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Silole-Incorporated Polysilanes[1a]

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Siloles,[2] silacyclopentadienes, have long attracted considerable interest because of their unique electronic structures.[3] Facile photochemical dimerization[4] and reduction to radical anions and dianions[5] indicate existence of low-lying LUMO orbitals for siloles. We have previously reported low reduction potentials for both diphenyl- and tetraphenyldimethylsiloles by cyclic voltammetry.[6] Recently, Tamao and co-workers have indicated by MO calculations that the parent silole, 1-silacyclopentadiene, has a relatively low LUMO energy level due to the $\sigma^*-\pi^*$ conjugation in comparison with a carbon analogue, cyclopentadiene.[7,8] Although the HOMO energy level is also somewhat lowered, lowering of the LUMO energy is quite characteristic for siloles. Since polysilanes are characterized by their high-lying HOMO energy levels,[9] polysilanes incorporating siloles should be interesting polymers, in which the polysilane chain is expected to behave as an electron donor while the silole ring should act as an acceptor. A combination of the donor and acceptor systems should result in an interesting polymer. Herein, we report synthesis and properties of the first polysilane polymer with tetraphenylsilole in the polymer chain.[10]

Our synthetic strategy for the silole-incorporated polymer is based on the ring opening polymerization of tetraphenylsilolespirooctamethylcyclopentasilane (**1**), which can be prepared by the reaction of the silole dianion and 1,4-dichlorooctamethyltetrasilane in 30% yield as shown in Scheme 1. Fortunately, information on silole dianions has accumulated considerably in recent years.[11]

Compound **1** forms pale yellow crystals, and spectroscopic evidence as well as X-ray crystallographic analysis of **1** indicates that it has the spiro structure.[12] Next, anionic ring opening polymerization of **1** with a catalytic amount of butyllithium as an initiator was examined (Scheme 2). In a typical example, polymerization of **1** in THF at −40 °C proceeded smoothly, the polymer **2** being obtained in 41% yield (M_n = 17 000, M_w/M_n = 1.3, determined by SEC with polystyrene standards).[13] The structure of the polymer was highly ordered as evidenced by NMR analyses. Figure 1 shows ^{29}Si NMR spectra of the polymer in which only three different kinds of signals are observed. These signals are assigned to the silole silicon (C), the central two silicon atoms of the original tetrasilane units (B), and the two silicon atoms adjacent to the silole silicon (A), respectively. Thus the ^{29}Si NMR spectrum is consistent with a highly regulated structure for the polymer chain. The ^{1}H and ^{13}C NMR spectra also supported the structure. These results indicate that the anionic ring opening polymerization process itself must be highly regioselective.

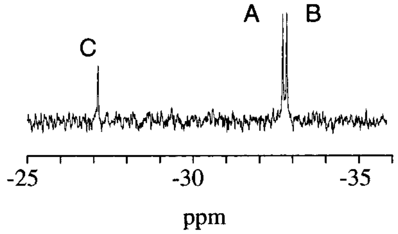
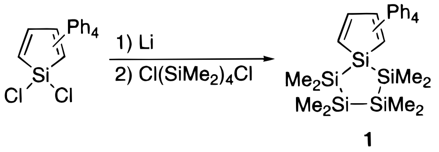
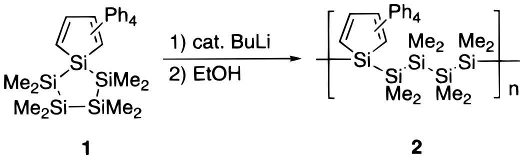


Figure 1. ^{29}Si NMR spectra of the polymer **2** in $CDCl_3$.

Scheme 1



Scheme 2



To elucidate the polymerization mechanism, the reaction of **1** with a large excess methyllithium at −40 °C, followed by addition of methanol (or deuterium oxide), was examined. The reaction gave **3** exclusively as shown in Scheme 3. The structure of **3**

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[10] Similar low-molecular-weight polymers may be prepared by the condensation reaction of the tetraphenylsilole dianion with dichlorosilanes (R. West, private communication).

