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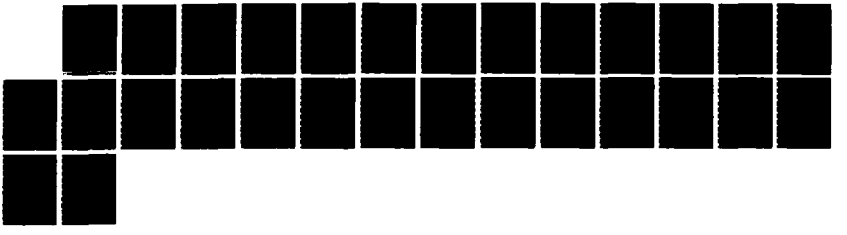

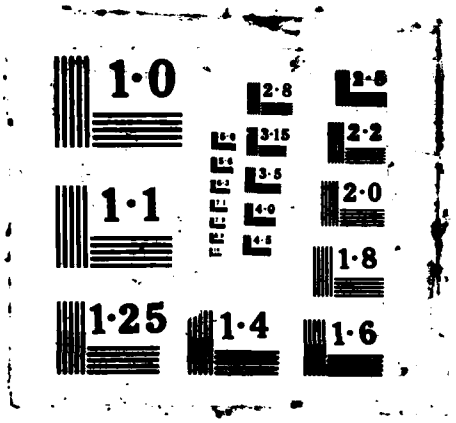
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ORGANOSILICON POLYMERS AS PRECURSORS FOR SILICON-CONTAINING CERAMICS

by

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Following general comments about the preceramic polymer approach to the preparation of ceramic materials, we describe the preparation of a novel polysilazane by dehydrocyclodimerization of the ammonolysis product of CH_3SiHCl_2, the conversion of such polymers to ceramic products and their use in upgrading polysilanes of type $[(CH_3SiH)_x(CH_3Si)_y]_n$ and $[CH_3Si(H)CH_2]_n$ to more useful ceramic precursors.

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ABSTRACT

Following general comments about the preceramic polymer approach to the preparation of ceramic materials, we describe the preparation of a novel polysilazane by dehydrocyclodimerization of the ammonolysis product of CH_3SiHCl_2, the conversion of such polymers to ceramic products and their use in upgrading polysilanes of type $[(CH_3SiH)_x(CH_3Si)_y]_n$ and $[CH_3Si(H)CH_2]_n$ to more useful ceramic precursors.

INTRODUCTION AND GENERAL COMMENTS

Silicon-containing ceramics include the oxide materials, silica and the silicates; the binary compounds of silicon with non-metals, principally silicon carbide and silicon nitride; silicon oxynitride and the sialons; main group and transition metal silicides, and, finally, elemental silicon itself. There is a vigorous research activity throughout the world on the preparation of all of these classes of solid silicon compounds by the newer preparative techniques. In this report we will focus on silicon carbide and silicon nitride.

Silicon carbide, SiC [1] and silicon nitride, Si_3N_4 [2], have been known for some time. Their properties, especially their high thermal and chemical stability, their hardness, their high strength, as well as other properties have led to useful applications for both of these materials. Silicon carbide has been an article of commerce since the development of the Acheson process for its manufacture just

before the turn of the century, but silicon nitride is a relative newcomer as far as commercial utilization goes [3].

The "conventional" methods for the preparation of SiC and Si_3N_4, the high temperature reaction of fine grade sand and coke (with additions of sawdust and NaCl) in an electric furnace (the Acheson process) for the former and usually the direct nitridation of elemental silicon or the reaction of silicon tetrachloride with ammonia (in the gas phase or in solution) for the latter, do not involve soluble or fusible intermediates. For many applications of these materials this is not necessarily a disadvantage (e.g., for the application of SiC as an abrasive), but for some of the more recent desired applications soluble or fusible (i.e., processable) intermediates are required.

The need for soluble or fusible precursors whose pyrolysis will give the desired ceramic material has led to a new area of macromolecular science, that of preceramic polymers [4]. Such polymers are needed for a number of different applications. Ceramic powders by themselves are difficult to form into bulk bodies of complex shape. Although ceramists have addressed this problem using the more conventional ceramics techniques with some success, preceramic polymers could, in principle, serve in such applications, either as the sole material from which the shaped body is made or as a binder for the ceramic powder from which the shaped body is to be made. In either case, pyrolysis of the green body would then convert the polymer to a ceramic material, hopefully of the desired composition. In the latter alternative, shrinkage during pyrolysis should not be great, but when the green body is made entirely of preceramic polymer, shrinkage on pyrolysis could be considerable.

Ceramic fibers of diverse chemical compositions are sought for application in the production of metal-, ceramic-glass- and polymer-matrix composites [5]. The presence of such ceramic fibers in a matrix, provided they have the right length-to-diameter ratio and are distributed uniformly throughout the matrix, can result in very considerable increases in the strength (i.e., fracture toughness) of the resulting material. To prepare such ceramic fibers, a

suitable polymeric precursor is needed (which can be spun by melt-spinning, dry-spinning, or wet-spinning techniques) to fibers which then can be pyrolyzed (with or without a prior cure step).

Some materials with otherwise very useful properties such as high thermal stability and great strength and toughness are unstable with respect to oxidation at high temperatures. A notable example of such a class of materials is that of the carbon-carbon composites. If these materials could be protected against oxidation by infiltration of their pores and the effective coating of their surface by a polymer whose pyrolysis gives an oxidation-resistant ceramic material, then one would have available new dimensions of applicability of such carbon-carbon composite materials.

