Synthesis and Characterization of a Soluble, Highly Branched Organo-Silicon−Nitride Polymer

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A highly soluble organopolysilazane was generated from the reaction of $CySiCl_3$ with Li_3N in diglyme. On the basis of light scattering, elemental analysis, NMR spectra, and solubility data, this polymer is believed to be highly branched with a molecular weight of approximately 26 000 Da. The polymer is characterized by excellent solubility in all organic solvents, a highly economical method of synthesis, a hyperbranched topology, and potential applicability to a wide range of R group modification. The use of lithium nitride has allowed the generation of highly branched structures without the need to further treat the polymer with insolubilizing cross-linking agents.

I. Introduction

Silicon nitride and carbosilicon nitride materials have attracted great interest over the last 20 years due to their exceptional properties as strong, refractory, chemically inert ceramics.[1−4] Processing of these materials is hampered by the classical synthesis method, cocondensation of silicon tetrachloride/ammonia mixtures, which typically produces intractable materials.[1] The reaction releases large amounts of corrosive HCl, and the resulting material cannot be further processed except by sintering. Soluble polysilazane precursors are a promising solution to the problems with current preceramic silicon nitride materials; however, the moisture sensitivity of most polysilazanes has made structural characterizations challenging.[5−7] Seyferth and co-workers developed polysilazanes of ∼3000 Da from base-induced condensations. These soluble preceramics can be applied to the syntheses of carbosilicon nitride and silicon nitride ceramics (eq 1).[8,9] Several other groups have explored the synthesis of polysilicon nitride from simple alkylsilicon chlorides and amines, but they also obtained low molecular weight polymers and intractable solids.[10−15] Lithiated amines have been used as sources of nucleophilic nitrogen, with results similar to those for the reactions of amines.[16−18] With the exception of a study by Burns et al.,[19] it was consistently observed that high molecular weight polysilazanes could not be synthesized by these methods. Solubility also dropped off rapidly upon cross-linking with strong base. This is unfortunate as cross-linking appears to be responsible for an improvement in ceramic yield over the more linear polymer structures.[8]

$$H_2SiCl_2/Me_2SiCl_2 + NH_3 \xrightarrow{CH_2Cl_2 \text{ or } Et_2O} \text{polysilazane oil } (\sim 3000 \text{ daltons}) \quad (\mathbf{1})$$

The cross-linked polymers are proposed to have a flat, fused-ring structure.[8,9] Soluble, high molecular weight materials with this topology are needed to improve processability closer to the final pyrolysis step. A novel approach explored by several groups is transition-metal-based catalytic polymerization of silicon and nitrogen compounds, leading to silicon−nitrogen bond formation. These methods involve catalytic ring opening polymerization or dehydrocoupling by a variety of catalysts (eq 2).[20−23] Observation of high molecular weight materials has been unsuccessful via these routes, though this may

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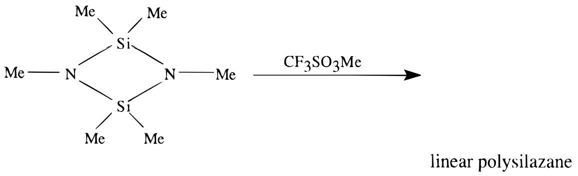
$$R_2SiH_2/RSiH_3 + RNH_2 \xrightarrow[-H_2]{\text{metal catalyst}} \text{oligomers and cyclics} \qquad (2)$$

only be a function of catalyst design. The low molecular weight polymers produced by these methods are proposed to have structures which are linear, cyclic, or chains of Si−N linked together. These catalytic methods have the advantage of operating under very mild conditions and the ability to act on simple, readily obtainable substrates.

A major breakthrough was made by Soum and coworkers in 1992. Ring-opening polymerization of organocyclosilazanes gave high molecular weight, linear polysilazanes (eq 3).[24] The substrates with which this reaction will work appear to be limited to organocyclodisilazanes with small R groups. However, polymers of up to 100 000 Da can be obtained, and these materials are soluble and stable to air oxidation.



(3)

We have discovered a new method for generating high molecular weight polysilazanes from Li_3N and $RSiCl_3$ in diglyme solvent. The polymers have a highly branched Si−N framework yet retain excellent solubility in all organic solvents. All starting materials are cheap and commercially available. The synthesis and characterization of these materials are reported.

