

## Dehydrogenative Polymerization of Hydrosilanes to Silicon Polymers

Myoung-Hee Kim, Jun Lee, Soo-Yong Mo, Jong-Hyun Kim and Hee-Gweon Woo<sup>†</sup>

### Abstract

Hydrosilanes possessing reactive Si-H bond are used in synthesizing various types of polysilanes by dehydrocoupling under the influence of various organometallic promoters.<sup>4,2</sup> Catalytic Si-Si/Si-O coupling of hydrosilanes with hydrosilanes, alcohols, and lactones to silicon-based polymers are described in this article as selective examples of our recent research developments. These silicon-containing polymers can be used as a precursor to prepare useful functional materials for fabricating electronic devices.

**Key words** : Polysilane, Dehydrocoupling, Hydrosilanes, Catalyst

### 1. Introduction

Organic polymers have been very essential for our daily life. The polymers are composed of mainly carbon (group 4A or group 14) elements connected together or separated by heteroatoms such as oxygen or nitrogen.<sup>[1]</sup> Most of them seldom decompose in nature and burn with the release of toxic chemicals as well, leading to serious environmental pollution and fatal damage. Furthermore, the availability of raw materials for organic polymers is limited by the expected shortage of petroleum/coal natural resources.<sup>[2]</sup> Main group metal-containing and transition metal-containing inorganic polymers have been heavily reviewed by many authors<sup>[3]</sup> and are beyond the scope of this article. Main group metalloid-containing inorganic polymers possessing unusual properties are made up of mainly boron (group 3A or group 13), silicon/germanium/tin (group 14), phosphorous (group 5A or group 15), and sulfur (group 6A or group 16) atoms, which do not stem from petroleum/coal resources.<sup>[1b,2]</sup> In particular, silicon-based polymers exhibit quite unusual properties as advanced specialty materials.<sup>[4]</sup>

For the heavier elements in group 14 the formation of D-D bonds to produce a long chain polymer has proven to be difficult because stable unsaturated D=D

species, analogues of vinyl compounds, can be prepared only in the combination with sterically bulky substituents, which will deter their polymerization.<sup>[1,4-6]</sup> Wurtz-type coupling of dichlorosilanes using an alkali metal dispersion has widely been used in industry, but is very problematic. As an alternative, dehydrocoupling of hydrosilanes to polysilanes is a useful synthetic route. Hydrosilanes possess an Si-H bond (bond energy of 320 kJ/mole) that is more reactive than the C-H bond of hydrocarbons (bond energy of 416 kJ/mol).<sup>[7]</sup> This article mainly describes some of the recent advances that have been made by us with respect to silicon-based polymers prepared by dehydrocoupling of hydrosilanes.

### 2. Result and Discussion

#### 2.1. Linear-Selective Dehydrocoupling of Hydrosilanes to Polysilanes

Polysilanes are used for many applications in ceramics/composites, photoelectronics, photoresistors, and nonlinear optics.<sup>[8,9]</sup> The peculiar optoelectronic properties of polysilanes are due to sigma-conjugation of the silicon atoms in the polymer chain, varying with the molecular weight, conformation, and substituents of the polymer.<sup>[10a]</sup> Wurtz-type coupling of dihalosilanes with an alkali metal dispersion in toluene- or xylene-refluxing temperature has some serious problems: (1) intolerance of certain reducible functional groups, (2) lack of reproducibility from the heterogeneous reaction medium, and (3) limitations for controlling stereochemistry and molecular weight distribution. Some improve-

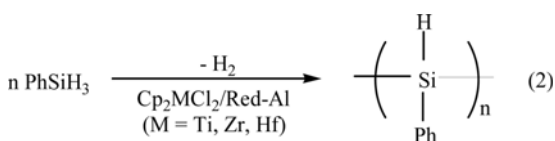
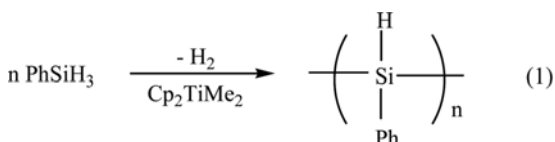
Nanotechnology Research Center and Department of Chemistry, Chonnam National University, Gwangju 500-757, Korea

<sup>†</sup>Corresponding author: hgwoo@jnu.ac.kr  
(Received : June 8, 2010, Revised : June 21, 2010,  
Accepted : June 24, 2010)

ments have been made by tuning several factors under ultrasonic activation.<sup>[10b]</sup> As an alternative, the catalytic dehydrocoupling of hydrosilanes, mediated by transition metal group 4 metallocene such as dimethyltitanocene or dimethylzirconocene, was first reported by Harrod and coworkers (eq. 1).

The dehydrocoupling of hydrosilanes generally produces a mixture of linear polysilanes and cyclic oligosilanes, leading to the decrease of polymer molecular weights and improper molecular weight distribution. Following studies to improve the disadvantage were intensively made with great efforts by many researchers worldwide.<sup>11-13</sup> For the selective production of linear polysilane the careful design of new group 4 metallocene-based catalyst systems is important with proper tuning of other factors such as addition rate/order of reagents, reaction temperature, etc.<sup>[12a]</sup> Linear (high molecular weight) polysilanes can be used as precursors for making functional polysilanes by introducing useful functional groups on the silicon atoms of linear polysilane backbone. Tilley group reported the synthesis of high molecular weight polyphenylsilanes with number-average molecular weight ( $M_n$ ) of *ca.* 5300 and 4700 g/mol by careful control of dehydrocoupling reaction conditions of phenylsilane using zirconocene-based catalysts.<sup>[12a,14]</sup> Tanaka<sup>[15]</sup> and Harrod<sup>[16]</sup> groups also prepared polyphenylsilanes with  $M_n$  of *ca.* 4600 and 7300 g/mol, respectively, from the dehydrocoupling of phenylsilane by using the zirconocene-based combination catalysts of  $[\text{Me}_2\text{N}(\text{CH}_2)_3\text{-H}_4\text{C}_5](\text{Me}_5\text{C}_5)\text{ZrCl}_2/2\text{MeLi}$  and  $\text{Cp}(\text{Me}_5\text{C}_5)\text{ZrCl}_2/2n\text{-BuLi}/(\text{C}_6\text{F}_5)_3\text{B}$ , respectively. A comprehensive survey of the catalytic dehydrocoupling of hydrosilanes under the influence of a wide range of early and late transition metal complexes was recently provided by Corey.<sup>[13b]</sup>

Woo and co-workers recently developed a facile, highly linear-selective dehydrocoupling catalyst system



of phenylsilane:  $\text{Cp}'_2\text{MCl}_2/\text{Hydride}$  ( $\text{Cp}' = \text{C}_5\text{H}_5$  or  $\text{C}_5\text{Me}_5$ ;  $\text{M} = \text{Ti, Zr, Hf}$ ; Hydride = Red-Al, Selectride, Super Hydride) combination catalysts (eq. 2).<sup>[11, 17]</sup>

