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Dehydrocoupling of 1,1-Dihydrotetraphenylsilole to an Electroluminescent Polysilole

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*Summary: Catalytic dehydrocoupling of 1,1-dihydrotetraphenylsilole (**1**) with various inorganic hydrides produces electroluminescent polysiloles (**2**) in high yield. The polymerization yield and molecular weight increase in the order* $LiB[CH(CH_3)C_2H_5]_3H < NaB[CH(CH_3)C_2H_5]_3H < KB[CH(CH_3)C_2H_5]_3H$*. The polymerization yields are almost equal for* $Na[H_2Al(OCH_2CH_2OCH_3)_2]$, $KB[CH(CH_3)C_2H_5]_3H$*, and* $LiB(C_2H_5)_3H$*, but the molecular weights increase in the order* $Na[H_2Al(OCH_2CH_2OCH_3)_2] < KB[CH(CH_3)C_2H_5]_3H < LiB(C_2H_5)_3H$*. The polysiloles emit green light at 520 nm and are electroluminescent at 520 nm.*

Introduction

Polysilanes with low oxidation potentials and a high-lying HOMO show unusual optical and electronic properties due to σ-conjugation along the silicon backbone chain.[1] Applications of polysilanes as ceramic precursors, third-order NLO materials, deep-UV photoresists, photoconductors, and photoinitiators have been mentioned.[2,3] The Wurtz coupling reaction of dichlorosilanes to polysilanes is intolerant of some functional groups, and this procedure possesses other limitations such as in controlling the stereochemistry and molecular weight. The discovery of group 4 metallocene-catalyzed dehydrocoupling reactions of primary hydrosilanes to polysilanes provides an alternative route in polyorganosilane synthesis.[4−6]

Siloles, silacyclopentadienes, with low reduction potential and a low-lying LUMO, have attracted considerable attention because of their peculiar electronic properties.[7] They may be used for electron-transporting materials in devices.[8] The silacyclopentadiene moiety could be essential to the luminescent property because silacycloheptadienes do not luminesce.[9] Tang and collaborators reported that a silole did not luminesce in diluted solution but did luminesce in concentrated solution.[7] Polysiloles could thus show different luminescent behavior from that of monomeric siloles. Polysiloles can be synthesized by 1,1- or 2,5-coupling reaction of siloles by various synthetic coupling methods.[10] The electroluminescent poly(silole-*co*-silane)s have also been synthesized in several laboratories.[11] West and co-workers reported recently the synthesis of polysiloles ($M_w = 5200-5700$) that have methoxy end groups in 30−37% yield by heterogeneous Wurtz coupling of 1,1-dichlorotetraphenylsilole with 2.0 equiv of Li, Na, or K metal in refluxing THF for 3 days.[10a] Some oligomers were also isolated along with the polysilole when 1.2 equiv of the metal was used at room temperature for 1 day. Tamao and collaborators had earlier reported the Wurtz coupling synthesis of polysiloles.[10d] The homogeneous dehydrocoupling of 1,1-dihydrotetraphenylsilole (**1**) to a polysilole (**2**) having hydrogen end groups was reported in our recent preliminary report[12] and Tanaka's earlier report of the dehydrocoupling synthesis of poly(dibenzosilole).[13] Here we report our detailed study on the high-yield synthesis under mild conditions (room temperature for 1 day) of electroluminescent **2** having hydrogen end groups by the catalytic dehydrocoupling reaction of **1** with inorganic hydrides such as Selectrides ($MB[CH(CH_3)C_2H_5]_3H$; M = Li, Na, K), Red-Al ($Na[H_2Al(OCH_2CH_2OCH_3)_2]$), and Super-Hydride ($LiB(C_2H_5)_3H$).

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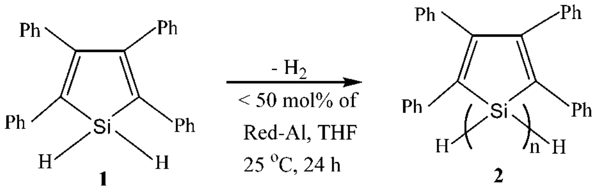
Results and Discussion

Synthesis of 1. 1,1-Dihydrotetraphenylsilole (**1**) is best prepared by the nucleophilic ring formation of 1,4-dilithiotetraphenylbutadiene with an excess of H_2SiCl_2 in THF at liquid nitrogen temperature with subsequent warming to room temperature.[14] The reduction of 1,1-dichlorotetraphenylsilole[15] with $LiAlH_4$ is not a good route to **1** since the latter will undergo premature and uncontrolled dehydrocoupling to polysilole (**2**).

