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# Stepwise synthesis of siloxane chains†

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**Siloxane chains of designated lengths can be synthesized with high yields by reacting tris(*tert*-butoxy)silanol alternately with dichlorosilane and silanediol.**

Siloxanes are common precursors for the synthesis of silicone and various silica-based materials. For example, silicone oligomers and polymers can be synthesized by reaction of dichlorosilane with dihydroxysilane, and silica and other ceramic materials can be formed by hydrolysis of siloxanes followed by calcination. Procedures for synthesis of finite-length silicone oligomers have been reported over forty years ago,[1] and trisiloxanes[2,3] and tetrasiloxanes[1] were synthesized. More recently, methods that would permit extension of a linear chain were reported by Makarova *et al*. involving reaction between trichlorosilane and siloxanediol,[4] and by Klingebiel and coworkers involving reaction of a silanediol with lithium alkyl and a chloro or fluorosilane.[5] Syntheses of polysiloxanes of other structures and compositions have also been reported, including cyclic siloxanes of different ring sizes[6–8] and stereoisomers,[9] aluminosiloxanes[10] and germanosiloxanes.[11] In these other syntheses, the schemes were devised to produce a *specific* siloxane of definite size and structure and are not easily amenable to modification for extension of the siloxane chain.

In spite of the many studies related to siloxane, to our knowledge, no general method has been reported to synthesize siloxane chains of a uniform but designated size that is analogous to peptide synthesis. In principle, this can be achieved by extending the method of Klingebiel.[5] The generalized methods to synthesize peptides involve forming an amide bond between two amino acids. By applying this method to various amino acids consecutively, peptides of well-defined sequences of pre-selected amino acids can be made. Here we report a method to form siloxane–siloxane bonds that can be repetitively applied to form a chain that offers precise control of its size and sequence. We illustrate the method by synthesizing various siloxane chains from disiloxane to pentasiloxane.

Our method makes use of a starting siloxane that contains one hydroxyl ligand and three less reactive alkoxy ligands, such as tris(*tert*-butoxy)silanol (**I**), that serves as the terminal unit. This is then reacted with a dichlorosilane to form a disiloxane with one reactive chloro ligand (Eqn. 1). Addition of a third siloxy unit to form a trisiloxane can be accomplished by reacting the disiloxane unit with a silanediol (Eqn. 2), and the resulting trisiloxane unit contains a reactive hydroxyl ligand. The next unit can be added by reacting the hydroxyl ligand with dichlorosilane, similar to reaction (1), and the unit after that by reaction with silanediol, similar to reaction 2. Thus, the chain growth process can continue one unit at a time by repeating the reactions with dichlorosilane and silanediol sequentially. Pyridine is used to remove the by-product HCl in order to facilitate the transformation.

$$HOSi(OR)_3 + (R')_2SiCl_2 + Py \rightarrow (RO)_3SiOSi(R')_2Cl + PyHCl \quad (1)$$

$$(RO)_3SiOSi(R')_2Cl + R''_2Si(OH)_2 + Py \rightarrow (RO)_3SiOSi(R')_2OSi(R'')_2OH + PyHCl \quad (2)$$

† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b3/b310472a/

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Starting with **I**, we used this method to synthesize the disiloxane $(Bu^tO)_3SiOSi(CH_3)_2Cl$ **II**, the trisiloxane $(Bu^tO)_3SiOSi(CH_3)_2O$-$SiPh_2OH$ **III**, the tetrasiloxane $(Bu^tO)_3SiOSi(CH_3)_2OSiPh_2O$-$Si(CH_3)_2Cl$ **IV**, and the pentasiloxane $(Bu^tO)_3SiOSi(CH_3)_2OSi$-$Ph_2OSi(CH_3)_2OSiPh_2OH$ **V**, using as the chain growth agents dichlorodimethylsilane **VI** and diphenylsilanediol **VII**. The yield and the purity of the purified products were determined with solution nuclear magnetic resonance (NMR) spectroscopy collected at room temperature in a toluene-$d_8$ solvent with a Varian INOVA-500 spectrometer at 500 MHz for $^1H$ and $^{13}C$ and a Varian INOVA-400 at 79.5 MHz for $^{29}Si$. The $^1H$ peaks were reference to a toluene peak at $\delta$ = 7.025 ppm (from toluene-$h_1$ impurity in toluene-$d_8$), and the $^{13}C$ peaks and the $^{29}Si$ peaks were referenced to the corresponding tetramethylsilane peaks. After the purification procedure described in the supplementary information†, which typically involved extraction and/or distillation, the products obtained were pure as determined by lack of impurity peaks in the NMR spectra and the fact that the elemental C, H, and Cl contents agreed with theoretical values. These purified products were used for all subsequent synthesis steps.

All syntheses were performed under nitrogen in the tetrahydrofuran solvent employing standard Schlenk techniques and/or a Vacuum Atmospheres Drybox. Dichlorodimethylsilane (99.9%), pyridine, tetrahydrofuran and pentane, all from SigmaAldrich, were distilled in the presence of calcium hydride under nitrogen before use, and toluene-$d_8$ also with calcium hydride. Tris(*tert*-butoxy)silanol (99.999%, SigmaAldrich) and diphenylsilanediol (97%, Gelest) were used as purchased.