Woo's in-situ catalyst system of  $\text{Cp}'_2\text{MCl}_2/\text{Hydride}$  is different from the catalyst systems using  $\text{Cp}'_2\text{MCl}_2/2\text{RLi}$  of Corey, Tanaka, and Harrod. True catalytic species in the dehydrocoupling of hydrosilanes could be a metallocene-based hydride according to the sigma-bond metathesis mechanism.<sup>[12,13b]</sup> Inorganic hydrides effectively can produce a metallocene hydride by Cl/H metathesis between inorganic hydride and metallocene dichloride whereas two alkyllithiums produce a metallocene hydride *via* a complex process (*e.g.*, reductive elimination of metallocene alkyls or reaction with hydrosilane after Cl/R metathesis). No appreciable induction period is observed for the  $\text{Cp}'_2\text{MCl}_2/\text{Hydride}$  combination catalyst. For  $\text{Cp}'_2\text{TiCl}_2/\text{Hydride}$  combination catalyst the molecular weight distributions measured from the GPC traces were bimodal, indicating the presence of linear polysilanes and cyclic oligosilanes. The formation of cyclic oligosilanes can be estimated by integration of the GPC peaks. The peaks corresponding to SiH in the  $^1\text{H}$  NMR spectrum can visually be separated as linear polysilane ( $\delta$  4.2 ~ 4.8 ppm range) and cyclic oligosilane ( $\delta$  4.9 ~ 5.3 ppm range). The formation of the cyclic oligosilanes can be also estimated by integration of the  $^1\text{H}$  NMR peaks, and is used as a means of cross-checking the cyclic/linear ratio. Woo *et al.* also examined the other group 4 metallocene-based combination catalysts for the dehydrocoupling of phenylsilane under various reaction conditions. The dehydrocoupling of phenylsilane with  $\text{Cp}'_2\text{MCl}_2/\text{Red-Al}$  ( $\text{M} = \text{Zr, Hf}$ ) combination catalysts rapidly produces mainly linear polyphenylsilanes. The linear selectivity increases in the order:  $\text{Cp}_2\text{Ti}$  (64%) <  $\text{Cp}_2\text{Zr}$  (92%) <  $\text{Cp}(\text{C}_5\text{Me}_5)\text{Zr}$  (95%) <  $\text{Cp}_2\text{Hf}$  (99%) <  $\text{Cp}(\text{C}_5\text{Me}_5)\text{Hf}$  (<99%).<sup>[17b]</sup> The higher linear-selectivity of the hafnocene relative to the zirconocene is likely due to the lower intrinsic dehydrocoupling activity (originating from stronger Hf-H and Hf-Si bond strengths). The lower linear-selectivity of titanocene relative to zirconocene and hafnocene is due probably to the combined effect of greater intrinsic dehydrocoupling activity (stemming from much weaker Ti-H and Ti-Si bond strengths) and much smaller atomic size (overriding steric crowding around the metal center) of Ti.<sup>[18]</sup> The change in linear selectivity is more pronounced than in other catalytic combination

systems:  $\text{Cp}_2\text{TiCl}_2/2\text{MeLi}$  (55%) <  $\text{Cp}_2\text{ZrCl}_2/2\text{MeLi}$  (75%),  $\text{Cp}_2\text{TiCl}_2/2n\text{-BuLi}$  (75%) <  $\text{Cp}(\text{C}_5\text{Me}_5)\text{ZrCl}_2/2n\text{-BuLi}$  (80%) <  $\text{Cp}_2\text{HfCl}_2/2\text{MeLi}$  (85%).<sup>[16,18]</sup> The coordinating environment around the metal center of the  $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$  combination catalysts could be different from other catalytic systems such as  $\text{Cp}_2\text{MCl}_2/2\text{R}'\text{Li}$ .<sup>[14,15,18,20]</sup> Red (or Vitride; sodium bis(2-methoxyethoxy)aluminum hydride;  $\text{Na}[\text{H}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OMe})_2]$ , soluble in toluene and commercially available) will be stoichiometrically converted into  $\text{Na}[\text{Cl}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OMe})_2]$  after reacting with dichlorometalocene. The coordinating structure of the present catalytic system could be similar to the zwitterionic structure in the  $\text{Cp}_2\text{ZrCl}_2/2n\text{-BuLi}/(\text{C}_6\text{F}_5)_3\text{B}$  catalytic system.<sup>[16,19]</sup> The  $\text{Na}[\text{Cl}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OMe})_2]$  moiety may influence by simply coordinating to the metal through an H, Cl-bridge or H, OMe-bridge between the group 4 metal and Al metal. The favorable steric demands imposed by the Cp ring and cocatalyst moiety could prevent the formation of the inactive dimer of metallocene hydride and could suppress the cyclic oligomer formation by chain scission reaction as well, leading to greater chain elongation.<sup>[15,16]</sup> However, an overriding steric demand results in low dehydrocoupling activity. The order of dehydrocoupling activity for the various zirconocenes turned out to be the same as the sequence of Tilley<sup>[12]</sup> and Harrod<sup>[16]</sup>:  $(\text{C}_5\text{Me}_5)_2\text{Zr} \ll \text{Cp}_2\text{Zr} < \text{Cp}(\text{C}_5\text{Me}_5)\text{Zr}$ . The  $(\text{C}_5\text{Me}_5)_2\text{ZrCl}_2/\text{Red-Al}$  combination catalyst thus slowly produces a mixture of dimer, trimer, and tetramer. In addition, the order of linear-selectivity for the dehydrocoupling of phenylsilane catalyzed by hydrides with  $\text{Cp}_2\text{ZrCl}_2$  was found to be Super Hydride (82%) < N-Selectride (88%) < Red-Al (92%).<sup>[17c]</sup> The dehydrocoupling of  $\text{PhCH}_2\text{SiH}_3$  yields only low-molecular weight oligomers since an alkylsilane is generally less reactive than an arylsilane.<sup>[20]</sup> The molecular weights of polymers increase with higher catalyst concentration (1 mol% versus 5 mol%), but it is little affected by longer reaction times (1 day versus 5 days).<sup>[17b]</sup> As expected, linear selectivity and molecular weights decrease with adding solvent and with heating, which was similarly observed in other catalytic systems.<sup>[12a,16]</sup> The reason could be because dilution and heating could hamper the tight coordination of the  $\text{Na}[\text{Cl}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OMe})_2]$  moiety to the metal center. The proper coordination of the aluminium moiety to the catalyst center should be necessary for the linear selectivity. Linear selectivity and molecular weights decrease