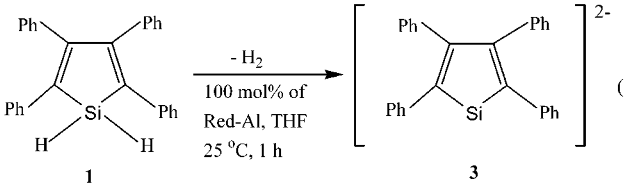
Synthesis of 2. Dehydrocoupling of **1** catalyzed by <50 mol % (i.e., M−H/Si−H = 0.5 or less) of Red-Al was initiated rapidly, as evidenced by the immediate evolution of hydrogen gas (eq 1). To complete the reaction,



(1)

the mixture was stirred at room temperature for 24 h.

Polymers with molecular weight (M_w) of 4600 and 4100 were isolated in 86% and 78% yields when 15 and 50 mol % of Red-Al was used, respectively, after workup including column chromatography and precipitation from methanol as light yellow powders. As expected, when 15 mol % of Red-Al was used, the polymer yield and the molecular weight were higher compared to when 50 mol % of Red-Al was used. Products from the reaction of **1** with 15, 25, and 50 mol % Red-Al were subjected to separation by preparative GPC and characterization by NMR spectroscopy. Shorter oligomers such as silole dimer or trimer were not found in products. However, when 100 mol % of Red-Al (i.e., M−H/Si−H = 1) was used, the silole dianion **3**[15,16] was obtained without forming **2** (eq 2).



(2)

Similar dehydrocoupling of **1** to **2** also was carried out using 15 mol % of Selectrides and Super-Hydride at 25 °C for 24 h. The polysiloles were obtained in 77−87% isolated yield, respectively. The molecular weight (M_w) and polydispersity index (PDI) of all the polysiloles were in the range 4300−5800 and 1.1−1.2, respectively. End-group analysis was performed to determine the chain length by integrating the peak area for the phenyl protons and Si−H protons in the proton NMR spectra. A ratio of about 15−17 siloles to 2 Si−H groups was observed. To confirm the result of the end-group analysis, the Si−H end groups were transformed to Si−OMe by reacting **2** with an excess of CCl_4 for 48 h to convert Si−H to Si−Cl, followed by reaction with methanol. A ratio of about 14−16 siloles to 2 Si−OMe groups was found, which is in reasonably good agreement with the Si−H derived value. The chain length from the end-group analysis is consistent with the polymer molecular weight determined by GPC. The polymerization yield and molecular weight increased in the order L-Selectride < N-Selectride < K-Selectride. The trend appears to be related to the ionic character of the Selectrides. The polymerization yields were almost equal for Red-Al, K-Selectride, and Super-Hydride, but the molecular weight increased in the order Red-Al < K-Selectride < Super-Hydride. The results are summarized in Table 1.

Table 1. Characterization for the Catalytic Dehydrocoupling of 1 to 2[a]

catalyst	yield (%)	mol wt M_w	mol wt M_n
Red-Al	86	4600	3900
Red-Al[b]	78	4100	3600
Red-Al[c]	0	silole dianion formed	
L-Selectride	77	4300	3900
N-Selectride	82	4800	4100
K-Selectride	88	5700	4800
Super-Hydride	87	5800	4900
n-BuLi	0	substitution occurred	
heating[d]	0	no reaction observed	
UV-irradiation[e]	0	no reaction observed	

[a] Reaction in THF at 25 °C for 24 h, a catalyst concentration (M−H/Si−H) of 15 mol % except where stated otherwise. [b] Catalyst concentration of 50 mol %. [c] Catalyst concentration of 100 mol %. [d] In neat at 150 °C for 12 h. [e] 300 nm for 12 h in THF.

When Super-Deuteride was used instead of Super-Hydride, the end groups of Si−H of **2** were found to be deuterium-incorporated (confirmed by ^2H NMR spectroscopy). However, BH_3-THF was ineffective for the dehydrocoupling at 25 °C for 24 h. Like the polysiloles prepared by West and co-workers,[10a] these polysiloles have a characteristic UV absorption around 300 nm, assigned to the $\sigma-\sigma^*$ transition of the Si−Si backbone chain. They are photoluminescent, emitting green light at 520 nm when the excitation is at 330 nm. These polysiloles are strongly electroluminescent around 520 nm. No appreciable characteristic Si−O−Si band was observed in the IR spectra of the polysiloles.

