

stitution along with the minor chain propagation, resulting in a branched polymer. This result suggests that the polymerization of a vinyl monomer having an activating aromatic ring with a Lewis acid should yield a highly branched polymer if the reactivities of the aromatic ring and the vinyl group toward the carbocation are controlled properly.

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Catalytic Dehydropolymerization of Di-*n*-butylstannane $n\text{-Bu}_2\text{SnH}_2$ by Group 4 and 6 Transition Metal Complexes

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The catalytic dehydrocoupling of di-*n*-butylstannane $n\text{-Bu}_2\text{SnH}_2$ by the $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$ ($\text{M} = \text{Ti, Zr, Hf}$) and $\text{M}(\text{CO})_6/\text{Red-Al}$ *in situ* combination catalysts yielded a mixture of two kinds of catenated products: one is a cross-linked insoluble solid, and the other is a non-cross-linked soluble solid ($\approx \text{Sn}_2$) or viscous oil ($\approx \text{Sn}_2$). The soluble oligostannanes could be produced by simple dehydrocoupling of $n\text{-Bu}_2\text{SnH}_2$, whereas the insoluble polystannanes could be obtained *via* disproportionation/dehydrocoupling combination process of $n\text{-Bu}_2\text{SnH}_2$. The disproportionation/dehydrocoupling combination process may initially produce a low-molecular-weight oligostannane with partial backbone Sn-H bonds which could then undergo an extensive cross-linking reaction of backbone Sn-H bonds, resulting in the formation of an insoluble polystannane.

Introduction

For many special applications, inorganic polymers possessing various superior properties over organic polymers have been employed.¹ In particular, polysilanes with unique optoelectronic and chemical properties attributed to σ electron-conjugation along the one-dimensional silicon polymer backbone have received extensive attentions as SiC pre-ceramic polymers,^{2a} electroluminescent materials,^{2b} deep-UV photoresists of positive image,^{2c} electroconductors,^{2d} and photoinitiators.^{2e-f} The Wurtz coupling reaction of organodichlorosilanes using an alkali metal dispersion in toluene-re-

fluxing temperature is the conventional method for synthesizing polysilanes. However, the synthetic method has several disadvantages such as intolerance of some functional groups, lack of reproducibility, and danger due to the strongly reduced reaction conditions.³ Other synthetic methods include anionic polymerization of masked disilenes,^{4a} ring-opening polymerization of cyclic oligosilanes,^{4b} electroreductive polymerization of organodichlorosilanes,^{4c} sonochemical polymerization of organodichlorosilanes,^{4d} and electrochemical polymerization of hydrosilanes.^{4e} Harrod recently discovered an alternative group 4 metallocene-catalyzed dehydropolymerization of hydrosilanes, resulting in

great progress in poly(organosilane) synthesis.⁵ Worldwide efforts have been intensively made to refine the synthetic method.⁶⁻¹¹

Polystannane, a tin analogue of polysilane, has not been thoroughly studied because of its synthetic difficulties. Recently, the synthesis of poly(di-*n*-butylstannane)s by Wurtz-type coupling of *n*-Bu₂SnCl₂ using molten Na metal¹² and by hydrostannolysis of *n*-Bu₂Sn(CH₂CH₂OEt)NMe₂ in the presence of DIBAL-H¹³ have been reported. Very recently, Tilley *et al.* described the catalytic dehydropolymerization of secondary stannanes by the group 4 zirconocene complexes, producing soluble (uncross-linked) mixtures of cyclic oligostannanes (up to 50%) and linear polystannanes (*M_w* up to 70000).¹⁴ The group 4 Cp₂MCl₂/Red-Al (M=Ti, Zr, Hf) combination catalyst and the group 6 M(CO)₆ or M(CO)₆/Red-Al (M=Cr, Mo, W) combination catalyst have been developed in our laboratory for dehydropolymerization of hydrosilanes to polysilanes.^{11,15,16} We reported the redistribution/dehydrocoupling of 2-phenyl-1,3-disilapropane by the Cp₂MCl₂/Red-Al (M=Ti, Zr, Hf) catalyst and the catalytic dehydropolymerization of 2-phenyl-1,3-disilapropane by the Cp₂MCl₂/*n*-BuLi combination catalyst (M=Ti, Zr, Hf).¹⁵ We also reported the dehydropolymerization of 3-aryl-1-silabutanes catalyzed by the group 4 Cp₂MCl₂/Red-Al and the group 6 Cr(CO)₆.^{11,16} In this paper, we wish to report our result on the catalytic dehydrocoupling of *n*-Bu₂SnH₂ by the group 4 Cp₂MCl₂/Red-Al (M=Ti, Zr, Hf) combination catalyst and by the group 6 M(CO)₆/Red-Al (M=Cr, Mo, W) combination catalyst to compare their catalytic effects with the Tilley's results using zirconocene catalysts.¹⁴