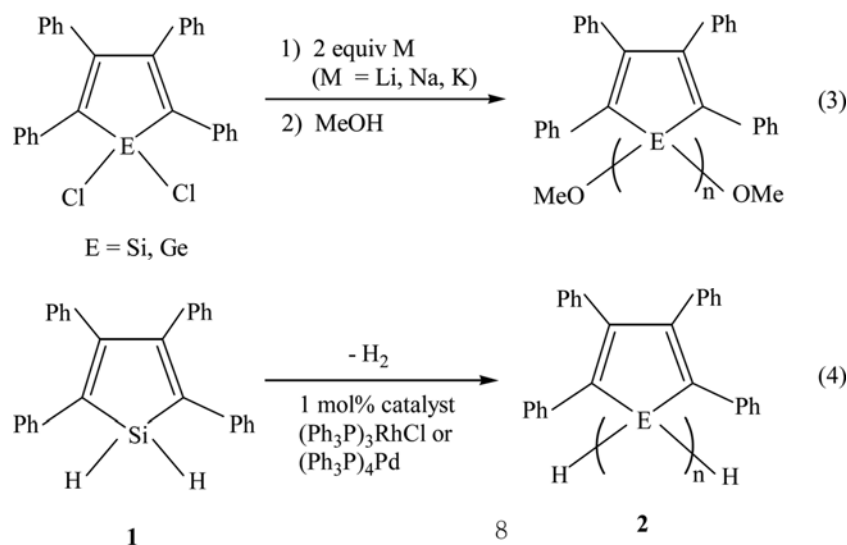
drastically by adding 4 Å molecular sieve (MS 4Å). The interaction of  $\text{Na}[\text{Cl}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OMe})_2]$  moiety with MS 4Å might prevent the close coordination of  $\text{Na}[\text{Cl}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OMe})_2]$  moiety to the metal center.<sup>[17b]</sup> An exact molar ratio of Red-Al to dichlorometalocene is necessary to replace both chlorines to attain high reactivity. The inactivity observed for higher molar ratios of Red-Al to dichlorometalocene could be attributed to over-complexation of Red-Al moieties to the metal, blocking the empty coordination site necessary for the dehydrocoupling of silane.<sup>[18]</sup> The poor activity is observed for lower molar ratios of Red-Al to dichlorometalocene. All the experimental results above described firmly suggest that better catalysts affording higher linear-selectivity and higher-molecular-weight polymer can be properly designed by tuning the steric and electronic character of the catalyst environment, including metal, ligand and co-catalyst moieties.

It is interesting to note that the dehydrocoupling of *p*-fluorophenylsilane using  $\text{Cp}_2\text{ZrCl}_2/\text{Red-Al}$  produced soluble amorphous polysilane (*ca.* 75%) and sparingly-soluble crystalline polysilane (*ca.* 25%) in toluene and chloroform. The two polysilanes are soluble in THF and pyridine. In comparison, the dehydrocoupling of *p*-fluorophenylsilane using  $\text{Cp}_2\text{TiCl}_2/\text{Red-Al}$  gives soluble polysilane only.<sup>[17c]</sup> The crystalline polysilane may have interactions<sup>[17b]</sup> in the polymer molecules either between Si and F with high possibility or between F and phenyl ring with low possibility according to the medium level of MO calculation.

Linear high molecular weight polysilanes can be used as precursors for making functional polysilanes by introducing functional groups on the linear polysilane. The Si-H bonds in the backbone chain of poly(hydrophenylsilane) are transformed to Si-Cl bonds using a mild chlorinating reagent,  $\text{CCl}_4$ . The Si-Cl bonds in the poly(chlorophenylsilane) can be replaced by various nucleophiles such as cyclopropyl, epoxy, aziridinyl, pyridyl, bipyridyl, phosphinyl, poly(ethylene oxide), thiol, etc. to give new functional polymers which can be used for applications in sensors, ion-exchange resins, batteries, drug delivery, metal nanomaterials preparation, etc.<sup>[17e]</sup>

## 2.2. Homodehydrocoupling and Codehydrocoupling of 1,1-Dihydrotetraphenylsilole and 1,1-Dihydrotetraphenylgermole to Electroluminescent Polymers

Polysilanes<sup>[21-23]</sup> having low oxidation potentials and



a high-lying HOMO display interesting optoelectronic properties due to sigma-conjugation along the silicon backbone chain in the polymer.<sup>[10,24]</sup> Siloles (silacyclopentadienes), with low reduction potential and low-lying LUMO's, have attracted considerable attention because of their unusual electronic properties.<sup>[25,26]</sup> They can be used as electron-transporting materials in devices.<sup>[27]</sup> A silole does not luminesce in diluted solution but does luminesce in concentrated solution, implying that polysiloles could exhibit different luminescent behavior from that of monomeric siloles.<sup>[25]</sup> Polysiloles, which are expected to have hybrid properties of polysilane and silole by nature in the structure, can be prepared by 1,1- or 2,5-coupling reactions of siloles using various synthetic coupling methods.<sup>[28]</sup> Electroluminescent poly(silole-co-silane)s have also been synthesized in several laboratories.<sup>[29]</sup> West *et al.* reported recently the synthesis of polysiloles and polygermole ( $M_w$  ca. 5200-5700 g/mol) that have methoxy end groups in 30-37% yield by heterogeneous Wurtz 1,1-dehydrocoupling of 1,1-dichlorotetra-phenylsilole with 2.0 equivalents of Li, Na, K metal in refluxing THF for 3 days (eq. 3).<sup>[28a]</sup>

Tamao and collaborators had earlier reported the Wurtz coupling synthesis of polysiloles.<sup>[28d]</sup>

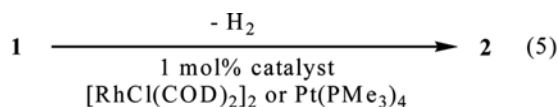
As an alternative to the Wurtz coupling of 1,1-dichlorosilole, the homogeneous dehydrocoupling methodology was demonstrated in Tanaka's earlier report of the dehydrocoupling synthesis of poly(dibenzosilole).<sup>[30a]</sup> Trogler and co-workers recently reported the 1,1-dehydrocoupling of 1,1-dihydro-tetra-phenylsilole (1) to an

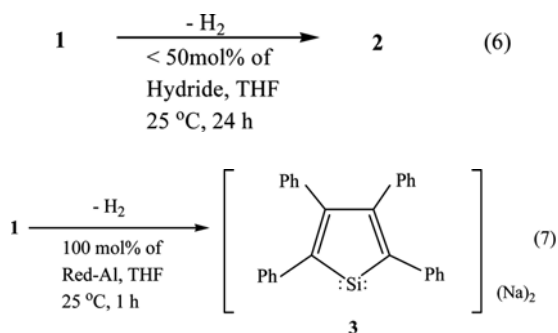
electroluminescent polysilole (2) ( $M_w$  ca. 4000-6000 g/mol), having hydrogen end groups, in high yield 80-90% yield using 1 mol% of the late transition metal complexes  $[(\text{Ph}_3\text{P})_3\text{RhCl}]$  and  $(\text{Ph}_3\text{P})_4\text{Pd}$  as catalysts (eq. 4).<sup>[29b,30b]</sup>

Similarly, Woo and co-workers prepared 2 ( $M_w$  ca. 5500-6200 g/mol) in > 95% yield by dehydrocoupling of 1 using  $[\text{RhCl}(\text{COD})_2]_2$  and  $\text{Pt}(\text{PMe}_3)_4$  as catalyst (eq. 5).<sup>[31]</sup>

