This article is published as part of the *Dalton Transactions* themed issue entitled:

New Horizon of Organosilicon Chemistry

Guest Editor: Professor Mitsuo Kira
Tohoku University, Japan

Published in issue 39, 2010 of *Dalton Transactions*

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Rapid assembly of explicit, functional silicones†

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Received 30th April 2010, Accepted 17th June 2010
DOI: 10.1039/c0dt00400f

The impressive surface activity of silicones can be enhanced by the incorporation of hydrophilic organic functional groups and polymers. Traditional routes to such compounds, which typically involve platinum-catalyzed hydrosilylation, suffer from incompatibility with certain functional groups. $B(C_6F_5)_3$-catalyzed condensation of hydrosilanes with alkoxysilanes offers new opportunities to prepare explicit silicone structures. We demonstrate here that conversion of alcohols to silyl ethers competes unproductively with alkoxysilane conversion to disiloxanes. By contrast, a wide range of structurally complex alkyl halide and oligovinyl compounds can be readily made in high yield. Thermal 3+2-cycloadditions and thiol-ene click reactions are used to convert these compounds into surface active materials.

Introduction

Silicone polymers are widely used in commerce. While they have many attributes that are unmatched by organic polymers, it is perhaps their surface activity in particular that has been the basis of most applications. With the exception of some surfactants that are based on small siloxanes, such as the superwetters[1,2] – commonly used to disperse agricultural chemicals on leaves – most silicone surfactants involve ill-defined mixtures of silicones polymers modified by oligo- or poly(ethylene glycol)(PEG) or propylene glycol (PPG) chains (Fig. 1).[3]

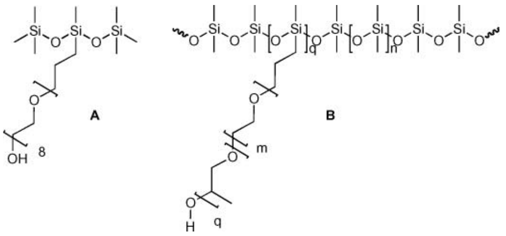

Fig. 1 Typical silicone surfactants; A: superwetters; B: rake copolymers.

A much wider range of surface activities is available when alternate hydrophiles to glycol oligomers are used, including such functional groups as amines, phosphates, sulfonates, carboxylic acids,[4,5] or clusters of acids[6,7] amino acids[8,9] and saccharides.[10–14] However, in these cases too, a clear correlation between structure and surface activity is generally not possible because the silicone constituents are typically poorly defined mixtures.

Recently, we[15] and others[16–19] have described the preparation of silicone polymers using the Piers–Rubinsztajn reaction[20–23] in which an alkoxysilane is combined with a hydrosilane in the presence of $B(C_6F_5)_3$. Explicit silicone structures can be the result of such reactions.[15] We were interested in establishing if the Piers–Rubinsztajn process could also be used to create functional, explicit silicones that may be linked to hydrophilic organic moieties.[24] Such compounds could be the basis of a new class of well-defined silicone surfactants. An examination of the tolerance of $B(C_6F_5)_3$ to a variety of organic functional groups, and the conversion of functional silicones into surface active materials is described below.

Experimental

Materials

Allyltriethoxysilane, allyltrimethoxysilane, vinyltriethoxysilane, methylphenylvinylsilane, dimethylphenylsilane, diphenylmethylsilane, pentamethyldisiloxane, 1,1,1,3,5,5,5-heptamethyltrisiloxane, (3-glycidoxy)propyltrimethoxysilane (3-iodopropyl)-trimethoxysilane, 1,3-dimethyltetramethoxy-disiloxane, (3-chloropropyl)methyldimethoxysilane, and vinyltetramethyldisiloxane were purchased from Gelest and used as received. Vinyltrimethoxysilane (98%), tetramethyl orthosilicate (98%), tetraethyl orthosilicate (98%), (3-chloropropyl)trimethoxysilane (97%), (3-chloropropyl)-triethoxysilane (95%), 1-thioglycerol (98%), (3-aminopropyl)trimethoxysilane (97%), propiolic acid (95%), poly(ethyleneglycol) methyl ether av. mol. wt: 350, *p*-toluenesulfonic acid (98%), 2,2-dimethoxy-2-phenylacetophenone (99%), allyloxytrimethylsilane (98%), allyl benzyl ether (99%), chromium(III) acetylacetonate, anhydrous dimethylformamide, sodium azide and tris(pentafluorophenyl)borane (95%) were purchased from Aldrich and used as received. Commercial solvents: hexane, dichloromethane and toluene were dried over activated alumina prior to use.

Instrumentation

^{1}H NMR, ^{13}C NMR and ^{29}Si NMR experiments were recorded at room temperature and performed on Bruker Avance 200, 500 and 600 MHz nuclear magnetic resonance spectrometers, respectively. High-resolution MS Spectrometry was performed with a Hi-Res Waters/Micromass Quattro Global Ultima (Q-TOF mass spectrometer).

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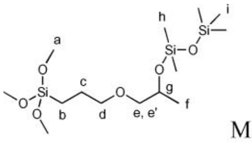
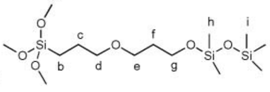
† Electronic supplementary information (ESI) available: NMR spectra of the compounds presented in Fig. 2 and 3. See DOI: 10.1039/c0dt00400f

General synthesis of functional silicones

Reaction of pentamethyldisiloxane with (3-glycidoxypropyl)-trimethoxysilane. To a solution of (3-glycidoxypropyl)trimethoxysilane (0.150 g, 0.63 mmol) in dry hexane (5 ml), was added pentamethyldisiloxane (0.376 g, 2.5 mmol). The mixture was stirred at room temperature for 5 min before the addition of $B(C_6F_5)_3$ (10 µl of a solution containing 40 mg dissolved in 1 ml of toluene, 7.8×10^{-4} mmol). After a 30 s induction time, the reaction flask became warm, signifying the onset of an exothermic reaction, lasting roughly 10 min. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1.5 g). The resulting solution was filtered and examined *via* NMR. The obtained spectrum showed evidence of complete loss of epoxide, with no evidence of reaction at the methoxy moieties. The major and minor products deduced by proton and carbon NMR experiments are shown below.



Major



Minor

Major Product: (~ 88% by NMR). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.01–4.05 (m, 1 H, **g**, $J = 6.0$ Hz) 3.56 (s, 9 H's, **a**), 3.39–3.39–3.43 (m, 2 H's, **d**), 3.37 (dd, 1 H, **e**, $J = 6.0, 9.6$ Hz), 3.24 (dd, 1 H, **e′**, $J = 6.0, 9.6$ Hz), 1.66 (m, 2 H's, **c**), 1.17 (d, 3 H's, **f**, $J = 6$ Hz), 0.65–0.68 (m, 2 H's, **b**), 0.09 (s, 9 H's, **i**), 0.07 ppm (s, 6 H's, **h**). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 76.53, 73.56, 67.23, 50.64, 22.93, 20.94, 5.39, 1.92, –0.15 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1% w/v $Cr(acac)_3$): δ 7.07 (M), –13.56 (D), –42.01 ppm (T). HRMS (ES Positive mode): m/z [M + H$^+$] calculated = 385.1898, found = 385.1878.

Minor Product: (~ 12% by NMR). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.72 (t, 2 H, **g**, $J = 6.4$ Hz), 3.48 (t, 2 H, **e**, $J = 6.4$ Hz), 3.56 (s, 9 H's, **a**), 3.39–3.43 (m, 2 H's, **d**), 1.79 (m, 2 H, **f**) 1.66 (m, 2 H's, **c**), 0.67 (m, 2 H's, **b**), 0.09 (s, 9 H's, **i**), 0.06 ppm (s, 6 H's, **h**). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 73.12, 67.56, 59.33, 50.64, 33.61, 22.93, 5.39, 1.92, –0.17 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1% w/v $Cr(acac)_3$): δ 7.31 (M), –13.02 (D), –42.01 ppm (T).

When the same reaction was run in dichloromethane (otherwise identical protocol), the outcome was somewhat different. Rather than the explicit reaction observed in hexane at the epoxide, the methoxy groups also started to react. The reaction was, therefore, not particularly useful in a synthetic sense. In either solvent, even with excess hydrosilane it was not possible to convert all OMe groups into disiloxanes (see ESI†).