Experimental Section

All reactions and manipulations were performed under prepurified nitrogen using Schlenk techniques. Dry, oxygen-free solvents were employed throughout. Glassware was flame-dried or oven-dried before use. Infrared spectra were obtained using a Perkin-Elmer 1600 Series FT-IR or a Nicolet 520P FT-IR spectrometer. Proton NMR spectra were recorded on a Varian Gemini 300 spectrometer using CDCl₃/CHCl₃ as a reference at 7.24 ppm downfield from TMS. Gel permeation chromatography (GPC) was carried out on a Waters Millipore GPC liquid chromatograph. The calibrant (monodisperse polystyrene) and the sample were dissolved in toluene and separately eluted from an Ultrastaygel GPC column series (sequence 500, 10³, 10⁴ 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. Thermogravimetric analysis (TGA) of the polymer sample was performed on a Perkin-Elmer 7 Series thermal analysis system under an argon flow. The polymer sample was heated from 25 to 900 °C at a rate of 20 °C/min. Ceramic residue yield (as a matter of convenience, read at 400 °C) is reported as the percentage of the sample remaining after completion of the heating cycle. Cp₂MCl₂ (M=Ti, Zr, Hf), M(CO)₆ (M=Cr, Mo, W), *n*-Bu₂SnCl₂, and Red-Al (or Vitride; sodium bis(2-methoxyethoxy)aluminum hydride; 3.4 M in toluene) were purchased from Aldrich Chemical Co. and were used without further purification. The di-*n*-butylstannane *n*-Bu₂SnH₂ was prepared by reduc-

tion of *n*-Bu₂SnCl₂ with LiAlH₄ in diethyl ether.¹⁷

Dehydropolymerization of *n*-Bu₂SnH₂ Catalyzed by Cp₂MCl₂/Red-Al (M=Ti, Zr, Hf). The following procedure is the representative of the dehydropolymerization of neat di-*n*-butylstannane *n*-Bu₂SnH₂ with the group 4 metallocene Cp₂MCl₂/Red-Al (M=Ti, Zr, Hf) combination catalysts. *n*-Bu₂SnH₂ (0.30 g, 1.28 mmol) was injected to a Schlenk flask containing *in situ*-generated dark purple catalytic mixture of Cp₂TiCl₂ (6.5 mg, 0.026 mmol) and Red-Al (6.7 μL, 0.026 mmol) which was protected from room light. The reaction mixture instantly turned dark red-brown, and the reaction medium became quickly gelatinous with rapid gas evolution. The catalyst was inactivated 30 min later by exposure to the air for a few minutes. The dark red-brown gelatinous material was washed well with dry THF and dried at reduced pressure to give 0.117 g (39% yield) of yellow solid which was insoluble in most organic solvents. The combined washing solutions were pumped to dryness and the resulting solid was dissolved in 20 mL of dry hexane. Dry methanol was added to the hexane solution to separate the oligomer as a yellow viscous oil. Removal of solvents by decantation followed by drying under vacuum yielded 0.183 g (61% yield) of yellow solid which was soluble in most organic solvents. For the insoluble solid: IR (KBr pellet, cm⁻¹): 1807 w (ν_{SnH}); TGA ceramic residue yield: 38% at 400 °C and 33% at 900 °C (grey solid), onset temperature for decomposition = 300 °C. For the soluble solid: ¹H NMR (δ, CDCl₃, 300 MHz): 0.91 (m, CH₃), 1.19-1.60 (m, CH₂CH₂), 1.70-1.90 (m, CH₂); GPC: *M_w*=1050, *M_n*=1030, *M_w*/*M_n* (PDI)=1.02.

