

Hydrosilylation reactions of tetramethyldisilazanes and their derivatives

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Abstract

Hydrosilylation between 1,1,3,3-tetramethyldisilazane (**A**) and 1,3-divinyl-1,1,3,3-tetramethyldisilazane (**B**) occurs rapidly at 90 °C in the presence of Karstedt's catalyst to give a product mixture consisting mainly of large macrocycles. Deprotonation–substitution reactions of these macrocycles were largely unsuccessful. Trimethylsilylated and methylated derivatives of **A** and **B** were prepared and used in hydrosilylation reactions. High-yield formation of large macrocycles was observed when the trimethylsilylated or methylated derivative of **B** was reacted with unmodified **A**. The methylated product was successfully deprotonated and functionalized with trimethylsilyl groups. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Hydrosilylation; Silazane; Polymerization

1. Introduction

The use of hydrosilylation as a polymerization reaction is well-documented in the literature. One particular widespread application is the synthesis of linear poly(carbosilanes) and poly(carbosiloxanes) from hydrosilylation polymerizations between A_2 and B_2 monomers [1–12]. By carefully controlling the monomer ratios, it is possible to obtain polymers of high molecular weight [1,2]. While a variety of functional groups have been incorporated into the A_2 and B_2 monomer structures, we have not seen any report of hydrosilylation reactions between 1,1,3,3-tetramethyldisilazane (**A**) and 1,3-divinyl-1,1,3,3-tetramethyldisilazane (**B**), both containing the –NH– moiety [13] (Fig. 1). Among the attractive features of these monomers are their commercial availability and the potential modification and donor chemistry involving the –NH– groups. In this report we describe our investigations concerning the hydrosilylation reaction between **A** and **B**, characterization of the products, and chemical modifications of both the monomers and the products.

2. Experimental

2.1. Materials and general information

Unless otherwise noted, all reactions were carried out in a nitrogen atmosphere. 1,1,3,3-Tetramethyldisilazane (**A**) and 1,3-divinyl-1,1,3,3-tetramethyldisilazane (**B**) were obtained from Gelest and used as received. Karstedt's catalyst (platinum-divinyltetramethyldisiloxane complex in xylene, 2 wt.% Pt) was obtained from United Chemical Technologies. All NMR spectra were obtained on a Bruker AVANCE 400 MHz spectrometer using $CDCl_3$ as solvent. All NMR data were referenced to tetramethylsilane. Vapor pressure osmometry (VPO) measurements were obtained using a Wescan Model 233 Molecular Weight Apparatus with chloroform as solvent. Elemental analysis data were obtained from Galbraith Analytical Laboratory or from a ThermoQuest CE Elantech Flash EA1112 elemental analyzer.

2.2. Reaction of **A** with **B** in the presence of Pt catalyst

A 100 ml, round-bottomed, three-necked flask equipped with a magnetic stir bar, condenser, and gas inlet adapter was charged with **B** (5.85 g, 0.03 mol), 12 ml of toluene, and six drops of Karstedt's catalyst solution (80 ppm). This mixture was stirred at room

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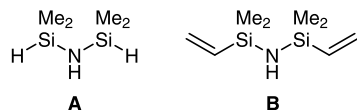


Fig. 1. Monomers 1,1,3,3-tetramethyldisilazane (A) and 1,3-divinyl-1,1,3,3-tetramethyldisilazane (B).

temperature (r.t.) for ca. 15 min. After stirring, an equimolar amount of A (4.20 g, 0.03 mol) was added and the reaction flask was placed into a 90 °C oil bath. After ca. 2 min, the mixture turned from colorless to a clear brown color and began to reflux for ca. 45 s. The mixture was heated for a total of 1 h in the 90 °C oil bath. After the heating period, most of the volatiles were removed using a rotary evaporator. The flask was then attached to a vacuum line (~0.1 mm Hg) and heated for ca. 3 h in a 50 °C oil bath. The crude product was purified by dissolution in a minimum amount of chloroform, and then adding the solution dropwise to a large excess of rapidly stirred methanol that was cooled in an isopropyl alcohol–dry ice bath. After ca. 15 min, the product had conglomerated as a sticky, gray mass on the bottom of the flask. The methanol was slowly decanted and the sticky product was redissolved in chloroform and transferred to another round-bottomed flask. The chloroform was removed first by rotary evaporation, and then by exposure to high vacuum for 3 h in a 50 °C oil bath. The purified product (**1P**) was obtained in 85% yield as a clear, light brown, viscous liquid. IR (neat, cm^{-1}): 3375 (m, NH), 2953 (s), 2902 (m), 2788 (w), 1406 (m), 1252 (s), 1178 (s), 1130 (m), 1050 (w), 931 (s), 830 (s), 793 (s). $^1\text{H-NMR}$: 0.003 (s, SiCH_3 , 12H), 0.35 (s, $\text{SiCH}_2\text{CH}_2\text{Si}$, 4H). M_n (VPO): 1234. Anal. Calc. for $\text{C}_{12}\text{H}_{34}\text{N}_2\text{Si}_4$: C, 45.22; H, 10.75. Found: C, 44.92; H, 11.10%.

