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Synthesis of inorganic polymers as glass precursors and for other uses: Pre-ceramic block or graft copolymers as potential precursors to composite materials

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Pre-ceramic block or graft copolymers may offer entrée into nanocomposite ceramics provided the two homopolymers are immiscible and one can carefully control the size of the blocks or grafts. We are exploring the possibility of making copolymers from methylsilsesquioxane, —$[MeSi(O)_{1.5}]_x$—, (SiO), a precursor to 'black glass' and the polysilazane, —$[MeHSiNH]_x$—, (SiMe), a precursor to silicon carbide nitride. Our initial efforts have been directed towards delineating the chemical transformations that SiO, prepared by room-temperature catalytic redistribution of —$[MeHSiO]_x$— using Cp_2 $TiMe_2$ as the catalyst (0.1 wt %), undergoes as it is heated to 900 °C in nitrogen. We find that, although Cp_2 $TiMe_2$ will not catalyze the redistribution of SiMe at room temperature, in the presence of even small amounts of —$[MeHSiO]_x$— it is an active catalyst precursor and a copolymer can be formed. Spectra and chemical composition studies on the pyrolysis products of the copolymers and SiO are described.

Keywords: Copolymer, silicon carbide nitride, pyrolysis, chemical transformation, ceramic precursor

INTRODUCTION

The alloying or blending of one polymer with another is often used as a means of enhancing the physical and chemical properties of one or both polymers. Mixing is obtained by dissolution in a common solvent or by melt-mixing. This 'comingling' of properties is effective only if the two polymers are compatible and do not segregate (on a macroscopic level) upon heating, with time, or if they segregate only under a specific (narrow) set of conditions.

Segregation in polymer blends or alloys can sometimes be avoided through the synthesis of block or graft copolymers wherein oligomeric chains of polymer A are chemically bonded to chains of polymer B. However, if the physical properties of A and B are quite disparate, then segregation can occur on a mesoscopic (nano) scale. In some instances, mesoscopic segregation can be beneficial, especially for 'toughening' purposes.

For example, the block copolymerization of A with B, or grafting of A to B, can lead to the formation of unique three-dimensional microstructures, as illustrated by Fig. 1.[1–4] Thus, if A is the minority phase in a block or graft copolymer of A and B, then one obtains a segregated structure, as shown in the figure, in which spheres of A form in a matrix of B. The converse is true if small quantities of B oligomers are copolymerized with A oligomers. As the mole fraction of A oligomers increases relative to B oligomers one obtains, progressively, spheres, cylinders and then lamellar structures when $A \approx B$. These structures offer considerable potential for 'toughening', provided certain design criteria are met.[1–4]

The diameter and definition of the spherical and cylindrical microstructures are controlled by the polymer, the chain lengths and the polydispersity of the minority component. Likewise, the thickness and definition of each lamella is controlled by the number of monomer units in the chain segments of A and B as well as the polydispersity. Furthermore, A must be immiscible in B. If these design criteria are met, it should be possible to tailor the microstructures of block or graft copolymer shapes and thereby obtain precise control of the physical and mechanical properties of the resultant piece.

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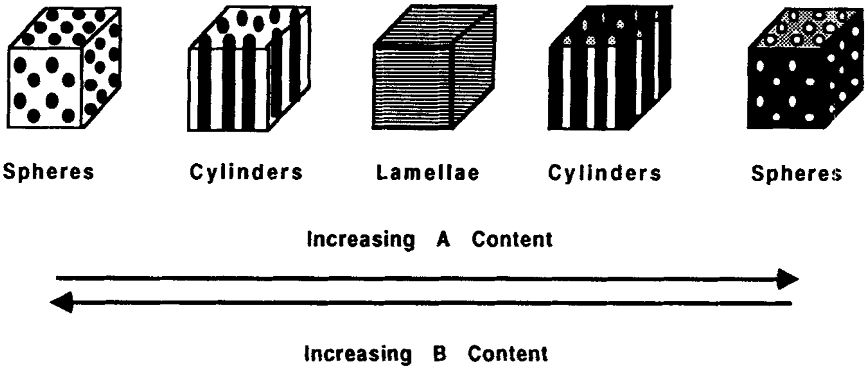

Figure 1 Effect of changes of composition on the microstructure of a block copolymer.

