

THE STRUCTURAL CHARACTERIZATION OF POLYSILAZANES

The following is provided to assist researchers in the structural characterization of polysilazanes:

I. CYCLIC CONTENT

The stubborn propensity for silazanes to form low molecular weight cyclic species (i.e. cyclosilazanes having a number average molecular weight of less than about 500 grams/mol) was recognized by Kruger and Rochow as early as 1964 [Kruger, C.R, Rochow, E.G., "Polyorganosilazanes", J. Polymer Sci.; Part A, Vol. 2, 3179-3189 (1964)]. To generate more linear structures from the cyclic species generated from a simple ammonolysis of dialky/dichlorosilanes, these researchers developed a secondary processing step involving the heating of the dialky/cyclosilazanes such as hexamethylcyclotrisilazane (MW = 219) in anhydrous, liquid ammonia in a bomb, under pressure, in the pressence of an ammonium bromide catalyst. It was later disclosed by Rochow in 1966 [Rochom, E.G., "Polymeric Methylsilazanes", Pure Appl. Chem.; Vol. 13, No. 1-2, 247-262 (1966)] that the same effect could be achieved at 4 bars pressure without the addition of the ammonium bromide catalyst.

The transformation of cyclic to linear structure in the dimethyl case could be demonstrated through ¹H NMR spectral analysis. For instance, Rochow reports that the simple ammonolysis of dimethyldichlorosilane in liquid ammonia appears to give about 50% cyclic material (in the form of a trimer and a tetramer), and about 50% polymer. The cylosilazanes exhibited methyl proton chemical shifts in ¹H NMR spectra at approximately 0.02 ppm for the trimer, 0.04 ppm for the tetramer, 0.04 ppm to 0.08 ppm for the linear polymer, and between 0.12 ppm and 0.25 ppm for the crosslinked polymer. Based on the relative intensity of peaks, the composition was about 21% crosslinked. On the other hand, upon pressure-induced ring opening about 88% of the material was recovered as linear polymer with no crosslinked polymer evident, while 12% of the material was cyclic.

While the above chemical shifts are representative of polysilazanes which comprise two methyl groups bonded to silicon, a similar trend and correlation can be made for polysilazanes in which the silicon atoms are bonded to just one methyl group (or alkyl group in general), and a hydrogen atom (HSiC). In such polysilazanes 1H NMR chemical shifts for Si-CH₃ groups can be detected at about 0.19 ppm for the trimer, 0.22 for the tetramer, 0.26 for the pentamer, and 0.31 for the hexamer. Peaks for Si-CH₃ groups contained in linear segments of polysilazane occur between about 0.31 ppm and 0.38 ppm, while peaks for the Si-CH₃ groups contained in crosslink junctures of the polysilazane can be seen at between about 0.38 ppm and 0.45 ppm. [Zhang, L., Luo, Y., Zhang, Z., Zhang M., Xu, C.,, "Preparation of Si3N4 Materials by Catalytic Polymerization and Pyrolysis of Silazane Rings, Journal of Aerospace Materials Technology, 2015, 45(2), 43-47]. The comparative ¹H NMR chemical shifts for the Si-CH₃ methyl group for these, as well as two other polysilazanes [Durazane 1500: Lo, T.N.H., Hong, S.W., Hwang, H.S., Park, I., "Facile Synthesis of Fluorinated Polysilazanes and Their Durable Icephobicity on Rough Al Surfaces", Polymers, 2022, 14, 330, Durazane 1800: Sourangsu, S., "The Fabrication of Polymer-Derived SiCN/SiBCN Ceramic Nanostructures and Investigation of their Structure-Property Relationship", Thesis, University of Central Florida, 2010] are shown in Figure 1, below.

