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Metal-Catalyzed Dehydropolymerization of Secondary Stannanes to High Molecular Weight Polystannanes[†]

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Abstract: The first high molecular weight polystannanes, $H(SnR_2)_nH$ (R = ^nBu, ^nHex, ^nOct), result from dehydropolymerization of secondary stannanes R_2SnH_2 by zirconocene catalysts. Good catalysts include zirconocenes based on both $CpCp^*Zr$ ($Cp^* = \eta^5-C_5Me_5$) and Cp_2Zr fragments, and the most active catalyst with respect to production of high molecular weight polystannanes was $Me_2C(\eta^5-C_5H_4)_2Zr[Si(SiMe_3)_3]Me$. The latter catalyst produced $H(Sn^nBu_2)_nH$ chains ($M_w/M_n = 66\,900/20\,300$) that were contaminated by ca. 18% (by weight) low molecular weight cyclic oligomers. Lower molecular weights resulted from dehydropolymerizations of Me_2SnH_2, $PhMeSnH_2$, and Ph_2SnH_2. At room temperature, $H(SnR_2)_nH$ (R = alkyl group) polystannanes have λ_{max} values at ca. 380–400 nm, attributed to $\sigma \rightarrow \sigma^*$ transitions. Thermal gravimetric analyses on the polystannanes reveal that these polymers are as thermally stable as related poly(dialkylsilane)s and have onset temperatures for thermal decomposition in the range 200–270 °C, under both nitrogen and air. The $H(Sn^nBu_2)_nH$ polymer has been shown to be a good precursor to SnO_2, as shown by bulk pyrolysis in air (ceramic yield: 56%). Preliminary results also indicate that these polymers may be useful as precursors to elemental tin. The polystannanes are photosensitive, and their photobleaching behavior has been characterized by UV−vis spectrometry and ^{119}Sn NMR spectroscopy, which demonstrated that $H(Sn^nBu_2)_nH$ is photochemically depolymerized to a 2:1 mixture of $cyclo$-$(Sn^nBu_2)_5$ and $cyclo$-$(Sn^nBu_2)_6$. The polymers $H(Sn^nHex_2)_nH$ and $H(Sn^nOct_2)_nH$ exhibit thermochromic behavior which is visibly evident as a discoloration from yellow to colorless upon warming above room temperature. This reversible behavior is associated with an abrupt change in λ_{max} (e.g., from 402 to 378 nm for films of $H(Sn^nOct_2)_nH$) and a phase change at ca. 40 °C (by differential scanning calorimetry). Thin films of $H(Sn^nBu_2)_nH$ and $H(Sn^nOct_2)_nH$ on glass slides were doped by exposure to SbF_5 vapor to conductivities of 10^{-2} and 0.3 S cm^{-1}, respectively. Preliminary experiments suggest that the dehydropolymerization occurs by a σ-bond metathesis mechanism involving four-center transition states. A previous report on production of high molecular weight poly(dibutylstannane) by the reductive coupling of $^nBu_2SnCl_2$ by Na/15-crown-5 was reinvestigated and found to produce only low molecular weight material with $M_w/M_n = 2400/1200$.

There is rapidly growing interest in charge-transporting polymers, fueled by the identification of numerous potential applications in electronic devices.[1] Much of the focus on synthesis of new polymer structures has targeted π-conjugated

organic systems, but considerable effort has also been devoted to development of delocalized polymers with inorganic backbones.[2] Prominent among polymers of the latter type are the polysilanes, $(SiRR')_n$, which may be viewed as soluble, processible, one-dimensional metalloids.[3] Interest in polysilanes stems from their unusual electronic, optical, and chemical

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properties, and potential applications derived therefrom. Because of their delocalized electronic structure and relatively narrow band gap (*ca.* 4 eV), polysilanes provide a new class of charge-transporting and photoconducting materials. They exhibit a strong near-UV absorption that results from σ-conjugation along the silicon backbone, and the radiation sensitivity associated with this transition makes these polymers suitable for applications in microlithography. The primary synthetic route that has been used to explore polysilanes is the Wurtz-coupling of dichlorosilanes by alkali metals.[3] This method has proven very useful for research purposes, but it is severely limited as a general method since it produces moderate yields, and does not tolerate many functional groups.

In principle, heavier atoms in the polymer backbone (with their more diffuse bonding orbitals) might be expected to give rise to greater σ-conjugation, narrower band gaps, and more metallic character.[4–6] Recent theoretical calculations by Takeda and Shiraishi indicate that polystannanes should have inherently more narrow band gaps, even though the degrees of delocalization for polysilanes, polygermanes, and polystannanes are similar.[4b] West[7] and Miller[8] have reported that polygermane polymers, prepared by the reductive coupling of R_2GeCl_2, exhibit absorptions that are *ca.* 20 nm red-shifted from the corresponding polysilanes. Well-characterized polystannane polymers, however, have not been available and early speculation suggested that such materials might be inherently unstable.[9] Attempts to obtain polystannanes by the Wurtz-coupling method that has been used to synthesize polysilanes and polygermanes have generally given only low molecular weight oligomers (≤ 10

Sn atoms).[9c,10] A recent, preliminary account of the synthesis of higher molecular weight polystannanes via Wurtz coupling[11] is discussed in detail below. Other methods for forming polystannanes[6,10,12] have also produced only oligomers. Investigations on polystannane properties have therefore been limited to small chromophores, but these studies have strongly indicated that polystannanes would be significantly more delocalized than comparable polysilanes and polygermanes.[5,6]

Polystannanes therefore represent a promising class of electroactive polymers with a high degree of σ-delocalization. Extrapolations from polysilane properties suggest that polystannanes should be photolabile and therefore potentially useful in microlithography. Soluble polystannane polymers may also provide versatile routes to thin films containing elemental tin or tin oxides, which can be employed as conductors or coatings in semiconductors. Such tin-containing films are typically formed by ion or electron beam-induced deposition using tin tetrachloride or tetramethyltin.[13] Films produced by these methods generally retain an undesirable amount of carbon, hydrogen, and/or halogen from the precursor molecules, as high conductivities are found to require significant loss of these impurities.

New synthetic procedures for polystannanes are clearly desired, and in particular methods which would allow some control over the polymer structure and the degree of catenation. A new synthetic route to polystannanes was suggested to us by the newly-developed dehydropolymerization of silanes to polysilanes, as catalyzed by titanocene and zirconocene derivatives.[14,15] This reaction works best for primary arylsilanes such as $PhSiH_3$, for which degrees of polymerization of over 100 ($M_n \approx 5000-7000$) have been achieved.[15,16] With secondary silanes $RR'SiH_2$, the dehydrocoupling reactions are much slower and give only oligomers with up to ca. 8 monomer units.[17] Harrod has shown that $PhGeH_3$ is more active toward dehydropolymerization than $PhSiH_3$, such that with Cp_2TiMe_2 as catalyst, extensive cross-linking occurs to give an insoluble, three-dimensional gel.[18] Thus, even though previous studies indicated that Zr—Sn and Hf—Sn bonds are relatively unreac-

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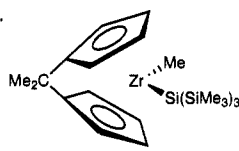
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Table 1. Molecular Weight Data for Dehydropolymerization of $^nBu_2SnH_2$, as a Function of Catalyst (Reactions Were Run with Neat Monomer and 2–4 mol % Catalyst)[a]

| catalyst	reactn time	% cyclic[b]	cyclics + linears		linear fraction	
			M_n	M_w	M_n	M_w
1. CpCp*Zr[Si(SiMe₃)₃]Me	15 min		900	1 300		
	1 h		2 100	5 800		
	5 h	16	2 900	14 500	5 800	17 200
	24 h[c]	29	2 700	12 700	7 800	17 500
2. CpCp*Zr[Si(SiMe₃)₃]Me + PhMe₂NH⁺BPh₄⁻	17 h	20	1 600	6 000	3 200	6 800
3. CpCp*ZrMe₂	15 min	15	3 600	34 700	12 400	40 800
	1 h	11	4 500	47 200	12 700	53 400
	3 h	11	5 000	50 000	14 200	55 900
	5 h	10	3 700	66 500	10 700	74 000
	24 h	12	4 500	62 500	12 800	71 400
4. CpCp*Zr[Si(SiMe₃)₃]Cl	24 h		2 000	7 200		
5. CpCp*Hf[Si(SiMe₃)₃]Cl	24 h		1 200	5 200		
6. CpCp*HfMe₂	3 h		1 600	2 000		
7. Cp₂Zr[Si(SiMe₃)₃]Me	3 h	18	2 000	17 800	6 300	22 100
8. Cp₂Zr[Si(SiMe₃)₃]Me + PhMe (1 equiv/monomer)	6 h	25	2 400	22 500	8 800	29 900
9. Cp₂ZrMe₂	12 h	13	3 900	32 600	11 900	35 700
	24 h	18	3 300	38 000	13 900	46 000
	81.5 h	22	2 800	30 600	12 500	39 500
10. Cp₂ZrMe₂ + PhMe (1 equiv/monomer)	24 h	13	4 200	25 100	10 600	28 600
11. Cp₂ZrMe₂ + PhMe (0.05 equiv/monomer)	22 h	44	1 500	20 600	15 300	35 500
12. Cp₂ZrMe₂ + C₆H₆ (0.05 equiv/monomer)	24 h	33	2 300	26 200	14 500	35 200
13. Cp₂ZrMe₂ + n-pentane (0.05 equiv/monomer)	24 h	20	2 900	35 200	14 300	42 800
14. [Cp₂Zr(H)Me]ₙ	0.5 h	7 (58)[d]	2 900	13 200	5 400	13 400
	3.5 h	43 (18)[d]	2 300	11 100	6 600	17 100
	6 h	45 (27)[d]	1 100	7 600	6 100	14 300
	18 h	57 (17)[d]	1 000	5 700	8 700	18 800
	2 days	98	900	1 000		
15.	4 h	34	2 000	30 300	17 400	48 100
	8 h	25	2 600	40 200	17 900	52 400
	11 h	18	3 300	53 100	20 300	66 900
	28 h	21	2 700	40 800	15 400	51 800
16. Cp*₂ZrMe₂	20 h		800	1 000		
17. Cp*₂SmCH(SiMe₃)₂	7 h		600	1 000		

