

Dehydrocoupling of Bis(1-sila-3-butyl)benzene and 2-Phenyl-1,3-disilapropane to Polymers Using Zirconocene Combination Catalysts

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Abstract

The catalytic dehydrocoupling of bis(1-sila-3-butyl)benzene **1** and 2-phenyl-1,3-disilapropane **2** by $\text{Cp}_2\text{ZrCl}_2/\text{Red-Al}$ and $\text{Cp}_2\text{ZrCl}_2/n\text{-BuLi}$ was reported to compare their catalytic efficiency. The dehydrocoupling of monomeric silanes **1** with the $\text{Cp}_2\text{ZrCl}_2/\text{Red-Al}$ and $\text{Cp}_2\text{ZrCl}_2/n\text{-BuLi}$ combination catalysts produced two phases of polymers: one is a highly cross-linked insoluble solid, and the other is noncross-linked or slightly cross-linked soluble oil and could be a precursor for the solid polymer. The dehydrocoupling of **2** with the $\text{Cp}_2\text{ZrCl}_2/n\text{-BuLi}$ combination catalyst similarly produced two phases of polymers. By contrast, the catalytic reaction of **2** with the $\text{Cp}_2\text{ZrCl}_2/\text{Red-Al}$ combination catalyst produced a soluble polymer *via* redistribution/dehydrocoupling process.

Key words : Dehydrocoupling, Catalyst, Polymers, Silanes

1. Introduction

Inorganic polymers with various superior properties over organic polymers have been employed for many advanced applications^[1]. Especially, polysilanes possessing unusual optoelectronic properties attributed to electron-conjugation along the silicon backbone have particularly received extensive attentions as SiC ceramic precursors^[2a], luminescent materials^[2b], deep-UV photoresists^[2c], electroconductors^[2d], and photoinitiators^[2e-f]. The conventional synthetic method of polysilanes is the Wurtz coupling reaction of organodichlorosilanes using an alkali metal dispersion in toluene-refluxing temperature, which is intolerant of some functional groups, lack of reproducibility, and dangerous due to the strongly reduced reaction conditions^[3]. Other synthetic methods include anionic polymerization of masked disilenes^[4a], ring-opening polymerization of

organodichlorosilanes^[4c], onochemical polymerization of organodichlorosilanes, 4d and electrochemical polymerization of hydrosilanes^[4e].

Harrod recently discovered an alternative group 4 metallocene-catalyzed dehydropolymerization leading to great progress in poly(organosilane) synthesis^[5]. A major handicap of this synthetic which affects mechanical and optical properties^[5-6]. Intensive efforts have been made to increase the molecular weight of the polysilanes by studying the polymerization mechanism, by varying reaction conditions, and by adding either an additive or a cross-linking agent^[6-10]. Here we report the catalytic dehydrocoupling of bis(1-sila-3-butyl)benzene **1** and 2-phenyl-1,3-disilapropane **2** by $\text{Cp}_2\text{ZrCl}_2/\text{Red-Al}$ and $\text{Cp}_2\text{ZrCl}_2/n\text{-BuLi}$ to compare their catalytic efficiency.

2. Experimental

2.1. Materials

All reactions and manipulations were performed under prepurified nitrogen atmosphere using Schlenk line techniques. Dry, oxygen-free solvents were employed throughout. Glasswares was flamed-dried or oven-dried before use. Cp_2ZrCl_2 , *n*-BuLi (2.67 M solution in hexane), and Red-Al (or Vitride; sodium bis(2-methoxyethoxy)aluminum hydride; 3.4 M in

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toluene) were purchased from Aldrich Chemical Co. and were used without further purification.

2.2. Instrumentation

Infrared spectra were obtained using a Perkin-Elmer 1600 series FT-IR spectrometer. Proton NMR spectra were recorded on a Varian Gemini 300 spectrometer using $\text{CDCl}_3/\text{CHCl}_3$ as a reference at 7.24 ppm downfield from TMS. Silicon-29 NMR spectra were obtained on a Varian XL-300 spectrometer operating at 59.59 MHz with CDCl_3 as a solvent utilizing a DEPT (Distortionless Enhancement of Polarization Transfer) pulse sequence. An external reference of 50/50 by volume of TMS (0.00 ppm) in CDCl_3 was used. Gel permeation chromatography (GPC) was carried out on a Waters Millipore GPC liquid chromatography. Thermogravimetric analyses (TGA) of samples were performed on a Perkin Elmer 7 Series Thermal Analysis System under an argon flow. X-ray powder diffraction (XRD) measurements were done on an APD 3600 X-ray powder diffractometry.

