Silole Polymer and Cyclic Hexamer Catenating through the Ring Silicons

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Poly(1,1-silole)s, silole (silacyclopentadiene)[1] polymers catenated through the ring silicons, are of keen interest as a new class of polysilanes.[2] Recent theoretical calculations have suggested their unique electronic structures with low LUMO levels due to the $\sigma^*-\pi^*$ conjugation along the main chain.[3,4] Experimentally, oligo(1,1-silole)s,[5,6] silole-incorporated polysilanes,[7] and poly(dibenzosilole)[8] have recently been synthesized as their models and related polymers, respectively, suggesting their unique optical properties and high potentials as new functional materials such as organic light-emitting diodes.[7] However, the polymers consisting of only silole rings are still unknown. We have now succeeded in the syntheses of poly(1,1-silole) as well as a silole cyclic hexamer by a simple Wurtz-type polycondensation.[9]

The Wurtz-type coupling of **1** using Li affords the well-defined poly(1,1-silole), as shown in Scheme 1. Thus, the 1,1-dichlorosilole **1** was allowed to react with just 2 molar amounts of granular Li in THF at −20 °C for 20 h followed by treatment with EtMgBr to quench any reactive terminal groups.[10] The GPC analysis of the reaction product after reprecipitation from MeOH revealed that the reaction indeed afforded polymeric materials, together with an oligomer. The oligomer was completely removed by repeated (twice) reprecipitations from *i*-PrOH to give pure poly(1,1-silole) **2** in 61% yield. The polymer **2** is slightly soluble in THF and CHCl₃ and stable enough to be handled in air without special care. The structure of **2** was unequivocally characterized by ¹H, ¹³C, and ²⁹Si NMR spectra, IR spectra, and molecular weight determination.[11] For instance, the solid state ²⁹Si NMR of **2** shows a sharp peak ascribed to the silole ring silicon atoms at −28.0 ppm, together with small broad peaks around 0 ppm,

Scheme 1
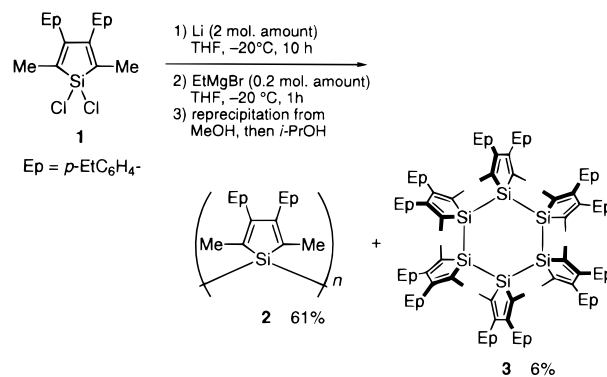
Ep = *p*-EtC₆H₄-

assignable to the terminal silole rings.[12] The molecular weight estimated by GPC using polystyrene standards is $M_w = 7200$ and $M_n = 6300$ ($n \approx 20$) with a very narrow polydispersity ($M_w/M_n = 1.14$).

The oligomer soluble in *i*-PrOH was a cyclic hexamer **3**, which was isolated in pure form in 6% yield by recrystallization from ethyl acetate.[13] No other cyclic oligomers were detected. As for the X-ray crystal structure of **3** shown in Figure 1,[14] while the geometries of the silole rings and the Si−Si bonds are in the normal range, the central cyclohexasilane skeleton has a considerably flat chair conformation in comparison with the known cyclohexasilanes. The averaged Si−Si−Si−Si dihedral angle and the averaged Si−Si−Si bond angle is 37.5 and 116.3°, respectively.[15] This flat geometry is mainly due to the widening of the Si−Si−Si angles arising from the small C−Si−C angles (av 93.3°) of the silole skeletons.

The keys to achieving the synthesis of the poly(1,1-silole) are the choice of starting materials and reaction condition. We employed the dichlorosilole **1** which has small methyl groups at the 2,5-positions and *p*-ethyl groups on the 3,4-phenyl groups in order to reduce the steric congestion[16] and increase the solubility of the resulting polymers. The compound **1** can be readily prepared by our method reported previously.[17] Also, the use of Li metal in THF is crucial. The polycondensation of **1** under the standard conditions for the Wurtz-type polysilane synthesis using Na in refluxing toluene only gave a mixture of oligomeric

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(2) Review for polysilanes: Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359.

(3) Yamaguchi, Y. *Synth. Met.* **1996**, *82*, 149.

(4) Yamaguchi, S.; Tamao, K. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2327.

(5) Yamaguchi, S.; Jin, R.-Z.; Tamao, K.; Shiro, M. *Organometallics* **1997**, *16*, 2486.

(6) Kanno, K.; Ichinohe, M.; Kabuto, C.; Kira, M. *Chem. Lett.* **1998**, 99.

(7) Sanji, T.; Sakai, T.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1998**, *120*, 4552.

(8) Chauhan, B. P. S.; Shimizu, T.; Tanaka, M. *Chem. Lett.* **1997**, 785.

