

# One-pot synthesis of poly(alkoxysilane)s by Si–Si/Si–O dehydrocoupling of silanes with alcohols using Group IV and VIII metallocene complexes

Bo-Hye Kim, Myong-Shik Cho, Mi-Ae Kim, Hee-Gweon Woo\*

*Department of Chemistry and Institute of Basic Sciences, Chonnam National University, Kwangju 500-757, South Korea*

Received 9 January 2003; received in revised form 26 April 2003; accepted 22 May 2003

## Abstract

Si–Si/Si–O dehydrocoupling reactions of silanes with alcohols (1:1.5 mole ratio), catalyzed by  $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$  ( $\text{M} = \text{Ti}, \text{Zr}$ ) and  $\text{Cp}_2\text{M}'$  ( $\text{M}' = \text{Co}, \text{Ni}$ ), produced poly(alkoxysilane)s in one-pot in high yield. The silanes included  $p\text{-X-C}_6\text{H}_4\text{SiH}_3$  ( $\text{X} = \text{H}, \text{CH}_3, \text{OCH}_3, \text{F}$ ),  $\text{PhCH}_2\text{SiH}_3$ , and  $(\text{PhSiH}_2)_2$ . The alcohols were MeOH, EtOH,  $i\text{-PrOH}$ , PhOH, and  $\text{CF}_3(\text{CF}_2)_2\text{CH}_2\text{OH}$ . The weight average molecular weight of the poly(alkoxysilane)s ranged from 600 to 8000. The dehydrocoupling reactions of phenylsilane with ethanol (1:1.5 mole ratio) using  $\text{Cp}_2\text{HfCl}_2/\text{Red-Al}$  and phenylsilane with ethanol (1:3 mole ratio) using  $\text{Cp}_2\text{TiCl}_2/\text{Red-Al}$  gave only triethoxyphenylsilane as product.

© 2003 Elsevier Science B.V. All rights reserved.

**Keywords:** Hydrosilanes; Dehydrocoupling; Metallocene; Catalyst; Poly(alkoxysilane)

## 1. Introduction

Polysilanes have recently attracted considerable attention due to their peculiar electronic and photophysical properties as well as their potential applications in microlithography [1], in ceramics [2], as photoconducting polymers [3], and as third-order nonlinear optical materials [4]. The unique properties of polysilanes stem from the extensive delocalization of  $\sigma$ -electrons along the silicon backbone and depend on the nature of the substituents attached to the polymer backbone, the polymer conformation, and the polymer molecular weight [5]. Polysilanes are generally prepared by Wurtz coupling of dichlorosilanes using sodium metal in refluxing hydrocarbon solvents such as toluene [5]. The introduction of functionality onto the polymer chain is quite limited due to the harsh reaction conditions employed in the reductive coupling reaction [6]. Some recent success has been achieved in functionalizing

polysilanes prepared by Wurtz coupling, particularly for phenyl-substituted polysilanes [7–10]. Recently developed transition-metal mediated dehydrocoupling syntheses of polysilanes provide exciting opportunities for the synthesis of polymers with defined structure and functionality [11]. One of the appealing characteristics of polysilanes synthesized by the catalytic Si–Si dehydrocoupling of primary silanes is the reactive Si–H functionality in the backbone of the polysilanes. The Si–H functional group can be transformed to other useful functional groups by simple chemical reactions. Very recently, Waymouth and co-workers [12,13] reported a free-radical method for selectively substituting the backbone Si–H bonds of polyphenylsilane. Free-radical chlorination of polyphenylsilane  $[-\text{Si}(\text{H})\text{Ph}-]_n$  with  $\text{CCl}_4$  afforded poly(chlorophenylsilane)  $[-\text{Si}(\text{Cl})\text{Ph}-]_n$ , which was subsequently reacted with nucleophiles to produce a new polysilane  $[-\text{Si}(\text{X})\text{Ph}-]_n$  ( $\text{X} = \text{Me}, \text{OMe}$ ).

A wide range of catalysts have been reported for Si–O dehydrocoupling of OH-containing compounds with silanes [14,15]. These catalysts include acids, bases, and both homogeneous and heterogeneous transition

\* Corresponding author. Tel.: +82-62-530-3378; fax: +82-62-530-3389.

E-mail address: [hwoo@chonnam.ac.kr](mailto:hwoo@chonnam.ac.kr) (H.-G. Woo).

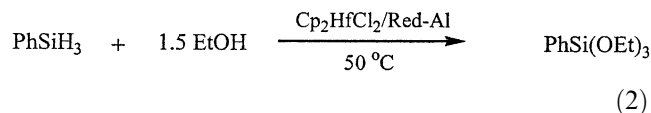
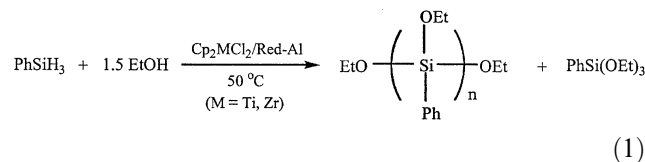
metal catalysts. Bedard and Corey [16] carried out a survey of the dehydrocoupling of a range of organosilanes and alcohols under the influence of  $\text{Cp}_2\text{TiCl}_2/2^\text{n}\text{BuLi}$ . The transition metal complexes of Group VIII (Ni, Co, Rh, Pd, Ir, Pt etc.) have been extensively applied for the catalytic dehydrocoupling of hydrosilanes with various nucleophilic reagents [17–21]. In the presence of Raney nickel and Pd/C catalysts, dehydrocoupling of triallylsilane with excess alcohol produced trialkoxysilane [22]. Si–Si dehydrocoupling of hydrosilanes with late transition metal catalysts produced a mixture of oligomers along with a significant amount of redistributed by-products [23].

