Using Hydrosilylation To Assemble Organometallic Polymers Containing Combinations of Silicon-Based Functional Groups

Thomas Kuhnen, Ralph Ruffolo, Mark Stradiotto, Dagmar Ulbrich,
Michael J. McGlinchey, and Michael A. Brook*

Department of Chemistry, McMaster University, 1280 Main Street West,
Hamilton, Ontario, Canada L8S 4M1

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A set of silicon-based monomers has been prepared by a series of hydrosilylation reactions. These compounds serve as a molecular set of organosilicon compounds from which well-defined oligomers can be assembled. The organic functional groups contained in the monomers include alkynes, diynes, and arylsilanes for use as ligands for transition metals, and also disiloxanes. Depending upon the catalyst and temperature used, it was possible to prepare symmetric or asymmetric molecules from Ph_2SiH_2, **2**. The direct polymerization of these small molecules was limited by the degree to which the concentration of functional groups could be matched; decamers were the highest molecular weight materials prepared. These fragments were also oligomerized with a HSi-terminated silicone to give a functional organosilicone polymer of molecular weight $\bar{M}_w = 140\ 000$.

Introduction

Functionalized organosilanes have been shown to possess silicon-dependent electronic properties that operate over both short and long distances. Typically, α,ω-bis(trimethylsilyl)polyalkynes exhibit red-shifted UV absorptions relative to their non-silylated analogues.[1] A number of silicon-containing "molecular wires" have been reported,[2,3] and very recently, this concept has been extended to silylated poly-ynes tethered to a surface.[4]

These short-range interactions are complemented by the longer range phenomena observed when 1,2-bis(trimethylsilyl)ethyne or 1,4-bis(trimethylsilyl)butadiyne are cationically polymerized; these systems, once approximately doped, are exceptionally conductive.[5] Polysilanes also exhibit long-range electronic interactions: the maximum UV absorption wavelengths increase with growing chain length before leveling off at a degree of polymerization of about 20.[6] Interestingly, the irradiation of polysilanes can lead to the production of a range of silicon-based reactive intermediates including disilenes, silenes, silicon radicals, and silylenes.[7,8]

The combination of functionalized silanes and transition metals also leads to materials with unusual electronic properties. For instance, the very intriguing poly(ferrocenyl)silanes, described by Manners and co-workers,[9] conjugate through the silicon atoms, as evidenced by the longer wavelength UV absorption maxima and lower ionization potentials than those found in their carbon analogues.

Although molecular fragments possessing these electronic properties are of interest in their own right, we are particularly interested in the potential interactions between different electronically active, functionalized silanes *within the same molecule*. We, therefore, chose to develop a flexible methodology that would allow the combination of a variety of different fragments from a molecular "set". Moreover, we chose to impose the additional constraint that these different components should be combined in a polymeric matrix that could be adapted to different applications. In particular, it would be desirable to establish conditions for homo- or copolymerization that are compatible with the facile incorporation of transition metal moieties (either pre- or post-polymerization) at relatively mild temperatures.

While the polymeric species discussed above are generally amorphous or crystalline solids, silicones, at least for the polydimethylsiloxanes, are liquids irrespective of their molecular weight. Moreover, silicones often possess an array of properties that are quite different from those of their organic analogues, including high electri-

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* To whom correspondence should be addressed. E-mail: mabrook@mcmaster.ca. Phone: (905) 525-9140 ext. 23483. Fax: (905) 522-2509.

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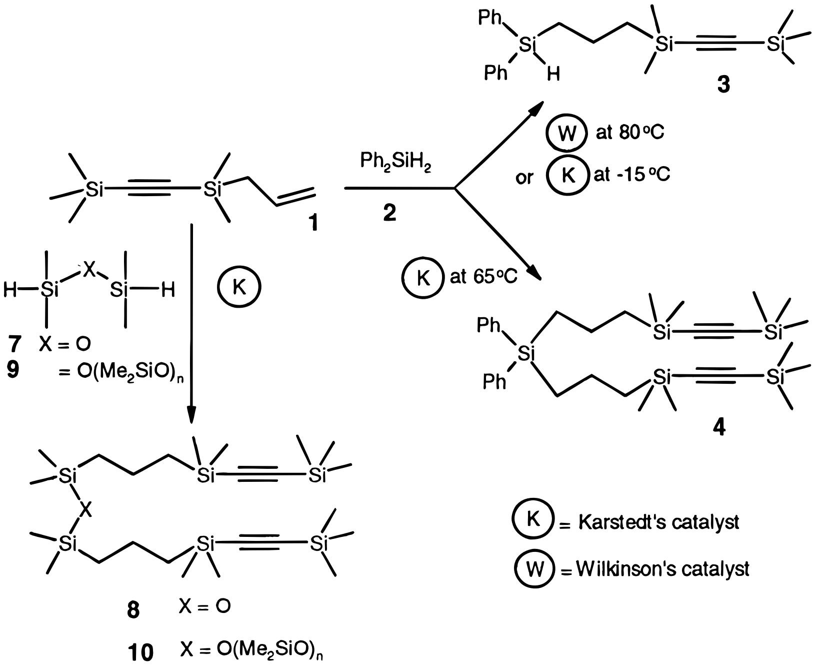
Scheme 1



cal resistivity, thermal and electrical stability, and exceptional hydrophobicity.[10] Furthermore, silicones are not affected to a great extent by neutral transition metal complexes, except that Si−H species can yield oxidative addition products.[11] Consequently, we decided to use silicones as the matrix within which to interchangeably place selected combinations of sila-functional species with the goal of preparing polymers with potentially interesting optical and electronic properties.[12]

Results and Discussion

Hydrosilylation was chosen to connect the molecular fragments. Among the many advantages of this reaction are high yields, very low catalyst loadings and, with the exception of colloidal platinum, no byproducts.[13] In order to develop the hydrosilylation chemistry required for the assembly of our desired functionalized polymers, a series of model studies were carried out with allyldimethyl((trimethylsilyl)ethynyl)silane, **1**, which may be prepared by the reaction of $Me_3SiC{\equiv}CLi$ with $ClMe_2SiCH_2CH{=}CH_2$.[14] To mimic the difunctional nature of the monomers that will eventually be needed for polymerization, hydrosilylation reactions were performed with dihydrosilicon compounds, as illustrated in Scheme 1.

The 2:1 reaction of $Me_3SiC{\equiv}CSiMe_2CH_2CH{=}CH_2$, **1**, with diphenylsilane, **2**, using Wilkinson's catalyst, $(Ph_3P)_3RhCl$, at room temperature gave exclusively the mono-addition product, **3**, in good yield, even in refluxing tetrahydrofuran (65 °C). In contrast, Karstedt's catalyst, $Pt_2[(CH_2{=}CHSiMe_2)_2O]_3$,[13,15] gave the monoadduct **3** at −15 °C, but yielded the bisadduct, **4**, at elevated temperatures. At room temperature, a mixture of starting material, **1**, and the mono- and bisadducts was obtained. In neither case did the alkyne participate in the hydrosilylation.

