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Convenient Approach to Novel Organosilicon Polymers

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Reactions of α,ω-bis[[(trifluoromethyl)sulfonyl]oxy]–substituted organosilicon compounds with organic dilithio reagents (or the corresponding di-Grignard compounds) lead to the formation of new organosilicon polymers, which show a regular alternating arrangement of silylene or disilylene groups and ethynylene, diethynylene, or phenylene units in the polymer backbone. Conversions of the silyl triflates with hydroquinone or diphenylsilanediol afford various structured polysiloxanes. The required silyl triflates are prepared by protodesilylation of the corresponding phenyl- or aminosilanes with triflic acid.

Introduction

In recent years, much attention has been directed to silicon-containing polymers as sources of novel materials.[1,2] Numerous polymers have been prepared in which regular alternating arrangements of organosilicon groups and π-electron-containing units such as phenylene,[3] ethenylene,[4] ethynylene,[5] diethynylene,[6] thienylene,[7] dithienylene,[8] furylene,[9] butenyne-1,4-diyl,[10] and dipyridylene[11] are found in the polymer backbone. Such derivatives are of interest in order to explore the ability of a silicon atom to allow charge transport properties in a conjugated carbon backbone. Silyl or polysilyl groups are known to be involved in conjugation with unsaturated groups either through a $(d{-}p)_\pi$ overlap[12] or a $(\sigma^*{-}p)_\pi$-type interaction.[13] Therefore, the above polymer systems can be expected to be polymeric conductors.

It is well-known that the sodium condensation reaction of bis(chlorosilyl)-substituted compounds (Wurtz reaction) and the coupling reaction of dilithio derivatives of compounds bearing π-electron systems with dichlorosilanes or dichlorodisilanes offer a convenient route to various silicon-containing polymers. However, the polymers prepared by these methods always contain a small proportion of siloxy units in the polymer backbone, which would interrupt the electron delocalization.

Therefore, new synthetic routes to organosilicon polymers have been developed in which no alkali-metal halide condensations are involved.[5a,c,10,14] In this paper we report the synthesis of organosilicon polymers, based on silyl triflate derivatives, which is characterized by a high regioselectivity and excellent yields (>90%). Siloxy units are not found in the resulting polymers. On the other hand we show that silyl triflates are also versatile starting materials for special structured polysiloxanes, e.g. silarylene–siloxane copolymers, which are known to be materials with an optimum combination of mechanical properties and thermal stability.[15]

Results and Discussion

The highly reactive silyl triflates are valuable reagents in organosilicon chemistry.[16] The determination of the rate constants in reactions of ketones with silylating agents of the type R_3SiX gave the following sequence of the silylating potential:[17] $(X=)\ Cl < CH_3SO_3 < C_6H_5SO_3 < Me_3SiOSO_3 < CF_3CH_2SO_3 < Br < CF_3SO_3 \approx I$. Therefore, organolithium and organomagnesium compounds react rapidly with silyl triflates at low temperatures. Interest-

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ingly, it was found that no exchange processes analogous to metal–halogen exchange occur.[18] The very simple preparation of many silyl triflates is another important aspect.[19] Systematic investigations of the cleavage of the silicon–element bond (Si–E) by triflic acid (eqs 1 and 2)

$$R_3Si\text{-}E + CF_3SO_3H \rightarrow R_3SiOSO_2CF_3 + EH \quad (1)$$

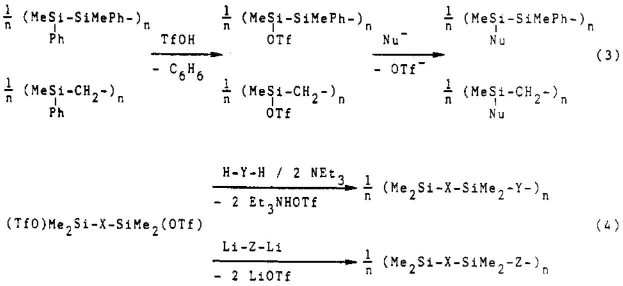
$$R_3Si\text{-}NEt_2 + 2CF_3SO_3H \rightarrow R_3SiOSO_2CF_3 + Et_2NH_2OSO_2CF_3 \quad (2)$$

have shown that the reaction rate decreases significantly in the sequence (E=) amino > allyl > α-naphthyl > phenyl > Cl > H, alkynyl > alkyl.[20,21] Particularly pure silyl triflates were obtained by protodesilylations of amino-, allyl-, or arylsilanes with CF_3SO_3H. These general results allow the synthesis of a large number of variously structured silyl triflates.

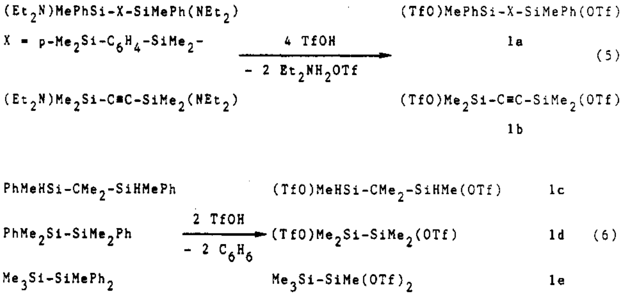
In principle two synthetic routes to new organosilicon polymers based on triflate derivatives are realizable. Firstly, derivatizations can be carried out on finished polymers. Recent papers by Matyjaszewski and by our group have shown the feasibility of this route.[22] The method is illustrated in eq 3 using as examples polysilanes and polycarbosilanes. We describe here the second synthetic route, which consists of formation of the polymer chains by condensation of bis[[(trifluoromethyl)sulfonyl]oxy]-substituted organosilicon compounds with dinucleophiles (eq 4).