In spite of numerous reported studies on the alcoholysis of hydrosilanes and on the dehydropolymerization of silanes in the presence of transition metal catalysts, to our knowledge there is no single report regarding the one-pot synthesis of poly(alkoxysilane)s by direct Si–Si/Si–O dehydrocoupling of hydrosilanes with alcohols. Poly(alkoxysilane)s can be used as precursors for preparing interesting polysilane–siloxane hybrids by sol–gel methods [24]. Herein we report a mild and simple one-pot procedure for the introduction of alkoxy groups (OMe, OEt, O<sup>i</sup>Pr,  $\text{OCH}_2(\text{CF}_2)_2\text{CF}_3$ ) onto the polysilane backbone with Group IV metallocene  $\text{Cp}_2\text{MCl}_2$  (M = Ti, Zr)/Red-Al combination and Group VIII metallocene  $\text{Cp}_2\text{M}'$  (M' = Co, Ni) catalysts.

## 2. Results and discussion

### 2.1. Si–Si/Si–O dehydrocoupling of silanes and alcohols catalyzed by $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$ (M = Ti, Zr)

For 48 h at 50 °C, a 1.5:1 mole ratio of alcohols (EtOH, <sup>i</sup>PrOH) and hydrosilanes [*p*-X-C<sub>6</sub>H<sub>4</sub>SiH<sub>3</sub> (X = H, F, CH<sub>3</sub>, OCH<sub>3</sub>), PhSiH<sub>3</sub>, PhCH<sub>2</sub>SiH<sub>3</sub>, PhSiH<sub>2</sub>-SiH<sub>2</sub>Ph] reacted in the presence of 2 mol% of  $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$  (M = Ti, Zr) catalyst to produce poly(alkoxysilane)s along with the respective trialkoxysilane as a minor product. The reaction of phenylsilane and ethanol with  $\text{Cp}_2\text{TiCl}_2/\text{Red-Al}$  catalyst produced 30% substituted poly(ethoxyphenylsilane) (mole ratio of 1:0.5) in 91% isolated yield and fully substituted poly(ethoxyphenylsilane) (mole ratio of 1:1.5) in 76% yield (Eq. 1). The only isolated product from the dehydrocoupling reaction of a 1:3 mole ratio of PhSiH<sub>3</sub> and ethanol with  $\text{Cp}_2\text{TiCl}_2/\text{Red-Al}$  catalyst was PhSi(OEt)<sub>3</sub>. The dehydrocoupling reaction of PhSiH<sub>3</sub> and ethanol (1:1.5 mole ratio) with  $\text{Cp}_2\text{HfCl}_2/\text{Red-Al}$  catalyst did not result in polymerization, with the only product being PhSi(OEt)<sub>3</sub> (Eq. 2). The results of the reactions of hydrosilanes and alcohols, catalyzed by  $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$  (M = Ti, Zr, Hf), are summarized in Table 1.



The weight average molecular weight of the produced polymers ranged from 700 to 2800. In the Si–Si dehydrocoupling of phenylsilane catalyzed by  $\text{Cp}_2\text{TiCl}_2/\text{Red-Al}$ , 30–40% of cyclic formation was reported [11]. By comparison, small amount (~3%; judged by Gel permeation chromatography (GPC) analysis) of cyclic formation was observed in the Si–Si/Si–O dehydrocoupling of phenylsilane with ethanol (1:1.5 mole ratio) catalyzed by  $\text{Cp}_2\text{TiCl}_2/\text{Red-Al}$ . However, no appreciable cyclic formation was found in the Si–Si/Si–O dehydrocoupling of phenylsilane with ethanol (1:1.5 mole ratio) catalyzed by  $\text{Cp}_2\text{ZrCl}_2/\text{Red-Al}$ . The <sup>1</sup>H-NMR spectra of the poly(alkoxysilane)s showed no appreciable Si–H resonances. Nonetheless, the IR spectra of the poly(alkoxysilane)s exhibited an extremely weak  $\nu_{\text{SiH}}$  band around 2100 cm<sup>-1</sup>. Therefore, we can assume that the polymers are almost fully substituted poly(alkoxysilane)s. In the catalytic reaction of hydrosilane and ethanol with  $\text{Cp}_2\text{TiCl}_2/\text{Red-Al}$  catalyst, as expected, the mole ratio of hydrosilane to alcohol largely affected the degree of alkoxy-substitution and the weight average molecular weight ( $M_w$ ) of the polymer products. It is interesting to note that reaction time also affected the degree of substitution and  $M_w$  as shown in Table 1. In the Si–Si/Si–O dehydrocoupling of phenylsilane with ethanol (1:1.5 mole ratio) catalyzed by  $\text{Cp}_2\text{TiCl}_2/\text{Red-Al}$ , ~70% (judged by <sup>1</sup>H-NMR spectroscopy) of ethoxy-substituted polymer with 960 of  $M_w$  was obtained for 24 h of reaction time where as ~100% of ethoxy-substituted polymer with 1220 of  $M_w$  was obtained for 480 h of reaction time. In terms of the catalyst, the degree of polymerization decreased in the order Ti > Zr >> Hf. When the dehydrocoupling reactions of PhSiH<sub>3</sub> with EtOH (1:1.5 mole ratio) using  $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$  (M = Ti, Zr) were performed for 5 days at ambient temperature, the only isolated product was triethoxyphenylsilane.

