J. Am. Chem. Soc. **1996,** *118,* 12481−12482

Highly Branched, High Molecular Weight Polystannane from Dibutylstannane via a Novel Dehydropolymerization/Rearrangement Process

Jason R. Babcock and Lawrence R. Sita*

Searle Chemistry Laboratory, Department of Chemistry
The University of Chicago
5735 South Ellis Avenue, Chicago, Illinois 60637

Received September 16, 1996

The development of new methods for the production of high molecular weight materials that possess structural frameworks composed of σ-bonded arrays of group 14 heavy atoms (i.e., polysilanes, polygermanes, and polystannanes) remains a topic of current interest given the unique optical/electronic/chemical properties and potential applications that exist for these special polymers.[1−7] In this regard, new classes of two- and three-dimensional hyperbranched and dendritic polysilane materials have recently been synthesized that expand both the scientific and technological horizons for the investigation of group 14 polymetallanes.[5−7] For instance, it has been documented that 2- and 3-D polysilane materials possess photophysical properties that are quite different than those of their linear counterparts.[5] Furthermore, with respect to future use, it is known that, relative to linear polymers, hyperbranched materials often possess unusual viscoelastic properties, are more soluble at high molecular weights, and due to a greater amount of free volume that exists between the chains, can provide the basis for the development of new classes of materials that can be utilized for the size- or shape-selective inclusion of molecular species.[8] Finally, as pointed out by Lambert and co-workers,[6a,d] branched or dendritic structures may offer a greater robustness of polymetallanes to the chemical environment, and for optical applications, redundant pathways for σ-delocalization through the framework should photochemical cleavage of a metal−metal bond occur. Against this backdrop, we have been interested for some time in the synthesis and characterization of polystannane materials, since the potential exists to discover new properties or physical phenomena associated with these heavier group 14 polymetallane structures that are absent in their lighter polysilane or polygermane counterparts.[9] However, for the production of high molecular weight polystannanes, it has not been possible to routinely utilize the alkali metal reductive coupling of organometal halides that has been successfully used previously for the silicon and germanium polymers.[4] Indeed, only very recently, have high molecular weight *linear* polystannanes been accessible through the dehydropolymerization of secondary organostannanes (i.e., R_2SnH_2) that is catalyzed by zirconocene-based catalysts, such as (η^5-C_5H_5)$_2$ZrMe$_2$, or the most active complex, Me$_2$C(η^5-C_5H_5)$_2$Zr[Si(SiMe$_3$)$_3$]Me.[4b,c,e] Herein, we now report the preparation and characterization of the first example of a high molecular weight, highly *branched* polystannane that is produced from the same class of secondary organostannane starting material and, more specifically, Bu$_2$SnH$_2$ (**1**) through an unprecedented dehydropolymerization/rearrangement process that is catalyzed by commercially available carbonyltris(triphenylphosphine)rhodium(I) hydride, HRh(CO)(PPh$_3$)$_3$ (**2**).

Following the Tilley protocol,[4b,c] our first attempt at dehydropolymerization involved adding neat **1** all at once to the rhodium catalyst **2** (2 mol %).[10] While this satisfactorily resulted in vigorous hydrogen evolution and the generation of heat, detailed analysis of the crude product by ^{119}Sn NMR spectroscopy and gel permeation chromatography (GPC) revealed that only the cyclic oligomers (Bu$_2$Sn)$_5$ and (Bu$_2$Sn)$_6$ (**3** and **4**, respectively)[11] were produced together with other low molecular weight material. Given that other late transition metal complexes, such as dichlorobis(triphenylphosphine)palladium, have previously been shown to serve as efficient cyclodehydrogenation catalysts for secondary organostannanes,[11] this result was not too surprising. What was quite unexpected, however, was the discovery that a modification of the reaction conditions could lead to such a dramatic change in product composition. Hence, by slowly adding a solution of 0.1 mol % of the rhodium complex **2** in 7.5 mL of toluene, dropwise over a period of 1 h, to a solution of 0.9 g (3.84 mmol) of **1** in 6 mL of toluene, noticeable hydrogen evolution was still observed, but now the temperature of the reaction remained fairly constant at room temperature. The mixture was stirred for 12 h, during which time it became dark amber in color, and then the volatiles were removed *in vacuo* to provide 0.3 g of a gumlike material (**5**) (31% yield).[12] Subsequent spectroscopic and chemical analyses of this product now revealed some interesting features when compared side-by-side with the high molecular weight linear polystannane, H−(Bu$_2$Sn)$_n$−H (M_w/M_n = 33 430/14 800) (**6**), that was produced by the published procedure which involves dehydropolymerization of **1** using (η^5-C_5H_5)$_2$ZrMe$_2$ as the