Protected alcohols

Synthesis of trimethylsilyl protected (3-hydroxypropyl)-trimethoxysilane 6. In a round bottom flask equipped with a stir bar and water jacket condenser under a nitrogen atmosphere was added trimethoxysilane (2.5 g, 20.5 mmol) in dry toluene (8 ml). Allyloxytrimethylsilane (3.19 g, 24.5 mmol) was then added, followed by Karstedt's platinum complex (5 µl, 2% solution in xylenes, 1.0 µmol of Pt). The reaction was then monitored *via* NMR to ensure full conversion (3 h). Once complete, activated charcoal was added (~ 0.25 g) to the solution. The resulting mixture was stirred for an additional 2 h. The crude reaction mixture was filtered over Celite, and residual solvent and excess starting material was removed *in vacuo*, affording pure trimethylsilyl-protected (3-hydroxypropyl)trimethoxy-silane (4.51 g, 88% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.55 (s, 9 H, $(\mathbf{H_3}CO)_3Si$), 3.52 (t, 2 H, $O_3SiCH_2CH_2\mathbf{CH_2}O$–, $J = 6.8$ Hz), 1.60–1.63 (m, 2 H, $O_3SiCH_2\mathbf{CH_2}CH_2O$–), 0.61–0.64 (m, 2 H, $O_3Si\mathbf{CH_2}CH_2CH_2O$), 0.09 ppm (s, 9 H, $OSi(\mathbf{CH_3})_3$). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 64.73, 50.45, 25.72, 4.94, –0.52 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1% w/v $Cr(acac)_3$): δ 16.69 (M), –41.95 ppm (T).

Reduction of trimethylsilyl-protected (3-hydroxypropyl)-trimethoxysilane with pentamethyldisiloxane. To a solution of trimethylsilyl-protected (3-hydroxypropyl)-trimethoxysilane **6** (0.250 g, 0.99 mmol) in dry hexane (5 ml) was added pentamethyldisiloxane (0.661 g, 4.45 mmol). The mixture was stirred at room temperature for 5 min before the addition of $B(C_6F_5)_3$ (20 µl of a prepared solution containing 40 mg dissolved in 1 ml of toluene, 1.6×10^{-3} mmol). After a 60 s induction time, moderate evolution of gas and heat from the solution occurred, lasting roughly 5 min. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1 g). The resulting solution was filtered, concentrated under reduced pressure and examined *via* ^{1}H NMR. The obtained spectrum showed complete cleavage of both methoxy and trimethylsiloxy groups (see ESI†) consistent with a propyl-modified silicone. As this product was not of synthetic interest, it was not isolated. When fewer equivalents of hydrosilane were employed, little to no control was observed, giving mixtures of products **8**, **9** and related silicones with various degrees of reaction at both methoxy and trimethylsiloxy moieties.

Synthesis of benzyl protected (3-hydroxypropyl)trimethoxysilane 7. In a round bottom flask equipped with a stir bar and water jacket condenser under a nitrogen atmosphere was added trimethoxysilane (9.07 g, 74.25 mmol) in dry toluene (15 ml). Allyl benzyl ether (10 g, 67.5 mmol) was then added, followed by Karstedt's platinum complex (5 µl, 2% solution in xylenes, 1.0 µmol of Pt). The reaction was then monitored *via* NMR to ensure full conversion (16 h). Once complete, solvent was removed under reduced pressure. The resulting mixture was then subjected to distillation (150 °C, 2 mmHg) yielding pure benzyl-protected (3-hydroxypropyl)trimethoxysilane. (11.46 g, 88% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.27–7.29 (m, 4 H, phenyl), 7.23–7.26 (m, 1 H, phenyl), 4.45 (s, 2 H, $O\mathbf{CH_2}(C_6H_5)$), 3.51 (s, 9 H, $(\mathbf{H_3}CO)_3Si$), 3.40 (t, 2 H, $O_3SiCH_2CH_2\mathbf{CH_2}O$–, $J = 6.5$ Hz), 1.66–1.70 (m, 2 H, $O_3SiCH_2\mathbf{CH_2}CH_2O$), 0.63–0.66 ppm (m, 2 H, $O_3Si\mathbf{CH_2}CH_2CH_2O$). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 138.64, 128.30, 127.57, 127.43, 72.73, 72.43, 50.49, 22.84, 5.34 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1% w/v $Cr(acac)_3$): δ –42.11 ppm (T).

Reaction of benzyl-protected (3-hydroxypropyl)trimethoxysilane with pentamethyldisiloxane. To a solution of benzyl-protected (3-hydroxypropyl)trimethoxysilane (0.100 g, 0.37 mmol) in dry hexane (5 ml), was added pentamethyldisiloxane **1** (0.33 g, 2.2 mmol). The mixture was stirred at room temperature for 5 min before the addition of $B(C_6F_5)_3$ (10 µl of a solution containing 40 mg dissolved in 1 ml of toluene, 7.8×10^{-4} mmol). After a 30 s induction time, the reaction flask became warm, and evolution of gas occurred, signifying the onset of an exothermic reaction, lasting roughly 5 min. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1 g). The resulting solution was filtered, concentrated under reduced pressure and examined *via* ^{1}H NMR. When only one equivalent of hydrosilane was added, both OMe and O-benzyl groups simultaneously reacted (see ESI†). Even with excess hydrosilane it was not possible to convert all OMe groups into disiloxanes. *Peaks associated with compound **10*** (although compound **10** was not isolated, characteristic peaks were observed *via* ^{1}H and COSY experiments. See ESI for COSY data†) ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.31–1.36 (m, 2 H, $(MeO)_3SiCH_2\mathbf{CH_2}CH_3$), 0.853–0.882 (t, 2 H, $(MeO)_3SiCH_2CH_2\mathbf{CH_3}$, $J = 7.5$ Hz), 0.486–0.519 ppm (m, 2 H, $(MeO)_3Si\mathbf{CH_2}CH_2CH_3$).

*Peaks associated with compound **11*** (although compound **11** was not isolated, characteristic peaks were observed *via* ^{1}H and COSY experiments. See ESI for COSY data†) ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.51–3.49 (t, 2 H, $(MeO)_3SiCH_2CH_2\mathbf{CH_2}O$–, $J = 7$ Hz), 1.58–1.53 (m, 2 H, $(MeO)_3SiCH_2\mathbf{CH_2}CH_2O$–), 0.57–0.54 ppm (m, 2 H, $(MeO)_3Si\mathbf{CH_2}CH_2CH_2O$–).

Haloalkanes

Synthesis of (3-chloropropyl)tris(pentamethyldisiloxy)silane 12. To a solution of chloropropyltriethoxysilane (0.500 g, 2.07 mmol) in dry hexane (10 ml), was added pentamethyldisiloxane (1.38 g, 9.34 mmol). The mixture was stirred at room temperature for 5 min before the addition of $B(C_6F_5)_3$ (25 µl of a solution containing 40 mg dissolved in 1 ml of toluene, 1.95×10^{-3} mmol). After a 2 min induction time, rapid evolution of gas and heat from the solution occurred. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1.5 g). The resulting solution was filtered and concentrated on a rotary evaporator. The remaining solvent and excess reagents were removed *in vacuo*, affording pure (3-chloropropyl)tris(pentamethyldisiloxy)silane (1.08 g, 1.81 mmol, 87.8% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.51 (t, 2 H, $O_2SiCH_2CH_2\mathbf{CH_2}Cl$, $J = 7.0$ Hz), 1.83–1.86 (m, 2 H, $O_2SiCH_2\mathbf{CH_2}CH_2Cl$), 0.62–0.65 (m, 2 H, $O_2Si\mathbf{CH_2}CH_2CH_2Cl$), 0.09 (s, 27 H, $OSi(\mathbf{CH_3})_3$), 0.07 (s, 18 H, $(\mathbf{CH_3})_2SiO_2$). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 47.70 ($O_2SiCH_2CH_2\mathbf{C}H_2Cl$), 27.09 ($O_2SiCH_2\mathbf{C}H_2CH_2Cl$), 12.10 ($O_2Si\mathbf{C}H_2CH_2CH_2Cl$), 1.95 ($(\mathbf{C}H_3)_3SiO$), 1.26 ppm ($(\mathbf{C}H_3)_2SiO_2$). ^{29}Si NMR ($CDCl_3$, 99 MHz, 1% w/v $Cr(acac)_3$): δ 7.05 (M), –21.90 (D), –70.19 ppm (T). HRMS (ES Positive mode): *m*/*z* [M + NH_4^+] calculated = 612.2103, found = 612.2079.

