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References

1. (a) Arnett, E. M.; Bentrude, W. G.; Duggleby, P. McG. *J. Am. Chem. Soc.* 1965, *87*, 2048. (b) Arnett, E. M.; Duggleby, P. McG.; Burke, J. J. *J. Am. Chem. Soc.* 1963, *85*, 1350. (c) Arnett, E. M.; Bentrude, W. G.; Burke, J. J.; Duggleby, P. McG. *J. Am. Chem. Soc.* 1965, *87*, 1541. (d) Arnett, E. M. *Phisicochemical Processes in Mixed Aqueous Solvents*; Franks, F., Ed.; Heinemann, London, 1967.
2. (a) Abraham, M. H.; Grellier, P. L.; Nasehzadeh, A.; Walker, R. A. C. *J. Chem. Soc., Perkin Trans. 2*, 1988, 1717. (b) Hyun, J. B. *Hydrogen-Bonded Solvent System*; Covington, A. K. Jones, P., Eds.; Taylor and Francis: London, 1968; p 99.
3. (a) Abraham, M. H. *J. Chem. Soc.(B)*, 1971, 299. (b) Abraham, M. H. *J. Chem. Soc., Perkin Trans. 2*, 1972, 1343. (c) Abraham, M. H. *J. Chem. Soc., Perkin Trans. 2*, 1975, 1856. (d) Abraham, M. H. *Advanced in Solution Chemistry*; Bertini, I.; Lunazzi, L.; Dei, A., Eds.; Plenum: New York, 1981; p 341.
4. Abraham, M. H.; Grellier, P. L. *J. Chem. Soc., Perkin Trans. 2*, 1976, 1735.
5. Kondo, Y.; Fujiwara, T.; Hayashi, A.; Kusabayashi, S. *J. Chem Soc., Perkin Trans. 2*, 1990, 741.
6. (a) Lee, I.; Shim, C. S.; Chung, S. Y.; Lee, H. W. *J. Chem. Soc Perkin Trans. 2*, 1988, 975. (b) Lee, I.; Shim, C. S.; Chung, S. Y.; Kim, H. Y.; Lee, H. W. *J. Chem. Soc., Perkin Trans. 2*, 1988, 1919.
7. (a) Lee, I.; Choi, Y. H.; Rhyu, K. W.; Shim, C. S. *J. Chem. Soc., Perkin Trans. 2*, 1989, 1881. (b) Lee, I.; Choi, Y. H.; Lee, H. W. *J. Chem. Soc., Perkin Trans. 2*, 1988, 1537.
8. (a) Lee, I.; Kang, C. H.; Lee, B-S.; Lee, H. W. *J. Chem. Soc. Faraday Trans. 86*, 1990, 1477. (b) Lee, I.; Kang, C. H.; Lee, B. S.; Lee, H. W. *Bull. Korean Chem. Soc.* 1990, *11*, 546.
9. Abraham, M. H. *Chem. Soc. Rev.* 1993, *22*, 73.
10. Klump, G. W. *Reactivity in Organic Chemistry*; Wiley: New York, 1982; p 275.
11. Cox, B. G.; Waghorne, W. E. *J. Chem. Soc., Faraday Trans. 1*, 1984, *80*, 1267.

Dehydrogenative Polymerization of New Alkylsilanes Catalyzed by Cp₂MCl₂/Red-Al System (M=Ti, Hf): Synthesis of Poly(substituted 3-phenyl-1-silabutanes)

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Substituted 3-phenyl-1-silabutanes such as 3-phenyl-1-silabutane (1), 3-(2,5-dimethylphenyl)-1-silabutane (2), 3-(p-chlorotolyl)-1-silabutane (3), and 3-naphthyl-1-silabutane (4) were prepared in 62-96% yield by reduction of the corresponding substituted 3-phenyl-1,1-dichloro-1-silabutanes with LiAlH₄. The dehydrogenative polymerization of the monomer silanes was carried out with Cp₂MCl₂/Red-Al (M=Ti, Hf) catalyst system. The molecular weight of the polymers produced ranged from 700 to 1300 (vs polystyrene) with degree of polymerization (DP) of 5 through 16 and with polydispersity index (PDI)=1.1-2.1. The dehydrogenative polymerization of the monomer silanes with Cp₂TiCl₂/Red-Al catalyst system occurred at a faster rate and produced somewhat higher molecular weights of polysilane than that with Cp₂HfCl₂/Red-Al catalyst system.