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[12] Sonication of 1,1-dichloro-2,3,4,5-tetraphenylsilole (6.3 g, 14 mmol) with lithium (1.9 g, 270 mmol) in THF (60 mL) for 5 h gave a dark brown solution. After removal of excess lithium, a solution of 1,4-dichloro-1,1,2,2,3,3,4,4-octamethyltetrasilane (10.7 g, 35 mmol) in THF (20 mL) was added to the solution at room temperature. The resulting mixture was refluxed for 40 h and then allowed to cool to room temperature. The reaction mixture was quenched by adding a small amount of ethanol and filtered. After removal of the solvent, crystallization from hexane afforded pale yellow crystals of **1** (2.6 g, 30%). **1**: mp 164−169 °C; ^{1}H NMR (C_6D_6, 300 MHz) δ 0.14 (s, 12H), 0.27 (s, 12H), 7.3−6.9 (brd m, 20H); ^{13}C NMR (C_6D_6, 75.4 MHz) δ −5.5, −4.1, 126.0, 126.7, 128.0, 128.5, 130.4, 131.1, 140.3, 142.1, 146.2, 155.0; ^{29}Si NMR (C_6D_6, 59 MHz) δ −23.1, −34.4, −40.4; GC−MS (70 eV) *m/z* (%) 616 (2.0, M^+), 538 (11.5), 135 (66.9), 105 (16.6), 73 (100); HRMS calcd for $C_{36}H_{44}Si_5$ 616.2289, found 616.2289.

[13] A typical run of the polymerization is as follows. In a 30-mL two-necked flask, equipped with a magnetic stirring bar, a rubber septum, and a three-way stopcock, were placed **1** (298 mg, 0.484 mmol) and THF (5 mL) under dry argon. A hexane solution of *n*-butyllithium (9.6×10^{-2} mmol) was added to the solution at −40 °C. After the mixture was stirred at −40 °C for 4 h, a few drops of ethanol were added to the mixture. After removal of the solvent, the residual mass was dissolved in benzene and the polymer was precipitated by pouring the solution into methanol. The second cycle of dissolving−precipitation followed by freeze-drying gave the polymer as a pale yellow powder (122 mg, 41%).

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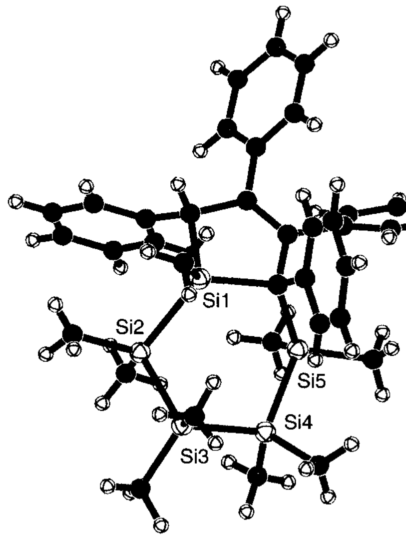
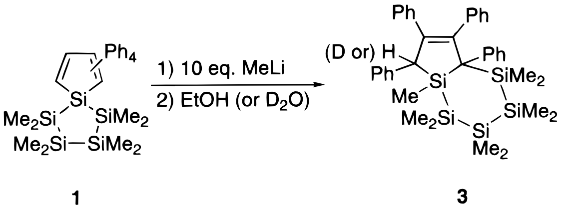


Figure 2. ORTEP view of the crystal structure of **3**.

Scheme 3



was determined unequivocally by ^{1}H, ^{13}C, and ^{29}Si NMR and X-ray crystallography (Figure 2).[14,15]

Scheme 4 shows a possible reaction mechanism for the formation of **3**. In the initial step of the reaction, methyllithium attack at the silole silicon atom of **1** to form a pentacoordinate silicate intermediate (**4**). The formation of the pentacoordinate silicate anions by the reaction of several siloles has been indicated before.[16] Then the silicon−silicon bond could be cleaved to form a silyl anion (**5**) which should be quite reactive and could attack the silole carbon to form an allyl anionic species (**6**). The resulting allyl anionic species should be stable due to resonance stabilization by the two phenyl groups. These two species may be in an equilibrium but in favor of the allyl anionic species. Then, quenching by ethanol gives the ring compound **3**. It is noteworthy that, due to the steric hindrance, the proton enters from the opposite side of the large pentasilacyclohexane ring of **6** to give only one diastereomer.

Polymerization proceeds similarly by the attack of the silyl-anions on the silole silicon of **1** to form polymeric anions. The reactive end should always be in an equilibrium between the silyl anion ends and ring allyl anions. This is an interesting new kind of degenerate living anionic polymerization.