Polymer Units	Si(CH3)2	Si(H)(CH3)	[Si(CH3)2]0.22[Si(H)(CH3)]0.44 [NH(CH2)3Si(OCH2CH3)3]0.34	[Si(CH3)(Vi)]0.20 [Si(H)(CH3)]0.80
			Durazane 1500	Durazane 1800
Reference	Rochow, 1966	Zhang, 2015	Lo, 2022	Sourangsu, 2010
Trimer	0.02 ppm	0.19 ppm	0.17 ppm	0.15 ppm
Tetramer	0.04 ppm	0.22 ppm	0.21 ppm	0.16 ppm
Pentamer	Not Observed	0.26 ppm	0.25 ppm	0.17 ppm
Linear	0.04-0.08 ppm	0.31-0.38 ppm	0.28-0.37 ppm	0.20-0.29 ppm
Crosslinked	0.12-0.25 ppm	0.38-0.45 ppm	Not Observed	0.29-0.37 ppm

¹H NMR chemical shifts for Si-CH₃ methyl groups for Polysilazanes

Figure 1

Cyclic versus linear structure can thus be determined through Si-CH₃ chemical shift analysis using ¹H NMR.

It should be noted here that while the multi-step procedure followed by Rochow does, indeed, lead to dialkylpolysilazanes having a low cyclic to linear ratio, the process is cumbersome in that it is multi-step and involves both heat and high pressure to effect cyclic ring opening, making large-scale manufacturing difficult. Moreover, it is not applicable to polysilazanes comprising Si-H containing bonds, since these condense with N-H bonds in the polysilazane with added heat through a dehydrocoupling reaction, giving highly crosslinked, and often gelled structures (typically at temperatures of greater than 120°C, but at lower temperatures by adding a catalyst).

II. CROSSLINKING

To clarify the mechanisms pertinent to polysilazane crosslinking, the following is provided. Polysilazanes comprising Si-H bonds can crosslink through three mechanisms: 1) dehydrocoupling, wherein the number of Si-H bonds decrease during crosslinking by reaction with N-H bonds to form hydrogen gas, 2) transamination, wherein only the number of N-H bonds decrease during crosslinking, or, alternatively, 3) amminolysis of Si-Cl bonds in polymer by Si-NH-Si groups, which generate crosslinks by their reaction with "secondary" amine groups in low molecular weight silazanes before full condensation to polymer occurs. A brief summary of each of these crosslinking mechanisms is now provided for clarity.

When a polysilazane comprising Si-H bonds undergoes a *dehydrocoupling* reaction to crosslink, configurations of silicon atoms bonded to three nitrogen atoms as well as nitrogen atoms bonds to three silicon atoms are formed: $N_2^1Si-H + Si-HN^2-Si \rightarrow N_2^1SiN^2Si_2$ ("Si₃N" / "SiN₃") + H₂]. Both the total number of Si-H groups and the total number of N-H groups are thus diminished with the formation of conjoined "SiN₃" groups and "Si₃N" groups at the crosslink sites.

A polysilazane can also undergo *transamination* reactions wherein a "secondary" NH group in a linear silazane chain reacts at an existing Si-N bond in a linear silazane chain, resulting in the formation of "Si₃N" groups. The reaction proceeds in the following manner: Si-HN¹-Si + Si-HN²-Si \rightarrow SiN²Si₂ ("Si₃N") + SiN¹H₂. In such transamination reactions "SiN₃" groups are not formed, since this would require cleavage of an Si-H or Si-C bond. It is important to note that transamination reactions in polysilazanes are thermally induced and are evidenced by the evolution of NH3 gas in the pyrolysis of polysilazanes at temperatures greater than about 200°C, not at typical synthesis temperatures [*Flores, O., Schmalz, T., Krenkel, W., Heymann, L., Motz, G. "Selective Cross-Linking of Oligosilazanes to Tailored Meltable Polysilazanes for the Processing of Ceramic SiCN Fibres", J. Mater. Chem A, 2013, 1, 15406-15415].* When characterizing polysilazanes that have not been exposed to such temperatures, this mechanism does not apply.

