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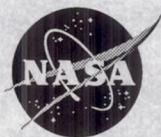
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CONVERSION OF POLYMERS OF METHYL- AND VINYLSILANE TO SIC CERAMICS

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ABSTRACT

Poly(methylsilane) and poly(vinylsilane) were synthesized using a titanocene catalyst, and their pyrolytic conversion to ceramics was followed using a combination of thermal analysis and infrared spectroscopy. The two polymers have distinctly different backbone structures, as determined by ^{29}Si NMR; methylsilane polymerizes to a polysilane, while vinylsilane polymers have a predominately polycarbosilane backbone, with some polysilane structure as well. The pyrolysis path and char yield were dependent primarily on backbone structure, with little influence of polymer molecular weight. The majority of the weight loss on conversion occurs below 650 °C, although bond rearrangement continues to 1400 °C. Poly(vinylsilane) produced a C-rich Si-C ceramic in which the carbon was dispersed on a sufficiently fine level to show resistance to oxidation on heating in air to 1400 °C.

INTRODUCTION

Use of organometallic polymers as precursors to ceramics enables fabrication techniques not attainable with more traditional powder sintering approaches, particularly in the areas of fiber and film formation and in the development of fiber reinforced ceramic matrix composites having complex shapes. The composition and structure of the precursor polymer, as well as the pyrolysis cycle and atmosphere, determine the composition and morphology of the final ceramic, as well as its physical and mechanical properties. Control of polymer structure, molecular weight and curing mechanism permits tailoring the polymer rheology for fiber spinning or composite matrix fabrication, and can determine ceramic yield and ultimate properties.

We previously¹⁻³ have reported on the synthesis and characterization of a number of polymers of alkyl and alkenylsilanes. The present work is concerned with characterizing the pyrolytic conversion of these polymers to Si-C ceramics, with the objective of understanding the relationship between polymer structure and the conversion process, as well as on ceramic stoichiometry. The intent of the work is the development of a series of polymers having tailorable rheological behavior that are suitable precursors to ceramic composite matrices and ceramic coatings.

EXPERIMENTAL

Poly(methylsilane) and poly(vinylsilane) were synthesized using a titanocene catalyst^{1, 3-6}. Two types of synthesis conditions were employed: a room temperature synthesis, for periods of nominally 30 days (condition A), and a protocol in which polymerization was started at room temperature for a period of seven days, and then continued at a temperature of 50 °C for an additional seven days (condition B). One of two solvents, tetrahydrofuran (THF) or cyclohexene, was used for polymerization.

The polymers were characterized by ¹H, ¹³C and ²⁹Si nuclear magnetic resonance to determine backbone structure, using a Bruker AC-300 NMR spectrometer and chloroform-d as the solvent. FTIR spectra of as-synthesized polymer samples were obtained using a Perkin-Elmer Model 1750 (Perkin-Elmer, Norwalk, CT) Fourier transform infrared spectrometer at a resolution of 2 cm⁻¹. Characterization of partially pyrolyzed materials was performed using standard diffuse reflectance techniques (DRIFTS).

The pyrolysis process was studied by thermogravimetry (TG) to 1400 °C, thermogravimetric analysis coupled with infrared spectroscopy of evolved gases (TG-IR) to 1000 °C, and x-ray diffraction (XRD) of polymers pyrolyzed to various final temperatures under argon atmosphere in a tube furnace.

POLYMER CHARACTERIZATION

Poly(methylsilane) was determined by NMR analysis to have a polysilane backbone structure as synthesized. Cyclic structures are not excluded based on NMR. Vinylsilane polymerization produced a mixture of polycarbosilanes, including -C-SiH₂-CH(CH₃)-Si- and -C-SiH₂-CH₂-CH₂-Si- linkages (nominally 80 percent), the remainder consisting of polysilane backbone (-Si-SiH(CH₂CH₃)-Si-) arising predominantly from dehydrogenative coupling and reduction of the double bond. No unsaturation was present in the polymer.