2.3. Synthesis of bis(vinyl dimethylsilyl) trimethylsilylamine (**2**)

This procedure follows the reported synthesis of tris(vinyl dimethylsilyl)amine [14]. A 100 ml, round-bottomed, single-necked flask equipped with a magnetic stir bar, septum, and a gas inlet needle was charged with B (7.22 g, 0.039 mol) and ca. 50 ml of THF. The flask was placed in an ice bath, and 17.1 ml of *n*-BuLi (2.5 M solution, 0.043 mol) was added via cannula. This mixture was stirred for 1 h in the ice bath, after which chlorotrimethylsilane (5.4 ml, 0.043 mol) was added via syringe. The reaction mixture was stirred in the ice bath for 15 additional minutes, then taken out of the ice bath and allowed to warm up to r.t. On warming to r.t., the lithium chloride salt precipitated out of the solution turning the color of the mixture from clear yellow to white. The mixture was stirred overnight at r.t. The mixture was then poured into an excess of ice-cold, saturated aqueous ammonium chloride solution. All

solids were removed by vacuum filtration through a Celite pad. The organic and aqueous layers were separated, and the aqueous layer was extracted twice with ether. The organic layers were combined and washed twice with distilled water and once with saturated aqueous sodium chloride solution. The clear organic layer was dried over anhydrous magnesium sulfate and then gravity filtered. As the volatiles were being removed on the rotary evaporator, the mixture suddenly turned from a clear liquid to a semi-crystalline, light brown solid. NMR spectroscopy indicated that the product was pure and did not require additional purification. Compound **2** was obtained in 91% yield. $^1\text{H-NMR}$: 0.17 (s, $\text{Si}(\text{CH}_3)_3$, 9H), 0.23 (s, $\text{Si}(\text{CH}_3)_2$, 12H), 5.64 (dd, $\text{C}=\text{CHH}$, $^2J=3.9$ Hz, $^3J=20.4$ Hz, 2H), 5.86 (dd, $\text{C}=\text{CHH}$, $^2J=3.7$ Hz, $^3J=14.8$ Hz, 2H), 6.24 (dd, $\text{SiCH}=\text{CH}_2$, $^3J=14.7$, 20.3 Hz, 2H). Anal. Calc. for $\text{C}_{11}\text{H}_{27}\text{NSi}_3$: C, 51.29; H, 10.56. Found: C, 51.48; H, 10.53%.

2.4. Reaction of A with 2 in the presence of Pt catalyst

Using the procedure described above, compound **2** (0.67 g, 0.0026 mol) was reacted with A (0.35 g, 0.0026 mol) in toluene (3 ml) after the addition of four drops of Karstedt's catalyst solution (15 800 ppm). The mixture was heated at 90 °C for ca. 21 h. The volatiles were removed first by rotary evaporation and then by high vacuum with heating in a 50 °C oil bath for 3 h. The product could not be purified by precipitation due to its solubility in hexane (even at low temperatures) and its sensitivity towards methanol. The product **2P** was obtained in 94% yield as a very viscous, dark brown liquid. $^1\text{H-NMR}$: 0.011 (s, $\text{NHSi}(\text{CH}_3)$, 12H), 0.14 (s, $\text{N}(\text{SiMe}_3)\text{Si}(\text{CH}_3)$, 12H), 0.16 (s, $\text{N}(\text{Si}(\text{CH}_3)_3)$, 9H), 0.35 (m, $-\text{CH}_2\text{CH}_2-$, 4H), 0.48 (m, $-\text{CH}_2\text{CH}_2-$, 4H). M_n (VPO): 1164. Anal. Calc. for $\text{C}_{15}\text{H}_{42}\text{N}_2\text{Si}_5$: C, 46.08; H, 10.83. Found: C, 45.69; H, 10.81%.