Synthesis of (3-chloropropyl)tris(1,1,1,3,5,5,5-heptamethyltrisiloxy)silane 13. To a solution of chloropropyltrimethoxysilane (0.500 g, 4.15 mmol) in dry hexane (10 ml), was added 1,1,1,3,5,5,5-heptamethyltrisiloxane (1.98 g, 12.4 mmol). The mixture was stirred at room temperature for 5 min before the addition of tris(pentafluorophenyl)borane (25 µl of a solution containing 40 mg dissolved in 1 ml of toluene, 1.95×10^{-3} mmol). After a 1 min induction time, rapid evolution of gas and heat from the solution occurred. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1.5 g). The resulting solution was filtered and concentrated on a rotary evaporator. The remaining solvent and excess reagents were removed *in vacuo*, affording pure chloropropyltris-(1,1,1,3,5,5,5-heptamethyltrisiloxy)silane (1.51 g, 90% yield).

^{1}H NMR ($CDCl_3$, 200 MHz): δ 3.51 (t, 2 H, $O_3SiCH_2CH_2\mathbf{CH_2}Cl$, $J = 7.1$ Hz), 1.83–1.98 (m, 2 H, $O_3SiCH_2\mathbf{CH_2}CH_2Cl$), 0.63–0.72 (m, 2 H, $O_3Si\mathbf{CH_2}CH_2CH_2Cl$), 0.12 (s, 54 H, $OSi(\mathbf{CH_3})_3$), 0.07 (s, 9 H, $(\mathbf{CH_3})SiO_3$). ^{13}C NMR ($CDCl_3$ 50 MHz): δ 47.65 ($O_3SiCH_2CH_2\mathbf{C}H_2Cl$), 26.97 ($O_3SiCH_2\mathbf{C}H_2CH_2Cl$), 12.14 ($O_3Si\mathbf{C}H_2CH_2CH_2Cl$), 1.91 ($(\mathbf{C}H_3)_3SiO$), –1.89 ppm ($(\mathbf{C}H_3)SiO_3$). ^{29}Si NMR ($CDCl_3$, 99 MHz, 1% w/v $Cr(acac)_3$): δ 7.71 (M), –66.09 (D), –71.29 ppm (T). HRMS (ES Positive mode): *m*/*z* [M + NH_4^+] calculated = 834.2643, found = 834.2667.

Synthesis of (3-chloropropyl)bis(1,1,1,3,5,5,5-heptamethyltrisiloxy)methylsilane 14. To a solution of chloropropyldimethoxymethylsilane (0.500 g, 2.73 mmol) in dry dichloromethane (10 ml), was added 1,1,1,3,5,5,5-heptamethyltrisiloxane (1.52 g, 6.84 mmol, 2.5 fold excess). The mixture was stirred at room temperature for 5 min before the addition of tris(pentafluorophenyl)borane (20 µl of a prepared solution containing 40 mg dissolved in 1 ml of toluene, 1.6×10^{-3} mmol). After a 5 min induction time, rapid evolution of gas and heat from the solution occurred. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1 g). The resulting solution was filtered and concentrated under reduced pressure. The remaining solvent and excess reagents were removed *in vacuo*, affording pure (3-choloropropyl)di(1,1,1,3,5,5,5-heptamethyltrisiloxy)methylsilane (1.48 g, 91% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.50 (t, 2 H, $O_2SiCH_2CH_2\mathbf{CH_2}Cl$, $J = 7.0$ Hz), 1.82–1.88 (m, 2 H, $O_2SiCH_2\mathbf{CH_2}CH_2Cl$), 0.62–0.66 (m, 2 H, $O_2Si\mathbf{CH_2}CH_2CH_2Cl$), 0.102 (s, 36 H, $OSi(\mathbf{CH_3})_3$), 0.09 (s, 3 H, $O_2Si(\mathbf{CH_3})(CH_2CH_2CH_2Cl)$), 0.03 (s, 6 H, $(\mathbf{CH_3})SiO_3$). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 47.81 ($O_2SiCH_2CH_2\mathbf{C}H_2Cl$), 26.80 ($O_2SiCH_2\mathbf{C}H_2CH_2Cl$), 15.13 ($O_2Si\mathbf{C}H_2CH_2CH_2Cl$), 1.81 ($(\mathbf{C}H_3)_3SiO$), –0.58 $O_2Si(\mathbf{C}H_3)(CH_2CH_2CH_2Cl)$), –2.0 ppm ($\mathbf{C}H_3SiO_3$). ^{29}Si NMR ($CDCl_3$, 99 MHz, 1% w/v $Cr(acac)_3$): δ 7.29 (M), –24.49 (D), –65.82 ppm (T). HRMS (ES Positive mode): *m*/*z* [M + NH_4^+] calculated = 595.1837, found = 595.1819.

Synthesis of (3-chloropropyl)tris(dimethylphenylsilyloxy)silane 15. To a solution of chloropropyltriethoxysilane (0.100 g, 0.5 mmol) in dry hexane (4 ml), was added dimethylphenylsilane (0.308 g, 2.3 mmol). The mixture was stirred at room temperature for 5 min before the addition of tris(pentafluorophenyl)borane (10 µl of a solution containing 40 mg dissolved in 1 ml of toluene, 7.8×10^{-4} mmol). After a 2 min induction time, rapid evolution of gas and heat from the solution occurred. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1 g). The resulting solution was filtered and concentrated on a rotary evaporator. The remaining solvent and excess reagents were removed *in vacuo*, affording pure chloropropyltris(dimethylphenylsilyl)silane (0.260 g, 91% yield).

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.38–7.54 (m, 6 H, phenyl) 7.27–7.33 (m, 9 H, phenyl), 3.36 (t, 2 H, $O_2SiCH_2CH_2\mathbf{CH_2}Cl$, $J =$ 6.8 Hz), 1.54–1.67 (m, 2 H, $O_2SiCH_2\mathbf{CH_2}CH_2Cl$), 0.31–0.57 (m, 2 H, $O_2Si\mathbf{CH_2}CH_2CH_2Cl$), 0.31 (s, 18 H, $OSi(\mathbf{CH_3})_2(C_6H_5)$). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 139.3, 133.2, 129.5, 127.9, 47.7, 26.9, 12.1, 0.64 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1% w/v $Cr(acac)_3$): δ –1.98 (M), –66.90 ppm (T). HRMS (ES Positive mode): *m*/*z* [M + NH_4^+] calculated = 576.2009, found = 576.2003.

Synthesis of (3-iodopropyl)tris(diphenylmethylsiloxy)silane 16. To a solution of iodopropyltrimethoxysilane (1.0 g, 3.45 mmol) in dry hexane (10 ml), was added methyldiphenylsilane (3.07 g, 15.5 mmol). The mixture was stirred at room temperature for 5 min before the addition of $B(C_6F_5)_3$ (25 µl of a solution containing 40 mg dissolved in 1 ml of toluene, 1.95×10^{-3} mmol). After a 6 min induction time, rapid evolution of gas and heat from the solution occurred. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1.5 g). The resulting solution was filtered and concentrated on a rotary evaporator. The remaining solvent and excess reagents were removed *in vacuo*, affording pure (3-iodopropyl)tris(diphenylmethylsiloxy)silane (2.18 g, 76% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.46–7.48 (m, 12 H, phenyl), 7.38–7.41 (m, 6 H, phenyl), 7.25–7.29 (m, 12 H, phenyl), 2.89 (t, 2 H, $O_3SiCH_2CH_2\mathbf{CH_2}I$ J = 7.0 Hz), 1.59–1.64 (m, 2 H, $O_3SiCH_2\mathbf{CH_2}CH_2I$), 0.54–0.55 (m, 2 H, $O_3Si\mathbf{CH_2}CH_2CH_2I$), 0.52 ppm (s, 9 H, $OSi(\mathbf{CH_3})(C_6H_5)_2$). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 137.21, 134.11, 129.76, 127.89, 27.83, 16.29, 10.77, −0.84 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1% w/v Cr(acac)$_3$): δ −11.48 (M), −67.51 (T) ppm. HRMS (ES Positive mode): m/z [M + NH_4^+] calculated = 854.1834, found = 854.1863.