Absorption, excitation, and fluorescence spectra (excited at 323 nm) of **2** are shown in Figure 3. In the absorption spectrum, the polymer **2** has two absorptions around 320 and 360 nm, assignable to the polysilane skeleton and the silole ring, respectively. It is quite interesting that the excitation spectrum, monitored at 520 nm, reproduced the absorption spectrum almost completely, indicating the extensive energy transfer between the silole ring and the polysilane chain. It should also be noted that the quantum yield of fluorescence of the polymer (4.1×10^{-2}) is about 10 times greater than that of the parent hexaphenylsilole (4.5×10^{-3}).[17,18]

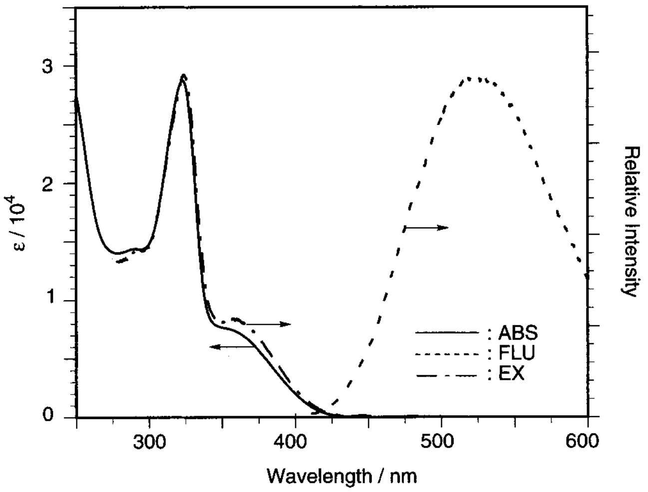
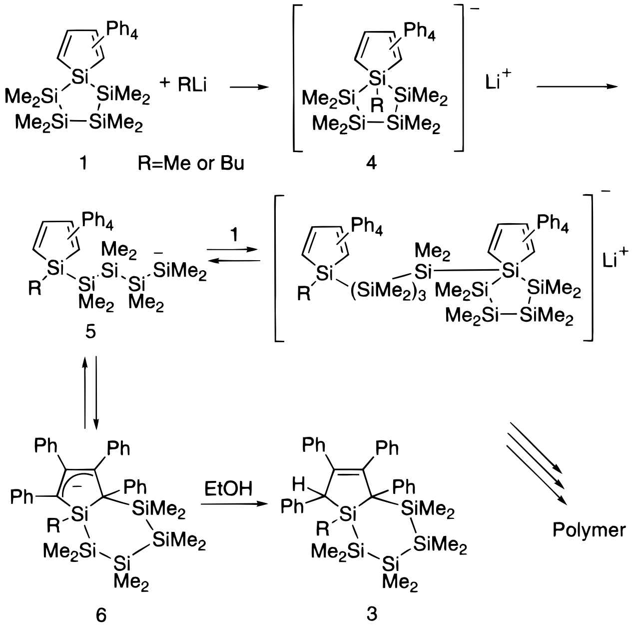


Figure 3. Absorption, fluorescence, and excited spectra of the polymer **2**.

Scheme 4



Further works on the silole-incorporated polysilanes, including application to electroluminescence devises, are now in progress.

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Supporting Information Available: Crystallographic data for **1** and **3** (32 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[14] Spectral data for **3**: transparent crystals; 203.4−206.4 °C; ^{1}H NMR (CDCl$_3$, 300 MHz) δ −0.38 (s, 3H), −0.22 (s, 3H), −0.14 (s, 3H), −0.11 (s, 3H), 0.20 (s, 9H), 0.39 (s, 3H), 0.46 (s, 3H), 3.93 (s, 1H), 7.5−7.0 (m, 20H); ^{13}C NMR (CDCl$_3$, 75.4 MHz) δ −6.6, −4.9, −4.7, −4.4, −4.1, −4.0, −2.9, −1.0, −0.1, 44.0, 48.8, 124.4, 124.9, 126.5, 127.4, 127.7, 128.40, 128.5, 128.9, 129.5, 130.64, 132.0, 142.2, 142.3, 145.2, 146.5, 148.6; ^{29}Si NMR (CDCl$_3$, 59 MHz) δ −47.0, −44.4, −43.7, −14.4, −12.8; GC−MS (70 eV) *m/z* (%) 632 (100, M$^+$), 559 (45.1), 501 (31.0), 481 (34.5), 439 (40.0), 423 (30.5), 220 (64.3); HRMS calcd for $C_{37}H_{48}Si_5$ 632.2602, found 632.2585.

[15] Crystal data for **3**: MF = $Si_5C_{37}H_{48}$, MW = 632.21, monoclinic, $a = 18.027(7)$ Å, $b = 11.282(3)$ Å, $c = 19.155(5)$ Å, $\beta = 107.05(2)°$, $V = 3724(2)$ Å^{-3}, space group = $P21/c$, $Z = 4$, $D_{\mathrm{calcd}} = 1.127$ g cm^{-3}, μ (Cu Kα) = 19.56 cm^{-1}. The final R factor was 0.035 ($R_w = 0.036$) for 4426 reflections with $F_0 > 3\sigma(F_0)$.

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