---

[1] For general reviews of polysilanes, see: (a) West, R. *J. Organomet. Chem.* **1986**, *300*, 327. (b) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359.

[2] For some recent syntheses of linear polysilanes, see: (a) Aiken, C. T.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1986**, *108*, 4059. (b) Woo, H. G.; Tilley, T. D. *J. Am. Chem. Soc.* **1989**, *111*, 3757. (c) Sakamoto, K.; Obata, K.; Hirata, H.; Nakajima, M.; Sakurai, H. *J. Am. Chem. Soc.* **1989**, *111*, 7641. (d) Sakamoto, K.; Yoshida, M.; Sakurai, H. *Macromolecules* **1990**, *23*, 4494. (e) Matyjaszewski, K. *Makromol. Chem., Makromol. Symp.* **1991** *42/43*, 269. (f) Fossum, E.; Gordon-Wylie, S. W.; Matyjaszewski, K. *Organometallics* **1994**, *13*, 1695. (g) Frey, H.; Möller, M.; Matyjaszewski, K. *Macromolecules* **1994**, *27*, 1814. (h) Fossum, E.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 1618. (i) Jones, R. G.; Benfield, R. E.; Evans, P. J.; Swain, A. C. *J. Chem. Soc., Chem. Commun.* **1995**, 1465.

[3] For some recent syntheses of linear polygermanes, see: (a) Trefonas, P.; West, R. *J. Polym. Sci.* **1985**, *23*, 1099. (b) Hallmark, V. M.; Zimba, C. G.; Sooriyakumaran, R.; Miller, R.; Rabolt, J. F. *Macromolecules* **1990**, *23*, 2346. (c) Hayashi, T.; Uchimaru, Y.; Reddy, N. P.; Tanaka, M. *Chem. Lett.* **1992**, 647. (d) Mochida, K.; Chiba, H. *J. Organomet. Chem.* **1994**, *473*, 45.

[4] For syntheses of linear polystannanes, see: (a) Zou, W. K.; Yang, N.-L. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1992**, *33*, 188. (b) Imori, T.; Tilley, T. D. *J. Chem. Soc., Chem. Commun.* **1993**, 1607. (c) Imori, T.; Lu, V.; Cai, H.; Tilley, T. D. *J. Am. Chem. Soc.* **1995**, *117*, 9931. (d) Yokoyama, Y.; Hayakawa, M.; Azemi, T.; Mochida, K. *J. Chem. Soc., Chem. Commun.* **1995**, 2275. (e) Lu, V.; Tilley, T. D. *Macromolecules* **1996**, *29*, 5763. (f) Devylder, N.; Hill, M.; Molloy, K. C.; Price, G. J. *J. Chem. Soc., Chem. Commun.* **1996**, 711.

[5] For the synthesis of branched polysilanes, see: (a) Bianconi, P. A.; Weidman, T. W. *J. Am. Chem. Soc.* **1988**, *110*, 2342. (b) Bianconi, P. A.; Schilling, F. S.; Weidman, T. W. *Macromolecules* **1989**, *22*, 1697. (c) Wilson, W. L.; Weidman, T. W. *J. Phys. Chem.* **1991**, *95*, 4568. (d) Maxka, J.; Chrusciel, J.; Sasaki, M.; Matyjaszewski, K. *Macromol. Symp.* **1994**, *77*, 79.