2.5. Synthesis of bis(vinyl dimethylsilyl) methylamine (**4**)

A 100 ml, round-bottomed, single-necked flask equipped with a magnetic stir bar, septum, and a gas inlet needle was charged with B (8.37 g, 0.045 mol) and ca. 55 ml of THF. The flask was placed in an ice bath, and 19.8 ml of *n*-BuLi (2.5 M solution, 0.050 mol) was added via cannula. This mixture was stirred for 1 h in the ice bath, and then placed in an isopropanol–dry ice bath. Methyl iodide (3.09 ml, 0.050 mol) was added via syringe. The reaction mixture was stirred for 15 min and then taken out of the cold bath and allowed to warm to r.t. After overnight stirring at r.t., all volatiles were removed by rotary evaporation. Hexane was added and the resulting suspension was filtered. The hexane was then removed by rotary evaporation and the residue was distilled at reduced pressure. Compound **4** was collected

as a clear, colorless liquid in 86% yield (7.7 g) at 63–75 °C/17 mm Hg (lit boiling point [15] 110 °C/83 mm Hg). $^1\text{H-NMR}$: 0.13 (s, $\text{Si}(\text{CH}_3)$, 12H), 2.45 (s, $\text{N}(\text{CH}_3)$, 3H), 5.66 (dd, $\text{C}=\text{CHH}$, $^2J=4.0$ Hz, $^3J=20$ Hz, 2H), 5.90 (dd, $\text{C}=\text{CHH}$, $^2J=4.1$ Hz, $^3J=15$ Hz, 2H), 6.12 (dd, $\text{SiCH}=\text{CH}_2$, $^3J=15, 20$ Hz, 2H).

2.6. Reaction of **A** with **4** in the presence of Pt catalyst

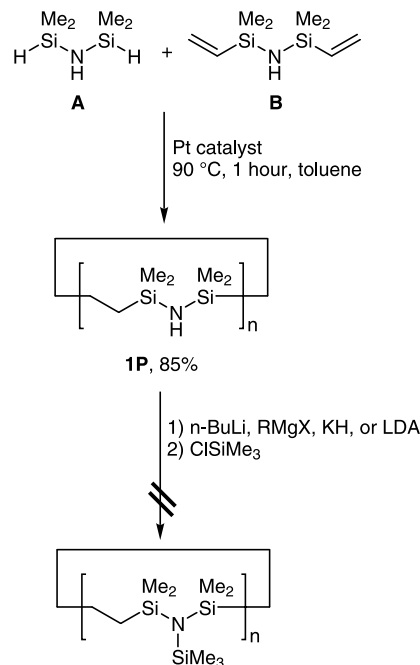
Using the procedure described above, compound **4** (0.6 g, 0.003 mol) was reacted with **A** (0.4 g, 0.003 mol) in toluene (2.5 ml) after the addition of three drops of Karstedt's catalyst solution (13 500 ppm). The mixture was heated at 90 °C for up to 72 h (until the Si–H absorbance in the IR had disappeared). The volatiles were removed first by rotary evaporation and then by high vacuum with heating in a 50 °C oil bath for 3 h. The product could not be purified by precipitation due to its solubility in hexane (even at low temperatures) and its sensitivity towards methanol. The product **4P** was recovered in quantitative yield as a clear brown, viscous liquid. $^1\text{H-NMR}$: 0.00 (s, $\text{Si}(\text{CH}_3)$, 12H), 0.028 (s, $\text{Si}(\text{CH}_3)$, 12H), 0.38 (m, $-\text{CH}_2\text{CH}_2-$, 8H), 2.42 (s, $\text{N}(\text{CH}_3)$, 3H). M_n (VPO): 1183. Anal. Calc. for $\text{C}_{13}\text{H}_{36}\text{N}_2\text{Si}_4$: C, 46.92; H, 10.90. Found: C, 47.33; H, 11.06%.

2.7. Deprotonation of **4P** and reaction with Me_3SiCl

A 100 ml, round-bottom, single-necked flask equipped with a magnetic stir bar, septum, and a gas inlet needle was charged with **4P** (0.66 g, 0.0019 mol) and 10 ml of THF. The flask was placed in an ice bath, and $n\text{-BuLi}$ (0.88 ml of 2.5 M solution, 0.0022 mol) was added via syringe. After 1 h, chlorotrimethylsilane (0.28 ml, 0.0022 mol) was added via syringe. The flask was left in the ice bath for 15 additional minutes, and then allowed to warm to r.t. As the reaction mixture warmed to r.t., lithium chloride precipitated out of the solution. The mixture was stirred overnight at r.t. All volatiles were removed by rotary evaporation, and hexane was added to the residue. The suspension was centrifuged and the supernatant was removed. All volatiles were removed first by rotary evaporation and then by high vacuum (~ 0.1 mm Hg) for 3 h in a 50 °C oil bath. The TMS-modified **4P** was obtained as a cloudy, viscous oil in 83% yield. $^1\text{H-NMR}$: 0.035, 0.14, 0.16 (s, SiCH_3 , 33H total), 0.43 (m, $-\text{CH}_2\text{CH}_2-$, 8H), 2.43 (s, $\text{N}(\text{CH}_3)$, 3H). M_n (VPO): 1311.

