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Dehydropolymerization of Bis- and Tris(silyl)arenes to Highly Cross-Linked Disilanylenearylene Polymers, Catalyzed by $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)ZrH_2]_2$

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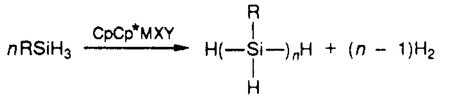
Introduction

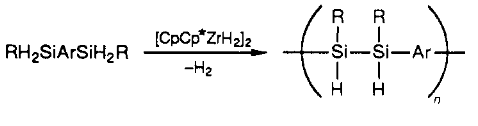
Recent research has addressed the synthesis of polysilanes[1] and other silicon-containing polymers[2] having unusual optical and electronic properties. While interest in polysilanes has dramatically increased over the last 10 years, there has been comparatively less attention given to other silicon-containing polymers that might have similar properties. Polymers containing both silylene and unsaturated hydrocarbon fragments in the backbone are particularly interesting in this respect. A few polymers of this general type have been synthesized, primarily via Wurtz coupling methods.[2b,i–m,o,p] In some cases the electronic spectra suggest extensive σ–π delocalization in the polymer backbone,[2d,j–m,3] and oxidative doping has been reported to give conductive or semiconductive materials.[2a–c,e,f,i]

We have previously described mechanistic details for Zr- and Hf-catalyzed dehydrocoupling reactions of hydrosilanes (eq 1; Cp = η^5-C_5H_5, Cp* = η^5-C_5Me_5; M = Zr, Hf; X = Y = H; X = silyl, Y = silyl, alkyl, or halide) which have characterized these reactions as metal-mediated condensation polymerizations.[4] These dehydrocoupling reactions, originally described by Harrod and co-workers,[5] represent an important new method for forming Si–Si bonds and generating Si-containing polymers. Generally, however, this method has produced polymers of only modest chain lengths (generally ≤ ca. 50 silicon atoms).


$$n\text{RSiH}_3 \xrightarrow{\text{CpCp*MXY}} \text{H}(\text{—}\overset{\text{R}}{\underset{\text{H}}{\text{Si}}}\text{—})_n\text{H} + (n-1)\text{H}_2 \qquad (1)$$

Given the step-growth nature of these polymerizations, it seemed that higher molecular weights might be obtained through incorporation of two or more hydrosilyl functionalities into the monomer, since then reaction of only one Si–H group per silicon center would be required for chain growth. Furthermore, reaction of more than one Si–H group per silicon center (as in eq 1) would lead to the cross-linking of chains and increased molecular weights.

Here we report the application of this synthetic method to the synthesis of high molecular weight, cross-linked poly(disilanylenearylene)s from bis(silyl) monomers, using $[CpCp^*ZrH_2]_2$ as a catalyst (eq 2).


$$\text{RH}_2\text{SiArSiH}_2\text{R} \xrightarrow[-\text{H}_2]{[\text{CpCp*ZrH}_2]_2} \left(\text{—}\overset{\text{R}}{\underset{\text{H}}{\text{Si}}}\text{—}\overset{\text{R}}{\underset{\text{H}}{\text{Si}}}\text{—Ar—}\right)_n \qquad (2)$$

