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*-Bu₂SnH₂ by Group 4 and 6 Transition Metal Complexes

Hee-Gweon Woo*, Jong-Mok Park, Sun-Jung Song, Soo-Yeon Yang, Ik-Sik Kim, and Whan-Gi Kim†

Department of Chemistry, Chonnam National University, Kwangju 500-757, Korea
†*Department of Applied Chemistry, Kon-Kuk University, Choongju 380-701, Korea*
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The catalytic dehydrocoupling of di-*n*-butylstannane *n*-Bu₂SnH₂ by the Cp₂MCl₂/Red-Al (M = Ti, Zr, Hf) and M(CO)₆/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 (≈Sn₅) or viscous oil (≈Sn₂). The soluble oligostannanes could be produced by simple dehydrocoupling of *n*-Bu₂SnH₂, whereas the insoluble polystannanes could be obtained *via* disproportionation/dehydrocoupling combination process of *n*-Bu₂SnH₂. 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] electro-reductive polymerization of organodichlorosilanes,[4c] sono-chemical polymerization of organodichlorosilanes,[4d] and electrochemical polymerization of hydrosilanes.[4e] Harrod recently dicovered an alternative group 4 metallocene-catalyzed dehydropolymerization of hydrosilanes, resulting in

1292 *Bull. Korean Chem. Soc.* **1997**, Vol. 18, No. 12

Hee-Gweon Woo et al.

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*-Bu$_2$SnCl$_2$ using molten Na metal[12] and by hydrostannolysis of *n*-Bu$_2$Sn(CH$_2$CH$_2$OEt)NMe$_2$ in the presence of DIBAL-H[13] 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 Cp$_2$MCl$_2$/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 Cp$_2$MCl$_2$/Red-Al (M = Ti, Zr, Hf) catalyst and the catalytic dehydropolymerization of 2-phenyl-1,3-disilapropane by the Cp$_2$MCl$_2$/*n*-BuLi combination catalyst (M = Ti, Zr, Hf).[15] We also reported the dehydropolymerization of 3-aryl-1-silabutanes catalyzed by the group 4 Cp$_2$MCl$_2$/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*-Bu$_2$SnH$_2$ by the group 4 Cp$_2$MCl$_2$/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 empolyed 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 CDCl$_3$/CHCl$_3$ 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 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. 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. Cp$_2$MCl$_2$ (M =Ti, Zr, Hf), M(CO)$_6$ (M = Cr, Mo, W), *n*-Bu$_2$SnCl$_2$, 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*-Bu$_2$SnH$_2$ was prepared by reduc-

tion of *n*-Bu$_2$SnCl$_2$ with LiAlH$_4$ in diethyl ether.[17]

Dehydropolymerization of *n*-Bu$_2$SnH$_2$ Catalyzed by Cp$_2$MCl$_2$/Red-Al (M = Ti, Zr, Hf). The following procedure is the representative of the dehydropolymerization of neat di-*n*-butylstannane *n*-Bu$_2$SnH$_2$ with the group 4 metallocene Cp$_2$MCl$_2$/Red-Al (M = Ti, Zr, Hf) combination catalysts. *n*-Bu$_2$SnH$_2$ (0.30 g, 1.28 mmol) was injected to a Schlenk flask containing *in situ*-generated dark purple catalytic mixture of Cp$_2$TiCl$_2$ (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 (v$_{SnH}$); 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: ^{1}H NMR (δ, CDCl$_3$, 300 MHz): 0.91 (m, CH$_3$), 1.19-1.60 (m, CH$_2$CH$_2$), 1.70-1.90 (m, CH$_2$); GPC: M_w=1050, M_n=1030, M_w/M_n (PDI)=1.02.
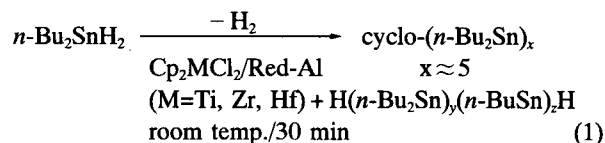
Dehydropolymerization of *n*-Bu$_2$SnH$_2$ Catalyzed by M(CO)$_6$/Red-Al (M=Cr, Mo, W). As a typical dehydropolymerization of neat dibutylstannane *n*-Bu$_2$SnH$_2$ with the group 6 metallocene M(CO)$_6$/Red-Al (M = Cr, Mo, W) combination catalysts, a Schlenk flask was charged with *n*-Bu$_2$SnH$_2$ (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 (v$_{SnH}$); 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 (v$_{SnH}$); ^{1}H NMR (δ, CDCl$_3$, 300 MHz): 0.89 (m, CH$_3$), 1.21-1.40 (m, CH$_2$CH$_2$), 1.87 (m, CH$_2$), 4.47 (m, SnH); GPC: M_w=450, M_n=430, M_w/M_n (PDI)=1.05.