One can prepare a large number of different bis[[[(trifluoromethyl)sulfonyl]oxy]silyl] compounds by relatively simple methods and consequently obtain the corresponding organosilicon polymers. Moreover, it is remarkable that bis[[[(trifluoromethyl)sulfonyl]oxy]silyl] derivatives are often easily formed, when the synthesis of the corresponding chloro- or bromosilanes is difficult or does not appear to have been attempted. Normally, the required silyl triflates are obtained from the corresponding phenyl derivatives, as is shown for the disilanes **1d** and **1e**[19a,b] and the disilylmethane **1c**[23] in eq 6. The 1,4-bis(disilyl)benzene **1a**[24] and the disilylethyne **1b**[25] were also prepared in high purity and yields, albeit only from aminosilyl compounds, as the protodesilylation of the corresponding phenylsilanes with CF_3SO_3H does not avoid the cleavage of the silyl–ethyne and the silyl–phenylene bond, respectively (eq 5). Moreover, the crude products of high purity are necessary, because the triflate derivatives often cannot be distilled without decomposition. Therefore, they should be used for the polycondensation without purification.

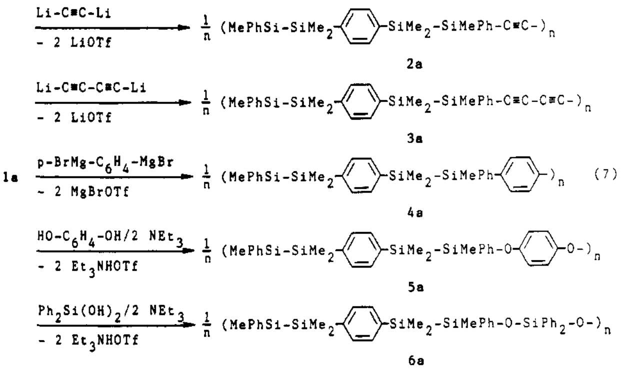
Scheme 1



Scheme 2



Scheme 3



We prepared numerous new organosilicon polymers using **1a–1e** as electrophilic starting materials. The dinucleophilic reactants were either organic or organometallic compounds. The reactions of **1a–1e** with 1,4-$BrMgC_6H_4MgBr$, Li_2C_2, Li_2C_4, p-HOC_6H_4OH, and $Ph_2Si(OH)_2$ illustrate the potential of this method. Cocondensations of the five dielectrophiles with the five dinucleophiles gave 25 different structured polymers. We could confirm their formation at low temperatures, in short reaction times, and with high yields. The syntheses of the silylphenylene copolymers **2a–6a** are shown in eq 7. The polymeric products obtained from **1b–1e**, by analogous reactions, and their ^{29}Si NMR chemical shifts are listed in Tables 1 and 2.

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Table 1. Polymer Products Prepared by the Reaction of 1b and 1c with Dinucleophiles and Their ^{29}Si NMR Data

	(TfO)Me$_2$Si—C≡C—SiMe$_2$(OTf) (**1b**)	(TfO)MeHSi—CMe$_2$—SiHMe(OTf) (**1c**)
Li—C≡C—Li	(Me$_2$Si—C≡C—SiMe$_2$—C≡C–)$_n$ (**2b**)	(MeHSi—CMe$_2$—SiHMe—C≡C–)$_n$ (**2c**)
δ, ppm (CDCl$_3$)	−37.3	−36.5
Li—C≡C—C≡C—Li	(Me$_2$Si—C≡C—SiMe$_2$—C≡C—C≡C–)$_n$ (**3b**)	(MeHSi—CMe$_2$—SiHMe—C≡C—C≡C–)$_n$ (**3c**)
δ, ppm (CDCl$_3$)	−38.6	−37.0
p-BrMg—C$_6$H–*MgBr*	(Me$_2$Si—C≡C—SiMe$_2$—C$_6$H$_4$–)$_n$ (**4b**)	(MeHSi—CMe$_2$—SiHMe—C$_6$H$_4$–)$_n$ (**4c**)
δ, ppm (CDCl$_3$)	−23.7	−21.9
p-HO—C$_6$H$_4$—OH	(Me$_2$Si—C≡C—SiMe$_2$—O—C$_6$H$_4$—O–)$_n$ (**5b**)	(MeHSi—CMe$_2$—SiHMe—O—C$_6$H–*O*–)$_n$ (**5c**)
δ, ppm (CDCl$_3$)	−4.9	−5.0
Ph$_2$Si(OH)$_2$	(Me$_2$Si—C≡C—SiMe$_2$—O—SiPh$_2$—O–)$_n$ (**6b**)	(MeHSi—CMe$_2$—SiHMe—O—SiPh$_2$—O–)$_n$ (**6c**)
δ, ppm (CDCl$_3$)	−9.4, −44.2	−11.6, −43.2

Table 2. Polymer Products Prepared by the Reaction of 1d and 1e with Dinucleophiles and Their ^{29}Si NMR Data

	(TfO)Me$_2$Si—SiMe$_2$(OTf) (**1d**)	Me$_3$Si—SiMe(OTf)$_2$ (**1e**)
Li—C≡C—Li	(Me$_2$Si—SiMe$_2$—C≡C–)$_n$ (**2d**)	[(Me$_3$Si)MeSi—C≡C–]$_n$ (**2e**)
δ, ppm (CDCl$_3$)	−38.6	−19.3, −57.1
Li—C≡C—C≡C—Li	(Me$_2$Si—SiMe$_2$—C≡C—C≡C–)$_n$ (**3d**)	[(Me$_3$Si)MeSi—C≡C—C≡C–]$_n$ (**3e**)
δ, ppm (CDCl$_3$)	−37.9	−20.1, −56.8
p-BrMg—C$_6$H$_4$—MgBr	(Me$_2$Si—SiMe$_2$—C$_6$H$_4$–)$_n$ (**4d**)	[(Me$_3$Si)MeSi—C$_6$H$_4$–]$_n$ (**4e**)
δ, ppm (CDCl$_3$)	−23.1	−19.4, −25.0
p-HO—C$_6$H$_4$—OH	(Me$_2$Si—SiMe$_2$—O—C$_6$H$_4$—O–)$_n$ (**5d**)	[(Me$_3$Si)MeSi—O—C$_6$H$_4$—O–]$_n$ (**5e**)
δ, ppm (CDCl$_3$)	−7.5	−21.0, −28.3
Ph$_2$Si(OH)$_2$	(Me$_2$Si—SiMe$_2$—O—SiPh$_2$—O–)$_n$ (**6d**)	[(Me$_3$Si)MeSi—O—SiPh$_2$—O–]$_n$ (**6e**)
δ, ppm (CDCl$_3$)	−12.5, −43.3	−18.9, −37.5, −44.1

