

Reductive halocyclosilazane polymerization

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The synthesis of a chloro-functionalized six-membered cyclosilazane (Si5N) is reported. Subsequent reductive polymerizations yielded low molecular weight polysilazanes. ¹H and ²⁹Si NMR characterization suggest the identity of the reducing metal influences the polysilazane structure. Optical characterization is consistent with extended σ -conjugation upon polymerization.

Introduction

σ -Conjugation in oligo- and polysilanes, small molecules and polymers with catenated Si–Si bonds, arises from the interaction of the orbitals that comprise the σ -bonded inorganic core.^{1,2} The unusual properties of σ -conjugated silanes, including bathochromically shifted absorption spectra relative to alkanes³ and conformation-dependent optoelectronic properties,^{4,5} have long sparked both fundamental and applied studies.^{6–9} Our research group studies how incorporation of heteroatoms such as boron and nitrogen perturb σ -conjugation. We have previously described charge transfer characteristics in emissive hybrid σ,π -oligosilanes and Si–B rings,^{10–12} as well as nitrogen's ability to bridge σ - and π -conjugated fragments in Si–N rings (cyclosilazanes).¹³ We also reported the synthesis of the poly(cyclosilanes), a class of silicon-inspired conjugated polymers obtained from dehydrocoupling polymerization of cyclic precursors.^{14–18}

Herein, we explore nitrogen incorporation into molecular and polymeric cyclosilane frameworks. Our goals were to investigate the synthetic limits of Wurtz polymerization and identify new functional polysilanes. Reductive dichlorodialkylsilane (Cl₂SiR₂) polymerization is typically performed with molten sodium (110 °C, toluene) which limits the scope of compatible side chain functionality;^{1,19} for example, monomers bearing Si–X (X = O, N) bonds are a traditional limitation.²⁰ Likely for these reasons, the synthesis of SiN polymers (polysilazanes) has focused on ring-opening polymerization^{21,22} or condensation of halosilanes and amines.^{23–25}

Inspired by Tamao's seminal synthesis of nitrogen-functionalized silyl anions via lithium-mediated chlorosilane

reduction,^{26–28} we targeted the preparation of nitrogen-functionalized poly(cyclosilane)s via comparison of sodium- and lithium-mediated reductive polymerization of a suitable halo-functionalized cyclosilazane precursor. While polysilazanes with random cyclic subunits have been reported,^{25,29} well-ordered poly(cyclosilazane) structures have not.

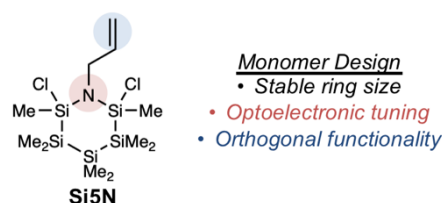


Figure 1. Design of Si5N monomer.

Strategic monomer design facilitates the synthesis of complex polymers. Like carbocyclic cyclohexane, six-membered cyclohexasilane is minimally ring-strained.^{30,31} Inspired by this stability, we targeted **Si5N** as a system combining a six-membered SiN heterocycle that might be resistant to ring-opening pathways and Si–Cl bonds amenable to Wurtz polymerization (Figure 1). We further appreciated that the **Si5N** nitrogen side chain provided an opportunity to introduce an orthogonal functional group. An allyl side chain was chosen, as it provides a functional handle that aids in structural characterization. An additional advantage of the allyl group is that it is not π -conjugated, as our earlier work on N-aryl cyclosilazanes showed that nitrogen can influence σ,π -conjugation. Finally, we appreciated that the allyl group could facilitate future postpolymerization functionalization.^{32,33} Stüger and West previously reported the reductive polymerization of dichlorodialkylsilanes bearing remote olefinic side chains and demonstrated postpolymerization olefin functionalization.³⁴

Experimental

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General information

All experiments were performed using either standard Schlenk line techniques under a dry argon atmosphere or in a UNILab Plus Glove Box by MBRAUN under a dry nitrogen atmosphere. All glassware was oven dried overnight in a 175 °C oven. 1,3-dichloro-1,1,2,2,3,3-hexamethyltrisilane was prepared by adaptation to a previously reported procedure.³⁵

All reaction solvents were dried and degassed on a J. C. Meyer Solvent Dispensing System. Granular lithium, triethylamine, allylamine, isopropylmagnesium chloride (2.0 M in THF), methylmagnesium bromide (3.0 M in Et₂O), NEt₃•HCl, naphthalene and dichlorodimethylsilane were purchased from Sigma Aldrich. Chloromethyldiphenylsilane and cyclohexane were purchased from Alfa Aesar. Trifluoromethanesulfonic acid was purchased from Acros Organics. Chlorodimethylphenylsilane was purchased from Gelest. Triethylamine (NEt₃) was freshly distilled from KOH under Ar prior to each use. Allylamine was distilled from CaCl₂ and degassed via freeze-pump-thaw. Naphthalene was recrystallized with methanol. Cyclohexane was sparged with N₂. All other purchased chemicals were used without further purification.

