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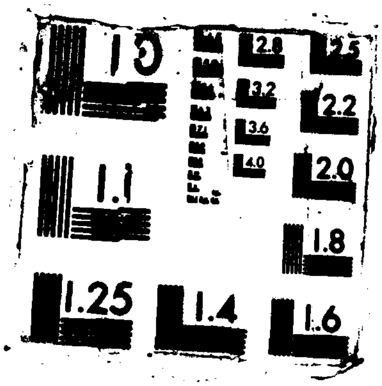
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We have examined the polymerization kinetics of transition metal dehydrocoupling of the Si-H and N-H bonds of oligomers of the type $HNMe-[H_2SiNMe]_x-H$ by size exclusion chromatography and correlated molecular weight changes with changes in shear viscosity. Analysis using simplified statistical theory that branching is a mechanism for polymerization and lends to gelation.

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POLYMERIZATION KINETICS OF POLYSILAZANE BY TRANSITION METAL CATALYZED DEHYDROCOUPLING REACTION

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and the Inorganic and Organometallic Chemistry Programs
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INTRODUCTION

In recent years, considerable interest has been directed to synthesizing inorganic or organometallic polymers as precursors to nonoxide ceramic materials such as silicon carbide (SiC), silicon nitride (Si_3N_4), boron nitride (BN), and boron carbide (BC_4).[1] This method offers potential routes to shape forms of nonoxide ceramics (e.g. fibers, coatings) if the synthesized polymers can be processed at low temperature using known organic polymer fabricating techniques, and if they can be pyrolytically transformed into the desired ceramic products. Nicalon®, a commercialized SiC continuous fiber, is one example of product fabrication via the preceramic polymer approach not feasible via conventional ceramic processing techniques.

Transition metal catalyzed polymerization of polysilazanes has been reported as one of several potential routes to silicon nitride precursor synthesis.[2] In this communication, we report a study of the polymerization kinetics of N-methylpolysilazane (NMPS) catalyzed by $Ru_3(CO)_{12}$. The polymerization reaction of NMPS proceeds from oligosilazanes as follows:[3]

$$\mathrm{MeNH\text{-}[H_2SiNMe]_x\text{-}H} \xrightarrow{\mathrm{Ru_3(CO)_{12}/90^{o}C}} \mathrm{H_2} + \text{polymer} \qquad (1)$$

$x \quad 19$

The starting oligomers in Reaction (1) can be obtained from a reaction of dichlorosilane and monomethylamine described by Seyferth and Wiseman:[4]

$$\mathrm{xH_2SiCl_2} + \mathrm{(3x+1)MeNH_2} \xrightarrow{\mathrm{0^{o}C/ether}} \mathrm{2xMeNH_3Cl} + \mathrm{MeNH\text{-}[H_2SiNMe]_x\text{-}H} \qquad (2)$$

The changes in molecular weight, molecular weight distribution and rheology with reaction time have been investigated to elucidate the reaction kinetics and mechanism of Reaction (1). Size exclusion chromatography (SEC), vapor phase osmometry (VPO), and rheometry techniques were used to characterize polymer products. To our knowledge, these techniques have rarely been applied to the study of the complicated structural changes of silazane polymers during the polymerization reaction.

EXPERIMENTAL

Size Exclusion Chromatography

The SEC equipment used for this study includes a Waters 6000 pump, Waters R401 differential refractometer, and four Waters Ultrastyragel columns--500 Å, 10^3 Å, 10^4 Å, and 10^5 Å. The mobile phase was tetrahydrofuran (THF) freshly purified by distillation over sodium-benzophenone-ketyl. The solvent delivery reservoir was maintained under a KOH-dried helium blanket to minimize the absorption of moisture. The elution volume was calibrated to molecular weight by using 15 monodispersed polystyrene standards of 240 to 3×10^6 daltons. Measurements were performed at room temperature of 25°C. All procedures used in the preparation of samples were done in a dry box.

Vapor Phase Osmometry

The VPO measurements were performed using a Mechrolab model 301 osmometer. The solvent used was toluene, and the measurement chamber was maintained at 65.0 ± 0.2°C.

Rheometry

Shear viscosity measurements were performed on a Rheometrics Mechanical Spectrometer 605 with environmental control. A dried nitrogen blanket was used throughout the experiment, including the sample loading. The measurement temperature was maintained at 29 ± 1°C.