In order to have a <u>useful</u> preceramic polymer, considerations of structure and reactivity are of paramount importance. Not every inorganic or organometallic polymer will be a useful preceramic polymer. Some more general considerations merit discussion. Although preceramic polymers are potentially "high value" products <u>if</u> the desired properties result from their use, the more generally useful and practical systems will be those based on commercially available, relatively cheap starting monomers. Preferably, the polymer synthesis should involve simple, easily effected chemistry which proceeds in high yield. The preceramic polymer itself should be liquid or, if a solid, it should be fusible and/or soluble in at least some organic solvents, i.e., it should be processable. It would simplify matters if the polymer were stable on storage at room temperature and stable toward atmospheric oxygen and moisture. Its pyrolysis should provide a high yield of ceramic residue and the pyrolysis volatiles preferably should be non-hazardous and non-toxic. In the requirement of high ceramic yield, economic considerations are only secondary. If the weight loss on pyrolysis is low, shrinkage will be minimized as will be the destructive effects of the gases evolved during the pyrolysis.

There are important considerations as far as the chemistry is concerned. First, the design of the preceramic

polymer is of crucial importance. Many linear organometallic and inorganic polymers, even if they are of high molecular weight, decompose thermally by formation and evolution of small cyclic molecules, and thus the ceramic yield is low. In such thermolyses, chain scission is followed by "back-biting" of the reactive terminus thus generated at a bond further along the chain. Thus high molecular weight, linear poly(dimethylsiloxanes) decompose thermally principally by extruding small cyclic oligomers, $(Me_2SiO)_n$, n = 3,4,5 . . . When a polymer is characterized by this type of thermal decomposition, the ceramic yield will be low and it will be necessary to convert the linear polymer structure to a cross-linked one by suitable chemical reactions prior to its pyrolysis. In terms of the high ceramic yield requirement, the ideal preceramic polymer is one which has functional substituent groups which will give an efficient thermal cross-linking process so that on pyrolysis non-volatile, three-dimensional networks-- which lead to maximum weight retention--are formed. Thus, preceramic polymer design requires the introduction of reactive or potentially reactive functionality.

In the design of preceramic polymers, achievement of the desired elemental composition in the ceramic obtained from them (SiC and Si_3N_4 in the present cases) is a major problem. For instance, in the case of polymers aimed at the production of SiC on pyrolysis, it is more usual than not to obtain solid residues after pyrolysis which, in addition to SiC, contain an excess either of free carbon or free silicon. In order to get close to the desired elemental composition, two approaches have been found useful in our research: (1) The use of two comonomers in the appropriate ratio in preparation of the polymer, and (2) the use of chemical or physical combinations of two different polymers in the appropriate ratio.

Preceramic polymers intended for melt-spinning require a compromise. If the thermal cross-linking process is too effective at relatively low temperatures (100-200°C), then melt-spinning will not be possible since heating will induce cross-linking and will produce an infusible material prior to the spinning. A less effective cross-linking process is

required so that the polymer forms a stable melt which can be extruded through the holes of the spinneret. The resulting polymer fiber, however, must then be "cured", i.e., cross-linked, chemically or by irradiation, to render it infusible so that the fiber form is retained on pyrolysis. Finally, there still are chemical options in the pyrolysis step. Certainly, the rate of pyrolysis, i.e., the time/temperature profile of the pyrolysis, is extremely important. However, the gas stream used in the pyrolysis also is of great importance. One may carry out "inert" or "reactive" gas pyrolyses. An example of how one may in this way change the nature of the ceramic product is provided by one of our preceramic polymers which will be discussed in more detail later in this paper. This polymer, of composition $[(CH_3SiHNH)_a(CH_3SiN)_b]_m$, gives a <u>black</u> solid, a mixture of SiC, Si_3N_4, and some free carbon, on pyrolysis to 1000°C in an inert gas stream (nitrogen or argon). However, when the pyrolysis is carried out in a stream of ammonia, a <u>white</u> solid remains which usually contains less than 0.5% total carbon and is essentially pure silicon nitride. At higher temperatures (>400°C), the NH_3 molecules effect nucleophilic cleavage of the Si-C bonds present in the polymer and the methyl groups are lost as CH_4. Such chemistry at higher temperatures can be an important and sometimes useful part of the pyrolysis process.

The first useful organosilicon preceramic polymer, a silicon carbide precursor, was developed by S. Yajima and his coworkers at Tohoku University in Japan [6]. The chemistry leading to the Yajima polycarbosilane has been described in the paper of Bacqué, Pillot, Birot and Dunogués. As might be expected on the basis of the 2 C/1 Si ratio of the $(CH_3)_2SiCl_2$ starting material, the ceramic fibers contain free carbon as well as silicon carbide. A typical analysis [6] showed a composition 1 SiC/0.78 C/0.22 SiO_2. (The latter is introduced in the oxidative cure step of the polycarbosilane fiber).

The Yajima polycarbosilane, while it was one of the first, is not the only polymeric precursor to silicon carbide which has been developed. Another useful system which merits mention is the polycarbosilane which resulted

from research carried out by C.L. Schilling and his coworkers in the Union Carbide Laboratories in Tarrytown, New York [7].

NEW PRECERAMIC POLYMER SYSTEMS: RESEARCH AT M.I.T.

Our own research has been aimed at polymer precursors for silicon nitride, silicon carbide as well as SiC/Si_3N_4 combinations.