Instrumentation

¹H NMR, ¹³C {¹H} NMR, ²⁹Si {¹H} NMR, and ¹⁹F {¹H} NMR spectra were recorded either on a Bruker Avance 300 or 400 MHz Spectrometer and chemical shifts are reported in parts per million (ppm). NMR spectra were recorded in CDCl₃ or THF-*d*₆ with tetramethylsilane (TMS) or the residual solvent as the internal standard. Multiplicities are as indicated: s (singlet), d (doublet), t (triplet), q (quartet), dt (doublet of triplets), ddt (doublet of doublet of triplets), dtd (doublet of triplet of doublets), and m (multiplet). Coupling constants, *J*, are reported in Hertz and integration is provided. IR spectra were collected on a Thermo Scientific Nicolet iS5 spectrometer equipped with iD5 ATR laminated diamond crystal attachment.

High Resolution Mass Spectrometry (HRMS) was performed at the Columbia University mass spectrometry facility using a Waters XEVO 62XS QToF mass spectrometer equipped with a UPC2 SFC inlet, electrospray ionization (ESI) probe, atmospheric pressure chemical ionization (APCI) probe, and atmospheric solids analysis probe (ASAP). All column chromatography was performed on a Teledyne ISCO Combiflash Rf+ using Redisep Rf silica columns. Elemental analysis was performed by Robertson Microlit Laboratories. For **Si5N**, carbon content was lower than expected by more than 0.4%. Although these results are outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date. Additionally, low carbon content in organosilane elemental analysis has previously been attributed to incomplete combustion related to SiC formation.^{36,37} HRMS and elemental analysis of **2** and **3** were not obtained due to poor stability of the Si-OTf bond.

Polymer molecular weights were measured by gel permeation chromatography (GPC) on a Tosoh Bioscience EcoSEC GPC workstation with UV detection at 254 nm using butylated hydroxytoluene stabilized tetrahydrofuran (THF) as

the eluent (0.35 mL min⁻¹, 40 °C) through TSKgel SuperMultipore HZ-M guard column (4.6 mm ID x 2.0 cm, 4 μm, Tosoh Bioscience) and a TSKgel SuperMultipore HZ-M column (4.6 mm ID x 15 cm, 4 μm, Tosoh Bioscience). Polystyrene standards (EasiVial PS-M, Agilent) were used to build a calibration curve. Processing was performed using EcoSEC Data Analysis software (Version 1.14, Tosoh Bioscience). Polymers were dissolved in THF inside a glove box (1 mg mL⁻¹), filtered (Millex-FG Syringe Filter Unit, 0.20 μm, PTFE, EMD Millipore), and injected using an auto-sampler (10 μL).

UV-vis spectra were collected with a Shimadzu UV-1800 UV-vis spectrophotometer. Emission spectra were collected with a Horiba Scientific Fluorolog-3 Spectrofluorometer with a 450 W xenon short arc light source, single excitation and emission monochromator at a Czerny-Turner design (0.3 nm resolution), reference photodiode, 2 nm slit width, and a PMT emission detector R928P. The UV-vis and emission spectra were measured at room temperature in THF for **Si5N**, **P1**, and **P2** in a quartz cuvette (10 mm) with an analyte concentration = 1.25 x 10⁻⁵ M for Si5N and 0.0124 g/L for **P1** and **P2** prepared in a nitrogen glove box. Emission spectra of **P1**, **P2**, and air exposed **P2** were excited with a wavelength at 280 nm and Si5N was excited at 250 nm. Each emission spectra were subtracted by the emission spectrum of a solvent blank. Absorption and emission measurements used to determine the quantum yield of **P2** relative to a naphthalene standard in cyclohexane³⁸ are shown in Figures S8-12.