Introduction

Polysilanes have received a considerable amount of attention as ceramic precursors, third-order NLO materials, deep-UV photoresists, photoconductors, and photoinitiators.[1-3] The only viable method to get high molecular weight polysilanes to date has been the Wurtz coupling reaction of dichlorosilanes, which has several commercial drawbacks.

A major breakthrough in polyorganosilane synthesis was Harrod's recent discovery of the group 4 metallocene-catalyzed dehydrogenative polymerization.[4] Two mechanisms have been so far proposed: (1) the oxidative addition/reductive elimination sequences via the intermediacy of transition-metal silylene complexes[4] and (2) the four-center sigma bond metathesis processes among silicon, hydrogen, and a d⁰ metal center via the intermediacy of transition-metal silyl and hydride complexes.[5] The latter mechanism is strongly supported by many model reactions[5] and thermochemical results.[6]

A major disadvantage of the metallocene-catalyzed dehydrogenative coupling method is to produce low molecular weights of polysilanes.[4,5] Copious efforts have been made to increase the molecular weight of the polysilanes: (1) employment of multi(silyl)arene as a cross-linking agent,[7] (2) polymerization of sterically less hindered silanes such as SiH₄

and MeSiH$_3$.[8] (3) employment of new catalyst systems,[9] and (4) polymerization under the optimum reaction conditions.[10]

^{29}Si NMR technique has been useful in analyzing polysilane chain microstructure.[11] The structures of all polysilanes so far synthesized *via* dehydrogenative coupling method are predominantly random atactic although some diastereomeric selection was observed in the special reaction conditions.[12] To date, most of silanes which have been employed in the literature are arylsilanes. There are few reports on the dehydrogenative coupling of alkylsilanes.[8,13]

The dehydrogenative coupling route of substituted 3-phenyl-1-silabutanes may provide the possibility of controlling the molecular weight distribution and stereochemistry of polymer as well as introducing functionality into the polymer. In this contribution, we report the dehydrogenative coupling of substituted 3-phenyl-1-silabutanes to poly(substituted 3-phenyl-1-silabutanes) catalyzed by *in situ* generated metallocene complexes.

Experimental

All manipulations were performed under an atmosphere of nitrogen using Schlenk techniques. Dry, oxygen-free sovlents were employed throughout. Glassware was flame-dried or oven-dried before use. Elemental analyses were performed by Advanced Analysis Center of Korea Institute of Science and Technology, Seoul, Korea. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FT-IR or a Nicolet 520P FT-IR spectrometer. Electronic spectra were acquired using an IBM 9420 UV-vis spectrophotometer. 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. 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. Gas chromatography (GC) analyses were carried out using Varian 3300 chromatograph equipped with a packed column (10% OV-101 on Chromosorb, W/AW-DMCS 1.5 m×1/8″ od) in conjunction with a flame ionization detector. GC/MS data were obtained using a Hewlett-Packard 5890II chromatograph (HP-5, 5% phenylmethylsiloxane, 0.25 mm id×30.0 m, film thickness 0.25 µm) connected to a Hewlett-Packard 5972A mass selective detector. Gel permeation chromatography (GPC) was performed on a Waters Millipore GPC Liquid Chromatograph. The calibrant (monodisperse polystyrene) and the sample were dissolved in toluene 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. Data analyses were carried out using a Waters Data Module 570. Cp$_2$TiCl$_2$, Cp$_2$HfCl$_2$, Red-Al (3.4 M in toluene), and LiAlH$_4$ were purchased from Aldrich Chemical Co. and were used without further purification.

Monomer Synthesis

Substituted 3-phenyl-1,1-dichloro-1-silabutanes were prepared according to the literature procedure.[14] The following reduction procedure is representative of the other monomers. (**Warning**: In the absence of diethyl ether solvent, AlCl$_3$ can catalyze silane redistribution reactions to produce

SiH$_4$ which is an explosive gas upon contact with air. Therefore, the LiAlH$_4$ reduction of the silicon chlorides should be performed in ether and quenched properly with isopropyl alcohol solution of HCl and then with water.)