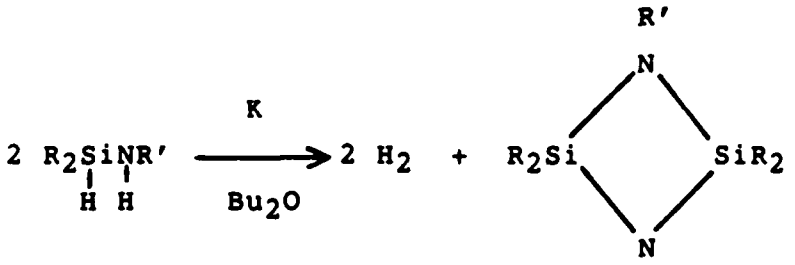
Our initial work involved the preparation of polysilazanes by the ammonolysis of dichlorosilane [8], but a useful product did not result. Our further studies of the polysilazanes obtained using methyldichlorosilane as starting material were more successful and useful preceramic polymers were obtained [9].

Methyldichlorosilane is commerically available; it is a by-product of the "Direct Process", the high temperature, copper-catalyzed reaction of methyl chloride with elemental silicon and it is potentially inexpensive. The ammonolysis of CH_3SiHCl_2 has been reported to give a mixture of cyclic and (possibly) linear oligomers, $[CH_3SiHNH]_x$ [10]. The ammonolysis product, after removal of the precipitated NH_4Cl which also is produced, can be isolated as a clear, mobile liquid in high yield. Its C, H and N analysis and its spectroscopic (^1H NMR, IR) data are in agreement with the $[CH_3SiHNH]_x$ formulation. Molecular weight determinations (cryoscopy in benzene) of several preparations ranged from 280-320 g/mol ($x = 4.7$-5.4). The product is quite stable at room temperature, but it is sensitive to moisture and must be protected from the atmosphere. This mixture of $[CH_3SiHNH]_x$ oligomers is not suitable for ceramics preparation without further processing. On pyrolysis to 1000°C in a stream of nitrogen the ceramic yield is only 20%. Clearly, it is necessary to convert these cyclic $[CH_3SiHNH]_x$ oligomers to material of higher molecular weight.

The conversion of the cyclopolysilazanes obtained by ammonolysis of diorganodichlorosilanes was investigated by Rochow and his coworkers some years ago when there was

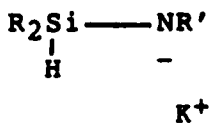
interest in polysilazanes as polymers in their own right [11]. Their procedure, the ammonium salt-induced polymerization, which in the case of hexamethyl-cyclotrisilazane appears to give polymers containing both linear and cyclic components, was applied to the CH_3SiHCl_2 ammonolysis product. It produced a very viscous oil of higher molecular weight, but the ceramic yield obtained in pyrolysis was a disappointing 36%. The $Ru_3(CO)_{12}$-catalyzed ring-opening polymerization of cyclo-$[(CH_3)_2SiNH]_4$, reported recently by Zoeckler and Laine [12], could not be adapted to the conversion of the $[CH_3SiHNH]_x$ cyclics to a soluble polymer. An insoluble, rubbery solid was formed, which suggests that Si-H bonds as well as the Si-N bonds were activated by the transition metal catalyst.

The solution to our problem of converting the $[CH_3SiHNH]_x$ cyclics to a useful preceramic polymer was provided by earlier workers [13] who had described the conversion of silylamines of type 1 to cyclodisilazanes, 2, in high yield by the action of potassium in di-n-butyl ether (eq. 1). In this dehydrocyclodimerization reaction, the



1 2 (1)

potassium serves to metallate the NH functions to give 3. This then either eliminates H^- from silicon to give an



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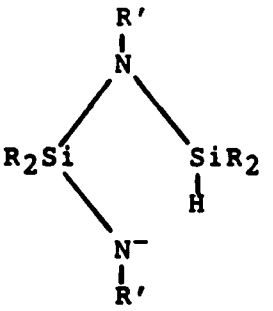

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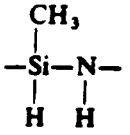
intermediate with a silicon-nitrogen double bond, $R_2Si{=}NR'$, which then undergoes head-to-tail dimerization to form 2, or alternatively, reacts with a molecule of $R_2Si(H)NHR'$ to give intermediate 4 which undergoes cyclization to 2 with displacement of H^-. This interesting mechanistic question still needs to be resolved.

The repeating unit in the $[CH_3SiHNH]_x$ cyclics is 5. For



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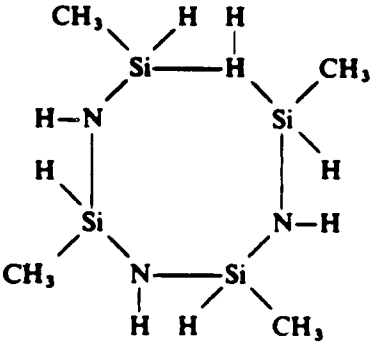

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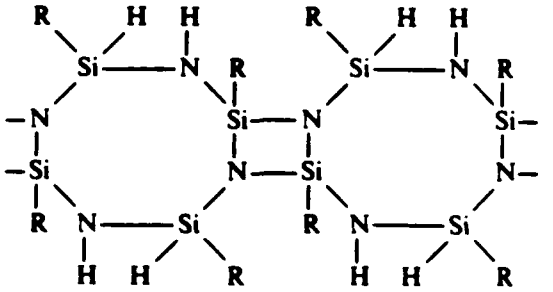
example, the cyclic tetramer is the 8-membered ring compound 6. On the basis of equation 1, the adjacent NH and SiH groups provide the functionality which permits the molecular weight of the $[CH_3SiHNH]_x$ cyclics to be increased. It may be expected that a sheet polymer will be formed.