3. Results and Discussion

Dehydropolymerization of **1** with 2 mol% of the $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$ and $\text{Cp}_2\text{ZrCl}_2/n\text{-BuLi}$ combination catalysts initiated immediately, as monitored by the immediate release of hydrogen gas, and the reaction medium became rapidly gelatinous. The polymers were isolated in > 85% total yield as two phases after workup including washing and column chromatography. The first part of the polymers was obtained in 50-52% yield as an off-white solid which was insoluble in most organic solvents. The TGA ceramic residue yield of the insoluble solids was acquired in 37-38% yield as a very viscous clear oil which was soluble in most organic solvents. The TGA ceramic residue yield of the soluble oils ranged from 8% to 9%. The weight average molecular weight (M_w) and number average molecular weight (M_n) of the oily polymers were in range of 1070-1090 and 850-890, respectively. The characterization data are summarized in Table 1.

The solid-state ^1H NMR spectra of the insoluble solid polysilanes showed only a single, broad ($\Delta\nu_{1/2}=360$ Hz) peaks centered at *ca.* 3.0 ppm assigned to the C-H and Si-H resonances. The ^1H NMR spectra of the soluble oily polysilanes apparently show nearly one broad unre-

Table 1. Characterization of Catalytic Dehydrocoupling of **1** with Zirconocene Combination Catalysts^a

Catalyst	% yiled	mol wt ^b		% ceramic residue yield ^c
		M_w	M_n	
$\text{Cp}_2\text{ZrCl}_2/$	50 (solid)	—	—	67
$n\text{-BuLi}$	37 (oil)	1070	850	8
$\text{Cp}_2\text{ZrCl}_2/$	52 (solid)	—	—	64
Red-Al	38 (oil)	1090	890	9

^a $[\text{Zr}]/[\text{Si}] = 0.02$; at ambient temperature for 24 h. ^bMeasured with GPC (*vs* polystyrene) in toluene. ^cMeasured with TGA up to 800 °C.

Table 2. Characterization of Catalytic Dehydrocoupling of **2** with Zirconocene Combination Catalysts

Catalyst	% yiled	mol wt ^c		% ceramic residue yield ^c
		M_w	M_n	
$\text{Cp}_2\text{ZrCl}_2/$	95 (solid)	—	—	73
$n\text{-BuLi}^a$	1 (oil)	9020	1050	14
$\text{Cp}_2\text{ZrCl}_2/$	25 (oil)	750	510	2
Red-Al ^b				

^a $[\text{Zr}]/[\text{Si}] = 0.02$; at ambient temperature for 24 h. ^b $[\text{Zr}]/[\text{Si}] = 0.004$; at ambient temperature for 8 h. ^cMeasured with GPC (*vs* polystyrene) in toluene. ^dMeasured with TGA up to 800 °C.

solved mountain-like resonances centered at *ca.* 3.4 ppm. The IR spectra of the polysilanes exhibit an intense SiH band at *ca.* 2140 cm^{-1} .

Dehydropolymerization of **2** with 2 mol% of the $\text{Cp}_2\text{ZrCl}_2/n\text{-BuLi}$ combination catalyst commenced immediately, as monitored by the instant evolution of hydrogen gas, and the reaction medium became promptly gelatinous.

The polymer was isolated in 96% total yield as two phases after workup including washing and column chromatography. The first part of the polysilane was obtained in 95% yield as an off-white solid which was insoluble in most organic solvents. The TGA ceramic residue yield of the insoluble solids was 73%. The second part of the polysilane was acquired in 1% yield as a very viscous opaque oil which was soluble in most organic solvents. The TGA ceramic residue yield of the soluble oil was 14%. The M_w and M_n of the oily polymer were 9020 and 1050, respectively. The characterization data are given in Table 2.