RESULTS AND DISCUSSION

N-methyloligosilazane (NMOP) produced by aminolysis, Reaction (2), is mixed with $Ru_3(CO)_{12}$ in a mole ratio of 5400:1. The homogeneous solution is heated at 90°C for up to 100 hours. Figure 1 shows the calibrated SEC results of aliquots removed periodically from the polymerizing medium. The starting oligomers, labeled as zero hour, are characterized by a Gaussian distribution in molecular weight with the peak at 2,100 daltons. After 10 hours of heating, a second distribution of molecular species centering around 26,000 dalton appears, and the apex of the low molecular weight peak is now shifted slightly to 2,600 daltons. The second peak grows in size with time, and a slight shoulder at about 50,000 daltons is noticeable after 20 hours of reaction. This broad, multimodal distribution in molecular weight persists throughout the reaction. Up to 65 hours, the polymer is still soluble in THF, toluene, and hexane. When the medium is allowed to react to 100 hours, however, the product is no longer completely soluble in THF, and a small amount of gel particles can be detected during filtration.

Figure 2 shows graphically the changes in molecular weights and polydispersity as a function of reaction time. The salient features of the SEC results are the initial sharp increase in M_n in the first 10 hours, a plateau region for M_n, M_w, and M_z between 10 and 65 hours, followed by a drastic increase in M_w and M_z and slight drop in M_n at 65 to 100 hours.

To facilitate discussion, we will divide the reaction kinetics into three regions. Region 1 is the initial polymerization in which bimodality in the molecular weight develops rapidly. Region 2 corresponds to the relatively slow molecular weight growth period. Region 3 corresponds to the exponential growth in M_w and M_z.

Qualitatively, the behavior in region 3 is the easiest to elucidate. It is reminiscent of behavior characterizing step-reaction polymerization of polyfunctional reactants.[5] Based on a statistical analysis of simple three-dimensional step polymerization in which all functional groups are assumed to be equally reactive and independent of molecular weight or viscosity, gelation is predicted to occur when the branching coefficient (the probability of a given functional group on a branch unit to cross-link another branch unit) reaches a critical value. One salient feature of the onset of gelation is that the value for M_n is low, but M_w becomes infinite. In other words, the polydispersity increases exponentially near gelation, which also characterizes the polysilazane polymerization reaction under investigation (Figure 2d). The onset of gelation is further confirmed by the decrease in polymer solubility after 100 hours of reaction, followed by the formation of a rubbery, highly crosslinked product at longer times.

The analysis of regions 1 and 2, on the other hand, is much more complicated. Several possible mechanisms may explain the formation of bimodality in molecular weight distribution in region 1. Before discussing these mechanisms, however, we should first examine the catalytic reactivity. One proposed hypothesis is that the ruthenium catalyst most likely activates Si-H bonds through oxidative addition as is known to occur in hydrosilylation, and then the active species is dehydrocoupled with an N-H bond to form an Si-N bond and release H_2 gas.[2] Moreover, the same ruthenium catalyst is known to be capable of cleaving Si-N bonds, but this reaction is believed to be slow at 90°C.

One proposed mechanism to explain the formation of bimodality in the molecular weight is the dependency of reactivity on molecular structure--linear, branched, or cyclic--of the starting oligomers.

Preliminary mechanistic studies suggest that the terminus Si-H bonds of MeNH-$[H_2SiNMe]_x$-H are likely to be more reactive than the internal Si-H bonds because the Si-H steric environment strongly controls reactivity; thus, chain extension of linear and branched species will be statistically favored over cyclic species. Such selectivity in active sites could give rise to a bimodal distribution in molecular weight.

As these preferred structures grow in chain length and molecular weight, the concentration of terminus Si-H bonds decreases accordingly. At the same time, the concentration of internal pendant MeNH functional groups increases. The decrease in concentration of terminal sites can cause a decrease in the chain extension kinetics, leading to the slower polymer growth of region 2. The reaction of the less reactive, internal Si-H, Si-N, and internal pendant N-H bonds may now become important because of the increasing relative concentration of the bonds. Their reaction causes an increasing degree of branching and reaction with cyclic oligomers and eventually gelation of region 3.