Treatment of the CH_3SiHCl_2 ammonolysis product, cyclo-$[CH_3SiHNH]_x$, with a catalytic amount of a base (generally an alkali metal base) strong enough to deprotonate the N-H function in a suitable solvent results in evolution of

hydrogen. The resulting solution contains polymeric basic species and these are quenched by addition of methyl iodide or a chlorosilane. After filtration to remove alkali metal halide, evaporation of the filtrate gives the product in essentially quantitative yield. In our experiments we generally have used catalytic amounts of potassium hydride as the base. When THF was used as reaction solvent, the product was isolated in the form of a white powder (average molecular weight, 1180) which was found to be soluble in hexane, benzene, diethyl ether, THF, and other common organic solvents. It is imperative to exclude atmospheric moisture since the $[CH_3SiHNH]_x$ cyclics are readily hydrolyzed. The product polymer on the other hand, is of greatly diminished sensitivity to hydrolysis.

The composition of the polysilazane product of the experiment detailed above, ascertained by proton NMR spectroscopy, was $(CH_3SiHNH)_{0.39}(CH_3SiHNCH_3)_{0.04}(CH_3SiN)_{0.57}$ and its combustion analysis (C,H,N,Si) agreed with this formulation. These results are compatible with a process in which $(CH_3SiHNH)_n$ rings are linked together via Si_2N_2 bridges. Thus, if for example, the silazane 6 were to be polymerized by such a dehydrocyclodimerization process, the eight-membered rings could be linked as shown in 7. The ex-



R = CH_3

7

perimental $(CH_3SiN)/(CH_3SiHNH)$ ratio of ~1.3 indicates that further linking via Si_2N_2 rings must have taken place,

probably to give a sheet-like structure. Many cross-links obviously are not formed, but the molecular weight is increased sufficiently so that pyrolysis proceeds satisfactorily.

A better understanding of the chemistry leading to these polysilazanes and of their structure is needed. For instance, in our various preparations the average molecular weights of the products obtained after the methyl iodide quench varied between 800 and 2000. Before the methyl iodide quench, silylamide functions (i.e., catalytically active functions) still were present, yet growth to higher molecular weights did not occur. The reason for this must be connected with the solution structure and conformation of the polymers.

Whatever the structure of the silazane polymers obtained by KH treatment of the $[CH_3SiHNH]_x$ cyclics, these polymers are excellent ceramic precursors. Examination of the polymers from various preparations by TGA showed the weight loss on pyrolysis to be only between 15 and 20%. The pyrolysis appears to take place in three steps: a 5% weight loss (involving evolution of H_2) from 100°C to 350°C; a 2% weight loss from 350-550°C and a 9% weight loss from 550°C to 900°C. During the 550-900°C stage a mixture of H_2 and methane was evolved. A trace of ammonia, in addition to H_2, was lost between 350 and 550°C.

In a typical bulk pyrolysis experiment, pyrolysis was conducted under a slow stream of nitrogen. The sample was heated quickly to 500°C and then slowly (over 8 h) to 1420°C and was held at 1420°C for 2 h. The ceramic powder was a single body and black. Powder X-ray diffraction (CuK_α with Ni filter) showed only very small, broad peaks for α-Si_3N_4. (At 1490°C, lines due to β-SiC also appeared). Scanning electron microscopy analysis showed little discernible microstructure with only a few very fine grains appearing at high magnification. The bulk appearance of the ceramic suggested that pyrolysis took place after the polymer had melted. There were many large holes and craters where the liquid bubbles apparently had burst. In such experiments ceramic yields usually were between 80 and 85%. The polymer used in the experiment above had been prepared in diethyl

ether. It had a molecular weight of around 900 and went through a melt phase when it was heated. This could be shown when it was heated in a sealed capillary: it began to soften around 65°C, becoming more fluid with increasing temperature. The polymer prepared in THF is of higher molecular weight (MW = 1700-2000) and does not soften when heated to 350°C. It gave an 83% yield of a black ceramic material on pyrolysis under nitrogen to 1000°C.

The pyrolysis of the silazane polymer may be represented by eq. 2. Here the ceramic yield (Si_3N_4 + SiC + C)

$$2\ (CH_3SiHNH)(CH_3SiN) \longrightarrow Si_3N_4 + SiC + C + 2\ CH_4 + 4\ H_2 \quad (2)$$

would be 83 wt%. An analysis of such a ceramic product gave 12.87% C, 26.07% N, and 59.52% Si. This analysis is compatible with eq. 2 and leads to a ceramic constitution, based on the 4 Si of eq. 2, of 0.88 Si_3N_4, 1.27 SiC, 0.75 C.

Thus the chemistry leading to the desired ceramic product is quite satisfactory: most of the requirements mentioned earlier are met.

Initial ceramic studies have been promising. Isostatically pressed (40,000 psi) bars of the polymer on pyrolysis to 1100°C gave a coherent, rectangular ceramic bar which had not cracked or bloated and could not be broken by hand.

In collaboration with ceramists at the Celanese Research Company it was found that our meltable polysilazane cannot be melt-spun. Apparently, the thermal cross-linking process which is so effective in giving a high ceramic yield on pyrolysis takes place in the heated chamber of the spinning machine and quickly gives infusible polymer. However, the infusible polysilazane which is obtained when the preparation is carried out in THF solution can be dry-spun. In this process the solid polysilazane is dissolved in an appropriate solvent and then is extruded through a spinneret into a heated drying chamber in which the solvent is volatilized, leaving the solid polymer. These polymer fibers could be pyrolyzed to give ceramic fibers. In simpler experiments, it was shown that fibers one to two

feet in length could be drawn from the sticky, waxy solid which remained when a toluene solution of the polysilazane was evaporated. Pyrolysis of these fibers under nitrogen produced long, flexible black fibers. This aspect of our work is in only at a very early stage, but these initial observations are encouraging.