Synthesis of (3-iodopropyl)tris(methylphenylvinylsilyloxy)silane 17. To a solution of iodopropyltrimethoxysilane (0.500 g, 1.7 mmol) in dry hexane (10 ml), was added methylphenylvinylsilane (1.14 g, 7.75 mmol). The mixture was stirred at room temperature for 5 min before the addition of tris(pentafluorophenyl)borane (20 µl of a solution containing 40 mg dissolved in 1 ml of toluene, 1.6×10^{-3} mmol). After a 1 min induction time, rapid evolution of gas and heat from the solution occurred. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1.5 g). The resulting solution was filtered and concentrated under reduced pressure affording pure iodopropyltris(methylphenylvinylsilyloxy)silane (1.1 g, 93% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.49–7.51 (m, 6 H, phenyl), 7.36–7.39 (m, 3 H, phenyl), 7.29–7.32 (m, 6 H, phenyl), 6.15–6.23 (m, 3 H, $R_3Si\mathbf{CH}CHH$), 6.02–6.06 (m, 3 H, $R_3SiCHC\mathbf{H}H$), 5.75–5.80 (m, 3 H, $R_3SiCHCH\mathbf{H}$), 3.03 (t, 2 H, $O_3SiCH_2CH_2\mathbf{CH_2}I$, J = 7.0 Hz), 1.71–1.77 (m, 2 H, $O_3SiCH_2\mathbf{CH_2}CH_2I$), 0.57–0.60 (m, 2 H, $O_3Si\mathbf{CH_2}CH_2CH_2I$), 0.371 ppm (t, 9 H, $OSi(\mathbf{CH_3})(C_6H_5)(CHCH_2)$, J = 3.5 Hz). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 137.36, 136.89, 134.20, 133.74, 129.69, 127.84, 27.93, 16.16, 10.94, −1.18 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1% w/v Cr(acac)$_3$): δ −13.38 (M), −67.49 ppm (T). HRMS (ES Positive mode): m/z [M + NH_4^+] calculated = 704.1365, found = 704.1349.

Vinylsilanes

Synthesis of tris(phenyldimethylsilyloxy)vinylsilane 20. To a solution of vinyltrimethoxysilane (0.250 g, 1.68 mmol) in dry hexane (10 ml) and dichloromethane (5 ml) was added dimethylphenylsilane (0.919 g, 6.74 mmol). The mixture was stirred at room temperature for 5 min before the addition of tris(pentafluorophenyl)borane (15 µl of a solution containing 40 mg dissolved in 1 ml of toluene, 1.2×10^{-3} mmol). After a 40 s induction time, rapid evolution of gas and heat from the solution occurred. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1.5 g). The resulting solution was filtered and concentrated under reduced pressure. The remaining solvent and excess reagents were removed *in vacuo*, affording pure tris(phenyldimethylsilyloxy)vinylsilane (0.79 g, 1.55 mmol, 92%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.50–7.52 (m, 6 H, phenyl), 7.34–7.37 (m, 3 H phenyl), 7.28–7.31 (m, 6 H phenyl), 5.78–5.92 (m, 3 H, vinyl), 0.29 ppm (s, 18 H $(C_6H_6)(\mathbf{H_3}C)_2SiO$). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 139.45, 134.46, 133.30, 133.21, 129.37, 127.76,.71 ppm. ^{29}Si NMR (99 MHz 1% w/v Cr(acac)$_3$): δ −1.58 (M), −78.86 (T). HRMS (ES Positive mode): m/z [M + NH_4^+] calculated = 526.2085 [M + NH_4^+] found = 526.2051.

Synthesis of allyltris(dimethylphenylsilyloxy)silane 21. To a solution of allyltrimethoxysilane (0.500 g, 3.10 mmol) in dry hexane (10 ml) was added phenyldimethylsilane (1.67 g, 12.3 mmol). The mixture was stirred at room temperature for 5 min before the addition of $B(C_6F_5)_3$ (20 µl of a solution containing 40 mg dissolved in 1 ml of toluene, 1.6×10^{-3} mmol). After a 1 min induction time, rapid evolution of gas and heat from the solution occurred. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1 g). The resulting solution was filtered and concentrated under reduced pressure. The remaining solvent and excess reagents were removed *in vacuo*, affording pure allyltris(dimethylphenylsilyloxy)silane (1.38 g, 2.6 mmol, 86% yield)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.54–7.56 (m, 6 H, phenyl) 7.38–7.41 (m, 3 H, phenyl), 7.33–7.36 (m, 6 H, phenyl) 5.70–5.75 (m, 1 H, $O_3SiCH_2\mathbf{CH}{=}CH_2$), 4.85–4.89 (m, 2 H, $O_3SiCH_2CH{=}\mathbf{CH_2}$), 1.55 (d, 2 H, $O_3Si\mathbf{CH_2}CH{=}CH_2$, J = 8 Hz), 0.34 ppm (s, 18 H's, $(C_6H_6)Si(\mathbf{CH_3})_2O$). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 139.47, 133.48, 133.21, 129.41, 127.79, 133.48, 114.53, 22.33, 0.69 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1% w/v Cr(acac)$_3$): δ −2.14 (M), −70.62 ppm (T). HRMS (ES Positive mode): m/z [M + NH_4^+] calculated = 540.2242, found = 540.2267.

Synthesis of bis(methylphenylvinylsiloxy)methyldisiloxane 22. To a solution of 1,3-dimethyltetramethoxydisiloxane (0.250 g, 1.1 mmol) in dry hexane (5 ml), was added methylphenylvinylsilane (0.90 g, 6.1 mmol). The mixture was stirred at room temperature for 5 min before the addition of tris(pentafluorophenyl)borane (15 µl of a solution containing 40 mg dissolved in 1 ml of toluene, 1.2×10^{-3} mmol). After a 4 min induction time, rapid evolution of gas and heat from the solution occurred. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1.5 g). The resulting solution was filtered and concentrated under reduced pressure affording pure bis(methylphenylvinylsiloxy)methyldisiloxane (0.63 g, 76% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.52–7.54 (m, 8 H, phenyl), 7.34–7.37 (m, 4 H, phenyl), 7.28–7.30 (m, 8 H, phenyl) 6.16–6.23 (m, 4 H, $Si\mathbf{CH}{=}CHH$), 5.99–6.02 (m, 4 H, $SiCHC{=}\mathbf{H}H$), 5.78–5.80 (m, 4 H, $SiCH{=}CH\mathbf{H}$), 0.370 (s, 12 H, $(C_6H_5)(CH{=}CH_2)(\mathbf{CH_3})SiO$), 0.04 ppm (d, 6 H, $O_3Si\mathbf{CH_3}$). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 137.7, 137.1, 133.9, 133.7, 129.5, 127.8, −1.12, −2.01 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1% w/v Cr(acac)$_3$): δ −13.81 (M), −65.83 ppm (T). HRMS (ES Positive mode): m/z [M + NH_4^+] calculated = 772.2624, found = 772.2624.

Synthesis of $((M^{Vi}D)_2T)_2$ 23. To a solution of 1,3-dimethyltetramethoxydisiloxane (0.250 g, 1.10 mmol) in dry hexane (10 ml), was added vinyltetramethyldisiloxane (0.97 g, 0.061 mol). The mixture was stirred at room temperature for 5 min before the addition of tris(pentafluorophenyl)borane (15 µl of a solution containing 40 mg dissolved in 1 ml of toluene, 1.2 × 10^{-3} mmol). After a 90 s induction time, rapid evolution of gas and heat from the solution occurred. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1 g). The resulting solution was filtered and concentrated under reduced pressure. The remaining solvent and excess reagents were removed *in vacuo*, affording pure $((M^{Vi}D)_2T)_2$ (0.85 g, 1.1 mmol, 96% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.13 (dd, 4H, OSi($CH_3)_2$(C**H**CHH), J = 15, 19.8 Hz), 5.92 (dd, 4 H, OSi($CH_3)_2$(CHC**H**H), J = 4.6, 15 Hz), 5.72 (dd, 4 H, OSi($CH_3)_2$(CHCH**H**), J = 4.6, 19.8 Hz), 0.153 (s, 24 H, OSi(C**H$_3$**)$_2$(CHCH$_2$)), 0.071 ppm (s, 30 H (C**H$_3$**)SiO$_3$, (C**H$_3$**)$_2$SiO$_2$). ^{13}C NMR ($CDCl_3$ 50 MHz): δ 139.48, 131.80, 1.29, 0.43, −2.09 ppm. ^{29}Si NMR (99 MHz 1% w/v Cr(acac)$_3$): δ = −4.47 (M), −21.35 (D), −68.35 (T) ppm.