The solid-state ^1H NMR spectrum of the insoluble

polysilane showed only a single, broad ($\Delta\nu_{1/2}=208$ Hz) peaks centered at *ca.* 3.2 ppm assigned to the C-H and Si-H resonances. The ^1H NMR spectrum of the soluble polysilanes apparently show nearly one broad unresolved mountain-like resonances centered at *ca.* 4.0 ppm. The IR spectrum of the polysilanes exhibit an intense ν_{SiH} band at *ca.* 2145 cm^{-1} .

As shown in Table 1, two combination catalysts in the dehydropolymerization of **1** produce the polysilanes with similar molecular weight and percent ceramic residue yield in the similar polymerization yield. Interestingly, as shown in Table 1 and 2, with the $\text{Cp}_2\text{ZrCl}_2/n\text{-BuLi}$ combination catalyst, the molecular weight and percent ceramic residue yield of the polysilane prepared from the catalytic dehydropolymerization of **2** were higher than those of the polysilanes prepared from the catalytic dehydropolymerization of **1**. Compared to the other group 4 metallocene combination catalysts,^{12a} zirconocene combination catalysts produced the polysilanes with the similar molecular weights and percent ceramic residue yield as the titanocene and hafnocene combination catalysts in the catalytic dehydropolymerization of **1**. Zirconocene combination catalyst produced the oily polysilane with the higher molecular weights than the titanocene and hafnocene combination catalysts in the dehydropolymerization of **2** catalyzed by $\text{Cp}_2\text{ZrCl}_2/n\text{-BuLi}$. Differential scanning calorimetry (DSC) for these solid polymers did not show the presence of a glass transition temperature (T_g) between 25 and 400°C. X-ray powder pattern ($2\theta = 5\text{-}80^\circ$) for the solid polymers were featureless, which suggests that the polymers adopt an amorphous, glass-like structure. The carbon analyses were consistently lower than the calculated values due presumably to SiC formation leading to incomplete carbon combustion. Thermogravimetric analysis (TGA) of these insoluble polysilanes remained unchanged after and before irradiation for 2 h using a medium-pressure mercury lamp, indicating that the solid polymers are not appreciably photodegradable. The TGA data of the insoluble polysilanes showed that the ceramic residue yields were consistently higher than the theoretical yields (*i.e.*, $2\text{SiC}/\text{Si}_2\text{C}_{12}\text{H}_{18}=36.6\%$ for **1**; $2\text{SiC}/\text{Si}_2\text{C}_{12}\text{H}_{18}=53.8\%$ for **2**), probably due to extra free carbon formation, promoted by the crosslinking, along with SiC formation under the pyrolysis conditions. One might naturally think that the polymerization first produced a low-molecular-weight polymer

which then underwent as extensive cross-linking reaction of backbone Si-H bonds, leading to as insoluble polymer.

4. Conclusions

The monomeric silanes bis(1-sila-3-butyl)benzene **1** was dehydrocoupled by the $\text{Cp}_2\text{ZrCl}_2/\text{Red-Al}$ and $\text{Cp}_2\text{ZrCl}_2/n\text{-BuLi}$ combination catalysts to produce two phases of polymers: one is a highly cross-linked insoluble solid, and the other is noncross-linked or slightly cross-linked soluble oil and could be a precursor for the solid polymer. 2-phenyl-1,3-disilapropane **2** was dehydrocoupled by the $\text{Cp}_2\text{ZrCl}_2/n\text{-BuLi}$ combination catalyst, similarly yielding two phases of polymers. By contrast, the catalytic reaction of **2** with the $\text{Cp}_2\text{ZrCl}_2/\text{Red-Al}$ combination catalyst produced a soluble polymer *via* redistribution/dehydrocoupling process. A plausible mechanism for the formation of the soluble polymer was provided.