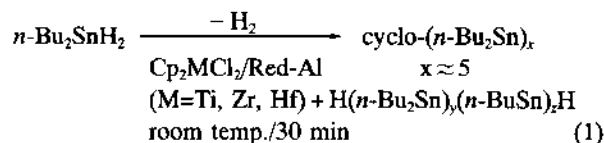
Dehydropolymerization of *n*-Bu₂SnH₂ Catalyzed by M(CO)₆/Red-Al (M=Cr, Mo, W). As a typical dehydropolymerization of neat dibutylstannane *n*-Bu₂SnH₂ with the group 6 metallocene M(CO)₆/Red-Al (M=Cr, Mo, W) combination catalysts, a Schlenk flask was charged with *n*-Bu₂SnH₂ (0.30 g, 1.28 mmol), Cr(CO)₆ (5.7 mg, 0.026 mol) and Red-Al (6.7 μL, 0.026 mmol), keeping room light avoided. The reaction mixture slowly turned light green, and the reaction medium became gelatinous over 16 h. The catalyst was then destroyed by exposure to the air for a few minutes. The light green gelatinous material was washed well with dry THF and dried *in vacuo* to give 0.12 g (40% yield) of yellow solid which was insoluble in most organic solvents. The volatiles were removed from the combined washing solutions at reduced pressure and the resulting solid was taken in 20 mL of dry hexane. Dry methanol was added to the hexane solution to separate the oligomer as a yellow oil. Removal of solvents by decantation followed by drying *in vacuo* afforded 0.18 g (60% yield) of yellow viscous oil. For the insoluble solid: IR (KBr pellet, cm⁻¹): 1807 w (ν_{SnH}); TGA ceramic residue yield: 38% at 400 °C and 33% at 900 °C (grey solid), onset temperature for decomposition=300 °C. For the viscous oil: IR (neat, KBr, cm⁻¹): 1808 w (ν_{SnH}); ¹H NMR (δ, CDCl₃, 300 MHz): 0.89 (m, CH₃), 1.21-1.40 (m, CH₂CH₂), 1.87 (m, CH₂), 4.47 (m, SnH); GPC: *M_w*=450, *M_n*=430, *M_w*/*M_n* (PDI)=1.05.

Results and Discussion

Group 4 zirconocenes such as Cp₂ZrMe₂,⁵ Cp₂Zr[Si

(SiMe₃)₃Me,⁶ and Cp₂ZrCl₂/*n*-BuLi¹⁸ are known to be the active catalysts for the dehydropolymerization of primary silanes. *Inter alia*, CpCp*Zr[Si(SiMe₃)₃]Me and (CpCp*ZrH₂)₂ were the most active catalyst previously examined.⁶ Nonetheless, we decided to employ a novel *in situ* combination catalyst, Cp₂MCl₂/Red-Al (M = Ti, Zr, Hf) because the catalyst was recently found to give predominantly linear, higher molecular weight of polysilanes than for any other catalyst system.¹⁹ In general, sterically hindered silanes such as R₂SiH₂ (R = *n*-Bu, Ph, mesityl) were known to be very slow to polymerize and to give low-molecular-weight oligosilanes.^{5,6} However, a hydrostannane is more reactive toward various reactants than a hydrosilane²⁰ because the bond energy of Sn-H bond (74 kcal/mol) is smaller than that of Si-H bond (90 kcal/mol).²¹ As expected, Tilley *et al.* reported the dehydropolymerization of sterically hindered secondary stannanes catalyzed by the group 4 zirconocene complexes, producing a THF-soluble mixture of cyclic oligostannanes (up to 50%) and linear polystannanes (*M_w* up to 70000).¹⁴ We also decided to use another new *in situ* combination catalyst, M(CO)₆/Red-Al (M = Cr, Mo, W) because the group 6 transition metal carbonyl catalysts produce higher-molecular-weight polysilanes in the dehydrocoupling of alkylsilanes than the group 4 metallocene catalysts do.¹⁶

Dehydropolymerization of *n*-Bu₂SnH₂ with 2 mol% of the Cp₂MCl₂/Red-Al (M = Ti, Zr, Hf) combination catalysts initiated immediately, as monitored by the immediate release of hydrogen gas, and the reaction medium became rapidly gelatinous (eq. 1).



The products were isolated in quantitative yield as two phases after workup including washing and precipitation. The first part of the polymers was obtained in 26-39% yield as a yellow solid which was insoluble in most organic solvents. The TGA ceramic residue yields at 900 °C of the insoluble solids were *ca.* 33%. The second part of the polymers was acquired in 61-74% yield as a yellow solid which was soluble in most organic solvents. The weight average molecular weight (*M_w*) and number average molecular weight (*M_n*) of the oily polymers (closely equivalent to Sn₂) were in the range of 1010-1120 and 990-1110, respectively. The characterization data are summarized in Table 1.