Synthesis of 3-Phenyl-1-silabutane (1). To a diethyl ether suspension of lithium aluminum hydride (3.07 g, 0.08 mol) in 70 mL of diethyl ether in a 250 mL three-necked, round-bottomed flask equipped with a reflux condenser topped with an inlet/outlet tube was slowly added 3-phenyl-1,1-dichloro-1-silabutane (10.1 g, 0.04 mol) in 70 mL of diethyl ether in a pressure equalizing addition funnel. After completion of addition, the mixture was stirred at room temperature for 3 h. The reaction mixture was filtered, cooled to 0 ℃, slowly quenched with an isopropyl alcohol (150 mL) solution of HCl (20 mL), and then poured into ice water. The resulting slurry was extracted with diethyl ether. The combined ether phases were washed twice with water, dried over anhydrous MgSO$_4$, and concentrated on rotary vacuum evaporator. The solution was then fractionally distrilled at 74-76 ℃ / 20 mmHg to yield 1 (3.70 g, 62%). Anal. Calcd for SiC$_9$H$_{14}$: C, 71.92; H, 9.31. Found: C, 71.72; H, 9.42. IR (neat, KBr, cm^{-1}): 2155 s (vSiH), 910 s (δSiH). ^{1}H NMR (δ, CDCl$_3$, 300 MHz): 1.14-1.20 (m, 2H, CH$_2$), 1.36 (d, J=3.5 Hz, 3H, CH$_3$), 2.92 (sextet, J=3.6 Hz, 1H, CH), 3.43 (t, J=3.9 Hz, 3H, SiH), 7.19-7.35 (m, 5H, ArH). ^{13}C{^{1}H} NMR (δ, CDCl$_3$, 75.5 MHz): 16.16 (SiCH$_2$), 24.54 (CH$_3$), 37.77 (CH), 126.13, 126.55, 128.43, 148.26 (ArC). GC/MS, m/e (relative intensity): 150 (23) (M$^+$), 135 (18), 119 (5), 109 (4), 108 (17), 107 (66), 105 (100), 91 (16), 79 (12), 77 (18), 72 (13), 65 (4), 51 (8).

Synthesis of 3-(2,5-Dimethylphenyl)-1-silabutane (2). 96% yield, bp 62-65 ℃ /0.6 mmHg. Anal. Calcd for SiC$_{11}$H$_{18}$: C, 74.08; H, 10.17. Found: C, 74.21; H, 10.22. IR (neat, KBr, cm^{-1}): 2150 s (vSiH), 905 s (δSiH). ^{1}H NMR (δ, CDCl$_3$, 300 MHz): 1.11-1.16 (m, 2H, CH$_2$), 1.29 (d, J=7.0 Hz, 3H, CH$_3$), 2.29, 2.32 (s, 3H, CH$_3$), 3.13 (sextet, J=7.0 Hz, 1H, CH), 3.44 (t, J=3.5 Hz, 3H, SiH), 6.89-7.04 (m, 3H, ArH) (isomer ratio=3 : 2). ^{13}C{^{1}H} NMR (δ, CDCl$_3$, 75.5 MHz): 15.35 (SiCH$_2$), 19.35, 21.26, 23.77 (CH$_3$), 32.44 (CH), 125.72, 126.50, 130.13, 131.92, 135.96, 146.15 (ArC). GC/MS, m/e (relative intensity): 178 (22) (M$^+$), 163 (10), 136 (31), 135 (55), 133 (100), 131 (20), 119 (15), 117 (18), 115 (22), 105 (38), 91 (27), 77 (14).