References

- [1] J. E. Mark, H. R. Allcock, and R. West, "Inorganic Polymers", Prentice Hall, New Jersey, 1992.
- [2] (a) S. Yajima, M. Omori, J. Hayashi, K. Okamura, T. Matsuzawa, and C. F. Liaw, "Molecular weight distribution of polycarbosilane as a starting material of the silicon carbide fiber with high tensile strength", *Chem. Lett.*, p. 551, 1976. (b) P. A. Bianconi and T. W. Weidman, "Poly(*n*-hexylsilylene): synthesis and properties of the first alkyl silicon [RSi] $_n$ network polymer", *J. Am. Chem. Soc.*, Vol. 110, p. 2342, 1988. (c) B. F. Griffing and R. West, "Contrast enhanced photoresists—processing and modeling", *Polym. Eng. Sci.*, Vol. 23, p. 947. 1983. (d) R. West, L. D. David, P. I. Djurovich, K. S. V. Stearley, and H. Y. Srinivasan, "Phenylmethylpolysilanes: formable silane copolymers with potential semiconducting properties", *J. Am. Chem. Soc.*, Vol. 103, p. 7352, 1981. (e) R. D. Miller and J. Michl, "Polysilane high polymers", *Chem. Rev.*, Vol. 89, p. 1359, 1989. (f) R. West, "The polysilane high polymers", *J. Organomet. Chem.*, Vol. 300, p. 327, 1986.
- [3] (a) P. Trefonas III, J. R. Damewood, R. West, and R. D. Miller, "Organosilane high polymers: thermochromic behavior in solution", *Organometallics*, Vol. 4, p. 1318, 1985. (b) L. A. Harrah and J. M.