[a] Polymerization were run at 23 °C under 1 atm of nitrogen. Polystyrene standards were used for the GPC measurements. [b] These values probably have large errors associated with them, unless there is good peak separation (M_n for linears ≥ ca. 3000). [c] This sample was isolated by precipitation with methanol (see Experimental Section). [d] The number in parantheses represents the approximate percentage of material remaining as monomer.

tive,[19] it seemed that secondary stannanes might be good substrates for dehydropolymerization. Here we report a simple and convenient method for forming polystannane polymers, based on dehydropolymerizations catalyzed by zirconocene derivatives. The new polystannanes are significantly σ-delocalized, as indicated by λ_{max} values for the σ → σ* transitions which are the highest yet observed. Our initial observations of this polymerization chemistry have been communicated.[20]

Results and Discussion

Synthesis of Polystannanes. Results from representative dehydropolymerizations of $^nBu_2SnH_2$ are summarized in Table 1. Conditions were optimized for a metal-catalyzed polymerization with step-growth character, assuming a mechanism analogous to the one we have proposed for the dehydropolymerization of silanes.[14c,15a] The polymerizations were initiated by addition of neat monomer to the catalyst (2 mol %) under nitrogen. In most cases, immediate gas evolution occurs and the reaction mixture develops a yellow color which then darkens to orange and then to dark red or dark brown as gas evolution slows. For polymerizations that afford relatively high molecular weight polystannanes, the reaction mixture solidifies rapidly. Molecular weight distributions were measured by gel permeation chromatography (GPC) utilizing polystyrene standards and

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tetrahydrofuran solvent. In general, mixtures of cyclic oligomers (predominantly the pentamer) and linear $H(Sn^nBu_2)_nH$ chains are produced (eq 1), the ratio of which depends on the reaction

$$^nBu_2SnH_2 \xrightarrow[-H_2]{catalyst} cyclo\text{-}(Sn^nBu_2)_m + H(Sn^nBu_2)_nH \quad (1)$$
$$m = 5, 6$$
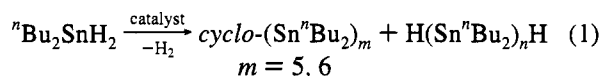
conditions and the nature of the catalyst. The isolated polymers (yields ≥90%) are air- and light-sensitive yellow solids.

The first catalyst examined was the "mixed-ring" silyl complex CpCp*Zr[Si(SiMe₃)₃]Me, which is one of the most active catalysts for the dehydropolymerization of phenylsilane.[15b] As seen by the data in Table 1 (entry 1), this catalyst results in a gradual increase in the average molecular weight for the polystannane mixture over 24 h. The resulting polymer was extracted into pentane and then precipitated as a yellow oil by addition of methanol. Separation of the oil by decantation and drying under vacuum resulted in 93% yield of the polystannane as a yellow solid. Analysis of this polymer by GPC revealed a bimodal molecular weight distribution composed of a sharp peak at *ca.* 1000 amu (29%), assigned to *cyclo*-(Sn^{n}Bu₂)₅ (*vide infra*), and a broader molecular weight fraction (M_w/M_n = 17 500/7 800) attributed to H(Sn^{n}Bu₂)$_n$H chains. A rough estimate for the average degree of polymerization for these

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chains, made by simply accounting for the difference in length between styrene and Sn^nBu_2 monomer units, is ca. 80.[21]

Entry 2 of Table 1 presents data obtained for a cationic catalyst, generated by addition of $[PhMe_2NH]^+[BPh_4]^-$ to $CpCp*Zr[Si(SiMe_3)_3]Me$, which gives molecular weights that are only about half those obtained with the catalyst derived from $CpCp*Zr[Si(SiMe_3)_3]Me$ alone. In related studies we have determined that cationic zirconocene derivatives are not remarkably more active than analogous neutral catalysts toward chain elongation in the dehydropolymerization of $PhSiH_3$.[15b] Surprisingly, the mixed-ring dimethyl catalyst $CpCp*ZrMe_2$ produces polystannane chains that are nearly twice as long as those obtained with $CpCp*Zr[Si(SiMe_3)_3]Me$ (entry 3), even though these compounds presumably provide similar active species in solution. The molecular weights produced in this polymerization are observed to increase steadily over 24 h, with little degradation to cyclic material. As observed for the dehydropolymerization of hydrosilanes, the chloride derivatives $CpCp*M$-$[Si(SiMe_3)_3]Cl$ (M = Zr, Hf) are comparatively inactive toward chain elongation in hydrostannane dehydrocoupling (entries 4 and 5). Also, hafnium derivatives react more sluggishly compared to analogous zirconium derivatives (entries 5 and 6).

Considering the numerous similarities to silane dehydropolymerization, it is somewhat surprising that Cp_2Zr derivatives are comparable to analogous $CpCp*Zr$ compounds as catalysts for $^nBu_2SnH_2$ dehydrocoupling (entries 7−14). Entries 7 and 8 show that addition of a small amount of solvent (1 equiv of toluene per monomer) significantly increases the molecular weights obtained. This effect may be attributed to increased fluidity for the reaction medium, which allows more complete transformation of functional groups to chain linkages in the condensation process.[15] Dimethylzirconocene is quite active toward chain elongation (entry 9), and addition of slight amounts of solvent (entries 10−13) affords significantly higher molecular weights. Note, however, that substantial dilution of the monomer leads to predominant cyclic formation, as in the polymerization of $^nBu_2SnH_2$ (0.30 g) by $CpCp*Zr[Si(SiMe_3)_3]$-Me in 1 mL of toluene, which gives mostly low molecular weight, cyclic oligomer $(M_w/M_n = 1400/1200)$.[20] For $[Cp_2Zr$-$(H)Me]_n$ (entry 14), significant quantities of monomer were detected throughout the reaction (by GPC), indicating that in this polymerization, distannanes and other small oligomers are much more reactive than monomer toward dehydrocoupling. It is also possible that the low solubility of this catalyst leads to low conversion rates. At high conversion, extensive deoligomerization occurs to give a high yield of *cyclic* $(Sn^nBu)_n$ species (by GPC).

The most active catalyst with respect to chain elongation is the *ansa*-zirconocene derivative of entry 15, which after 11 h gives $H(Sn^nBu_2)_nH$ chains containing several hundred tin atoms $(M_w/M_n = 66\,900/20\,300)$, while converting only about 20% of the monomer to *cyclo*-$(Sn^nBu_2)_5$. Longer reaction times under these conditions (atmospheric pressure, room temperature, no solvent) result in some depolymerization.

The final entries in Table 1, for the bis(pentamethylcyclopentadienyl) catalysts $Cp*_2ZrMe_2$ (entry 16) and $Cp*_2SmCH$-$(SiMe_3)_2$ (entry 17), describe production of only small oligomers. This is consistent with earlier observations on the dehydropolymerization of $PhSiH_3$.[15a]

Tables 2 and 3 present molecular weight data for polymerizations of various secondary hydrostannane monomers as cata-

Table 2. Molecular Weight Data for Dehydropolymerizations of Various Secondary Hydrostannanes with $CpCp*Zr[Si(SiMe_3)_3]Me$ (2−4 mol %) Catalyst[a]

monomer	reactn time	% cyclics[b]	cyclics + linears		linear fraction	
			M_n	M_w	M_n	M_w
1. $^nBu_2SnH_2$	24 h	29	2 700	12 700	7 800	17 500
2. $^nHex_2SnH_2$	1 h	65	1 500	5 300	9 900	14 800
	3 h	75	1 400	3 700	9 700	14 300
	5 h	78	1 300	4 700	12 600	22 000
	23 h	48	2 000	16 000	15 300	36 800
	82 h	56	1 700	7 500	12 100	20 900
3. $^nOct_2SnH_2$	15 h	11	6 800	84 800	14 300	95 700
4. Me_2SnH_2[c]	17 h		590	3 600		
5. $PhMeSnH_2$[c]	48 h		700	1 600	900	1 700
6. Ph_2SnH_2[c]	5 min		700	730		
	24 h	75	930	2 200	5 000	6 700

[a] Polymerizations were run at 23 °C under 1 atm of nitrogen. Polystyrene standards were used for the GPC measurements. [b] These values probably have large errors associated with them, unless there is good peak separation (M_n for linears ≥ ca. 3000). [c] The polystannanes resulting from these reactions were slightly soluble in tetrahydrofuran.