Previous work has shown that internal alkynes react more rapidly in hydrosilylations than do terminal olefins, the exact opposite of the results presented here.[16] This difference may be attributed to the accessibility of the alkyne in this case. The $SiMe_2$ groups which flank the alkyne serve to protect it from chelation by the catalyzing metal: we have had difficulty in finding conditions in which the alkyne will react.[17] In the previous work, less sterically constrained alkynes $PhC{\equiv}CPh$ and 2-decyne were utilized.[16]

It is somewhat more difficult to explain the differences in reactivity between Wilkinson's and Karstedt's catalyst. Wilkinson's catalyst has been shown to be more reactive than Karstedt's catalyst in the bishydrosilylation of dihydrosilanes with octene as the reacting olefin.[18,19] It is clear from this work and the referenced papers that temperature, reaction time, catalyst preparation, the presence of metals in colloidal form, and the structures of the reagents all play a part in the relative rates of hydrosilylation. However, we are unable to ascertain the specific factors in this case that result in the observed selectivity in the production of **3** and **4** (Scheme 1).

The ready availability of the monoadduct, **3**, was exploited by subsequent conversion at higher temper-

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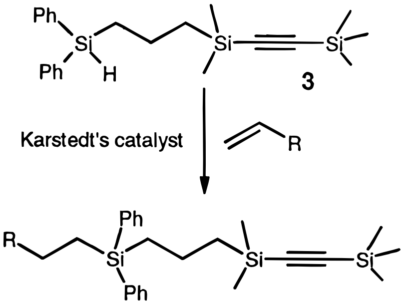
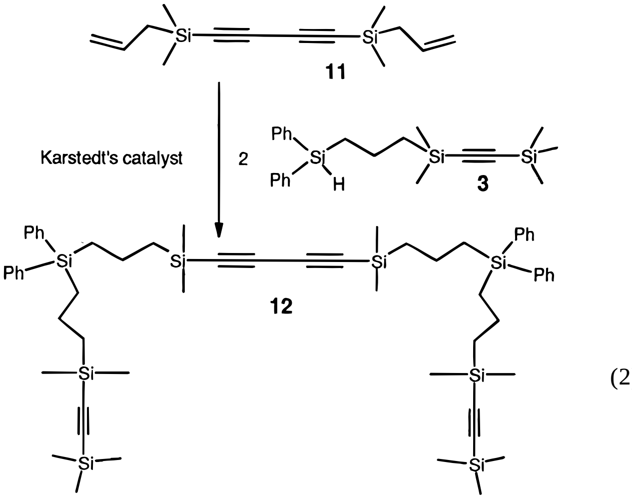


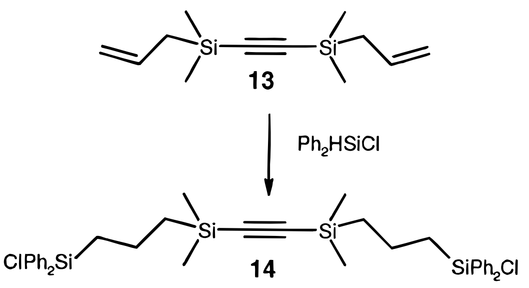
(1)

5 R = C_4H_9
6 R = Ph

atures to the unsymmetrical products **5** or **6** by reaction with 1-hexene or styrene, respectively (eq 1). Another difunctional hydrosilane was found to react readily with $Me_3SiC{\equiv}CSiMe_2CH_2CH{=}CH_2$, **1**. Thus, condensation of **1** with tetramethyldisiloxane, **7**, in the presence of Karstedt's catalyst yielded the bishydrosilylation product **8**, in excellent yield (Scheme 1). Similarly, the higher molecular weight hydrogen-terminated silicone **9** gave the corresponding bishydrosilylation product **10**. Presumably, a variety of other interesting silicon-containing "spacer" fragments could be similarly incorporated into the backbone of an organometallic polymer. As an example, the "reverse" reaction between 2 equiv of the initial monoadduct **3** with the difunctional system 1,4-bis(allyldimethylsilyl)butadiyne, **11**, yielded the bishydrosilylation product **12** (eq 2). Yet another example appears in eq 3 whereby the chloro-functionalized species **14** is easily generated by double addition of Ph_2SiHCl to bis(allyldimethylsilyl)ethyne, **13**.

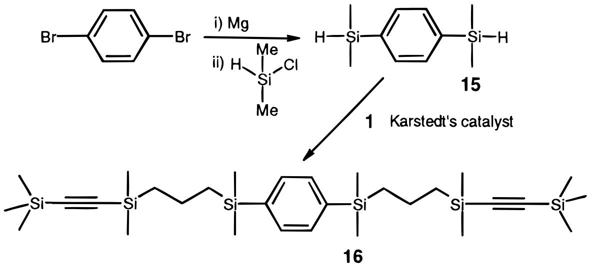


(2)



(3)

This technique can also be applied to arylhydrosilanes; in this case, the phenyl ring is not an appendage of the linear chain but a component of it. The dihydrosilane **15**, prepared by a traditional Grignard approach, undergoes a bishydrosilylation with 2 equiv of **1** to yield **16** (eq 4).



(4)

Having demonstrated that the model systems work efficiently, the preparation of block copolymers possessing various functional fragments was examined. If the stoichiometry between the divinyl and di(Si−H) monomers is perfectly matched (*i.e.*, $[Si{-}H]/[RCH{=}CH_2] = 1$), then high molecular weights will result. However, even small deviations from this ratio will lead to much lower molecular weights.[20] A 2:1 reaction between diphenylsilane, **2**, and bis(allyldimethylsilyl)ethyne, **13**, gave the bishydrosilylation product **17** (Scheme 2). The iterative process can be continued with consequent enhancement of the molecular weight: thus, double addition of **1** to **17** yielded the octasilyl−triyne **18**. The Karstedt-catalyzed reaction of Ph_2SiH_2 and **13** produced polymer **20**, which was found by GPC to have a molecular weight of approximately 4200.

The use of higher molecular weight components (macromonomers) similarly led to efficient oligomerization. Thus, the reaction between the hydrogen-terminated silicone **9** ($\bar{M}_w = 28\,000$) and bis(allyldimethylsilyl)ethyne, **13**, gave a clear, highly viscous oil **20** having a molecular weight of 140 000 (Scheme 2). Better control of the functional group stoichiometry should lead to even higher molecular weight, functionalized organometallic polymers.

While, *prima facie*, the GPC results suggest that a large difference exists between the extent of the polymerization reactions giving **19** and **20**, respectively, these results are deceiving owing to the fact that the monomers employed in the two reactions differ greatly in molecular weight. Upon closer inspection, it is apparent that both polymerization products, **19** and **20**, are the result of 5−10 hydrosilylation cycles.