Results and Discussion

Group 4 zirconocences such as Cp$_2$ZrMe$_2$,[5] Cp$_2$Zr[Si

Catalytic Dehydropolymerization of Di-n-butylstannane

Bull. Korean Chem. Soc. **1997**, Vol. 18, No. 12   1293

$(SiMe_3)_3]Me$,[6] and Cp_2ZrCl_2/n-BuLi[18] are known to be the active catalysts for the dehydropolymerization of primary silanes. *Inter alia*, $CpCp^*Zr[Si(SiMe_3)_3]Me$ and $(CpCp^*ZrH_2)_2$ were the most active catalyst previously examined.[6] Nonetheless, we decided to employ a novel *in situ* combination catalyst, Cp_2MCl_2/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 R_2SiH_2 (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 hydrosilane[20] 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-Bu_2SnH_2 with 2 mol% of the Cp_2MCl_2/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).

$$n\text{-}Bu_2SnH_2 \xrightarrow[\substack{Cp_2MCl_2/Red\text{-}Al \\ (M=Ti, Zr, Hf)}]{-H_2} \text{cyclo-}(n\text{-}Bu_2Sn)_x$$

$$x \approx 5$$
$$+ H(n\text{-}Bu_2Sn)_y(n\text{-}BuSn)_zH$$
$$\text{room temp./30 min} \qquad (1)$$

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 accquired 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 Sn_5) were in the range of 1010-1120 and 990-1110, respectively. The characterization data are summarized in Table 1.
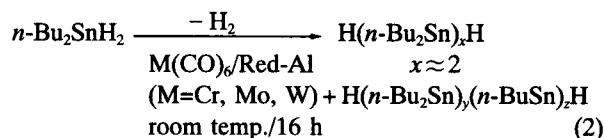
The IR spectra of the insoluble solids exhibit a very weak v_{Sn-H} band at *ca.* 1807 cm^{-1}. The ^{1}H NMR spectra of the soluble oligostannanes (Sn_5 cyclic?) apparently show mountain-like multiple resonances only assigned to n-Bu_2 groups. Therefore, the IR spectra of the soluble solids do not exhibit an appreciable v_{Sn-H} band at *ca.* 1807 cm^{-1}.

Dehydropolymerization of n-Bu_2SnH_2 with 2 mol% of the $M(CO)_6/Red$-Al (M = Cr, Mo, W) combination catalyst commenced slowly, as monitored by the moderate evolution of hydrogen gas, and the reaction medium became slowly gelatinous (eq. 2).

$$n\text{-}Bu_2SnH_2 \xrightarrow[\substack{M(CO)_6/Red\text{-}Al \\ (M=Cr, Mo, W)}]{-H_2} H(n\text{-}Bu_2Sn)_xH$$

$$x \approx 2$$
$$+ H(n\text{-}Bu_2Sn)_y(n\text{-}BuSn)_zH$$
$$\text{room temp./16 h} \qquad (2)$$

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 accquired 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 Sn_2) 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 v_{Sn-H} band at *ca.* 1807 cm^{-1}. The ^{1}H NMR spectra of the soluble oligostannanes (Sn_2 dimer?) apparently show mountain-like multiple resonances assigned to n-Bu_2 groups along with resonances centered at 4.47 ppm assigned to Sn-H. The IR spectra of the yellow viscous oils exhibit a weak v_{Sn-H} band at *ca.* 1808 cm^{-1}.