II. Experimental Section

All air-free manipulations were carried out using standard vacuum line and drybox techniques. Anhydrous diglyme was used as received from Aldrich in a Sure-Seal bottle. Identical results were obtained using freshly distilled diglyme dried by refluxing over sodium metal. All other solvents were distilled from Na/benzophenone just prior to use. $C_6H_{11}SiCl_3$, $LiAlH_4$, Me_3SiCl, NH_3, and $HN(SiMe_3)_2$ were purchased from Aldrich or Gelest and used as received. Lithium nitride was purchased from Alfa Aesar and used as received. ^{1}H NMR spectra were recorded at 400 MHz and referenced to the residual protons in C_6D_6 at 7.15 ppm. ^{13}C NMR spectra were recorded at 100 MHz and referenced to the natural abundance of ^{13}C in C_6D_6 (128.0 ppm). ^{29}Si NMR spectra were recorded at 71 MHz and referenced to the natural abundance of ^{29}Si in $SiMe_4$ (0.0 ppm). IR spectra were recorded on Nicolet model 5DXB and 740 spectrometers. Light-scattering data were collected on a Dawn DSP multiangle laser light scattering photometer in conjunction with an Optilab differential refractometer. Sample solutions were prepared in an inert atmosphere glovebox using THF and filtered through a 0.02 μm filter. The solutions were placed in 20 mL scintillation vials, sealed before removal from the glovebox, and centrifuged at 3200 rpm for 15 min immediately before MW analysis. Elemental analyses were submitted to Galbraith Analytical services (C, H, N, Cl) or performed in-house on a Perkin-Elmer model 2400 analyzer (C, H, N). X-ray photoelectron spectroscopy (XPS) was performed using a conventional Mg X-ray source and a Physical Electronics model 10-360 spherical capacitor analyzer fitted with a multichannel detector.

$(C_6H_{11}SiN)_n(diglyme)_{0.10n}Cl_{0.10n}$ (1). A 2.86 mL (16.4 mmol) portion of $C_6H_{11}SiCl_3$ and 572 mg (16.4 mmol) of Li_3N were refluxed in diglyme for 2 h, the solvent was cooled, and all volatiles were removed followed by continued drying in vacuo for 12 h. The solids were dissolved in toluene, filtered to remove LiCl, and dried again for 12 h in vacuo to give a flaky, pale amber powder (2.02 g, 87% yield based on silicon). The LiCl byproduct was isolated and recovered in an 83% yield. ^{1}H NMR (C_6D_6): δ 4.2−3.2 (br, diglyme), 1.81 (br, Cy), 1.41 (br, Cy). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 75−59 (diglyme), 30−26 (br, cyclohexyl-C). IR (KBr): 1194−851 (br, Si−N, overlapped with Si−C and C−H). Elem Anal. Found: C, 51.6; H, 8.6; N, 8.8; Cl, 3.0. MW (light scattering, THF): 26 000 Da.

$[(C_6H_{11})SiCl_2]_3N$ (2). A 2.50 g (11.6 mmol) sample of $C_6H_{11}SiCl_3$ and 150 mg (4.31 mmol) of Li_3N were refluxed for 4 h in THF. During this time the deep maroon color of undissolved Li_3N was observed to give way to a solution with only white insoluble solids visible. The THF was removed in vacuo, and the solids were washed away from the insoluble salts with hexane (10 mL, 14×). The product was isolated as a white powder by recrystallization and filtration from 5 mL of hexane (620 mg, 24% yield). ^{1}H NMR (C_6D_6): δ 2.09 (d, 2H, $J = 13.6$ Hz), 1.99 (t of t, 1H, $J = 12.6, 2.8$ Hz), 1.64 (d of t, 2H, $J = 12.8, 3.2$ Hz), 1.50 (d of m, 1H, $J = 12$ Hz), 1.39 (q of d, 2H, $J = 12.5, 2.8$ Hz), 1.08 (m, 3H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 34.54, 27.53, 26.87, 26.44. MS (CI mode, ammonia): m/e 577 ($[M + NH_4]^+$), 524 ($[M - Cl]^{\bullet +}$), 476 ($[M - \text{cyclohexyl}]^{\bullet +}$). Anal. Calcd for $C_{18}H_{33}Cl_6NSi_3$: C, 38.6; H, 5.9; N, 2.3: found C, 38.7; H, 5.9; N, 2.6.

III. Results and Discussion

To the best of our knowledge, lithium nitride has not been previously employed to synthesize organosilazanes. Solubilizing the lithium nitride is the key to modulating the reactivity. Diglyme was noted to be the best solvent for this purpose, although the reaction also proceeded in THF and diethyl ether. Reactions did not proceed to any appreciable extent in aliphatic or aromatic solvents. Small molecules and oligomers could be observed in this system, especially for reactions run at low temperature or in THF and diethyl ether. The use of refluxing diglyme eliminated the presence of small molecules in the product mixture. The bimodal product distribution is reminiscent of the observed reactivity when ammonia or amines are used as the nitrogen source. Amines and ammonia typically produce a mixture of polymers and ring compounds.[25,26] Anionic sources of nucleophilic nitrogen besides lithium nitride have been explored in silicon−nitrogen bond-forming reactions. There have been several instances where lithiated amines were shown to be useful in the controlled synthesis of silicon−nitrogen bonds, but not high molecular weight polymers.[15−17,27,28]