The main goal of this phase of the project was to establish that hydrosilylation allowed the sequential assembly of a variety of different functional groups and spacers. This has been efficiently accomplished by using an iterative procedure. In an accompanying paper,[12] we describe the coordination of single and mixed organo-transition-metal fragments to the ligands described in this paper. We further show an example in which a transition metal cluster was incorporated along the chain of a relatively high molecular weight siloxane polymer.

Experimental Section

Instrumentation. ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded using Bruker AC-200, AC-300, and DRX-500 spectrometers. Proton spectra on the latter instrument were acquired using a 5 mm broad-band inverse probe with triple-axis gradient capability. Spectra were obtained with eight scans in 32K data points over a 3.788 kHz spectral width

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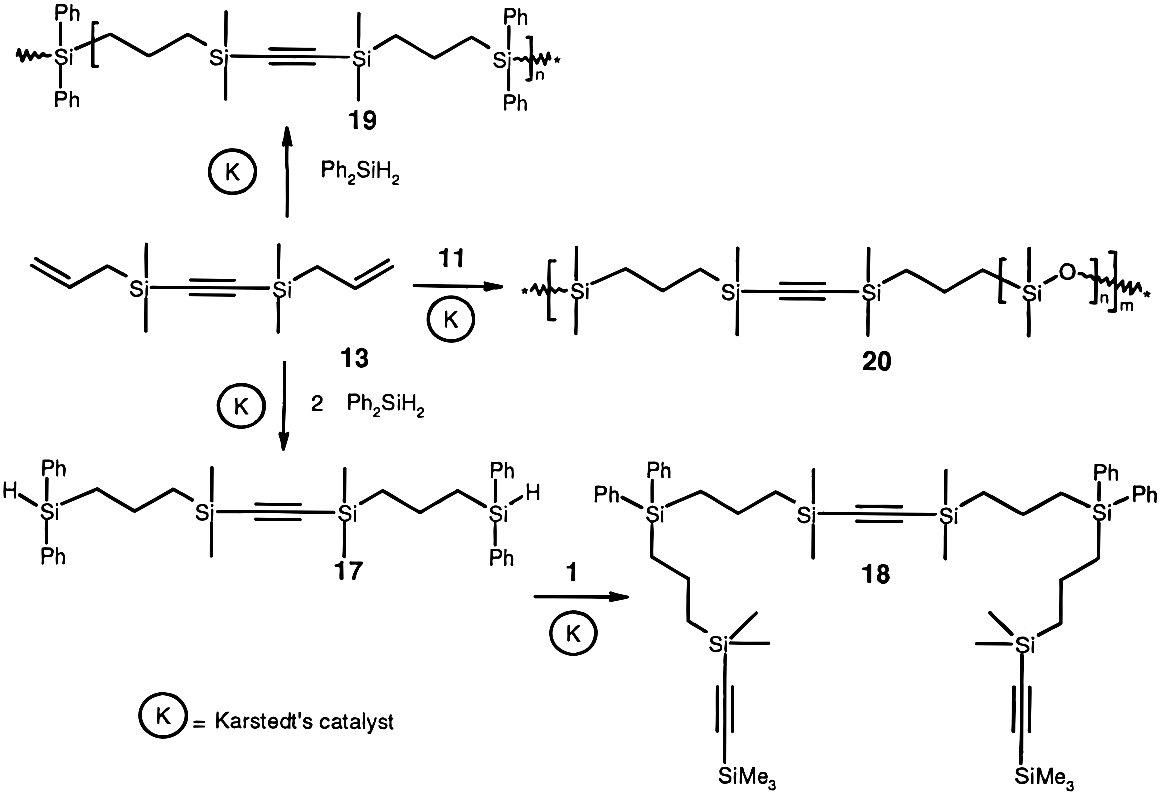
(20) Fried, J. R. *Polymer Science and Technology*; Prentice Hall PTR: Englewood Cliffs, NJ, 1995.

Scheme 2



(4.325 s acquisition time). The sample temperature was maintained at 30 °C by a Bruker Eurotherm variable-temperature unit. The free induction decay (FID) was processed using exponential multiplication (line broadening, 0.2 Hz) and was zero-filled to 64K before Fourier transformation.

Infrared spectra were obtained on a Bio-Rad FTS-40 Fourier transform spectrometer, using NaCl windows. Electron impact (EI) and chemical ionization (CI, NH_3) mass spectra were recorded at 70 eV with a source temperature of 200 °C on a VG analytical ZAB-E mass spectrometer equipped with a VG 11-250 data system.

The molecular weights of the hydrophobic polymers were analyzed using a Waters gel permeation chromatograph (GPC) equipped with a Waters 510 HPLC pump and a Waters 410 differential refractive index detector. Two Jordi mixed-bed columns and one Waters 4E column in series were utilized with 1,1,1-trichloroethane as the solvent flowing at 1 mL/min. Pretreatment of the HPLC grade 1,1,1-trichloroethane involved filtration through a 400 μm Teflon filter. Narrow molecular weight polystyrene and silicone standards from Scientific Polymer Products, Inc., were used for calibration of the chromatographic system. While we recognize that neither standard will give an accurate molecular weight value for compounds **10**, **19**, and **20**, comparison of the retention volumes of the standards and the known molecular weights of the starting materials with those of the products allows us to estimate the number of interative hydrosilylations which occurred. Data manipulation was done using Waters Millenium Chromatography Manager software.

Materials. Diethyl ether (Caledon) was distilled from lithium aluminum hydride. Tetrahydrofuran (Caledon) was distilled from potassium/benzophenone. CH_2Cl_2 (Caledon) was distilled prior to use from P_2O_5. Cyclohexane (Caledon) and hexane (Caledon) were distilled prior to use. Only distilled water was used.

Dimethyldichlorosilane (Aldrich) was distilled prior to use. Otherwise, the compounds from Aldrich (*n*-butyllithium, 1,4-dibromobenzene, diphenylsilane, 1-hexene, lithium aluminum hydride, magnesium turnings, styrene, trichloroethylene, (trimethylsilyl)ethyne, and Wilkinson's catalyst ($(Ph_3P)_3RhCl$)) and from Gelest (allyldimethylchlorosilane, hydride-terminated silicone ($\bar{M}_w = 17\,000$), Karstedt's catalyst (platinum divinyltetramethyldisiloxane complex in xylene)) were used without further purification. *p*-$HMe_2SiC_6H_4SiMe_2H$ (**15**) was prepared using the method detailed by Merker and co-workers.[21]

All experiments were carried out under an atmosphere of dry nitrogen, using standard Schlenk techniques. For all hydrosilylations, 1 mol % of either Wilkinson's or Karstedt's catalyst was used. Unless otherwise specified, the compounds were purified by flash chromatography on silica gel using hexane/acetone mixtures.