The structural characterization of **2a–6e** was mainly based on NMR spectroscopy. ^{29}Si NMR chemical shifts are particularly useful for structural characterization. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra of all compounds are consistent with the proposed structures of the polymer chains. As expected, one observes the broad signals, which are typical for organosilicon polymers. However, the half-band widths of the ^{29}Si NMR signals, 1.5–3.0 ppm, are much narower than those in the case of the polysilanes and polycarbosilanes prepared by Wurtz reactions.[22a,26] The narrower signals of **2a–6e** indicate the regular alternating arrangements in the polymer backbones resulting from the fact that the condensation reactions are not accompanied by exchange processes. The ^{13}C NMR data also support this view. Thus, only isolated ethynyl groups are detectable in the spectra of **2a** and **2c–2e**. Diethynyl units –C≡C—C≡C–, which are produced in variable yields (5–20%) by the reaction of Li$_2$C$_2$ with dihalogenosilanes, are not observed.

Weight-average molecular weights in the range M_w = 2000–7000, relative to polystyrene standards, were found by size exclusion chromatography (SEC). They correspond to polymerization degrees of n = 10–25. The polydispersities (M_w/M_n) were found in the range 1.4–2.0 and are consistent with purely linear structures for all polymers described. The molecular weights were determined by the reaction conditions. Higher values of M_w were obtained using relatively more concentrated solutions of the reactants and short reaction times. However, molecular weights can also fall below 2000 when diluted solutions are needed. Other changes such as the use of different solvents and reaction temperatures are being currently investigated. Thus, molecular weights reported in the Experimental Section are those found under the conditions specified there. Normally, the polymers are yellow-brown solids when molecular weights exceed values of about 4000. Defined melting points are not observed. The solids become highly viscous fluids, with contraction of volume, at temperatures between 70 and 200 °C. These conversions occur within temperature intervals of about 20 deg. Polymers **5a–6e**, which contain siloxy groups, in some cases form highly viscous oils. They change to thin liquids at high temperatures. They are not decomposed at temperatures to 250 °C. All polymers are soluble in the usual organic solvents such as benzene, chloroform, and THF. Further work will be directed to investigations of the physical properties (thermal behavior, conductivity) of the new polymers.

Conclusions

Obviously, the polymer syntheses described here are too expensive for technical applications. However, the essential advantage of the method consists of the possibility of synthesizing, with relatively little effort, small amounts of numerous differently structured organosilicon polymers for investigations in material science. In the future we are interested in the question whether other "superelectrophiles" such as the cheaper fluorosulfonates are also useful starting materials for organosilicon polymers.

Experimental Section

All reactions were carried out under nitrogen or argon using Schlenk tubes. Solvents were dried and distilled before use. The dichlorosilanes used were obtained from Wacker. Diphenylsilanediol was purchased from Fluka; trifluoromethanesulfonic acid, from Merck. The strongly hygroscopic triflic acid must be distilled before use and should subsequently be kept under nitrogen. Detailed information about its purification is included in ref 16. It must be emphasized that traces of moisture in CF$_3$SO$_3$H always lead to the formation of undesirable siloxanes. The following derivatives were prepared by published methods: 1,2-dilithioethyne,[5d] 1,4-dilithiobutadiyne,[6b] 1,4-bis(bromomagnesio)benzene,[27] 1,4-bis[[(diethylamino)methylphenylsilyl]dimethylsilyl]benzene,[24] 1,2-bis[(diethylamino)dimethylsilyl]ethyne,[25a,b] 2,2-bis(methylphenylsilyl)propane,[23,28] 2,2-diphenyl-1,1,2,2-tetramethyldisilane,[29a] 1,1-diphenyl-1,2,2,2-tetramethyldisilane.[29b]

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The ^{1}H NMR spectra were obtained on a Bruker AC-80 instrument, and the ^{13}C and ^{29}Si NMR spectra, on a Bruker WP-200 spectrometer; the chemical shifts are relative to tetramethylsilane. The ^{29}Si NMR chemical shifts of triflate-substituted silicon atoms and the ^{13}C NMR chemical shifts of neighboring carbon atoms are concentration dependent over a range of 5 ppm. The molecular weights of the monomers were verified by the M^{+} peaks of mass spectra (Varian CH 7 A). The molecular weights of polymers were obtained by SEC, using a Knauer HPLC instrument (toluene, 1 mL/min, 25 °C, relative to a polystyrene standard).