### 2.2. Si–Si/Si–O dehydrocoupling of silanes and alcohols catalyzed by $\text{Cp}_2\text{M}'$ (M' = Co, Ni)

The Si–Si/Si–O dehydrocoupling of hydrosilanes and alcohols with 2 mol.% of  $\text{Cp}_2\text{M}'$  (M' = Co, Ni) yielded poly(alkoxysilane)s at room temperature in high yields

Table 1  
Results for the reactions of hydrosilane and alcohol with Group IV metallocene-based Cp<sub>2</sub>MCl<sub>2</sub>/Red-Al combination catalysts

Silane:Alcohol (mole ratio)	Catalyst <sup>a</sup> [M]	Polymer isolated yield (%)	Mol wt. <sup>b</sup>		
			M <sub>w</sub>	M <sub>n</sub>	M <sub>w</sub> /M <sub>n</sub>
PhSiH <sub>3</sub> :EtOH (1:0.5)	Ti	91	1540	1180	1.3
PhSiH <sub>3</sub> :EtOH (1:1.5)	Ti	76	1220	580	2.1
PhSiH <sub>3</sub> :EtOH (1:1.5) <sup>c</sup>	Ti	50	960	600	1.6
PhSiH <sub>3</sub> :EtOH (1:3)	Ti	PhSi(OEt) <sub>3</sub> (98)	–	–	–
PhSiH <sub>3</sub> :EtOH (1:1.5)	Zr	76	1030	690	1.5
PhSiH <sub>3</sub> :EtOH (1:1.5)	Hf	PhSi(OEt) <sub>3</sub> (43)	–	–	–
(PhSiH <sub>2</sub> ) <sub>2</sub> :EtOH (1:2)	Ti	70	1620	670	1.7
PhCH <sub>2</sub> SiH <sub>3</sub> :EtOH (1:1.5)	Ti	77	1010	360	2.8
PhSiH <sub>3</sub> : <sup>i</sup> PrOH (1:1.5)	Ti	64	750	570	1.3
Poly( <i>p</i> -F-C <sub>6</sub> H <sub>4</sub> SiH <sub>3</sub> ):EtOH (1:1.5)	Ti	82	2300	1920	1.2
Poly( <i>p</i> -F-C <sub>6</sub> H <sub>4</sub> SiH <sub>3</sub> ):EtOH (1:1.5)	Zr	87	1120	1020	1.1
Poly( <i>p</i> -CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> SiH <sub>3</sub> ):EtOH (1:1.5)	Ti	76	2800	2000	1.4
Poly( <i>p</i> -CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> SiH <sub>3</sub> ):EtOH (1:1.5)	Zr	74	1400	1270	1.1
Poly( <i>p</i> -OCH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> SiH <sub>3</sub> ):EtOH (1:1.5)	Ti	79	2560	1970	1.3
Poly( <i>p</i> -OCH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> SiH <sub>3</sub> ):EtOH (1:1.5)	Zr	83	1310	940	1.4

Heated at 50 °C in neat for 48 h.

<sup>a</sup> [M]/[Si] = 0.02.

<sup>b</sup> Measured by GPC in THF (vs. polystyrene).

<sup>c</sup> Heated at 50 °C in neat for 24 h.

after workup and column chromatography. The results of these reactions are given in Table 2.

<sup>1</sup>H-NMR spectra of the polymers prepared from the Si–Si/Si–O dehydrocoupling reaction of silanes (PhSiH<sub>3</sub>, PhCH<sub>2</sub>SiH<sub>3</sub>, PhSiH<sub>2</sub>SiH<sub>2</sub>Ph) and alcohols ROH (R = Et, <sup>i</sup>Pr) with Cp<sub>2</sub>Co and Cp<sub>2</sub>Ni catalysts showed no appreciable Si–H resonances. The IR spectra of all the polymers exhibited a strong ν<sub>Si–O</sub> band around 1100–1000 cm<sup>-1</sup>. The FT-IR spectra reflected the disappearance of the ν<sub>Si–H</sub> band. The weight average molecular weight of the produced polymers ranged from 600 to 8100. The GPC characterization data of these reactions are given in Table 3.