Synthesis of 3-(p-Chlorotolyl)-1-silabutane (3). 93% yield, bp 50-52 ℃ /0.6 mmHg. Anal. Calcd for SiC$_{10}$H$_{15}$Cl: C, 60.42; H, 7.61. Found: C, 60.70; H, 7.89. IR (neat, KBr, cm^{-1}): 2160 s (vSiH), 910 s (δSiH). ^{1}H NMR (δ, CDCl$_3$, 300 MHz): 1.10-1.17 (m, 2H, CH$_2$), 1.33 (1.31) (d, J=7.0 Hz, 3H, CH$_3$), 2.34 (2.31) (s, 3H, CH$_3$), 3.44 (3.13) (sextet, J=7.0 Hz, 1H, CH), 3.48 (t, J=4.0 Hz, 3H, SiH), 6.93-7.27 (m, 3H, ArH) (isomer ratio=4 : 1). ^{13}C{^{1}H} NMR (δ, CDCl$_3$, 75.5 MHz): 14.86 (15.23) (SiCH$_2$), 22.10 (18.90) (CH$_3$), 22.79 (22.52) (CH$_3$), 33.05 (32.56) (CH), 125.29, 125.72, 127.51, 127.84, 129.16, 130.16, 131.51, 133.10, 136.66, 144.90, 148.36 (ArC). GC/MS, m/e (relative intensity): 198 (26) (M$^+$), 157 (27), 156 (16), 155 (100), 154 (11), 153 (93), 145 (12), 121 (18), 119 (18), 117 (34), 116 (18), 115 (64), 105 (10), 93 (10), 92 (10), 91 (51), 89 (11), 77 (14), 65 (21), 63 (29).

Synthesis of 3-Naphthyl-1-silabutane (4). 66% yield, bp 72-75 ℃ /0.6 mmHg. Anal. Calcd for SiC$_{13}$H$_{16}$: C, 77.93; H, 7.98. Found: C, 77.83; H, 7.99. IR (neat, KBr, cm^{-1}): 2145 s (vSiH), 918 s (δSiH). ^{1}H NMR (δ, CDCl$_3$, 300 MHz): 1.26

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-1.45 (m, 2H, CH₂), 1.58 (1.52) (d, J=3.5 Hz, 3H, CH₃), 3.61 (3.56) (t, J=3.9 Hz, 3H, SiH), 3.91 (3.17) (sextet, J=3.9 Hz, 1H, CH), 7.41-8.18 (m, 7H, ArH) (isomer ratio=3 : 1). $^{13}C\{^1H\}$ NMR (δ, CDCl₃, 75.5 MHz): 15.64 (16.10) (SiCH₂), 23.55 (24.63) (CH₃), 31.75 (37.99) (CH), 122.57, 123.21, 124.67, 125.36, 125.46, 125.70, 125.94, 126.04, 126.71, 127.75, 128.23, 129.16, 131.32, 132.42, 133.75, 134.12, 144.35, 145.75 (ArC). GC/MS, m/e (relative intensity): 200 (37) (M⁺), 185 (7), 183 (6), 169 (5), 158 (30), 157 (41), 156 (16), 155 (100), 153 (27), 152 (20), 141 (8), 129 (9), 128 (18), 115 (7), 63 (2), 53 (1).

Polymerization Catalyzed by Cp₂TiCl₂/Red-Al

Polymerization of 1. The following procedure is representative of the polymerization reactions. To a Schlenk flask charged with Cp₂TiCl₂ (0.20 g, 0.80 mmol) and Red-Al (24 mL, 0.80 mmol) was added slowly 1 (1.20 g, 8.00 mmol). The reaction immediately turned dark green, and the reaction medium became rapidly viscous with strong gas evolution. The mixture was stirred under a stream of nitrogen for 24 h and then heated at 90 ℃ until the mixture became rigid. The catalyst was allowed to oxidize by exposure to the air for a few second, and the solution was then passed rapidly through a Silica gel column (70-230 mesh, 20 cm×2 cm). The column was rinsed with 200 mL of toluene. The removal of volatiles at reduced pressure yielded 1.00 g (83% yield) of off-white tacky product. IR (neat, KBr, cm⁻¹): 2150 s (vSiH). ¹H NMR (δ, CDCl₃, 300 MHz): 0.68-1.96 (m, 5H, SiCH₂, CH₃), 2.56-3.10 (m, 1H, CH), 3.10-3.85 (m, 2H, SiH), 6.88-7.47 (m, 5H, ArH). GPC: M_w=821; M_n=455; M_w/M_n=1.78.

Polymerization of 2. 79% yield. IR (neat, KBr, cm⁻¹): 2105 s (vSiH). ¹H NMR (δ, CDCl₃, 300 MHz): 0.80-1.50 (m, 5H, SiCH₂, CH₃), 2.10-2.40 (m, 6H, Ar-CH₃), 2.92-3.26 (m, 1H, CH), 3.26-3.72 (m, 2H, SiH), 6.77-7.40 (m, 3H, ArH). GPC: M_w=1292; M_n=1162; M_w/M_n=1.11.