"Aminolysis" crosslinking occurs when a chlorosilane monomer reacts with a "secondary" amine present in an already-formed silazane oligomer as shown below:

 $(R)(H)SiCl_2 + -NH-Si(R)(H)-NH-Si(R)(H)-NH- ----> (R)(H)(Cl)Si-N-[Si(R)(H)-NH-]_2$. Aminolysis crosslinking results in the formation of conjoined "Si₃N" and "SiN₃" groups at crosslink sites similar to what occurs in *transamination*. Typically, such amminolysis crosslinking is observed when synthetic routes

which could result in an ammonia deficieny, such as ammonolysis using gaseous ammonia, are employed.

A straighforward method to determine crosslink density resulting from the above mechanisms involves FTIR analysis. When both "Si₃N" and "SiN₃" groups are formed in a conjoined configuration at a crosslink site, new signals at about 850 cm⁻¹ (N-Si₃ asymmetric stretching) and 950 cm⁻¹ (N-SiN₂ stretching) in the polymer's FTIR spectrum are observed. These two peaks bracket the "Si₂N₂" (Si₂NH) signals at about 920 cm⁻¹. The presence of a conjoined "SiN₃" and "Si₃N" crosslink configuration was demonstrated in the '487 patent upon exposure of a polysilazane to catalytic ammonium chloride over time, resulting in crosslinking through dehydrocoupling, wherein two new peaks at 845 cm^{-1} and 960 cm^{-1} emerged (Figure 5 in the '487 patent). The wavenumber assignments for such conjoined "SiN₃" and "Si₃N" crosslinking groups are disclosed in the literature [Silva, J.A., Quoizola, S., Hernandez, E., Thomas, L., Massines, F. "Silicon Carbon Nitride Films as Passivation and Antireflective Coatings for Silicon Solar Cells", Surface & Coatings Technology 242 (2014) 157-163; Ermakova, E., Kolodin, A., Fedorenko, A., Yushina, I., Shayapov, V., Maksimovskiy, E., Kosinova, M., "Controlling of Chemical Bonding Structure, Wettability, Optical Characteristics of SiCN:H (SiC:H) Films Produced by PECVD Using Tetramethylsilane and Ammonia Mixture, Coatings 2023, 13, 310] and are supported by related work assigning "Si₃N" and "SiN₄" FTIR wavenumbers in the highly crosslinked structure of silicon nitride (Si₃N₄) [Scardera, G., Puzzer, T., Conibeer, G., Green, M.A., "Fourier Transform Infrared Spectroscopy of Annealed Silicon-Rich Silicon Nitride Thin Films", J. Appl. Phys. 104, 104310 (2008); Tugay, E., Yilmaz, E., Turan, R., "Influence of Gamma Irradiation on the C-V Characteristics of the Al/SiN_x/Si MIS Capacitors", J. Vac. Sci. Technol. A 30(4), Jul/Aug 2012]. A very strong peak at about 838 cm⁻¹, characteristic of silicon nitride's pronounced "Si₃N" crosslinking, is depicted in the FTIR spectrum published in trade literature by Thermo Fisher Scientific /Boyle, R., Sukumaran, S., Chen, R., "Quantitative Determination of Hydrogen Concentration in Silicon Nitride Dielectric Films on Silicon Wafers using FTIR Spectroscopy", Thermo Fisher Scientific, Madison, Wisconsin. This FTIR peak at around 840 cm⁻¹ is, perhaps, the most revealing indicator of polymer crosslinking in a polysilazane, since the peak at around 950 cm⁻¹ that accompnies this peak is often obscured by the large, wide peak at around 920 cm⁻¹ characteristic of the

many "Si₂N₂" (Si₂NH) links in the polymer chain.

Apart from such considerations, prior art gas phase ammonolysis processes, such as those described above have all also demonstrated additional deficiencies.