Table 3. Molecular Weight Data for Dehydropolymerizations of Various Secondary Hydrostannanes with Cp_2ZrMe_2 (2−4 mol %) Catalyst[a]

monomer	reactn time	% cyclics[b]	cyclics + linears		linear fraction	
			M_n	M_w	M_n	M_w
1. $^nBu_2SnH_2$	24 h	18	3 300	38 000	13 900	46 000
2. $^nHex_2SnH_2$	40 min		1 300	2 700		
3. $^nOct_2SnH_2$	15 min	4	8 500	22 200	11 100	23 100
	15 h	11	9 100	82 800	21 700	92 600
4. $PhMeSnH_2$	15 min		800	1 800		
	1 h		900	2 300		

[a] Polymerizations were run at 23 °C under 1 atm of nitrogen. Polystyrene standards were used for the GPC measurements. [b] These values probably have large errors associated with them, unless there is good peak separation (M_n for linears ≥ ca. 3000).

lyzed by $CpCp*Zr[Si(SiMe_3)_3]Me$ and Cp_2ZrMe_2, respectively. The largest macromolecules are obtained for secondary stannanes with long alkyl chains (as expected). Notably, the dihexyl monomer exhibits a marked tendency to dehydrocouple to cyclic oligomers. With both Cp_2ZrMe_2 and $CpCp*ZrMe_2$ catalysts, $^nHex_2SnH_2$ is converted almost quantitatively to a cyclic polystannane $(M_w/M_n = 1200/1100)$, which was characterized as *cyclo*-$(Sn^nHex_2)_5$ on the basis of its ^{119}Sn NMR signal at δ −202.1.[22] With the $Me_2C(\eta^5$-$C_5H_5)_2Zr[Si(SiMe_3)_3]Me$ catalyst, $^nHex_2SnH_2$ is polymerized in 10 min to $H(Sn^nHex_2)_nH$ chains with $M_w/M_n = 34\,600/14\,400$ and production of 20% cyclics by weight.

Other monomers (entries 4−6 of Table 2; entry 4 of Table 3) produced slightly soluble polystannanes with rather low molecular weights. In these cases, we attribute the low molecular weights to insolubility of the oligomeric polystannanes, which leads to low conversion of functional groups. The dehydropolymerization of Ph_2SnH_2 gives relatively low molecular weight oligomers, and after 5 min the reaction has proceeded selectively to a single product which has not yet been fully characterized (M = ca. 700 amu; probably a dimer or trimer). At longer reaction times, the majority of $(SnPh_2)_n$ species formed have molecular weights (ca. 2000) comparable to those observed by Kuivila et al. for certain "modifications of diphenyltin".[23] A higher molecular weight mode (ca. 25%, $M_w/M_n = 6700/5000$) is also produced.

(21) This estimate is made by accounting for differences in size between styrene and SnR_2 monomer units, via the following equation: degree of polymerization = (molecular weight based on polystyrene standard/104) × 2 × (covalent radius of C/covalent radius of Sn). We thank Prof. John Harrod for suggesting this method of estimation.

(22) Jousseaume, B.; Noiret, N.; Pereyre, M.; Saux, A.; Francès, J.-M. *Organometallics* **1994**, *13*, 1034.

(23) Kuivila, H. G.; Sawyer, A. K.; Armour, A. G. *J. Org. Chem.* **1961**, *26*, 1426.
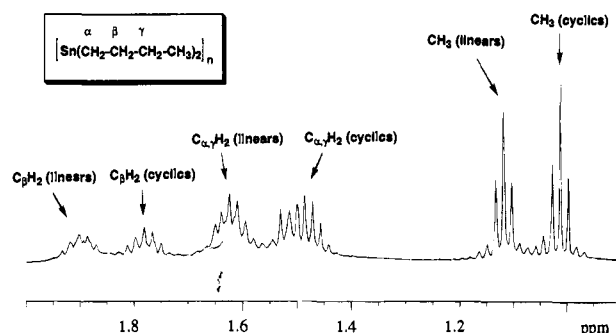
Figure 1. ¹H NMR spectrum of a sample containing a 1:1 mixture of linear $H(Sn^nBu_2)_nH$ ($M_w/M_n = 35\ 200/14\ 500$) and cyclic $(Sn^nBu_2)_{5,6}$ polystannanes.

The observed molecular weight distributions are sensitive to the purity of the monomer. Prolonged storage (over weeks, under nitrogen and in the presence of fluorescent room lighting) of neat $^nBu_2SnH_2$ results in decomposition to a mixture of small oligomers (dimers, trimers, and tetramers, by GPC). Such mixtures are polymerized by the catalysts described above to polystannanes that typically have slightly higher average molecular weights than polystannanes obtained under comparable conditions from pure monomer. The purification procedure for the R_2SnH_2 monomers (prepared by reduction of R_2SnCl_2 with $LiAlH_4$) is also critical. Monomers isolated without an aqueous workup give somewhat different results, presumably because these samples contain Al—H derivatives that are not completely removed by distillation. Such monomer samples are polymerized even by Cp_2ZrCl_2. For example, $^nBu_2SnH_2$, prepared by the $LiAlH_4$ reduction of $^nBu_2SnCl_2$ but distilled without an aqueous quench, was polymerized by Cp_2ZrCl_2 to give a polystannane sample with $M_w/M_n = 31\ 000/4\ 200$ (entire sample, 20% cyclics) and $M_w/M_n = 38\ 800/15\ 300$ (linear fraction). We assume that in this reaction, catalyst formation occurs by reaction of Cp_2ZrCl_2 with the Al—H species present, to produce an active zirconium hydride catalyst.

Characterization of Polystannanes. ¹H NMR shifts for the cyclic and linear fractions of poly(dibutylstannane) samples are clearly separated, and peak assignments were readily made by comparisons with the corresponding GPC traces. Figure 1 displays the ¹H NMR spectrum of a sample composed of a 1:1 mixture of $H(Sn^nBu_2)_nH$ chains ($M_w/M_n = 35\ 200/14\ 500$) and $(Sn^nBu_2)_n$ cyclics. The terminal —CH_3 hydrogens are shifted to highest field, and give rise to distinct triplets ($J = 7$ Hz) which are separated for the linear and cyclic materials. This is also true for poly(dihexylstannane)s but not for the dioctyl derivatives, for which the ¹H resonances overlap too extensively. Thus, ¹H NMR spectroscopy is a useful tool for measuring the cyclic/linear ratio in polymerizations of $^nBu_2SnH_2$ and $^nHex_2$-SnH_2.

In general, the cyclic polystannanes formed in the above polymerizations appear to be monodisperse by GPC. These species give GPC molecular weights (vs polystyrene standards) that are only moderately underestimated (by ca. 5—30%). A few reactions, such as the one in entry 2 of Table 3, proceed almost quantitatively to cyclic material, which may be purified by washing away the more soluble linear polymers with pentane. Generally, fractionation or rinsing procedures are useful in purifying the cyclic and linear polystannanes. Mass spectroscopy revealed the presence of both $cyclo$-$(SnR_2)_5$ and $cyclo$-$(SnR_2)_6$ in samples containing significant fractions of cyclics. Figure 2 shows a representative ¹¹⁹Sn NMR spectrum and GPC trace for a poly(dibutylstannane) sample. The linear $H(Sn^nBu_2)_nH$ chains give rise to a resonance at δ —189.6, and this chemical shift is consistent with values reported earlier for ^nBu-

Table 4. Spectroscopic Data for Polystannanes

repeat unit	¹¹⁹Sn NMR shift (linear chains)[a]	¹¹⁹Sn NMR shift (Sn₅, Sn₆ cyclics)	$\lambda_{max}(\sigma \rightarrow \sigma^*)$, nm
Sn^nBu_2	−189.6	−200.9, −202.1	384 (6300)[b]
Sn^nBu_2 (ref 11)	−267.9		365
Sn^nHex_2	−190.9	−202.1, −202.7	384 (4700)[b]
Sn^nOct_2	−190.7	−201.8, −202.4	388 (4200)[b]

[a] For linear samples with $M_n \geq 10\ 000$. [b] Extinction coefficient based on single Sn—Sn bond chromophores (THF solvent).