(9) Poly(1,1-silole) consisting of 2,3,4,5-tetraphenylsilole units has recently been prepared by R. West and co-workers: Sohn, H.; Huddleston, R.; Powell, D. R.; West, R.; Oka, K.; Yonghua, X. *J. Am. Chem. Soc.* **1999**, *121*, 2935.

(10) We could not define the terminal groups of the polymer despite the use of several quenching reagents such as EtMgBr, *i*-PrOH/NEt₃, or water, all of which gave almost the same molecular weight polymers.

(11) **2**: ¹H NMR spectrum of **2** in CDCl₃ at room temperature only shows uncharacterizable broad signals, probably due to heavy hindered rotation of the polysilane main chain, but in C₆D₅NO₂ at elevated temperature, characterizable signals are observed: (C₆D₅NO₂, 413 K) δ 0.95−1.29 (br m, 6H, ethyl CH₃), 2.41−2.79 (br m, 10H, ethyl CH₂ and 2,5-CH₃), 6.75−7.23 (br m, 8H, 3,4-C₆H₄). ¹³C NMR (C₄D₈O, 293 K) δ 15.83, 19.03 (br), 29.27, 127.42 (br), 130.90 (br), 136.72 (br), 137.37 (br), 142.10 (br), 156.25 (br). ²⁹Si NMR (solid state) δ −28.0. ²⁹Si NMR spectrum in solution could not be measured due to the low solubility. IR (KBr) 2963, 1903, 1494, 830 cm⁻¹. Anal. Calcd for (C₂₂H₂₄Si)ₙ C, 83.48; H, 7.64. Found C, 82.24; H, 7.20. The molecular weight of the polymer part after reprecipitation from MeOH is $M_w = 7600$ and $M_n = 6000$ ($n \approx 19$) according to the GPC approximation, which is almost the same as that after reprecipitation twice from *i*-PrOH.

(12) The small broad peaks around 0 ppm in the solid state ²⁹Si NMR become larger as the molecular weights of the polymer become lower, indicating that the peaks are ascribed to the terminal silole rings. The spectra of **2** and **2′** are shown in the Supporting Information.

(13) **3**: No melting point was observed up to 400 °C. ¹H NMR (CDCl₃) δ 1.14 (t, *J* = 7.6 Hz, 36H), 2.12 (s, 36H), 2.53 (q, *J* = 7.6 Hz, 24H), 6.69 (d, *J* = 7.8 Hz, 24H), 6.91 (d, *J* = 7.8 Hz, 24H). ¹³C NMR (CDCl₃) δ 15.35, 17.74, 28.47, 126.72, 129.42, 133.85, 136.95, 141.47, 155.51. ²⁹Si NMR (CDCl₃) −33.24. HRMS(FAB) Calcd for C₁₃₂H₁₄₄Si₆ 1897.9946. Found 1897.9928. Anal. Cacld for C₁₃₂H₁₄₄Si₆ C, 83.48; H, 7.64. Found C, 83.19; H, 7.65.

(14) Crystal data of **3** (instrument; Rigaku RAXIS-IV): C₁₃₂H₁₄₄Si₆, fw = 1899.10, crystal size 0.40 × 0.10 × 0.10 mm, triclinic, *P1̄* (No. 2), *a* = 16.809-(5) Å, *b* = 17.708(6) Å, *c* = 10.432(2) Å, *a* = 106.55(2)°, *b* = 93.27(1)°, *γ* = 105.22(1)°, *V* = 2842.8701 Å³, *Z* = 1, *D*c = 1.109 g cm⁻³, *μ* (Mo Kα) = 1.22 cm⁻¹, number of unique reflections = 4592, temperature −50 °C, *R* = 0.059, *R*w = 0.082, and GOF = 1.23. Hydrogen atoms were included but not refined.

(15) According to a search of the Cambridge Structural Database (CSD), cyclohexasilane derivatives generally have the averaged Si−Si−Si−Si torsion angles of 53−57°. An irregularly small averaged torsion angle of 33.6° has been reported for [Si(PhCH₂)H]₆: Li, H.; Butler, I. S.; Harrod, J. F. *Organometallics* **1993**, *12*, 4553.

(16) For the formation of the polymer, the size of the 2,5-substituents is critical. When 2,5-bis(trimethylsilyl)-3,4-diphenyl-1,1-dichlorosilole was employed in place of the 2,5-dimethyl derivative **1**, the Wurtz-type coupling using Li only gave silole dimers due to the steric congestion.