Synthesis of the Silyl Triflate Derivatives 1a–e. 1,4-Bis[[[[(trifluoromethyl)sulfonyl]oxy]methylphenylsilyl]dimethylsilyl]benzene (1a). A solution of triflic acid (1.5 g, 0.01 mol), in 20 mL of diethyl ether, was added to 1,4-bis[[[(diethylamino)methyl]phenyl]dimethylsilyl]benzene (1.45 g, 0.0025 mol) in 100 mL of diethyl ether at 0 °C. The mixture was stirred at room temperature for 2 h. The ammonium triflate precipitated as a white solid and was filtered off. The solvent was removed under vacuum to give **1a** (1.75 g, 96%) as a colorless liquid. The purity was controlled by NMR spectroscopy. **1a** was used without further treatment for subsequent reactions. **1a** contains two asymmetric silicon atoms. Therefore, three stereoisomers were produced. The D and L forms are enantiomeric, while the meso form is diastereomeric to the others. Therefore, all NMR signals are doubled. The product is the mixture of the racemate and the meso form in a 1:1 ratio, as indicated by integrals of ^{1}H NMR spectra. ^{1}H NMR (CDCl$_3$; δ, ppm): 0.35/0.38 (s, 12H, Me$_2$Si), 0.59/0.63 (s, 6H, MeSi), 6.91–7.85 (m, 14H, Ph). ^{13}C NMR (CDCl$_3$; δ, ppm): −2.98/−2.17 (Me$_2$Si), 5.67/6.23 (MeSiOTf), 117.45/118.62 (q, CF$_3$), 127.0–140.5 (Ph). ^{29}Si NMR (CDCl$_3$; δ, ppm): −23.6/−22.6 (Me$_2$Si), 25.3/26.8 (MeSiOTf).

1,2-Bis[[[(trifluoromethyl)sulfonyl]oxy]dimethylsilyl]ethyne (1b). The procedure described for **1a** was used, using 3.00 g (0.02 mol) of CF$_3$SO$_3$H and 1.42 g (0.005 mol) of 1,2-bis[(diethylamino)dimethylsilyl]ethyne; 2.12 g (97%) of **1b** was obtained. ^{1}H NMR (CDCl$_3$; δ, ppm): 0.38 (s, MeSi). ^{13}C NMR (CDCl$_3$; δ, ppm): 4.26 (MeSi), 111.84 ($C\equiv C$), 118.59 (q, J_{CF} = 314 Hz, CF$_3$). ^{29}Si NMR (CDCl$_3$; δ, ppm): 24.1. Mass spectrum (*m/e* (relative intensity)): 289 (M^{+} − CF$_3$SO$_3$, 11), 73 (Me$_3$Si^{+}, 100). Anal. Calcd for $C_8H_{12}F_6O_6S_2Si_2$ (438.3): C, 21.92; H, 2.74. Found: C, 21.55; H, 2.54.

2,2-Bis[[[(trifluoromethyl)sulfonyl]oxy]methylsilyl]propane (1c). A solution of CF$_3$SO$_3$H (2.90 g, 0.0195 mol) in 50 mL of diethyl ether was added to 2,2-bis(methylphenylsilyl)propane (2.84 g, 0.01 mol) in 250 mL of diethyl ether at 0 °C. The reaction mixture was stirred for 2 h. The solvent and the benzene formed were removed to give 4.07 g (95%) of **1c** as a colorless liquid. Its purity was controlled by NMR spectroscopy. **1c** can be distilled under reduced pessure, but purification is not necessary for further use. Distillation gave **1c**: 2.40 g, 56% yield (racemic mixture of two diastereomers). Bp$_{0.9}$: 88–91 °C. ^{1}H NMR (CDCl$_3$; δ, ppm): 0.35/0.37 (d, 6H, MeSi), 1.16/1.19 (s, 6H, CH$_3$C), 5.05/5.11 (m, 2H, SiH). ^{13}C NMR (CDCl$_3$; δ, ppm): 6.45/7.23 (MeSi), 28.09/29.87 (*C*H$_3$C), 35.54/37.02 (CH$_3$*C*), 117.94/118.56 (q, J_{CF} = 312 Hz/313 Hz, CF$_3$). ^{29}Si NMR (CDCl$_3$; δ, ppm): 24.5/25.7. Mass spectrum (*m/e*): 279 (M^{+} − CF$_3$SO$_3$, 17), 101 (Me$_2$PrSi^{+}, 100). Anal. Calcd for $C_7H_{14}O_6F_6S_2Si_2$ (428.3): C, 19.63; H, 3.27. Found: C, 19.97; H, 3.06.

1,2-Bis[[(trifluoromethyl)sulfonyl]oxy]-1,1,2,2-tetramethyldisilane (1d). The procedure described for **1c** was used, using 3.00 g (0.02 mol) of triflic acid and 2.70 g (0.01 mol) of 1,2-diphenyl-1,1,2,2-tetramethyldilsilane; 4.04 g (97%) of **1d** was obtained before distillation, 2.62 g (63%) after distillation (see ref 20d). Bp$_8$: 94–96 °C. ^{1}H NMR (CDCl$_3$; δ, ppm): 0.70 (s, MeSi). ^{13}C NMR (CDCl$_3$; δ, ppm): −0.35 (MeSi), 118.75 (q, J_{CF} = 314 Hz, CF$_3$). ^{29}Si NMR (CDCl$_3$; δ, ppm): 38.9. Mass spectrum (*m/e*): 416 (M^{+}, 24), 73 (Me$_3$Si^{+}, 100). Anal. Calcd for $C_6H_{12}F_6O_6S_2Si_2$ (416.3): C, 17.31; H, 2.88. Found: C, 17.21; H, 2.70.

1,1-Bis[[(trifluoromethyl)sulfonyl]oxy]-1,2,2,2-tetramethyldisilane (1e). The same procedure as for **1c** was used, with 3.00 g (0.02 mol) of triflic acid and 2.70 g (0.01 mol) of 1,1-diphenyl-1,2,2,2-tetramethyldisilane; 3.86 g (93%) of **1e** was obtained before and 2.45 g (59%) after distillation. Bp$_5$: 89–91 °C. ^{1}H NMR (CDCl$_3$; δ, ppm): 0.26 (s, 9H, Me$_3$i), 0.81 (s, 3H, MeSi). ^{13}C NMR (CDCl$_3$; δ, ppm): −3.35 (Me$_3$Si), 4.14 (MeSi), 118.86 (q, J_{CF} = 313 Hz, CF$_3$). ^{29}Si NMR (CDCl$_3$; δ, ppm): −17.9 (Me$_3$Si), 1.4 (MeSi). Mass spectrum (*m/e*): 416 (M^{+}, 3), 73 (Me$_3$Si^{+}, 100). Anal. Calcd for $C_6H_{12}F_6O_6S_2Si_2$ (416.3): C, 17.31; H, 2.88. Found: C, 17.45; H, 3.07.