A round-bottom flask was charged with a 1:1 ratio of Li_3N and $CySiCl_3$. Dry diglyme was added via syringe under an argon atmosphere and the mixture refluxed for 2 h. Diglyme was removed in vacuo and the soluble, polymeric material washed away from the insoluble LiCl using hexane or toluene. The isolated yield of silazane

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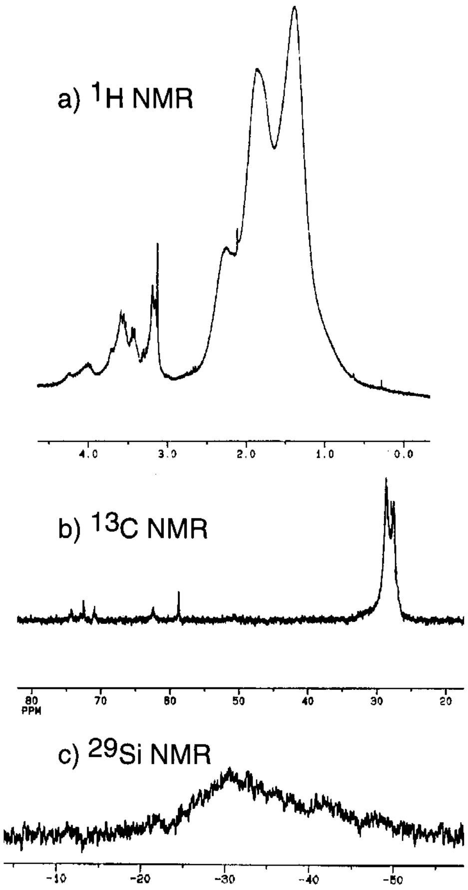

Figure 1. NMR data for **1**: (a) ^{1}H NMR (4.3−3.0 ppm, diglyme; 2.5−1.0 ppm, cyclohexyl group), (b) ^{13}C NMR, (c) ^{29}Si NMR.

polymer was typically ~90%, although inclusion of diglyme made exact calculation of the yield problematic. Relative integration of the diglyme and cyclohexyl peaks allowed an estimate to be made that the isolated material was approximately 10% diglyme by weight. Attempts to further reduce the amount of diglyme present failed. Indeed, **1** can be heated past its melting point of ~100 °C as high as 200 °C in vacuo without detectable decomposition, as monitored by ^{1}H NMR or further loss of diglyme, although a visible darkening of the amber color does occur. The results obtained for the reaction of $CySiCl_3$ and Li_3N in refluxing diglyme are summarized in eq 4.

$$CySiCl_3 + Li_3N \xrightarrow[\text{reflux}]{\text{diglyme}} (CySiN)_n{*}(\text{diglyme})_{0\cdot 10n}Cl_{0\cdot 10n} + 2.5\ LiCl \qquad (4)$$

The lithium chloride byproduct was isolated in 83% yield. Polysilazane **1** is infinitely soluble in aprotic organic solvents and relatively stable as a solid in air. However, **1** is highly water sensitive when dissolved in solution, rapidly forming white precipitates with evolution of ammonia detected.

Multinuclear NMR spectra of **1** are provided in Figure 1. The broad cyclohexyl features are present between 0.5 and 3.0 ppm. The diglyme can be seen between 3.0 and 4.5 ppm. The spectra suggest that solvent molecules are trapped into the polymer matrix, as the resonances for the residual solvent are broad and shifted. The diglyme oxygens may interact with the silicon atoms; however, the details of the interaction are not known. The ^{13}C NMR spectra are similarly broad, as is the primary feature in the ^{29}Si NMR data. Several attempts were made to endcap **1** under the assumption that the end groups consisted of reactive Si−Cl or Si−N functionality. It was hoped that such experiments could help to provide an estimate of molecular weight and help to stabilize the material. Reagents used included $LiAlH_4$, NH_3, $HN(SiMe_3)_2$, and Me_3SiCl. Reaction was observed only for $LiAlH_4$, and in that case the infrared spectrum for the soluble polymeric product revealed that Si−H, N−H, and Al−H bonds were present. The polymer treated with $LiAlH_4$ exhibited increased solution stability, but did not lend itself to end group analysis by ^{1}H NMR.