Synthesis of tetrakis(vinyltetramethyldisiloxy)silane 24. To a solution of tetraethyl orthosilicate (0.200 g, 0.96 mmol) in dry hexane (5 ml), was added vinyltetramethyldisiloxane (0.85 g, 5.28 mmol). The mixture was stirred at room temperature for 5 min before the addition of tris(pentafluorophenyl)borane (10 µl of a solution containing 40 mg dissolved in 1 ml of toluene, 7.81 × 10^{-4} mmol). After a 2 min induction time, rapid evolution of gas and heat from the solution occurred. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1 g). The resulting solution was filtered and concentrated under reduced pressure. The remaining solvent and excess reagents were removed *in vacuo*, affording pure tetrakis(vinyltetramethyl-disiloxy)silane (0.520 g, 75% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.13 (dd, 4 H, R$_3$SiC**H**CHH, J = 15.0, 20.5 Hz), 5.93 (dd, 4 H, R$_3$SiCHCH**H**, J = 4.0, 15.0 Hz), 5.74 (dd, 4 H, R$_3$SiCHC**H**H, J = 4.0, 20.5 Hz), 0.166 (s, 24H, O(**H$_3$**C)$_2$Si(CHCH$_2$)), 0.09 ppm (s, 24 H, (C**H$_3$**)$_2$SiO$_2$)). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 139.47 (CH vinyl), 131.82 (CH$_2$ vinyl), 1.17 (SiCH$_3$), 0.45 ppm (SiCH$_3$). ^{29}Si NMR ($CDCl_3$, 99 MHz, 1% w/v Cr(acac)$_3$): δ −4.34 (M), −20.95 (D), −110.18 ppm (D). HRMS (ES Positive mode): m/z [M + NH_4^+] calculated = 746.2555, found = 746.2564.

Synthesis of $(M^YD)_4Si$, Y = $CH_2CH_2Si(OEt)_3$ 25. In a round bottom flask equipped with a stir bar and water jacket condenser with drying tube (Drierite desiccant) was added tetrakis(vinyltetramethyldisiloxy)silane (0.50 g, 0.68 mmol) in dry toluene (5 ml). Triethoxysilane (0.56 g, 3.4 mmol) was then added, followed by Karstedt's platinum complex (5 µl, 2% solution in xylenes, 1.0 µmol of Pt). The reaction flask was then immersed in an oil bath at 50 °C. The reaction was allowed to proceed for 48 h, at which time activated charcoal was added (~ 0.25 g). The resulting solution was stirred for an additional 2 h. The crude reaction mixture was filtered over Celite, and residual solvent and excess starting material was removed *in vacuo*, affording pure $(M^YD)_4Si$, Y = $CH_2CH_2Si(OEt)_3$ (0.74 g, 80% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.81 (q, 24 H, (CH$_3$C**H$_2$**O)$_3$-SiO, J = 7.0 Hz), 1.22 (t, 36 H, (C**H$_3$**CH$_2$O)$_3$SiO, J = 7.0 Hz), 0.54 (s, 16 H, O$_3$SiC**H$_2$**C**H$_2$**Si(CH$_3$)$_2$O), 0.07 (s, 24 H, CH$_2$Si(C**H$_3$**)$_2$OSi(CH$_3$)$_2$OSi), 0.06 ppm (s, 24 H, CH$_2$Si(CH$_3$)$_2$OSi(C**H$_3$**)$_2$OSi). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 58.50, 18.45, 9.21, 1.93, 1.17, −0.42 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1% w/v Cr(acac)$_3$): δ 7.90 (M), −21.60 ppm (D), −45.01(T), −110.0 (Q) ppm.

Coupling to hydrophilic moieties

Thermal cycloaddition.

Synthesis of (3-azidopropyl)tris(pentamethyldisiloxy)silane ***18***. To a 10 ml round bottom flask equipped with a magnetic stir bar was added a solution of (3-iodopropyl)tris(pentamethyldisiloxy)silane (0.500 g, 0.72 mmol) in anhydrous DMF (2 ml). To the solution was added sodium azide (0.095 g, 1.45 mmol). The mixture was then allowed to stir for 5 h at 90 °C. To the mixture was added 20 ml of water and the desired product was extracted with 25 ml of hexane. The aqueous layer was washed three times with hexane (10 ml) to ensure maximum product recovery. The organic layers were combined and dried over magnesium sulfate (10 g). The resulting solution was filtered and concentrated under reduced pressure affording pure (3-azidopropyl)tris(pentamethyldisiloxy)silane (0.38 g, 88% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 3.42 (t, 2 H, O$_3$SiCH$_2$CH$_2$-C**H$_2$**N$_3$ J = 7.0 Hz), 1.65–1.72 (m, 2 H, O$_3$SiCH$_2$C**H$_2$**CH$_2$N$_3$), 0.55–0.58 (m, 2 H, O$_3$SiC**H$_2$**CH$_2$CH$_2$N$_3$), 0.09 (s, 27 H's, OSi(C**H$_3$**)$_3$), 0.07 ppm (s, 18 H's, (C**H$_3$**)$_2$SiO$_2$). ^{13}C NMR ($CDCl_3$ 150 MHz): δ 54.20, 23.19, 11.61, 1.96, 1.28 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1% w/v Cr(acac)$_3$): δ 7.06 (M), −21.88 (D), −70.20 ppm (T). HRMS (ES Positive mode): m/z [M + Na$^+$] calculated = 624.2061, found = 624.2064.

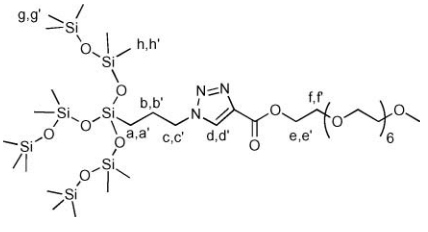
Synthesis of (3-azidopropyl)tris(1,1,1,3,5,5,5-heptamethyltrisiloxy)silane ***19***. To a 10 ml round bottom flask equipped with a magnetic stir bar was added a solution of (3-iodopropyl)tris(1,1,1,3,5,5,5-heptamethyltrisiloxy)silane (1.0 g, 1.1 mmol) in anhydrous DMF (2 ml). To the solution was added sodium azide (0.141 g, 2.18 mmol). The mixture was then allowed to stir for 5 h at 90 °C. To the mixture was added 40 ml of water and the desired product was extracted with 25 ml of hexane. The aqueous layer was washed three times with hexane (10 ml) to ensure maximum product recovery. The organic layers were combined and dried over magnesium sulfate (10 g). The resulting solution was filtered and concentrated under reduced pressure affording pure pale yellow (3-azidopropyl)tris(1,1,1,3,5,5,5-heptamethyltrisiloxy)silane (0.78 g, 87% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 3.23 (t, 2 H, O$_3$SiCH$_2$CH$_2$-C**H$_2$**N$_3$ J = 7.2 Hz), 1.70–1.73 (m, 2 H, O$_3$SiCH$_2$C**H$_2$**CH$_2$N$_3$), 0.57–0.60 (m, 2 H, O$_3$SiC**H$_2$**CH$_2$CH$_2$N$_3$), 0.11 (s, 54 H, OSi(C**H$_3$**)$_3$), 0.06 ppm (s, 9 H, (C**H$_3$**)SiO$_3$). ^{13}C NMR ($CDCl_3$ 150 MHz): δ 53.68, 22.40, 10.89, 1.44, −2.54 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1% w/v Cr(acac)$_3$): δ 7.81 (M), −66.01 (T), −71.28 ppm (T).