Synthetic procedures

Synthesis of 1. Li metal (1.90 g, 274 mmol, 8 equiv) was added to an oven dried 250 mL round bottom Schlenk flask with stir bar cooled under vacuum. An oven dried addition funnel was equipped to the Schlenk flask, sealed with a septum, and cooled under vacuum. The apparatus was cycled under argon three times. THF (69 mL) was added through the addition funnel into the flask and the flask was cooled to 0 °C in an ice water bath. Chloromethyldiphenylsilane (14.4 mL, 68.4 mmol, 2 equiv) was added to the funnel via syringe and the solution was added dropwise at 0 °C for one hour. Once the addition finished, the reaction mixture was warmed to room temperature and stirred overnight (16 hours) and a dark yellow-green colour formed. The reaction mixture was filtered under Ar into a separate 250 mL Schlenk flask and the filtrate was cooled to 0 °C. *i*-PrMgCl (34 mL, 68 mmol, 2 equiv) was added dropwise to the filtrate via syringe and stirred at 0 °C for 20 min. 1,3-dichloro-1,1,2,2,3,3-hexamethyltrisilane (8.39 g, 34.2 mmol, 1 equiv) was added dropwise at 0 °C and stirred at room temperature for 3 h under Ar. The reaction was quenched at 0 °C by dropwise addition of water (15 mL) followed by saturated ammonium chloride (15 mL). The mixture was liquid-liquid extracted three times with diethyl ether, dried with brine and Na₂SO₄. Solvent was concentrated via rotary evaporation to give a yellow liquid. The crude product was purified through column chromatography, eluting with a 95:5 ratio of hexanes:CH₂Cl₂, as the second fraction. A white solid was obtained (15.39 g, 79%). δ ¹H (300 MHz, CDCl₃) 7.48 – 7.41 (m, 8H), 7.35 – 7.29 (m, 12H), 0.61 (s, 6H), 0.18 (s, 12H), -0.17 (s, 6H). δ ¹³C (101 MHz, CDCl₃) 137.81,

134.97, 128.85, 127.94, -3.65, -4.43, -4.48. $\delta^{29}\text{Si}$ (79 MHz, CDCl_3) -19.07, -39.58, -42.75. HRMS (ASAP+): $[\text{M}^+]$ calcd. for $\text{C}_{32}\text{H}_{44}\text{Si}_5$ 568.2289, found 568.2285. Anal. calcd. C, 67.53; H, 7.79; N, 0; found C, 67.31; H, 7.73; N, <0.10.

Synthesis of 2. **1** (3.00 g, 5.27 mmol, 1 equiv) was added an oven dried 100 mL Schlenk flask with stir bar and cycled three times under Ar. Pentane (27 mL) was then added via syringe. An oven dried addition funnel was cooled in the antechamber of a glove box. Inside a glove box, trifluoromethanesulfonic acid (TfOH, 1.87 mL, 21.1 mmol, 4 equiv) was added to the addition funnel, the funnel was sealed with a dummy flask on the male joint, then brought out of the glove box under N_2 . The funnel was quickly swapped with the Schlenk flask with a heavy flow of Ar and TfOH was added to the reaction mixture dropwise at 0 °C. Once the addition completed, the reaction mixture was warmed to room temperature and stirred for 1.5 h. Solvent was removed under vacuum to yield **2** as a yellow liquid. **2** was carried forward without further purification. $\delta^1\text{H}$ (300 MHz, CDCl_3) 0.95 (s, 6H), 0.47 (s, 12H), 0.41 (s, 6H). $\delta^{13}\text{C}$ (101 MHz, CDCl_3) 118.31 (q, $J = 318.1$ Hz), 2.38, -5.49, -6.44. $\delta^{29}\text{Si}$ (79 MHz, CDCl_3) 26.79, -38.69, -41.01. $\delta^{19}\text{F}$ (282 MHz, CDCl_3) -75.41.

Synthesis of 3. Continuing from the synthesis of **2**, Et_2O (27 mL) was added to the Schlenk flask. Freshly distilled NEt_3 (1.47 mL, 10.5 mmol, 2 equiv) was added via syringe, shortly followed by allylamine (0.40 mL, 5.27 mmol, 1 equiv). A biphasic mixture quickly formed, and the reaction was stirred overnight at room temperature (16 hours). The next morning, the reaction mixture was cooled to -78 °C with a dry ice/acetone bath. The bottom ionic liquid layer ($\text{NEt}_3 \cdot \text{HOTf}$) froze and the top Et_2O layer was cannulated under vacuum to an oven dried 100 mL Schlenk flask under Ar. The solvent was removed under vacuum yielding **3**, a colourless liquid. The product was inspected by ^1H NMR and carried forward without further purification. Due to the presence of two diastereomers and minor impurities, tabulated integrations are not included. $\delta^1\text{H}$ (400 MHz, CDCl_3) 5.92 – 5.76 (m), 5.20 – 5.11 (m), 5.05 (m), 3.96 (dt, $J = 5.1, 1.9$ Hz), 3.92 (dt, $J = 5.1, 1.8$ Hz), 3.88 (dt, $J = 4.2, 1.9$ Hz), 3.81 (dt, $J = 5.4, 1.8$ Hz), 3.78 – 3.74 (m), 0.68 (s), 0.63 (s), 0.37 (s), 0.34 (s), 0.34 (s), 0.32 (s), 0.32 (s), 0.29 (s), 0.28 (s). $\delta^{13}\text{C}$ (101 MHz, CDCl_3) 137.56, 136.95, 118.50 (q, $J = 317.8$ Hz), 116.45, 115.33, 48.40, 47.09, 0.07, -1.04, -6.22, -6.65, -6.73, -7.47. $\delta^{29}\text{Si}$ (79 MHz, CDCl_3) 25.63, -44.87, -49.78. $\delta^{19}\text{F}$ (282 MHz, CDCl_3) -76.10, -76.17.