Our polysilazane also serves well as a binder for ceramic powders. The preparation of such composites (using commercial samples of fine α-SiC, β-SiC and α-Si_3N_4 of 0.36-0.4 μm mean particle size) required appropriate dispersion studies. The ceramic powder was dispersed in a solution of toluene containing the appropriate weight of polysilazane and then the toluene was evaporated using a rotary evaporator, leaving a waxy residue. Vacuum distillation removed the remaining solvent and left chunks of solid material. These were finely ground and pressed into a bar at 5000 psi. Isostatic pressing to 40,000 psi followed and then the bars were pyrolyzed in a tube furnace under nitrogen (10°C a minute, to 1100°C). The maximum density (~2.4 g/cc) was achieved in these experiments with a polymer loading of 30%.

Our research also has been directed at SiC precursors. It began with an examination of a potential starting material in which the C:Si ratio was 1, the ratio desired in the derived ceramic product.

Available methylsilicon compounds with a 1 C/1 Si stoichiometry are CH_3SiCl_3 and CH_3SiHCl_2. The former gives highly cross-linked, insoluble products on treatment with an alkali metal in a suitable diluent. The latter, in principle, could give $[CH_3SiH]_n$ cyclic oligomers and linear polymers on reaction with an alkali metal. In practice, the Si-H linkages also are reactive toward alkali metals. Thus, mixed organochlorosilane systems containing some CH_3SiHCl_2 have been treated with metallic potassium by Schilling and Williams [14]. It was reported that the CH_3SiHCl_2-based contribution to the final product was $(CH_3SiH)_{0.2}(CH_3Si)_{0.8}$, i.e., about 80% of the available Si-H bonds had reacted. Such Si-H reactions lead to cross-linking in the product, or to formation of polycyclic species if cyclic products are preferred. Nevertheless, we have used this known reaction

of CH_3SiHCl_2 with an alkali metal as an entry to new preceramic polymers.

When the reaction of CH_3SiHCl_2 with sodium pieces was carried out in tetrahydrofuran medium, a white solid was isolated in 48% yield. This solid was poorly soluble in hexane, somewhat soluble in benzene, and quite soluble in THF. Its molecular weight could not be determined by cryoscopy in benzene because of its limited solubility in that solvent. Its ^1H NMR spectrum (in $CDCl_3$) indicated that extensive reaction of Si-H bonds had occurred. The $\delta(SiH)/\delta SiCH_3$ integration led to a constitution $[(CH_3SiH)_{0.4}(CH_3Si)_{0.6}]_n$. Here the CH_3SiH units are ring and chain members which are not branching sites; the CH_3Si units are ring and chain members which are branching sites. In our reactions it is expected that mixtures of polycyclic and linear (possibly cross-linked) polysilanes will be formed. (Attempts to distill out pure compounds from our preparations were not successful. Less than 10% of the product was volatile at higher temperatures at 10^{-4} torr.)

The ceramic yield obtained when the $[(CH_3SiH)_{0.4}(CH_3Si)_{0.6}]_n$ polymer was pyrolyzed (TGA to 1000°C) was 60%; a gray-black solid was obtained whose analysis indicated a composition 1.0 SiC + 0.49 Si.

The reaction of methyldichlorosilane with sodium in a solvent system composed of six parts of hexane and one of THF gave a higher yield of product which was soluble in organic solvents. Such reactions give a colorless, cloudy oil in 75 to over 80% yield which is soluble in many organic solvents. In various experiments the molecular weight (cryoscopic in benzene) averaged 520-740 and the constitution (by ^1H NMR) $[(CH_3SiH)_{0.76}(CH_3Si)_{0.24}]_n$ to $[(CH_3Si)_{0.9}(CH_3Si)_{0.1}]_n$. This less cross-linked material (compared to the product obtained in THF alone) gave much lower yields of ceramic product on pyrolysis to 1000°C (TGA yields ranging from 12-27% in various runs). Again, the product was (by analysis) a mixture of SiC and elemental silicon, 1.0 SiC + 0.42 Si being a typical composition.

The results described above are not especially promising. The CH_3SiHCl_2/Na product which on pyrolysis gives a reasonable ceramic yield is of limited solubility in

organic solvents and its conversion to ceramic fibers requires a photolysis/oxidation cure step. The CH_3SiHCl_2/Na product in which crosslinking is not as extensive and which is very soluble in organic solvents gives unacceptably low ceramic yields on pyrolysis. Furthermore, only in the case of the preparations carried out in 6-7/1 hexane/THF solvent medium were the yields of soluble product satisfactory. Finally, in all cases the ceramic product contained a considerable excess of "free" silicon over the ideal SiC composition. It was obvious that further chemical modification of the $[(CH_3SiH)_x(CH_3Si)_y]_n$ products obtained in the CH_3SiHCl_2/Na reactions was required.

A number of approaches which we tried did not lead to success, but during the course of our studies we found that treatment of the $[(CH_3SiH)_x(CH_3Si)_y]_n$ products with alkali metal amides (catalytic quantities) serves to convert them to materials of higher molecular weight whose pyrolysis gives significantly higher ceramic yields. Thus, in one example, to 0.05 mol of liquid $[(CH_3SiH)_{0.85}(CH_3Si)_{0.15}]$ in THF was added, under nitrogen, a solution of about 1.25 mmol (2.5 mol%) of $[(CH_3)_3Si]_2NK$ in THF. The resulting red solution was treated with methyl iodide. Subsequent nonhydrolytic workup gave a soluble white powder in 68% yield, molecular weight 1000, whose pyrolysis to 1000°C gave a ceramic yield of 63%.