$Me_3SiC{\equiv}C{-}SiMe_2(CH_2CH{=}CH_2)$ (1). *n*-Butyllithium (96 mL, 2.5 M in hexane, 0.25 mol) was added dropwise to a solution of (trimethylsilyl)ethyne (25 g, 0.25 mol) in diethyl ether (100 mL) at −78 °C via syringe over 30 min, after which the solution was allowed to warm to room temperature. After the mixture was stirred for 2 h, the solution was cooled to −78 °C and allyldimethylchlorosilane (36 mL, 0.25 mol) in diethyl ether (15 mL) was added dropwise. The solution was allowed to warm to room temperature and stirred for 24 h. The crude mixture was extracted with water, and the separated organic phase was dried over $MgSO_4$. Removal of the solvent and other volatile organic components by rotary evaporation yielded **1** as a clear oil (44.8 g, 0.24 mol, 96%). ^1H NMR ($CDCl_3$, 300.13 MHz): δ 5.77 (m, 1H, $CH_2{=}CHCH_2$), 4.89 (m, 2H, $CH_2{=}CHCH_2$), 1.60 (m, 2H, $CH_2{=}CHCH_2$), 0.14 (s, 6H, $Si(CH_3)_2$), 0.12 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR ($CDCl_3$, 75.03 MHz): δ 133.8 ($CH_2{=}CHCH_2$), 114.8 ($CH_2{=}CHCH_2$), 112.0 ($C{\equiv}C$), 113.9 ($C{\equiv}C$), 24.0 ($CH_2{=}CHCH_2$), −0.1 ($Si(CH_3)_2$), −2.3 ($Si(CH_3)_3$). ^{29}Si NMR (CH_2Cl_2, 59.6 MHz): δ −19.0 ($Si(CH_3)_2(CH_2{=}CHCH_2)$), −19.2 ($Si(CH_3)_3$). Mass spectrum (DEI, m/z (%)): 181 (76, $[M - CH_3]^+$), 166 (87, $[M - 2(CH_3)]^+$), 155 (100, $[M - CH_2{=}CHCH_2]^+$), 73 (65, $[Si(CH_3)_3]^+$). Mass spectrum (DCI (NH_3), m/z (%)): 214 (78, $[M + 18]^+$), 197 (41, $[M + 1]^+$). Mass spectrum (high resolution, (DEI)): calcd for mass $^{12}C_9H_{17}Si_2$ ($[M - CH_3]^+$), 181.0869 amu; found, 181.0866. amu; Anal. Calcd for $C_{10}H_{20}Si_2$: C, 61.14; H, 10.26. Found: C, 61.40; H, 10.95.

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[21] Merker, R. L.; Scott, M. J. *J. Polym. Sci. A* **1964**, *2*, 15.

$Me_3SiC{\equiv}CSiMe_2(CH_2CH_2CH_2)SiPh_2H$ (3). A mixture of diphenylsilane **2** (2.08 g, 0.0115 mol) and compound **1** (2.26 g, 0.0115 mol) was cooled to −15 °C, and Karstedt's catalyst (or Wilkinson's catalyst at 25 °C stirred for 72 h) was added. After a few seconds, gas bubbles developed and the solution turned bright yellow. The reaction mixture was stirred for an additional 2 h at −15 °C and then slowly allowed to warm to ambient temperature with stirring over an additional 18 h. The crude mixture was subjected to flash chromatography on silica gel. Elution with hexane/acetone (10:1) gave **3** as a clear oil (3.84 g, 0.0103 mol, 92%). ^{1}H NMR ($CDCl_3$, 200.13 MHz): δ 7.40 (m, 10H, aromatic), 4.88 (t, 1H, $J_{Si-H} = 3.7$ Hz, $Si{-}\mathit{H}$), 1.60 (m, 2H, $CH_2C\mathit{H}_2CH_2$), 1.27 (t, 2H, $J = 8.2$ Hz, $SiPh_2C\mathit{H}_2$), 0.75 (t, 2H, $J = 8.2$ Hz, $SiMe_2C\mathit{H}_2$), 0.16 (s, 6H, $Si(C\mathit{H}_3)_2$), 0.14 (s, 9H, $Si(C\mathit{H}_3)_3$). ^{13}C NMR ($CDCl_3$, 75.03 MHz): δ 135.2, 134.6, 129.4, 128.0 (aromatic), 113.1, 110.0 ($C{\equiv}C$), 20.1 ($CH_2CH_2CH_2$), 19.0 ($SiPh_2\mathit{C}H_2$), 16.2 ($SiMe_2\mathit{C}H_2$), −0.6 ($Si(\mathit{C}H_3)_2$), −1.66 ($Si(\mathit{C}H_3)_3$). ^{29}Si NMR (CH_2Cl_2, 59.6 MHz): δ −19.67 ($Si(CH_3)_3$), −18.58 ($Si(CH_3)_2$), −11.38 ($Si{-}H$). IR (neat): ν_{Si-H} 2116 cm^{-1}(sh). Mass spectrum (DEI, *m/z* (%)): 379 (25, $[M - H]^+$), 365 (16, $[M - CH_3]^+$), 307 (28, $[M - Si(CH_3)_3]^+$), 73 (100, $[Si(CH_3)_3]^+$). MS (high resolution, (DEI)): calcd for mass $^{12}C_{22}H_{31}Si_3$ ($[M - H]^+$), 379.1734 amu; found, 379.1723 amu. Anal. Calcd for $C_{22}H_{32}Si_3$: C, 69.44; H, 8.48. Found: C, 69.28; H, 8.99.

$(Me_3SiC{\equiv}CSiMe_2CH_2CH_2CH_2)_2SiPh_2$ (4). Using methods analogous to those detailed for the preparation of compound **3**, diphenylsilane, **2**, (0.92 g, 5.51 mmol) and compound **1** (2.26 g, 11.5 mmol) were reacted at ambient temperature in the presence of Karstedt's catalyst. The desired product, **4,** was isolated as a clear oil (3.04 g, 5.35 mmol, 93%). ^{1}H NMR ($CDCl_3$, 200.13 MHz): δ 7.34 (m, 10H, aromatic), 1.61 (m, 4H, $CH_2C\mathit{H}_2CH_2$), 1.22 (t, 4H, $J = 8.2$ Hz, $SiPh_2C\mathit{H}_2$), 0.70 (t, 4H, $J = 8.2$ Hz, $SiMe_2C\mathit{H}_2$), 0.16 (s, 12H, $Si(C\mathit{H}_3)_2$), 0.14 (s, 18H, $Si(C\mathit{H}_3)_3$). ^{13}C NMR ($CDCl_3$, 75.03 MHz): δ 135.5, 134.8, 129.6, 129.0 (aromatic), 114.0, 110.9 ($C{\equiv}C$), 20.7 ($CH_2CH_2CH_2$), 18.3 ($SiPh_2\mathit{C}H_2$), 16.8 ($SiMe_2\mathit{C}H_2$), −0.04 ($Si(\mathit{C}H_3)_2$), −1.64 ($Si(\mathit{C}H_3)_3$). ^{29}Si NMR (CH_2Cl_2, 59.6 MHz): δ −18.6 ($SiPh_2$), −19.4 ($Si(CH_3)_2$), −19.7($Si(CH_3)_3$). IR (neat): $\nu_{C\equiv C}$ 1250 cm^{-1} (m). Mass spectrum (DEI, *m/z* (%)): 576 (8, $[M]^+$), 379 (100, $[M - Me_3SiC{\equiv}CSiMe_2CH_2CH_2CH_2]^+$), 73 (15, $[Si(CH_3)_3]^+$). Mass spectrum (high resolution, (DEI)): calcd for mass $^{12}C_{31}H_{49}Si_5$ ($[M - CH_3]^+$), 561.2681 amu; found, 561.2684 amu. Anal. Calcd for $C_{32}H_{52}Si_5$: C, 66.63; H, 9.09. Found: C, 66.98; H, 10.06.