Experimental Section

Manipulations were carried out under an atmosphere of nitrogen or argon using Schlenk techniques and/or a Vacuum Atmospheres glovebox. Dry, oxygen-free solvents were employed unless otherwise noted. Elemental analyses were performed by Microanalytisches Labor Pascher. Infrared spectra were recorded on a Perkin-Elmer 1330 infrared spectrometer. NMR spectra were obtained with a GE QE-300 instrument at 300 MHz (^{1}H), 75.5 MHz (^{13}C), and 59.6 MHz (^{29}Si). The solid-state combined rotation and multiple-pulse spectroscopy (CRAMPS) ^{1}H NMR spectra and the solid-state cross polarization/magic angle spinning (CP/MAS) ^{29}Si NMR spectra were obtained on a modified Nicolet spectrometer operating at 149.32 MHz (^{1}H) and 29.8 MHz (^{29}Si) by C. F. Ridenour at the Regional NMR Center, Colorado State University. Rapid sample rotation at the magic angle averages chemical shift anisotropy, and the multiple-pulse sequence averages the strong proton–proton dipolar interaction. The proton spectra were referenced by assigning the methyl resonance of tetrakis(trimethylsilyl)silane (TTMSS) a shift of 0.38 ppm. The silicon spectra were referenced to external TTMSS at −9.7 ppm vs $SiMe_4$. Values for the average degree of cross-linking were determined by comparing the empirical formulas calculated from the solid-state CRAMPS ^{1}H NMR spectrum or the combustion analysis with those for a linear disilanylenearylene polymer ($-H_2SiArSiH_2-$, 0% cross-linking) and for a polymer that had undergone dehydrocoupling at two sites per silicon (=HSiArSiH=, 100% cross-linking). The cross-linking values calculated from the combustion analyses were based on the hydrogen analyses only, because the carbon analyses were consistently too low to correspond to a reasonable empirical formula, possibly due to SiC formation under the conditions of the analysis. The specific surface area was measured by the BET adsorption analysis method on a Quantachrome QSJR-3 instrument using N_2 gas. X-ray powder diffraction measurements were obtained with an APD 3600 X-ray powder diffractometer. Thermal analyses were performed on a Du Pont Model 2000 thermal analysis system. Transmission electron micrographs were recorded using a Hitachi H-500 microscope. Conductivities were determined using pressed pellets of each polymer and were measured under an inert atmosphere by the four-point probe method.[6] Doping with SbF_5 vapor was performed by placing the pellet in a chamber with SbF_5 at its vapor pressure. Melting points were determined with a Thomas Hoover Unimelt apparatus and are uncorrected. 1,2-Dibromobenzene, 1,3-dibromobenzene, 2,5-dibromothiophene, and 1,3,5-tribromobenzene were purchased from Aldrich and were dried over molecular sieves and degassed before use. 1,4-Dibromobenzene and 4,4′-dibromobiphenyl (Aldrich) were used as received. Tetraethyl orthosilicate (Aldrich) was distilled before use. $LiAlH_4$ (Aldrich) was recrystallized from diethyl ether before use. 1,4-Bis(triethoxysilyl)benzene and 4,4′-bis(triethoxysilyl)biphenyl were obtained by the method of Shea,[7] and $[CpCp^*ZrH_2]_2$[8] was prepared according to the literature procedure. The compounds 1,4-$(H_3Si)_2C_6H_4$[9] and 1,3-$(H_3Si)_2C_6H_4$[10] have previously been reported.

1,3-Bis(triethoxysilyl)benzene. The method is essentially the same as that previously described for 1,4-bis(triethoxysilyl)benzene.[7] Magnesium chips (28.0 g, 1.15 mol) and freshly distilled tetraethoxysilane (450 mL, 2 mol) in tetrahydrofuran (750 mL) were placed under nitrogen in a 2-L three-neck flask equipped with a magnetic stirbar, a condenser, and an addition funnel. A small crystal of iodine was added to activate the magnesium. A solution of 1,3-dibromobenzene (100.0 g, 0.424 mol) in tetrahydrofuran (250 mL) was added slowly. When ca. 25 mL of the dibromide had been added, the addition was stopped and stirring was continued until a mildly exothermic reaction began (usually within 20–30 min). The addition of dibromobenzene was continued and held at such a rate as to maintain the solution at reflux. After the addition was complete, the reaction mixture was stirred for an additional 2 h. The resulting brown solution was filtered from the remaining magnesium metal, and the tetrahydrofuran was removed by evacuation. The brown residue was extracted with dry hexane (500 mL), and the combined extracts were concentrated in vacuo. Unreacted tetraethyl orthosilicate was removed in vacuo (10^{-3} Torr), leaving a tea brown oil. Two distillations gave the product as a clear, colorless oil (0.1 mmHg, 126–128 °C, 58.0 g, 34%). Anal. Calcd for $C_{18}H_{34}O_6Si_2$: C, 53.7; H, 8.51. Found: C, 54.1; H, 8.59. IR (neat, CsI, cm^{-1}): 3060 w, 2970 s, 2920 s, 2880 s, 2730 w, 1577 m, 1478 w, 1439 m, 1390 s, 1365 m, 1290 m, 1160 s, 1090 vs, 958 s, 805 s, 770 s, 715 m, 705 m, 670 m, 485 s. ^{1}H NMR (benzene-d_6, 22 °C): δ 1.15 (t, J = 7.1 Hz, 18 H, OCH_2CH_3), 3.91 (q, J = 7.1 Hz, 12 H, OCH_2-

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CH_3), 7.30 (t, J = 7.2 Hz, 1 H, C_6H_4), 7.89 (d, J = 7.2 Hz, 2 H, C_6H_4), 8.37 (s, 1 H, C_6H_4). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ 18.43 (OCH_2CH_3), 58.89 (OCH_2CH_3), 127.59, 131.52, 137.06, 141.70 (C_6H_4).

1,3,5-Tris(triethoxysilyl)benzene. The procedure used for the preparation of 1,3-bis(triethoxysilyl)benzene was followed by using 1,3,5-tribromobenzene (100.0 g, 0.318 mol) in place of 1,3-dibromobenzene. Two distillations gave a clear, colorless oil (0.1 mmHg, 196–198 °C, 23.4 g, 13%). Anal. Calcd for $C_{24}H_{48}O_9Si_3$: C, 51.0; H, 8.56. Found: C, 51.2; H, 8.53. IR (neat, CsI, cm^{-1}): 2964 s, 2920 s, 2880 s, 2730 w, 1560 m, 1480 w, 1440 m, 1386 s, 1290 m, 1160 s, 1090 vs, 955 s, 825 s, 775 s, 710 m, 670 m, 487 s. ^1H NMR (benzene-d_6, 22 °C): δ 1.16 (t, J = 7.1 Hz, 18 H, OCH_2CH_3), 3.87 (q, J = 7.1 Hz, 12 H, OCH_2CH_3), 8.55 (s, 1 H, C_6H_5). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ 18.43 (OCH_2CH_3), 58.92 (OCH_2CH_3), 130.83, 143.60 (C_6H_4).