Synthesis of the Organosilicon Polymers (2a–6e). General Procedures. A (2a–4e): The silyl triflate (**1a**–**1e**) (0.01 mol) dissolved in 50 mL of diethyl ether was added to a slurry, or solution, of the corresponding lithium or magnesium organic compound (0.01 mol), in 100 mL of a 1:1 mixture THF/diethyl ether, at 0 °C within 5 min. The reaction mixture was stirred at room temperature for 2 h. The solvent was removed under reduced pressure and replaced by 150 mL of toluene. Lithium or magnesium triflate precipitated as a white solid and was filtered off. Toluene was removed under vacuum leaving yellow-brown powders in high yields.

B (5a–6e). A solution of the silyl triflate (**1a**–**1e**) (0.01 mol) in 50 mL of diethyl ether was added to a mixture of hydroquinone or diphenylsilanediol (0.01 mol) and triethylamine (0.022 mol) dissolved in 100 mL of diethyl ether at 0 °C. Triethylammonium triflate precipitated quantitatively as a light-yellow oil and was separated. Removal of the diethyl ether under reduced pressure left the product as a yellow-brown powder or yellow high viscous oil in high yield.

Poly[[[[[(methylphenylsilyl)dimethylsilyl]phenyl]dimethylsilyl]methylphenylsilyl]acetylene] (2a). Method A was used and gave 4.37 g (97%) of a yellow powder. Mp: 180–200 °C. ^{1}H NMR (CDCl$_3$; δ, ppm): 0.21–0.34 (18H, Me$_2$Si, MePhSi), 7.0–7.8 (14H, Ph). ^{13}C NMR (CDCl$_3$; δ, ppm): −1.25 to +1.65 (Me$_2$Si, MePhSi), 112.10 ($C\equiv C$), 128.9, 129.5, 133.8, 134.6, 139.5, 140.7 (Ph). ^{29}Si NMR (CDCl$_3$; δ, ppm): −37.1 (MePhSi), −22.8 (Me$_2$Si). IR, $\nu(C\equiv C)$: 2143 cm^{-1}. M_w = 6550. M_w/M_n = 1.45. Anal. Calcd for $(C_{26}H_{32}Si_4)_n$ (456.6): C, 68.39; H, 7.01. Found: C, 67.99; H, 6.70.

Poly[[[[[(methylphenylsilyl)dimethylsilyl]phenyl]dimethylsilyl]methylphenylsilyl]diacetylene] (3a). Method A was used and gave the title compound (4.46 g; 93%) as a yellow-brown powder. Mp: 170–185 °C. ^{1}H NMR (CDCl$_3$; δ, ppm): 0.28–0.46 (18H, Me$_2$Si, MePhSi), 7.0–7.8 (14H, Ph). ^{13}C NMR (CDCl$_3$; δ, ppm): −2.35 to +0.13 (Me$_2$Si, MePhSi), 82.54 ($SiC\equiv C$), 89.55 ($SiC\equiv C$), 127.5, 128.6, 133.0, 134.7, 138.5, 140.7 (Ph). ^{29}Si NMR (CDCl$_3$; δ, ppm): −38.5 (MePhSi), −21.0 (Me$_2$Si). IR, $\nu(C\equiv C)$: 2075 cm^{-1}. M_w = 5470. M_w/M_n = 1.76. Anal. Calcd for $(C_{28}H_{32}Si_4)_n$ (480.6): C, 69.97; H, 6.66. Found: C, 69.45; H, 6.40.

Poly[(1-phenyl-1,2,2-trimethyldisilanylene)phenylene] (4a). Method A was used and gave 4.56 g (90%) of a yellow powder. Mp: >210 °C dec. ^{1}H NMR (CDCl$_3$; δ, ppm): 0.30–0.64 (18H, Me$_2$Si, MePhSi), 7.02–7.89 (18H, Ph). ^{13}C NMR (CDCl$_3$; δ, ppm): −3.05 to −0.25 (Me$_2$Si, MePhSi), 126.5–140.5 (Ph). ^{29}Si NMR (CDCl$_3$; δ, ppm): −23.6 (MePhSi), −20.5 (Me$_2$Si). M_w = 6200. M_w/M_n = 1.80. Anal. Calcd for $(C_{30}H_{36}Si_4)_n$ (508.6): C, 70.84; H, 7.08. Found: C, 71.22; H, 7.30.

Poly[[[[[(methylphenylsilyl)dimethylsilyl]phenyl]dimethylsilyl]methylphenylsilyl]-1,4-benzenediolate] (5a). Method B was used and gave 4.97 g (92%) of a brown powder. Mp: >250 °C dec. ^{1}H NMR (CDCl$_3$; δ, ppm): 0.28 (12H, Me$_2$Si), 0.57 (6H, MePhSi), 6.95–7.97 (18H, Ph). ^{13}C NMR (CDCl$_3$; δ, ppm): −2.10 to +1.45 (Me$_2$Si, MePhSi), 121.57, 152.05 (PhO), 127.8–141.1 (PhSi). ^{29}Si NMR (CDCl$_3$; δ, ppm): −22.0 (Me$_2$Si), −5.1 (MePhSi). M_w = 5950. M_w/M_n = 1.56. Anal. Calcd for $(C_{30}H_{36}O_2Si_4)_n$ (540.6): C, 66.65; H, 6.66. Found: C, 66.26; H, 6.40.