$(Me_3SiC{\equiv}CSiMe_2CH_2CH_2CH_2)SiPh_2C_6H_{13}$ (5). A neat mixture of compound **3** (1.0 g, 2.67 mmol), 1-hexene (0.224 g, 2.67 mmol), and Karstedt's catalyst was stirred for 72 h at 25 °C. The desired product, **5,** was isolated by distillation (185 °C/1.0 mmHg) as a clear, viscous oil (1.16 g, 2.53 mmol, 95%). ^{1}H NMR ($CDCl_3$, 200.13 MHz): δ 7.36 (m, 10H, aromatic), 1.51 (m, 2H, $CH_2C\mathit{H}_2CH_2$), 1.24 (m, 10H, hexyl $C\mathit{H}_2$'s), 1.08 (t, 2H, $J = 8.1$ Hz, $SiPh_2C\mathit{H}_2$), 0.85 (t, 3H, $J = 8.2$ Hz, hexyl $C\mathit{H}_3$), 0.70 (t, 2H, $J = 8.2$ Hz, $SiMe_2C\mathit{H}_2$), 0.14 (s, 6H, $Si(C\mathit{H}_3)_2$), 0.10 (s, 9H, $Si(C\mathit{H}_3)_3$). ^{13}C NMR ($CDCl_3$, 50.03 MHz): δ 136.6, 134.8, 129.0, 127.7 (aromatic), 114.4, 113.2 ($C{\equiv}C$), 33.4, 31.4, 23.7, 22.6, 20.7, 18.2, 16.7, 14.1, 12.6 (aliphatic), −0.1 ($Si(\mathit{C}H_3)_2$), −1.6 ($Si(\mathit{C}H_3)_3$). IR (neat): $\nu_{C\equiv C}$ 1250 cm^{-1}(m). Mass spectrum (DEI, *m/z* (%)): 464 (8, $[M]^+$), 379 (31, $[M - C_6H_{13}]^+$), 302 (100, $[M - C_{12}H_{18}]^+$), 73 (57, $[Si(CH_3)_3]^+$).

$(Me_3SiC{\equiv}CSiMe_2CH_2CH_2CH_2)SiPh_2CH_2CH_2Ph$ (6). Using methods analogous to those detailed for the preparation of compound **5**, a mixture of compounds **3** (1.0 g, 2.67 mol), styrene (0.277 g, 2.67 mmol), and Karstedt's catalyst was stirred for 72 h at 25 °C. The resulting mixture was subjected to flash chromatography on silica gel. Elution with cyclohexane/CH_2Cl_2 (50:50) yielded **6** (1.049 g, 2.19 mmol, 82%). ^{1}H NMR ($CDCl_3$, 200.13 MHz): δ 7.47 (m, 15H, aromatic), 2.74 (t, 2H, $J = 8.5$ Hz, $C\mathit{H}_2Ph$), 1.46 (m, 2H, $CH_2C\mathit{H}_2CH_2$), 1.18 (m, 4H, $SiPh_2C\mathit{H}_2$), 0.71 (t, 2H, $J = 8.2$ Hz, $SiMe_2C\mathit{H}_2$), 0.13 (s, 6H, $Si(C\mathit{H}_3)_2$), 0.10 (s, 9H, $Si(C\mathit{H}_3)_3$). ^{13}C NMR ($CDCl_3$, 50.03 MHz): δ 135.5, 134.9, 129.2, 128.3, 127.8, 127.7, 127.6, 125.6 (aromatic), 114.5, 113.2 ($C{\equiv}C$), 20.7, 18.3, 18.2, 16.7, 14.9 (aliphatic carbons), −0.1 ($Si(\mathit{C}H_3)_2$), −1.6 ($Si(\mathit{C}H_3)_3$). ^{29}Si NMR (CH_2Cl_2, 59.6 MHz): δ −17.9 ($SiPh_2$), −16.8 ($Si(CH_3)_2$), −9.6 ($Si(CH_3)_3$). IR (neat): $\nu_{C\equiv C}$ 1250 cm^{-1}(m). Mass spectrum: (DEI, *m/z* (%)): 469 (8, $[M - CH_3]^+$), 407 (30, $[M - Ph]^+$), 379 (86, $[M - PhCH_2CH_2]^+$), 73 (100, $[Si(CH_3)_3]^+$). Mass spectrum (DCI (NH_3), *m/z* (%)): 502 (78, $[M + 18]^+$). Mass spectrum (high resolution, (DEI)): calcd for mass $^{12}C_{29}H_{37}Si_3$ ($[M - CH_3]^+$), 469.2203 amu; found, 469.2187 amu.

$(Me_3SiC{\equiv}CSiMe_2CH_2CH_2CH_2SiMe_2)_2O$ (8). A mixture of **1** (0.75 g, 0.00383 mol), tetramethyldisiloxane **7** (0.26 g, 0.00191 mol), and Karstedt's catalyst in 50 mL of freshly distilled THF was stirred at ambient temperature for 18 h. The crude mixture was then subjected to flash chromatography on silica gel. Elution with pentane/CH_2Cl_2 (5:1) gave **8** as clear oil (0.82 g, 1.56 mmol, 82%). ^{1}H NMR ($CDCl_3$, 200.13 MHz): δ 1.42 (m, 4H, $CH_2C\mathit{H}_2CH_2$), 0.62 (m, 8H, $C\mathit{H}_2CH_2C\mathit{H}_2$), 0.11 (s, 18H, $Si(C\mathit{H}_3)_3$), 0.08 (s, 12H, $Si(C\mathit{H}_3)_2$), 0.03 (s, 12H, $OSi(C\mathit{H}_3)_2$). ^{13}C NMR ($CDCl_3$, 75.03 MHz): δ 114.2, 113.2 ($C{\equiv}C$), 22.6, 20.3, 17.6 ($CH_2CH_2CH_2$), 1.2 ($Si(\mathit{C}H_3)_2$), 0.3 ($OSi(\mathit{C}H_3)_2$), −1.6 ($Si(\mathit{C}H_3)_3$). Mass spectrum (DEI, *m/z* (%)): 526 (50, $[M]^+$), 511 (15, $[M - CH_3]^+$), 271 (12, $[M - C_{12}H_{27}Si_3]^+$), 255 (100, $[C_{12}H_{27}Si_3]^+$), 73 (47, $[Si(CH_3)_3]^+$). Mass spectrum (high resolution, (DEI)): calcd for mass $^{12}C_{24}H_{54}Si_6O$ ($[M]^+$), 526.2790 amu; found, 526.2779 amu.