2,5-Bis(triethoxysilyl)thiophene. The procedure used for the preparation of 1,3-bis(triethoxysilyl)benzene was followed by using 2,5-dibromothiophene (100.0 g, 0.413 mol) in place of 1,3-dibromobenzene. Two distillations gave a clear, colorless oil (0.1 mmHg, 126–128 °C, 64.1 g, 38%). Anal. Calcd for $C_{16}H_{32}O_6SSi_2$: C, 47.0; H, 7.89. Found: C, 47.3; H, 7.91. IR (neat, CsI, cm^{-1}): 2970 s, 2920 s, 2880 s, 2730 w, 1485 m, 1440 m, 1388 s, 1362 w sh, 1290 m, 1268 w, 1200 s, 1165 s, 1090 vs, 1025 s, 960 s, 780 s, 750 m, 695 s, 520 s. ^1H NMR (benzene-d_6, 22 °C): δ 1.14 (t, J = 6.9 Hz, 18 H, OCH_2CH_3), 3.85 (q, J = 6.9 Hz, 12 H, OCH_2CH_3), 7.66 (s, 2 H, C_4H_2S). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ 18.38 (OCH_2CH_3), 59.17 (OCH_2CH_3), 137.61, 137.78 (C_4H_2S).

1,4-$(H_3Si)_2C_6H_4$. A solution of 1,4-bis(triethoxysilyl)benzene (44.4 g, 0.110 mol) in ether (50 mL) was added dropwise to a vigorously stirred suspension of $LiAlH_4$ (7.85 g, .206 mol) in ether (400 mL) at 0 °C. A white precipitate formed immediately. After the addition was complete the solution was allowed to warm to room temperature and was then stirred at room temperature for 36 h. The reaction mixture was filtered, and the filtrate was then concentrated to ca. 50 mL and bulb to bulb distilled in vacuo (10^{-3} Torr) at 35 °C (no warmer, due to the presence of unreacted $LiAlH_4$). Pure 1,4-$(H_3Si)_2C_6H_4$ (9.5 g, 63%) was obtained by fractional distillation through a 20-cm Vigreux column at atmospheric pressure [bp 140–142 °C; lit.[9] bp 31 °C (10 mmHg)]. IR (neat, CsI, cm^{-1}): 3400 m, 3000 m, 2940 w, 2150 s, 1374 s, 1130 s, 1020 m, 910 s, 840 m, 810 m, 650 s, 490 s. ^1H NMR (benzene-d_6, 22 °C): δ 4.17 (s, 6 H, SiH_3), 7.29 (s, 4 H, C_6H_4). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ 130.16, 135.58 (C_6H_4). ^{29}Si NMR (benzene-d_6, 22 °C): δ −62.65 (q, J_{SiH} = 202 Hz).

1,3-$(H_3Si)_2C_6H_4$. A procedure analogous to that described above for 1,4-$(H_3Si)_2C_6H_4$ was used, starting from 1,3-bis(triethoxysilyl)benzene (15.0 g, 37.3 mmol) and lithium aluminum hydride (4.24 g, 112 mmol), to yield 3.5 g (68%) of 1,3-$(H_3Si)_2C_6H_4$ after two vacuum distillations [bp 58–59 °C (25 mmHg); lit.[10] bp 59 °C (25 mmHg)]. Anal. Calcd for $C_6H_{10}Si_2$: C, 52.1; H, 7.29. Found: C, 52.2; H, 7.41. IR (neat, CsI, cm^{-1}): 3060 w, 3030 w, 3007 w, 2980 w, 2150 s, 1570 w, 1460 w, 1373 m, 1137 w, 1130 w, 1102 s, 910 s, 710 s, 640 s sh, 625 s, 595 w sh, 386 m. ^1H NMR (benzene-d_6, 22 °C): δ 4.17 (s, 6 H, SiH_3), 6.98 (t, J = 7.5 Hz, 1 H, C_6H_4), 7.33 (t, J = 7.5 Hz, 2 H, C_6H_4), 7.66 (s, 1 H, C_6H_4). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ 128.00, 135.59, 137.43, 143.55 (C_6H_4). ^{29}Si NMR (benzene-d_6, 22 °C): δ −62.60 (q, J_{SiH} = 200 Hz).