As shown in Table 1, the group 4 combination catalysts in the dehydropolymerization of n-Bu_2SnH_2 produce the polystannanes with similar molecular weights in the similar polymerization yields. Similarily, as shown in Table 2, the group 6 combination catalysts in the dehydropolymerization of n-Bu_2SnH_2 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 (Sn_5?) prepared from the catalytic dehydropolymerization by the group 4 combination catalysts were higher than those of the soluble oligostannanes (Sn_2?) prepared from the catalytic dehydropolymeri-
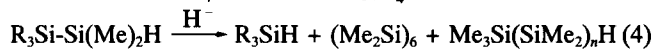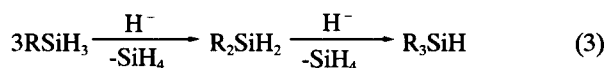
Table 1. Characterization of Catalytic Dehydropolymerization of n-Bu_2SnH_2 with Group 4 Transition Metal Complex[a]

Catalyst	% Yield[b]	mol wt[c]	
		M_w	M_n
Cp_2TiCl_2/Red-Al	61 (39)	1050	1030
Cp_2ZrCl_2/Red-Al	73 (27)	1120	1110
Cp_2HfCl_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.

Table 2. Characterization of Catalytic Dehydropolymerization of n-Bu_2SnH_2 with Group 6 Transition Metal Complex[a]

Catalyst	% Yield[b]	mol wt[c]	
		M_w	M_n
$Cr(CO)_6/Red$-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-Bu_2SnH_2 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-Bu_2SnH_2 by Cp_2MCl_2/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 tri-hydrosilanes[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]

$$3RSiH_3 \xrightarrow[-SiH_4]{H^-} R_2SiH_2 \xrightarrow[-SiH_4]{H^-} R_3SiH \qquad (3)$$

$$R_3Si\text{-}Si(Me)_2H \xrightarrow{H^-} R_3SiH + (Me_2Si)_6 + Me_3Si(SiMe_2)_nH \quad (4)$$

$$PhCH(SiH_3)_2 \xrightarrow{H^-} PhCH_2SiH_3 + SiH_4 \qquad (5)$$

We believe that a small portion of n-Bu_2SnH_2 may be disproportionated into n-$BuSnH_3$ and n-Bu_3SnH in the presence of Red-Al although we failed up to now to prove the presence of n-Bu_3SnH in the reaction mixture. n-$BuSnH_3$ may be immediately dehydrocoupled with n-Bu_2SnH_2 to produce soluble co-polystannane, $(n\text{-}Bu_2Sn)_x(n\text{-}Bu(H)Sn)_z$ of which the backbone Sn-H may then undergo the cross-linking process due to reactive Sn-H bonds. $PhGeH_3$ and $PhSnH_3$ 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 ploymer as a co-polymer. We are making our effort to elucidate the structure of the copolymer using solid-state ^{13}C and ^{119}Sn 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/SnC_8H_{18}= 51%), probably due to loss of some volatile tin-constituents fromed under the pyrolysis conditions although the polystannanes have a cross-linked structure.

Conclusions

Unlike Tilley's report, the di-n-butylstannane n-Bu_2SnH_2

was dehydrocoupled by the Cp_2MCl_2/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; $\approx Sn_5$) for Cp_2MCl_2/Red-Al (M = Ti, Zr, Hf) catalyst or a viscous oil (M_w = 450; PDI = 1.0; $\approx Sn_2$) for $M(CO)_6$/Red-Al (M = Cr, Mo, W) catalyst. While the soluble oligostannanes could be produced by simple dehydrocouplig of n-Bu_2SnH_2, the insoluble polystannanes could be obtained by *via* disproportionation/dehydrocoupling combination process of n-Bu_2SnH_2. 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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