$(Me_3SiC{\equiv}CSiMe_2CH_2CH_2CH_2SiMe_2O)_2((SiMe_2O)_n\text{-}SiMe_2)$ (10). Using methods similar to those detailed for the preparation of compound **3**, hydrogen-terminated silicone **9** (8.75 g, 0.5 mmol, 17 500 molecular weight) and compound **1** (0.196 g, 1.0 mmol) were reacted at ambient temperature in the presence of Karstedt's catalyst for 2 h. The desired compound **10** was isolated as a clear oil (8.81 g). ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ 1.45 (m, 4H, $CH_2C\mathit{H}_2CH_2$), 1.23 (m, 4H, $C\mathit{H}_2CH_2CH_2$), 0.66 (m, 4H, $CH_2CH_2C\mathit{H}_2$), 0.15 (s, 18H, $Si(C\mathit{H}_3)_3$), 0.12 (s, 12H, $Si(C\mathit{H}_3)_2$), 0.06 (s, *ca.* 1480 H, $(Si(C\mathit{H}_3)_2O)_n$). ^{13}C NMR ($CDCl_3$, 75.03 MHz): δ 22.5, 20.4, 17.7 (aliphatic carbons), 1.2 ($Si(\mathit{C}H_3)_2$), 0.3 ($Si(\mathit{C}H_3)_3$), 0.0, −1.0 ($(Si(\mathit{C}H_3)_2O)_n$). ^{29}Si NMR (CH_2Cl_2, 59.6 MHz): δ −17.1, −17.5, −17.9, −20.4. $\bar{M}_w = 29\,000$, $\bar{M}_w/\bar{M}_n = 2.45$.

$(CH_2{=}CHCH_2)Me_2Si{-}C{\equiv}C{-}C{\equiv}C{-}SiMe_2(CH_2CH{=}CH_2)$ (11).[14] *n*-Butyllithium (150 mL, 1.6 M, 0.24 mol) was added dropwise to a solution of hexachlorobutadiene (15.7 g, 61 mmol) in diethyl ether (30 mL) at −78 °C via syringe over 30 min. After the mixture was stirred for 2 h, the solution was cooled to −78 °C and allyldimethylchlorosilane (18 mL, 15.7g, 0.13 mol) in diethyl ether (5 mL) was added dropwise. After the mixture was stirred for an additional 24 h at room temperature, the reaction was quenched by slow addition of distilled water (50 mL) and extracted with diethyl ether (3 × 25 mL). Removal of the volatile organics yielded **11** (11.0 g, 47 mmol, 80%) as an oil. ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ 5.75 (m, 2H, $CH_2{=}C\mathit{H}CH_2$), 4.88 (m, 4H, $C\mathit{H}_2{=}CHCH_2$), 1.61 (m, 4H, $CH_2{=}CHC\mathit{H}_2$), 0.15 (s, 12H, $Si(C\mathit{H}_3)_2$). ^{13}C NMR ($CDCl_3$, 125.03 MHz): δ 133.0 ($CH_2{=}\mathit{C}HCH_2$), 114.6 ($\mathit{C}H_2{=}CHCH_2$), 88.8, 84.3 ($C{\equiv}C$), 23.3 ($CH_2{=}CH\mathit{C}H_2$), −2.8 ($Si(\mathit{C}H_3)_2$). ^{29}Si NMR (CH_2Cl_2, 59.6 MHz): δ −16.5 ($\mathit{Si}(CH_3)_2$). Mass spectrum (DEI, *m/z* (%)): 231 (17, $[M - CH_3]^+$), 205 (100, $[M - C_3H_5]^+$), 190 (12, $[M - C_4H_8]^+$). Mass spectrum (DCI (NH_3), *m/z* (%)): 264 (100, $[M + 18]^+$), 247 (27, $[M + 1]^+$). Mass spectrum (high resolution, (DEI)): calcd for mass $^{12}C_{13}H_{19}Si_2$ ($[M - CH_3]^+$), 231.1025 amu; found, 231.1023 amu.

$(Me_3Si{-}C{\equiv}C{-}SiMe_2CH_2CH_2CH_2Ph_2SiCH_2CH_2CH_2{-}SiMe_2C{\equiv}C)_2$ (12). Using methods similar to those detailed for the preparation of compound **3**, compound **11** (0.255 g, 1.00 mmol) and compound **3** (0.787 g, 2.00 mmol) were reacted at ambient temperature in the presence of Karstedt's catalyst for 2 h. The crude mixture was subjected to flash column chromatography over silica, and **12** was eluted with hexane/CH_2Cl_2 (20:1) as a clear, yellow oil (0.301 g, 0.26 mmol, 26%). ^{1}H NMR ($CDCl_3$, 200.13 MHz): δ 7.36 (m, 20H, aromatic), 1.90 (m, 8H), 1.31 (m, 8H), 0.76 (m, 8H), 0.14 (s, 24H, $Si(C\mathit{H}_3)_2$), 0.07 (s, 18H, $Si(C\mathit{H}_3)_3$). ^{13}C NMR ($CDCl_3$, 75.03 MHz): δ 136.0, 135.5, 129.0, 127.6 (aromatic), 116.1 ($C{\equiv}C$), 19.3, 18.4, 15.1

(aliphatic), 0.50 ($Si(\mathit{C}H_3)_2$), 0.03 ($Si(\mathit{C}H_3)_3$). ^{29}Si NMR (CH_2Cl_2, 59.6 MHz): δ −6.5, −9.6, −16.9, −17.9. Mass spectrum (DEI, *m*/*z* (%)): 627 (18, $[M - C_{22}H_{21}Si_3]^+$), 585 (10, $[M - C_{25}H_{27}Si_3]^+$), 248 (85, $[C_{14}H_{24}Si_2]^+$), 73 (100, $[Si(CH_3)_3]^+$).