The present dehydrocoupling of moisture-insensitive **1** to **2** is a homogeneous reaction, while the Wurtz dechlorocoupling of moisture-sensitive 1,1-dichlorotetraphenylsilole to **2**[10a] is a heterogeneous reaction. The dehydrocoupling reaction possibly can be monitored and controlled. Although the molecular weights of the polysiloles produced via the dehydrocoupling reaction are similar to those produced via Wurtz coupling, the present dehydrocoupling reaction occurred under milder conditions (e.g., room temperature/1 day vs THF-refluxing temperature/3 days) and produced polysiloles in higher yield when compared to the Wurtz coupling reaction (e.g., 82−86% vs 30−37%). For the dehydrocoupling reaction of **1** to **2**, K-Selectride and Super-Hydride were the most active catalysts examined. Catalysis of the **1** to **2** conversion by Cp_2MCl_2/Red-Al (M = Ti, Zr, Hf) (a system that was recently found to give predominantly linear polysilanes of higher molec-

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ular weight than any other catalyst system for phenylsilane) was found to be ineffective in the dehydrocoupling of **1** because **1** is sterically hindered. Therefore, the dehydrocoupling mechanism of **1** catalzed by the inorganic complex hydrides must be different from that (i.e., σ-bond metathesis[5a−e]) of phenylsilane catalyzed by the Cp_2MCl_2/Red-Al (M = Ti, Zr, Hf). Although enough experimental data are not currently available, some comments on the mechanism of the dehydrocoupling of **1** to **2** seem appropriate based on the following facts: (1) when Super-Deuteride was used for the dehydrocoupling of **1** instead of Super-Hydride, the end groups of Si−H of **2** were found to be deuterium-incorporated (<5%, determined using benzene-d_6 as an internal reference by ^{2}H NMR spectroscopy, when 20 mol % Super-Deuteride was used as catalyst) and (**2**) **1** could not be dehydrocoupled upon heating at 150 °C and UV-irradiating in the absence of inorganic hydride. We thus propose a mechanism involving the preferential attack of a hydride ion on either the silicon atom or silole ring of **1** to form an activated anionic intermediate such as either a pentacoordinated σ-complex or a π-complex.[16] The activated anionic intermediate could lose both a dihydrogen molecule and a hydride ion (this hydride may participate again in the catalytic cycle) sequentially to form a silylene type of silole. If the activated anionic intermediate accepts another hydride ion, a silole dianion **3** will be formed after losing two dihydrogen molecules.[17] The silylene type of silole will then either self-couple or keep inserting into the Si−H bond of **1**, forming **2**. A study of codehydrocoupling of **1** and 1,1-dihydrotetraphenylgermole using the inorganic hydrides is in progress, and the results will be published elsewhere in due course.[18]