1,3,5-$(H_3Si)_3C_6H_3$. A procedure analogous to that described above for 1,4-$(H_3Si)_2C_6H_4$ was used, with 1,3,5-tris(triethoxysilyl)benzene (15.0 g, 26.6 mmol) reacting with lithium aluminum hydride (4.90 g, 130 mmol) to yield 2.60 g (58%) of 1,3,5-$(H_3Si)_3C_6H_3$ after two vacuum distillations [bp 88–90 °C (25 mmHg)]. Anal. Calcd for $C_6H_{12}Si_3$: C, 42.8; H, 7.18. Found: C, 42.4; H, 7.16. IR (neat, CsI, cm^{-1}): 3060 w, 3000 m, 2150 s, 1845 w, 1795 w, 1550 w, 1380 m, 1150 w, 1130 w, 915 s, 790 w, 720 s, 640 s, 612 s, 595 m, 385 m. ^1H NMR (benzene-d_6, 22 °C): δ 4.14 (s, 9 H, SiH_3), 7.65 (s, 3 H, C_6H_3). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ 128.07, 144.76 (C_6H_4). ^{29}Si NMR (benzene-d_6, 22 °C): δ −62.40 (q, J_{SiH} = 199 Hz).

4,4′-$(H_3Si)_2C_6H_4C_6H_4$. A procedure analogous to that described above for 1,4-$(H_3Si)_2C_6H_4$ was used, with 4,4′-bis(triethoxysilyl)biphenyl (20.0 g, 41.8 mmol) reacting with lithium aluminum hydride (4.74 g, 125 mmol) to yield crude solid 4,4′-$(H_3Si)_2C_6H_4C_6H_4$, which was recrystallized from hexane/benzene (9:1) to yield 6.1 g (68%) of 4,4′-$(H_3Si)_2C_6H_4C_6H_4$ melting at 166–168 °C. Anal. Calcd for $C_{12}H_{14}Si_2$: C, 67.2; H, 6.58. Found: C, 67.4; H, 6.54. IR (nujol, CsI, cm^{-1}): 3070 w, 3010 w, 2142 s, 1590 w, 1525 w, 1385 m, 1345 w, 1250 w, 1115 m, 920 s, 806 s, 730 s, 690 w, 644 s, 635 s sh, 380 w. ^1H NMR (benzene-d_6, 22 °C): δ 4.29 (s, 6 H, SiH_3), 7.34 (d, J = 8.1 Hz, 4 H, biphenyl), 7.44 (d, J = 8.1 Hz, 4 H, biphenyl). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ 127.12, 127.40, 136.68, 142.46. ^{29}Si NMR (benzene-d_6, 22 °C): δ −62.88 (q, J_{SiH} = 199 Hz).

2,5-$(H_3Si)_2C_4H_2S$. A procedure analogous to that described above for 1,4-$(H_3Si)_2C_6H_4$ was used, with 2,5-bis(triethoxysilyl)thiophene (15.0 g, 36.7 mmol) reacting with lithium aluminum hydride (3.48 g, 92.0 mmol) to yield 2.65 g (50%) of 2,5-$(H_3Si)_2C_4H_2S$ after two vacuum distillations [bp 58–62 °C (25 mmHg)]. Anal. Calcd for $C_4H_8Si_2S$: C, 33.3; H, 5.59. Found: C, 36.5; H, 6.24. ^1H NMR (benzene-d_6, 22 °C): δ 4.23 (s, 6 H, SiH_3), 7.13 (s, 2 H, C_4H_2S). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ 133.31, 139.98 (C_4H_2S). ^{29}Si NMR (benzene-d_6, 22 °C): δ −73.0 (q, J_{SiH} = 212 Hz). This material was contaminated with small amounts of 2,5-$(H_3Si)_2C_4H_6S$. ^1H NMR (benzene-d_6, 22 °C): δ 1.16 (m, β-CH_2), 3.86 (m, α-CH_2), 4.29 (d, J = 6.5 Hz, SiH_3).

Polymerization of 1,3-$(H_3Si)_2C_6H_4$. 1,3-$(H_3Si)_2C_6H_4$ (2.00 g, 14.5 mmol) was added to a benzene solution (5 mL) of $[CpCp^*ZrH_2]_2$ (85 mg, 0.29 mmol). The reaction immediately turned dark brown, and the reaction medium became rapidly viscous with strong gas evolution. Benzene (ca. 20 mL) was added to the reaction mixture. The mixture was vigorously stirred under a stream of argon for 24 h, resulting in a heterogeneous, chocolate solution. The catalyst was oxidized by exposure of the solution to air, and then the polymer product was collected on a glass fritted funnel by suction filtration in air. The collected polymer was washed with benzene (500 mL) and ethyl ether (200 mL) and dried under vacuum giving 1.71 g of off-white solid. All the polymers described here were insoluble in organic solvents and did not melt or decompose when heated to 300 °C. Anal. Calcd for $(C_6H_6Si_2)_n$: C, 53.67; H, 4.50. Found: C, 54.8; H, 5.18. IR (nujol, CsI, cm^{-1}): 3600 m, 3300 m, 2110 s (Si–H stretch), 1310 m, 1244 w, 1175 w, 1130 w, 1096 s, 990 w, 910 s (SiH_2 bend), 750 s br, 645 s, 600 s, 440 w, 405 m, 384 m. CRAMPS ^1H NMR: δ 4.29 ($w_{1/2}$ = 266 Hz, 2.34 H, SiH), 6.86 ($w_{1/2}$ = 281 Hz, 4.0 H, C_6H_4). CP/MAS ^{29}Si NMR: δ −60.6 ($w_{1/2} = 4 \times 10^2$ Hz).