Synthesis of Si5N. Continuing from the synthesis of **3**, crude **3** was dissolved in Et_2O (27 mL). Under a positive pressure of Ar, $\text{NEt}_3 \cdot \text{HCl}$ (1.45 g, 10.5 mmol, 2 equiv) was added through a powder funnel. The reaction was stirred at room temperature for 1.5 h. A biphasic mixture formed with the ionic liquid $\text{NEt}_3 \cdot \text{HOTf}$ being the bottom layer. The organic layer was isolated at -78 °C using same procedure described in the synthesis of **3**. Et_2O was removed under vacuum to yield a viscous yellow liquid. The crude mixture was sublimed under vacuum (0.7 torr, 70 °C) to give a colourless, waxy solid (1.69 g, 82% overall from **1**). Due to the presence of diastereomers, relative integrations of the Si-Me peaks for the *trans* and *cis*

isomers are provided. Allyl peaks for each diastereomer overlapped and could not be integrated relative to each diastereomer. $\delta^1\text{H}$ (400 MHz, CDCl_3) allyl peaks: 5.93 – 5.81 (m), 5.24 (dtd, $J = 17.1, 1.9, 1.5$ Hz), 5.14 – 5.06 (m), 3.83 (dt, $J = 4.9, 1.9$ Hz), 3.79 (m), 3.70 (dt, $J = 4.6, 1.9$ Hz), 3.66 (dt, $J = 4.6, 1.9$ Hz); *trans*-**Si5N** Si-Me (70%): 0.57 (s, 6H), 0.33 (s, 6H), 0.27 (s, 6H), 0.26 (s, 6H); *cis*-**Si5N** Si-Me (30%): 0.52 (s, 6H), 0.33 (s, 6H), 0.31 (s, 3H), 0.23 (s, 3H), 0.23 (s, 6H). $\delta^{13}\text{C}$ (101 MHz, CDCl_3) 139.03, 138.67, 115.33, 114.73, 48.00, 47.16, 3.39, 2.29, -5.61, -5.73, -5.75, -5.77, -5.93, -6.19, -6.31. $\delta^{29}\text{Si}$ (79 MHz, CDCl_3) 19.85, 19.24, -43.08, -43.44, -49.08, -49.30. (ASAP+) calcd. HRMS (ASAP+): $[\text{M}^+]$ calcd. $\text{C}_{11}\text{H}_{30}\text{Si}_5\text{NCl}_2$ 386.0602, found 386.0602. Anal. calcd. C, 34.17; H, 7.56; N, 3.62, found C, 33.59; H, 7.59; N 3.69.

Polymerization procedures

For Table 1, entries 1 and 2. An oven dried 25 mL 2 neck round bottom flask with stir bar was cooled under vacuum. Sodium metal (0.47 g, 4.4 equiv) was weighed and quickly added to the flask and cycled under Ar 3 times. The residual mineral oil on the sodium surface was rinsed 3 times with 10 mL of pentane via syringe then dried under vacuum for 10 min. The flask was brought into a glove box where **Si5N** (1.9 g, 4.91 mmol) was weighed and added to the flask. The flask was brought out of the glovebox under nitrogen and equipped with a reflux condenser on a Schlenk line. Toluene (5 mL) was added and the reaction mixture was heated to 110 °C. The reaction mixture turned dark purple. At 4 h, an anhydrous aliquot (0.5 mL) was taken and dried under vacuum in a 10 mL round bottom flask. At 24 h, the reaction mixture was cooled to room temperature and the reaction mixture was filtered through a Schlenk funnel under Ar, giving a clear, slightly yellow filtrate. The filtrate was dried under vacuum to yield a slightly yellow gel.

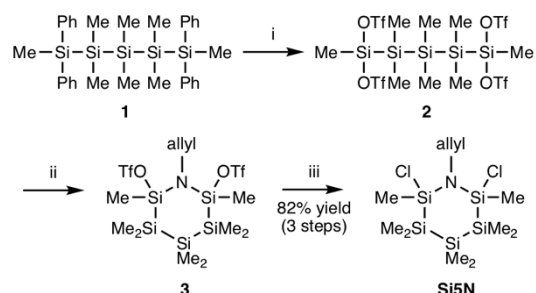
For Table 1, entries 3-5. The same procedure for weighing sodium and removing mineral oil described above was used. Inside the glove box, sodium metal was finely cut with a razor blade (use caution when handling sharp objects inside the glove box). **Si5N** (1.90 g, 4.91 mmol) was added to the flask followed by THF and the reaction mixture was stirred at room temperature. Similar aliquots described above were taken at 6 and 24 h. At 72 h the reaction mixture was filtered under Ar and concentrated under vacuum same as above.