Poly[[[[[(methylphenylsilyl)dimethylsilyl]phenyl]dimethylsilyl]methylphenylsilyl]diphenylsilanediolate] (6a). Method B was used and gave 6.08 g (94%) of a yellow, high viscous oil. ^{1}H NMR (CDCl$_3$; δ, ppm): 0.27 (12H, Me$_2$Si), 0.56 (6H, MePhSi). ^{13}C NMR (CDCl$_3$; δ, ppm): −3.80 to −0.05 (Me$_2$-

Si, MePhSi); 127.0–139.1 (Ph). ^{29}Si NMR (CDCl$_3$; δ, ppm): −42.9 (D^{Ph}2), −22.5 (Me$_2$Si), −15.9 (MePhSi). M_w = 5990. M_w/M_n = 1.40. Anal. Calcd for $(C_{36}H_{42}O_2Si_5)_n$ (646.8): C, 66.85; H, 6.49. Found: C, 66.50; H, 6.68.

Poly[(dimethylsilylene)ethynylene] (2b). Method A was used and gave 1.60 g (98%) of a yellow solid. See Table 1 for ^{29}Si NMR. See also ref 5d. Mp: 135–150 °C. ^{1}H NMR (CDCl$_3$; δ, ppm): 0.29 (Me$_2$Si). ^{13}C NMR (CDCl$_3$; δ, ppm): 1.55 (Me$_2$Si), 112.77 (C≡C). IR, ν(C≡C): 2046 cm^{-1}. M_w = 5450. M_w/M_e = 1.65. Anal. Calcd for $(C_4H_6Si)_n$ (82.1): C, 58.50; H, 7.31. Found: C, 58.17; H, 7.07.

Poly[(dimethylsilylene)ethynylene(dimethylsilylene)diethynylene] (3b). Method A was used and gave 1.78 g (95%) of a yellow-brown solid. See Table 1 for ^{29}Si NMR. Mp: 145–165 °C. ^{1}H NMR (CDCl$_3$; δ, ppm): 0.33 (Me$_2$Si). ^{13}C NMR (CDCl$_3$; δ, ppm): −0.30 (Me$_2$Si), 81.59 (Si*C*≡C), 88.40 (SiC≡*C*), 111.95 (C≡C). IR, ν(C≡C): 2076, 2048 cm^{-1}. M_w = 3890. M_w/M_n = 1.87. Anal. Calcd for $(C_{10}H_{12}Si_2)_n$ (188.3): C, 63.79; H, 6.37. Found: C, 63.38; H, 6.12.

Poly[(dimethylsilylene)ethynylene(dimethylsilylene)phenylene] (4b). Method A was used and gave 1.92 g (89%) of a yellow-brown powder. See Table 1 for ^{29}Si NMR. Mp: 155–165 °C. ^{1}H NMR (CDCl$_3$; δ, ppm): 0.31 (12H, Me$_2$Si), 7.29 (4H, Ph). ^{13}C NMR (CDCl$_3$; δ, ppm): −2.50 (Me$_2$Si), 112.15 (C=C), 133.05 (*o*-Ph), 137.64 (*ipso*-Ph). M_w = 5140. M_w/M_n = 1.78. Anal. Calcd for $(C_{12}H_{16}Si_2)_n$ (216.3): C, 66.64; H, 7.40. Found: C, 65.96; H, 7.68.

Poly[[[(dimethylsilyl)ethynyl]dimethylsilyl]-1,4-benzenediolate] (5b). Method B was used and gave 2.25 g (91%) of a yellow, viscous oil. See Table 1 for ^{29}Si NMR. ^{1}H NMR (CDCl$_3$; δ, ppm): 0.27 (12H, Me$_2$Si), 6.88 (4H, Ph). ^{13}C NMR (CDCl$_3$; δ, ppm): 0.65 (Me$_2$Si), 113.03 (C≡C), 122.12, 151.84 (Ph). M_w = 5400. M_w/M_n = 1.46. Anal. Calcd for $(C_{12}H_{16}O_2Si_2)_n$ (248.28): C, 58.05; H, 6.44. Found: C, 57.67; H, 6.31.

Poly[[[(dimethylsilyl)ethynyl]dimethylsilyl]diphenylsilanediolate] (6b). Method B was used and gave 3.40 g (96%) of a yellow solid. See Table 1 for ^{29}Si NMR. Mp: 85–105 °C. ^{1}H NMR (CDCl$_3$; δ, ppm): 0.12 (Me$_2$Si), 7.05–7.49 (Ph). ^{13}C NMR (CDCl$_3$; δ, ppm): 2.85 (Me$_2$Si), 111.92 (C≡C) 126.95, 129.34, 134.08, 139.89 (Ph). M_w = 2370. M_w/M_n = 1.39. Anal. Calcd for $(C_{18}H_{22}O_2Si_3)_n$ (354.4): C, 61.00; H, 6.21. Found: C, 60.51; H, 5.88.

Poly[(methylsilylene-*co*-dimethylmethylene)methylsilylene-*co*-ethynylene] (2c). Method A was used and gave 1.50 g (97%) of a yellow-brown solid. See Table 1 for ^{29}Si NMR. Mp: 115–130 °C. ^{1}H NMR (CDCl$_3$; δ, ppm): 0.09 (6H, MeSi), 1.09 (6H, CH$_3$C), 4.35 (2H, SiH). ^{13}C NMR (CDCl$_3$; δ, ppm): −0.64 (MeSi), 25.65 (*C*H$_3$C), 29.61 (CH$_3$*C*), 111.60 (C≡C). M_w = 4200. M_w/M_n = 1.59. Anal. Calcd for $(C_7H_{14}Si_2)_n$ (154.2): C, 54.51; H, 9.08. Found: C, 54.27; H, 8.87.