Extension of the concept of tailored block or graft copolymers to pre-ceramic polymers offers the unique opportunity to fabricate ceramic shapes wherein one can control the size, configuration and distribution of heterogeneities in the ceramic body by controlling the nanostructural features of the precursor polymer. Thus, small amounts of precursor oligomer A, copolymerized with oligomers of precursor B, should lead to ceramics, following pyrolysis, that have approximately spherical *reinforcing* heterogeneities. This assumes that the oligomers of A are not miscible with B and that their chain lengths and molecular weights are narrowly defined. It also assumes that segregation is maintained during pyrolysis.

To our knowledge, no one has attempted to develop pre-ceramic block or graft copolymers for the express purpose of introducing controlled heterogeneities into the resultant ceramic product. Seyferth *et al.*[5] have synthesized —$[(MeSiH)_a(MeSi)_b$ $(MeSiNH)_c(MeSiN)_d$-$(MeHSiNMe)_e]_n$— graft copolymers to adjust the composition ($SiC{:}Si_3N_4$) of the final ceramic product. However, with the exception of Seyferth *et al*'s work, little has been done to develop systems of mixed pre-ceramic polymers either by chemical linkage (grafting or copolymerization) or by physical mixture, despite the potential for forming nanocomposite materials.

The long-term objective of the work discussed here is to explore the use of pre-ceramic copolymers as a means of preparing ceramic materials with controlled heterogeneities—nanocomposite ceramics. However, to achieve this objective it is first necessary to develop two distinct pre-ceramic polymer systems wherein we can exert control of both the macromolecular properties (degree of polymerization, polydispersity, rheology) and pyrolytic selectivity to specific ceramic products. It will also be necessary to establish that physical mixtures and then copolymers of these pre-ceramics will segregate and will, when pyrolyzed, give ceramic products that maintain the pre-ceramic segregation. Furthermore, we must also develop methods of characterizing both the pre-ceramics and the expected amorphous ceramic products so that we can identify the individual product phases. Finally, the choice of both pre-ceramics must be such that on pyrolysis they do not react to form a third ceramic material.

To this end, we are exploring the use of two types of pre-ceramic polymers. One, based on —$[MeHSiO]_x$—, when catalytically polymerized and pyrolyzed to 900 °C, gives 'black glass', which consists primarily of species of the type SiC_xO_{4-x} where x is normally in the range of 1–2. The second pre-ceramic is the nitrogen analog, —$[MeHSiNH]_x$—, (SiMe), which when pyrolyzed to 900 °C gives an amorphous ceramic which consists of species of the type SiC_xN_{4-x} where x is typically in the range of 1–2. In this paper, we discuss our preliminary studies on the pyrolysis and characterization of the black glass precursors, and results of our studies on pyrolysis of that precursor with the SiMe polysilazane, —$[MeHSiNH]_x$—. The synthetic and experimental details have been already been described in detail.[6,7]

RESULTS AND DISCUSSION

Alkyl silsesquioxanes, —$[RSi(O)_{1.5}]_x$–, prepared by sol–gel processing of alkylsiloxanes, $RSi(OEt)_3$, have been studied by Fox and co-workers[8,9] as precursors to silicon carbide powders and to silicon-carbide-reinforced black glass (reaction [1]).

$$\mathrm{RSi(OEt)_3 + 1.5H_2O \xrightarrow{\text{catalyst = acid}} 3EtOH + —[RSi(O)_{1.5}]_x—} \qquad [1]$$

Kamiya *et al.*[10] have recently described the use of methyl silsesquioxane as a precursor for the processing of nitrided glass fibers. Zhang and Pentano[11] are currently exploring the utility of black glasses as a matrix for the fabrication of graphite fiber composites.