$(H_2C{=}CHCH_2)Me_2Si{-}C{\equiv}C{-}SiMe_2(CH_2CH{=}CH_2)$ (13). Following a modified version of the synthetic procedure previously described by Uhlig and co-workers,[22] *n*-butyllithium (100 mL of a 1.6 M diethyl ether solution, 0.16 mol) was added dropwise to a solution of trichloroethylene (6.9 g, 0.053 mol) in diethyl ether (30 mL) at −78 °C via syringe over 30 min. After the mixture was stirred for 2 h, the solution was cooled to −78 °C and allyldimethylchlorosilane (16.6 mL, 14.8 g, 0.12 mol) in diethyl ether (5 mL) was added dropwise. The solution was allowed to warm to room temperature and stirred for 24 h. The reaction mixture was washed with water, and the organic phase was dried over $MgSO_4$. After removal of solvents under reduced pressure, the organic phase yielded **13** (10 g, 45 mmol, 85%) as an oil. ^1H NMR ($CDCl_3$, 300.13 MHz): δ 5.75 (m, 2H, $CH_2{=}C\mathit{H}CH_2$), 4.84 (m, 4H, $C\mathit{H}_2{=}CHCH_2$), 1.59 (m, 4H, $CH_2{=}CHC\mathit{H}_2$), 0.13 (s, 12H, $Si(C\mathit{H}_3)_2$). ^{13}C NMR ($CDCl_3$, 50.03 MHz): δ 132.5 ($CH_2{=}\mathit{C}HCH_2$), 114.4 ($C{\equiv}C$), 113.2 ($\mathit{C}H_2{=}CHCH_2$), 23.9 ($CH_2{=}CH\mathit{C}H_2$), −2.4 ($Si(\mathit{C}H_3)_2$). ^{29}Si NMR (CH_2Cl_2, 59.6 MHz): δ −18.4 ($\mathit{Si}(CH_3)_2$). Mass spectrum (DEI, *m*/*z* (%)): 207 (16, $[M - CH_3]^+$), 181 (62, $[M - C_3H_5]^+$) , 41 (100, $[C_3H_5]^+$). Mass spectrum (DCI (NH_3), *m*/*z*): 240 (19, $[M + 18]^+$), 223 (65, $[M + 1]^+$). Mass spectrum (high resolution, (DEI)): calcd for mass $^{12}C_{11}H_{19}Si_2$ ($[M - CH_3]^+$), 207.1025 amu; found, 207.1016 amu.

$ClPh_2SiCH_2CH_2CH_2SiMe_2C{\equiv}CSiMe_2CH_2CH_2CH_2SiPh_2Cl$ (14). Using methods detailed for the synthesis of compound **3**, compound **13** (1.20 g, 0.0055 mol) and diphenylchlorosilane (2.49 g, 0.011 mol) were reacted at ambient temperature in the presence of Karstedt's catalyst for 2 h. Removal of the volatile organics yielded the product **14** as a clear, viscous oil (3.50 g, 0.0052 mol, 95% conversion). ^1H NMR ($CDCl_3$, 200.13): δ 7.70 (m, 20H, aromatic), 1.89 (m, 4H, $CH_2C\mathit{H}_2CH_2$), 1.67 (m, 4H, $Ph_2SiC\mathit{H}_2$), 0.92 (m, 4H, $Me_2SiC\mathit{H}_2$), 0.28 (s, 12H, $Si(C\mathit{H}_3)_2$). ^{13}C NMR ($CDCl_3$, 75.03 MHz): δ 134.3, 133.8, 130.4, 128.1 (aromatic), 113.9 ($C{\equiv}C$), 20.2 ($CH_2\mathit{C}H_2CH_2$), 19.9 ($SiPh_2\mathit{C}H_2$), 17.6 ($SiMe_2\mathit{C}H_2$), −1.70 ($Si(CH_3)_2$). ^{29}Si NMR (CH_2Cl_2, 59.6 MHz,): δ 11.4, −16.7. Mass spectrum (DEI, *m*/*z* (%)): 623 (29, $[M - Cl]^+$), 399 (71, $[M - C_{15}H_{16}SiCl]^+$), 317 (100, $[C_{17}H_{22}Si_2Cl]^+$). Mass spectrum (high resolution, (DEI)): calcd for mass $^{12}C_{36}H_{44}Si_4Cl$ ($[M - Cl]^+$), 623.2209 amu, found 623.2223 amu. Anal. Calcd for $C_{36}H_{44}Cl_2Si_4$: C, 65.63; H, 6.74. Found: C, 65.76; H, 6.95.

[*p*-$(Me_3SiC{\equiv}CSiMe_2CH_2CH_2CH_2Me_2Si)_2C_6H_4$] (16). A mixture of **15** (1.97 g, 0.0102 mol), compound **1** (3.92 g, 0.0200 mol), and Karstedt's catalyst was stirred at ambient temperature for 18 h. From the crude mixture was distilled **16** (150−160 °C/1 mmHg) as a clear oil (5.3 g, 9.1 mmol, 90%). ^1H NMR ($CDCl_3$, 200.13 MHz): δ 7.54 (s, 4H, aromatic), 1.53 (m, 4H, $CH_2C\mathit{H}_2CH_2$), 0.88 (m, 4H, $SiPh_2C\mathit{H}_2$), 0.71 (m, 4H, $SiMe_2C\mathit{H}_2$), 0.28 (s, 12H, $Si(C\mathit{H}_3)_2$), 0.18 (s, 18H, $Si(C\mathit{H}_3)_3$), 0.18 (s, 12H, $Si(C\mathit{H}_3)_2$). ^{13}C NMR ($CDCl_3$, 75.03 MHz): δ 140.1, 132.8 (aromatic), 114.4, 113.2 ($C{\equiv}C$), 20.5, 19.8, 18.4 ($\mathit{C}H_2\mathit{C}H_2\mathit{C}H_2$), 0.0 ($Si(\mathit{C}H_3)_3$), −1.9, −3.9 ($Si(\mathit{C}H_3)_2$). ^{29}Si NMR (CH_2Cl_2, 59.6 MHz): δ −2.4 ($Ph\mathit{Si}$), −16.5 ($\mathit{Si}(CH_3)_2$), −17.9 ($\mathit{Si}(CH_3)_3$). IR (neat, cm^{-1}): 3048 (w), 2958 (s), 2916 (m), 2875 (m) 1250(s). Mass spectrum (DEI, *m*/*z* (%)): 586 (11, $[M]^+$), 571 (56, $[M - CH_3]^+$), 489 (44, $[M - C_5H_9Si]^+$), 255 (100, $[C_{12}H_{27}Si_3]^+$). Mass spectrum (high resolution, (DEI)): calcd for mass $^{12}C_{30}H_{58}Si_6$ (M^+), 586.3154 amu, found, 586.3151 amu; Anal. Calcd for $C_{30}H_{58}Si_6$: C, 61.40; H, 9.97. Found: C, 61.96; H, 10.61.