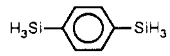
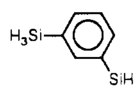
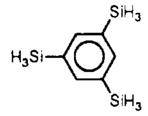
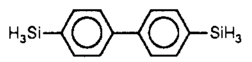
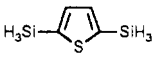
Polymerization of 1,4-$(H_3Si)_2C_6H_4$. The procedure for the polymerization of 1,3-$(H_3Si)_2C_6H_4$ was used, yielding 1.69 g of $[1,4\text{-}(H_xSi)_2C_6H_4]_n$. Anal. Calcd for $(C_6H_6Si_2)_n$: C, 53.67; H, 4.50. Found: C, 52.9; H, 5.13. IR (nujol, CsI, cm^{-1}): 3030 m, 2100 s (Si–H stretch), 1295 m, 1230 w, 1115 m, 1010 w, 906 s (SiH_2 bend), 840 w, 805 m sh, 765 s sh, 740 s sh, 715 s, 640 m, 600 m, 590 m sh, 475 m. CRAMPS ^1H NMR: δ 4.42 ($w_{1/2}$ = 230 Hz, 2.64 H, SiH), 7.05 ($w_{1/2}$ = 218 Hz, 4.0 H, C_6H_4). CP/MAS ^{29}Si NMR: δ −60.6 ($w_{1/2} = 4 \times 10^2$ Hz).

Polymerization of 1,3,5-$(H_3Si)_3C_6H_3$. The procedure for the polymerization of 1,3-$(H_3Si)_2C_6H_4$ was used, yielding 1.80 g of $[1,3,5\text{-}(H_xSi)_3C_6H_3]_n$. Anal. Calcd for $(C_6H_6Si_3)_n$: C, 44.38; H, 3.72. Found: C, 43.7; H, 5.04. IR (nujol, CsI, cm^{-1}): 2120 s (Si–H stretch), 1300 w, 1130 w, 910 s (SiH_2 bend), 870 w, 790 s, 730 s, 650 m, 610 w, 430 w, 385 w. CRAMPS ^1H NMR: δ 4.10 ($w_{1/2}$ = 218 Hz, 4.8 H, SiH), 7.45 ($w_{1/2}$ = 257 Hz, 3.0 H, C_6H_3). CP/MAS ^{29}Si NMR: δ −60.6 ($w_{1/2} = 4 \times 10^2$ Hz).

Polymerization of 4,4′-$(H_3Si)_2C_6H_4C_6H_4$. The procedure for the polymerization of 1,3-$(H_3Si)_2C_6H_4$ was used, yielding 1.74 g of $[H_xSiC_6H_4SiH_x]_n$. Anal. Calcd for $(C_{12}H_{10}Si_2)_n$: C, 68.51; H, 4.79. Found: C, 66.2; H, 5.34. IR (nujol, CsI, cm^{-1}): 3600 w, 3010 m, 2120 s (Si–H stretch), 1590 m, 1525 w, 1300 w, 1250 w, 1105 m, 998 m, 913 s (SiH_2 bend), 840 w, 800 s, 740 w, 646 m, 605 w, 540 w, 490 w, 380 w. CRAMPS ^1H NMR: δ 4.60 ($w_{1/2}$ = 303 Hz, 3.43 H, SiH), 6.80 ($w_{1/2}$ = 269 Hz, 8.0 H, C_6H_3). CP/MAS ^{29}Si NMR: δ −60.6 ($w_{1/2} = 4 \times 10^2$ Hz).