Our recent discovery[12–14] that dimethyltitanocene-derived catalysts can be used to catalyze the redistribution of hydridosiloxanes (reaction [2]), at room temperature, prompted us to consider using the same system as in reaction [3], to produce the silsesquioxane, $—[\mathrm{MeSi(O)_{1.5}}]_x—$ from $—[\mathrm{MeHSiO}]_x—$.

$$\mathrm{MeHSi(OEt)_2 \xrightarrow{Cp_2TiMe_2/RT} MeSiH_3 + MeSi(OEt)_3} \qquad [2]$$

$$\mathrm{—[MeHSiO]_x— \xrightarrow{Cp_2TiMe_2/RT} \tfrac{1}{3}x\ MeSiH_3 + —[MeSi(O)_{1.5}]_{2x/3}—} \qquad [3]$$

Furthermore, the tetrameric and pentameric cyclomers of $—[\mathrm{MeHSiO}]_x—$, or well-defined (by DP or M_n) linear chain analogs, are commercially available (Hüls). This suggested that these species, when used in conjunction with reaction [3], might serve as a potential second pre-ceramic system with the well-studied SiMe polysilazane system[5, 7, 15–17] to test the feasibility of the block copolymer approach to nanocomposite structures. Of importance to our above stated goal is the fact that the siloxane precursor is not miscible with either $—[\mathrm{MeHSiNH}]_x—$ or the isostructural $—[\mathrm{H_2SiNMe}]_x—$.[7]

Methylsilsequioxane

Our first objective was to define the pyrolysis characteristics of the methylsilsesquioxane, $—[\mathrm{MeSi(O)_{1.5}}]_x—$, produced in reaction [3] (the silsesquioxane can contain up to 25% residual MeHSiO groups). We have studied the chemical evolution of $—[\mathrm{MeSi(O)_{1.5}}]_x—$ during pyrolysis from 25 °C to 1000 °C by chemical analysis and diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS). A good portion of this work is reported elsewhere;[5] however, the DRIFTS data shown in Fig. 2 are pertinent to the present work. The most useful absorption bands are those that correspond to ν(O–H) (3250–3600 cm^{-1}, ν(C–H) (2750–3000 cm^{-1}) and ν(Si–H) (2100–2230 cm^{-1}) (from residual MeHSiO groups). The starting polymer has no bands attributable to an O–H stretching frequency, as expected, given that reaction [3] does not involve hydrolysis.

As the polymer is heated from 25 to 600 °C, very little change is observed in the shapes of these peaks; however, the Si–H bonds diminish with increasing temperature. By 600 °C, the peak corresponding to ν(Si–H) disappears and some broadening of the C–H peak is observed as the polymer undergoes extensive crosslinking which 'freezes' individual polymer chain segments in multiple conformations. What is extremely intriguing is that as the polymer is heated to 800 °C, Si–H peaks reappear at 2200 and 2250 cm^{-1}. Coincident with the reappearance of Si–H bonds, we also see the formation of a broad peak corresponding to *n* O–H. This was verified by exchange with $\mathrm{D_2O}$, which shifts a good portion of the O–H stretching vibrations to 2400 cm^{-1} [ν(O–D)].

The disappearance of Si–H bonds in the 600 °C intermediate suggests that this material contains only Si–O, Si–C, C–H and possible Si–Si bonds. Therefore, we must conclude that the reappearance of Si–H bonds and the appearance of O–H bonds in the 800 °C intermediate results as a consequence of the reaction of C–H bonds with Si–O bonds. We assume that Si–C bonds are formed coincidentally with the formation of the Si–H and O–H bonds. This then is evidence for the first chemical steps in the carbothermal reduction of silica by hydrocarbons. In addition, it also partially delineates the reaction pathway(s) whereby SiC is formed during the pyrolysis of $—[\mathrm{MeSi(O)_{1.5}}]_x—$. Of primary importance is the fact that we have a partial picture of the decomposition pattern of the $—[\mathrm{MeSi(O)_{1.5}}]_x—$ polymer for use in characterizing the decomposition patterns of any potential copolymer.