(17) (a) Yamaguchi, S.; Jin, R.-Z.; Tamao, K.; Shiro, M. *Organometallics* **1997**, *16*, 2230. (b) Tamao, K.; Yamaguchi, S.; Shiro, M. *J. Am. Chem. Soc.* **1994**, *116*, 11715.
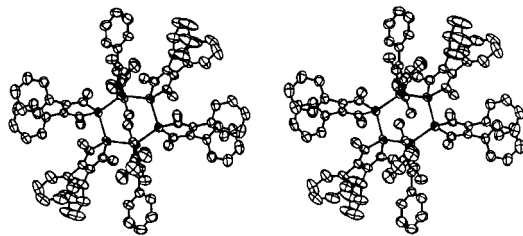
Figure 1. Stereoview of the crystal structure of the cyclic hexamer **3**. Silicon atoms are shaded and hydrogen atoms and *p*-ethyl groups on 3,4-phenyl rings are omitted for clarity.
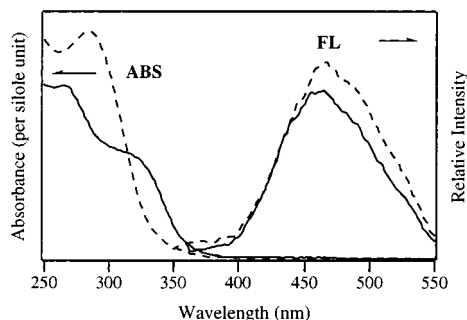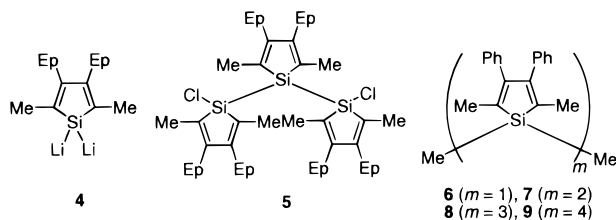

Figure 2. UV absorption and fluorescence spectra in chloroform; **2**, solid line: **3**, dashed line.

materials, which might contain the Si–O–Si linkages in light of the broad band around 1000–1100 cm⁻¹ in the IR spectrum.

As an alternative route to the poly(1,1-silole)s, the coupling reaction of the silole dianion **4** with chlorine-terminated tersilole **5**[18] in THF at −78 °C has also been examined. The polymer **2′** having essentially the same spectroscopic data as that of **2** was obtained in 48% yield,[12] although the molecular weight was relatively low; $M_w = 3000$ and $M_n = 2400$ ($n \approx 8$) with $M_w/M_n = 1.25$. In this reaction, the cyclic hexamer was no longer obtained.


The polymer **2** and the cyclic hexamer **3** showed interesting photophysical properties. Their UV absorption and fluorescence spectra are shown in Figure 2 and the data are summarized in Table 1, together with the data for the oligosiloles **6**–**9** for comparison, which we previously reported.[5] Polymer **2** has broad absorption bands with a shoulder at 320 nm, which is about 30–

(18) For the preparation of compound **5**, see the Supporting Information.

Table 1. UV Absorption and Fluorescence Spectral Data for Poly(1,1-silole) and Oligo(1,1-silole)s

compd	UV absorption[a]		fluorescence[a]	
	λ_{max}/nm	log ε	λ_{max}/nm[b]	$\Phi_f \times 10^{3\ c}$
2	320(sh)	4.02[d]	460	0.314
3	285	5.07	467	0.353
6	307	3.22[e]	393	0.372
7	255	4.42[e]	415	1.94
8	279	4.60[e]	439	1.27
9	289	4.59[e]	441	1.39

[a] In chloroform. [b] Excited at the absorption maximum wavelength. [c] Quantum yield determined with reference to quinine sulfate. [d] Per silole ring unit. [e] Yamaguchi, S.; Jin, R.-Z.; Tamao, K.; Shiro, M. *Organometallics* **1997**, *16*, 2483.

Scheme 2
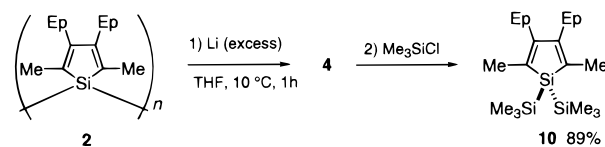
40 nm red-shifted relative to those of the trimer **8** and tetramer **9**, whereas the cyclic hexamer **3** has an absorption maximum comparable to those of the oligomers. In the fluorescence spectra, the poly(1,1-silole) **2** and the cyclic hexamer **3** have broad emission bands around 460 nm, although the quantum yields are rather low. The emission maximum wavelengths tend to shift to a longer region going from the monosilole to polymer, probably due to the mixing of the orbitals between the silole moieties and polysilane moiety.

The most notable chemical properties of poly(1,1-silole) **2** may be the complete degradation of the polysilane skeleton with lithium. Thus, as shown in Scheme 2, polymer **2** ($M_n = 5,400$) was reacted with an excess amount of Li in THF at 10 °C to form the silole dianion **4** within 1 h as the sole product, which was trapped with Me₃SiCl to give 1,1-bis(trimethylsilyl)silole **10** in 89% isolated yield. This unique exhaustive degradation up to the silole dianion is totally different from those of the conventional polysilanes, which result only in the formation of the oligomeric mixtures at most, and may be consistent with the expected low-lying LUMO level of the poly(1,1-silole)s. More detailed elucidation of the chemical properties of the present silole-based σ-conjugated systems is now in progress, especially, the formation of the radical anion of the silole cyclic hexamer.

Supporting Information Available: Experimental procedures and data including the solid state ²⁹Si NMR spectra of **2** and **2′** and crystal data of compound **3** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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