Typical IR spectra are shown in Figure 1. Both polymers exhibit characteristic C-H stretching between 3000 and 2700 cm⁻¹ and Si-H stretching near 2100 cm⁻¹. In poly(methylsilane) the Si-H stretching peak is asymmetric, with a maximum at 2079 cm⁻¹, indicative of a mixture of SiH and terminal SiH groups (Figure 1a). The IR spectrum for poly(vinylsilane), Figure 1b, exhibits a sharp Si-H stretching peak at 2119 cm⁻¹. Three characteristic bands are observed at 1457 (CHCH₃⁷), 1410 (SiCH₃ asymmetric bending plus possible scissoring of CH₂ groups attached to Si⁸) and 1377 cm⁻¹ (likely symmetric bending of CH₃ groups not attached to Si). Also characteristic are a pair of bands at 941 and 837 cm⁻¹ (SiH₂ bending modes). A small 1136 cm⁻¹ (Si-CH₂-CH₂-Si) peak⁷ also is observed. Peaks in the 1615-1590 cm⁻¹ range, where vinyl groups occur, were notably absent, supporting the NMR findings of no unsaturation (see above).

Synthesis from either THF or cyclohexene produced similar spectra. The relative ratios of the Si-H and C-H stretching peaks varied, with fewer Si-H groups when cyclohexene was the solvent, as observed by infrared spectroscopy, as well as by integration of the SiH region of the ¹H NMR spectra.

The influence of polymerization conditions on molecular weight is summarized in Table I. In the case of methylsilane polymers maximum molecular weights were obtained in cyclohexene under condition B. Cyclohexene polymerization also led to higher molecular weight poly(vinylsilane), although the increase was less pronounced than for poly(methylsilane),

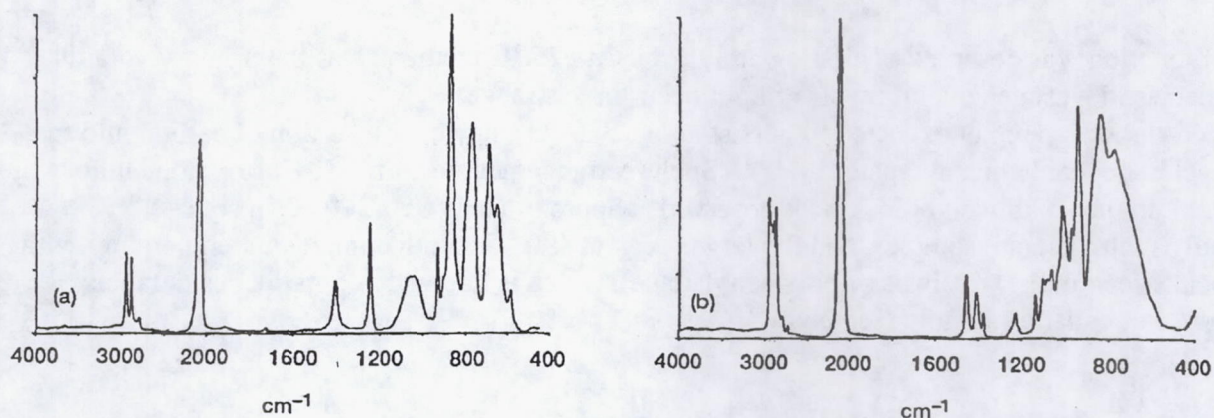


Figure 1.—Typical infrared spectra of (a) poly(methylsilane) and (b) poly(vinylsilane).

Table I. Influence of polymerization conditions on molecular weight (Daltons).

Polymer	Condition	Solvent	M_n	M_w
Methylsilane	A	THF or Cyclohexene	200-800	950-2230
	B	THF	365-760	765-1500
	B	Cyclohexene	1236, 1503*	5800, 9800*
Vinylsilane	A	THF or Cyclohexene	250-670	1170-3030
	B	THF	260-510	1080-1300
	B	Cyclohexene	370-980	1700-3900

Condition A= 30 days room temperature

B = 7 days room temperature, 7 days 50°C

*Two experiments only

possibly because the presence of the vinyl group already provides a mechanism for absorbing hydrogen formed during polymerization.

PYROLYSIS STUDIES

Poly(methylsilane)

The thermogravimetry trace of poly(methylsilane) pyrolyzed in flowing argon was characterized by a major weight loss centered at 310-325 °C with a shoulder, or sometimes a resolved derivative peak at 350-360 °C and a smaller, broad weight loss at nominally 500 °C, as shown in Figure 2. In some instances a low temperature weight loss region was seen at 135-195 °C. This lowest temperature reaction seemed to correlate with lower molecular weight polymers, and may correspond with the elimination of small cyclics.