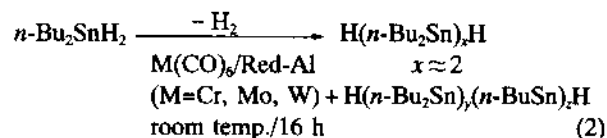
Table 1. Characterization of Catalytic Dehydropolymerization of *n*-Bu₂SnH₂ with Group 4 Transition Metal Complex^a

Catalyst	% Yield ^b	mol wt ^c	
		<i>M_w</i>	<i>M_n</i>
Cp ₂ TiCl ₂ /Red-Al	61 (39)	1050	1030
Cp ₂ ZrCl ₂ /Red-Al	73 (27)	1120	1110
Cp ₂ HfCl ₂ /Red-Al	74 (26)	1010	990

^a [M]/[Sn]=0.02; at ambient temperature for 30 min. ^b Yield of THF-soluble product; the number in bracket is yield of THF-insoluble product. ^c Measured with GPC (*vs* polystyrene) in THF.

The IR spectra of the insoluble solids exhibit a very weak ν_{Sn-H} band at *ca.* 1807 cm⁻¹. The ¹H NMR spectra of the soluble oligostannanes (Sn₅ cyclic?) apparently show mountain-like multiple resonances only assigned to *n*-Bu₂ groups. Therefore, the IR spectra of the soluble solids do not exhibit an appreciable ν_{Sn-H} band at *ca.* 1807 cm⁻¹.

Dehydropolymerization of *n*-Bu₂SnH₂ with 2 mol% of the M(CO)₆/Red-Al (M = Cr, Mo, W) combination catalysts commenced slowly, as monitored by the moderate evolution of hydrogen gas, and the reaction medium became slowly gelatinous (eq. 2).



The polymer was isolated in quantitative yield as two phases after workup including washing and precipitation. The first part of the polymers was obtained in 39-48% yield as a yellow solid which was insoluble in most organic solvents. The TGA ceramic residue yields at 900 °C of the insoluble solids were *ca.* 33%. The second part of the polymers was acquired in 52-61% yield as a yellow viscous oil which was soluble in most organic solvents. The weight average molecular weight (*M_w*) and number average molecular weight (*M_n*) of the oily polymers (closely equivalent to Sn₂) were in the range of 440-450 and 430, respectively. The characterization data are given in Table 2. The IR spectra of the insoluble solids exhibit a very weak ν_{Sn-H} band at *ca.* 1807 cm⁻¹. The ¹H NMR spectra of the soluble oligostannanes (Sn₂ dimer?) apparently show mountain-like multiple resonances assigned to *n*-Bu₂ groups along with resonances centered at 4.47 ppm assigned to Sn-H. The IR spectra of the yellow viscous oils exhibit a weak ν_{Sn-H} band at *ca.* 1808 cm⁻¹.

As shown in Table 1, the group 4 combination catalysts in the dehydropolymerization of *n*-Bu₂SnH₂ produce the polystannanes with similar molecular weights in the similar polymerization yields. Similarly, as shown in Table 2, the group 6 combination catalysts in the dehydropolymerization of *n*-Bu₂SnH₂ produce the polystannanes with similar molecular weights in the similar polymerization yields. Interestingly, as shown in Table 1 and 2, the molecular weights of the soluble oligostannanes (Sn₅?) prepared from the catalytic dehydropolymerization by the group 4 combination catalysts were higher than those of the soluble oligostannanes (Sn₂?) prepared from the catalytic dehydropolymeri-

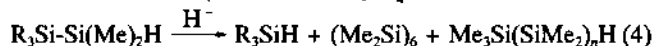
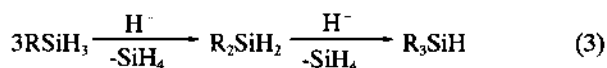
Table 2. Characterization of Catalytic Dehydropolymerization of *n*-Bu₂SnH₂ with Group 6 Transition Metal Complex^a

Catalyst	% Yield ^b	mol wt ^c	
		<i>M_w</i>	<i>M_n</i>
Cr(CO) ₆ /Red-Al	60 (40)	450	430
Mo(CO) ₆ /Red-Al	52 (48)	440	430
W(CO) ₆ /Red-Al	61 (39)	450	430

^a [M]/[Sn]=0.02; at ambient temperature for 16 h. ^b Yield of THF-soluble product; the number in bracket is yield of THF-insoluble product. ^c Measured with GPC (*vs* polystyrene) in THF.

zation by the group 6 combination catalysts.