SiMe polysilazane

A number of researchers[5, 6, 15, 18–21] have previously shown that pyrolysis of the SiMe polysilazane, $—[\mathrm{MeHSiNH}]_x—$, leads to the formation at 900 °C in nitrogen) of silicon carbide nitride. Typical DRIFTS spectra are shown in Fig. 3.[16]

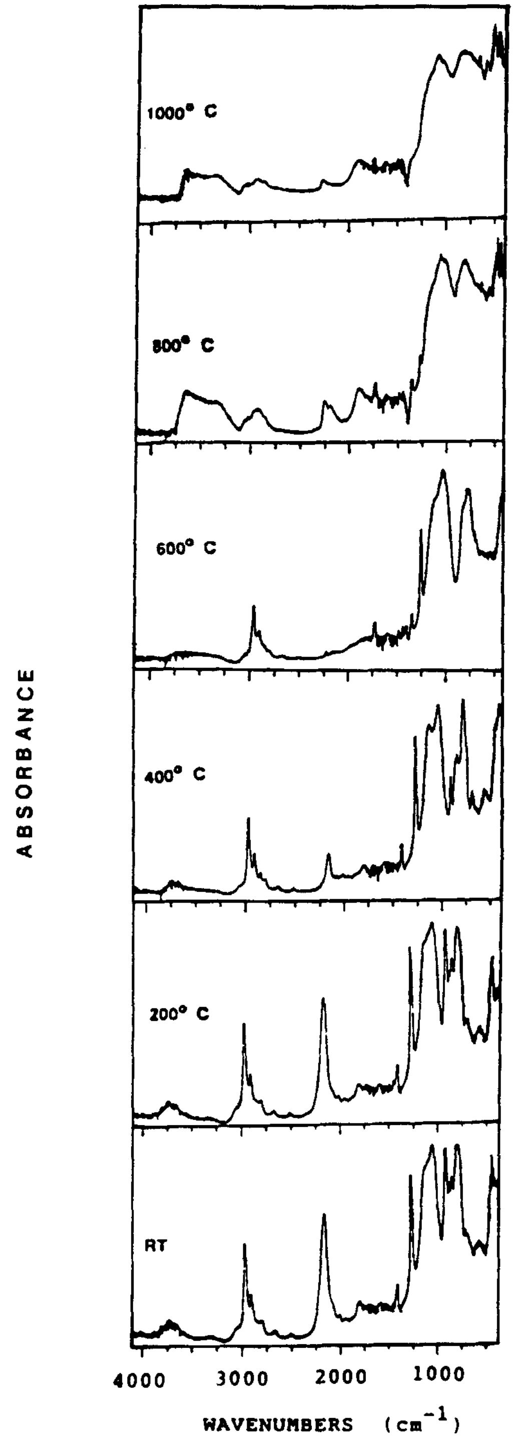

Figure 2 DRIFT spectra for samples of —[MeSi(O)$_{1.5}$]$_x$— pyrolyzed under nitrogen to various temperatures. Precursor prepared by reaction of —[MeHSiO]$_x$— ($M_n \approx 2000$ D) with 0.1 wt% Cp_2TiMe_2 catalyst at room temperature.