3. Results and discussion

The Pt-catalyzed hydrosilylation reaction between 1,1,3,3-tetramethyldisilazane (**A**) and 1,3-divinyl-1,1,3,3-tetramethyldisilazane (**B**) in toluene proceeded



Scheme 1. Polymerization of **A** and **B** and failed attempt at functionalizing **1P**.

smoothly at 90 °C in 1 h to give the expected product **1P** as a clear, light brown, viscous liquid in 85% yield after precipitation (Scheme 1). The Pt concentration in this reaction was 80 ppm [16], and we utilized the Karstedt's catalyst due to its widespread use in the silicone industry [17]. The reactivity of the **A–B** polymerization is roughly comparable to the analogous disiloxanes, which polymerize within 2.5 h at 42 °C with a Pt concentration of ca. 56 ppm and a monomer concentration ca. one-half of our values [1]. The reaction was monitored with IR spectroscopy and total loss of the Si–H absorbance was indicative of the reaction being complete. Heterogeneous catalysis using Pt on carbon (at a concentration as high as 3159 ppm) gave unsatisfactory results. While most of the polymerizations were performed under a nitrogen atmosphere, we found little difference in reactivity when the reactions were run under air.

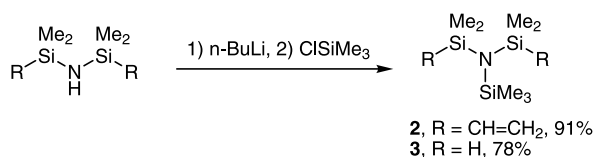
$^1\text{H-NMR}$ spectroscopy indicated that the structure of **1P** corresponded to that shown in Scheme 1, without the presence of any α -hydrosilylation products. The molecular weight determination of the product, or the magnitude of 'n' in Scheme 1, was next determined. Although the lack of endgroup resonances in the $^1\text{H-NMR}$ spectrum might suggest high molecular weight product, the sharpness of the peaks in the spectrum and the liquidity of the product suggested otherwise. Number-average molecular weight of **1P** was determined using VPO and found to be 1234, corresponding to $n = 7.75$. Thus **1P** can best be described as consisting mainly of oligomeric macrocycles, which would explain the lack

of endgroup resonances in the $^1\text{H-NMR}$ spectrum [18]. Macrocyclic formation from $\text{A}_2\text{-B}_2$ hydrosilylation reactions is not unusual, as we have observed this previously [5].

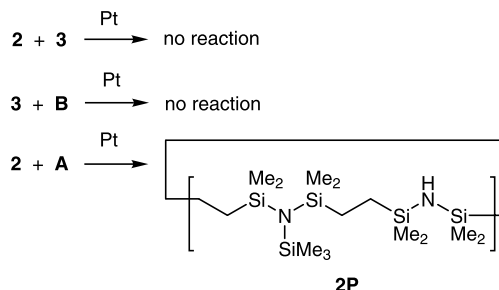
Chemical modification of **1P** proved to be difficult. Our goal was to do a simple replacement of the hydrogen on nitrogen with a trimethylsilyl group using deprotonation followed by reaction with chlorotrimethylsilane (Scheme 1). While normally a straightforward reaction, we were unable to obtain satisfactory results. For deprotonation reagents we used *n*-BuLi (both stoichiometric and deficient molar amounts), Grignard compounds, KH, and LDA. The reactions were performed in either THF or diethyl ether with aqueous or non-aqueous workups. In almost all cases, the $^1\text{H-NMR}$ spectra of the products were messy and no products were clearly identifiable. When the reaction was performed in diethyl ether with *n*-BuLi as the deprotonation reagent, **1P** was recovered unchanged.