Experimental Section

General Considerations. All reactions and manipulations were performed under prepurified argon atmosphere using Schlenk techniques. Dry, oxygen-free solvents were employed throughout. Glassware was flame-dried or oven-dried before use. Elemental analyses were performed by the Advanced Analysis Center of the Korea Institute of Science and Technology, Seoul, Korea. Infrared spectra were obtained using a Perkin-Elmer 1600 Series FT-IR spectrometer. Electronic spectra were acquired using an IBM 9420 UV−vis spectrophotometer. The photoluminescence spectra of polysilole thin films, which were prepared by spin-casting from a toluene solution of polysilole, were measured at ambient temperature using a Shimadzu RF-5300PC fluorescence spectrometer. The LEDs (active area: 2.4×3 mm^2) were prepared by the spin-coating of polysilole on a clean ITO glass plate (resistance: 30 hm/cm^{-2}) and the subsequest vacuum-deposition of an Mg:Ag layer as a cathode at a pressure of 1×10^{-6} mmHg. The LEDs were operated at 100 μA of pulse current. Proton NMR spectra were recorded on a Varian Gemini 300 spectrometer using $CDCl_3/CHCl_3$ as a reference at 7.24 ppm downfield from TMS. Deuterium NMR spectra were obtained using a Varian Gemini 300 (operating at 46.1 MHz) spectrometer using $CHCl_3/CDCl_3$ as a reference. Carbon-13 NMR spectra were obtained using a Varian Gemini 300 (operating at 75.5 MHz) spectrometer using $CDCl_3$ as a reference at 77.0 ppm. Silicon-29 NMR spectra were obtained using a Varian Gemini 300 (operating at 59.6 MHz) spectrometer using TMS as a reference at 0.0 ppm and an INEPT sequence to enhance signals. Gel permeation chromatography (GPC) was carried out on a Waters Millipore GPC liquid chromatograph. The calibrant (monodisperse polystyrene) and the sample were dissolved in THF and separately eluted from an Ultrastyragel GPC column series (sequence 500, 10^3, 10^4 Å columns). Molecular weights were extrapolated from the calibration curve derived from the polystyrene standard, assuming that the solution structure of polysilole **2** is similar to that of polystyrene. Data analyses were carried out using a Waters Data Module 570. For the photolysis experiments a Raynot photochemical reactor model RPR-2080 made by the Southern N. E. Ultraviolet Co. was used. The built-in monochromatic UV light sources (RUL-300 nm UV lamp; lamp intensity = 6.93×10^{18} hν mL^{-1} min^{-1}) was positioned approximately 17 cm from the reaction quartz tubes. $PhSiH_3$, Cp_2MCl_2 (M = Ti, Zr, Hf), BH_3-THF (1.0 M in THF), *n*-BuLi (1.6 M in hexane), Red-Al ($Na[H_2Al(OCH_2CH_2OCH_3)_2]$; 3.4 M in toluene), Selectrides ($MB[CH(CH_3)C_2H_5]_3H$; M = Li, Na, K; 1.0 M in THF), Super-Hydride ($LiB(C_2H_5)_3H$; 1.0 M in THF), and Super-Deuteride ($LiB(C_2H_5)_3D$; 1.0 M in THF) were purchased from Aldrich Chemical Co. and were used as received. **1** [IR (neat, film, cm^{-1}): 2126 s (ν_{Si-H}), 916 s (δ_{Si-H}). ^{1}H NMR (δ, $CDCl_3$, 300 MHz): 4.91 (s, 2H, SiH_2), 6.81−7.18 (m, 20H, PhH). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 75.5 MHz): 126.13, 126.55, 128.43, 128.54, 129.87, 129.96 (ph), 135.11, 139.51, 158.26 (silole carbons). ^{29}Si NMR (δ, $CDCl_3$, 59.6 MHz): −35.03] was prepared by the reaction of 1,4-dilithiotetraphenylbutadiene with excess dichlorosilane (purchased from Aldrich Chemical Co.; ***Precaution!*** *Dichlorosilane should be handled carefully under a dry argon atmosphere because it inflames in air*) in THF first at liquid nitrogen temperature and then at room temperature.[14]

Dehydrocoupling of 1 to 2 Catalyzed by Red-Al. The following procedure is representative of the dehydrocoupling reactions catalyzed by inorganic hydrides such as Red-Al, Selectrides, and Super-Hydride. To a Schlenk flask containing **1** (1.0 g, 0.58 mmol) in THF (5 mL) was injected Red-Al (13.2 μL, 0.045 mmol, 0.09 mmol equiv of H^-). The reaction mixture immediately turned burgundy red with mild gas evolution and finally yielded a clear orange solution. The mixture was stirred under a stream of nitrogen for 24 h. The catalyst was allowed to oxidize by exposure to the air for a few seconds, and the solution then was passed rapidly through a silica gel column (70−230 mesh, 20 cm × 2 cm) where the top was layered with a 3 cm thick pad of Celite. The column was rinsed with 200 mL of THF. The removal of volatiles at reduced pressure gave a yellow powder. The latter was taken up in 3 mL of THF, and the resulting solution was poured into 100 mL of methanol. Filtration and drying in vacuo yielded 0.86 g (86% yield) of **2** as a light yellow powder. Anal. Calcd for $C_{28}H_{20}Si$: C, 87.45; H, 5.24. Found: C, 87.50; H, 5.29. UV−vis (THF): $\lambda_{\sigma\to\sigma^*}$ 300 nm. PL (film): 520 nm (excitation at 330 nm). EL: 520 nm. IR (neat, film, cm^{-1}): 2130 s (ν_{Si-H}). ^{1}H NMR (δ, $CDCl_3$, 300 MHz): 4.46 (SiH), 6.80−7.40 (m, br, PhH). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 75.5 MHz): 125−132 (m, silole carbons), 137−147 (br, m, Ph). ^{29}Si NMR (δ, $CDCl_3$, 59.6 MHz): −34.21 (end group), −40.85 (backbone). GPC: $M_w = 4600$, $M_n = 3900$, $M_w/M_n = 1.18$). However, the similar reaction with *n*-BuLi instead of hydride did not give **2** but instead gave a small amount of butyl derivatives of **1** along with **1**.

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