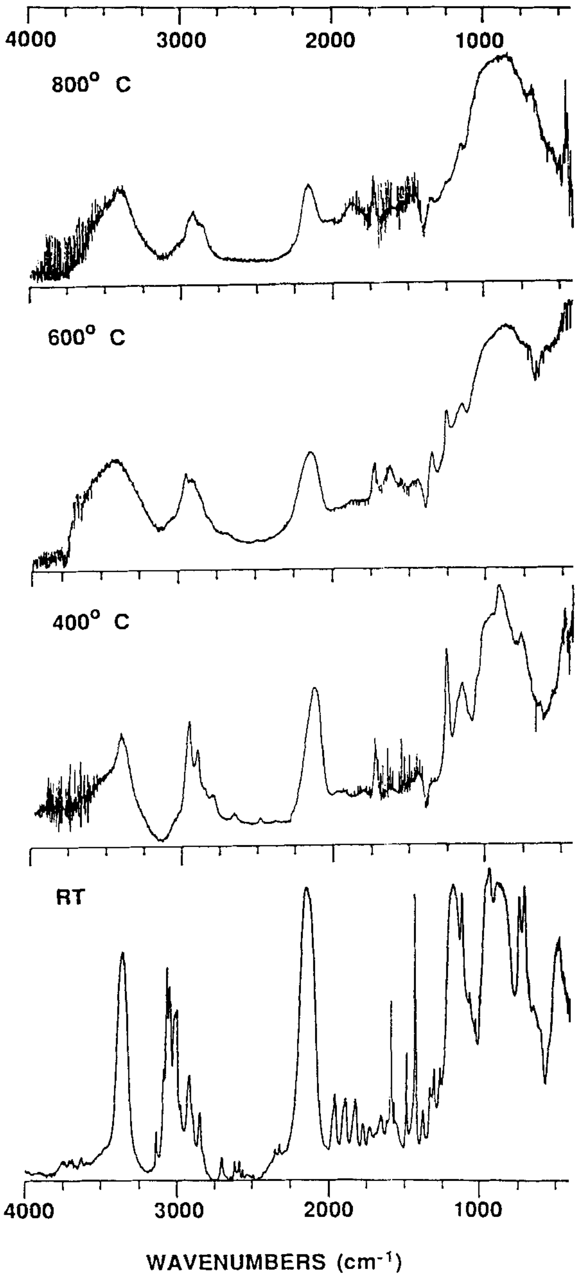

Figure 3 DRIFT spectra for samples of —[MeHSiNH]$_x$— pyrolyzed under nitrogen to various temperatures. Precursor prepared by reaction of —[MeHSiNH]$_x$— ($M_n \approx 600$ D) with 0.1 wt% $Ru_3(CO)_{12}$ catalyst at 40 °C for 48 h.

Unlike the DRIFTS studies of the —[MeSi(O)$_{1.5}$]$_x$— pyrolytic intermediates, the SiMe intermediates do not exhibit any noteworthy chemical changes apart from the typical broadening of the ν(N–H) and ν(C–H) peaks as the polymer becomes progressively more cross-linked (200–400 °C), chars (400–600 °C), and eventually becomes a true ceramic material (>600 °C). One difference between the SiMe spectra and the SiO spectra is that the ν(Si–H) peaks diminish but never really disappear, even at 800 °C.

Based on the spectra shown in Fig 2 and 3, it is not clear that we can use DRIFTS as the sole analytical tool with which to follow the chemical evolution of physical mixtures of the two pre-ceramics or true copolymers. Furthermore, studies[18, 19, 22] on the pyrolysis of polymers of the general type $\text{—[Me(NH)}_{0.5}\text{SiO]}_x\text{—}$ under nitrogen and especially under ammonia, show that the major product formed is silicon oxynitride (Si_2ON_2). Thus, it is quite possible that Si_2ON_2 will be one of the products formed upon pyrolysis of mixtures of the two-ceramics.

However, our initial objectives are: (1) to establish whether or not it is feasible to form copolymers from the two precursors we have chosen to study; and (2) to determine whether or not we can obtain defined microstructures from physical mixtures or copolymers of two inorganic polymers. Furthermore, even if these precursors do eventually produce silicon oxynitride upon pyrolysis, we are interested in following the kinetics of formation as a function of temperature, especially from segregated phases.