- Zeigler, "Electronic spectra of polysilanes", *Macromolecules*, Vol. 20, p. 601, 1987. (c) M. Fujino, T. Hisaki, M. Fujiki, and N. Matsumoto, "Preparation and characterization of a novel organopolysilane. (3,3,3-Trifluoropropyl)methylpolysilane", *Macromolecules*, Vol. 25, p. 1079, 1992.
- [4] (a) K. Sakamoto, M. Yoshida, and H. Sakurai, "Highly ordered high-molecular weight alternating polysilylene copolymer prepared by anionic polymerization of masked disilene", *Macromolecules*, Vol. 23, p. 4494, 1990. (b) K. Matyjaszewski, M. Cypryk, H. Frey, J. Hrkach, H. K. Kim, M. Moeller, K. Ruehl, and M. White, "Synthesis and characterization of polysilanes", *J. Macromol. Sci.-Chem.* A28, Vol. 11, p. 1151, 1991. (c) E. Hengge and G. K. Litscher, "A New Electrochemical Method of Forming SiSi Bonds", *Angew. Chem., Int. Ed. Engl.*, Vol. 15, p. 370, 1976. (d) K. Matyjaszewski, D. Greszta, J. S. Hrkach, and H. K. Kim, "Controlled radical polymerizations: the use of alkyl iodides in degenerative transfer", *Macromolecules*, Vol. 28, p. 59, 1995. (e) Y. Kimata, H. Suzuki, S. Satoh, and A. Kuriyama, "Electrochemical Polymerization of Hydrosilane Compounds", *Organometallics*, Vol. 14, p. 2506, 1995.
- [5] (a) C. Aitken, J. F. Harrod, and U. S. Gill, "Structural studies of oligosilanes produced by catalytic dehydrogenative coupling of primary organosilanes", *Can. J. Chem.*, Vol. 65, p. 1804, 1987. (b) J. F. Harrod and S. S. Yun, "Silyltitanocene complexes as catalysts for the hydrogenation, isomerization, and hydrosilylation of olefins", *Organometallics*, Vol. 6, p. 1381, 1987. (c) C. Aitken, J. P. Barry, F. Gauvin, J. F. Harrod, A. Malek, and D. Rousseau, "A survey of catalytic activity of .eta.5-cyclopentadienyl complexes of Groups 4-6 and uranium and thorium for the dehydrocoupling of phenylsilane", *Organometallics*, Vol. 8, p. 1732, 1989. (d) J. F. Harrod, T. Ziegler, and V. Tschinke, "Theoretical study of $Cp_2Ti(H)(SiH_3)$ and Cp_2TiSiH_2 and their possible role in the polymerization of primary organosilanes", *Organometallics*, Vol. 9, p. 897, 1990. (e) H. G. Woo, J. F. Harrod, J. Henique, and E. Samuel, "Titanocene-catalyzed dehydrocoupling of silanes in the presence of phosphines. Probing a complex organometallic catalysis by EPR spectroscopy", *Organometallics*, Vol. 12, p. 2883, 1993. (f) J. Britten, Y. Mu, J. F. Harrod, J. Polowin, M. C. Baird, and E. Samuel, "Crystal structures and conformational analysis of titanocene complexes of the type $Cp_2Ti(SiHRR')PMe_3$ (R, R' = H, Me, Ph): relationships between calculated molecular structures and observed solid-state structures", *Organometallics*, Vol. 12, p. 2672, 1993.
- [6] (a) H. G. Woo and T. D. Tilley, ".sigma.-Bond metathesis reactions of silicon-hydrogen and metal-silicon bonds. New routes to d⁰ metal silyl complexes", *J. Am. Chem. Soc.*, Vol. 111, p. 3757, 1989. (b) H. G. Woo and T. D. Tilley, "Dehydrogenative polymerization of silanes to polysilanes by zirconocene and hafnocene catalysts. A new polymerization mechanism", *J. Am. Chem. Soc.*, Vol. 111, p. 8043, 1989. (c) H. G. Woo, R. H. Heyn, and T. D. Tilley, ".sigma.-Bond metathesis reactions for d⁰ metal-silicon bonds that produce zirconocene and hafnocene hydrosilyl complexes", *J. Am. Chem. Soc.*, Vol. 114, p. 5698, 1992. (d) H. G. Woo, J. F. Walzer, and T. D. Tilley, ".sigma.-Bond metathesis mechanism for dehydropolymerization of silanes to polysilanes by d⁰ metal catalysts", *J. Am. Chem. Soc.*, Vol. 114, p. 7047, 1992. (e) J. P. Banovetz, H. Suzuki, and R. M. Waymouth, "Dehydrogenative coupling of substituted phenylsilanes: synthesis of poly[[(trifluoromethyl)phenyl]silanes]", *Organometallics*, Vol. 12, p. 4700, 1993.
- [7] (a) H. G. Woo, J. F. Walzer, and T. D. Tilley, "Dehydropolymerization of bis- and tris(silyl)arenes to highly crosslinked disilanylarenylene polymers, catalyzed by $[(\eta^5-C_5H_5)(\eta^5-C_5Me_5)ZrH_2]^{2+}$ ", *Macromolecules*, Vol. 24, p. 6863, 1991. (b) T. Imori, H. G. Woo, J. F. Walzer, and T. D. Tilley, "Disilanylarenylene oligomers and polymers from dehydropolymerization of 1,4-RH₂SiC₆H₄SiH₂R (R = methyl, ethyl, and hexyl)", *Chem. Mater.*, Vol. 5, p. 1487, 1993.
- [8] (a) J. F. Harrod, "In Transformation of Organometallics into Common and Exotic Materials", Amsterdam, p. 103, 1998. (b) Y. Mu, and J. F. Harrod, "In Inorganic and Organometallic Polymers and Oligomers", J. F. Harrod, R. M. Laine, Eds.; Kluwer Academic Publishers: Dordrecht, p. 23, 1991.
- [9] (a) V. K. Dioumaev and J. F. Harrod, "Catalytic Dehydrocoupling of Phenylsilane with "Cation-like" Zirconocene Derivatives: A New Approach to Longer Silicon Chains", *Organometallics*, Vol. 13, p. 1548, 1994. (b) V. K. Dioumaev, J. F. Harrod, Submitted for publication.
- [10] (a) T. D. Tilley, "The coordination polymerization of silanes to polysilanes by a ".sigma.-bond metathesis" mechanism. Implications for linear chain growth", *Acc. Chem. Res.*, Vol. 26, p. 22, 1993. (b) T. Imori and T. D. Tilley, "The influence of catalyst

- structure on the dehydropolymerization of phenylsilane”, *Polyhedron*, Vol. 13, p. 2231, 1994.
- [11] H. G. Woo, S. Y. Kim, M. K. Han, E. J. Cho, and I. N. Jung, “Dehydrohomopolymerization and Dehydrocopolymerization of New Alkylsilanes: Synthesis of Poly(3-aryl-1-silabutanes)”, *Organometallics*, Vol. 14, p. 2415, 1995.