Polymerization of 3. 81% yield. IR (neat, KBr, cm⁻¹): 2108 s (vSiH). ¹H NMR (δ, CDCl₃, 300 MHz): 0.78-1.49 (m, 5H, SiCH₂, CH₃), 2.09-2.49 (m, 3H, ArCH₃), 3.31-3.43 (m, 1H, CH), 3.43-3.62 (m, 2H, SiH), 6.78-7.38 (m, 3H, ArH). GPC: M_w=851; M_n=715; M_w/M_n=1.19.

Polymerization of 4. 83% yield. IR (neat, KBr, cm⁻¹): 2106 s (vSiH). ¹H NMR (δ, CDCl₃, 300 MHz): 0.79-1.73 (m, 5H, SiCH₂, CH₃), 2.71-3.08 (m, 1H, CH), 3.08-3.80 (m, 2H, SiH), 7.00-8.24 (m, 7H, ArH). GPC: M_w=831; M_n=699; M_w/M_n=1.19. UV-vis (hexane): $\lambda\sigma{\rightarrow}\sigma^*$=290 (ε=2800).

Polymerization Catalyzed by Cp₂HfCl₂/Red-Al

Polymerization of 1. The following procedure is representative of the polymerization reactions. 1 (0.14 g, 0.92 mmol) was slowly added to a Schlenk flask charged with Cp₂HfCl₂ (24 mg, 0.06 mmol) and Red-Al (18 μL, 0.06 mmol). The reaction immediately turned light yellow, and the reaction medium became slowly viscous with moderate gas evolution. The mixture was stirred under a stream of nitrogen for 30 min and then heated at 90 ℃ until the mixture became rigid. The catalyst was inactivated by exposure to the air for a few second, and the solution was then passed rapidly through a Silica gel column (70-230 mesh, 20 cm×2 cm). The column was rinsed with 200 mL of toluene. The removal of volatiles at reduced pressure yielded 0.043 g (31% yield) of off-white tacky product. IR (neat, KBr, cm⁻¹): 2150 s (vSiH). ¹H NMR (δ, CDCl₃, 300 MHz): 1.01-1.48 (m, 5H, SiCH₂,

Table 1. Physical Characteristics of Monomer Silanes

Monomer	Yield (%)	¹H NMR[a] (Si-H, ppm)	IR_{Si-H} (cm⁻¹)
1	62	3.43	2155
2	96	3.44	2150
3	93	3.48	2160
4	66	3.61	2145

[a] All measurements were carried out in CDCl₃ solvent.

CH₃), 2.70-2.90 (m, 1H, CH), 3.15-3.56 (m, 2H, SiH), 7.08-7.39 (m, 5H, ArH). GPC: M_w=807; M_n=410; M_w/M_n=1.97.

Polymerization of 2. 46% yield. IR (neat, KBr, cm⁻¹): 2105 s (vSiH). ¹H NMR (δ, CDCl₃, 300 MHz): 1.01-1.36 (m, 5H, SiCH₂, CH₃), 2.17-2.36 (m, 6H, Ar-CH₃), 2.98-3.19 (m, 1H, CH), 3.32-3.54 (m, 2H, SiH), 6.83-7.14 (m, 3H, ArH). GPC: M_w=948; M_n=488; M_w/M_n=1.94.

Polymerization of 3. 67% yield. IR (neat, KBr cm⁻¹): 2108 s (vSiH). ¹H NMR (δ, CDCl₃, 300 MHz): 0.78-1.49 (m, 5H, SiCH₂, CH₃), 2.09-2.49 (m, 3H, Ar-CH₃), 2.92-3.15 (m, 1H, CH), 3.20-3.70 (m, 2H, SiH), 6.78-7.38 (m, 3H, ArH). GPC: M_w=900; M_n=428; M_w/M_n=2.10.

Polymerization of 4. 84% yield. IR (neat, KBr, cm⁻¹): 2106 s (vSiH). ¹H NMR (δ, CDCl₃, 300 Mhz): 0.97-1.59 (m, 5H, SiCH₂, CH₃), 2.89-3.06 (m, 1H, CH), 3.27-3.79 (m, 2H, SiH), 7.16-8.21 (m, 7H, ArH). GPC: M_w=738; M_n=400; M_w/M_n=1.85.