With this in mind, we sought to establish the reactivity of the SiMe polysilazane with Cp_2TiMe_2. After repeated attempts, we were unable to obtain any type of catalysis. Thus, we assumed that the addition of catalytic amounts of Cp_2TiMe_2 to *well-stirred* physical mixtures of the SiMe polysilazane ($M_n \approx 500$–600 D) and $\text{—[MeHSiO]}_x\text{—}$ ($M_n \approx 2000$ D) would cause only the latter to polymerize. We also assumed that the TGA of a mixture of equivalent amounts of $\text{—[MeHSiNH]}_x\text{—}$ and $\text{—[MeHSiO]}_x\text{—}$ would give an average ceramic yield for the two polymers.

Figure 4 shows the TGA data for pure $\text{—[MeHSiNH]}_x\text{—}$ and $\text{[MeSi(O)}_{1.5}]_x\text{—}$ and for a 1:1 molar mixture of $\text{—[MeHSiNH]}_x\text{—}$ and $\text{—[MeHSiO]}_x\text{—}$ treated with Cp_2TiMe_2

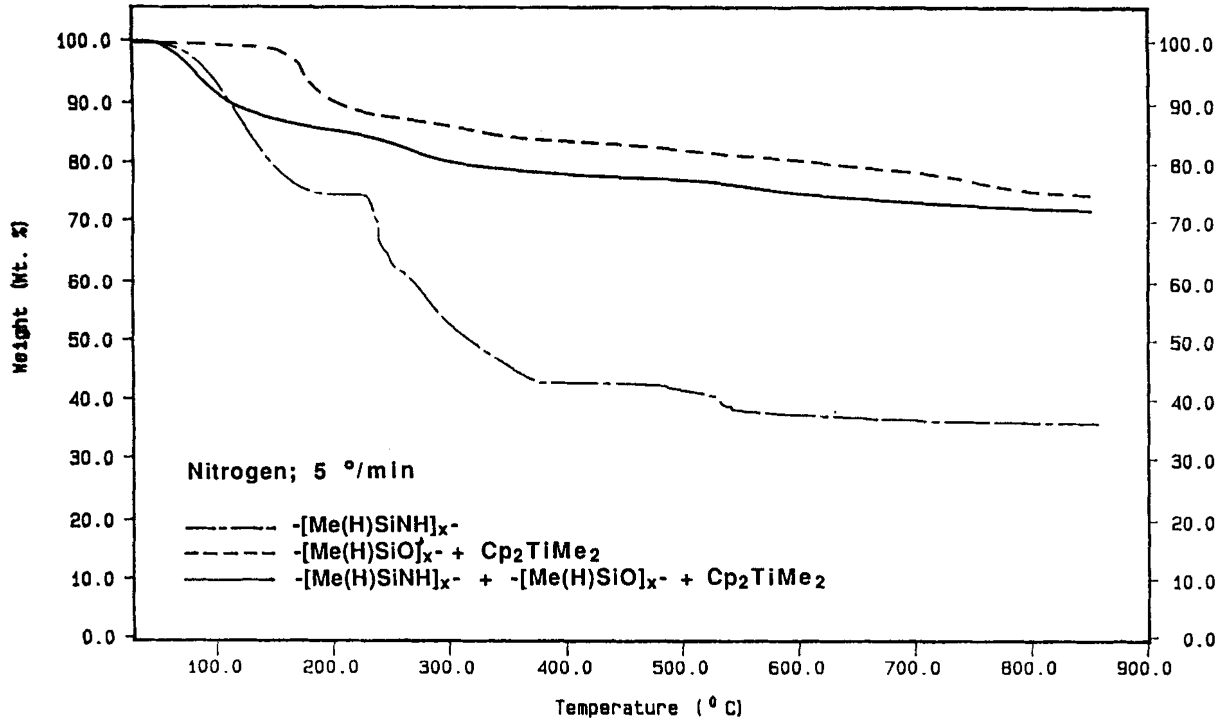

Figure 4 Thermogravimetric analysis of $\text{—[MeSi(O)}_{1.5}]_x\text{—}$ (a), $\text{—[MeHSiNH]}_x\text{—}$ (c) and a 1:1 copolymer of $\text{—[MeHSiNH]}_x\text{—}$ and $\text{—[MeSi(O)}_{1.5}]_x\text{—}$ (b). Pyrolyzed under nitrogen at a heating rate of 5 °C min^{-1}. SiO precursor and SiMe/SiO copolymer precursor prepared by reaction of $\text{—[MeHSiO]}_x\text{—}$ or a $\text{—[MeHSiO]}_x\text{—/—[MeHSiNH]}_x\text{—}$ mixture with 0.1 wt% Cp_2TiMe_2 catalyst at room temperature.