Another possible mechanism to account for bimodality in molecular weight is the mobility of the catalyst. $Ru_3(CO)_{12}$ forms a homogeneous catalytic species in this reaction. If, however, the active catalyst can be "trapped" inside a portion of the oligomers that the catalyst initially encounters, those species become reactive and leave the remaining species only as a supply of building blocks for the "living" polymers to grow. Immobilization of catalyst is possible by physical interference or chemical coordination of the polymer with the transition metal complex. The result of this could produce bimodality in molecular weight in region 1.

As the reactive species grow in size and lose mobility, the diffusion of oligomeric molecules to the vicinity of the activated Si-H or Si-N bonds becomes slower and could account for the plateau in growth of region 2. Gelation in region 3 would be expected because of the branching reaction. Branching can occur by internal Si-H bond activation, Si-N bond activation, or the reaction of the internal MeNH groups.

To distinguish among these plausible mechanisms, we attempted a number of experiments to increase the catalyst mobility by addition of solvent. Our preliminary results show that initially (region 1) no dramatic change occurs in the qualitative features of polymer growth. At intermediate time (region 2), however, the kinetics seems to be enhanced, and two more high molecular weight peaks develop. These results suggest that the selective reactivity mechanism may dominate in region 1 and that catalyst or chain mobility may be important in region 2 when the polymerizing mixture becomes more viscous.

The branching reaction makes the analysis of the SEC data more complicated. The hydrodynamic volume generally decreases with increasing degree of branching for a fixed molecular weight,[6] and the apparent values of M_n, M_w, and M_z measured by SEC may therefore be less than the true values. Nevertheless, the qualitative features of the molecular weights measured by SEC are not likely to be affected. As shown in Figure 2a, M_n measurements by VPO performed on similar aliquots in up to 65 hours of reaction time provide reasonable qualitative agreement with those by SEC--both results indicate decreasing reaction kinetics with time in regions 1 and 2. Quantitative agreement, however, is not very good possibly because of the insensitivity of our VPO apparatus to very high molecular weight species.

Viscosity measurements on the aliquots were also obtained. Figure 3 plots the zero shear viscosity of the polymers at $30^{o}C$ as a function of reaction time. A drastic increase in viscosity can be observed for reaction mixtures exceeding 65 hours--another classic characteristic of gelation. A study of the shear rate dependence of viscosity indicates that the properties of the reaction mixtures change from Newtonian to non-Newtonian behavior after 65 hours of reaction time; the 100-hour sample exhibits highly shear thinning properties (apparent viscosity decreases with increasing shear rate). Moreover, the first normal stress difference becomes measureable in the 100-hour sample. This is another indication of increasing non-Newtonian behavior of the reaction mixture with reaction time.

CONCLUSIONS

Despite the difficulties in analyzing SEC results due to the unknown extent of branching in the molecules, our molecular weight results are believed to be significant in revealing some information on the mechanism for polymer growth. Data analysis using the simplified statistical theory indicates that the gelation process caused by branching becomes important at reaction times after 65 hours. Viscosity and solubility data further confirm this conclusion.

On the other hand, the formation of the bimodal distribution in the beginning of the reaction (region 1), is much less understood. This development is qualitatively independent of solvent or temperature effects. It may be an indication of selective reactivity of species of certain structures in which chain extension dominates. At intermediate time (region 2), the solvent effect becomes apparent in the polymerization kinetics, indicating the importance of catalyst or molecular mobility. At later times in the reaction (region 3), polymer growth by branching must be important because of the onset of gelation.

In retrospect, the use of universal calibration, which requires additional information such as intrinsic viscosity or light-scattering measurements, could provide quantitatively more accurate elution volume-molecular weight calibration for branched polymers. In the future, such additional characterization will be required to obtain a more complete quantitation of the structural development and polymerization kinetics of multifunctional polysilazanes. Furthermore, a detailed investigation of the solvent and temperature effects will be useful.

In conclusion, this communication demonstrates the importance of molecular and structural characterization of the reacting medium to better understand the reaction mechanism of new types of polymer such as the polysilazane preceramic polymers. These characterization results will also serve as a data base for establishing structure-property-processing relationship for better molecular design of inorganic and organometallic polymers.

