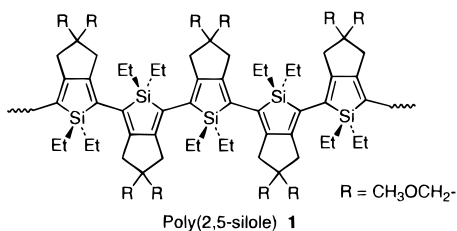# The First Synthesis of Well-Defined Poly(2,5-silole)

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Since the first proposal in 1989,[1] poly(2,5-silole)s, silole-2,5-linked homopolymers, have been target molecules for enthusiastic theoretical studies, because of their analogous structures to all-trans-*s*-cis polyacetylene as well as their potential applicability to organic electronic devices.[2–8] Experimentally, however, the structurally well-defined poly(2,5-silole)s are still unknown, despite a few attempts.[1,9] Quater(2,5-silole) is the longest silole oligomer reported to date.[9,10] The synthesis of the polymer has been hampered by the limited availability of their crucial precursors, the 2,5-difunctionalized siloles,[9,11,12] and, moreover, the intrinsic low reactivities of the functionalities at the 2,5-positions. Actually, although we have recently prepared some potential precursors such as the 5-stannyl- and 5-boryl-2-halosiloles, unfortunately, they did not react during the transition metal-catalyzed coupling reactions under various conditions.[9,11c] After several attempts, we have now succeeded in the synthesis of poly(2,5-silole) **1** by the Pd(0)-catalyzed cross-coupling reaction of 5-zincated 2-iodosilole, in situ generated from the newly prepared 2,5-diiodosilole **2**.

Poly(2,5-silole) **1**   R = CH₃OCH₂-

We have designed 2,5-diiodosilole **2** as a key precursor of the poly(2,5-silole), where methoxymethyl groups are introduced to

Scheme 1

Reagents and Conditions: i, Ti(O*i*-Pr)₄ (1.2 mol. amt.), *i*-PrMgCl (2.6 mol. amt.), Et₂O, −50 °C, 2 h; ii, I₂ (2.5 mol. amt.), rt, 10 h; iii, *n*-BuLi (2 mol. amt.), Et₂O, −78°C, 1 h; iv, (MeO)₄Si (1 mol. amt.), −78°C ∼ rt, 10 h; v, EtMgBr (4 mol. amt.), CuCN (1 mol. amt.), THF, reflux, 60 h; vi, I₂ (2 mol. amt.), AgBF₄ (2 mol. amt.), MeOH/THF = 2/1, −78 °C, 1 h, then, 0°C, 30 min.

facilitate the structure characterization and to provide sufficient solubility of the resulting polymer. Compound **2** was prepared in four steps starting from 1,7-disilyl-1,6-heptadiyne **3** by our procedure based on the halodesilylation reaction,[11] as shown in Scheme 1. Thus, the reaction of the diyne **3** with Ti(O*i*-Pr)₄/2*i*-PrMgCl produced a titanacyclopentadiene,[13] followed by iodonolysis which gave the diiodobutadiene **4** in 75% yield. Dilithiation of **4** followed by the treatment with Si(OMe)₄ afforded 1,1-dimethoxysilole **5** in 42% yield. The alkylation of **5** with EtMgBr in the presence of CuCN[14] gave 1,1-diethyl-2,5-disilylsilole **6** in 77% yield. The final step was the iododesilylation of **6** with iodine in the presence of a silver salt,[15] which successfully afforded the 2,5-diiodosilole **2** in 84% yield.