We first expected that the catalytic dehydrocoupling of *n*-Bu₂SnH₂ by the group 4 and 6 combination catalysts could give the same type of polystannane as Tilley's because both catalyst systems are known to produce same catalytic species in the presence of silane,⁵⁻¹¹ but they yielded different products. We found from the above results that the expected structures of uncross-linked oligostannanes are obtained along with unexpected structure of cross-linked polystannanes from the catalytic dehydrocoupling of *n*-Bu₂SnH₂ by Cp₂MCl₂/Red-Al (M = Ti, Zr, Hf) and M(CO)₆/Red-Al (M = Cr, Mo, W) combination catalysts. Red-Al (or Vitride; sodium bis(2-methoxyethoxy)aluminum hydride) is known to catalyze the exchange reactions of di- and trihydrosilanes^{22a} (eq. 3) and the oligomerization of disilanes^{22b} (eq. 4), catalyzed by inorganic hydrides (e.g., NaH, KH, etc.). Corriu *et al.* suggested a mechanism *via* the intermediacy of a pentacoordinated hydrosilyl anion,^{22c} which is formed by addition of hydride (H⁻) on the silanes. We recently found an intriguing redistribution of bis- and tris(silyl) methanes with Si-C-Si linkage(s) (eq. 5), catalyzed by Red-Al.^{22d}



We believe that a small portion of *n*-Bu₂SnH₂ may be disproportionated into *n*-BuSnH₃ and *n*-Bu₃SnH in the presence of Red-Al although we failed up to now to prove the presence of *n*-Bu₃SnH in the reaction mixture. *n*-BuSnH₃ may be immediately dehydrocoupled with *n*-Bu₂SnH₂ to produce soluble *co*-polystannane, (*n*-Bu₂Sn)_{*n*}(*n*-Bu(H)Sn)_{*n*}, of which the backbone Sn-H may then undergo the cross-linking process due to reactive Sn-H bonds. PhGeH₃ and PhSnH₃ are known to undergo the dehydrocoupling process, catalyzed by the group 4 metallocenes, to give the cross-linked polymers.²³ The mechanisms for the dehydrocoupling of hydrostannanes, hydrogermanes, and hydrosilanes could be same.^{5,6,10,14} We tentatively assign the polymer as a copolymer. We are making our effort to elucidate the structure of the copolymer using solid-state ¹³C and ¹¹⁹Sn NMR spectroscopy and other analytical techniques. The IR spectra of soluble and insoluble polymeric products are quite similar with each other except the Sn-H stretching frequency. The TGA ceramic residue yield at 400 °C of Tilley's uncross-linked poly(di-*n*-butylstannane) is 18% with onset temperature for decomposition of 255 °C,¹⁴ whereas the TGA ceramic residue yield at 400 °C of our cross-linked poly(di-*n*-butylstannane) is 38% with onset temperature for decomposition of 300 °C. The TGA data of our insoluble polystannanes show that the ceramic residue yields are consistently lower than the theoretical yields (*i.e.*, Sn/SnC₈H₁₈ = 51%), probably due to loss of some volatile tin-constituents formed under the pyrolysis conditions although the polystannanes have a cross-linked structure.

Conclusions

Unlike Tilley's report, the di-*n*-butylstannane *n*-Bu₂SnH₂

was dehydrocoupled by the Cp₂MCl₂/Red-Al (M = Ti, Zr, Hf) and M(CO)₆/Red-Al (M = Cr, Mo, W) *in situ* combination catalysts to produce two phases of polymers: one is a cross-linked insoluble solid (with TGA ceramic residue yield of *ca.* 38% and onset temperature for decomposition of 300 °C), and the other is a non-cross-linked soluble solid (*M_w* = 1100; PDI = 1.0; ≈ Sn_{*n*}) for Cp₂MCl₂/Red-Al (M = Ti, Zr, Hf) catalyst or a viscous oil (*M_w* = 450; PDI = 1.0; ≈ Sn_{*n*}) for M(CO)₆/Red-Al (M = Cr, Mo, W) catalyst. While the soluble oligostannanes could be produced by simple dehydrocoupling of *n*-Bu₂SnH₂, the insoluble polystannanes could be obtained by *via* disproportionation/dehydrocoupling combination process of *n*-Bu₂SnH₂. One might naturally think that the disproportionation/dehydrocoupling combination process first produced a low-molecular-weight oligostannane possessing partial backbone Sn-H bonds which then underwent an extensive cross-linking reaction of backbone Sn-H bonds, leading to an insoluble polystannane. This provides an example of forming different types of polymers, depending on the combination of transition metal complex and anionic additive.

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