The major loss region is shown by TG/IR to be related to evolution of mixed silanes, likely the result of cleavage of the Si-Si backbone ($D_{\text{Si-Si}} = 42 \text{ kcal/mole, } 25 \text{ }^\circ\text{C}$)⁹. Some methane

production was observed beginning at 395 °C. At 525 °C methane was the primary volatile species. Hydrogen evolution also might occur in this range⁷.

Si-Si bonds are not expected to persist above 380 °C⁷; however insertion of carbon into the backbone would be anticipated^{7, 10-12}. Such rearrangement to form -Si-C- backbone units would explain the small weight loss peak observed at approximately 350-360 °C in some poly(methylsilane) samples, and the larger peak at 490 °C. Both coincide in temperature with peaks seen in the pyrolysis of poly(vinylsilane), which is known to contain considerable polycarbosilane structure (see below).

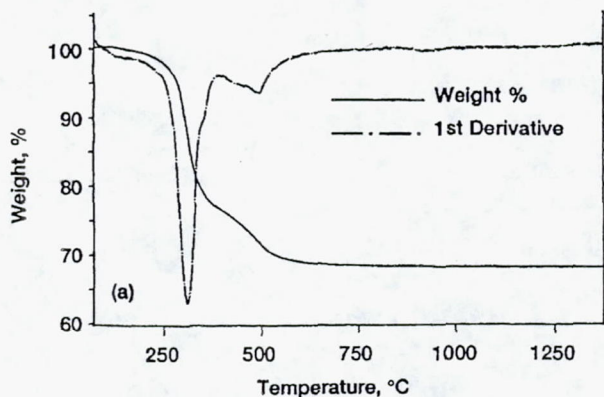


Figure 2.—Typical TG trace of poly(methylsilane) heated in flowing argon at 10 °C/min.

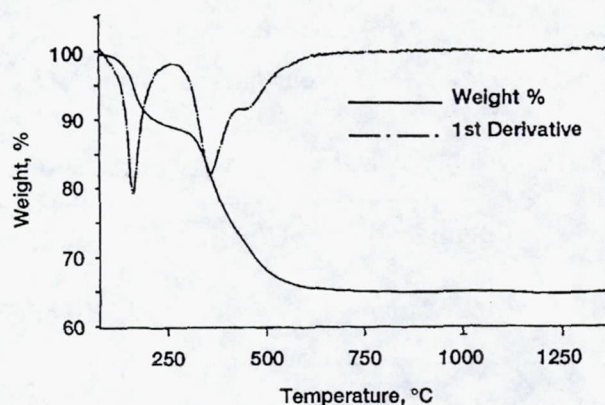


Figure 3.—Representative TG trace of poly(vinylsilane) heated in flowing argon at 10 °C/min.

Char yields at 1400 °C (30 min.) averaged 66.9 percent (standard deviation = 2.16). There was no correlation between char yield and molecular weight. XRD showed evidence of excess Si.

Poly(vinylsilane)

In contrast to the single major weight loss at 310-320 °C observed in the pyrolysis of poly(methylsilane), the TG trace for poly(vinylsilane) was characterized by two primary weight loss regions centered at 160-200 °C and 350-375 °C, and a third region overlapping the second at nominally 435-480 °C (Figure 3). A very small weight loss also is observed just above 1000 °C, which likely corresponds with elimination of hydrogen.

The infrared spectra of the evolved gases were identical in the first two areas of weight loss, and indicated silane evolution. The first of these weight loss regions is in the same temperature regime as the lowest temperature weight loss seen in poly(methylsilane), and may correspond with the evolution of cyclic silanes or small oligomers. It previously has been shown¹ that poly(vinylsilane) is comprised of a mixture of polysilane and polycarbosilane backbone structures, as determined by ²⁹Si NMR of the polymer. Absence of a substantial weight change at 310-320 °C, combined with the presence of a weight loss at 160-200 °C, suggest that the Si-Si backbone structures seen in the ²⁹Si NMR of the polymer coincide primarily with small cyclics which have been volatilized in the lower temperature range.