The synthesis of poly(2,5-silole) **1** has been examined by the coupling reactions of this diiodosilole **2** under several conditions. Although the homo-coupling reactions of **2** using Ni(0) catalysts all failed, the Pd(0)-catalyzed cross-coupling reaction[16] of a mono-zincated intermediate successfully produced the desired polymer. Thus, as shown in Scheme 2, compound **2** was selectively mono-

Scheme 2

X,Y = H, I, or Bu
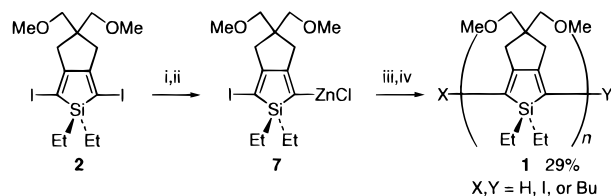
Reagents and Conditions: i, *n*-BuLi (1.1 mol. amt.), Et₂O, −78 °C, 1h; ii, ZnCl₂(tmen) (1.1 mol. amt.), −78 °C to rt; iii, removal of volatiles *in vacuo*; iv, PdCl₂(PPh₃)₂, (0.01 mol. amt.),THF, reflux, 44 h.

lithiated with *n*-BuLi in ether, followed by the treatment with ZnCl₂(tmen) to afford the mono-zincated silole **7**. After removal of the volatiles in vacuo, the cross-coupling reaction of **7** in the

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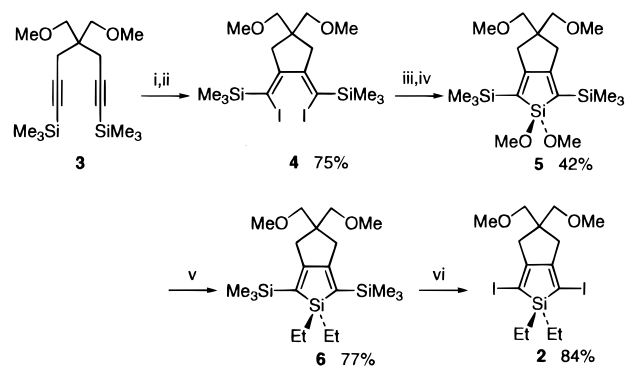
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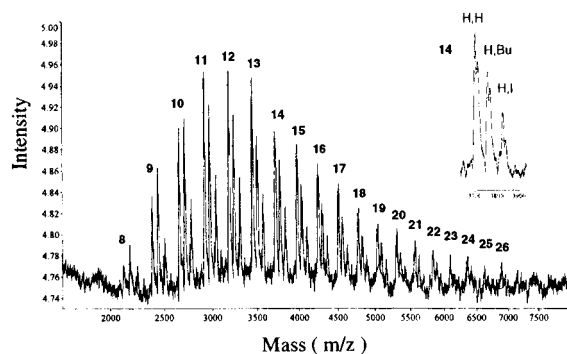
Figure 1. MALDI-TOF mass spectrum of poly(2,5-silole) **1**. The insert represents a magnification of the peaks of 14mers.

Figure 2. UV−vis absorption spectra of poly(2,5-silole) **1** in 2-methyl-tetrahydrofuran: at 293 K, solid line; at 153 K, dashed line.

presence of 0.01 molar amount of $PdCl_2(PPh_3)_2$ was carried out.[17] Reprecipitation from ethanol actually afforded poly(2,5-silole) **1** in 29% yield as a red powder.[18] The polymer is stable in the air and soluble in common organic solvents such as THF and chloroform.

The ^1H NMR spectrum of **1** shows three sharp singlet peaks in the aliphatic region, which are assigned to the methyl and methylene protons of the methoxymethyl groups and the ring-methylene protons, indicative of its regular structure. In addition, a small singlet peak observed at 5.45 ppm indicates the hydrogen atoms as one of the terminal groups. The structure of **1** was also confirmed by ^{13}C and ^{29}Si NMR spectroscopies[18] and by MALDI-TOF mass spectrometry. Figure 1 represents the mass spectrum, where the peaks from the 8mer to the 26mer are discernible. The number-averaged molecular weight (M_n) determined by this method is 3730, which confirms those estimated by GPC analysis using polystyrene standards: $M_w = 4560$ and $M_n = 3440$ (PDI = 1.33). The degree of polymerization is about 13. It should be noted here that, in the mass spectrum, three peaks are observed for each oligomer as shown in the insert of Figure 1, which correspond, with satisfactory accuracy, to oligomers having (H,H), (H,Bu), and (H,I) terminal group sets, respectively.[19] The incorporation of a butyl group as the terminal group suggests that one of the termination reaction for the present polymerization is the coupling with butyl iodide, which was generated in the lithium−halogen exchange step.[17]