Results

Monomer Synthesis. Substituted 3-phenyl-1,1-dichloro-1-silabutanes were prepared by Friedel-Crafts reaction of allyldichlorosilane with substituted aryl compounds in the presence of AlCl₃ as a catalyst.[14] The monomer silanes, substituted 3-phenyl-1-silabutanes, were prepared in 62-96% yield by reduction of the corresponding substituted 3-phenyl-1,1-dichloro-1-silabutanes with LiAlH₄ (Eq. 1).

X = H (1); CH₃,CH₃ (2); CH₃,Cl (3); c-(CH)₄ (4)
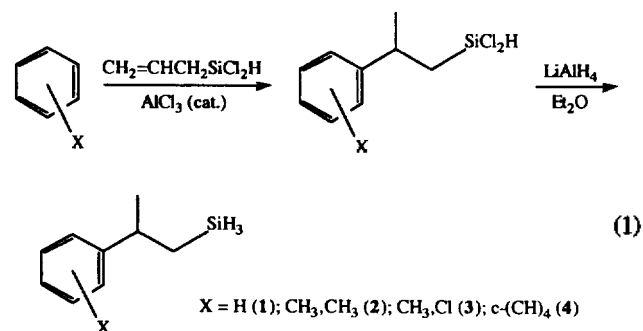
The monomer silanes such as 3-phenyl-1-silabutane (1), 3-(2,5-dimethylphenyl)-1-silabutane (2), 3-(p-chlorotolyl)-1-silabutane (3), and 3-naphthyl-1-silabutane (4) were purified by fractional distillation. The physical data of the monomer silanes are summarized in Table 1.
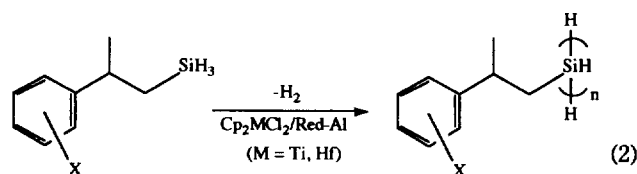
Polymerization of Monomer Silanes. Polymerization of the monomer silanes with Cp₂TiCl₂/Red-Al catalyst system commenced immediately, as evidenced by the immediate release of hydrogen gas, and the reaction medium became rapidly viscous (Eq. 2).

Table 2. Polymerization of Monomer Silanes with Cp_2TiCl_2/Red-Al[a]

Monomer	Yied (%)	mol wt[b]		
		M_w	M_n	PDI
1	83	821	455	1.78
2	79	1292	1162	1.11
3	81	851	715	1.19
4	83	831	699	1.19

[a][Ti]/[Si]=0.10. [b]GPC *vs* polystyrene.

Table 3. Polymerization of Monomer Silanes with Cp_2HfCl_2/Red-Al[a]

Monomer	Yied (%)	mol wt[b]		
		M_w	M_n	PDI
1	31	807	410	1.97
2	46	948	488	1.94
3	67	900	428	2.10
4	84	738	400	1.85

[a][Hf]/[Si]=0.065. [b]GPC *vs* polystyrene.

$$(2)$$

To drive the reaction toward completion, the mixture was stirred at room temperature for 24 h and then heated at 90 ℃ until the mixture became rigid. The polymers were isolated after workup including column chromatography as off-white tacky materials which are soluble in most organic solvents. The polymrization results are shown in Table 2.

Polymerization of the monomer silanes with Cp_2HfCl_2/Red-Al catalyst system initiated slowly, as noticed by the moderate release of hydrogen gas, and the reaction medium became slowly viscous. To drive the reaction toward completion, the mixture was stirred at room temperature for 30 min and then heated at 90 ℃ until the mixture became rigid. The polymers were obtained after workup including column chromatography as off-white tacky materials which are soluble in most organic solvents. The polymerization results are given in Table 3.

Discussion

The chemical shifts and coupling constants associated with the protons of the Si-H bonds in the ^1H NMR spectra of the monomer silanes are in the ranges of 3.4-3.6 ppm and 3.5-4.0 Hz, respectively. The Si-H stretching bands in the IR spectra of the silanes are in the 2145-2160 cm^{-1} range. The spectra data were in good agreement with similar products reported in the literature.