As in the case of Group IV metallocene catalysts, the mole ratio of hydrosilane to alcohol significantly affected the degree of alkoxy-substitution and the polymer molecular weights in the dehydrocoupling reaction of silane and alcohol with Cp<sub>2</sub>M' (M' = Co, Ni). The reaction of phenylsilane and ethanol (1:0.5 mole ratio) produced 40% partially substituted polymer. The dehydrocoupling reaction of phenylsilane and ethanol (1:3 mole ratio) produced triethoxyphenylsilane and unidentified materials as minor products (Eq. 3). The unidentified materials were believed to be by-products from the redistribution of aryl or alkoxy groups (e.g., Ph<sub>2</sub>Si(OEt)<sub>2</sub>, Ph<sub>3</sub>Si(OEt)). It has been

Table 2  
Results for the reactions of hydrosilane and alcohol with Group VIII metallocene Cp<sub>2</sub>M' catalysts

Silane:Alcohol (mole ratio)	Catalyst <sup>a</sup> [M]	Reaction time (h)	Product (isolated% yield)
PhSiH <sub>3</sub> :EtOH (1:0.5)	Co	23	poly(ethoxyphenylsilane) (83)
PhSiH <sub>3</sub> :EtOH (1:1.5)	Co	16	poly(ethoxyphenylsilane) (87)
PhSiH <sub>3</sub> :EtOH (1:3)	Co	24	PhSi(OEt) <sub>3</sub> (92)
PhSiH <sub>3</sub> :EtOH (1:1.5)	Ni	32	poly(ethoxyphenylsilane) (78)
PhSiH <sub>3</sub> :MeOH (1:1.5)	Co	10	poly(methoxyphenylsilane) (81)
PhSiH <sub>3</sub> : <sup>i</sup> PrOH (1:1.5)	Co	20	poly(isopropoxyphenylsilane) (81)
PhSiH <sub>3</sub> :PhOH (1:1.5)	Co	26	poly(phenoxyphenylsilane) (88)
PhSiH <sub>3</sub> :CF <sub>3</sub> (CF <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> OH (1:1.5)	Co	22	poly(alkoxyphenylsilane) (75)
(PhSiH <sub>2</sub> ) <sub>2</sub> :EtOH (1:2)	Co	16	poly(ethoxyphenylsilane) (92)
(PhSiH <sub>2</sub> ) <sub>2</sub> :MeOH (1:2)	Co	10	poly(methoxyphenylsilane) (84)
PhCH <sub>2</sub> SiH <sub>3</sub> :EtOH (1:1.5)	Co	24	poly(methoxyphenylsilane) (64)
PhCH <sub>2</sub> SiH <sub>3</sub> :MeOH (1:1.5)	Co	24	poly(methoxyphenylsilane) (68)
PhSiH <sub>3</sub> :EtOH (1:3)	Co	24	PhSi(OEt) <sub>3</sub> (92)

Stirred at ambient temperature in neat until the reaction mixture became rigid.

<sup>a</sup> [M]/[Si] = 0.02.

Table 3  
GPC characterization of hydrosilane and alcohol with Group VIII metallocene Cp<sub>2</sub>M' catalysts

Silane:Alcohol (ratio)	Catalyst <sup>a</sup> [M]	Mol wt. <sup>b</sup>		
		M <sub>w</sub>	M <sub>n</sub>	M <sub>w</sub> /M <sub>n</sub>
PhSiH <sub>3</sub> :EtOH (1:0.5)	Co	2010	1510	1.3
PhSiH <sub>3</sub> :EtOH (1:1.5)	Co	1470	790	1.9
PhSiH <sub>3</sub> :EtOH (1:1.5)	Ni	610	580	1.1
PhSiH <sub>3</sub> :MeOH (1:1.5)	Co	5900	1110	5.4
PhSiH <sub>3</sub> : <sup>i</sup> PrOH (1:1.5)	Co	3800	2400	1.6
PhSiH <sub>3</sub> :PhOH (1:1.5)	Co	5260	660	8.0
PhSiH <sub>3</sub> :CF <sub>3</sub> (CF <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> OH (1:1.5)	Co	2090	520	4.0
(PhSiH <sub>2</sub> ) <sub>2</sub> :EtOH (1:2)	Co	3910	2190	1.8
(PhSiH <sub>2</sub> ) <sub>2</sub> :MeOH (1:2)	Co	8130	2310	3.5
PhCH <sub>2</sub> SiH <sub>3</sub> :EtOH (1:1.5)	Co	3320	1970	1.7
PhCH <sub>2</sub> SiH <sub>3</sub> :MeOH (1:1.5)	Co	2870	820	3.5

Stirred at ambient temperature in neat until the reaction mixture became rigid.

<sup>a</sup> [M]/[Si] = 0.02.

<sup>b</sup> Measured with GPC (vs. polystyrene) in THF.

reported that the dehydrocoupling of hydrosilanes with late transition metal catalysts produced a mixture of oligomers along with significant amounts of redistribution products [23].

### 2.3. UV absorption spectrum of poly(ethoxyphenylsilane)

The UV absorption spectrum of polyphenylsilane contains a weak transition at 297 nm ( $\epsilon_{\text{Si-Si}} = 2062 \text{ cm}^{-1} \text{ M}^{-1}$ ). Substitution of the Si-H group with a Si-OEt group resulted in a red shift of 45 nm and an increase in the extinction coefficient (Fig. 1). The differences in the  $\lambda_{\text{max}}$  for the -H and -OEt substituents are likely a result of an electronic perturbation of the silicon backbone by the ethoxy substituent. The lone-pair electrons on the oxygen substituent might be expected to perturb the electronic structure of the polymer backbone by destabilizing the HOMO more than the LUMO, leading to a decrease of the transition energy.