As preliminary results of the characteristics, we have found the unique photophysical properties of polymer **1**. Figure 2 represents the UV−vis absorption spectra of **1**. The polymer has its absorption band at 482 nm in 2-MeTHF at 293 K. This is more than 140 nm longer than that of its model compound, silole dimer **8** (λ_{max} 340 nm),[11c] indicating that π-conjugation is extended to some extent in polymer **1**. Interestingly, the absorption is largely dependent on the measurement temperature. Thus, as the temperature is decreased, the λ_{max} of **1** shifts to longer wavelengths up to 542 nm at 153 K (Figure 2). This large bathochromic shift is probably due to the change in the effective conjugation length by the conformational change of the main chain. Actually, it has already been proven that the dimer **8** has a considerably twisted ($\sim 60°$) syn-arrangement of the two silole rings in the crystal structure due to the steric congestion by the substituents on the silole rings.[11c,20]

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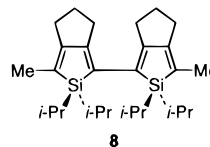
In summary, the Pd(0)-catalyzed cross-coupling reaction of the mono-zincated intermediate, derived from the newly synthesized 2,5-diiodosilole, successfully produced poly(2,5-silole). Although the molecular weight of the present polymer is still rather low, this is the first synthesis of the well-defined poly(2,5-silole). Further studies on the improvement of the molecular weight as well as other properties of the present polymer are currently in progress.

Supporting Information Available: Experimental procedures and data for all new compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) For the present polymerization, interestingly, the amount of the palladium catalyst was critical. The use of larger amounts of catalyst significantly decreased the molecular weight of the polymer and, when a 0.10 molar amount of catalyst was employed, no polymeric materials were obtained by reprecipitation from methanol. Under such conditions, the coupling reaction with butyl iodide seemed to significantly compete.

(18) **1**: ^1H NMR (CDCl₃) δ 0.66−1.05 (m, 10H, ethyl), 2.16 (s, 4H, ring CH_2), 3.27 (s, 4H, MeOCH_2), 3.31 (s, 6H, OCH_3), and a small singlet peak assignable to the terminal proton is observed at 5.45. ^{13}C NMR (CDCl₃) δ 5.59, 7.51, 37.06, 48.72, 59.18, 75.54, 131.45, 155.63, and, in addition, small peaks at 5.59, 8.00, 114.48, 134.14, 154.16, 164.92. The peaks only for the H-terminated silole ring seem to be observed among the several possible terminal silole rings. ^{29}Si NMR (CDCl₃) δ 23.24 and small peaks at 21.57 and 24.12 ppm. UV−vis (CHCl₃) λ_{max} 485 nm, log ϵ 3.73 (per silole unit) at 293K.

(19) For example, the calculated molecular weights for 14mers having (H,H), (H,Bu), and (H,I) terminal sets are 3700.18, 3756.24, and 3826.08, respectively. Their found masses are 3700.4, 3755.9, and 3825.1, respectively.
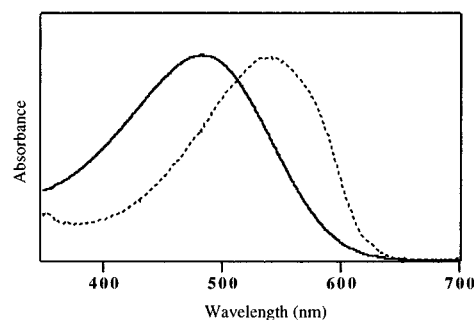
(20) Polymer **1** shows no fluorescence at room temperature, probably due to the noncoplanar conformation of the polymer main chain.