(0.1 mol %). The 900 °C ceramic yield for pure —$[MeHSiNH]_x$— is 37%, as expected for this molecular weight.[7] The 900 °C ceramic yield for —$[MeSi(O)_{1.5}]_x$—, produced by Cp_2TiMe_2— catalyzed polymerization of —$[MeHSiO]_x$—, averages about 76–80%.[6] The numerical average expected from a 1:1 equimolar mixture of the two would be 56–58%. As seen in Fig. 4, the catalytically transformed 1:1 equimolar mixture gives a polymer with a ceramic yield of approximately 74–76%, which is contrary to what is expected. In fact, it suggests that, in the presence of siloxane, the catalyst is now able to polymerize the polysilazane. To test this possibility and to determine whether or not we could make a range of copolymeric mixtures, we attempted to copolymerize various ratios of —$[MeHSiNH]_x$— (SiMe) to —$[MeHSiO]_x$— (HSiO).

Table 1 records the ceramic yields for 1:1, 3:1, 9:1 and 19:1 molar ratios of SiMe to HSiO (0.1 mol % Cp_2TiMe_2). These yields are all higher than the ceramic yield of pure SiMe polysilazane. We conclude that we have found an approach to polymerizing the SiMe alone. One simply needs a certain amount of the hydridosiloxane, which probably generates the active ligand/catalyst. We are currently attempting to determine the lower limit of hydridosiloxane required to generate the true active SiMe polymerization catalyst and to independently synthesize the catalyst.

Given that SiMe is the major component in all but the 1:1 version, these results indicate that we can successfully copolymerize the two preceramics. Tables 1 and 2 list the apparent ceramic compositions following pyrolysis of the preceramics to 900 °C in nitrogen. The apparent ceramic compositions reported in Table 1 are based on the assumption that pyrolysis of the copolymers leads to the formation of the ceramic products normally found for the individual preceramics. Table 2 lists apparent ceramic compositions that are calculated on the assumption that silicon oxynitride is formed as the major ceramic product.

Table 1 Apparent ceramic compositions[a] for copolymers of SiMe and SiO assuming that Si_2ON_2 does not form

SiMe:HSiO	Ceramic yield (wt%)	Si_3N_4	SiC	SiO_2	C
0:1	78	—	19	70	10
1:0	37	65	24	—	10
1:1	72	31.3	19.7	38.2	10.4
3:1	62	43.1	19.8	26.7	9.9
9:1	61	52.8	22.1	14.2	10.1
19:1	61	62.0	19.4	7.3	10.7

[a] Apparent compositions based on silicon as the limiting element. Precursors pyrolyzed to 900 °C in nitrogen.

Table 2 Apparent ceramic compositions[a] for copolymers of SiMe and SiO assuming that Si_2ON_2 forms

SiMe:HSiO	Si_2ON_2	Si_3N_4	SiC	SiO_2	C
1:1	44.7	0.0	19.7	24.8	10.4
3:1	61.6	0.0	19.9	8.2	9.9
9:1	47.5	19.6	22.1	0.0	10.1
19:1	24.3	45.0	19.4	0.0	10.7

[a] Apparent compositions based on silicon as the limiting element. Precursors pyrolyzed to 900 °C in nitrogen.