The same authors also synthesized poly(tetra-phenylgermole) ( $M_w$  ca. 5800-6500 g/mol) in > 92% yield by dehydrocoupling of 1,1-dihydro-tetra-phenylgermole using the same catalysts. The UV-vis spectrum of poly(tetra-phenylgermole) shows an absorption at 377 nm, which is assignable to both the  $\sigma$ - $\sigma^*$  transition of the Ge-Ge backbone chain and  $\pi$ - $\pi^*$  transition of the germole ring. The polygermole is intensively photoluminescent, emitting green light at 487 nm.<sup>[31]</sup> The hydrogen end groups of the polysiloles and polygermoles are then transformed to other useful functional groups by various chemical reactions in usual manner.<sup>[31]</sup>

As an alternative to the heterogeneous Wurtz reductive coupling of dichlorosilole and the homogeneous late-transition-metal-complex-catalyzed dehydrocoupling





of **1**, Woo *et al.* also synthesized **2** in high yield by homogeneous dehydrocoupling of **1** under mild conditions, catalyzed with inorganic hydrides such as Selectrides {MB[CH(CH<sub>3</sub>)C<sub>2</sub>H<sub>5</sub>]<sub>3</sub>H; M = Li, Na, K}, Red-Al {Na[H<sub>2</sub>Al(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>]}, and Super-Hydride [LiB(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>H] as shown in eq. 6.<sup>[32a,b]</sup>

Dehydrocoupling of **1** catalyzed by < 50mol% (*i.e.*, M-H/Si-H = 0.5) of Red-Al yielded **2** as light yellow powders. Polymers with molecular weights (*M<sub>w</sub>*) of 4600 and 4100 g/mol were isolated in 86% and 78% yields when 15 mol% and 50 mol% of Red-Al were used, respectively. Polymer yields and molecular weights when 15 mol% of Red-Al was used were higher compared to polymers obtained when 50 mol% of Red-Al was used. Products from the reaction of **1** with 15 mol%, 25 mol%, and 50 mol% Red-Al were separated by preparative GPC and were characterized 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 formation of silole dianion **3**<sup>[33]</sup> was observed without forming **2** (eq. 7).

In the similar manner, the dehydrocoupling of **1** using 15 mol% of Selectrides and Super-Hydride at 25°C for 24 hours produces **2** in 77-78% isolated yield. The molecular weight (*M<sub>w</sub>*) and polydispersity index (PDI) of all the polysiloles are in the range of 4300-5800 g/mol and 1.1-1.2, respectively. Polymerization yield and polymer molecular weight increased in the order: L-Selectride < N-Selectride < K-Selectride. This trend appears to be closely 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. Like the polysiloles prepared by West and co-workers,<sup>[28a]</sup> these polysiloles have a characteristic UV absorption around 300 nm, assigned to the σ-σ\* 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. The similar dehydrocoupling of 1,1-dihydro-tetraphenylgermole with the hydrides produced polygermole in high yield. Furthermore the *co*-dehydrocoupling of **1** and 1,1-dihydro-tetraphenylgermole (with varying the mixing mole ratio) with the hydrides produced poly(silole-*co*-germole)s in high yield.<sup>[31]</sup>

For the dehydrocoupling reaction of **1** to **2**, K-Selectride and Super-Hydride were the most active catalysts

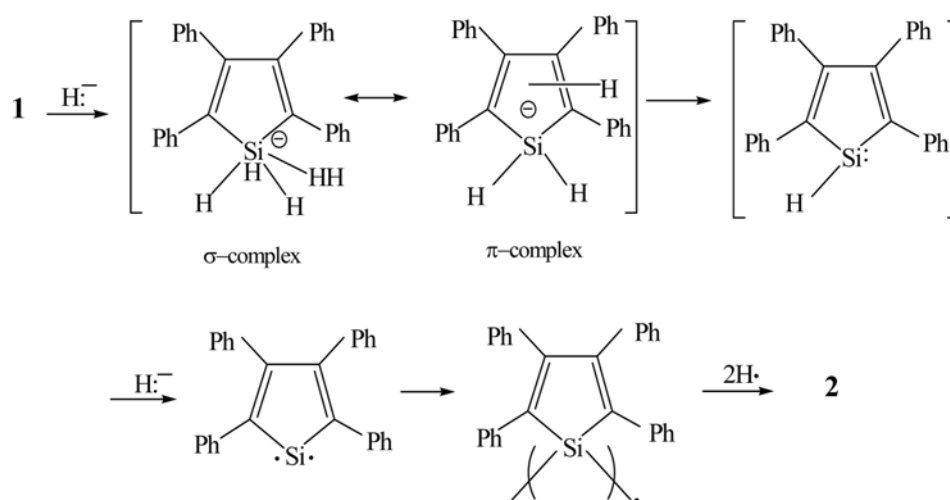


Fig. 1. Possible mechanism for the formation of polysilole **2** from the dehydrocoupling of **1**.

examined. **2** also can be prepared in high yield directly from the reaction of 1,1-dichlorotetraphenylsilole instead of **1** in the presence of < 1.5 equiv of Red-Al (instead of < 0.5 equiv).<sup>[32c]</sup> Unlike in the case of late-transition-metal-complex-catalyzed dehydrocoupling (generally proceeded by oxidative addition/reductive elimination processes),<sup>[30,31]</sup> catalysis for the conversion of **1** to **2** by early transition metallocenes, Cp<sub>2</sub>MCl<sub>2</sub>/Red-Al (M = Ti, Zr, Hf)<sup>[17]</sup> is ineffective in the dehydrocoupling of **1** because **1** is sterically demanding, considering that steric effect is dominant factor in the four-centered transition state in the sigma-bond metathesis mechanism.<sup>[12]</sup> Woo group proposed 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 a pentacoordinated sigma-complex or pi-complex (Figure 1).<sup>[32]</sup>

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 by losing two dihydrogen molecules. The silylene type of silole will then either self-couple or keep inserting into the Si-H bond of **1**, forming **2**. For the homodehydrocoupling of 1,1-dihydrogermole to polygermole or *co*-dehydrocoupling of 1,1-dihydrogermole with 1,1-dihydrosilole to poly(silole-*co*-germole)s the same mechanism in Figure 1 should be applied.