**II** was synthesized by reacting **I** and **VI** (1:2 molar ratio) at room temperature for 8 h in the presence of pyridine (1:1 molar ratio with **I**). The latter served to remove the by-product HCl as pyridine hydrochloride precipitate. Otherwise, the HCl formed would generate unwanted side reactions. The mixture was filtered, and the precipitate was washed with tetrahydrofuran. After removing the solvent and the excess **VI** in the filtrate by vacuum distillation and subsequently extracting **II** with pentane, a 94 wt.% yield of **II** was obtained. In this preparation, excess **VI** was important to minimize the undesirable reaction of both chloride ligands in **VI** with two molecules of **I** to form a trisiloxane without any functional groups. In toluene-$d_8$, **II** exhibited $^1H$ NMR peaks (Fig. 1 spectrum a) at $\delta$ = 1.386 ppm (*tert*-butyl) and 0.503 ppm (methyl) with the area ratio of 27.0:6.1, close to the expected value. These peaks were distinct from the methyl peak of **VI** ($\delta$ = 0.481 ppm) and the *tert*-butyl peak of **I** ($\delta$ = 1.434 ppm). The $^{29}Si$ spectrum of **II** (spectrum 2a, Fig. 2) showed two peaks at $\delta$ = −101.028 ($(Bu^tO)_3SiO$-) and 4.365 ppm (-$OSi(CH_3)_2Cl$], which were distinct from those for **I** ($\delta$ = −89.936 ppm) and **VI** ($\delta$ = 31.958 ppm). Its $^{13}C$ spectrum showed peaks at $\delta$ = 4.356 (Si–$CH_3$), 31.711 ($CH_3$ in *tert*-butyl), and 73.213 ppm (*t*-C).

**III** was synthesized by reacting **II** with **VII** in the presence of pyridine (1:2:1 molar ratio) at room temperature for 12 h. The white pyridine hydrochloride precipitate was removed by filtration. A side-product, $(Bu^tO)_3SiOSi(CH_3)_2OH$, was also formed that was probably due to the hydrolysis of $(Bu^tO)_3SiOSi(CH_3)_2Cl$ by the small amount of water introduced with diphenylsilanediol. This impurity could be removed from **III** by vacuum distillation at 100 °C for a 80 wt% yield of **III**. In toluene-$d_8$, **III** exhibited $^1H$ NMR peaks (spectrum 1b) at $\delta$ = 1.379 ppm (butyl), 0.357 ppm (methyl),

 

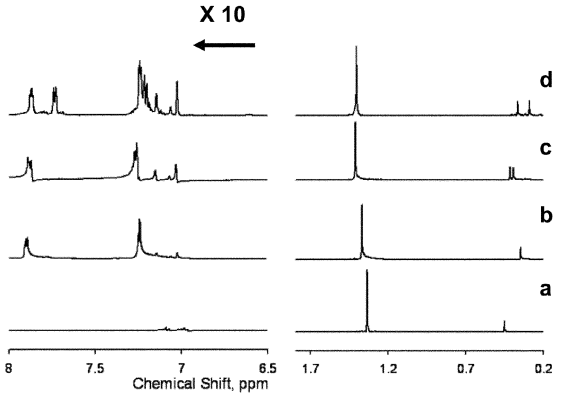


**Fig. 1** $^{1}$H NMR spectra of toluene-$d_8$ solutions of: a, $(Bu^tO)_3SiOSi(CH_3)_2Cl$ **II**; b, $(Bu^tO)_3SiOSi(CH_3)_2OSiPh_2OH$ **III**; c, $(Bu^tO)_3SiOSi(CH_3)_2OSiPh_2OSi(CH_3)_2Cl$ **IV**; and d, $(Bu^tO)_3SiOSi(CH_3)_2OSiPh_2OSi(CH_3)_2OSiPh_2OH$ **V**. Peaks at $\delta$ = 7.025, 7.062, and 7.145 are due to toluene-$h_1$ impurity.

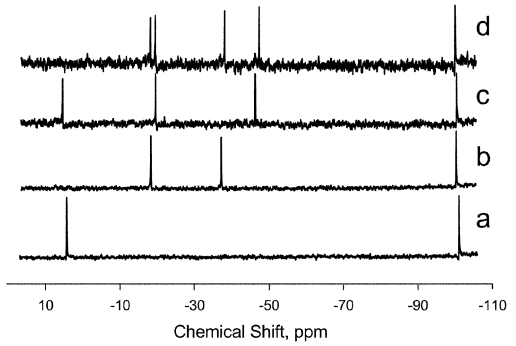


**Fig. 2** $^{29}$Si NMR spectra of toluene-$d_8$ solutions of: a, $(Bu^tO)_3SiOSi(CH_3)_2Cl$ **II**; b, $(Bu^tO)_3SiOSi(CH_3)_2OSiPh_2OH$ **III**; c, $(Bu^tO)_3SiOSi(CH_3)_2OSiPh_2OSi(CH_3)_2Cl$ **IV**; and d, $(Bu^tO)_3SiOSi(CH_3)_2OSiPh_2OSi(CH_3)_2OSiPh_2OH$ **V**.