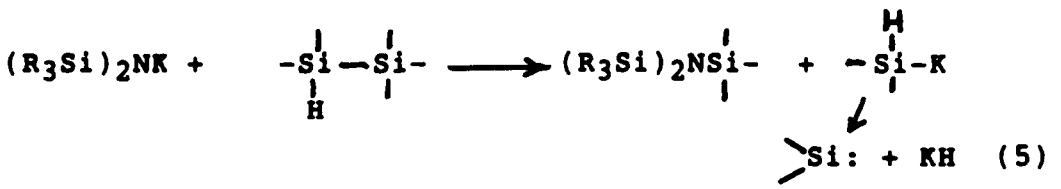
The proton NMR spectra of these products showed only broad resonances in the Si-H and $Si-CH_3$ regions. In the starting $[(CH_3SiH)_x(CH_3Si)_y]_n$ materials observed proton NMR integration ratios, $SiCH_3/SiH$, ranged from 3.27-3.74. This ratio was quite different in the case of the products of the silylamide-catalyzed processes, ranging from 8.8 to 14. Both Si-H and Si-Si bonds are reactive toward nucleophilic reagents. In the case of the alkali metal silylamides, the following processes can be envisioned:

$$(R_3Si)_2NK + -\overset{|}{\underset{|}{Si}}H \longrightarrow -\overset{|}{\underset{|}{Si}}N(SiR_3)_2 + KH \qquad (2)$$

$$(R_3Si)_2NK + -\overset{|}{\underset{|}{Si}}H \longrightarrow (R_3Si)_2NH + -\overset{|}{\underset{|}{Si}}K \qquad (3)$$

$$(R_3Si)_2NK + -\overset{|}{\underset{|}{Si}}-\overset{|}{\underset{|}{Si}}- \longrightarrow (R_3Si)_2N-\overset{|}{\underset{|}{Si}}- + -\overset{|}{\underset{|}{Si}}K \qquad (4)$$

In each process, a new reactive nucleophile is generated: KH in equation 2, a silyl alkali metal function in reactions 3 and 4. These also could undergo nucleophilic attack on the $[(CH_3SiH)_x(CH_3Si)_y]_n$ system and during these reactions some of the oligomeric species which comprise the starting material would be linked together, giving products of higher molecular weight. Other processes are possible as well, e.g., a silylene process as shown in equation 5. Thus not only anionic species but also neutral silylenes could be involved as intermediates. In any case, extensive loss of Si-H takes place during this catalyzed process: it is more



$$(R_3Si)_2NK + -\overset{|}{\underset{H}{Si}}-\overset{|}{Si}- \longrightarrow (R_3Si)_2N\overset{|}{Si}- + -\overset{H}{\overset{|}{Si}}-K \rightarrow \overset{|}{Si}: + KH \quad (5)$$

than a simple redistribution reaction. Further studies relating to the mechanism of this process must be carried out.

While these silylamide-catalyzed reactions have provided a good way to solve the problem of the low ceramic yield in the pyrolysis of $[(CH_3SiH)_x(CH_3Si)_y]_n$, the problem of the elemental composition of the ceramic product remained (i.e., the problem of Si/C ratios greater than one) since only catalytic quantities of the silylamide were used.

As noted above, KH-catalyzed polymerization of the CH_3SiHCl_2 ammonolysis product gives a polymeric silylamide of type $[(CH_3SiHNH)_a(CH_3SiN)_b(CH_3SiHNK)_c]$. In a typical example, a ~0.9, b~1.3, c~0.04, so there is only a low concentration of silylamide functions in the polymer. This polymeric silylamide reacts with electrophiles other than methyl iodide, e.g., with diverse chlorosilanes, and it has been isolated and analyzed. Since it is a silylamide, we expected that it also would react with $[(CH_3SiH)_x(CH_3Si)_y]_n$ polysilane-type materials. Not only would it be expected to convert the latter into material of higher molecular weight, but it also would be expected to improve the Si/C ratio (i.e., bring it closer to 1). As noted above, pyrolysis of $[(CH_3SiHNH)_a(CH_3SiN)_b(CH_3SiHNCH_3)_c]_n$ gives a ceramic product

in 80-85% yield containing Si_3N_4, SiC and excess carbon. Thus, combination of the two species in the appropriate stoichiometry, i.e., of $[(CH_3SiH)_x(CH_3Si)_y]_n$ and $[(CH_3SiHNH)_a(CH_3SiN)_b(CH_3SiHNK)_c]_n$, and pyrolysis of the product (which we will call a "graft" polymer) after CH_3I quench could, in principle, lead to a ceramic product in which the excess Si obtained in pyrolysis of the former and the excess C obtained in the pyrolysis of the latter combine to give SiC. A further benefit might be expected from such a combination in the formation of ceramic fibers: The $[(CH_3SiHNH)_a(CH_3SiN)_b(CH_3SiHNCH_3)_c]_2$ system is self-curing as the temperature is raised on the way to the production of a ceramic material; the $[(CH_3SiH)_x(CH_3Si)_y]_n$ system, as described above, is not. It might be expected that a combination of the two would give a self-curing system.

With these ideas in mind, experiments were carried out in which the two polymer systems, $[(CH_3SiH)_x(CH_3Si)_y]_n$ and the "living" polymer-silyl amide, $[(CH_3SiHNH)_a(CH_3SiN)_b(CH_3SiHNK)_c]_n$, were mixed in THF solution in varying proportions (2.4:1 to 1:2 mole ratio) and allowed to react at room temperature for 1 h and at reflux for 1 h. (Such experiments were carried out with the $[(CH_3SiH)_x(CH_3Si)_y]_n$ materials prepared in hexane/THF as well as with those prepared in THF alone.) After quenching with methyl iodide, nonhydrolytic workup gave a new polymer in nearly quantitative yield (based on weight of material charged). The molecular weight of these products was in the 1800-2500 range. Their pyrolysis under nitrogen gave ceramic products in 74-83% yield. Thus, the reaction of the two polymer systems gives a new polymer in close to quantitative yield which seems to be an excellent new preceramic polymer in terms of ceramic yield.