While the molecular weights of polysilanes produced by the dehydrogenative coupling reaction are lower than those

produced *via* Wurtz coupling of dichlorosilanes, this method is more tolerant of functional groups. The Wurtz coupling method cannot be used to polymerize chlorine-substituted arylsilanes due to cross-linking.[1] Although Cp_2ZrMe_2,[4] Cp_2Zr [(SiMe$_3$)$_3$]Me,[5] and Cp_2ZrCl_2/n-BuLi[12b] are the active catalysts for the dehydrogenative polymerization of primary silanes, we wanted to employ a new catalyst system, Cp_2MCl_2/Red-Al (M=Ti, Hf)[9] which was recently found to give predominantly linear, higher molecular weight of polysilanes than any other catalyst system, because the present monomer silanes, substituted 3-phenyl-1-silabutanes, are sterically hindered. Sterically hindered silanes were known to be very slow to polymerize and to give low molecular weights of oligosilanes.[5] Thus, in order to accelerate the rate of polymerization, higher catalyst concentration (*i.e.*, 10 mol% for Ti and 6.5 mol% for Hf) than usual concentration range of 0.5 -1.0 mol% and heating to 90 ℃ were employed in the polymerization. As anticipated from steric ground, the present monomer silanes dehydrogenatively polymerize slower than less hindered silane (*e.g.*, benzylsilane). However, substitution on the phenyl ring results in similar rates for both the methyl and chloro substituents. These results suggest that steric effect influences the rate of polymerization more than electronic effect in the present dehydrogenative polymerization. We cannot rationalize for the moment why **2** dehydropolymerizes to give somewhat higher molecular weight of polymer than the others in spite of similar rate of polymerization.

As expected from the reactivity of d^0 metallocene hydrides toward silanes, the monomer silanes with Cp_2TiCl_2/Red-Al catalyst system dehydrogenatively polymerize faster than with Cp_2HfCl_2/Red-Al catalyst system. The polymers reported here apparently show no sign of cross-linking due to coupling of the substituted chlorine and of the backbone Si-H bonds of polymer chains, evidenced by ^1H NMR, IR, and GPC. UV-vis spectrum in hexane of poly(3-naphthyl-1-silabutane) showed $\lambda_{o \to o^*}$=290 (ε=2800) which is in the normal range of polysilane.[1]

Although the molecular weights determined by GPC (*vs* polystyrene standard) are not directly comparable for various substituted polysilanes,[1] it appears that the polymers of present substituted 3-phenyl-1-silabutanes are lower degree of polymerization than those obtained from phenylsilane, but are approximately of the similar degree of polymerization as those obtained from benzylsilane[8] or n-butylsilane.[13] As seen in Table 2 and Table 3, the polymers with degree of polymerization (DP) of 5 through 16 were obtained. Cp_2TiCl_2/Red-Al system produced higher molecular weights of polysilane than Cp_2HfCl_2/Red-Al system, opposite trend to the polymerization of phenylsilane with Cp_2MCl_2/RLi system.[15] In comparison, the dehydrogenative polymerization of the monomer silanes with Cp_2MCl_2 (M=Ti, Hf)/n-BuLi catalyst system is currently underway. We are not presently certain of the percentage of cyclic and linear oligomers in the polymers. We expect some degree of diastereomeric selection in the polymerization due to the presence of 2-methyl group of the substituted 3-phenyl-1-silabutanes. To find out the percentage of cyclic and linear oligomers in the polymers and the degree of diastereomeric selection in the polymerization is currently in progress and will be the subject of a future paper.

Conclusion

Our work describes the preparation and the dehydrogenative polymerization of new alkylsilanes, substituted 3-phenyl-1-silabutanes, catalyzed by Cp_2MCl_2 (M = Ti, Hf)/Red-Al combined system. The polymers with degree of polymerization (DP) of 5 through 16 were obtained. The dehydrogenative polymerization of the monomer silanes with Cp_2TiCl_2/Red-Al catalyst system occurred at a faster rate and produced higher molecular weights of polysilane than that with Cp_2HfCl_2/Red-Al catalyst system, opposite trend to the polymerization of phenylsilane with Cp_2MCl_2/RLi system.