$(HPh_2Si(CH_2CH_2CH_2)SiMe_2C{\equiv}CSiMe_2(CH_2CH_2CH_2)SiPh_2H)$ (17). To a mixture of diphenylsilane **2** (4.14 g, 0.0225 mol) and compound **13** (2.5 g, 0.012 mol) at −15 °C was added Karstedt's catalyst. After 1.5 h, the mixture was allowed to warm to ambient temperature with stirring for an additional 18 h. The crude mixture was then subjected to flash chromatography on silica gel. Elution with pentane/CH_2Cl_2 (5:1) gave the desired compound **17** as a clear oil (6.6 g, 0.011 mol, 98%). ^1H NMR ($CDCl_3$, 200.13 MHz): δ 7.41 (m, 20H, aromatic), 4.90 (t, 2H, $J = 3.6$ Hz, $Si{-}\mathit{H}$), 1.65 (m, 4H, $CH_2C\mathit{H}_2CH_2$), 1.27 (m, 4H, $SiPh_2C\mathit{H}_2$), 0.74 (m, 4H, $SiMe_2C\mathit{H}_2$), 0.09 (s, 12H, $Si(C\mathit{H}_3)_2$). ^{13}C NMR ($CDCl_3$, 50.03 MHz): δ 135.8, 135.4, 135.1, 134.5 (aromatic), 113.8 ($C{\equiv}C$), 20.9, 20.0, 16.1 ($\mathit{C}H_2\mathit{C}H_2\mathit{C}H_2$), −1.7 ($Si(\mathit{C}H_3)_2$). ^{29}Si NMR (CH_2Cl_2, 59.6 MHz): δ −10.7 ($Ph\mathit{Si}$), −15.0 ($\mathit{Si}(CH_3)_2$). IR (neat): ν_{Si-H} 2116 cm^{-1}. Mass spectrum (DEI, *m*/*z* (%)): 365 (30, $[C_{21}H_{29}Si_3]^+$), 283 (55, $[C_{17}H_{23}Si_2]^+$), 183 (100, $[C_{12}H_{11}Si]^+$). Mass spectrum (CI, NH_3, m/z (%)): 608 (10, $[M + 18]^+$), 366 (100, $[C_{21}H_{29}Si_3 + 1]^+$). Anal. Calcd for $C_{36}H_{46}Si_4$: C, 73.19; H, 7.85. Found: C, 73.40; H, 8.10.

$(Me_3Si{-}C{\equiv}C{-}SiMe_2(CH_2CH_2CH_2)SiPh_2(CH_2CH_2CH_2)Me_2Si{-}C)_2$ (18). Using methods similar to those detailed for the preparation of compound **12**, a freshly prepared sample of **17** (1.0 g, 1.7 mmol) and compound **1** (0.66 g, 3.4 mmol) were reacted at ambient temperature in the presence of Karstedt's catalyst for 2 h. The crude mixture was then subjected to flash chromatography on silica gel. Elution with cyclohexane/CH_2Cl_2 (4:1) gave **18** as a colorless, viscous oil (0.814 g, 0.85 mmol, 49%). ^1H NMR ($CDCl_3$, 200.13 MHz): δ 7.50 (m, 20H, aromatic), 1.66 (m, 8H, $CH_2C\mathit{H}_2CH_2$), 1.38 (m, 8H, $SiPh_2C\mathit{H}_2$), 0.86 (m, 8H, $SiMe_2C\mathit{H}_2$), 0.30 (s, 24H, $Si(C\mathit{H}_3)_2$), 0.28 (s, 18H, $Si(C\mathit{H}_3)_3$). ^{13}C NMR ($CDCl_3$, 75.03 MHz): δ 135.4, 134.9, 129.0, 127.7 (aromatic), 113.8, 113.2 ($C{\equiv}C$), 20.7 ($CH_2\mathit{C}H_2CH_2$), 18.3 ($SiPh_2\mathit{C}H_2$), 16.9 ($SiMe_2\mathit{C}H_2$), −0.02 ($Si(\mathit{C}H_3)_2$), −1.60 ($Si(\mathit{C}H_3)_3$). ^{29}Si NMR (CH_2Cl_2, 59.6 MHz): δ −16.9, −17.0, −17.9 (double the intensity of the other 2 peaks). Anal. Calcd for $C_{56}H_{86}Si_8$: C, 68.40; H, 8.82. Found: C, 68.63; H, 9.50.

$[SiPh_2(CH_2CH_2CH_2)Me_2SiC{\equiv}CSiMe_2(CH_2CH_2CH_2)]_n$ (19). Using methods detailed for the synthesis of **3**, compounds **13** (0.22 g, 1.0 mmol) and **2** (0.184 g, 1.0 mmol) were reacted at ambient temperature in the presence of Karstedt's catalyst for 2 h. Removal of the volatile organics yielded the oligomeric product, **19**, as a clear, highly viscous oil (0.40 g, 98%). ^1H NMR ($CDCl_3$, 200.13 MHz): δ 7.43 (m, 10H, aromatic), 1.59 (m, 4H, aliphatic), 1.24 (m, 4H, aliphatic), 0.70 (m, 4H, aliphatic), 0.11 (s, 12H, $Si(C\mathit{H}_3)$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 136.5, 135.6, 129.0, 127.7 (aromatic), 113.8 ($C{\equiv}C$), 20.7, 18.3, 16.9 (aliphatic), −1.07 ($Si(\mathit{C}H_3)$). ^{29}Si NMR (CH_2Cl_2, 59.6 MHz): δ −8.2, −18.6. $\bar{M}_w = 4200$, $\bar{M}_w/\bar{M}_n = 1.56$.

$-[Me_2SiCH_2CH_2CH_2SiC{\equiv}CSiMe_2CH_2CH_2CH_2SiMe_2(OSiMe_2)_n]_mO-$ (20). Using methods described for the synthesis of compound **3**, compounds **13** (0.11 g, 0.5 mmol) and **9** (8.75 g, 0.5 mmol) were reacted at ambient temperature in the presence of Karstedt's catalyst for 2 h. After removal of the volatile organics, the desired product **20** was isolated as a clear, highly viscous oil (8.78 g). ^1H NMR ($CDCl_3$, 200.13 MHz): δ 1.43 (m, 4H, aliphatic), 0.64 (m, 8H, aliphatic), 0.05 (br, s, ca. 9200 H, $SiCH_3$ from silicone). ^{13}C NMR ($CDCl_3$, 75.03 MHz): δ 22.4, 20.3, 17.7 (aliphatic), 1.0 ($Si\mathit{C}H_3$), −1.7 ($Si\mathit{C}H_3$ from silcone). ^{29}Si NMR (CH_2Cl_2, 59.6 MHz): δ −16.6, −17.7, − 20.4. $\bar{M}_w = 140\,000$. $\bar{M}_w/\bar{M}_n = 2.06$.

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Supporting Information Available: ^1H NMR and ^{13}C NMR spectra of compounds **5**, **6**, **8**, **10**, **12**, **19**, and **20** (14 pages). Ordering information is given on any current masthead page.

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