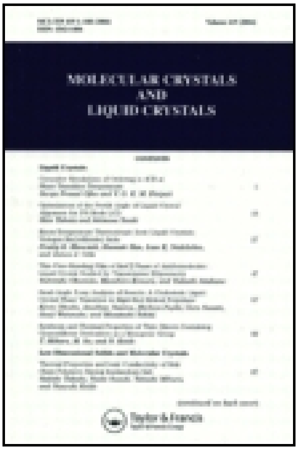

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Catenation of 1,1-dichlorotertaphenylsilole and 1,1-dichlorotetraphenylgermole to optoelectronic polymers

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CATENATION OF 1,1-DICHLOROTERTAPHENYLSILOLE AND 1,1-DICHLOROTETRAPHENYLGERMOLE TO OPTOELECTRONIC POLYMERS

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Combinative dechloro/dehydro catenation of 1,1-dichlorotetraphenylsilole **1** *with* < 150 *mol% of various inorganic hydrides in THF at 25°C produces optoelectronic polysiloles* **2** *in high yield. Similarly, cocatenation of* **1** *and 1,1-dichlorotetraphenylgermole* **4** *(9:1 mole ratio) using 110 mol% of Red-Al in THF at 25°C gives poly(silole-co-germole)* **5** *in high yield. The polymers emit green light at 520 nm and are strongly electroluminescent at 520 nm.*

Keywords: catenation; electroluminescence; green light; inorganic hydride; photoluminescence; polysilole

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INTRODUCTION

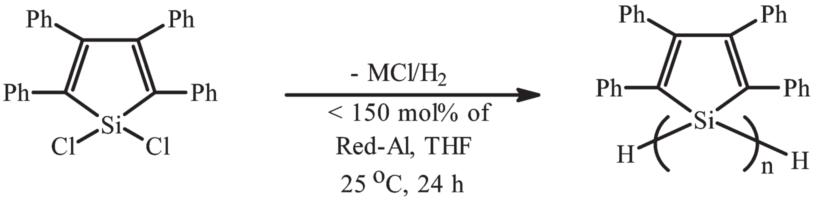
Polysilanes with low oxidation potentials and a high-lying HOMO exhibit unusual optoelectronic properties due to σ-conjuation along the silicon backbone chain [1]. Versatile applications of polysilanes as ceramic precursors, third-order NLO materials, deep-UV photoresists, photoconductors, and photoinitiators have been described [2]. The discovery of group 4 metallocene-catalyzed dehydrocoupling reactions of primary hydrosilanes to polysilanes provides an alternative route of Wurtz coupling in polyorganosilane synthesis [3–5].

Siloles, silacyclopentadienes, with low reduction potential and a low-lying LUMO, have attracted considerable attention because of their peculiar electronic properties [6]. Silicon-catenated polysiloles can be regarded as a new class of polysilanes with σ^*–π^* conjugation between the σ^*–orbital delocalized over the polysilane backbone chain and the π^*–orbital delocalized on the *cis*-butadiene moiety in every silole ring. They can be used for electron-transporting materials in devices such as light-emitting diodes (LED's) [7]. The silacyclopentadiene moiety could be essential to the luminescent property because silacycloheptadiene do not luminesce [8]. West and coworkers reported recently the synthesis of polysiloles ($M_w = 5.2 \times 10^3$–5.7×10^3) that have methoxy end groups in 30–37% of moderate yield by heterogeneous Wurtz-dechlorocoupling of 1,1-dichloro-tetraphenylsilole **1** with 2.0 equiv of Li, Na, or K metal in refluxing THF for 3 days [9]. Very recently, we reported the homogeneous catalytic dehydrocoupling in THF at 25°C for 1 day of 1,1-dihydrotetraphenylsilole to an optoelectronic polysilole ($M_w = 4.1 \times 10^3$–5.8×10^3) having hydrogen end groups in the presence of catalytic inorganic hydride [10]. In this paper we report the high-yield synthesis under mild conditions (25°C for 1 day) of optoelectronic polysiloles **2** and poly(silole-*co*-germole) **5** having hydrogen end groups by the combinative dechloro/dehydro catenation of **1** and 1,1-dichlorotetraphenylgermole **4** 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 ($LiB(C_2H_5)_3H$).