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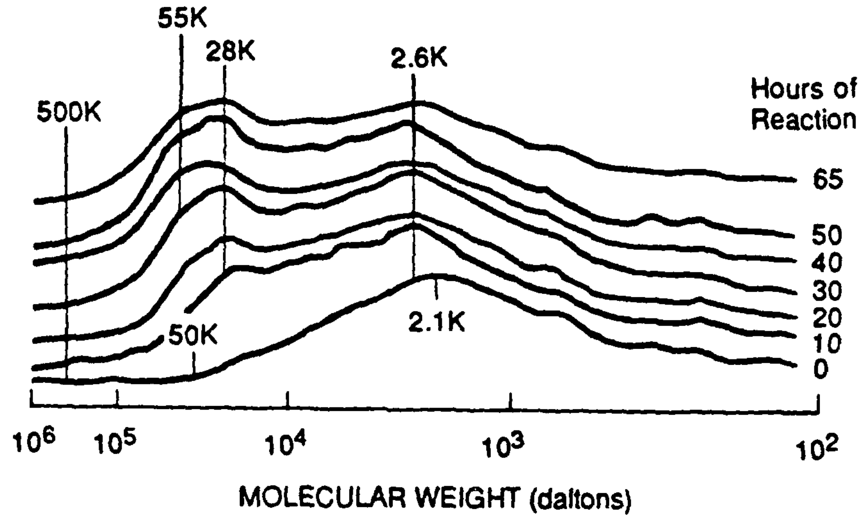
FIGURE CAPTIONS

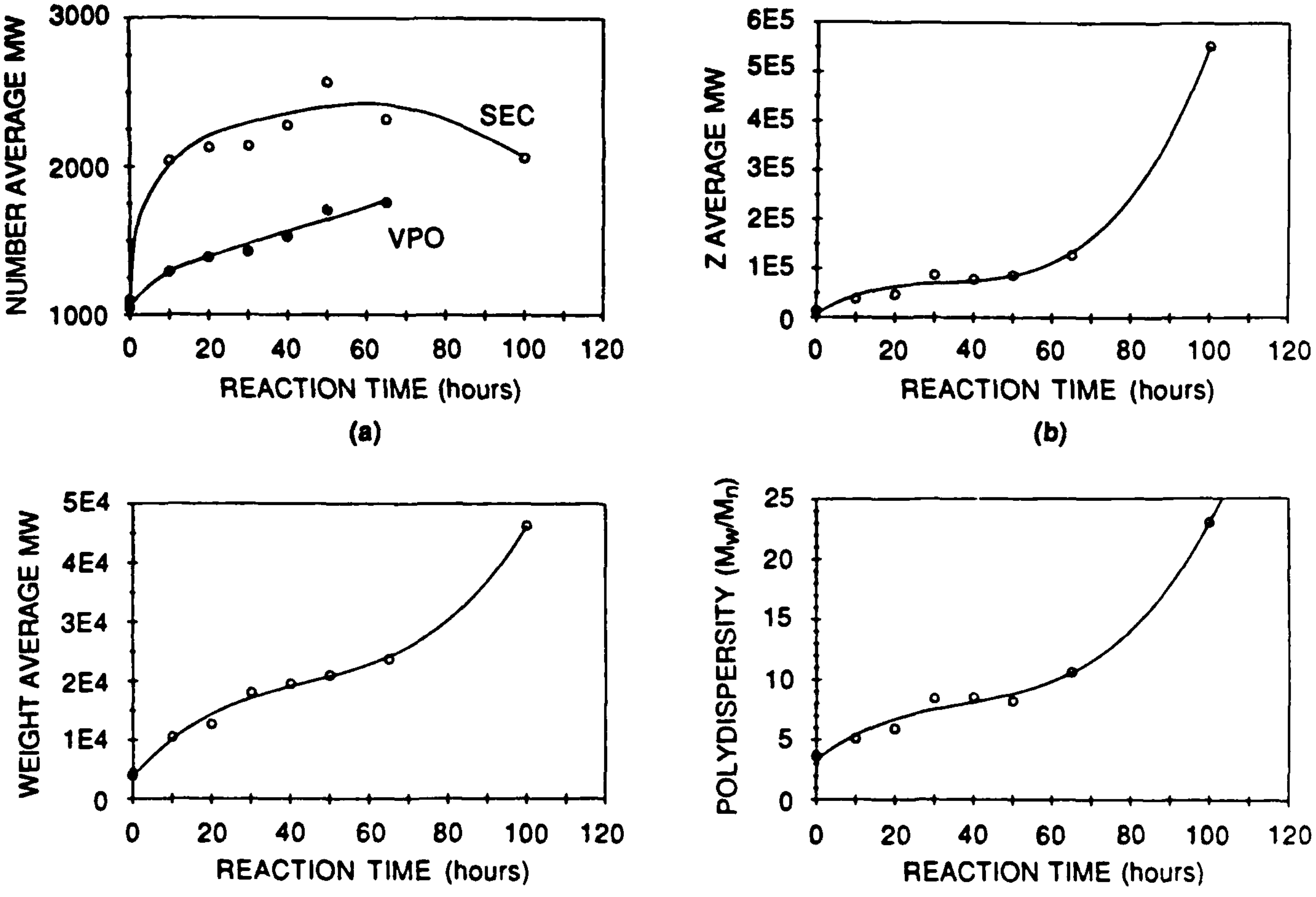
Figure 1 SEC results of $[H_2SiNMe]_x$ polymerization catalyzed by $Rn_3(CO)_{12}$. Polystyrene standards have been used to correlate elution volume to molecular weight.