$(Sn^nBu_2)_n{}^nBu$ oligomers ($n = 3$—5).[12f] The predominant cyclic species (δ —200.9) was identified as $cyclo$-$(Sn^nBu_2)_5$, based solely on comparison to recently reported ¹¹⁹Sn NMR shift data.[22] A weaker ¹¹⁹Sn resonance at δ —202.1 may be assigned to $cyclo$-$(Sn^nBu_2)_6$.[22] Similar characteristics were observed in spectra obtained from dehydropolymerizations of $^nHex_2SnH_2$ and $^nOct_2SnH_2$ (Table 4). In all cases, the pentamer is the dominant cyclic species formed by dehydrocoupling. The $cyclo$-$(Sn^nBu_2)_6$ compound was previously reported by Neumann et al., who synthesized it by a variety of methods including the dehydrocoupling of $^nBu_2SnH_2$ by pyridine and NaOMe catalysts.[24]

The ¹¹⁹Sn NMR spectra contain no discernible peaks assignable to branching positions ($\leq$ca. 2%), and though we have been unable to detect —$SnHR_2$ end groups in ¹H or ¹¹⁹Sn NMR spectra, this is expected given the high molecular weights. An extremely weak peak in the infrared spectrum of poly(dibutylstannane), at 1809 cm⁻¹, was assigned to —Sn^nBu_2H end groups.

At room temperature, $H(SnR_2)_nH$ (R = alkyl group) polystannanes have λ_{max} values at ca. 380—400 nm, attributed to $\sigma \rightarrow \sigma^*$ transitions (Table 4). This value may vary slightly depending upon the percentage of cyclics present, the temperature, and the polymer phase (e.g., solid vs solution). A sample of $H(Sn^nBu_2)_nH$ ($M_w/M_n = 41\ 200/13\ 900$, prepared with the $Me_2C(\eta^5$-$C_5H_4)_2Zr[Si(SiMe_3)_3]Me$ catalyst) containing few cyclics (6%) displays a transition at 390 nm (pentane solution). For comparison, the λ_{max} value for $Et(SnEt_2)_6Et$ is 325 nm,[25] and the λ_{max} value for the $(Sn^nBu_2)_n$ material reported by Zou and Yang is 365 nm. It has been established that the λ_{max} values increase with molecular weight, up to a limiting value, for polysilanes,[3] polygermanes,[7,8] and polystannanes.[5,6] In addition, the corresponding $(Si^nBu_2)_n$ polysilane and $(Ge^nBu_2)_n$ polygermane have limiting λ_{max} values of 314[3b] and 333 nm,[7] respectively. Thus, the $\sigma \rightarrow \sigma^*$ transitions for polystannanes are red-shifted by ca. 70 nm with respect to comparable polysilane polymers, and this is consistent with the presence of relatively long, σ-conjugated chromophores. The low molecular weight $(SnPh_2)_n$ material obtained in this study displays a slightly higher λ_{max} value of 402 nm (in tetrahydrofuran). This suggests the presence of some degree of σ/π conjugation in the aryl-substituted polystannane, but conclusions regarding the electronic influence of aryl substituents in polystannanes must await the availability of high molecular weight poly(arylstannane)s for comparison.

Long-chain polystannanes absorb strongly in the ultraviolet, as indicated by the extinction coefficients listed in Table 4. These values are only approximate, given the necessary assumptions that must be used in calculating the degrees of polymerization. Also, no corrections have been made to account for the different masses of the repeat units in the three polymers. However, we can say that the extinction coefficients are several thousand, and therefore comparable to values reported for polysilanes.[3b]

(24) Neumann, W. P.; Pedain, J.; Sommer, R. *Ann.* **1965**, *694*, 9.

(25) Creemers, H. M. J. C.; Noltes, J. G. *J. Organomet. Chem.* **1967**, *7*, 237.
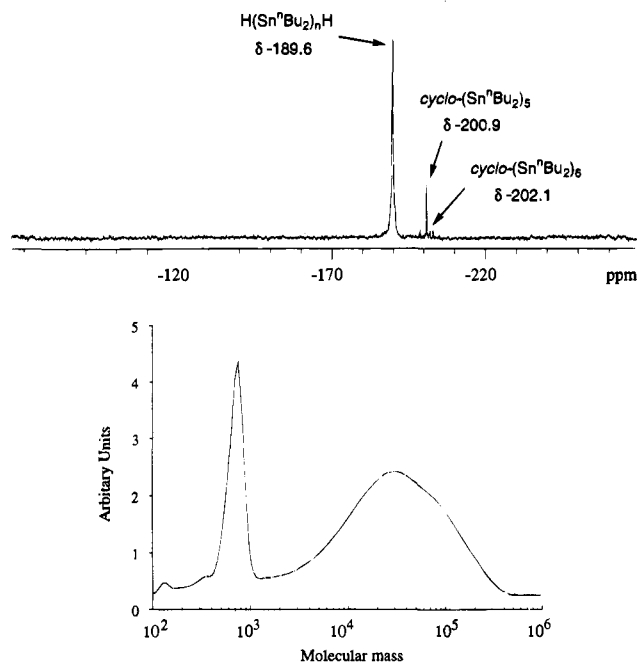
Figure 2. (a) ^{19}Sn NMR spectrum for a poly(dibutylstannane) sample containing cyclo-(Sn^{n}Bu$_2$)$_5$ (major cyclic, δ −200.9, J_{SnSn} = 467 Hz), cyclo-(Sn^{n}Bu$_2$)$_6$ (minor cyclic, δ −202.1), and linear H(Sn^{n}Bu$_2$)$_n$H chains (M_w/M_n = 35 200/14 500; 73% linears by GPC). (b) Gel permeation chromatogram (GPC) for the sample described in part a (polystyrene standards, THF solvent).

Although no emission (337.1 nm; N$_2$ laser) is observed for cyclo-(Sn^{n}Bu$_2$)$_5$ (in solution or solid state), the higher molecular weight polystannane chains give rise to an emission band centered at 505 nm (solid state). By comparison, high molecular weight polysilanes are known to exhibit 20−30 nm Stokes-shifted emissions.[3b] Future efforts are planned to more fully characterize the luminescent properties of these polystannanes.

Thermal Stability and Photostability of Polystannanes. The H(SnR$_2$)$_n$H polystannanes are thermally stable, but somewhat air- and light-sensitive. In air, solid samples decompose very slowly whereas solutions degrade rapidly. Therefore, routine handling of these polymers is best conducted under anaerobic conditions and with low levels of ambient lighting. A solution of H(Sn^{n}Bu$_2$)$_n$H (M_w/M_n = 32 000/10 100; 5% cyclics; 0.005 g in 0.6 mL of benzene-d_6) did not undergo observable decomposition after being heated to 120 °C for 12 h.

Thermal gravimetric analysis (TGA) of H(Sn^{n}Bu$_2$)$_n$H under nitrogen shows no weight loss below 200 °C, and then precipitous weight loss (81%) between 250 and 300 °C (Figure 3). The corresponding H(Sn^{n}Oct$_2$)$_n$H polymer is stable to about 250 °C, after which 66% of the material is lost between 250 and 325 °C.[26] Surprisingly, the thermogravimetry for these polystannanes corresponds very closely to results published for related poly(dialkylsilane)s, which have onset temperatures for thermal decomposition in the temperature range 220−260 °C.[27]

Table 5 summarizes the TGA data for polystannane polymers under various conditions. Interestingly, these materials do not degrade more rapidly under air or oxygen. The ceramic yield of material obtained at 400 °C is generally higher when thermolysis occurs in the presence of oxygen, which suggests the formation of tin oxide. When H(Sn^{n}Bu$_2$)$_n$H was heated

(26) Note that this weight loss corresponds to a quantitative formation of tin metal. This transformation is currently being investigated in more detail.

(27) Varma-Nair, M.; Cheng, J.; Jin, Y.; Wunderlich, B. *Macromolecules* **1991**, *24*, 5442.
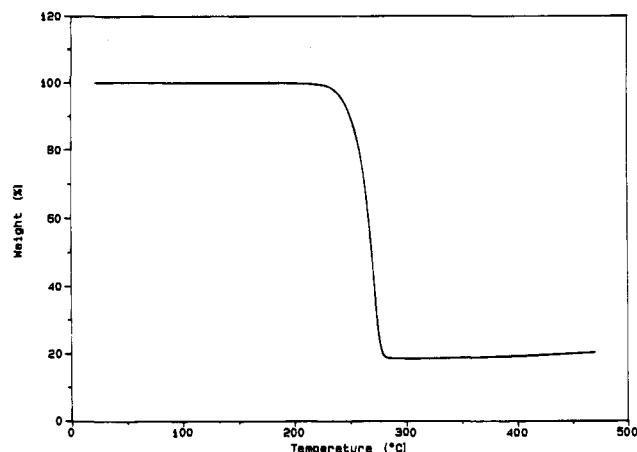
Figure 3. TGA curve for H(Sn^{n}Bu$_2$)$_n$H.