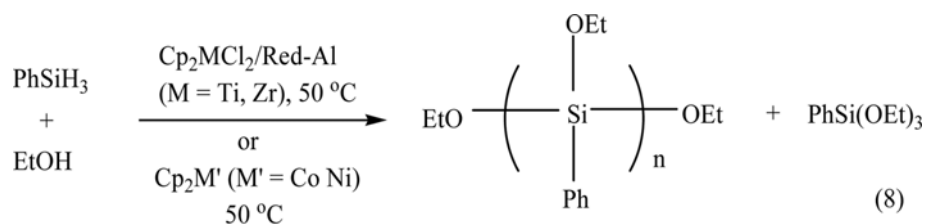
### 2.3. Si-O/Si-Si Dehydrocoupling of Hydrosilane with Alcohol to Poly(alkoxysilane)s

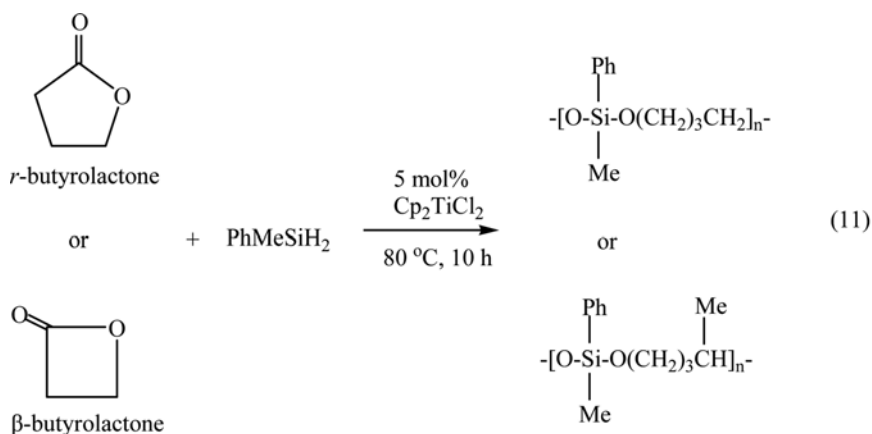
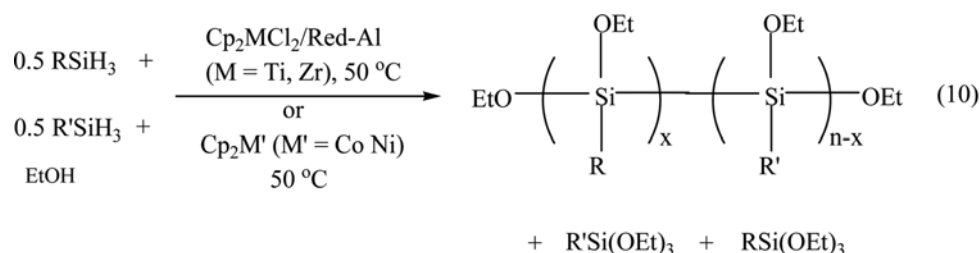
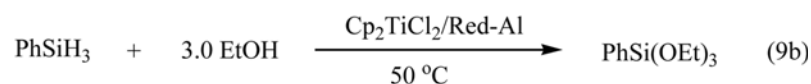
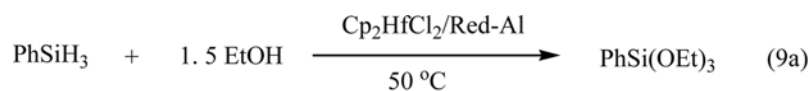
A wide range of catalysts (e.g., acids, bases, and homogeneous/heterogeneous transition metal catalysts) have been used for the Si-O dehydrocoupling of alcohols with silanes.<sup>[13a,34,35a]</sup> The Si-O dehydrocoupling of bis-hydrosilanes with diols, catalyzed by rhodium complex, yielding polysiloxanes was reported.<sup>35b,c</sup> The Si-S-

dehydrocoupling of hydrosilanes with dithiols to produce polysilathianes was also reported.<sup>[35d]</sup> Si-Si dehydrocoupling of hydrosilanes with late transition metal complex catalysts produces a mixture of oligomers along with significant amounts of disproportionated by-products.<sup>[13b]</sup> Harrod *et al.* reviewed the recent dehydrocoupling of hydrosilanes with alcohols.<sup>[11]</sup> The transition metal complexes of group VIII (Ni, Co, Rh, Pd, Ir, Pt, etc.) have been extensively used in the catalytic dehydrocoupling of hydrosilanes with various nucleophilic reagents.<sup>[36]</sup> A recent survey written by Corey was appeared on the catalytic dehydrocoupling of hydrosilanes in the presence of a range of early and late transition metal complexes.<sup>[13b]</sup>

Numerous studies were reported either on the alcoholysis of hydrosilanes (i.e., Si-O coupling) or on the dehydropolymerization of silanes (i.e., Si-Si coupling) under the influence of various transition metal complex catalysts.<sup>[13,34,35a-c,36]</sup> Poly(alkoxysilane)s can be used as important precursors for preparing interesting polysilane-siloxane hybrids by sol-gel methods in the presence of acid/base catalyst in the reverse micellar environment.<sup>[37a]</sup> Woo and co-workers first described the combinative Si-Si/Si-O dehydrocoupling reaction of hydrosilanes with alcohols (1:1.5 mole ratio) at 50°C, catalyzed by Cp<sub>2</sub>MCl<sub>2</sub>/Red-Al (M = Ti, Zr) and Cp<sub>2</sub>M' (M = Co, Ni), producing poly(alkoxysilane)s in one-pot in high yield (eq. 8).

The hydrosilanes include *p*-C<sub>6</sub>H<sub>4</sub>SiH<sub>3</sub> (X = H, CH<sub>3</sub>, OCH<sub>3</sub>, F), PhCH<sub>2</sub>SiH<sub>3</sub>, and (PhSiH<sub>2</sub>)<sub>2</sub>. The alcohols include MeOH, EtOH, *i*-PrOH, PhOH, and CF<sub>3</sub>(CF<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>OH. The weight average molecular weights (*M<sub>w</sub>*) of the resulting poly(alkoxysilane)s ranged from 600 to 8000 g/mol. However, Cp<sub>2</sub>M' (M' = Co, Ni) have no catalytic activity toward Si-Si dehydrocoupling of primary hydrosilanes in inert atmosphere (e.g., dry N<sub>2</sub> or Ar gas atmosphere).<sup>[37b]</sup> Interestingly, the dehydrocoupling reactions of phenylsilane with ethanol (1:1.5 mole ratio) using Cp<sub>2</sub>HfCl<sub>2</sub>/Red-Al, and phenylsilane with





ethanol (1:3 mole ratio) using  $\text{Cp}_2\text{TiCl}_2/\text{Red-Al}$  gave only triethoxyphenylsilane as product (eq. 9a-b).<sup>[38]</sup>

Similarly, the combinative Si-Si/Si-O dehydrocoupling reactions of mixed hydrosilanes with alcohols (two different hydrosilanes were used in the same mole ratio; 0.5:0.5:1.5 mole ratio) at  $50^\circ\text{C}$ , catalyzed by  $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$  ( $\text{M} = \text{Ti, Zr}$ ) and  $\text{Cp}_2\text{M}'$  ( $\text{M}' = \text{Co, Ni}$ ), producing copoly(alkoxysilane)s in one-pot in high yield (eq. 10) were reported.<sup>[37a]</sup>