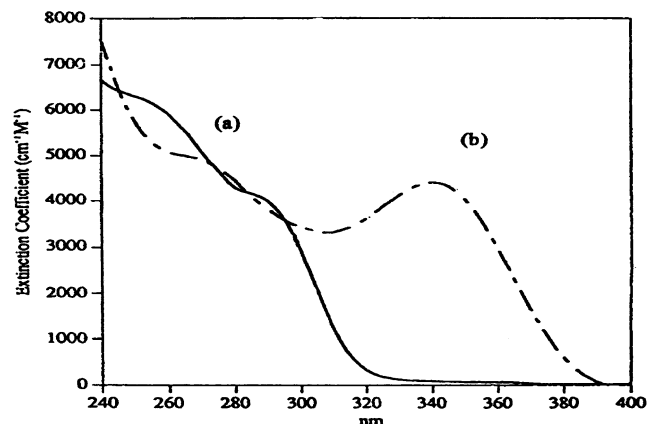


Fig. 1. UV spectra of  $-(\text{PhSiX})_n-$ : (a) polyphenylsilane; (b) poly(ethoxyphenylsilane).

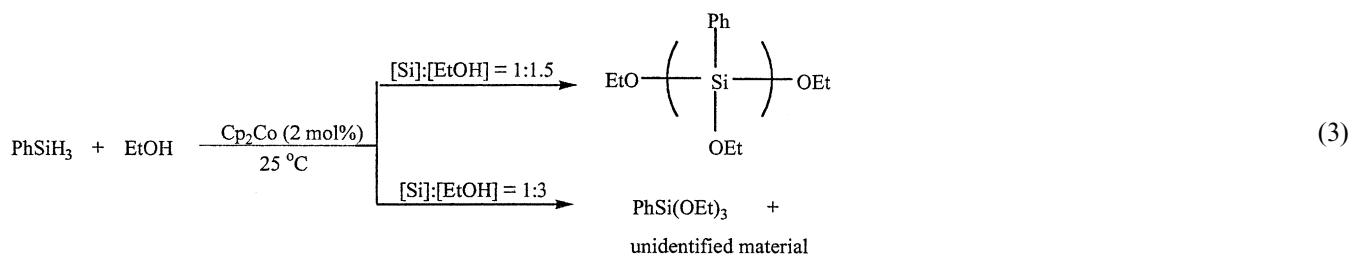
### 2.4. Conclusions

Poly(alkoxysilane)s were prepared in high yields from the Si-Si/Si-O dehydrocoupling reactions of silanes with alcohols (1:1.5 mole ratio) in the presence of Cp<sub>2</sub>MCl<sub>2</sub>/Red-Al (M = Ti, Zr) and Cp<sub>2</sub>M' (M' = Co, Ni) catalyst. Thus, this is a mild and one-pot procedure with considerable synthetic flexibility for the preparation of a wide variety of functionalized polysilanes.

## 3. Experimental

### 3.1. General procedures and materials

All reactions and manipulations were carried out under prepurified nitrogen atmosphere using Schlenk techniques. Dry, oxygen-free solvents were employed throughout. All glasswares were flamed-dried before use. Infrared spectra were obtained using a Nicolet 520 FT-IR or a Perkin-Elmer 1600 Series FT-IR spectrometer. Electronic spectra were acquired using an IBM 9420 UV-vis spectrophotometer. Proton NMR spectra were recorded on a Varian Gemini 300 spectrophotometer using CDCl<sub>3</sub>/CHCl<sub>3</sub> as a reference at 7.24 ppm downfield from Me<sub>4</sub>Si. 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 Ultrastyrigel GPC column series (sequence 500,  $10^3$ ,  $10^4$ ,  $10^5$  Å columns). Molecular weights were extrapolated from the calibration curve derived from the polystyrene standard. Data analyses were carried out using a Waters Data Module 570.  $\text{Cp}_2\text{TiCl}_2$ ,  $\text{Cp}_2\text{ZrCl}_2$ ,  $\text{Cp}_2\text{HfCl}_2$ , Red-Al,  $\text{Cp}_2\text{Co}$ , and  $\text{Cp}_2\text{Ni}$  were purchased from Aldrich Chemical Co and were used as received. Methanol, ethanol, isopropyl alcohol, phenol and 1,2,3-heptafluorobutanol were dried according to the literature procedure [25]. The  $p\text{-X-C}_6\text{H}_4\text{Si(OEt)}_3$  (X = H, F,  $\text{CH}_3$ ,  $\text{OCH}_3$ ) compounds were obtained by the reaction  $p\text{-X-C}_6\text{H}_4\text{MgBr}$  with  $\text{Si(OEt)}_4$ , respectively, in THF. The  $p\text{-X-C}_6\text{H}_4\text{SiH}_3$  reagents were prepared by reduction of the  $p\text{-X-C}_6\text{H}_4\text{Si(OEt)}_3$  with  $\text{LiAlH}_4$  in diethyl ether.