[6] For the synthesis of discrete polysilane dendrimers, see: (a) Lambert, J. B.; Pflug, J. L.; Stern, C. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 98. (b) Sekiguchi, A.; Nanjo, M.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1995**, *117*, 4195. (c) Suzuki, H.; Kimata, Y.; Satoh, S.; Kuriyama, A. *Chem. Lett.* **1995**, 293. (d) Lambert, J. B.; Pflug, J. L.; Denari, J. M. *Organometallics* **1996**, *15*, 615.

[7] After submission of this manuscript, the synthesis of a high molecular weight branched polygermane via a ruthenium-catalyzed *demethanative* coupling of HGeMe$_3$ was reported, see: Reichl, J. A.; Popoff, C. M.; Gallagher, L. A.; Remsen, E. E.; Berry, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 9430.

[8] (a) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638. (b) Kim, Y. H.; Webster, O. W. *J. Am. Chem. Soc.* **1990**, *112*, 4592. (c) Fréchet, J. M. J. *Science* **1994**, *263*, 1710.

[9] (a) Sita, L. R. *Acc. Chem. Res.* **1994**, *27*, 191. (b) Sita, L. R.; Terry, K. W.; Shibata, K. *J. Am. Chem. Soc.* **1995**, *117*, 8049.

[10] All manipulations, including GPC analyses, were conducted under an inert atmosphere using either dry and degassed, or just sparged (helium), solvents.

[11] Jousseaume, B.; Noiret, N.; Pereyre, M.; Saux, A.; Francés, J.-M. *Organometallics* **1994**, *13*, 1034.

[12] Analytically pure material was obtained by precipitation of **5**, under an inert atmosphere, from a tetrahydrofuran solution with methanol to provide a dark yellow gumlike solid. Anal. Calcd. for C$_8$H$_{18}$Sn: C, 41.2; H, 7.79. Found: C, 41.4; H, 7.28.

S0002-7863(96)03237-4 CCC: $12.00

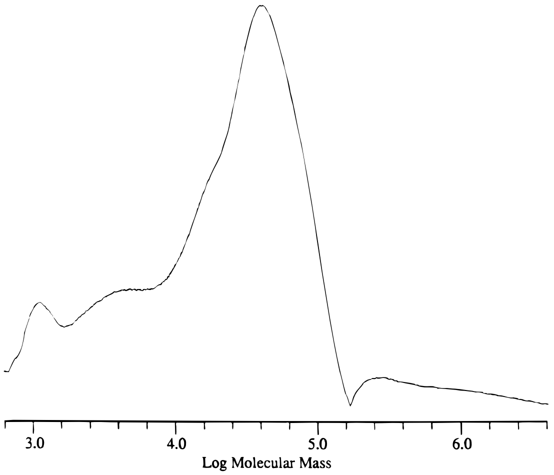

Figure 1. A gel permeation chromatogram of the polystannane material **5**.