Poly[(methylsilylene-*co*-dimethylmethylene)methylsilylene-*co*-diethynylene] (3c). Method A was used and gave 1.62 g (91%) of a beige powder. See Table 1 for ^{29}Si NMR. Mp: 135–150 °C. ^{1}H NMR (CDCl$_3$; δ, ppm): 0.13 (6H, MeSi), 1.12 (6H, CH$_3$C), 4.28 (2H, SiH). ^{13}C NMR (CDCl$_3$; δ, ppm): −1.36 (MeSi), 27.13 (*C*H$_3$C), 30.76 (CH$_3$*C*), 80.11 (Si*C*≡C), 89.90 (SiC≡*C*). M_w = 3460. M_w/M_n = 1.49. Anal. Calcd for $(C_9H_{14}Si_2)_n$ (178.3): C, 60.64; H, 7.85. Found: C, 60.19; H, 7.61.

Poly[(methylsilylene-*co*-dimethylmethylene)methylsilylene-*cophenylene*] (4c). Method B was used and gave 1.83 g (89%) of a yellow-brown solid. See Table 1 for ^{29}Si NMR. Mp: 165–180 °C. ^{1}H NMR (CDCl$_3$; δ, ppm): 0.33 (6H, MeSi), 1.15 (6H, CH$_3$C), 4.59 (2H, SiH), 7.31 (4H, Ph). ^{13}C NM (CDCl$_3$; δ, ppm): −1.35 (MeSi), 26.96 (*C*H$_3$C), 31.29 (CH$_3$*C*), 132.54 (*o*-Ph), 138.34 (*ipso*-Ph). M_w = 4650. M_w/M_n = 1.62. Anal. Calcd for $(C_{11}H_{18}Si_2)_n$ (206.27): C, 64.05; H, 8.73. Found: C, 63.79; H, 8.55.

Poly[[[(methylsilyl)dimethylmethyl]methylsilyl]-1,4-benzenediolate] (5c). Method B was used and gave 2.28 g (96%) of a yellow, viscous oil. See Table 1 for ^{29}Si NMR. ^{1}H NMR (CDCl$_3$; δ, ppm): 0.23 (6H, MeSi), 1.10 (6H, CH$_3$C), 4.44 (2H, SiH), 6.93 (4H, Ph). ^{13}C NMR (CDCl$_3$; δ, ppm): 1.78 (MeSi) 28.78 (*C*H$_3$C), 31.09 (CH$_3$*C*), 122.05, 149.67 (Ph). M_w = 3120. M_w/M_n = 1.57. Anal. Calcd for $(C_{11}H_{18}O_2Si_2)_n$ (238.3): C, 55.45; H, 7.55. Found: C, 55.89; H, 7.67.

Poly[[[(methylsilyl)dimethylmethyl]methylsilyl]diphenylsilanediolate] (6c). Method B was used and gave 3.30 g (96%) of a yellow, high viscous oil. See Table 1 for ^{29}Si NMR. ^{1}H NMR (CDCl$_3$; δ, ppm): 0.11 (6H, MeSi), 1.09 (6H, CH$_3$C), 4.34 (2H, SiH), 6.98–7.52 (10H, Ph). ^{13}C NMR (CDCl$_3$; δ, ppm): 1.69 (MeSi), 24.63 (*C*H$_3$C), 29.95 (CH$_3$*C*), 127.34, 130.01, 134.44, 139.58 (Ph). M_w = 3900. M_w/M_n = 1.99. Anal. Calcd for $(C_{17}H_{24}O_2Si_3)_n$ (344.4): C, 59.28; H, 6.97. Found: C, 58.99; H, 6.71.

Poly[(tetramethyldisilanylene)ethynylene] (2d). Method A was used and gave 1.29 g (92%) of a light yellow solid. See Table 2 for ^{29}Si NMR. See also ref 5d. Mp: 100–110 °C. ^{1}H NMR (CDCl$_3$; δ, ppm): 0.24 (Me$_2$Si). ^{13}C NMR (CDCl$_3$; δ, ppm): −2.65 (Me$_2$Si), 113.80 (C≡C). IR, ν(C≡C): 2041 cm^{-1}. M_w = 4100. M_w/M_n = 1.68. Anal. Calcd for $(C_6H_{12}Si_2)_n$ (140.2): C, 51.39; H, 8.56. Found: C, 50.99; H, 8.49.

Poly[(tetramethyldisilanylene)diethynylene] (3d). Method A was used and gave 1.52 g (93%) of a beige solid. See Table 2 for ^{29}Si NMR. See also ref 6b. Mp: 120–135 °C. ^{1}H NMR (CDCl$_3$; δ, ppm): 0.28 (Me$_2$Si). ^{13}C NMR (CDCl$_3$; δ, ppm): −3.44 (Me$_2$Si), 83.94 (Si*C*≡C), 91.90 (SiC≡*C*). IR, ν(C≡C): 2065 cm^{-1}. M_w = 5250. M_w/M_n = 2.02. Anal. Calcd for $(C_8H_{12}Si_2)_n$ (164.2): C, 58.50; H, 7.31. Found: C, 58.24; H, 7.07.

Poly[(tetramethyldisilanylene)phenylene] (4d). Method A was used and gave 1.84 g (96%) of a yellow powder. See Table 2 for ^{29}Si NMR. See also ref 30. Mp: 125–140 °C. ^{1}H NMR (CDCl$_3$; δ, ppm): 0.39 (12H, Me$_2$Si), 7.34 (4H, Ph). ^{13}C NMR (CDCl$_3$; δ, ppm): −2.80 (Me$_2$Si), 133.65 (*o*-Ph), 138.99 (*ipso*-Ph). M_w = 6850. M_w/M_n = 1.95. Anal. Calcd for $(C_{10}H_{16}Si_2)_n$ (192.2): C, 62.47; H, 8.32. Found: C, 62.11; H, 8.50.