Synthesis of propiolate terminated monomethoxy poly-(ethyleneoxide), (av. mol. wt: 350) ***26***. In a round bottom flask containing monomethoxypoly(ethylene-oxide) (*av. mol. wt 350*) (7.0 g, 20 mmol), was successively added propiolic acid (2.8 g, 40 mmol), toluene (60 ml) and a catalytic amount of *para*-toluene sulfonic acid (0.2 g). The flask was equipped with a Dean Stark apparatus, and heated with azeotropic removal of water. Completion of the reaction was monitored by ^{1}H NMR, by comparison of the 3 protons of terminal methoxy compared to the appearance of the methylenic esters protons at 4.32 ppm (*ca.* 20 h). The mixture was then concentrated *in vacuo*, and the crude product directly loaded onto a chromatography column packed with silica gel. Elution started with pure dichloromethane, then increasing amounts of methanol were added to the eluent (up to 3%, v:v). The fractions containing the propiolate ester were combined, evaporated under reduced pressure to afford pure yellow propiolate, methyl-terminated poly(ethyleneoxide) (7.3 g, 91% yield).

^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.32 (t, 2 H, $COOCH_2$, J = 4.6 Hz), 3.74 to 3.50 (m, 29H, OCH_2CH_2), 3.35 (s, 3H, OCH_3), 2.96 to 2.93 (m, 1H, $HCCCOO$). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 75.44, 74.60, 71.99, 70.65, 68.62, 65.32, 59.12.

*Thermal cyclization of **18** with propiolate-modified PEG **27**.* To a 5 ml round bottom flask equipped with a magnetic stir bar and previously prepared azidopropyltris(pentamethy-ldisiloxy)silane (0.280 g, 0.47 mmol), was added propiolate, methyl-PEG (0.178 g, 0.47 mmol; av. mol. wt: 350, *mass calculated via NMR 382g/mol*) and dry toluene (1 ml). The mixture was then stirred at 65 °C and monitored *via* NMR for completion (typical time required is 48 h). Once complete, solvent was removed under reduced pressure, yielding pure **17** as two isomers, with a ratio of roughly 1 : 4. (0.324 g, 99.6% yield)



1,4-Isomer (~75%)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.05 (s, 1 H, **d**), 4.49 (t, 2 H, **e**, J = 5.0 Hz), 4.38 (t, 2 H, **c**, J = 7.3 Hz), 3.82 (t, 2 H, **f**, J = 5.0 Hz), 3.62–3.68 (m, ~ 24H, $-OC\mathbf{H_2}C\mathbf{H_2}O-$), 3.53 (t, 2 H, $-(CO)OCH_2CH_2OC\mathbf{H_2}CH_2O-$, J = 4.8 Hz), 3.36 (s, 3 H, $OC\mathbf{H_3}$), 1.96–2.03 (m, 3 H, **b**), 0.49–0.53 (m, 2 H, **a**), 0.063 (s, 27 H, **g**), 0.05 ppm (s, 18 H, **h**). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 159.10, 140.49, 128.08, 72.70, 71–28–71.48, 69.70, 64.81, 59.77, 53.69, 25.30, 11.90, 2.57, 1.90 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1% w/v $Cr(acac)_3$): δ 7.24 (M), –21.52 (D), –70.99 ppm (T).

1,5-Isomer (~25%):

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.13 (s, 1 H, **d′**), 4.68 (t, 2 H, **c′**, J = 7.5 Hz), 4.44 (t, 2 H, **e′**, J = 5.0 Hz), 3.79 (t, 2 H, **f′**, J = 5.0 Hz), 3.62–3.68 (m, ~ 24H, $-OC\mathbf{H_2}C\mathbf{H_2}O-$), 3.53 (t, 2 H, $-(CO)OCH_2CH_2OC\mathbf{H_2}CH_2O-$, J = 4.8 Hz), 3.36 (s, 3 H, $OC\mathbf{H_3}$), 1.93–1.97 (m, 3 H, **b′**), 0.49–0.53 (m, 2 H, **a′**), 0.051 (s, 27 H, **g′**), 0.03 ppm (s, 18 H, **h′**). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 161.45, 138.78, 128.08, 72.70, 71.28–71.48, 69.52, 65.26, 59.77, 53.56, 25.30, 11.99, 2.57, 1.85 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1% w/v $Cr(acac)_3$): δ 7.06 (M), –21.85 (D), –70.74 ppm (T).

Thiol-ene click 29

To a solution of allyltris(1,1,1,3,5,5,5-heptamethyltrisiloxy)-silane (0.500 g, 0.64 mmol) in dry THF, previously passed through neutral alumina (1 ml), was added 1-thiogylcerol (0.103 g, 0.96 mmol) and 2,2-dimethoxy-2-phenylacetophenone (0.016 g, 0.0625 mmol). The mixture was then irradiated under ultraviolet light (254 nm) and monitored *via* NMR until complete disappearance of the allyl functionality was observed (typically 30–40 min). Once complete, the mixture was subjected to column chromatography (10% acetone, 90% dichloromethane) to remove the photoinitiator and excess starting materials. The collected fractions were combined and concentrated under reduced pressure yielding the sulfide-modified silicone (0.392 g, 69% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.76 (m, 1 H, $SCHH'C\mathbf{H}(OH)CHH''(OH)$), 3.73 (m, 1 H, $SCHH'CH(OH)C\mathbf{H}H''(OH)$), 3.52–3.55 (m, 1 H, $SCHH'CH(OH)CH\mathbf{H}''(OH)$), 2.68–2.72 (m, 1 H, $SC\mathbf{H}H'CH(OH)CHH''(OH)$), 2.56–2.60 (m, 1 H, $SCH\mathbf{H}'CH(OH)CHH''(OH)$), 2.53 (t, 2 H's, $O_3SiCH_2CH_2C\mathbf{H_2}S$, J = 7.5 Hz), 1.64–1.73 (m, 2 H's, $O_3SiCH_2C\mathbf{H_2}CH_2S$), 0.58–0.69 (m, 2 H's, $O_3SiC\mathbf{H_2}CH_2CH_2S$), 0.10 (s, 54 H's, $(C\mathbf{H_3})_3SiO$), 0.047 ppm (s, 9 H's, $(CH_3)SiO_3$). ^{13}C NMR ($CDCl_3$ 150 MHz): δ 69.60, 65.57, 36.01, 35.72, 23.63, 14.07, 1.91, –1.88 ppm. ^{29}Si NMR ($CDCl_3$, 119 MHz, 1% w/v $Cr(acac)_3$): δ 7.75 (M), –66.01 (T), –71.20 ppm (T). HRMS (ES Positive mode): m/z $[M + NH_4^+]$ calculated = 906.3145 found = 906.3204.

Results

Incorporation of functional synthetic handles

3-(Glycidoxy)propyltrimethoxysilane was reacted with one equivalent of pentamethyldisiloxane **1** in the presence of catalytic amounts of $B(C_6F_5)_3$. No evidence of disiloxane formation was observed: instead, selective reductive epoxide ring opening occurred (Fig. 2), but only in hexanes as solvent. Surprisingly, there was no further reaction with the addition of excess **1**: the major product remained **2A** (**A** : **B**, 88 : 12). In the more polar solvent dichloromethane some competition occurred between the epoxide and the alkoxysilane: small amounts of disiloxane **3** were also formed. This trend in selectivity as a function of solvent polarity was also seen in the reaction of hydrosilanes with thiols ($R_3SiH + HS(CH_2)_3Si(OR)_3 \rightarrow R_3SS(CH_2)_3Si(OR)_3 + H_2$).[24]

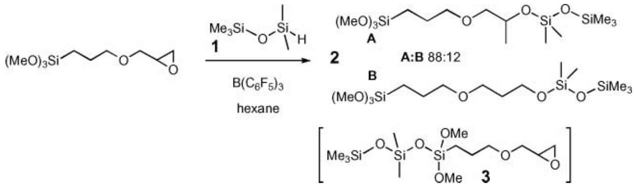


Fig. 2 Reductive epoxide ring opening.