### 3.2. Synthesis of poly(alkoxysilane)s with Group IV metallocene combination catalysts

#### 3.2.1. General procedure for the reaction of $\text{PhSiH}_3$ and EtOH ( $[\text{Si}]:[\text{EtOH}] = 1:1.5$ ) catalyzed by $\text{Cp}_2\text{ZrCl}_2/\text{Red-Al}$

To a Schlenk flask containing  $\text{Cp}_2\text{ZrCl}_2$  (0.01 g, 0.03 mmol) and Red-Al (0.01 ml, 0.03 mmol; 3.4 M solution in toluene) were injected phenylsilane (0.18 g, 1.66 mmol) and ethanol (0.11 g, 2.43 mmol) in that order at room temperature. The reaction mixture immediately turned deep yellow with vigorous gas evolution. After disappearance of the gas evolution the reaction mixture was heated at 50 °C. The reaction medium became viscous. After 48 h, the catalyst was deactivated by exposure to the air for a minute. The mixture was passed rapidly through a silica gel column (28–200 mesh,  $20 \times 2$  cm) using 200 ml diethyl ether as an eluent. Removal of the volatiles in vacuo yielded a pale yellow tacky product. The tacky product was washed well with dry *n*-hexane (10 ml  $\times$  3) and dried in vacuo to give 0.21 g of off-white brittle powder which was soluble in most organic solvents. The combined washing solution was evaporated at reduced pressure to yield 0.04 g of a clear oil ( $\text{PhSi(OEt)}_3$ ).

Off-white powder, yield 76%,  $M_w = 1030$ ,  $M_n = 690$ . IR (KBr pellet): 3052, 2919, 2878, 2166, 1424, 1137, 1050, 845, 732.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  0.93–1.19 (br,  $\text{OCH}_2\text{CH}_3$ ), 3.54–3.83 (br,  $\text{OCH}_2\text{CH}_3$ ), 6.80–7.80 (br, Ph).

Clear oil, yield 10%, IR (KBr pellet): 3.67, 3.37, 2929, 2883, 1588, 1424, 1396, 1260, 1169, 958.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.14–1.19 (t,  $J = 7.0$  Hz, 3H,  $\text{OCH}_2\text{CH}_3$ ), 3.75–3.83 (q,  $J = 7.0$  Hz, 2H,  $\text{OCH}_2\text{CH}_3$ ), 7.21–7.41 (m, 3H, Ph), 7.57–7.63 (m, 2H, Ph). 7.57–7.63 (m, 2H, Ph).

#### 3.2.2. Reaction of $\text{PhSiH}_3$ and EtOH ( $[\text{Si}]:[\text{EtOH}] = 1:1.5$ ) catalyzed by $\text{Cp}_2\text{TiCl}_2/\text{Red-Al}$

Off-white powder, yield 76%,  $M_w = 1220$ ,  $M_n = 580$ . IR (KBr pellet): 3067, 3047, 2924, 2162, 1962, 1823, 1593, 1429, 1127, 1040, 850, 738.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.04–1.18 (br,  $\text{OCH}_2\text{CH}_3$ ), 3.10–3.65 (br,  $\text{OCH}_2\text{CH}_3$ ), 6.80–7.80 (br, Ph).

#### 3.2.3. Reaction of $\text{PhSiH}_3$ and EtOH ( $[\text{Si}]:[\text{EtOH}] = 1:3$ ) catalyzed by $\text{Cp}_2\text{TiCl}_2/\text{Red-Al}$

Clear oil, yield 95%. IR (KBr pellet): 3067, 3032, 2919, 1961, 1731, 1594, 1429, 1388, 1301, 1152, 947, 789.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.22–1.27 (t,  $J = 7.0$  Hz, 3H,  $\text{OCH}_2\text{CH}_3$ ), 3.84–3.91 (quartet,  $J = 7.0$  Hz, 2H,  $\text{OCH}_2\text{CH}_3$ ), 7.36–7.41 (m, 3H, Ph), 7.66–7.69 (m, 2H, Ph).

#### 3.2.4. Reaction of $\text{PhSiH}_3$ and EtOH ( $[\text{Si}]:[\text{EtOH}] = 1:1.5$ ) catalyzed by $\text{Cp}_2\text{HfCl}_2/\text{Red-Al}$

Clear oil, yield 43%. IR (KBr pellet): 3067, 3032, 2919, 1961, 1731, 1594, 1429, 1388, 1301, 1152, 947, 789.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.22–1.27 (t,  $J = 7.0$  Hz, 3H,  $\text{OCH}_2\text{CH}_3$ ), 3.84–3.91 (quartet,  $J = 7.0$  Hz, 2H,  $\text{OCH}_2\text{CH}_3$ ), 7.36–7.41 (m, 3H, Ph), 7.66–7.69 (m, 2H, Ph).

#### 3.2.5. Reaction of $\text{PhSiH}_2\text{-SiH}_2\text{Ph}$ and EtOH ( $[\text{Si}]:[\text{EtOH}] = 1:2.0$ ) catalyzed by $\text{Cp}_2\text{TiCl}_2/\text{Red-Al}$

Off-White powder, yield 70%.  $M_w = 1620$ ,  $M_n = 670$ . IR (KBr pellet): 3062, 3030, 2976, 2883, 2126, 1583, 1434, 1137, 897.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.10–1.28 (m, br,  $\text{OCH}_2\text{CH}_3$ ), 3.60–3.91 (m, br,  $\text{OCH}_2\text{CH}_3$ ), 7.0–7.4 (br, Ph).