In the similar manner, Woo and co-workers performed the combinative Si-Si/Si-O dehydrocoupling reactions of hydrosilanes with mixed alcohols (two different alcohols were used in the same mole ratio; 1:0.75:0.75 mole ratio) at  $50^\circ\text{C}$ , catalyzed by  $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$  ( $\text{M} = \text{Ti, Zr}$ ) and  $\text{Cp}_2\text{M}'$  ( $\text{M}' = \text{Co, Ni}$ ), producing copoly(alkoxysilane)s in one-pot in high yield.<sup>[37a]</sup> The bonding characters [mixing interaction between  $\sigma$

(silicon) orbital and  $n$  (oxygen) orbital] of Si-O bonds in poly(dialkoxysilylene)s were studied in detail using various levels of molecular orbital calculations.<sup>[37c]</sup>

#### 2.4. Ring-Opening/Dehydrocoupling of Hydrosilane and Lactone

Harrod and coworkers first reported the reductive ring-opening/dehydrocoupling copolymerization of  $\beta$ - and  $\gamma$ -butyrolactones (four- and five-membered cyclic esters) and a secondary hydrosilane  $\text{PhMeSiH}_2$  using  $\text{Cp}_2\text{TiMe}_2$  catalyst to give polysiloxane type copolymers,  $[\text{OSiPhMeO}(\text{CH}_2)_4]_n$  and  $[\text{OSiPhMeO}(\text{CH}_2)_2(\text{CH})\text{CH}_3]_n$ , respectively, which have the regularly alternating structure of reduced lactone (i.e., dialkoxylefinic unit) and silylene moieties without ester functional groups in the polymer chain (eq. 11).<sup>[39]</sup>

In contrast, Woo and coworkers first reported the





- D.C., 1990.
- [10] (a) R. D. Miller, "Polysilane high polymers", *J. Chem. Rev.* Vol. 89, p. 1359, 1989. (b) K. Matyjaszewski, Y. L. Chen, H. K. Kim, M. Zeldin, K. J. Wynne and H. R. Allcock, "in *Inorganic and Organometallic Polymers ACS Symposium Series 360*", American Chemical Society: Washington D. C., 1988.
- [11] F. Gauvin, J. F. Harrod and H.-G. Woo, "Catalytic Dehydrocoupling: A General Strategy for the Formation of Element-Element Bonds", *Adv. Organomet. Chem.* Vol. 42, p. 363, 1998.
- [12] (a) T. D. Tilley, "The coordination polymerization of silanes to polysilanes by a sigma-bond metathesis" mechanism. Implications for linear chain growth", *Acc. Chem. Res.* Vol. 26, p. 22, 1993. (b) T. D. Tilley, "Mechanistic Aspects of Transition-Metal Catalyzed Dehydrogenative Silane Coupling Reactions", *Comments Inorg. Chem.* Vol. 10, p. 37, 1990.
- [13] (a) J. Y. Corey, "Catalytic dehydrocoupling of organosilanes", *Adv. Silicon Chem.* Vol. 1, p. 327, 1991. (b) J. Y. Corey, "Dehydrocoupling of Hydrosilanes to Polysilanes and Silicon Oligomers: A 30 Year Overview", *Adv. Organomet. Chem.* Vol. 51, p. 1, 2004.
- [14] J. P. Banovetz, R. M. Stein and R. M. Waymouth, "Stereoselectivity in the catalytic oligomerization of phenylsilane", *Organometallics* Vol. 10, p. 3430, 1991.
- [15] N. Choi, S. -Y. Onozawa, T. Sakakura and M. Tanaka, "Palladium-Catalyzed Borylstannylative Carbocyclization of Dienes and an Enyne Compound", *Organometallics* Vol. 16, p. 2765, 1997.
- [16] V. K. Dioumaev and J. F. Harrod, "Catalytic Dehydrocoupling of Phenylsilane with Cation-like" Zirconocene Derivatives: A New Approach to Longer Silicon Chains", *Organometallics* Vol. 13, p. 1548, 1994.
- [17] (a) H.-G. Woo, S.-Y. Kim, M. K. Han, E. J. Cho and I. N. Jung, "Dehydrohomopolymerization and dehydrocopolymerization of new alkylsilanes: synthesis of poly (3-aryl-1-silabutanes)", *Organometallics* Vol. 14, p. 2415, 1995. (b) H.-G. Woo and S.-J. Song, "Rapid, highly linear-selective dehydrocoupling of phenylsilane with new group 4 metallocene-based combination catalysts", *Chem. Lett.* p. 457, 1999, (c) H.-G. Woo and B.-H. Kim, manuscript in preparation. (d) R. Resel, G. Leising, F. Lunzer and C. Marschner, "Structure in amorphous polysilanes determined by diffuse X-ray scattering", *Polymer* Vol. 39, p. 5257, 1998. (e) H.-G. Woo and B.-H., Kim manuscript in preparation.
- [18] H. Li, F. Gauvin and J. F. Harrod, "Observations concerning the inactivity of dimethylhafnocene as a catalyst for the dehydrocoupling of phenylsilane", *Organometallics* Vol. 12, p. 575, 1993.
- [19] V. K. Dioumaev and J. F. Harrod, "Unusual Cation-like Zirconocene Hydrosilyl Complex; Silylium Ligand or a Nonclassically Bonded Si-H", *Organometallics* Vol. 15, p. 3859, 1996.
- [20] W. H. Campbell, T. K. Hilty and L. Yurga, "Dimethylzirconocene-catalyzed polymerization of alkylsilanes", *Organometallics* Vol. 8, p. 2615, 1989.
- [21] (a) C. Aitken, J. F. Harrod and U. S. Gill, "Titanocene-catalyzed dehydrocoupling of phenylsilane", *Can J. Chem.* Vol. 65, p. 1804, 1987. (b) J. F. Harrod and S. S. Yun, "Silyltitanocene complexes as catalysts for the hydrogenation, isomerization, and hydrosilylation of olefins", *Organometallics*, Vol. 6, p. 1381, 1987. (c) C. Aitken, J.-P. Barry, F. Gauvin, J. G. Harrod, A. Malek and D. Rousseau, "A survey of catalytic activity of eta. 5-cyclopentadienyl complexes of Groups 4-6 and uranium and thorium for the dehydrocoupling of phenylsilane", *Organometallics* Vol. 8, p. 1732, 1989. (d) J. F. Harrod, T. Ziegler and V. Tschinke, "Theoretical study of Cp<sub>2</sub>Ti(H)(SiH<sub>3</sub>) and Cp<sub>2</sub>TiSiH<sub>2</sub> and their possible role in the polymerization of primary organosilanes", *Organometallics* Vol. 9, p. 897, 1990. (e) H.-G. Woo, J. F. Harrod, J. Henique and E. Samuel, "Titanocene-catalyzed dehydrocoupling of silanes in the presence of phosphines. Probing a complex organometallic catalysis by EPR spectroscopy", *Organometallics* Vol. 12, p. 2883, 1993. (f) J. Britten, Y. Mu, J. F. Harrod, J. Polowin, M. C. Baird and E. Samuel, "Crystal structures and conformational analysis of titanocene complexes of the type Cp<sub>2</sub>Ti(SiHRR')PMe<sub>3</sub> (R, R' = H, Me, Ph): relationships between calculated molecular structures and observed solid-state structures", *Organometallics* Vol. 12, p. 2672, 1993.
- [22] (a) H.-G. Woo and T. D. Tilley, "Dehydrogenative polymerization of silanes to polysilanes by zirconocene and hafnocene catalysts. A new polymerization mechanism", *J. Am. Chem. Soc.* Vol. 111, p. 3757, 1989. (b) H.-G. Woo and T. D. Tilley, "sigma.-Bond metathesis reactions of silicon-hydrogen and metal-silicon bonds. New routes to d<sup>0</sup> metal silyl complexes", *J. Am. Chem. Soc.* Vol. 111, p. 8043, 1989 (c) H.-G. Woo, J. F. Walzer and T. D. Tilley, "Dehydropolymerization of bis- and tris

