

## Polymer Precursors to Silicon Nitride ( $\text{Si}_3\text{N}_4$ )

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Literature Seminar

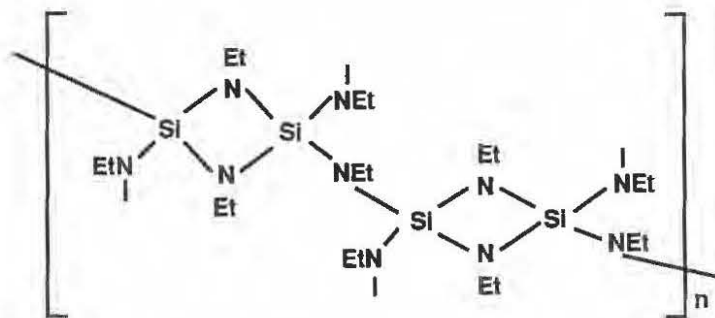
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The pyrolysis of organometallic polymers to form ceramic bodies [1] has attracted increasing interest over the past 15 years. The conversion of organosilicon polymers into silicon carbide by Yajima and colleagues [2] was the first major achievement in this area of materials chemistry [3]. Further progress is now being made in understanding the chemistry of the polymer precursors and effecting their conversion to ceramics [4].

The use of polymer processing has potential advantages over conventional powder processing by lowering processing temperatures, eliminating additives, and allowing the production of more complex ceramics [5]. An optimal preceramic polymer should have a large molecular weight, be tractable, contain some cross-linking, have latent chemical reactivity, and have appropriate elemental composition [4,5]. Preceramic polymers have been used to create ceramics such as BN,  $\text{B}_4\text{C}$ , SiC, and  $\text{Si}_3\text{N}_4$  [3].

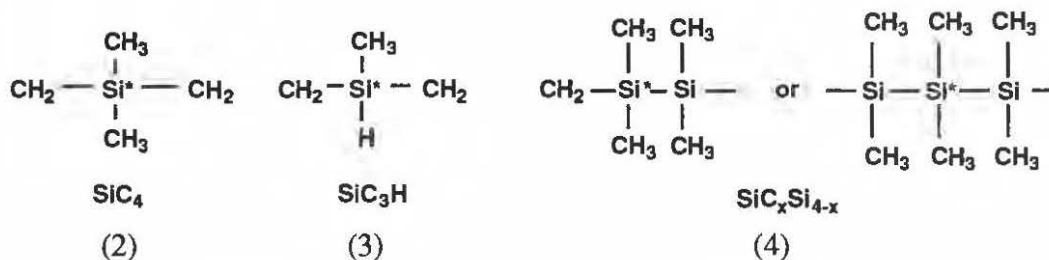
Silicon nitride is an important structural ceramic due to its high-temperature properties, its stability to oxidation, and its low thermal expansion coefficient [7]. Silicon nitride exists in two crystal modifications:  $\alpha$ , the low-temperature form, and  $\beta$ , the high-temperature form [8-10]. However, amorphous silicon nitride is generally used to yield a ceramic form. Three general types of organosilicon polymers are used to generate silicon nitride, poly(silazanes), poly(carbosilanes), and poly(silanes). Each of these types of polymers contain differing backbones and thus have slightly differing chemistry involved.

A study of poly(cyclosilazane-Et) found that this polymer decomposes to either silicon nitride or silicon carbide depending on the atmosphere used during pyrolysis. Most notable was the retention of the  $\text{SiN}_4$  structural environment throughout the conversion of the polymeric silazane to the amorphous ceramic. Upon heating to  $1600^\circ\text{C}$  in a nitrogen atmosphere,  $\alpha$ - $\text{Si}_3\text{N}_4$  with a minor amount of  $\beta$ -SiC is obtained [11].

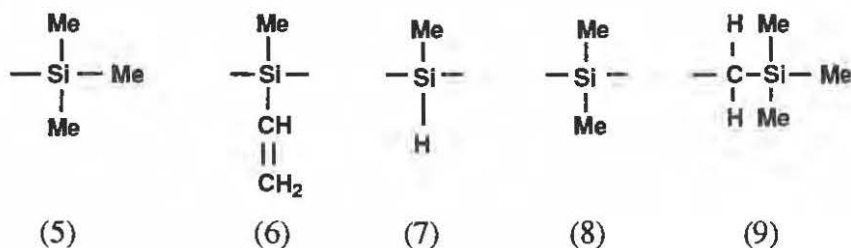


(1)

Poly(carbosilane) has a structure with four basic silicon environments (see 2-4 below) [12-14]. The ceramic transformation is believed to begin with nucleophilic substitution of Si-H bonds by ammonia. At higher temperatures, the substitution of Si-C bonds is believed to involve homolytic cleavages. Pyrolysis to  $1200^\circ\text{C}$  in an ammonia/argon (30/70) atmosphere gives amorphous  $\text{Si}_3\text{N}_4$  with some residual carbon [15].



Vinylc polysilane has at least five different silicon environments (see 5-9 below) [16, 17]. The major difference due to atmosphere ( $\text{N}_2$ -vs- $\text{NH}_3$ ) is seen during pyrolysis, between 300-650°C, where the largest weight loss occurs. In this temperature range there is substantial cleavage of the polysilane backbone and methylene insertion. Also occurring in this temperature range is the  $\text{NH}_3$ -assisted elimination of hydrocarbons and the replacement of Si-C bonds by Si-N bonds. Heating to temperatures of 1000°C in  $\text{NH}_3$  followed by higher temperatures in  $\text{N}_2$  causes the loss of residual carbon and hydrogen and the eventual crystallization of  $\alpha$ - $\text{Si}_3\text{N}_4$  [18].



The understanding of the pyrolysis of polymers to form ceramics is improving. With better understanding of the mechanisms involved, polymers might be designed and synthesized to give specific properties upon transformation to a desired ceramic material.

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