RESULTS AND DISCUSSION

Combinative dechloro/dehydro catenation of **1** catalyzed by < 150 mol% (*i.e.,* $M{-}H/Si{-}Cl = 1.5$ or less) of Red-Al was initiated rapidly, as evidenced by the immediate evolution of hydrogen gas (Fig. 1).

Polysiloles **2** with the weight average molecular weights (M_w) of 4.65×10^3 (PDI index = 1.19) and 4.05×10^3 (PDI index = 1.13) were isolated 24 h later in 82% and 75% yields when 110 mol% and 150 mol% of

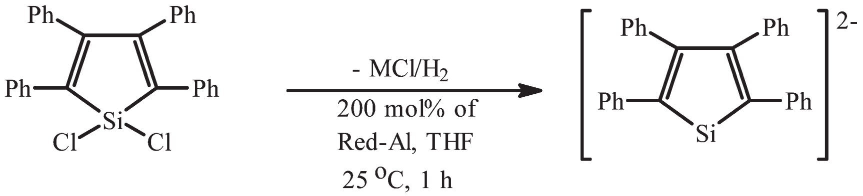


1 **2**

FIGURE 1 Catenation of **1** to **2** using < 150 mol% of Red-Al in THF at 25°C.

Red-Al were used, respectively, after workup including column chromatography and precipitation from methanol as yellow powders. As expected, when 110 mol% of Red-Al was used, the polymer yield and the polymer molecular weight were higher compared to when 150 mol% of Red-Al was used. However, when 200 mole% of Red-Al (*i.e.*, M-H/Si-Cl = 2) was used, the silole dianion **3** [11] was obtained without forming **2** (Fig. 2).

Similar dechloro/dehydro catenation of **1** to **2** was also carried out using 110 mol% of Selectrides and Super-Hydride at 25°C for 24 h. The polysiloles were obtained in 75–85% isolated yield, respectively. The NMR and IR spectral data are the same as those of polysiloles prepared by the dehydrocoupling of 1,1-dihydrotetraphenylsilole, catalyzed by the inorganic hydrides [10]. The molecular weight (M_w) and polydispersity index (PDI) of all the polysiloles were in the range of 4.05×10^3–5.80×10^3 and 1.1–1.2, respectively. The polymerization yield and polymer molecular weight increased in the order of 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 polymer molecular weight increased in the order of Red-Al < K-Selectride < Super-Hydride. However, the similar reaction of **1** with *n*-BuLi instead of the inorganic hydride did not give **2** but instead gave only the butyl derivative of **1**. The results are summarized in Table 1.



1 **3**

FIGURE 2 Formation of silole dianion **3** from **1** using 200 mol% of Red-Al in THF at 25°C.

TABLE 1 Characterization for the Catenation of **1** to **2**[a]

Hydrides	Yield (%)	Mol wt[d] $M_w \times 10^{-3}$	$M_n \times 10^{-3}$
Red-Al	82	4.65	3.92
Red-Al[b]	75	4.05	3.58
Red-Al[c]	0	silole dianion formed	
L-Selectride	75	4.35	3.90
N-Selectride	80	4.85	4.13
K-Selectride	85	5.75	4.85
Super-Hydride	85	5.80	4.91
n-BuLi	0	substitution occurred	

[a] Reactions were carried out in THF at 25°C for 24 h.; a mole ratio of M-H/Si-Cl = 1.1:1.0 was used except where stated otherwise.

[b] A mole ratio of M-H/Si-Cl = 1.5:1.0 was used.

[c] A mole ratio of M-H/Si-Cl = 2.0:1.0 was used.

[d] Determined by GPC in THF (*vs* polystyrene).

Dechloro/dehydro catenation of **1** and 1,1-dichlorotetraphenylgermole **4** (9:1 mole ratio) using 110 mol% of Red-Al in THF at 25°C gave poly(silole-*co*-germole) **5** in 83% isolated yield (Fig. 3).

