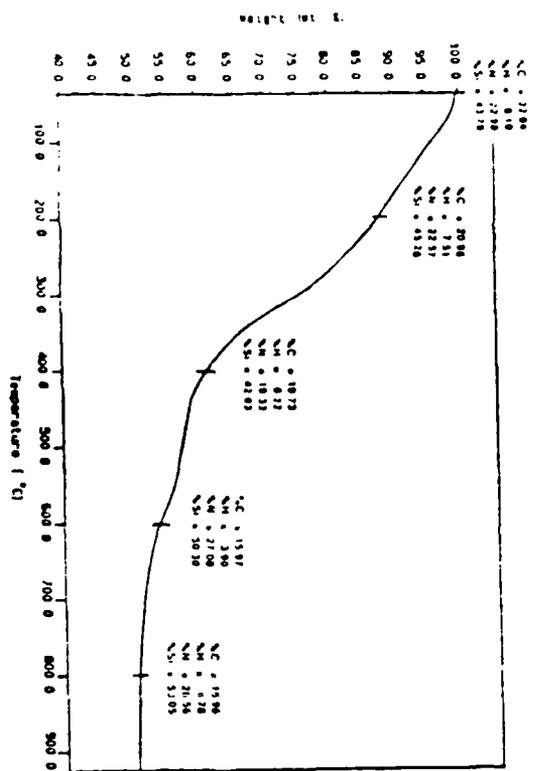
Figure 1. TGA and chemical analyses for $-\text{[MeHSiNH]}_x-$ at 25, 200, 400, 600, and 800 °C (pyrolyzed in nitrogen at a heating rate of 5 °C/min).

Figure 2. TGA and chemical analyses for $-\text{[H}_2\text{SiNMe]}_x-$ at 25, 200, 400, 600, and 800 °C (pyrolyzed in nitrogen at a heating rate of 5 °C/min).

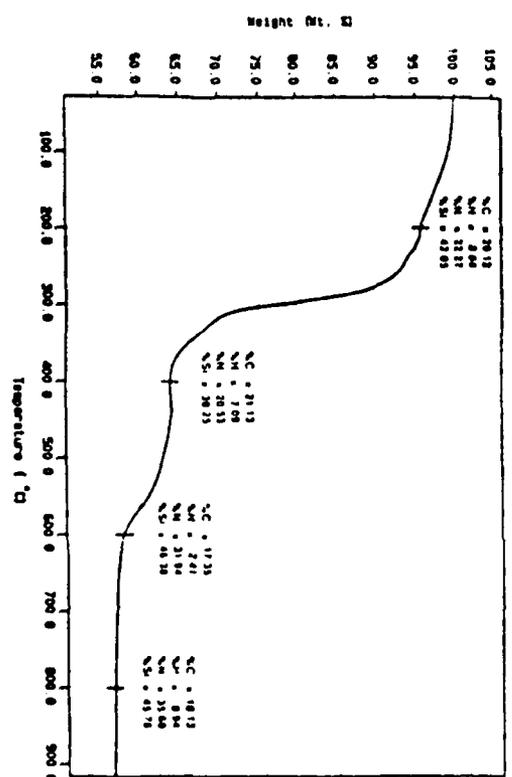
Figure 3. DRIFT spectra for $-\text{[MeHSiNH]}_x-$ at 25, 200, 400, 600, and 800 °C (pyrolyzed in nitrogen at a heating rate of 5 °C/min).

Figure 4. DRIFT spectra for $-\text{[H}_2\text{SiNMe]}_x-$ at 25, 200, 400, 600, and 800 °C (pyrolyzed in nitrogen at a heating rate of 5 °C/min).

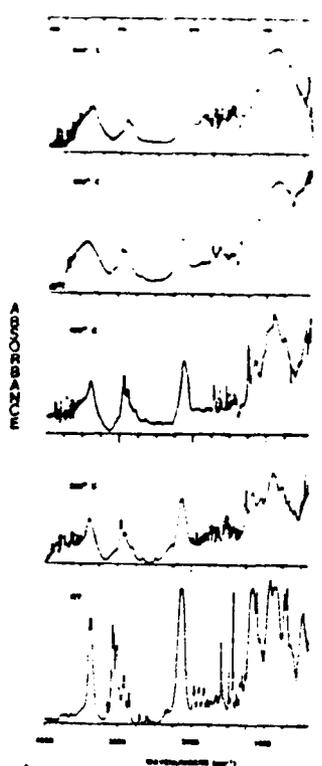
1A



1B



2A



2B