Polymerization of 2,5-$(H_3Si)_2C_4H_2S$. The procedure for the polymerization of 1,3-$(H_3Si)_2C_6H_4$ was used, yielding 1.81 g of $[2,5\text{-}(H_xSi)_2C_4H_2S]_n$. Reduction of the thienyl rings (ca. 24% reduction based on CRAMPS ^1H NMR, assuming no hydrosilation of the thienyl ring) apparently occurred by $[CpCp^*ZrH_2]_2$-catalyzed hydrogenation. The cross-linking calculations in Table I are based on this assumption. Anal. Calcd for $(C_4H_4Si_2S)_n$: C, 34.24; H, 2.87; S, 22.85. Found: C, 35.7; H, 4.05; S, 21.4. IR (nujol, CsI, cm^{-1}): 3400 w, 2100 s (Si–H stretch), 1260 m, 1196 s, 1070 s br, 1000 s br, 900 s (SiH_2 bend), 700 s br, 470 m. CRAMPS

Table I
Disilanylenearylene Polymers

monomer	CRAMPS ¹H NMR formula	CRAMPS ¹H NMR % cross-linking	combustion anal.[a] formula	combustion anal.[a] % cross-linking	UV-vis λ_{max},[b] nm
	$[H_{1.4}SiC_6H_4Si_{1.4}]_n$	65	$[H_{1.5}SiC_6H_4Si_{1.5}]_n$	55	260
	$[H_{1.5}SiC_6H_4Si_{1.5}]_n$	55	$[H_{1.5}SiC_6H_4Si_{1.5}]_n$	55	
	$[C_6H_3(SiH_{1.8})_3]_n$	20	$[C_6H_3(SiH_{1.7})_3]_n$	27	240
	$[H_{1.6}SiC_6H_4C_6H_4SiH_{1.6}]_n$	45	$[H_{1.6}SiC_6H_4C_6H_4SiH_{1.6}]_n$	45	295
	$[H_{1.1}SiC_4H_2SSiH_{1.1}]_n$	12	$[H_{1.8}SiC_4H_2SSiH_{1.8}]_n$	80	295

[a] Hydrogen analysis only. [b] Nujoll mull, ε not calculated.

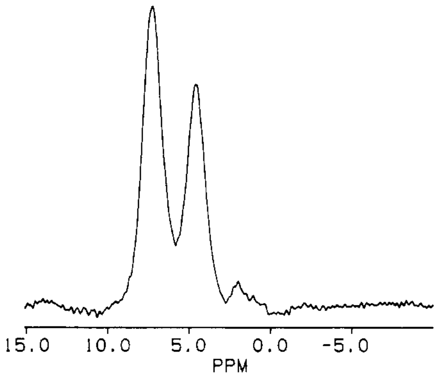


Figure 1. ¹H CRAMPS spectrum (149.32 MHz; t_d = 10 s; δ 4.42 ($w_{1/2}$ = 230 Hz, 2.64 H, SiH), 7.05 ($w_{1/2}$ = 218 Hz, 4.0 H, C_6H_4)) of $[1,4\text{-}(H_xSi)_2C_6H_4]_n$.

¹H NMR: δ 1.10 ($w_{1/2}$ = 230 Hz, 0.63 H, C_4H_4S), 4.20 ($w_{1/2}$ = 87 Hz, 3.13 H, SiH), 6.50 ($w_{1/2}$ = 230 Hz, 2.0 H, C_4H_2S).

Results and Discussion

Convenient routes to bis(trialkoxysiloxy)arene compounds have recently been described by Shea and coworkers,[7] who employed the procedure outlined in eq 3. We have used this method to synthesize 1,3-bis(triethoxysilyl)benzene, 1,3,5-tris(triethoxysilyl)benzene, and 2,5-bis(triethoxysilyl)thiophene. Reductions of these compounds with lithium aluminum hydride give the corresponding hydrosilanes in 50–70% isolated yields. Except for 4,4'-$(H_3Si)_2C_6H_4C_6H_4$ (mp 166–168 °C), these hydrosilanes are liquids at room temperature.

$$\text{BrArBr} \xrightarrow[\text{Si(OEt)}_4,\ \Delta]{\text{Mg, THF}} (\text{EtO})_3\text{SiArSi(OEt)}_3 \xrightarrow{\text{LiAlH}_4} \text{H}_3\text{SiArSiH}_3 \quad (3)$$

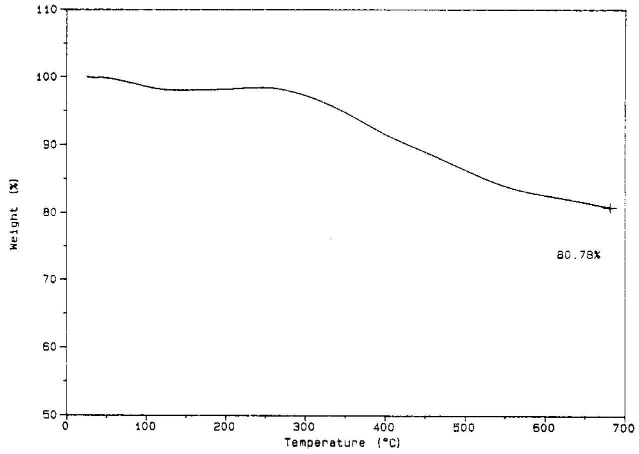


Figure 2. TGA of $[4,4'\text{-}(H_xSi)_2C_6H_4C_6H_4]_n$ taken at 5 °C/min under argon.