Poly[(tetramethyldisilanyl)-1,4-benzenediolate] (5d). Method B was used and gave 2.10 g (94%) of a white solid. See Table 2 for ^{29}Si NMR. Mp: 110–125 °C. ^{1}H NMR (CDCl$_3$; δ, ppm): 0.11 (12H, Me$_2$Si), 6.83 (4H, Ph). ^{13}C NMR (CDCl$_3$; δ, ppm): −0.09 (Me$_2$Si), 120.87, 151.32 (Ph). M_w = 5800. M_w/M_n = 1.55. Anal. Calcd for $(C_{10}H_{16}O_2Si_2)_n$ (224.3): C, 53.55; H, 7.13. Found: C, 53.21; H, 6.90.

Poly[(tetramethyldisilanyl)diphenylsilanediolate] (6d). Method B was used and gave 3.26 g (99%) of a colorless, high viscous oil. See Table 2 for ^{29}Si NMR. ^{1}H NMR (CDCl$_3$; δ, ppm): 0.09 (12H, Me$_2$Si), 7.01–7.56 (10H, Ph). ^{13}C NMR (CDCl$_3$; δ, ppm): −0.80 (Me$_2$Si), 128.00, 129.78, 135.43, 138.89 (Ph). M_w = 2850. M_w/M_n = 1.38. Anal. Calcd for $(C_{16}H_{22}O_2Si_3)_n$ (330.4): C, 58.15; H, 6.66. Found: C, 58.65; H, 6.92.

Poly[(methyl(trimethylsilyl)silylene)ethynylene] (2e). Method A was used and gave 1.30 g (93%) of a yellow-brown powder. See Table 2 for ^{29}Si NMR. Mp: 80–95 °C. ^{1}H NMR (CDCl$_3$; δ, ppm): −0.04 (9H, Me$_3$Si), 0.14 (3H, MeSi). ^{13}C NMR (CDCl$_3$; δ, ppm): −2.05 (Me$_3$Si), 1.13 (MeSi), 113.06 (C≡C). IR, ν(C≡C): 2046 cm^{-1}. M_w = 2750. M_w/M_n = 1.34. Anal. Calcd for $(C_6H_{12}Si_2)_n$ (140.2): C, 51.39; H, 8.56. Found: C, 51.67; H, 8.87.

Poly[(methyl(trimethylsilyl)silylene)diethynylene] (3e). Method A was used and gave 1.44 g (88%) of a beige solid. See Table 2 for ^{29}Si NMR. Mp: 75–85 °C. ^{1}H NMR (CDCl$_3$; δ, ppm): −0.06 (9H, Me$_3$Si), 0.17 (3H, MeSi). ^{13}C NMR (CDCl$_3$; δ, ppm): −2.85 (Me$_3$Si), 0.54 (MeSi), 79.98 (Si*C*≡C), 91.76 (SiC≡*C*). IR, ν(C=C): 2072 cm^{-1}. M_w = 2120. M_w/M_n = 1.60. Anal. Calcd for $(C_8H_{12}Si_2)_n$ (164.2): C, 58.50; H, 7.31. Found: C, 58.68; H, 7.52.

Poly[(methyl(trimethylsilyl)silylene)phenylene] (4e). Method A was used and gave 1.74 g (91%) of a yellow solid. See Table 2 for ^{29}Si NMR. Mp: 95–110 °C. ^{1}H NMR (CDCl$_3$; δ, ppm): −0.02 (9H, Me$_3$Si), 0.36 (3H, MeSi), 7.36 (4H, Ph). ^{13}C NMR (CDCl$_3$; δ, ppm): −3.55 (Me$_3$Si), 0.98 (MeSi), 133.67, 138.55

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(Ph). $M_w = 3500$. $M_w/M_n = 1.49$. Anal. Calcd for $(C_{10}H_{16}Si_2)_n$ (192.2): C, 62.47; H, 8.32. Found: C, 62.36; H, 8.01.

Poly[[methyl(trimethylsilyl)silyl]-1,4-benzenediolate] (5e). Method B was used and gave 2.20 g (98%) of a light yellow oil. See Table 2 for ^{29}Si NMR. ^{1}H NMR ($CDCl_3$; δ, ppm): −0.01 (9H, Me_3Si), 0.21 (3H, MeSi), 6.88 (4H, pH). ^{13}C NMR ($CDCl_3$; δ, ppm): −1.98 (Me_3Si), 2.00 (MeSi), 119.67, 150.55 (Ph). $M_w = 4500$. $M_w/M_n = 183$. Anal. Calcd for $(C_{10}H_{16}O_2Si_2)_n$ (224.3): C, 53.55; H, 7.13. Found: C, 53.87; H, 7.30.

Poly[[methyl(trimethylsilyl)silyl]diphenylsilanediolate] (6e). Method B was used and gave 3.20 g (97%) of a colorless oil. See Table 2 for ^{29}Si NMR. ^{1}H NMR ($CDCl_3$; δ, ppm): 0.01 (9H, Me_3Si), 0.17 (3H, MeSi), 6.99–7.61 (10H, Ph). ^{13}C NMR ($CDCl_3$; δ, ppm): −2.89 (Me_3Si), 0.05 (MeSi), 127.10, 129.09, 134.89, 139.90 (Ph). $M_w = 2370$. $M_w/M_n = 1.41$. Anal. Calcd for $(C_{16}H_{22}O_2Si_3)_n$ (330.4): C, 58.16; H, 6.66. Found: C, 57.77; H, 6.30.

All reported NMR chemical shifts are mean values of the broadened signals (signal breadth in ^{29}Si and ^{13}NMR spectra, 1.5–3.0 ppm; in ^{1}H NMR spectra, 0.1–0.2 ppm).

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