peaks around 7.243 ppm (H3 and H4 of phenyl), and around 7.888 ppm (H2 of phenyl) with the intensity ratios of 27:6:6.3:4, close to the theoretical ratios of 27:6:6:4. There was a peak at $\delta$ = 4.808 ppm due to hydroxyl. Compared with the $^{1}$H NMR of **II**, **III** showed the new peaks from the phenyl groups and shifting of the methyl peaks to $\delta$ = 0.357 ppm from $\delta$ = 0.503 ppm in the disiloxane. There were three silicon resonances for **III** at $\delta$ = −100.260 (assigned to $(Bu^tO)_3SiO$-), −18.250 ppm (-OSi-$(CH_3)_2O$-) and −37.178 ppm (-$OSiPh_2OH$) (spectrum 2b), indicating the presence of Si in three different environment. The $^{13}$C spectrum showed peaks at $\delta$ = 1.277 (Si–$CH_3$), 31.471 ($CH_3$ in *tert*-butyl), 73.727 (*t*-C), and a group at 127.872, 130.073, 134.673, and 136.268 ppm due to the phenyl group.

Further chain lengthening to form the tetrasiloxane **IV** was achieved by applying reaction 1 to **III**, since **III** contains a hydroxyl group that can react with **VI**. Thus, **IV** could be synthesized at 95.5% yield by reacting **III** with excess **VI** in the presence of pyridine, followed by purification. $^{1}$H NMR of **IV** (spectrum 1c) showed peaks at $\delta$ = 1.406 ppm (*tert*-butyl), 0.389 ppm (3-methyl), 0.410 ppm (1-methyl), ~7.260 ppm (H3 + H4 of phenyl), ~7.870 ppm (H2 of phenyl) with area ratios of 27.0:5.9:5.7:6.3:4.2 (theoretical ratios are 27:6:6:6:4). $^{29}$Si NMR (spectrum 2c) showed peaks at $\delta$ = 5.441 ppm ($OSi(CH_3)_2Cl$), −19.510 ppm (-OSi-$(CH_3)_2O$-), −46.273 ppm (-$OSiPh_2O$-), and −100.353 ppm ($(Bu^tO)_3SiO$-), consistent with the presence of four non-equivalent Si atoms. Likewise, the $^{13}$C spectrum showed peaks at $\delta$ = 1.493 (1-methyl), 4.526 (3-methyl), 31.730 ($CH_3$ in *tert*-butyl), 72.780 (*t*-C), and 128.031, 130.383, 134.688 and 135.501 ppm (phenyl).

The terminal chloride in **IV** can be utilized to add another siloxane unit to the tetrasiloxane to form pentasiloxane **V** by reaction with **VII**, as in Eqn. 2. After purification, **V** was obtained with 89.8% yield. Its $^{1}$H NMR spectrum (spectrum 1d) showed resonances at $\delta$ = 1.404 ppm (*tert*-butyl), 0.289 ppm (2-methyl), 0.365 ppm (4-methyl), ~7.230 ppm (H3 and H4 of 1- and 3-phenyl), ~7.730 ppm (H2 of 3-phenyl) and ~7.870 ppm (H2 of 1-phenyl) with area ratios of 27.0:5.9:6.1:11.7:4.1:4.0 (theoretical ratio being 27:6:6:12:4:4). Its $^{29}$Si NMR spectrum (spectrum 2d) showed resonances that can be assigned to the fifth ($\delta$ = −99.86 ppm, first being SiOH), fourth (−19.86 ppm), third (−47.32 ppm), second (−18.10 ppm) and first Si atom (−38.04 ppm). Its $^{13}$C spectrum showed resonances at $\delta$ = 1.530 (2-methyl), 1.627 (4-methyl) 31.710 ($CH_3$ in *tert*-butyl), 72.162 (*t*-C), one group at 127.959, 130.144, 134.644, 135.514 and another at 128.083, 130.388, 134.760, and 136.253 ppm for the 1- and 3-phenyl groups, respectively.

Longer siloxane chains can be synthesized by repeating the procedure described here. Since the siloxane units are added one at a time, this method offers the possibility of introducing specific alkyl side chains at specific locations by using the appropriate chain growth agents analogous to **VI** and **VII**. Additional flexibility in choice of chain growth agents is offered by the fact that the chloride ligands in a living chain can be converted easily to a hydroxyl ligand by hydrolysis. Similarly, reacting an active chain with trichlorosilane or silanetriol can lead to branching at specific locations. The chain can also be terminated by reacting an active chain with monochlorosilane or silanol, such that the resulting chain does not possess any reactive ligands. These possibilities will be tested in the future.

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