- (silyl) arenes to highly crosslinked disilanylene-arylene polymers, catalyzed by [(*eta*-5-C<sub>5</sub>H<sub>5</sub>)(*eta*-5-C<sub>5</sub>Me<sub>5</sub>)ZrH<sub>2</sub>]<sup>2+</sup>”, *Macromolecules* Vol. 24, p. 6863, 1991. (d) H.-G. Woo, R. H. Heyn and T. D. Tilley, “sigma-Bond metathesis reactions for d0 metal-silicon bonds that produce zirconocene and hafnocene hydrosilyl complexes”, *J. Am. Chem. Soc.* Vol. 114, p. 5698, 1992. (e) H.-G. Woo, J. F. Walzer, T. D. Tilley, “Platinum-mediated reactions of hydrosilanes. Isolation of a complex with bridging disilene and silylene ligands”, *J. Am. Chem. Soc.* Vol. 114, p. 7047, 1992. (f) J. P. Banovetz, H. Suzuki and R. M. Waymouth, “Dehydrogenative coupling of substituted phenylsilanes: synthesis of poly [(trifluoromethyl) phenyl] silanes”, *Organometallics* Vol. 12, p. 4700, 1993. (g) T. Imori, H.-G. Woo, J. F. Walzer and T. D. Tilley, “Disilanylene-arylene oligomers and polymers from dehydropolymerization of 1, 4-RH<sub>2</sub>SiC<sub>6</sub>H<sub>4</sub>SiH<sub>2</sub>R (R= methyl, ethyl, and hexyl)”, *Chem. Mater.* Vol. 5, p. 1487, 1993. (h) J. Y. Corey, J. L. Huhmann and X.-H. Zhu, “Coupling of deuteriosilanes in the presence of Cp<sub>2</sub>MCl<sub>2</sub>/nBuLi”, *Organometallics* Vol. 12, p. 1121, 1993.
- [23] (a) H.-G. Woo, S.-Y. Kim, W.-G. Kim, E. J. Cho, S. H. Yeon and I. N. Jung, “Dehydropolymerization of Bis (silyl) alkylbenzenes to Highly Cross-Linked Polysilanes, Catalyzed by Group 4 Metallocene Complex”, *Bull. Korean Chem. Soc.* Vol. 16, p. 1109 1995. (b) H.-G. Woo, S.-J. Song, M.-K. Han, E. J. Cho and I. N. Jung, “Photopolymerization of Methyl methacrylate with Phenylsilane”, *Bull. Korean Chem. Soc.* Vol. 16, p. 1242, 1995. (c) H.-G. Woo and S.-J. Song, “Catalytic Redistribution/Dehydrocoupling of 2-Phenyl-1, 3-disilapropane by Cp<sup>-</sup>2MCl<sup>-</sup>2/Red-Al System (M= Ti, Hf)”, *Bull. Korean Chem. Soc.* Vol. 17, p. 494, 1996. (d) H.-G. Woo and S.-J. Song, “Redistribution of Bis-and Tris (silyl) methanes Catalyzed by Red-Al”, *Bull. Korean Chem. Soc.* Vol. 17, p. 1040, 1996. (e) H.-G. Woo, B.-H. Kim, S.-J. Song, M.-K. Han, S.-Y. Kim, J.-H. Kim and J. S. Lee, “Dehalogenation of Monohalopyridines Catalyzed by Group 4 Metallocene Reagent”, *Bull. Korean Chem. Soc.* Vol. 21, p. 935, 2000.
- [24] R. West, “in *Comprehensive Organometallic Chemistry II*; Davis, A. G., Ed.; Pergamon Press”, Oxford, pp 77-110, 1995.
- [25] J. Luo, Z. Xie, J. W. Y. Lam, L. Cheng, H. Chen, C. Qiu, H. S. Kwok, X. Zhan, Y. Liu, D. Zhu and B. Z. Tang, “Gold-platinum alloy nanoparticle assembly as catalyst for methanol electrooxidation”, *J. Chem. Soc., Chem. Commun.* p. 1740, 2001.
- [26] (a) H. Sohn, H.-G. Woo and D. R. Powell, “Synthesis and structural characterization of a silacycloheptadiene”, *J. Chem. Soc., Chem. Commun.* P. 697, 2000. (b) H.-G. Woo, B.-H. Kim and H. Sohn, “Serendipitous Synthesis of Oligo(6-vinylsilyl-5-silacyclohepta-1,3-diene)s”, *Chem. Lett.* p. 544, 2000.
- [27] K. Tamao, M. Uchida, T. Izumizawa, K. Furukawa and S. Yamaguchi, “Silole derivatives as efficient electron transporting materials”, *J. Am. Chem. Soc.* Vol. 118, p. 11974, 1996.
- [28] (a) H. Sohn, R. R. Huddleston, D. R. Powell and R. West, “An electroluminescent polysilole and some dichlorooligosiloles”, *J. Am. Chem. Soc.* Vol. 121, p. 2935, 1999. (b) K. Tamao and S. Yamaguchi, “Regio-controlled intramolecular reductive cyclization of diynes”, *Pure Appl. Chem.* Vol. 68, p. 139, 1996. (c) S. Yamaguchi and K. Tamao, “Silole-containing  $\sigma$ - and  $\pi$ -conjugated compounds”, *J. Chem. Soc., Dalton Trans.* p. 3693, 1998. (d) S. Yamaguchi, R.-Z. Jin and K. Tamao, *J. Am. Chem. Soc.* Vol. 121, p. 2937, 1999. (e) K. Kanno, M. Ichinohe, C. Kabuto and M. Kira, “Synthesis and Structure of a Series of Oligo [1, 1-(2, 3, 4, 5-tetramethylsilole)] s”, *Chem. Lett.* p. 99, 1998.
- [29] (a) T. Sanji, T. Sakai, C. Kabuto and H. Sakurai, “Silole-Incorporated Polysilanes 1a”, *J. Am. Chem. Soc.* Vol. 120, p. 4552, 1998. (b) H. Sohn, M. J. Sailor, D. Magde and W. C. Trogler, “Detection of nitroaromatic explosives based on photoluminescent polymers containing metalloles”, *J. Am. Chem. Soc.* Vol. 125, p. 3821, 2003. (c) H.-G. Woo, B.-H. Kim, S.-J. Song, manuscript in preparation.
- [30] (a) B. P. S. Chauhan, T. Shimizu and M. Tanaka, “New Vistas in Dehydrocoupling Polymerization of Hydrosilanes: Platinum Complex-Catalyzed Dehydrocoupling of Cyclic and Acyclic Secondary Silanes”, *Chem. Lett.* p. 785 1997. (b) W. C. Trogler, H. Sohn, S. Liu, and S. Toal, Abstracts of Papers (225th ACS National Meeting, New Orleans, March 23-27, 2003), INOR-746.
- [31] B.-H. Kim, M.-S. Cho, J.-I. Kong and H.-G. Woo, manuscript in preparation.
- [32] B.-H. Kim and H.-G. Woo, “Dehydrocoupling of 1, 1-dihydrotetraphenylsilole to an electroluminescent polysilole”, *Organometallics* Vol. 21, p. 2796, 2002. (b) H.-G. Woo, S.-J. Song, B.-H. Kim and S. S. Yun, “Dehydrocoupling synthesis and optoelectronic properties of polysilole”, *Mol. Cryst. Liq. Cryst.* Vol. 349, p. 87, 2000. (c) B.-H. Kim, M.-S. Cho, J.-