Table 5. Thermal Gravimetric Analysis data for Polystannanes

| polymer	atmosphere	onset temp for dec (°C)	% ceramic yield at 400 °C
H(Sn^{n}Bu$_2$)$_n$H	N$_2$	255	18
	air	239	53
	O$_2$	196	66
H(Sn^{n}Hex$_2$)$_n$H	N$_2$	265	24
	air	220	50
H(Sn^{n}Oct$_2$)$_n$H	N$_2$	271	34
	air	245	44

under a flow of oxygen, the ceramic yield increased to 66% (by TGA), which is very close to the theoretical yield for SnO$_2$ (65%). To investigate the latter possibility, a 0.10-g sample of H(Sn^{n}Bu$_2$)$_n$H was heated under a flow of air to 400 °C. This gave an off-white powder in 61% ceramic yield. Further annealing of this sample to 1100 °C resulted in a material (ceramic yield 56%) that by XRD contained only SnO$_2$ (cassiterite). A combustion analysis showed that this material is essentially carbon and hydrogen free (0.06% and <0.01%, respectively). Thus, polystannane polymers appear to be useful precursors to tin oxide (eq 2).

$$H(Sn^nBu_2)_nH \xrightarrow{\text{400 °C/air}} SnO_2 \qquad (2)$$
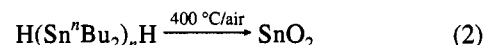
Polystannanes also appear to be useful precursors to elemental tin. By TGA, H(Sn^{n}Oct$_2$)$_n$H thermally decomposes under nitrogen to give the theoretical yield for tin (34%, Table 5). A bulk sample of this polymer was heated to 400 °C under flowing nitrogen, to give a 26% yield of a material that was identified (by XRD) as Sn metal (tetragonal), contaminated with some SnO$_2$ (cassiterite). Presumably, the sample was oxidized by adventitious air during experimental manipulations.

Figure 4 illustrates the photobleaching behavior of a dilute solution of the H(Sn^{n}Bu$_2$)$_n$H polymer by room light. Such behavior has been previously noted for polysilane and polygermane polymers, and is of interest with respect to photoresist technology.[3] Qualitatively, we have observed that H(Sn^{n}Bu$_2$)$_n$H polymers are significantly more stable to room light in tetrahydrofuran (vs pentane) solution. The photobleaching depolymerization produces mostly cyclic oligomers. Exposure of a H(Sn^{n}Bu$_2$)$_n$H sample (M_w/M_n = 32 000/10 100; 5% cyclics) to fluorescent room lighting for 2 h led to complete decomposition to two products, cyclo-(Sn^{n}Bu$_2$)$_5$ and cyclo-(Sn^{n}Bu$_2$)$_6$, in a roughly 2:1 ratio (by ^{119}Sn NMR spectroscopy).

Thermochromic behavior for H(SnR$_2$)$_n$H. As for a number of polysilanes,[3,27,28] poly(dioctylstannane) exhibits thermochromic behavior which is visibly evident as a discoloration of the material from yellow to colorless upon warming slightly above

Dehydropolymerization of Secondary Stannanes

J. Am. Chem. Soc., Vol. 117, No. 40, 1995 9937
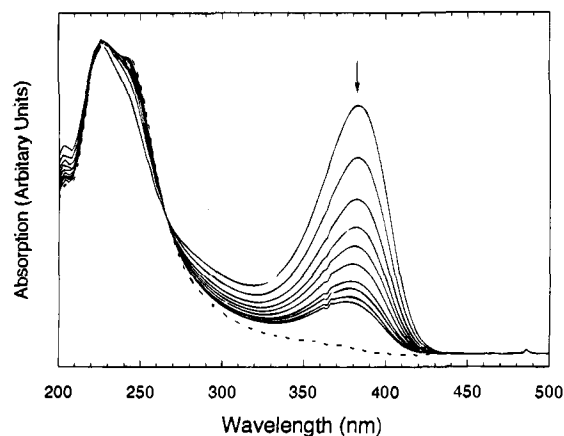
Figure 4. The UV–vis spectrum for $H(Sn^nBu_2)_nH$ ($M_n = 7800$), showing the photobleaching behavior in pentane solution upon irradiation by room light. Measurements were taken every 30 s. The final spectrum is given by the dotted line.

a)

b)
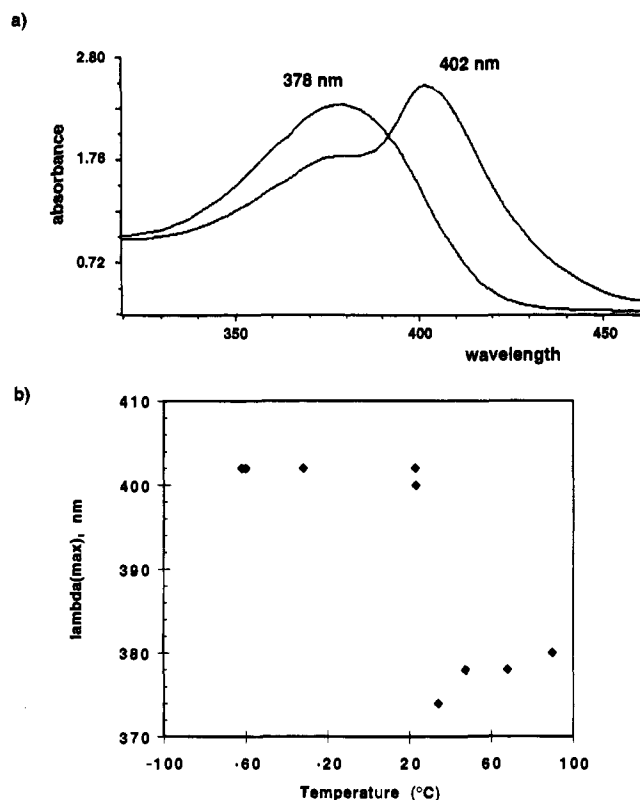
Figure 5. Temperature dependence of the UV–vis spectrum for a film of $H(Sn^nOct_2)_nH$ (M_w/M_n 149 000/17 000). (a) Spectra taken at 47 (λ_{max} = 378 nm) and 22 °C (λ_{max} = 402 nm). (b) Plot of λ_{max} vs temperature.

room temperature. Variable-temperature UV–vis spectrometry shows that this reversible behavior is associated with an abrupt change in the absorption maximum between 30 and 40 °C, from 384 to 369 nm in toluene solution. Figure 5 shows spectra taken of a film of $H(Sn^nOct_2)_nH$ (M_w/M_n = 149 000/17 000) cast onto the inner walls of a sealed UV–vis cuvette, at 22 (λ_{max} = 402 nm) and at 47 °C (λ_{max} = 378 nm). These λ_{max} values do not vary further as a function of temperature (Figure 5), and the observed thermochromism is clearly associated with a phase transition at 40 °C (ca. 18 J g^{-1}), as shown by the DSC curve of Figure 6.

Poly(dihexylstannane) is also thermochromic. Solid films of this polymer change their absorption characteristics between 30 and 40 °C (by variable-temperature UV–vis spectroscopy), such that the λ_{max} value reduces from 398 to 382 nm upon warming. The DSC curve for this polymer also displays an endothermic
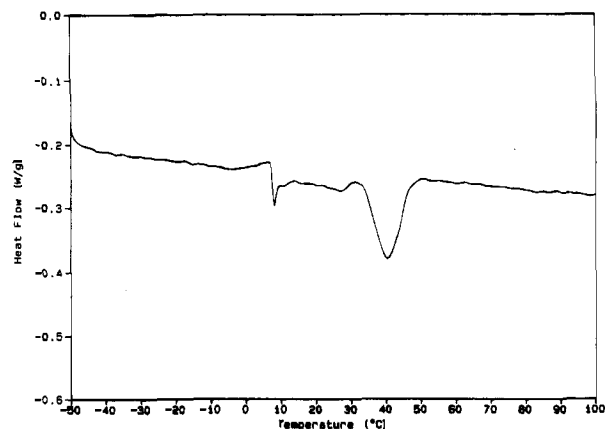
Figure 6. Differential scanning calorimetry trace for $H(Sn^nOct_2)_nH$ (M_w/M_n = 149 000/17 000). Heating rate 10 °C min^{-1}; nitrogen atmosphere.

event resulting from a phase transition, at 36 °C (ca. 17 J g^{-1}). Thermochromic behavior was not observed for $H(Sn^nBu_2)_nH$ (over the temperature range −10 to 90 °C), and this polymer does not exhibit a phase transition over the same temperature range (by DSC).