When Si-H containing organohalosilanes are employed as the raw material in the process taught in the '487 patent, and compared to the analogous ammonolysis products prepared by the traditional method of gaseous ammonia ammonolysis at ambient pressure (Example 6 of the '487 patent), novel polysilazanes result that are characterized in that they have both (1) a reasonably high molecular weight comprising a low ratio of cyclic to linear polymer segments due to the stabilization of the initially formed ammonolysis products of the reaction in the anhydrous liquid ammonia containing the ionized, dissolved ammonium halide, but (2) a high degree of crosslinking as evidenced spectroscopically by Fourier Transform Infrared Spectrometry (FTIR) in the reduced number of Si-H bonds and N-H bonds in the final product compared to the number of Si-H bonds introduced in the halosilane starting material. The number of N-H bonds which are detected in the polymer is observed to rapidly decrease in proportion to the decrease in the number of Si-H bonds in the polymer as it is left to dwell in the presence of the ionized, dissolved ammonium halide in the anhydrous liquid ammonia solvent, approaching 6.7% crosslink density after 6.5 hours of ammonium chloride/anhydrous liquid ammonia exposure in Example 7 of the '487 patent. This, based on the ratio of CH_3 to NH hydrogen content in the ¹H NMR of a freshly prepared sample versus a sample allowed to dwell in the presence of ammonium chloride/anhydrous liquid ammonia solution. This is also accompanied by crosslink density induced by transamination, which also results in a decrease in the number of N-H bonds in the polymer, although the number of Si-H bonds in the polymer is not affected by transamination crosslinking.

The following then summarizes the features of the polysilazanes prepared by the method taught in the '487 patent. The '487 patent thus describes a process utilizing no organic solvent, for the preparation of a highly crosslinked, but processable polysilazane produced by inducing crosslinking in the polymer structure through the catalytic action of ammonium halide on the Si-H and N-H bonds contained within the polymer. Fourier Transform Infrared Analysis of both the polysilazane prepared by the process of the '487 patent compared to the polysilazane prepared by the traditional process of ambient pressure, gaseous ammonia ammonolysis is described in Example 6 of the '487 patent. Figure 6 in that patent shows the decreased number of Si-H bonds in the polysilazane prepared by the '487 process, and Figure 7 in that patent shows the greater linear versus cyclic character of the polysilazane prepared by the '487 process.

It is important to note that the crosslinked polysilazane composition obtained by the process of the '487 patent is achieved because, in the batch process that is described, the ammonolysis product of the Si-H containing halosilane remains in intimate contact with the acidic, solubilized and ionized solution of ammonium halide in liquified ammonia for a sufficient time to cause condensation of Si-H and N-H bonds in the ammonolysis product with the evolution of hydrogen gas. Since the addition of the halosilane raw material in the batch process described can only be achieved over a certain period of time due to the need to limit the rise of temperature and pressure in the reaction vessel to remain within equipment specifications, the ammonolysis product that is formed with the initial charge of halosilane comprises such crosslinks by the time the full complement of halosilane is added to the reactor. Addition times of approximately about one hour for the halosilane are reported, during which time silazane or polysilazane products that are formed during the early stages of chlorosilane addition have sufficient time to crosslink. Since FTIR analysis can only detect levels of chemical crosslink density greater than about 5% of the composition analyzed, it is clear from the FTIR spectra presented in the '487 patent that crosslinking must begin well before addition of the halosilane is fully accomplished.

A low cyclic to linear polymer segment ratio is achieved in the '487 patent because the linear structure of the initially formed ammonolysis product is stabilized in the anhydrous liquid ammonia containing the ionized, dissolved ammonium halide salt until the crosslinking mechanism initiates. This stabilization of linear structure is analogous to that effected in the '549 patent described above.