For Table 2, entries 1-8. An oven dried 25 mL 2 neck round bottom flask with stir bar was cooled under vacuum inside a glove box antechamber. Inside the glove box, **Si5N** (1.4 g, 3.62 mmol) was weighed and the flask was brought out of the glove box under nitrogen. Lithium metal (0.111 g, 4.4 equiv or 0.057 g, 2.2 equiv) was weighed and quickly added to the flask. The flask was cycled under Ar three times. THF (4 mL) was then added. The reaction mixture turned cloudy yellow in 30 min for both 4.4 and 2.2 equiv of Li. Anhydrous aliquots (0.2 mL) were taken at 1, 2, 4, and 24 h for 4.4 equiv of Li and dried under vacuum in a 10 mL round bottom flask. Similar anhydrous aliquots were taken at 1, 2, and 4 h for 2.2 equiv. At 50 h (4.4 equiv) and 6 h (2.2 equiv), the reaction mixture was filtered under Ar and the yellow filtrate was concentrated under vacuum to yield a yellow solid for both reactions.

Results and discussion

Synthesis and characterization of Si5N

Our synthesis of **Si5N** began with oligosilane **1** (available in 1 step from known precursors),³⁹ which was dearylated to tetratriflate **2** (Scheme 1).^{40,41} Cyclization was achieved with allylamine/ NEt_3 , yielding **3**. Conversion of the triflates to chlorides was achieved with $\text{NEt}_3 \cdot \text{HCl}$, giving the target compound **Si5N** in 82% overall yield from **1**. Both **3** and **Si5N** bear two stereogenic centers and were isolated as 70:30 mixtures of diastereomers (vide infra). Control of relative stereochemistry in oligosilanes is a topical synthetic challenge⁴² as is understanding polysilane tacticity.¹⁷ We chose allylamine as the allyl group is not π -conjugated and contains characteristic NMR and IR signals that aid in the characterization of poly(**Si5N**).



Scheme 1. Synthesis of **Si5N**. i. TfOH (4 equiv.), pentane; ii. Allylamine (1 equiv.), NEt_3 (2 equiv.), Et_2O . iii. $\text{NEt}_3 \cdot \text{HCl}$ (2 equiv.), Et_2O

Analysis of ^1H and ^{29}Si 1-D NMR spectra (Figure 2) and the ^1H - ^{29}Si HMBC spectrum (Figure S1) allowed assignment of the major diastereomer to the *trans* isomer (*dr* = 70:30). Assignment of the major isomer to the *trans* diastereomer is based on the observation that the major isomer has a single methyl resonance assigned to position 3 (δ 0.27 ppm) while the minor isomer as two methyl resonances at the same position (δ 0.31 and 0.23 ppm, Figure 2a). *trans*-**Si5N** possesses a C2 rotational axis that renders these methyl groups equivalent (Figure S2, Table S1). Attempts to isolate pure diastereomers via chromatographic separation or crystallization have not been successful.

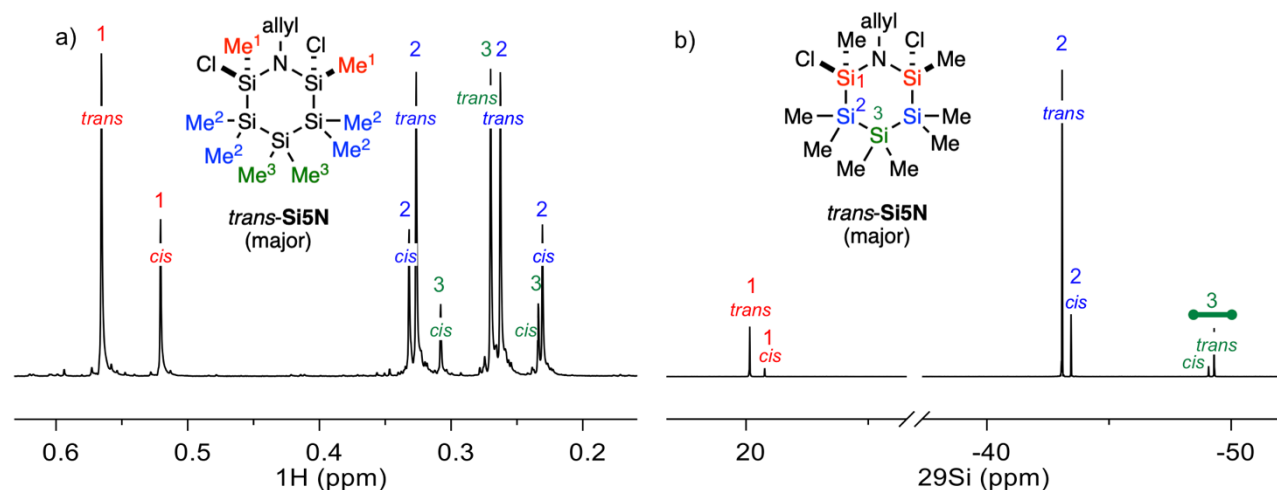
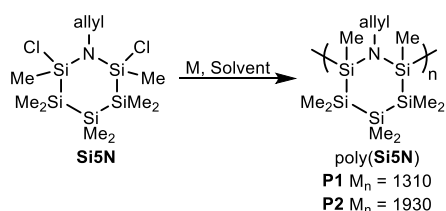