The transitions associated with the observed color changes have not as yet been characterized. It is interesting to note that the observed transition temperatures (ca. 40 °C) correspond closely to related transition temperatures observed for poly-(dialkylsilane)s.[26–28] It therefore seems that cooling of the polymer below 40 °C may result in alignment of the backbone Sn−Sn bonds into longer segments of planar, *trans* zigzag configurations, perhaps as a result of side-chain crystallization.[28a]

Conductivity Measurements on Doped Polystannanes. Films of the poly(dialkylstannane) polymers are readily cast from pentane solutions. Thin films of $H(Sn^nBu_2)_nH$ and $H(Sn^nOct_2)_nH$ on glass slides were doped by exposure to SbF_5 vapor at room temperature for 3 and 30 h, respectively. The resulting conductivities, measured by the four-point probe method, were 10^{-2} and 0.3 S cm^{-1}, respectively. Little attempt has been made to optimize these values with respect to doping time or oxidizing power of the dopant. We feel that these results are quite encouraging, particularly since SbF_5 is probably highly corrosive toward the Sn−Sn bonded chains. Future studies are planned to identify the mildest chemical dopants possible, and to optimize the conductivities of these polymers. For comparison, polysilanes have been doped to a conductivity of about 1 S cm^{-1}.[29]

Mechanistic Considerations. We assume that the polymerization reactions described here occur by a σ-bond metathesis mechanism, as has been described for hydrosilane polymerizations catalyzed by the same complexes (Scheme 1).[14c,15] However, we have been unable to observe isolated σ-bond metathesis reactions which would model either of the two steps in such a catalytic cycle. Numerous attempts have been made to observe "model reactions" between zirconocene or hafnocene silyl, hydride, or stannyl derivatives and a secondary stannane such as Ph_2SnH_2 or $^nBu_2SnH_2$. So far, these attempts have witnessed either rapid, multistep processes or no transformation

(28) (a) Miller, R. D.; Hofer, D.; Rabolt, J.; Fickes, G. N. *J. Am. Chem. Soc.* **1985**, *107*, 2172. (b) KariKari, E. K.; Greso, A. J.; Farmer, B. L.; Miller, R. D.; Rabolt, J. F. *Macromolecules* **1993**, *26*, 3937. (c) Yuan, C.-H.; West, R. *Macromolecules* **1993**, *26*, 2645. (d) Yuan, C.-H.; West, R. *Macromolecules* **1994**, *27*, 629. (e) Menescal, R.; Eveland, J.; West, R.; Leites, L. L.; Bukalov, S. S.; Yadritseva, T. D.; Blazsó, M. *Macromolecules* **1994**, *27*, 5885. (f) Sakamoto, K.; Yoshida, M.; Sakurai, H. *Macromolecules* **1994**, *27*, 881.

(29) West, R.; David, L. D.; Djurovich, P. I.; Stearley, K. L.; Srinivasan, K. S. V.; Yu, H. *J. Am. Chem. Soc.* **1981**, *103*, 7352.

Scheme 1
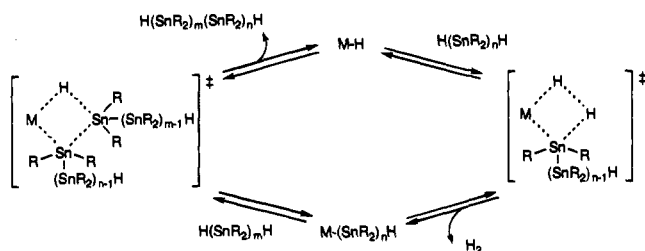
whatsoever. In many cases, the expected products of concerted, σ-bond metathesis reactions are observed, but a hydrostannyl derivative M—SnHR$_2$ has not been definitively characterized. For example, the silyl complex Cp*$_2$Hf(SiPh$_3$)Cl[19] is rapidly converted by ^{n}Bu$_2$SnH$_2$ to a mixture of Ph$_3$SiH, Cp*$_2$HfHCl, and polystannanes (by ^{1}H NMR spectroscopy). This would seem to occur by the sequence shown in eq 3, which passes through the (presumed) reactive intermediate Cp*$_2$Hf(SnH^{n}Bu$_2$)-Cl. This intermediate is not observed by room temperature
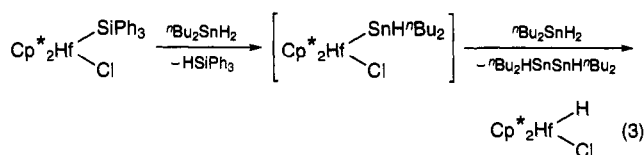
NMR spectroscopy, but monitoring the reaction at −20 °C revealed the appearance of an intermediate giving rise to a peak in the ^{1}H NMR spectrum at 4.28, which is shifted upfield from the resonance for ^{n}Bu$_2$SnH$_2$ by 0.48 ppm. The ^{119}Sn{^{1}H} NMR spectrum of this reaction mixture contains two weak resonances which may be assigned to hafnium stannyl derivatives, at δ 117.9 and 130.2. Hafnium stannyl derivatives appear to possess such downfield ^{119}Sn resonances; for example, Cp*$_2$Hf(SnPh$_3$)-Cl is characterized by a resonance at δ 114.7.[30]

It would therefore appear that d^0 metal stannyl complexes possessing α-hydrogens are highly reactive. Isolation and study of the first complexes of this type should prove very informative.

Polystannanes via Wurtz-Coupling Methods. A number of low molecular weight polystannanes have been obtained via reductive coupling of a dichlorostannane with an alkali metal.[9c,10] Typically, these reactions have given cyclic oligomers as the only isolated products. It was therefore somewhat surprising when a preliminary report appeared, by Zou and Yang, which described the Wurtz-type coupling of ^{n}Bu$_2$SnCl$_2$ by sodium/15-crown-5 to high molecular weight linear polystannane.[11] This reaction was reported to give an M_n value of 10 000 amu, as determined by vapor phase osmometry. We noted that the properties of this polystannane differed considerably from those observed by us for the same polymer (see Table 4). For example, the linear polystannanes were reported to give rise to a ^{119}Sn NMR shift of −267.9 ppm (vs −189.6 ppm for our sample) and a λ_{max} absorption at 365 nm (vs 384 nm reported here). For these reasons, we reinvestigated the reaction reported by Zou and Yang, using the exact synthetic conditions described by them.[11]

A solution of ^{n}Bu$_2$SnCl$_2$ in toluene was added dropwise to a toluene/heptane suspension of sodium dispersion containing 15-crown-5, and after completion of the reaction the polymer was isolated according to the literature procedure. Analysis of the resulting yellow product by GPC revealed a bimodal molecular weight distribution with M_w/M_n = 2400/1200. The ^{119}Sn NMR spectrum of this polystannane contained peaks that we have assigned to H(Sn^{n}Bu$_2$)$_n$H (at δ −189.5), cyclo-(Sn^{n}Bu$_2$)$_5$ (at δ

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(30) Lu, V.; Tilley, T. D. Unpublished results.

−200.9), and cyclo-(Sn^{n}Bu$_2$)$_6$ (at δ −202.0). The cyclic pentamer and hexamer were formed in a ratio of ca. 1:4 (by ^{119}Sn NMR spectroscopy). Thus, in our hands this reaction produces only low molecular weight oligomers. This result is in fact consistent with the UV−vis spectrum reported by Zou and Yang.

Conclusions

The results reported here are significant in that they show (1) that high molecular weight polystannanes are available via a straightforward synthetic method employing simple zirconocene reagents and (2) that a metal-catalyzed deydropolymerization reaction can be useful in providing a polymer that is not available via other methods. This work has produced high-yield syntheses to well-defined polystannane polymers containing at least several hundred Sn atoms, and the polymerization conditions may be modified to minimize production of low molecular weight cyclics.

Polystannanes give rise to electronic absorptions that are significantly more red-shifted than those for polysilane and polygermane analogues. Our initial survey of physical properties for polystannanes indicates that these polymers have potential applications in photoresist technology, as semiconductors, and as precursors to tin-based semiconducting materials. We are currently exploring dehydropolymerization routes to other polystannane structures which might exhibit novel electronic properties.

The limited research which has so far addressed optimization of catalyst structure indicates that polymerization activity is heavily influenced by the steric properties of the catalyst. Thus, the least hindered zirconocene fragment examined, Me$_2$C(η^5-C$_5$H$_4$)$_2$Zr, gave the highest activity toward chain elongation. This suggests a sterically crowded transition state, as one might predict for a secondary stannane.[14c,15] Clearly, hydrostannanes are much more active than corresponding silanes toward dehydrocoupling, as witnessed by the fact that secondary silanes are difficult to oligomerize with similar catalysts.[17] Although mechanistic information is currently lacking, many characteristics for the stannane dehydropolymerizations described here reflect observations made previously with related hydrosilane reactions. We are therefore tentatively basing our ongoing investigations on the mechanistic model summarized in Scheme 1.