#### 3.2.6. Reaction of $\text{PhCH}_2\text{SiH}_3$ and EtOH ( $[\text{Si}]:[\text{EtOH}] = 1:1.5$ ) catalyzed by $\text{Cp}_2\text{TiCl}_2/\text{Red-Al}$

Off-White powder, yield 77%.  $M_w = 1010$ ,  $M_n = 360$ . IR (KBr pellet): 3063, 2924, 2889, 2157, 1593, 1496, 1060.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.03–1.15 (m, br,  $\text{OCH}_2\text{CH}_3$ ), 1.88–2.13 (br,  $\text{PhCH}_2\text{Si}$ ), 3.55–3.69 (m, br,  $\text{OCH}_2\text{CH}_3$ ), 7.02–7.28 (br, Ph).

#### 3.2.7. Reaction of $\text{PhSiH}_3$ and $^i\text{PrOH}$ ( $[\text{Si}]:[{}^i\text{PrOH}] = 1:1.5$ ) catalyzed by $\text{Cp}_2\text{TiCl}_2/\text{Red-Al}$

Off-White powder, yield 64%.  $M_w = 750$ ,  $M_n = 570$ . IR (KBr pellet): 3073, 3046, 2927, 2896, 2166, 1963, 1822, 1593, 1431, 1129, 1036. 848.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  0.8–1.27 (br,  $\text{CH}(\text{CH}_3)_2$ ), 3.22–3.65 (br,  $\text{CH}(\text{CH}_3)_2$ ), 6.82–7.74 (br, Ph).



### 3.3. Synthesis of poly(alkoxysilane)s with Group VIII metallocene catalysts

#### 3.3.1. General procedure for the reaction of $\text{PhSiH}_3$ and $\text{EtOH}$ ( $[\text{Si}]:[\text{EtOH}] = 1:1.5$ ) catalyzed by $\text{Cp}_2\text{Co}$

Off-White powder, yield 87%.  $M_w = 1470$ ,  $M_n = 790$ . IR (KBr pellet): 3061, 2976, 2926, 2851, 1894, 1721, 1595, 1435, 1390, 1296, 1134, 1070, 736.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  0.79–1.04 (br,  $\text{OCH}_2\text{CH}_3$ ), 3.46–3.70 (br,  $\text{OCH}_2\text{CH}_3$ ), 7.08–7.20 (br, Ph), 7.26–7.49 (br, Ph).

#### 3.3.2. Reaction of $\text{PhSiH}_3$ and $\text{EtOH}$ ( $[\text{Si}]:[\text{EtOH}] = 1:1.5$ ) catalyzed by $\text{Cp}_2\text{Ni}$

Off-White powder, yield 78%.  $M_w = 610$ ,  $M_n = 580$ . IR (KBr pellet): 3078, 3047, 2975, 2929, 2176, 1962, 1823, 1579, 1424, 1393, 1163, 1040, 953, 735.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.04–1.18 (br,  $\text{OCH}_2\text{CH}_3$ ), 3.10–3.65 (br,  $\text{OCH}_2\text{CH}_3$ ), 6.78–7.82 (br, Ph).

#### 3.3.3. Reaction of $\text{PhSiH}_3$ and $\text{MeOH}$ ( $[\text{Si}]:[\text{MeOH}] = 1:1.5$ ) catalyzed by $\text{Cp}_2\text{Co}$

Off-White powder, yield 81%.  $M_w = 5900$ ,  $M_n = 1110$ . IR (KBr pellet): 3078, 3052, 2890, 1723, 1130, 1070, 998, 738, 698.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  3.00–3.33 (br,  $\text{OCH}_3$ ), 7.16–7.77 (br, Ph).

#### 3.3.4. Reaction of $\text{PhSiH}_3$ and $\text{PhOH}$ ( $[\text{Si}]:[\text{PhOH}] = 1:1.5$ ) catalyzed by $\text{Cp}_2\text{Co}$

Off-White powder, yield 88%.  $M_w = 5260$ ,  $M_n = 660$ . IR (KBr pellet): 3063, 1982, 1641, 1498, 1136, 928, 698.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  6.20–7.80 (br, Ph).

#### 3.3.5. Reaction of $\text{PhSiH}_3$ and $\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2\text{OH}$ ( $[\text{Si}]:[\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2\text{OH}] = 1:1.5$ ) catalyzed by $\text{Cp}_2\text{Co}$

Off-White powder, yield 75%.  $M_w = 2100$ ,  $M_n = 520$ . IR (KBr pellet): 3078, 3011, 1957, 1824, 1593, 1434, 1229, 1127, 1060, 912, 732, 697.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  3.41–4.13 (br,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2\text{OH}$ ), 6.81–7.74 (br, Ph).

#### 3.3.6. Reaction of $\text{PhSiH}_2\text{SiH}_2\text{Ph}$ and $\text{EtOH}$ ( $[\text{Si}]:[\text{EtOH}] = 1:2$ ) catalyzed by $\text{Cp}_2\text{Co}$

Off-White powder, yield 92%.  $M_w = 3910$ ,  $M_n = 2190$ . IR (KBr pellet): 3070, 3042, 2920, 2887, 1957, 1824, 1596, 1423, 1390, 1134, 1056, 956, 789, 733.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  0.60–1.20 (br,  $\text{OCH}_2\text{CH}_3$ ), 3.21–3.84 (br,  $\text{OCH}_2\text{CH}_3$ ), 7.62–7.82 (br, Ph).