In an alternative method of synthesis of $[(CH_3SiH)_x(CH_3Si)_y][(CH_3SiHNH)_a(CH_3SiN)_b]$ "combined" polymers, the polysilyl amide was generated <u>in situ</u> in the presence of $[(CH_3SiH)_x(CH_3Si)_y]_n$. This, however, gave materials that were somewhat different. In one such experiment, a mixture of $(CH_3SiHNH)_n$ cyclics (as obtained in the ammonolysis of CH_3SiHCl_2 in THF) and the $[(CH_3SiH)_x(CH_3Si)_y]_n$ material ($x = 0.76$; $y = 0.26$) in THF

was treated with a catalytic amount of KH. After the reaction mixture had been treated with methyl iodide, the usual workup gave an 89% yield of hexane-soluble white powder, molecular weight ~2750. On pyrolysis, this material gave a 73% yield of a black ceramic.

The "combined" polymer prepared in this way ("in situ polymer") was in some ways different from the "combined" polymer prepared by the first method ("graft" polymer). Principal differences were observed in their proton NMR spectra and in the form of their TGA curves. This suggests that the two differently prepared polymers have different structures. It is likely that in the "in situ" preparation intermediates formed by the action of KH on the $(CH_3SiHNH)_n$ cyclics are intercepted by reaction with the $[(CH_3SiH)_x(CH_3Si)_y]_n$ also present before the $[(CH_3SiHNH)_a(CH_3SiH)_b(CH_3SiHNK)_c]_n$ polymer (which is the starting reactant used in the "graft" procedure) has a chance to be formed to the extent of its usual molecular weight. Thus, less of the original CH_3SiHNH protons are lost and/or more of those of the $[(CH_3SiH)_x(CH_3Si)_y]_n$ system are reacted.

The TGA curves of the "graft" polymer and the "in situ" polymer are different as well. Noteworthy in the former is a small weight loss between 100°C and 200°C, which begins at around 100°C. This initial small weight loss occurs only at higher temperature (beginning at ~175°C) in the case of the "in situ" polymer. This difference in initial thermal stability could well have chemical consequences of importance with respect to ceramics and both kinds of polymers may be useful as preceramic materials.

Physical blends of $[(CH_3SiH)_x(CH_3Si)_y]_n$ (solid polymer, THF preparation) and $[(CH_3SiHNH)_a(CH_3SiN)_b(CH_3SiHNCH_3)_c]_n$ were also examined. When about equimolar quantities of each were mixed and finely ground together, pyrolysis to 1000°C gave a 70% ceramic yield (TGA). It appears that a reaction between the two polymers already occurs at lower temperatures. When such mixtures were heated, either in the absence of a solvent at 100°C under nitrogen or in toluene solution at reflux, white powders were obtained which were insoluble in hexane, benzene, and THF. The ceramic yields (by TGA) were 67& and 75%, respectively.

Further experiments showed that the "combined" polymers may be converted to black ceramic fibers. Pyrolysis of pressed bars of the "combined polymer to 1000°C gave a black, foam product of irregular shape (74-76% ceramic yield). In other experiments, SiC powder was dispersed in toluene containing 20% by weight of the "combined" polymer. The solution was evaporated and the residue, a fine powder of SiC with the "combined" polymer binder, was pressed into bars and pyrolyzed at 1000°C. A ceramic bar (6% weight loss, slightly shrunk in size) was obtained.

The ceramic products obtained in the pyrolysis of the "combined" polymers have not been studied in detail, but some of them have been analyzed for C, N, and Si. The compositions of the ceramic materials obtained cover the range 1 Si_3N_4 + 3.3 to 6.6 SiC + 0.74 to 0.85 C. Thus, as expected, they are rich in silicon carbide and the excess Si which is obtained in the pyrolysis of the $[(CH_3SiH)_x(CH_3Si)_y)_n$ materials alone is not present, so that objective has been achieved. By proper adjustment of starting material ratios, we find that the excess carbon content can be minimized.

The Yajima polycarbosilane discussed earlier, as obtained by thermal rearrangement of the poly(dimethylsilylene) is a polymeric silicon hydride, with $[(CH_3)(H)SiCH_2]$ as the main repeating unit. As such, it also might be expected to react with our $[(CH_3SiHNH)_a(CH_3SiN)_b(CH_3SiHNK)_c]$ poly(silylamide). This was found to be the case. The commercially available Yajima polycarbosilane (sold in the U.S. by Dow Corning Corporation; our sample, a white solid, had a molecular weight of 1210 and a ceramic yield of 58% was obtained on pyrolysis) was found to react with our poly(silylamide). A reaction carried out in THF solution, initially at room temperature, then at reflux, followed by treatment of the reaction mixture with methyl iodide, gave after appropriate workup a nearly quantitative yield of a white solid which was very soluble in common organic solvents including hexane, benzene, and THF. When the polycarbosilane-to-polysilylamide ratio was approximately one, pyrolysis of the product polymer gave a black ceramic solid in 84% yield

which analysis showed to have a composition (1 SiC + 0.22 Si_3N_4 + 0.7 C). When the polycarbosilane/polysilylamide ratio was ~5, the ceramic yield was lower (67%). In these experiments the cyclo-$(CH_3SiHNH)_n$ starting materials used to synthesize the polysilylamide had been prepared by CH_3SiHCl_2 ammonolysis in diethyl ether. When this preparation was carried out in THF, the final ceramic yields obtained by pyrolysis of the polycarbosilane/polysilylamide hybrid polymer were 88% (1:1 reactant ratio) and 64% (5:1 reactant ratio).