Experimental Section

used as recieved. The compounds Cp_2ZrMe_2,[31] Cp_2HfMe_2,[31] $CpCp^*Zr$-$[Si(SiMe_3)_3]Cl$,[32] $CpCp^*Zr[Si(SiMe_3)_3]Me$,[32] $CpCp^*Hf[Si(SiMe_3)_3]Cl$,[33] $Cp_2Zr[Si(SiMe_3)_3]Me$,[34] $CpCp^*ZrMe_2$,[35] $Cp^*_2ZrMe_2$,[36] $[Cp_2Zr(H)Me]_n$,[37] $Cp^*_2SmCH(SiMe_3)_2$,[38] $Me_2C(C_5H_4)_2ZrCl_2$,[39] and $(n\text{-hexyl})_2SnCl_2$[40] were obtained by literature procedures. Other R_2SnCl_2 compounds were purchased from Aldrich and used as received. The secondary hydrostannanes R_2SnH_2 were prepared by reduction of the corresponding dichlorides with $LiAlH_4$, according to the method described for Ph_2SnH_2.[23,41] Aqueous workup of the hydrostannanes is essential, since otherwise contamination of the sample with aluminum hydride species leads to less stable samples, and different resulting molecular weights for the polystannanes produced. Representative procedures are given below.

$^nHex_2SnH_2$. A solution of $^nHex_2SnCl_2$ (6.00 g, 16.70 mmol) in diethyl ether (60 mL) was added dropwise to a cooled (0 °C) suspension of $LiAlH_4$ (1.00 g, 26.40 mmol) in diethyl ether (50 mL). After the addition was complete, the reaction mixture was stirred at 0 °C for 2 h and was then allowed to warm to room temperature over ca. 1 h. The reaction mixture was then quenched with degassed, cold (0 °C) water, and the ether layer was separated and dried over $CaCl_2$. The solution was filtered, and the solvent was removed by vacuum transfer to give a yellow liquid. Addition of pentane (30 mL) gave a clear solution, which was cooled to −78 °C to yield colorless crystals of the product (3.90 g, 80%). The crystals melt upon warming to room temperature, to a slightly yellow liquid. ^1H NMR (300 MHz, benzene-d_6): δ 0.88 (t, $J = 7$ Hz, 6 H, CH_3), 0.97 (tt, $^3J_{HH} = 8$ Hz, $^3J_{HH} = 2$ Hz, 4 H, $SnCH_2$), 1.18−1.34 (br m, 12 H, CH_2), 1.49−1.59 (br m, 4 H, CH_2), 4.80 (quintet, $^3J_{HH} = 2$ Hz, $J(^{119}SnH) = 1667$ Hz, $J(^{117}SnH) = 1593$, 2 H, SnH). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene-d_6): δ 7.44, 14.28, 22.94, 28.45, 31.71, 33.83. $^{119}Sn\{^1H\}$ NMR (111.9 MHz, benzene-d_6): δ −202.8.

$^nOct_2SnH_2$. This compound was prepared by the method described above and shown to be pure by NMR and GPC. Anal. Calcd for $C_{16}H_{36}Sn$: C, 55.4; H, 10.45. Found: C, 55.8; H, 10.06. ^1H NMR (300 MHz, benzene-d_6): δ 0.90 (t, $J = 7$ Hz, 6 H, CH_3), 0.99 (tt, $^3J_{HH} = 7$ Hz, $^3J_{HH} = 2$ Hz, 4 H, $SnCH_2$), 1.20−1.32 (br m, 20 H, CH_2), 1.50−1.62 (br m, 4 H, CH_2), 4.75 (quintet, $^3J_{HH} = 2$ Hz, $J(^{119}SnH) = 1671$ Hz, $J(^{117}SnH) = 1597$, 2 H, SnH). $^{119}Sn\{^1H\}$ NMR (111.9 MHz, benzene-d_6): δ −202.7.

$^nBu_2SnH_2$. This compound (prepared by the method described above) was vacuum distilled[41] (42 °C, 4 mm Hg) rather than crystallized and shown to be pure by NMR and GPC. ^1H NMR (300 MHz, benzene-d_6): δ 0.85 (t, $J = 7$ Hz, 6 H, CH_3), 0.92 (tt, $^3J_{HH} = 8$ Hz, $^3J_{HH} = 2$ Hz, 4 H, $SnCH_2$), 1.27 (sextet, $^3J_{HH} = 7$ Hz, 4 H, CH_2), 1.43−1.64 (br m, 4 H, CH_2), 4.76 (quintet, $^3J_{HH} = 2$ Hz, $J(^{119}SnH) = 1669$ Hz, $J(^{117}SnH) = 1595$, 2 H, SnH). $^{13}C\{^1H\}$ NMR (100.6 MHz, benzene-d_6): δ 7.07 ($J(^{119}Sn^{13}C) = 1490$ Hz; $J(^{117}Sn^{13}C) = 1424$ Hz), 13.76, 27.11 ($^2J(^{119}Sn^{13}C) = 175$ Hz), 30.66 ($^3J(^{119}Sn^{13}C) = 71$ Hz). $^{119}Sn\{^1H\}$ NMR (111.9 MHz, benzene-d_6): δ −202.4.

Polymerization Reactions. In general, the polymerizations were carried out at ambient room temperature, under a blanket of vented nitrogen, with no solvent and a catalyst concentration of 2−4 mol %. The reactions were initiated in the inert atmosphere drybox, protected from ambient light by wrapping the Schlenk flask with aluminum foil,

and then rapidly transferred to a Schlenk line and vented to the nitrogen manifold. For most polymerizations, the molecular weights were determined by sampling ca. 1 mg of polymer, which was dissolved in dry, air-free tetrahydrofuran (ca. 1 mL). The resulting polymer solution was then filtered through a 1 μm filter. About 0.05 μL of the solution was then injected into the GPC instrument. Examples of specific polymerization reactions are given below.

(a) **Polymerization of $^nBu_2SnH_2$ with $CpCp^*Zr[Si(SiMe_3)_3]Me$.** Addition of neat $^nBu_2SnH_2$ (0.30 g, 1.28 mmol) to the catalyst (2 mol %) resulted in vigorous hydrogen evolution and a dark red mixture which was protected from room light. Hydrogen evolution slowed after a few minutes, but continued over the next 5 h while the reaction mixture solidified. The solid was dissolved in 20 mL of dry pentane, to which dry methanol (20 mL) was added to separate the polymer as a yellow oil. Removal of solvent by decantation followed by drying under vacuum resulted in 93% yield of the polystannane as a yellow solid. Anal. Calcd for $C_8H_{18}Sn$: C, 41.2; H, 7.79; Sn, 51.0. Found: C, 40.9; H, 7.84; Sn, 51.3. ^1H NMR (400 MHz, benzene-d_6): δ 1.02 (t, $J = 7$ Hz, CH_3, cyclic), 1.12 (t, $J = 7$ Hz, CH_3, linear), 1.45−1.53 (m, 2CH_2, cyclic), 1.60−1.63 (m, 2CH_2, linear), 1.77−1.83 (m, CH_2, cyclic), 1.87−1.95 (m, CH_2, linear). $^{13}C\{^1H\}$ NMR (100.6 MHz, benzene-d_6): δ 9.64, 14.00, 28.07, 33.37 (s, ^nBu, cyclic), 11.69, 14.00, 28.63, 33.62 (s, ^nBu, linear). $^{119}Sn\{^1H\}$ NMR (111.9 MHz, benzene-d_6): δ −189.6 (linear), −200.9 ($J_{SnSn} = 466.6$ Hz, cyclic pentamer), −202.1 (cyclic hexamer). IR (THF solution): 1809 cm^{-1} (ν_{SnH}).

(b) **Polymerization of $^nHex_2SnH_2$ with $CpCp^*Zr[Si(SiMe_3)_3]Me$.** In the inert atmosphere glovebox, the catalyst (4 mol %) was added to neat monomer (0.100 g) in a small vial. Rapid gas evolution was observed, and the mixture turned to dark brown. The molecular weight distribution of the sample was monitored periodically by GPC. After 82 h, the polystannanes were extracted into pentane (2 × 10 mL) and the combined extracts were evaporated to dryness to give a ca. 1:1 mixture of cyclic and linear polystannanes (by ^1H NMR spectroscopy). Anal. Calcd for $C_{12}H_{26}Sn$: C, 49.9; H, 9.07. Found: C, 49.7; H, 9.22. The remaining residue was mostly (ca. 90%, by GPC and NMR) *cyclo*-$(SnHex_2)_5$ (presumably with a minor amount of *cyclo*-$(SnHex_2)_6$). The mass spectrum of this sample actually gave a more intense peak for the hexamer, identified by EIMS (monoisotope mass 1740.634, average mass 1734.079, peak max mass 1734.64; the calculated isotope pattern matches the isotope pattern obtained by EIMS). ^1H NMR (500 MHz, benzene-d_6): δ 0.97 (m, CH_3, cyclic), 1.04 (t, $J = 7$ Hz, CH_3, linear), 1.37−1.60 (multiplets, CH_2, cyclic + linear), 1.68 (m, CH_2, linear), 1.86 (m, CH_2, cyclic), 1.97 (m, CH_2, linear). $^{13}C\{^1H\}$ NMR (100.6 MHz, benzene-d_6): δ 12.12, 14.45, 23.40, 31.68, 32.28, 35.75 (s, ^nHex, linear), 10.03, 14.39, 23.19, 31.28, 32.10, 35.01 (s, ^nHex, cyclic). $^{119}Sn\{^1H\}$ NMR (111.9 MHz, benzene-d_6): δ −190.9 (linear), −202.1 (cyclic pentamer), −202.7 (cyclic hexamer).