Figure 2. Molecular weight distribution of polymethylsilazane determined by SEC versus reaction time.

(a) Number-average molecular weight (M_n)
(b) Weight-average molecular weight (M_w)
(c) Z-average molecular weight (M_z)
(d) Polydispersity (M_w/M_n)

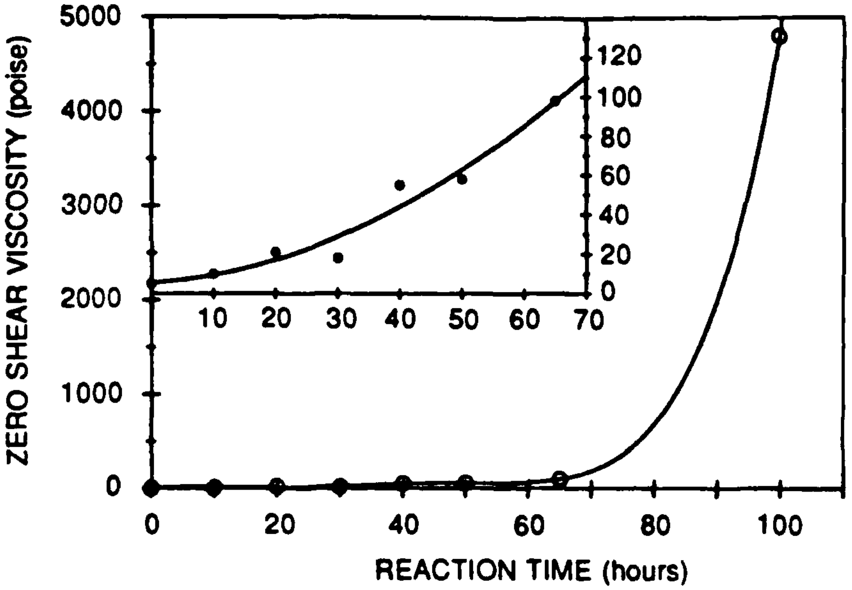
Figure 3. Zero shear viscosity of polymethylsilazane as a function of reaction time. The insert is an expanded plot of the viscosity increase in the first 70 hours of reaction.


55K
28K
2.6K
500K
Hours of Reaction
65
50
40
30
20
10
0
50K
2.1K
10^6
10^5
10^4
10^3
10^2
MOLECULAR WEIGHT (daltons)


NUMBER AVERAGE MW
3000
2000
1000
SEC
VPO
Z AVERAGE MW
6E5
5E5
4E5
3E5
2E5
1E5
0
WEIGHT AVERAGE MW
5E4
4E4
3E4
2E4
1E4
0
POLYDISPERSITY (M_w/M_n)
25
20
15
10
5
0
0
20
40
60
80
100
120
REACTION TIME (hours)

(a) **(b)**

(c) **(d)**


ZERO SHEAR VISCOSITY (poise)
5000
4000
3000
2000
1000
0
0
20
40
60
80
100
REACTION TIME (hours)
120
100
80
60
40
20
0
10
20
30
40
50
60
70

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