The "in situ" procedure in which the CH_3SiHCl_2 ammonolysis product, cyclo-$(CH_3SiHNH)_m$, was treated with a catalytic quantity of KH in the presence of the polycarbosilane, followed by a CH_3I quench and the usual work-up, gave equally good results in terms of high final ceramic yields, whether the starting cyclo-$(CH_3SiHNH)_m$ was prepared in Et_2O or THF.

It is clear from these results that a new polymer is formed when the polycarbosilane and the polymeric silylamide are heated together in solution and then quenched with methyl iodide. Proton NMR spectroscopy brought further evidence of such a reaction.

A physical mixture of the polycarbosilane and the polysilazane $[(CH_3SiHNH)_a(CH_3SiN)_b(CH_3SiHNCH_3)_c]_m$, also was found to react when heated to 1000°C, giving good yields of ceramic product. That appreciable reaction had occurred by 200°C was shown in an experiment in which a 1:1 by weight mixture of the initially soluble polymers was converted to a white, foamy solid which no longer was soluble in organic solvents by such thermal treatment.

The combined polymers obtained by the "graft", "in situ", and physical blend methods can be converted to black ceramic fibers. Pyrolysis of pressed bars of the combined polymers to 1000°C provides a black solid product. In other experiments, SiC powder was dispersed in a toluene solution containing 25% by weight of the combined powders. The solvent was evaporated and the residue, a fine powder of silicon carbide with combined polymer binder, was pressed into bars and pyrolyzed at 1000°C. A ceramic bar was obtained showing a low weight loss and slightly shrunken

size. Thus, the usual ceramic applications seem indicated. While this approach in which chemical combination of the Yajima polycarbosilane and our poly(silylamide) leads to new hybrid polymers successfully addreses the problem of ceramic yield, it does not deal with the problem of chemical composition. Pyrolysis of the polycarbosilane and of the polysilazane separately gives ceramic materials which in each case contain an excess of free carbon. As expected, the hybrid polymers produced by reaction of the polycarbosilane with the poly(silylamide) by either the "graft" or "in situ" procedures gives ceramic products which contain an excess of free carbon.

CONCLUSIONS

We have shown in this paper that useful preceramic organosilicon polymers can be prepared and that their design is an exercise in functional group chemistry. Furthermore, we have shown that an organosilicon polymer which seemed quite unpromising as far as application as a preceramic polymer is concerned could, through further chemistry, be incorporated into new polymers whose properties in terms of ceramic yield and elemental composition were quite acceptable for use as precursors for ceramic materials. It is obvious that the chemist can make a significant impact on this area of ceramics. However, it should be stressed that the useful applications of this chemistry can only be developed by close collaboration between the chemist and the ceramist.

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REFERENCES

1. Gmelin Handbook of Inorganic Chemistry, 8th Edition, Springer-Verlag: Berlin, Silicon, Supplement Volumes B2, 1984, and B3, 1986.

2. Messier, D.R.; Croft, W.J. in "Preparation and Properties of Solid-State Materials", Vol. 7, Wilcox, W.R., ed.; Dekker: New York, 1982, Chapter 2.

3. As recently as 1975, the statement "Silicon nitride has no established use." was applicable: Rochow, E.G., "The Chemistry of Silicon", Pergamon Texts in Inorganic Chemistry, Volume 9, Pergamon: Oxford, 1975, p. 1417.

4. (a) Wynne, K.J.; Rice, R.W. Ann. Rev. Mater. Sci. (1984) 14, 297.
   (b) Rice, R.W. Am. Ceram. Soc. Bull. (1983) 62, 889.

5. Rice, R.W. Chem. Tech. (1983) 230.

6. Yajima, S. Am. Ceram. Soc. Bull. (1983) 62, 893.

7. Schilling, C.L., Jr.; Wesson, J.P.; Williams, T.C. Am. Ceram. Soc. Bull. (1983) 62, 912.

8. (a) Seyferth, D.; Wiseman, G.H. and Prud'homme, C.C. J. Am Ceram. Soc. (1983) 66, C-13.
   (b) U.S. Patent 4,397,828 (August 9, 1983).

9. (a) Seyferth, D.; Wiseman, G.H. J. Am. Ceram. Soc. (1984) 67, C-132.
   (b) U.S. Patent 4,482,669 (13 Nov. 1984).
   (c) Seyferth, D.; Wiseman, G.H. in "Ultrastructure Processing of Ceramics, Glasses and Composites", 2, edited by L.L. Hench and D.R. Ulrich, Wiley: New York, 1986, Chapter 38.

10. Brewer, S.D.; Haber, C.P. J. Am. Chem. Soc. (1948) 70, 3888.

11. (a) Krüger, C.; Rochow, E.G. J. Polymer Sci., Part A (1964) 2, 3179.
(b) Rochow, E.G. Monatsh. Chem. (1964) 95, 750.

12. Zoeckler, M.T.; Laine, R.M. J. Org. Chem. (1983) 48, 2539.

13. Monsanto Company, Neth. Appl. 6,507,996 (December 23, 1965); Chem. Abstr. (1966) 64, 19677d.

14. (a) Schilling, C.L., Jr.; Williams, T.C., Report 1983, TR-83-1, Order No. AD-A141546; Chem. Abstr. 101. 196820p
(b) U.S. Patent 4,472,591 (18 Sept. 1984).

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