catalyst.[4b,c] To begin, as shown in Figure 1, GPC (THF, polystyrene standards) confirmed that **5** was indeed a high molecular weight material that possessed a fairly narrow polydispersity ($M_w/M_n = 50\ 240/35\ 130$) and that contained very little oligomeric or cyclic components. Both the ^{1}H and ^{119}Sn NMR spectra of **5** appear to support this conclusion, and quite importantly, virtually no trace of the cyclic oligomers **3** and **4** were now observed in the latter.[13,14] However, a direct comparison of these spectra with those recorded for the linear polystannane indicated that the two materials possessed different structural frameworks.[14] More specifically, the ^{119}Sn NMR spectrum of the unpurified linear polystannane displays, along with the resonances for **3** and **4**, a fairly narrow single resonance that is centered at −189 ppm for the high molecular weight material. In contrast, the ^{119}Sn NMR spectrum of crude **5** exhibits additional downfield resonances between −170 and −180 ppm that do not change in relative intensity upon purification of the material. In order to probe the nature of this structural difference further, a comparative chemical analysis of the two materials was conducted that involved (1) titration of a diethyl ether solution of the polystannane with iodine at −78 °C to effect exhaustive cleavage of the Sn−Sn bonds[15] and (2) conversion of the resulting $Bu_{4-x}SnI_x$ fragments into the $Bu_{4-x}SnPh_x$ products with phenylmagnesium bromide. When this procedure was followed, a ^{119}Sn NMR spectrum of the product obtained from the Tilley material **6** revealed only the presence of dibutyldiphenylstannane, which is the result expected for a purely linear polystannane structure.[14] When the same chemical analysis is performed on either crude or purified **5**, however, in addition to Bu_2SnPh_2, the ^{119}Sn NMR spectrum now showed the presence of significant amounts of butyltriphenylstannane and phenyltributylstannane, which is the result expected for a structure containing a large number of branch points but not one that is necessarily hyperbranched.[1b] Having established this structural difference, it was now of interest to compare the electronic spectrum of **5** with that of the linear polystannane material **6**. As Figure 2 shows, **6** exhibits a low-energy transition at a λ_{max} value of 378 nm that is essentially identical to that reported previously (*cf.* λ_{max} 380 nm). Although similar in shape, the absorption maximum for **5** is shifted to longer wavelengths (λ_{max} 394 nm), and it now extends further out to the visible. A similar red-shift in the absorption maxima of hyperbranched and dendritic polysilanes relative to their linear counterparts has also been observed.[5,6] Finally, as with the linear polystannane **6**, solutions of **5** are very light sensitive, as characterized by a rapid photobleaching that occurs with ambient light. Qualitatively, however, in the solid state, the branched material **5** is significantly more roboust to both air-oxidation and light than in solution.

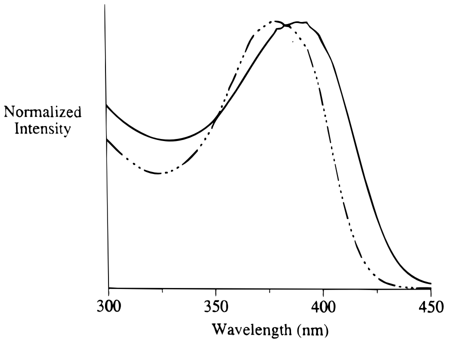

Figure 2. A comparison of the electronic spectra (pentane, 25 °C) for the linear polystannane **6** obtained from the dehydropolymerization of **1** with $(\eta^5\text{-}C_5H_5)_2ZrMe_2$ ($M_w/M_n = 33\ 430/14\ 800$) (dashed-dotted line) and the branched polystannane material **5** (solid line).

In summary, we present the first example of a high molecular weight, highly branched polystannane that can be accessed in a straightforward manner through the dehydropolymerization/rearrangement of a secondary organostannane that is catalyzed by a commerically available late transition metal complex. The extents, limitations and mechansim of this overall process, along with a detailed study of the physical and chemical properties of this new class of polymetallane material, are now currently under investigation.[17]

Acknowledgment. This work was supported by the National Science Foundation (CHE-9300022) for which we are grateful. L.R.S. is a Beckman Young Investigator (1995−1997) and a Camille Dreyfus Teacher−Scholar (1995−2000).

Supporting Information Available: A comparison of the ^{119}Sn NMR spectra for the polystannane materials **5** and **6** and a comparison of the ^{119}Sn NMR spectra of the products obtained from the chemical analysis of these two materials (3 pages). See any current masthead page for ordering and Internet access instructions.

JA963237X

---

[13] The ^{1}H NMR spectrum of **5** shows only a very small resonance for Sn−H end groups.

[14] Detailed information is provided in the Supporting Information.

[15] This method has previously been utilized for the analysis of polystannanes and is known to selectively cleave Sn−Sn bonds rather than Sn−C bonds, see: Neuman, W. P. *The Organic Chemistry of Tin*; Wiley: New York, 1970.

[16] An approximate ratio of Bu_2SnPh_2:$BuSnPh_3$:Bu_3SnPh_3, obtained from integrated intensities of the ^{119}Sn{^{1}H} NMR spectrum, is 8:2.5:1.

[17] To date, it has not been possible to identify or isolate any discrete products that might arise from the stoichiometric reaction between **1** and **2**.