Figure 2. a) Cropped ^1H NMR spectrum (400 MHz, CDCl_3) highlighting methyl region. b) Cropped ^{29}Si $\{^1\text{H}\}$ DEPT NMR spectrum (79 MHz, CDCl_3). Assignments based on ^1H - ^{29}Si HMBC spectrum (Figure S1).

Reductive polymerizations of Si5N

Polymerization studies were carried out with sodium or lithium metal (Scheme 2) and are summarized in Tables 1 and 2. Standard Wurtz polymerization conditions with molten sodium in toluene (Table 1, entries 1 and 2) only gave a minor increase in M_n compared to Si5N (entry 6). Reports by Jones have suggested room temperature Wurtz coupling in THF yields higher molecular weight polysilanes.^{43,44} Under room temperature conditions (entries 3-5), slight M_n increases were observed. A low molecular weight shoulder was observed in the GPC spectra for extended reaction times (entries 4 and 5) suggesting degradation occurs due to potential backbiting or bond breakage (see experimental section).



Scheme 2. Generic reductive polymerization of Si5N. P1 was obtained with Na, P2 by Li.

Table 1. Molecular weight characteristics of poly(Si5N) from sodium promoted polymerizations. [Si5N] = 0.905 M with 4.4 equiv of Na.

Entry	Solvent/Temperature	Time	M_n^a	M_w^a	\bar{D}^b
1	Toluene/110 °C	4 h	768	1180	1.54
2	Toluene/110 °C	24 h	854	1300	1.52
3	THF/rt	6 h	756	1440	1.91
4	THF/rt	24 h	1040	2520	2.43
5 (P1)	THF/rt	72 h	1310	4470	3.41
6 ^c	N/A	N/A	441	523	1.19

^a M_n and M_w of total peak area determined by gel permeation chromatography (GPC) with UV detection at 254 nm relative to a polystyrene standard. ^b $\bar{D} = M_w/M_n$. ^c GPC of Si5N.

Polymer formation was more rapid with lithium at room temperature (Table 2, entry 1) with a maximum M_n and M_w observed at 2 h (entry 2). However, both the M_n and M_w decreased beyond 2 h (entries 4 – 6). ¹H and ²⁹Si NMR spectroscopy revealed the growth of a sharp peak at δ 0.13 and -42.2 ppm respectively (Figures S3 and S4), consistent with permethylated 5- and 6-membered Si rings. West has previously shown that thermodynamic conditions (e.g. extended reaction times) promote polysilane depolymerization to cyclic oligomers.⁴⁵ Matyjaszewski previously reported that anionic ring opening polymerizations of cyclotetrasilanes degrades to 5- and 6-membered rings over extended reaction times.⁴⁶ Fewer equivalents of Li yielded a slightly longer polymer (entry 8), but a longer reaction time was needed. Similar to sodium polymerizations, a low molecular weight shoulder was observed in the GPC spectra, consistent with degradation to cyclic oligomers (see experimental section).

Table 2. Molecular weight characteristics of poly(Si5N) from lithium promoted polymerizations. Standard conditions: [Si5N] = 0.905 M in THF, room temperature.

Entry	Li equiv	Time	M_n^a	M_w^a	\bar{D}^b
1	4.4	1 h	1740	5370	3.09
2	4.4	2 h	1760	6210	3.52
3	4.4	4 h	1570	4420	2.81
4	4.4	24 h	1350	3150	2.33
5	4.4	50 h	1220	2450	2.00
6	2.2	1 h	1270	3030	2.39
7	2.2	2 h	1470	3500	2.38
8 (P2)	2.2	6 h	1930	6920	3.59

^a M_n and M_w of total peak area determined by gel permeation chromatography (GPC) with UV detection at 254 nm relative to a polystyrene standard. ^b $\bar{D} = M_w/M_n$.

The physical properties of polymers obtained by sodium and lithium promoted polymerizations were markedly different. Polymers formed from sodium gave a light-yellow gel while lithium gave a light-yellow powder. Sodium promoted polymers were soluble in conventional organic solvents (Et₂O, CHCl₃, CH₂Cl₂, THF) while lithium promoted polymers were soluble in THF and sparingly soluble in CHCl₃. The differences in solubility and physical appearance suggest different polysilazane structures were formed.