- I. Kong, H.-G. Woo, S.-W. Lee and C.-J. Lee, "Dehydrocoupling, redistributive coupling, and addition of main group 4 hydrides", *Mol. Cryst. Liq. Cryst.* Vol. 425, p. 243, 2004.
- [33] (a) J.-H. Hong and P. Boudjouk, "A stable aromatic species containing silicon. Synthesis and characterization of the 1-tert-butyl-2, 3, 4, 5-tetraphenyl-1-silacyclopentadienide anion", *J. Am. Chem. Soc.* Vol. 115, p. 5883, 1993. (b) J. -H. Hong, P. Boudjouk, and S. Castellino, "Synthesis and Characterization of Two Aromatic Silicon-Containing Dianions: The 2,3,4,5-Tetraphenylsilole Dianion and the 1,1'-Disila-2,2',3,3',4,4',5,5'-Octaphenylfulvalene Dianion", *Organometallics* Vol. 13, p. 3387, 1994. (c) R. West, H. Sohn, U. Bankwitz, J. Calabrese, Y. Apeloig and T. Mueller, "Dilithium Derivative of Tetraphenylsilole: An eta-1- eta-5 Dilithium Structure", *J. Am. Chem. Soc.* Vol. 117, p. 11608, 1995.
- [34] (a) E. Lukevics and M. Dzintara, "Hydrosilylation of unsaturated (hetero) aromatic aldehydes and related compounds catalyzed by transition metal complexes", *J. Organomet. Chem.* Vol. 295, p. 265, 1985. (b) C. G. Pitt, *Homoatomic "Rings, Chains, and Macromolecules of Main-Group Elements; Rheingold, A. L., Ed."* Elsevier Scientific Publishing Company: Amsterdam, p 203, 1977.
- [35] (a) T. C. Bedard and J. Y. Corey, "Conversion of hydrosilanes to alkoxy silanes catalyzed by Cp<sub>2</sub>TiCl<sub>2</sub>/nBuLi", *J. Organomet. Chem.* Vol. 428, p. 315, 1992. (b) Y. Li and Y. Kawakami, "Synthesis and properties of polymers containing silphenylene moiety via catalytic cross-dehydrocoupling polymerization of 1, 4-bis (dimethylsilyl) benzene", *Macromolecules* Vol. 32, p. 6871, 1999. (c) R. Zhang, J. E. Mark and A. R. Pinhas, "Dehydrocoupling Polymerization of Bis-silanes and Disilanols to Poly (silphenylenesiloxane) As Catalyzed by Rhodium Complexes", *Macromolecules* Vol. 33, p. 3508, 2000. (d) J. B. Baruah, K. Osakada and T. Yamamoto, "Polycondensation of Diarylsilanes with Aromatic Dithiols and the Model Reaction Involving RhCl (PPh<sub>3</sub>)<sub>3</sub>-Catalyzed Si-S Bond Formation", *Organometallics* Vol. 15, p. 456, 1996.
- [36] (a) L. H. Sommer and J. E. Lyons, "Stereospecific Substitution Reactions of Optically Active R<sub>3</sub>Si\*H Catalyzed by Palladium and Nickel", *J. Am. Chem. Soc.* Vol. 89, p. 1521, 1967. (b) R. J. P. Corriu and J. J. E. Moreau, "Asymmetric hydrosilylation of ketones catalyzed by a chiral rhodium complex", *J. Organomet. Chem.* Vol. 64, p. C51, 1973. (c) I. Ojima, T. Kogure, M. Nihonyanagi, H. Kono, S. Inaba and Y. Nagai, "Hydrosilane-rhodium(I) Complex Combinations As Silylating Agents Of Alcohols", *Chem. Lett.* p. 501, 1973.
- [37] (a) B.-H. Kim, S.-H. Park, M.-S. Kim and H.-G. Woo, manuscript in preparation. (b) B.-H. Kim and H.-G. Woo, manuscript in preparation. (c) J. R. Koe, M. Motonaga, M. Fujiki and R. West, "Synthesis and Spectroscopic Characterization of Heteroatom Polysilylenes: Poly (dialkoxy silylene)s and Evidence for Silicon [sigma]Oxygen n Mixing Interaction", *Macromolecules* Vol. 34, p. 706, 2001.
- [38] B.-H. Kim, M.-S. Cho, M.-A. Kim and H.-G. Woo, "One-pot synthesis of poly (alkoxy silane)s by Si-unknown; Si/Si-unknown; O dehydrocoupling of silanes with alcohols using Group IV and VIII metallocene Complex", *J. Organomet. Chem.* Vol. 685, p. 93, 2003.
- [39] R. Shu, J. F. Harrod and A. M. Lebus, "Catalytic reduction of benzoate esters and lactones in the presence of PhMeSiH<sub>2</sub> and a titanocene-based catalyst", *Can. J. Chem.* Vol. 80, p. 489, 2002.
- [40] B.-H. Kim, H.-G. Woo, W. Kim and H. Li, "Copolymerisation of ε-caprolactone where science meets business and hydrosilanes to poly(caprolactone-co-silane)s using Cp<sub>2</sub>MCl<sub>2</sub>/Red-Al (M = Ti, Zr, Hf) combination catalysts", *J. Chem. Tech. & Biotech.* Vol. 81, p. 746, 2006.
- [41] H. Li, C. Wang, F. Bai, J. Yue and H.-G. Woo, "Living ring-opening polymerization of L-lactide catalyzed by Red-Al", *Organometallics* Vol. 23, p. 1411, 2004.