The relative efficiency of silylation between free alcohols and alkoxysilanes in the presence of $B(C_6F_5)_3$ was examined using **4**, which was prepared in low yield by platinum-catalyzed hydrosilylation of allyl alcohol with $HSi(OEt)_3$.‡ Exposure of **4** to $B(C_6F_5)_3$ and one equivalent of **1** led preferentially to reaction at the alcohol giving **5** – the same process as occurs with platinum catalysts (Fig. 2). By contrast, once the alcohol was protected as a silyl **6** or benzyl ether **7**, reactions of both methyl and propyl ethers occurred competitively. In the case of **6**, the propyloxy group was

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‡ Problems with hydrosilylation in the presence of unprotected alcohols are well known: a reaction between the alcohol and silane can occur, leading to H_2 formation ($R_3SiH + H_2C{=}CHCH_2OH \rightarrow H_2C{=}CHCH_2OSiR_3 + H_2$).[43] Nevertheless, this direct route was attempted as it avoided protection/deprotection sequences.

reduced competitively with the SiOMe group to give mixtures of **8**, **9** and related products: tris(trimethylsiloxy)propylsilane was the product with an excess of **1**. The benzyl ether **7** gave an unhelpful mixture of regioisomeric cleavage products, **10** and **11**. Complete conversion to trifunctional propylsilicones could not be induced with an excess of **1** (Fig. 3).

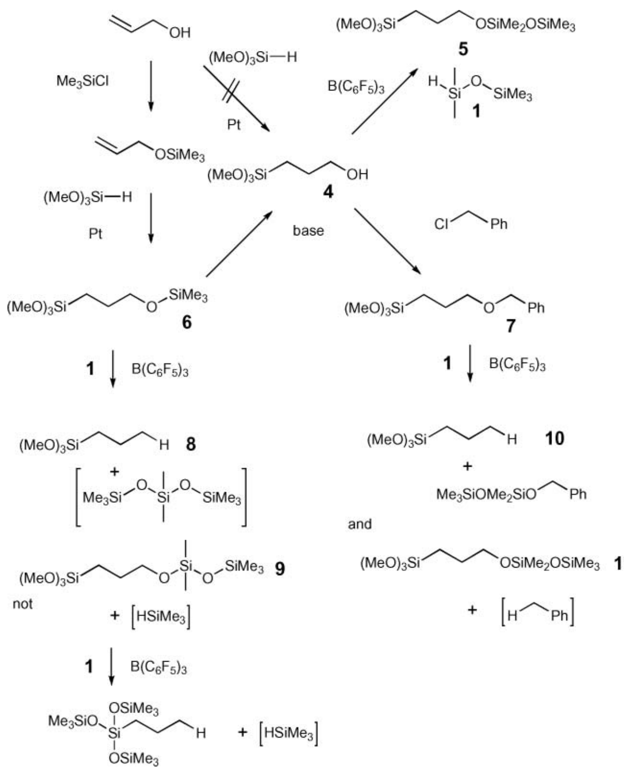

Fig. 3 Competitive reduction of benzyl and silyl ethers (products in '[]' were removed during workup at low vacuum and are inferred).

Compatible functional groups

Haloalkanes. Alkoxysilane compounds that also contain alkyl halides, including both iodo and chloro compounds, react cleanly in high yields with hydrosilanes in the presence of $B(C_6F_5)_3$ to give functional siloxanes **12**, **13**, **14**, **15**, **16** and **17** (Fig. 4). The alkyl halide can be further functionalized, as shown in the simple substitution of **12**, **13** to give organoazides **18** and **19**, respectively. The latter compounds provide a facile linkage to hydrophilically modified and functional materials, as is discussed further below. The latter substitution (and cyclization) processes do not affect the structure of the silicone framework.

Alkenes.

Oligoalkene-functionalized silicones. The hydrosilylation of alkynes, and particularly of alkenes, is broadly used in silicon chemistry to incorporate organic residues.[25] It has previously been reported that $B(C_6F_5)_3$ will catalyze the hydrosilylation of (thio)ketones, imines[26] and alkenes.[27,28] In addition, the hydrosilylation of alkenes catalyzed by $B(C_6F_5)_3$ has been described.[27] Therefore, it was not initially anticipated that vinyl-functional silicones could be prepared under the reaction conditions of the Piers–Rubinsztajn reaction. However, $C{=}C$ hydrosilylation typically requires catalyst loadings of ~5wt%. At the concentrations of $B(C_6F_5)_3$ used here, ~0.5%, very clean disiloxane formation occurred leading to highly functionalized silicones with both single and multiple alkene groups (Fig. 5) or mixed alkenes/alkyl halides **17** (Fig. 4): no silylation of the olefins were observed during the Piers–Rubinsztajn silicone formation. The yields are excellent and complex materials, including silicone crosslinkers **20**, **21**, **22**, **23** and **24** (see also Fig. 6), are readily prepared in a few steps.

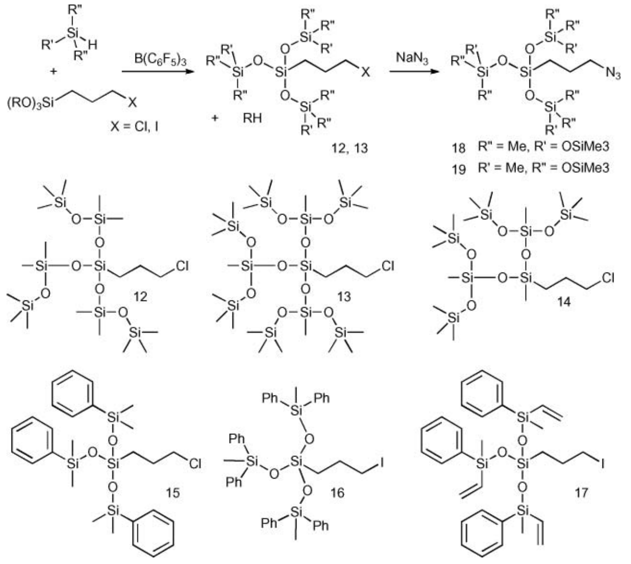

Fig. 4 Alkyl halide-derived silicones.

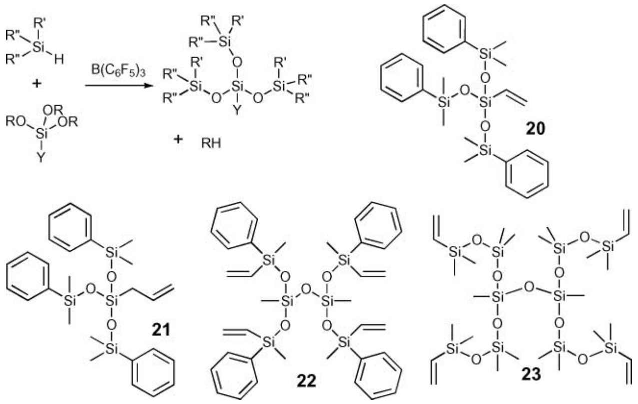

Fig. 5 Oligoalkene preparation.

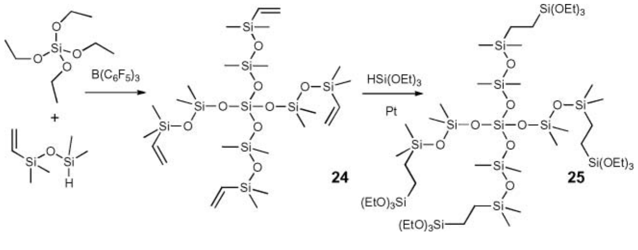

Fig. 6 Iterative Piers–Rubinsztajn/hydrosilylation.

Silicone functionalization – strategies for polymer coupling

As noted above, the key objective of this work was finding appropriate functional groups and reaction conditions that would permit organofunctionalization of silicones. We show three complementary strategies that demonstrate this point.

Iterative hydrosilylation. Silicones bearing both SiH and $SiCH{=}CH_2$ residues will self-polymerize in the presence of platinum or radical catalysts.[29,30] By contrast, the same compounds will selectively form siloxanes in the presence of $B(C_6F_5)_3$ without touching the alkenes. However, they can be converted into new alkoxysilanes **25** with platinum and compounds such as $HSi(OEt)_3$. Thus, a short iterative procedure can lead to large, highly functional compounds (Fig. 6) while maintaining silicone structural integrity. This obvious route to dendrimeric structures is currently being developed.