The dehydrogenative polymerizations of SiH_3-containing monomers were carried out in benzene solution employing ca. 2 mol % of $[CpCp^*ZrH_2]_2$ as catalyst. Empirical formulas for the polymers were determined by combustion analyses and by integration of CRAMPS solid-state ¹H NMR spectra (Table I). Both of these methods gave formulas of rather low accuracy. For the CRAMPS NMR spectra, low signal to noise ratios and the lack of base-line separation between peaks result in uncertainties of ca. 10% in the integrated areas from which the empirical formulas were determined. The spectrum of $[1,4\text{-}(H_xSi)_2C_6H_4]_n$ is shown in Figure 1. Cross-linking values determined from the combustion analyses were based on the hydrogen percentages only. The carbon analyses were variable and consistently low, apparently due to incomplete carbon combustion resulting from SiC formation. Despite the large errors inherent in these two methods, there is generally good agreement between them, and both support a high degree of cross-linking. A notable exception is $[2,5\text{-}(H_xSi)_2C_4SH_2]_n$, where a significant degree of ring reduction (ca. 25%) is observed, complicating the determination of empirical formulas and cross-linking values.

The cross-linking values in Table I are in general agreement with the extents of reaction at the gel point, as predicted by the Carothers equation[11] (p_c = 0.50 for $[1,4\text{-}(H_xSi)_2C_6H_4]_n$, $[1,3\text{-}(H_xSi)_2C_6H_4]_n$, and $[4,4'\text{-}(H_xSi)_2C_6H_4C_6H_4]_n$, assuming a tetrafunctional monomer; p_c = 0.33 for $[1,3,5\text{-}(H_xSi)_3C_6H_4]_n$, assuming a hexafunctional monomer). The values estimated from the empirical formulas are somewhat higher (e.g., p_c = 0.8 for $[1,4\text{-}(H_xSi)_2C_6H_4]_n$; p_c = 0.6 for $[1,3,5\text{-}(H_xSi)_3C_6H_4]_n$), suggesting that polymerization continues beyond the gel point.

The polymers are all insoluble in organic solvents and do not melt or decompose upon heating to 300 °C. Thermal gravimetric analysis (TGA) shows that $[4,4'\text{-}(H_xSi)_2C_6H_4C_6H_4]_n$ is thermally stable under argon, and only 5% of the polymer's initial weight is lost by 350 °C (Figure 2). At 700 °C, the residue remaining is equal to 80% of the initial sample weight, which corresponds to a substantially higher "ceramic yield" than has previously been reported for disilanylenearylene polymers.[2j–l] Differential scanning calorimetry (DSC) did not indicate the existence of a glass transition temperature (T_g) for $[1,4\text{-}(H_xSi)_2C_6H_4]_n$, $[1,3\text{-}(H_xSi)_2C_6H_4]_n$, or $[4,4'\text{-}(H_xSi)_2\text{-}$

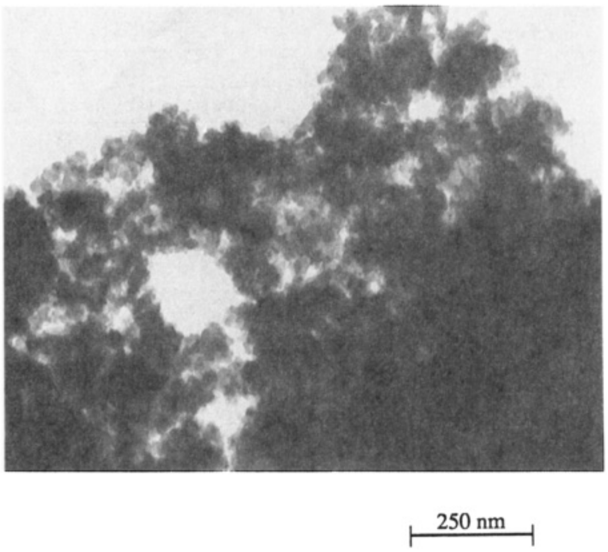
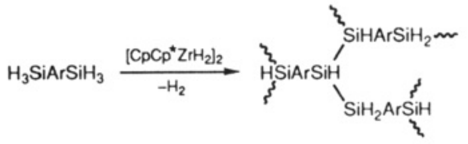


Figure 3. TEM micrograph of $[1,4\text{-}(H_xSi)_2C_6H_4]_n$; magnification 82 000.

$C_6H_4C_6H_4]_n$ between 25 and 450 °C. X-ray powder patterns for $[1,4\text{-}(H_xSi)_2C_6H_4]_n$ and $[4,4'\text{-}(H_xSi)_2C_6H_4C_6H_4]_n$ provide no evidence for crystallinity. It therefore appears that these materials adopt amorphous network structures as generalized in eq 4.