III. MOLECULAR WEIGHT

An example of the Weight Average Molecular Weight (M_w) of the polysilazane prepared from methyldichlorosilane by the process taught in the '487 process with minimal exposure time to by-product anhydrous liquid ammonia/ammonium chloride solution is 2495 g/mol, while its Number Average Molecular Weight (M_n) is 960. An example of the Weight Average Molecular Weight (M_w) of the polysilazane prepared from a mixture of dichlorosilanes comprising 80wt% methyldichlorosilane and 20wt% vinylmethyldichlorosilane by the process taught in the '487 process with minimal exposure time to by-product anhydrous liquid ammonia/ammonium chloride solution is 4836 g/mol, while its Number Average Molecular Weight (M_n) is 927 *[Flores, O., Schmalz, T., Krenkel, W., Heymann, L., Motz, G. "Selective Cross-Linking of Oligosilazaness to Tailored Meltable Polysilazanes for the Processing of Ceramic SiCN Fibres", J. Mater. Chem A, 2013, 1, 15406-15415].* These molecular weights are typical of state-of-the-art methods to prepare polysilazanes. Nevertheless, in the batch process taught in the '487 patent difficulties arise in having to handle large volumes of liquid ammonia in the separation of the two phases.

IV. THE CENTRIFUGAL PROCESS

A unique process feature of the CENTRIFUGAL PROCESS to prepare polysilazanes (U.S. Patent 12,091,513) whereby phase separation is effected inertially in a centrifugal device is, thus, two-fold: 1) low molecular weight aminosilanes and silazanes that are rapidly formed on halosilane ammonolysis and which are miscible in anhydrous, liquid ammonia are rapidly separated from the resulting ammonium halide and anhydrous, liquid ammonia by-product of the ammonolysis, and 2) the condensed polysilazane and anhydrous, liquid ammonia-ammonium halide by-product phases that form upon subsequent condensation of the initially formed aminosilanes can be continuously separated as the denser and less polar polysilazane phase is formed in the liquid phase containing the initial ammonolysis products of the reaction, and at a

much faster rate than under ambient conditions of settling. As stated above, this results, compositionally, in polysilazanes that, despite having Si-H bonds, do not have branched and, consequentially, crosslinked structures, and indeed these polysilazanes are also statistically predisposed to non-cyclic structures. Linear polysilazanes are obtained because the isolation of the diaminosilanes and low molecular weight silazanes that are formed in a liquid phase that is strictly separated and isolated from the anhydrous, liquid ammoniaammonium halide by-product eliminate all possibility of activation of Si-H bonds in those aminosilanes and low molecular weight silazanes to generate branching through dehydrocoupling or ammonolysis of sites originally containing Si-H radicals.

While the Molecular Weight of a polymer can be reported in several ways, the two most common are the polymer's Number Average Molecular Weight (M₀) and Weight Average Molecular Weight (M₀). Number Average Molecular Weight is typically important when one is considering polymer properties that are based on the number of polymer chains in a sample (like osmotic pressure), while Weight Average Molecular Weight is important when one is considering polymer properties that depend on polymer chain size and weight (like light scattering). In the case of preceramic polymers, such as polysilazanes, the yield of ceramic material upon pyrolysis ("ceramic" or "char" yield) is of prime importance. Thus, the Weight Average Molecular Weight (M₀) is more important than the Number Average Molecular Weight (M₀) for such polymers, since volatilization of material upon heating to pyrolysis temperatures needs to be minimized. Typically, it is desirable to employ preceramic polymers having Weight Average Molecular Weights of greater than about 500 g/mol in order to achieve high ceramic yields. For instance, for a composition comprising simply a mixture of equal parts of a cyclotrimer, cyclotetramer, cyclopentamer, and cyclohexamer having -Si(H)(CH₃)-NH- repeat units, the Weight Average Molecular Weight (M₀) can be calculated to be 281.43 g/mol. Weight Average Molecular Weights (M₀) of well over 500 g/mol can be achieved by employing the centrifugal process.

The prior art is replete with examples of the preparation of uncrosslinked polysilazanes that do not comprise Si-H bonds - which are prerequisite to a crosslinked structure when dihalosilanes are used as starting material. Examples cited in a paper by Andrianov [D. Ya. Zhinkin,

E.A. Semenova, L.M. Tartakovskaya, N.V. Markova, and K.A. Andrianov, "Ammonolysis and

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