Polymer characterization

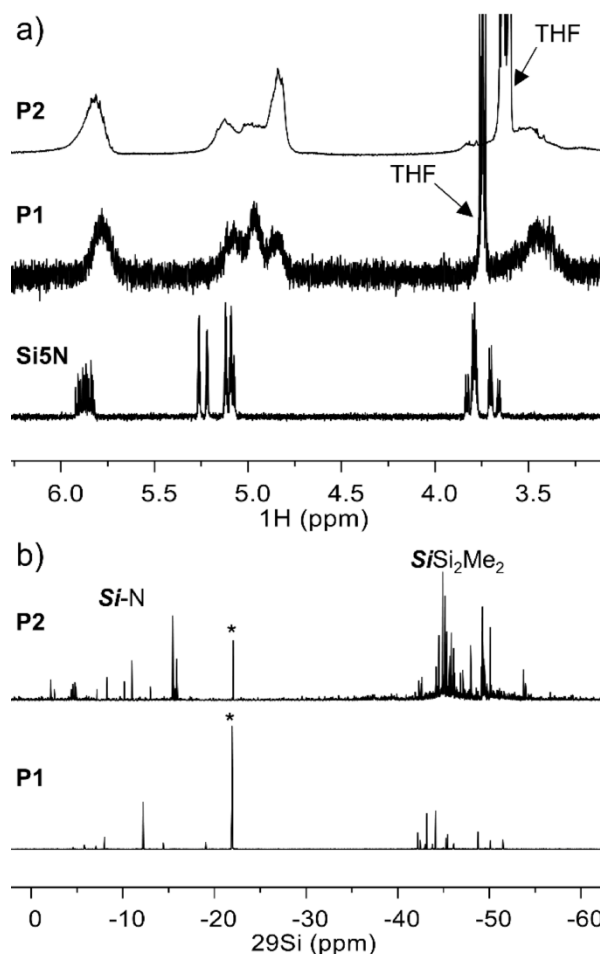


Figure 3. a) Cropped ¹H (400 MHz) NMR spectra of Si5N (CDCl₃), P1 (CDCl₃), and P2 (THF-*d*₈) and b) Cropped ²⁹Si (¹H) DEPT NMR spectra (79 MHz) of P2 (THF-*d*₈) and P1 (CDCl₃). * = silicon grease signal.

^1H NMR spectra of the highest molecular weight polymers derived from sodium (**P1**) and lithium (**P2**) exhibited broad resonances typical for polysilazanes. Similar N-allyl resonances were observed for **P1**, **P2**, and **Si5N**, suggesting the allyl substituent is preserved during polymerization (Figure 3a). Polarization transfer ^{29}Si NMR spectroscopy^{47,48} is a powerful tool for characterization of poly(cyclosilane)s.^{14–18} Figure 3b shows $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR spectra of **P1** and **P2**. Resonances between -40 and -55 ppm were assigned to SiSi_2 signals while the broad resonances between 0 and -15 ppm were assigned to SiN features. These assignments were made by comparison to literature compounds and Table S2 lists the Si-N resonances of related structures.^{49,50} The broad range of signals is consistent with an atactic polymer, but a mixture SiN(R)Si centers and SiN(R)H centers consistent with partial ring-opening cannot be definitively excluded.

While the NMR spectra of both **P1** and **P2** were consistent with similar functional groups, significant spectral differences were also observed. Most significantly, **P2** displayed more features in the $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR spectrum, especially between δ -40 and -55 (SiSi_2Me_2 region). Additional features unique to **P2** include sharp bands at δ -15 and -5. The increased number of chemical environments, combined with the decreased solubility of **P2**, suggests that **P2** could be cross-linked. A challenge in determining the chemical pathways that might lead to distinct structures is the mechanistic complexity of Wurtz coupling, in which silyl radicals, silyl radical anions, and silyl anions have all been implicated.⁴⁴ In light of the relatively well-preserved allyl signals, we speculate crosslinking arises from reactions across the silicon backbone such as ring-opening and interchain recombination.

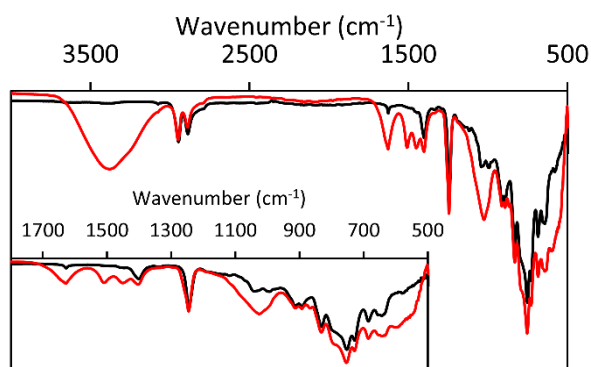


Figure 4. Attenuated Total Reflectance-Fourier Transform Infrared Spectra (ATR-FTIR) of **P2** (black) and **P2** exposed to air for one day (red).