The second weight loss region centered at 350-375 °C (Figure 3) likely arises from cleavage of the Si-C backbone (DSi-C = 69 kcal/mole⁹). The third weight loss region centered between 400 and 500 °C corresponded with evolution of silanes and ethylene as observed by TG/IR, and

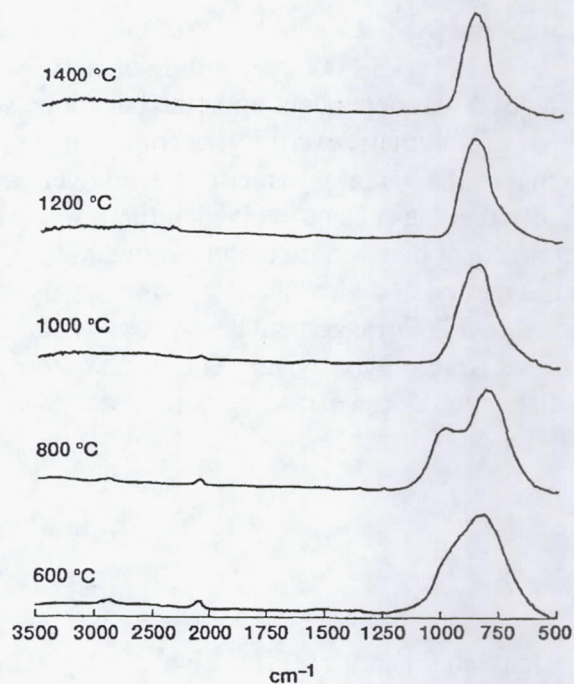


Figure 4.—DRIFTS spectra of poly (vinylsilane) pyrolyzed in a tube furnace under flowing argon to final temperatures of 600, 800, 1000, 1200 and 1400 °C.

occurs at the same temperature range as was reported for the pyrolysis of poly(silylethylene) as reported by Corriu and coworkers⁷.

DRIFTS spectra were obtained of samples pyrolyzed in a tube furnace under argon atmosphere (Figure 4). Si-H groups (2091 cm^{-1}) are seen to persist to $1000\text{ }^{\circ}\text{C}$. The Si-C peak is seen to shift from 818 cm^{-1} at $600\text{ }^{\circ}\text{C}$ to 883 cm^{-1} at $1400\text{ }^{\circ}\text{C}$, and at the same time to narrow considerably. This corresponds with formation of small SiC crystallites observed by XRD. The Si/C ratio in these materials averaged 0.82, as determined by elemental analysis. Only a slight increase in this ratio occurs in this temperature regime ($600\text{-}1400\text{ }^{\circ}\text{C}$), so that the infrared spectral changes are attributed primarily to bond rearrangement and structural ordering.

Although the ceramic product contains excess carbon, the material pyrolyzed in argon to $1400\text{ }^{\circ}\text{C}$ was extremely resistant to oxidation. Reheating the sample in the TGA in the presence of oxygen produced no change in weight. The presence of some excess carbon might actually be of benefit in the final material by inhibiting grain growth.

Char yield ($1400\text{ }^{\circ}\text{C}$, 30 min.) for poly(vinylsilane) averaged 59.57 percent (std. deviation = 0.90), and is significantly lower than the 67 percent char yield for poly(methylsilane) (at a confidence level of $\alpha = 0.001$). The differences are attributed to differences in polymer structure, and not to molecular weight.

SUMMARY AND CONCLUSIONS

Polymers of methyl- and vinylsilane have been prepared using a titanocene catalyst. While methylsilane polymerizes with a Si-Si backbone, vinylsilane produces predominantly

polycarbosilanes of mixed -Si-C- and -Si-C-C- backbone structures. The products are primarily oligomers, having a Mw range of 1,000 - 10,000, depending on solvent and polymerization conditions. Pyrolytic fragmentation was dependent upon the backbone structure, rather than molecular weight. In both types of polymers, evolution of fragments having structures identical to one another and similar to that of the parent polymer occurred over two separate temperature ranges, suggesting the possibility that the species evolved at the lower temperatures come from cyclic material, while that occurring at higher temperature is due to the cleavage of a linear, extended backbone. In both the methyl and vinylsilane polymers weight loss is mostly complete by 650 °C; however, significant bond rearrangement continues to occur to 1400 °C.

The C-rich SiC ceramic derived from poly(vinylsilane) is oxidation resistant to 1400 C, probably attributable to fine dispersion of the excess carbon.

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