Azide "click" chemistry. Click chemistry[31] has become a standard method to link disparate molecules. Initially, a thermally activated process described by Huisgen.[32–34] It was reinvented by Sharpless who used a copper catalyst to both increase reaction selectivity and decrease reaction temperatures.[31,35–37] We have previously examined both the copper-catalyzed and thermal versions to functionalize[38] and crosslink silicones.[39]

The reaction between azide **18** and poly(ethylene glycol) propiolate ester **26** occurred in the absence of a copper catalyst at 65 °C over 48 h to give the surface active graft copolymer **27** (Fig. 7); the silicone structure was not affected during the process. Because of this accessibility of well-defined silicone materials, it should be possible to prepare a wide range of polymeric surfactants using this protocol. An examination of the surface activity of these and related compounds is currently under way and will form the basis of a future report.

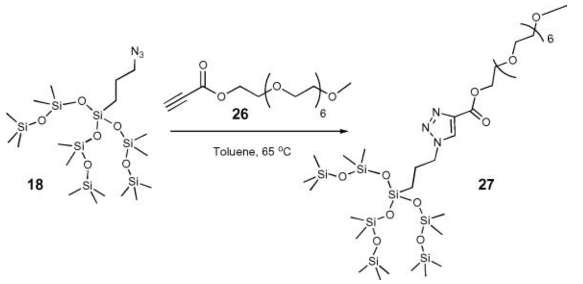

Fig. 7 Concise preparation of organofunctional silicones.

Thiol-ene "click" capable silicones thioglycerol. More recently, the "click" moniker has been applied to the thiol-ene reaction (Fig. 8).[40,41] Normally, this describes a radical chain addition of a thiol across an alkene to generate a sulfide. Thioglycerol cleanly added to **28**[24] in the presence of 2,2-dimethoxy-2-phenylacetophenone to give **29**: the process is photoinitiated at 254 nm. The thiol-ene reaction can therefore also be used to hydrophilize silicones under conditions that don't affect the silicone backbone.

Discussion

The Piers–Rubinsztajn reaction is understood to involve the formation of a Si–H–B complex **30** which, in the presence of oxygen-based nucleophiles, leads of an oxonium ion **31** that subsequently degrades to a disiloxane and alkane, regenerating the catalyst (Fig. 9). However, $B(C_6F_5)_3$ is a reasonably strong Lewis acid that can form Lewis acid–base complexes with other heteroatoms present in the reaction mixture **32**.[42] The interplay between formation of the required SiHB complex and other complexes controls the outcome of the reactions described above.

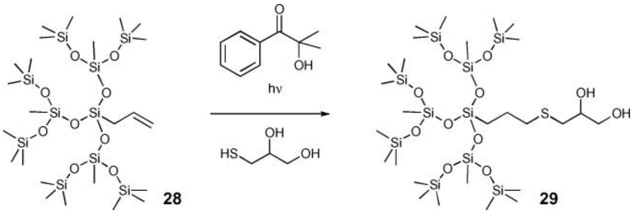

Fig. 8 Thiol-ene click.

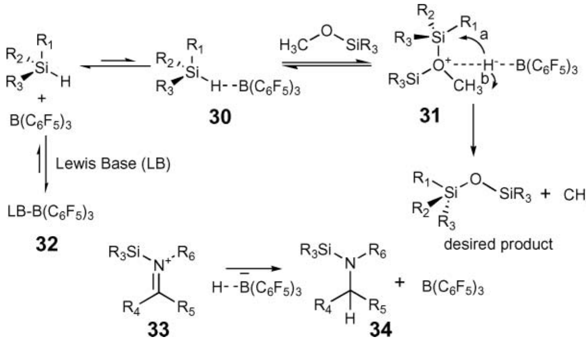

Fig. 9 Proposed mechanism for $B(C_6F_5)_3$-catalyzed siloxane formation.

Neither halides nor olefins provide sufficiently basic Lewis bases to compete with alkoxysilanes. Thus, at the low concentrations of $B(C_6F_5)_3$ used in this study (0.5 wt%), only activation *via* silyloxonium formation occurs, leading to clean disiloxane formation. The process can be repeated multiple times without loss of fidelity to produce complex structures in high yield in one or two steps (Fig. 4–6).

Less efficient reactions were observed when more powerful Lewis bases were present. Piers, in his examination of the hydrosilylation of imines, for example, showed that strong Lewis bases such as nitrogen can shut down any reaction involving SiH, because the equilibrium of N–B *vs.* H–B complexes lie almost exclusively on the side of the BN complex (Fig. 9, LB = $RR'C{=}NR''$).[26] As the N basicity is reduced, the equilibrium with SiH is established, and reduction occurs (**33** → **34**).

A similar set of complex equilibria will present in each of the cases studied here. The outcomes, in particular, the efficiency with which silicones are prepared, depend on the degree to which SiH–B complexes and silylated oxonium ions can form in the presence of other Lewis bases.

No reaction was observed to occur between **1** and aminopropyltriethoxysilane (APTS) in the presence of $B(C_6F_5)_3$. We ascribe this, following Piers' results, to essentially irreversible complexation between boron and the nitrogen (Fig. 9, LB = $H_2N(CH_2)_3Si(OR)_3$). Under such circumstances formation of the necessary B–H–Si complex is precluded. To examine this in more detail, proton NMR of the reaction medium containing tris(pentafluorophenyl)boron with aminopropyltriethoxysilane (APTS) and **1** over 3.5 h, a very long time when compared to the *ca.* 5 min normally needed for completion of Piers–Rubinsztajn reactions. No change in the multiplicity and integration of the different signals of APTS was observed. The only minor change was a small chemical shift of the amino protons, which can be attributed to the formation of the B–N complex, from 1.09 ppm in the free form to 1.32 in the presence of catalyst. It would be reasonable to expect that such complexes **35** could be relatively strong Brønsted acids and lead to silicone degradation/redistribution. However, as noted, there was no evidence of this.

The epoxide opened exclusively in hexane, and reacted competitively with the SiOMe groups in dichloromethane. The major reaction in both cases can be considered to arise from a B–H complex analogous to **30** and a silyloxonium ion: the Piers–Rubinsztajn reaction is as much about silicon-based Lewis acids as about borohydrides. Reduction of the silyl complex **36** preferentially occurs at the least hindered carbon (Fig. 10a), as would expected for nucleophilic driven reactions. In the more polar DCM, the less basic oxygen atoms of the SiOMe groups begin to compete, leading to some disiloxane formation (giving **3**, Fig. 2).

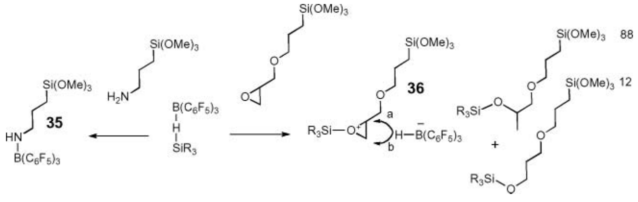

Fig. 10 Epoxide-ring opening.

The most significant contributions of this work are related to the synthetic flexibility provided. As shown in Fig. 6 (MW 1460), reasonably large silicones are available already after two steps. The orthogonality of the available processes suggest this strategy could be adopted to make explicit polymers or macrocrosslinkers.

The main objective of the work was to develop procedures to assembly amphiphilic polymers based on silicones. Both 3+2-cyclization reactions and thiol-ene reactions lend themselves to this objective (Fig. 7 and Fig. 8). As with hydrosilylation, they are orthogonal to dehydrogenative coupling, and both permit the linking of hydrophilic materials to silicones to give surface active materials.

Conclusions

The rapid assembly of explicit functional silicone polymers is facilitated by $B(C_6F_5)_3$-catalyzed condensation of hydrosilanes and alkoxysilanes. Efficiency of the process is reduced when more efficient Lewis bases than alkoxysilanes are present, including alcohols and epoxides: ethers are competitive. However, useful functional groups including alkyl halides and olefins are readily incorporated into complex silicone structures, and can then be converted into surface active polymers using 3+2-cycloadditions and thiol-ene click reactions.

Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada for financial support and Silcotech Canada and Siltech Inc. for support and helpful discussions.

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