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References

1. Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359.
2. West, R. *J. Organomet. Chem.* **1986**, *300*, 327.
3. Ziegler, J. M.; Fearon, F. W. G. *Silicon-based Polymer Science*; American Chemical Society: Washington, DC, 1990.
4. (a) Aitken, C.; Harrod, J. F.; Gill, U. S. *Can. J. Chem.* **1987**, *65*, 1804. (b) Harrod, J. F.; Yun, S. S. *Organometallics* **1987**, *6*, 1381. (c) Aitken, C.; Barry, J.-P.; Gauvin, F.; Harrod, J. F.; Malek, A.; Rousseau, D. *Organometallics* **1989**, *8*, 1732. (d) Harrod, J. F.; Ziegler, T.; Tschinke, V. *Organometallics* **1990**, *9*, 897.
5. (a) Woo, H.-G.; Tilley, T. D. *J. Am. Chem. Soc.* **1989**, *111*, 3757. (b) Woo, H.-G.; Tilley, T. D. *J. Am. Chem. Soc.* **1989**, *111*, 8043. (c) Woo, H.-G.; Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 5698. (d) Woo, H.-

6. (a) Nolan, S. P.; Porchia, M.; Marks, T. J. *Organometallics* **1991**, *10*, 1450. (b) Forsyth, C. M.; Nolan, S. P.; Marks, T. J. *Organometallics* **1991**, *10*, 2543.
7. (a) Woo, H.-G.; Walzer, J. F.; Tilley, T. D. *Macromolecules* **1991**, *24*, 6863. (b) Imori, T.; Woo, H.-G.; Walzer, J. F.; Tilley, T. D. *Chem. Mater.* **1993**, *5*, 1487.
8. (a) Harrod, J. F. in *Transformation of Organometallics into Common and Exotic Materials: Design and Activation*; Laine, R. M., Ed.; NATO ASI Series E: Appl. Sci. no. 141; Martinus Nijhoff Publishers: Amsterdam, 1988; p 103. (b) Mu, Y.; Harrod, J. F. in *Inorganic and Organometallic Polymers and Oligomers*; Harrod, J. F.; Laine, R. M., Eds.; Kluwer Academic Publishers: Dordrecht, 1991; p 23.
9. Woo, H.-G.; Harrod, J. F. Manuscript in preparation.
10. Tilley, T. D. *Acc. Chem. Res.* **1993**, *26*, 22.
11. (a) Wolff, A. R.; Nozue, I.; Maxka, J.; West, R. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 701. (b) Maxka, J.; Mitter, F. K.; Powell, D. R.; West, R. *Organometallics* **1991**, *10*, 660.
12. (a) Banovetz, J. P.; Stein, K. M.; Waymouth, R. M. *Organometallics* **1991**, *10*, 3430. (b) Corey, J. Y.; Huhmann, J. L.; Zhu, X.-H. *Organometallics* **1993**, *12*, 1121. (c) Li, H.; Butler, I. S.; Harrod, J. F. *Organometallics* **1993**, *12*, 4553.
13. Campbell, W. H.; Hilty, T. K. *Organometallics* **1989**, *8*, 2615.
14. Lee, B. W.; Yoo, B. R.; Kim, S.-I.; Jung, I. N. *Organometallics* **1994**, *13*, 1312.
15. Li, H.; Gauvin, F.; Harrod, J. F. *Organometallics* **1993**, *12*, 575.

A Potential Flame-retardant by Intumescence. Melaminium 2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-4-methoxy-sulfates

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New compounds of melaminium 2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-4-methoxy-sulfate have been synthesized and characterized by means of chemical analysis, ^1H, ^{13}C, and ^{31}P NMR, and IR spectroscopies. When the compounds are subjected to an open flame, they foam without melting to produce a light char with about 50 times volume of the initial compounds. The evaluation of these flame-retardants proves to be efficient for polypropylene. Thermogravimetric analysis discloses that the compounds are also thermally stable for compounding into polypropylene without decomposition.

Introduction

In recent years, the use of some traditional halogenated flame-retardants is limited on account of the possible forma-

tion of extremely toxic halogenated dioxines or dibenzofurans.[1,2] Among alternative candidates intumescent materials have a considerable attention because they provide fire protection with minimum of overall fire hazard.[3] Since the first