The Si-N bond is hydrolytically sensitive,⁵¹ suggesting that extended water exposure would convert an N-allyl poly(cyclosilazane) to a linear siloxane that contains a pentasilane unit (e.g. $-(\text{Si}_5\text{Me}_{10}\text{O})-$). ATR-FTIR spectra of **P2** before and after air exposure indicate that **P2** decomposed with loss of the allylamine fragment (Figure 4). Before air exposure, characteristic Si-CH₃ (1243 cm^{-1}) and olefin C=C (1625 cm^{-1}) stretches were observed, as well as a weak stretch at 912 cm^{-1} , consistent with reported Si-N stretches (950-920 cm^{-1}).^{52,53} A strong Si-O stretch ca. 1050 cm^{-1} was not observed prior to air exposure, supporting assignment of the initial structure to a

polysilane not a polysiloxane. However, after one week of air exposure, broad peaks at 3370 cm^{-1} and 1022 cm^{-1} consistent with O-H/N-H and Si-O stretches respectively were observed.

UV-Vis Spectroscopy

The optoelectronic properties of polysilazanes have received scant attention, with applications instead focusing on their use as precursors to silicon nitride and silicon carbonitride ceramics via pyrolysis.^{29,54–56} We therefore hoped that the synthesis of N-functionalized cyclosilanes and associated polymers would also expand our insights into heteroatom influence on polysilane optoelectronic properties. UV-vis absorption spectra were taken to identify structure-dependent properties (Figure 5). The UV-vis absorption spectra of both polymers were bathochromically shifted compared to **Si5N**, consistent with extended σ -conjugation.¹ **P1** and **P2** exhibit the same onset of absorption at 321 nm with the only difference being a more pronounced transition at ca. 280 nm for **P2**. The sharper features in the **P2** spectrum suggests a more ordered structure than observed in **P1**. While the structural heterogeneity of these polymers makes assignment of transitions to specific substructures a challenge, preliminary solution-phase emission spectra of **Si5N**, **P1** and **P2** were obtained (Figure S5). **Si5N** was not fluorescent, while both **P1** and **P2** emit blue light with a maximum intensity at 410 nm.

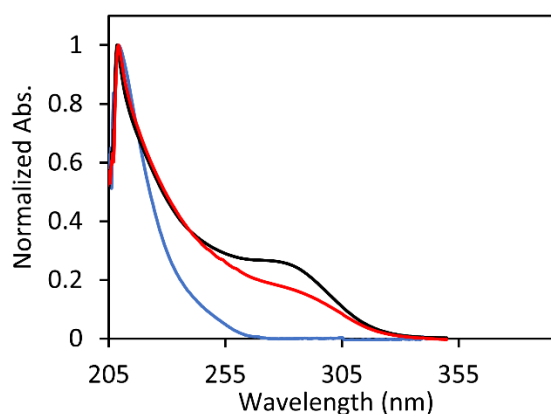


Figure 5. Absorption and spectra of **Si5N** (blue), **P1** (red), and **P2** (black). [polymer] = 0.0124 g/L in THF, [**Si5N**] = 1.25×10^{-5} M in THF.

Conclusions

In conclusion, a high yielding synthetic route to a functionalized dichlorocyclosilazane was developed. The dichlorocyclosilazane was isolated as a mixture of two diastereomers. Analysis of the ^1H - ^{29}Si HMBC and ^1H NMR spectra enabled assignment of the *trans* isomer as the major product. Sodium- and lithium-mediated reductive polymerization yielded low molecular weight oligomers (**P1** and **P2**, respectively). ^1H and ^{29}Si NMR spectra as well as FTIR spectra of **P1** and **P2** suggested functional groups common to both polymers: resonances consistent with an allyl group were observed and Si-N bonds were also present. However, the decreased solubility of **P2** in organic solvents, as well as a more

complex ^{29}Si $\{^1\text{H}\}$ DEPT NMR spectrum, suggested a different backbone structure (e.g. a higher degree of crosslinking) relative to **P1**. Both **P1** and **P2** displayed redshifted UV-vis absorption spectra upon polymerization consistent with extended σ -conjugation and supportive of a polysilane structure.

This work establishes the potential for amines to introduce new functionality into polysilane architectures. We anticipate future efforts including postpolymerization modification of the olefin towards crosslinked polymer networks and modulation of the optical properties via incorporation of π -conjugated side chains.¹³

Conflicts of interest

There are no conflicts of to declare.

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