(4)

Transmission electron microscopy (TEM) analysis of $[1,4\text{-}(H_xSi)_2C_6H_4]_n$ (Figure 3) shows a granular structure, with particle sizes ranging from 10 to 400 nm. No evidence for an ordered structure was found in the TEM analysis of $[1,4\text{-}(H_xSi)_2C_6H_4]_n$, $[1,3\text{-}(H_xSi)_2C_6H_4]_n$, or $[4,4'\text{-}(H_xSi)_2C_6H_4C_6H_4]_n$. All three of these polymers have very high surface areas (BET method, N_2: $[1,4\text{-}(H_xSi)_2C_6H_4]_n$, 420 m^2/g; $[1,3\text{-}(H_xSi)_2C_6H_4]_n$, 380 m^2/g; $[4,4'\text{-}(H_xSi)_2C_6H_4C_6H_4]_n$, 315 m^2/g). Solid-state CP/MAS ^{29}Si NMR spectra of $[1,4\text{-}(H_xSi)_2C_6H_4]_n$, $[1,3\text{-}(H_xSi)_2C_6H_4]_n$, $[1,3,5\text{-}(H_xSi)_3C_6H_3]_n$, and $[4,4'\text{-}(H_xSi)_2C_6H_4C_6H_4]_n$ showed only a single, broad ($w_{1/2}$ = 400 Hz) peak centered at −60.6 ppm.

Given the extended σ–π framework present in these polymers, it is not surprising that their UV–vis spectra are red-shifted compared to their respective monomers. Specifically, $[1,4\text{-}(H_xSi)_2C_6H_4]_n$ absorbs at 260 nm compared to $1,4\text{-}(H_3Si)C_6H_4$, which absorbs at 240 nm, and $[4,4'\text{-}(H_xSi)_2C_6H_4C_6H_4]_n$ absorbs at 295 nm compared with an absorbance of 265 nm for $4,4'\text{-}(H_3Si)_2C_6H_4C_6H_4$. The λ_{max} value for $[1,4\text{-}(H_xSi)_2C_6H_4]_n$ is similar to those reported for thin films of $[1,4\text{-}(MePhSi)_2C_6H_4]_n$ (254 nm) and $[1,4\text{-}(MeEtSi)_2C_6H_4]_n$ (262 nm).[2m] In contrast to these materials, however, $[1,4\text{-}(H_xSi)_2C_6H_4]_n$ does not photodegrade upon irradiation with a medium-pressure Hg lamp.

Conductivity measurements showed that all the polymers synthesized were insulators. Exposure to SbF_5 vapor caused the polymers to darken and turn dark blue or brown but did not result in measurable conductivity values, except in the case of $[4,4'\text{-}(H_xSi)_2C_6H_4C_6H_4]_n$, which was found to possess a conductivity of ca. 10^{-4} S/cm. Long-term exposure to SbF_5 led to a gradual decrease in conductivity, suggesting slow degradation of the polymer.

The polymers reported in this paper have very different properties than polymers that have been previously prepared by metal-catalyzed dehydropolymerization. Their physical properties are consistent with a substantial degree of cross-linking, and the UV–vis and conductivity data suggest σ–π delocalization in the –(SiArSi)– backbone. While the utility of these polymers may be limited by their intractability, uses that take advantage of their rigidity, high surface area, and chemical properties may well emerge (e.g., as catalyst supports). Currently we are focusing on modification of this polymerization to produce processable, linear polymers.

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Registry No. $1,4\text{-}(H_3Si)_2C_6H_4$, 3151-24-4; $1,4\text{-}(H_3Si)_2C_6H_4$ (homopolymer), 136892-88-1; $1,3\text{-}(H_3Si)_2C_6H_4$, 18135-87-0; $1,3\text{-}(H_3Si)_2C_6H_4$ (homopolymer), 136892-89-2; $1,3,5\text{-}(H_3Si)_3C_6H_3$, 63148-15-2; $1,3,5\text{-}(H_3Si)_3C_6H_3$ (homopolymer), 136892-90-5; $4,4'\text{-}(H_3Si)_2C_6H_4C_6H_4$, 136892-86-9; $4,4'\text{-}(H_3Si)_2C_6H_4C_6H_4$ (homopolymer), 136892-91-6; $2,5\text{-}(H_3Si)_2C_4H_2S$, 28920-20-9; $2,5\text{-}(H_3Si)_2C_4H_2S$ (homopolymer), 136892-92-7; $1,3\text{-}((EtO)_3Si)_2C_6H_4$, 16067-99-5; $1,3,5\text{-}((EtO)_3Si)_3C_6H_3$, 136892-87-0; $2,5\text{-}((EtO)_3Si)_3C_4H_2S$, 40190-22-5; $[CpCp^*ZrH_2]_2$, 81476-78-0; SbF_5, 7783-70-2; $(EtO)_4Si$, 78-10-4; $BrC_6H_4\text{-}m\text{-}Br$, 108-36-1; $1,3,5\text{-}Br_3C_6H_3$, 626-39-1; $2,5\text{-}Br_2C_4H_2S$, 3141-27-3.