Since deprotonation–substitution reactions were clearly difficult with **1P**, we investigated modifying **A** and/or **B** prior to the hydrosilylation reaction. To this end, compounds **2** and **3** were prepared from **B** and **A** in 91 and 78% yields, respectively (Scheme 2). When **2** and **3** were heated together in the presence of Karstedt's catalyst, no reaction occurred. This was also the case when **3** and **B** were heated together. However, hydrosilylation between **2** and **A** did occur albeit sluggishly, with complete reaction taking place within 21 h with a very high Pt concentration of 15 800 ppm. In this case, product **2P** was obtained in 94% yield as a very viscous, dark brown liquid. These results are summarized in Scheme 3. A number-average molecular weight for **2P** of 1164 in addition to the lack of endgroup resonances in the $^1\text{H-NMR}$ spectrum again indicated the formation of large macrocycles, with an average value for '*n*' of 3.21.

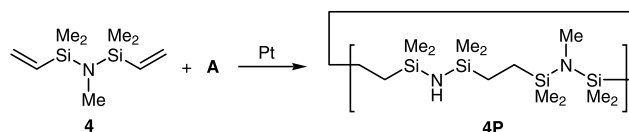
Due to the successful reaction between **2** and **A**, we investigated the reaction of bis(vinyl dimethylsilyl)methylamine (**4**) with **A**. This reaction did occur at 90 °C, but again more slowly and with a higher catalyst concentration than the reaction between **A** and **B**. Product **4P** was recovered in quantitative yield as a clear brown, viscous liquid (Scheme 4). Small amounts of impurities were present in the product (Fig. 2) but could not be removed; **4P** could not be precipitation purified due to its reactivity towards methanol and its excellent solubility in common solvents even at low temperatures. Molecular weight determination indicated



Scheme 2. Preparation of monomers **2** and **3**.



Scheme 3. Attempted polymerizations of modified monomers.



Scheme 4. Polymerization of **4** and **A**.

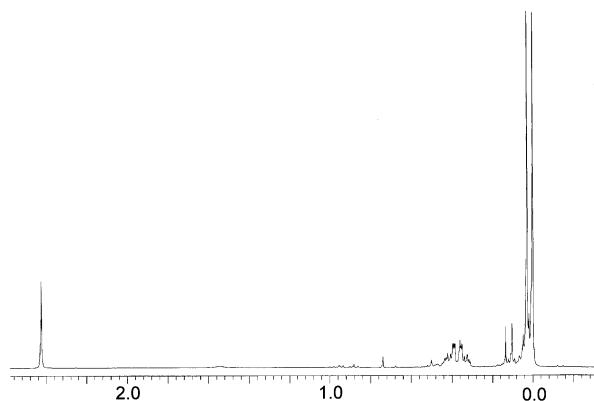
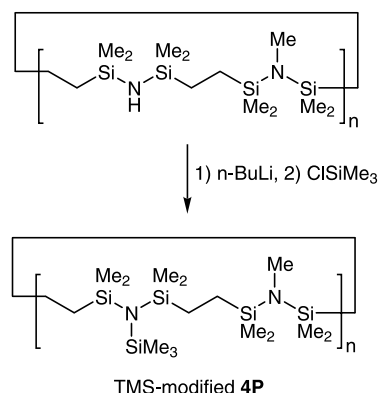


Fig. 2. $^1\text{H-NMR}$ spectrum of **4P**. Peaks at δ 0.10 and 0.13 due to impurities.

the formation of large macrocycles with an average value for '*n*' of 3.55.

Interestingly, product **4P** could be modified by deprotonation–substitution. Reaction of **4P** with *n*-BuLi followed by addition of chlorotrimethylsilane resulted in the formation of TMS-modified **4P** in 83% yield (Scheme 5). The $^1\text{H-NMR}$ spectrum correlated with the expected product, and the average ring-size



Scheme 5. Trimethylsilylation of polymer **4P**.

determination of the product also agreed closely with the previous value for unmodified **4P** ($n = 3.24$ vs. 3.55). Attempts to make methyl-modified **4P** using methyl iodide as the electrophile were unsuccessful.

4. Conclusion

Hydrosilylation between 1,1,3,3-tetramethyldisilazane (**A**) and 1,3-divinyl-1,1,3,3-tetramethyldisilazane (**B**) occurs readily to give a product mixture consisting primarily of large macrocycles. The difficulty in modifying these macrocycles via deprotonation can be partially circumvented by first modifying **A** or **B** and then performing the hydrosilylation reaction. The formation of macrocycles from the hydrosilylation reactions suggests that future efforts should be directed towards increasing the molecular weight of these materials, by decreasing monomer concentrations or perhaps using the 'one monomer deficient method' [12]. Furthermore, a wider variety of functionalization reactions should be examined.

Acknowledgements

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