#### 3.3.7. Reaction of $\text{PhCH}_2\text{SiH}_3$ and $\text{EtOH}$ ( $[\text{Si}]:[\text{EtOH}] = 1:1.5$ ) catalyzed by $\text{Cp}_2\text{Co}$

Off-White powder, yield 64%.  $M_w = 3320$ ,  $M_n = 1970$ . IR (KBr pellet): 30762, 2925, 1870, 1736, 1601, 1493, 1392, 1293, 1175, 1073, 959, 696.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300

MHz):  $\delta$  0.98–1.11 (br,  $\text{OCH}_2\text{CH}_3$ ), 1.94–2.13 (br,  $\text{PhCH}_2\text{Si}$ ), 3.53–3.71 (br,  $\text{OCH}_2\text{CH}_3$ ), 6.75–7.52 (br, Ph).

### Acknowledgements

This research was supported by the Leading Researcher Research Fund, Korea Research Foundation (Project No. 2000-041-D00165).

### References

- [1] J.M. Zeigler, L.A. Harrah, A.W. Johnson, Proc. SPIE-Int. Soc. Opt. Eng. 539 (1985) 166.
- [2] D. Seyferth, T.G. Wood, H.J. Tracy, J.L. Robinson, J. Am. Chem. Soc. 75 (1992) 1300.
- [3] R.G. Kepler, J.M. Zeigler, L.A. Harrah, S.R. Kurtz, Phys. Rev. B 35 (1987) 2818.
- [4] F. Kajzar, J. Messier, C. Rosilio, J. Appl. Phys. 60 (1986) 3040.
- [5] R.D. Miller, J. Michl, Chem. Rev. 89 (1989) 1359.
- [6] R.D. Miller, R. Sooriyakumaran, Macromolecules 21 (1988) 3120.
- [7] H. Stueger, R. West, Macromolecules 21 (1985) 2349.
- [8] K. Matyjaszewski, J. Inorganic. Organomet. Polym. 1 (1991) 463.
- [9] T. Seki, A. Thonai, T. Tamaki, K. Ueno, J. Chem. Soc. Chem. Commun. (1993) 1876.
- [10] Y. Nakano, S. Murai, R. Kani, S. Hayase, J. Polym. Sci. Part A: Polym. Chem. 31 (1993) 1876.
- [11] (a) C.T. Aitken, J.F. Harrod, E. Samuel, J. Organomet. Chem. 279 (1985) C11; (b) H.-G. Woo, T.D. Tilley, J. Am. Chem. Soc. 111 (1989) 8043; (c) J.Y. Corey, X.-H. Zhu, Organometallics 11 (1992) 672; (d) F. Gauvin, J.F. Harrod, H.-G. Woo, Adv. Organomet. Chem. 42 (1998) 363; (e) T.D. Tilley, Acc. Chem. Res. 26 (1993) 22.
- [12] J.P. Banovetz, Y.-L. Hsiao, R.M. Waymouth, J. Am. Chem. Soc. 115 (1993) 2540.
- [13] J.P. Banovetz, Y.-L. Hsiao, R.M. Waymouth, Polym. Prepr. 34 (1993) 228Am. Chem. Soc. Div. Polym. Chem..
- [14] E. Lukevics, M. Dzintara, J. Organomet. Chem. 295 (1985) 265.
- [15] C.G. Pitt, in: A.L. Rheingold (Ed.), Homoatomic Rings, Chains, and Macromolecules of Main-Group Elements, Elsevier Scientific Publishing Company, Amsterdam, 1977, p. 203.
- [16] T.C. Bedard, J.Y. Corey, J. Organomet. Chem. 428 (1992) 315.
- [17] L.H. Sommer, J.E. Lyons, J. Organomet. Chem. 89 (1967) 1521.
- [18] L.H. Sommer, J.D. Citron, J. Org. Chem. 32 (1967) 2470.
- [19] R.J.P. Corriu, J.J. Moreau, J. Chem. Soc. Chem. Commun. (1973) 38.
- [20] (a) R.J.P. Corriu, J.J. Moreau, Tetrahedron Lett. (1973) 4469; (b) R.J.P. Corriu, J.J. Moreau, J. Org. Chem. 114 (1976) 135; (c) R.J.P. Corriu, J.J. Moreau, J. Org. Chem. 127 (1977) 7; (d) R.J.P. Corriu, J.J. Moreau, J. Org. Chem. 120 (1976) 337.
- [21] I. Ojima, T. Kogure, M. Nihonyanagi, H. Kono, S. Inaba, Y. Nagai, Chem. Lett. (1973) 501.
- [22] (a) L.H. Sommer, J.E. Lyons, J. Am. Chem. Soc. 89 (1967) 1521; (b) L.H. Sommer, J.E. Lyons, J. Am. Chem. Soc. 91 (1967) 761.
- [23] J.Y. Corey, Adv. Silicon Chem. 1 (1991) 327.
- [24] B.-H. Kim, H.-G. Woo, in preparation.
- [25] W.L.F. Armarego, D.D. Perrin, Purification of Laboratory Chemicals, fourth ed., Butterworth Heinemann, Oxford, 1996.