The characterization data of **5** are as follows: IR (neat, film, cm^{-1}): 2130 s (ν_{SiH}), 1960 w (ν_{GeH}). ^1H NMR (δ, $CDCl_3$, 300MHz): 4.46 (SiH), 5.51 (GeH), 6.70–7.80 (m, br, PhH). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 75.5 MHz): 125–135 (m, silole-germole carbons), 137–147 (br, m, Ph). ^{29}Si NMR (δ, $CDCl_3$, 59.6 MHz): −34.21 (end group), −39.90, −40.80 (backbone). GPC: $M_w = 4.73 \times 10^3$; $M_n = 4.0 \times 10^3$, $M_w/M_n = 1.18$. Like the polysiloles prepared by West [9] and us [10], these polysiloles **2** and poly(silole-*co*-germole) **5** have a characteristic UV absorption around 300 nm assigned to the $\sigma-\sigma^*$ transition of the Si—Si (Ge) backbone chain.

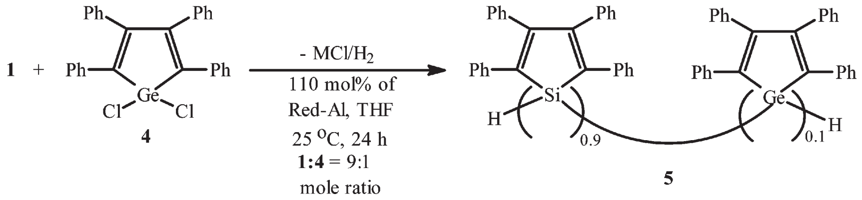


FIGURE 3 Cocatenation **1** and **4** (in 9:1 mole ratio) to **5** using 110 mol% of Red-Al in THF at 25°C.

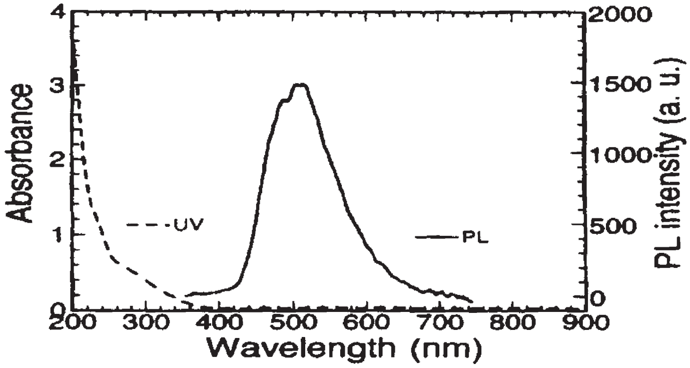


FIGURE 4 Absorption and photoluminescence spectra of **5** at 25°C.

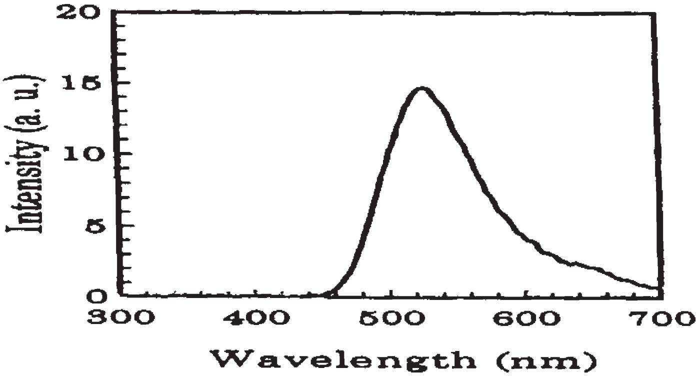


FIGURE 5 Electroluminescence spectrum of **5** at 25°C.

They are photoluminescent, emitting green light at 520 nm when the excitation is at 330 nm.

The photoluminescence spectra of polymer thin film, which were prepared by spin-casting from a toluene solution of polymer, were measured at ambient temperature using a Shimadzu RF-5300PC fluorescence spectrometer. They are strongly electroluminescent around 520 nm. The LEDs (active area: $2.4 \times 3\,\mathrm{mm}^2$) were prepared by the spin-coating of polymer on a clean ITO glass plate (resistance: $30\,\mathrm{ohm/cm}^{-2}$) and the subsequent 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. No appreciable characteristic Si–O–Si band was observed in the IR spectra of **2** and **5**.

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