Because the 900 °C ceramic products we obtain for the SiMe/SiO pre-ceramic mixtures are amorphous, it has not been possible to use X-ray powder diffractometry to determine whether their apparent ceramic compositions are best represented by those listed in Table 1 or Table 2. Furthermore, heating to higher temperatures, to obtain crystallization, will surely lead to formation of Si_2ON_2; therefore, use of this characterization method would be invalid.

The DRIFTS spectra for the 1:1 mixture (Fig. 5) offer some insight into what is probably ocurring in the polymerized species. Comparison with the spectra in Figs 2 and 3 shows some substantial differences, especially in the 600–800 °C range. There is one especially large peak at approximately 1780 cm^{-1}. We submit that this may be an amido $\nu(C{=}O)$ species trapped in the matrix. The set of spectra shown in Fig. 5 are distinctly different from the spectra found in Figs 2 and 3. This implies that segregation is not maintained even at temperatures as low as 600 °C, and the copolymer system is likely to be a useful precursor to Si_2ON_2-type materials but is probably not a useful model of a block or graft copolymer.

One important observation made in these studies is that under some conditions it is possible to use a titanium-based catalyst to polymerize the SiMe polysilazane *at room temperature*. We are pursuing this system as an alternative to the ruthenium-based catalysts we have used until recently.[7]

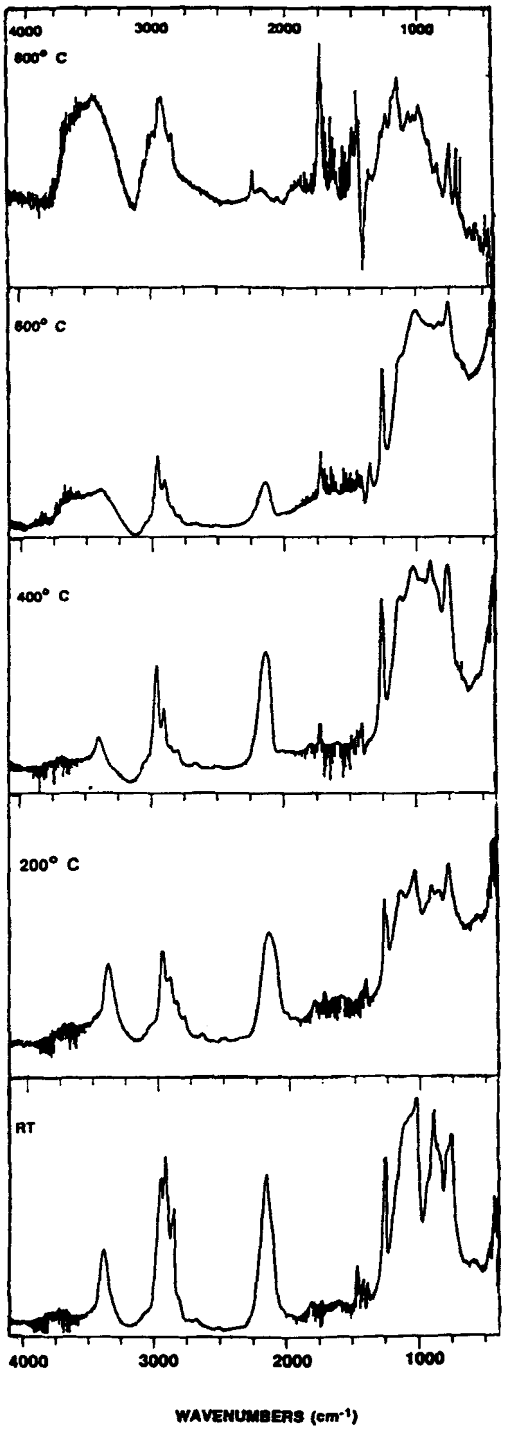

Figure 5 DRIFT spectra for samples of SiMe/HSiO copolymer precursor pyrolyzed under nitrogen to various temperatures. Precursor prepared by reacton of a 1:1 equimolar —$[MeHSiO]_x$—/$[MeHSiNH]_x$— mixture with 0.1 wt% Cp_2TiMe_2 catalyst at room temperature.

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