(c) **Polymerization of $^nOct_2SnH_2$.** Polymerizations of $^nOct_2SnH_2$ followed procedures similar to the one described above for $^nHex_2SnH_2$. Anal. Calcd for $C_{16}H_{34}Sn$: C, 55.7; H, 9.93. Found: C, 55.5; H, 9.90. ^1H NMR (500 MHz, benzene-d_6): δ 0.93−1.03 (br, CH_3, cyclic + linear), 1.35−1.80 (br combination of resonances, cyclic + linear), 1.81−2.05 (br, cyclic + linear). $^{119}Sn\{^1H\}$ NMR (111.9 MHz, benzene-d_6): δ −190.7 (linear), −201.8 (cyclic pentamer), −202.4 (cyclic hexamer).

(d) **Polymerization of Ph_2SnH_2 with $CpCp^*Zr[Si(SiMe_3)_3]Me$.** Addition of neat Ph_2SnH_2 (0.30 g, 1.09 mmol) to the catalyst (2 mol %) produced vigorous hydrogen evolution and a yellow-brown mixture. After 5 h, the solid mixture was washed with tetrahydrofuran−pentane (1:10) to give a light yellow solid. Analysis of the polymer by GPC revealed a molecular weight distribution of $M_w/M_n = 1480/620$. UV-vis (THF): λ_{max} 402 nm. Yield: 60%. Anal. Calcd for $C_{12}H_{10}Sn$: C, 52.8; H, 3.69. Found: C, 52.4; H, 3.63.

Wurtz-Coupling of $^nBu_2SnCl_2$ with Sodium. The experimental procedure according to Zou and Yang was rigorously followed.[11] A suspension of sodium dispersion (10.35 g, 0.137 mol, 30 wt % in toluene) and 15-crown-5 (1.51 g, 0.0069 mol) was added to toluene (144 mL) and heptane (26 mL), and the mixture was heated to 60 °C with an oil bath. A solution of freshly distilled $^nBu_2SnCl_2$ (20.32 g, 0.067 mol) in toluene (ca. 30 mL) was then added dropwise via an addition funnel over 3 h. The reaction mixture was stirred for another 14 h at 60 °C and then allowed to cool to ambient temperature over 2

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h before being filtered through Celite to remove unreacted sodium and sodium chloride. Solvent was removed by vacuum transfer, and then methanol was added to the resulting orange oil. After the mixture was stirred for another 2 h, the methanol was removed by vacuum transfer, and the resulting orange oil was dried under vacuum at 55 °C for 8 h to give a bimodal molecular weight distribution corresponding to a mixture of linear and cyclic polystannanes (ca. 1:1 by GPC; M_w/M_n = 2400/1200). ^{119}Sn NMR (186.5 MHz, 7:3 benzene-d_6 + THF) δ −202.0, −200.9, −189.6.

Me$_2$C(C$_5$H$_4$)$_2$Zr[Si(SiMe$_3$)$_3$]Cl. Toluene (ca. 15 mL) was added to a solid mixture of Me$_2$C(C$_5$H$_4$)$_2$ZrCl$_2$ (0.685 g, 2.06 mmol) and (THF)$_3$LiSi(SiMe$_3$)$_3$ (0.917 g, 1.95 mmol), and the resulting red solution was stirred for 4 h at ambient temperature. The reaction mixture was then filtered, evacuated to dryness, and extracted with pentane (3 × 15 mL). The combined pentane extracts were concentrated and cooled (−40 °C) to give the product as red crystals (0.780 g, 74%). Anal. Calcd for C$_{22}$H$_{41}$ZrSi$_4$Cl: C, 48.5; H, 7.59. Found: C, 48.3; H, 7.42. ^{1}H NMR (400.1 MHz, benzene-d_6): δ 0.44 (s, 27 H SiMe$_3$), 1.00 (s, 3 H, CMe), 1.08 (s, 3 H, CMe), 4.92 (q, J = 2.4 Hz, 2 H, C$_5$H$_4$), 5.54 (q, J = 2.4 Hz, 2 H, C$_5$H$_4$), 6.06 (q, J = 2.4 Hz, 2 H, C$_5$H$_4$), 7.68 (q, J = 2.4 Hz, 2 H, C$_5$H$_4$). ^{13}C{^{1}H} NMR (100.6 MHz, benzene-d_6): δ 4.50 (SiMe$_3$), 23.13, 23.46, 36.44 (CMe$_2$), 104.09, 107.67, 114.59, 116.36, 117.42 (C$_5$H$_4$).

Me$_2$C(C$_5$H$_4$)$_2$Zr[Si(SiMe$_3$)$_3$]Me. To a cold (−78 °C) solution of Me$_2$C(C$_5$H$_4$)$_2$Zr[Si(SiMe$_3$)$_3$]Cl (0.242 g, 0.445 mmol) in diethyl ether (ca. 20 mL) was added MeMgBr (0.35 mL, 1.4 M in diethyl ether, 0.49 mmol). The yellow reaction mixture was allowed to slowly warm to ambient temperature with continuous stirring over 4 h, and then the volatile material was removed by vacuum transfer. Extraction with pentane (2 × 50 mL) and concentration and cooling (to −40 °C) of the combined pentane extracts afforded the product as yellow crystals (0.100 g, 43%). Attempts to obtain reasonable combustion analysis data failed, even though NMR spectroscopy indicated that the recrystallized samples were quite pure. We assume that this is due to the slight thermal instability of the compound, or incomplete combustion. ^{1}H NMR (400.1 MHz, benzene-d_6): δ −0.14 (s, 3 H, ZrMe), 0.39 (s, 27 H, SiMe$_3$), 1.00 (s, 3 H, CMe), 1.04 (s, 3 H CMe), 4.94 (t, J = 2.4 Hz, 2 H, C$_5$H$_4$), 5.11 (t, J = 2.4 Hz, 2 H, C$_5$H$_4$), 6.31 (t, J = 2.4 Hz, 2H, C$_5$H$_4$), 7.67 (t, J = 2.4 Hz, 2 H, C$_5$H$_4$). ^{13}C{^{1}H} NMR (100.6 MHz, benzene-d_6): δ 4.75 (SiMe$_3$), 23.14, 23.71, 36.05 (CMe$_2$), 47.47 (ZrMe), 104.25, 107.41, 110.84, 113.03, 115.66 (C$_5$H$_4$).

Ceramic Conversion of H(Sn^{n}Bu$_2$)$_n$H to Tin Oxide. A sample of the polymer (M_n = 12 000) was placed in the tube furnace under a flow of air. The temperature of the sample was raised at a rate of 10 °C/min to 400 °C. The sample was then cooled to room temperature and weighed (ceramic yield: 61%). Further heating of the sample to 1100 °C gave a white powder (ceramic yield 56% based on original polymer) which was shown by XRD to contain SnO$_2$ (cassiterite) as the only crystalline phase. Anal. Found: C, 0.06; H, <0.01.

Ceramic Conversion of H(Sn^{n}Oct$_2$)$_n$H to Elemental Tin. A sample of the polymer (M_n = 12 000) was placed in a Schlenk flask under a blanket of vented nitrogen. The temperature of the sample was raised to 400 °C with a sand bath, and this temperature was maintained for 10 h. The sample was then cooled to room temperature and weighed (ceramic yield: 26%). The gray powder was shown by XRD to consist of Sn metal and SnO$_2$ (cassiterite).

Conductivity Measurements. A sample of H(Sn^{n}Bu$_2$)$_n$H (M_w/M_n = 58 000/17 000) was dissolved in pentane, and from this solution a film (0.5 mm thick) of the polymer was cast onto a glass slide. The film was exposed to SbF$_5$ vapor under vacuum in a doping chamber for 3 h. A standard four-point probe method was used to measure a conductivity of 10^{-2} ohm^{-1} cm^{-1} for the doped film. A film of H(Sn^{n}Oct$_2$)$_n$H polymer (M_w/M_n = 42 500/13 300) was doped similarly (film thickness = 0.34 mm, 30 h), and its conductivity was determined to be 0.3 ohm^{-1} cm^{-1}.