Static light scattering was used to determine the molecular weight of **1,** giving a value for M_w of 26 000 Da. On the basis of a repeat unit of CySiN, the degree of polymerization (DP) can be estimated to be ~200. The calculated radius of gyration is 20 nm. Combining the radius of gyration with the estimated DP of 200 and an average Si−N bond distance of 1.745 Å and using the relationships derived by Raleigh, Neugebauer, Debye, and Zimm,[29] the most consistent shape for this polymer in THF solution is approximated by a flexible coil. The observed radius of gyration is far too small for a rigid rod ladder polysilazane of DP 200 and is roughly twice as large as one would expect for an ideal sphere. The scatter in the Zimm plots suggests a polydisperse material, consistent with the broad NMR and IR spectra.[29,30] The moisture sensitivity of these polymers, particularly when in dilute solution, made these measurements very challenging. We were unable to obtain anhydrous enough conditions to avoid degradation of the polymers when attempting gel permeation chromotography, thus preventing us from obtaining more direct information regarding polydispersity.

Elemental analysis of **1** provides considerable insight into the structure of the polymer in tandem with the NMR and IR data (C, 51.6; H, 8.6; N, 8.8; Cl, 3.2). The carbon-to-hydrogen ratio is consistent with intact alkyl fragments, and after subtraction of diglyme carbon and hydrogen, the ratio of C_6H_{11} fragments to nitrogen is 1.0 to 1, supporting a structural repeat unit of $(RSiN)_n$. The chlorine analysis indicates approximately one unreacted chlorine termination for every seven silicon atoms, which is consistent with the observed 83% recovery of LiCl. XPS analysis of the polymer indicates the presence of less than 1 lithium per 100 nitrogen atoms. Given the stoichiometric constraints and the support from the NMR and Zimm plots showing a polydisperse, irregular structure, the polymer backbones one might propose for **1** are now rather limited. Spectroscopic and elemental analyses suggest that ~85% of silicon fragments are trifunctional and that all of the nitrogen fragments are trifunctional. No evidence of SiH, NH, or OH functional groups was seen in the infrared spectra. About 15% of silicon atoms may be difunctional, due to unreacted chlorine terminations.

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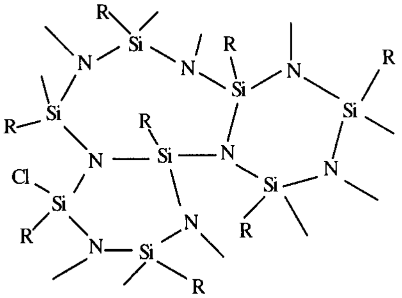

Figure 2. Proposed structure of polysilazane derived from $CySiCl_3/Li_3N$.

The most consistent structure is a hyperbranched polymer composed mostly of rings. Defects arising from remaining Si−Cl terminations contribute to the irregular distribution of rings and a mix of fused and nonfused ring cross-links. A schematic cross section of the proposed polymer structure is shown in Figure 2. Multiring structures are precedented in Si−N chemistry and have been invoked frequently in previous assignments of polysilazanes.[8,9,15] A ladder polymer, consisting of consecutive fused four-membered rings, appears unlikely on the basis of the observed physical properties, due to rigidity, and is also inconsistent with the light scattering data. Purely dendrimeric polymer backbones cannot converge to the observed stoichiometry without invoking a great deal of cross-linking. The amount of cross-linking required eventually brings one back to an irregular hyperbranched structure, as proposed above. This is consistent with the predicted flexible coil shape the polymer assumes in THF solution based on light scattering data and may explain the excellent solubility of these molecules. It is not certain which types of rings are present, but the need for an irregular structure supports the notion that a mixture of four-, six-, and eight-membered rings is possible.

Numerous trisilylamines have been reported in the literature, using ammonia, amines, or lithiated versions thereof as nitrogen sources.[16,23−25] In only one instance, however, have the silicon atoms remained completely chlorinated, and in that case no alkyl derivatives are known.[31] Trisilylamine **2** was prepared from reflux reaction in THF, isolated as a white powder, and characterized by ^1H and ^{13}C NMR, mass spectroscopy, and elemental analysis. On the basis of previous work regarding the structural characteristics of the Si_3N moiety, the expected geometry around nitrogen is trigonal planar.[32] Trisilylamine **2** contains a high density of reactive Si−Cl bonds and is very sensitive to moist air when in solution. **2** is also very reactive toward Li_3N, much more so than $CySiCl_3$. Whereas $CySiCl_3$ must be refluxed with lithium nitride in diglyme to ensure efficient conversion to polymer, **2** needs only to be stirred at room temperature with 2 equiv of lithium nitride for a few hours to observe complete conversion to silazane polymer. Apparently, starting with $CySiCl_3$ provides pathways to kinetically stable small molecules that are avoided when starting with pure **2**.

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Supporting Information Available: Details of the light-scattering measurements including Zimm plots (4 pages). Ordering information is given on any current masthead page.

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