Poly(diaryl)stannanes: Influence of Substituents on the $\sigma-\sigma^*$ Transition Energy

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ABSTRACT: Poly(diaryl)stannanes were prepared by the dehydropolymerization of secondary hydrostannanes Ar_2SnH_2 with dimethylzirconocene catalyst. At room temperature, $H(Ar_2Sn)_nH$ polystannanes (Ar = p-^{t}Bu-C_6H_4, p-^{n}Hex-C_6H_4, o-Et-C_6H_4, o-Et-p-^{n}BuO-C_6H_3, p-^{n}BuO-C_6H_4, p-$(Me_3Si)_2N$-C_6H_4) exhibit λ_{max} values attributed to $\sigma \rightarrow \sigma^*$ transitions in the range 430−506 nm. These values vary according to the polymer molecular weights and are independent of temperature between −20 and 90 °C. A sample of poly[bis(*o*-ethyl-*p*-^{n}butoxylphenyl)]stannane exhibits a strong UV−vis absorption at 506 nm (tailing to ca. 550 nm), which corresponds to the smallest band gap yet observed for a group 14, σ-conjugated polymer. The $H(Ar_2Sn)_nH$ polystannanes undergo photodecomposition in solution to give a mixture of the *cyclo*-hexamer and the *cyclo*-pentamer. Thermal gravimetric analyses for the polymers suggest that $H(Ar_2Sn)_nH$ polystannanes are thermally stable and have onset temperatures for thermal decomposition in the range 180−320 °C, under both nitrogen and air. The $H(Ar_2Sn)_nH$ polystannanes undergo clean thermal decompositions to elemental tin (under nitrogen) or tin oxide (under oxygen or air), as shown by bulk pyrolysis.

Introduction

The development of useful synthetic routes to soluble polysilanes in the early 1980s introduced a new class of charge-transporting materials that have attracted considerable attention.[1] The interesting electronic and optical properties exhibited by these polymers derive from delocalization of electron density in the silicon backbone and have focused attention on σ-delocalization in polymeric systems. However, there remains much to be learned about the range of electronic properties accessible to σ-conjugated frameworks. Given our interest in this area, we recently developed a route to linear poly(dialkyl)stannanes, $(SnR_2)_n$, based on the metal-catalyzed dehydropolymerization of secondary stannanes, R_2SnH_2.[2] These polymers display strong $\sigma \rightarrow \sigma^*$ transitions at ca. 390−430 nm, which represent a red shift with respect to analogous polysilanes of ca. 70 nm. On the basis of previous studies on polysilanes, it seemed that even lower band gaps might be achieved with aryl substituents which could increase conjugation via $\sigma-\pi$ mixing.[1b] In a preliminary communication, we described the synthesis of poly(diaryl)stannanes which in fact exhibit $\sigma \rightarrow \sigma^*$ transitions that are red-shifted with respect to those for the poly(dialkyl)stannanes by about 40 nm.[3] In this contribution, we present results from our investigation on the influence of substituent effects on the band gaps in poly(diaryl)stannanes. This work has led to isolation of a polystannane, H[(*o*-Et-*p*-^{n}BuO-$C_6H_3)_2Sn]_nH$, which exhibits a band gap of about 2.3 eV (based on the band edge of 550 nm).

Results and Discussion

Our synthesis of poly(diaryl)stannanes is based on the metal-catalyzed dehydropolymerization of a diarylstannane. Typically, vigorous gas evolution was observed upon addition of the catalyst. As the polymerization proceeded, the reaction mixture changed from colorless to yellow to dark orange and finally to dark red or dark brown as the gas evolution slowed and the solid polymer formed. Molecular weight distributions were measured by gel permeation chromatography (GPC), utilizing polystyrene standards and tetrahydrofuran solvent. The isolated polymer samples are air- and light-sensitive solids. In general, mixtures of cyclic oligomers and linear polystannane chains were produced (eq 1), the ratio of which depended on the reaction conditions. The cyclic polystannanes appear to be monodisperse by GPC and predominantly hexameric (vide infra).

$$Ar_2SnH_2 \xrightarrow[-H_2]{Cp_2ZrMe_2} H(Ar_2Sn)_nH + (Ar_2Sn)_m \quad (m = 5, 6) \quad (1)$$

To investigate the effects of various substituents on the polystannane band gap, we prepared the series of monomers listed in Table 1 as precursors to polystannanes. The initial monomers chosen for study, $(p$-^{t}Bu-$C_6H_4)_2SnH_2$ (**1**) and $(p$-^{n}Hex-$C_6H_4)_2SnH_2$ (**2**), were synthesized in reasonable yields (ca. 80%) via $LiAlH_4$ reductions of the corresponding dichlorides, which were obtained by comproportionation of Ar_4Sn and $SnCl_4$.[4] Both **1** and **2** are air-sensitive, and whereas **1** is a white solid at room temperature, **2** is a colorless, viscous oil.

Results from representative dehydropolymerizations of $(p$-^{t}Bu-$C_6H_4)_2SnH_2$ (**1**) are summarized in Table 2. Conditions were optimized for a metal-catalyzed polymerization with step-growth character, assuming a mechanism analogous to the one proposed for the dehydropolymerization of silanes.[5] These conditions, expected to maximize the polystannane chain length while minimizing the production of oligomeric cyclic species, involve high monomer concentrations (ideally, neat monomer), mild temperatures, and low pressures. Such considerations have been used to optimize molecular weight properties for $H(SiHPh)_nH$ polysilanes obtained in the polymerization of $PhSiH_3$ with CpCp*Zr-based catalysts.[5c] However, it is difficult to employ such conditions for monomers **1** and **2**, given their solid (**1**) or viscous (**2**) nature.

The dehydropolymerization of **1** in the melt (at 120 °C with Cp_2ZrMe_2 catalyst) and under dynamic vacuum

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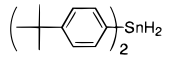
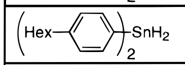
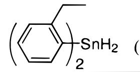
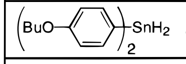
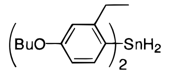
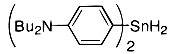
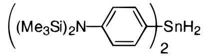
Table 1. Properties for Secondary Diarylstannanes

monomer	^{1}H NMR (δ_{SnH}, C_6D_6)	^{119}Sn NMR (δ, C_6D_6)	υ_{Sn-H} (cm^{-1})	mp (°C)
 (**1**)	6.15	-234.1	1871	73-74
 (**2**)	6.14	-232.1	1860	< -50
 (**3**)	6.13	-249.3	1852	< -50
 (**4**)	6.14	-228.6	1846	38-40
 (**5**)	6.14	-246.5	1863	23-24
 (**6**)	6.26	-226.7	1858	< -40
 (**7**)	6.10	-230.2	1858	< -40

(entry 1 in Table 2) resulted in solidification of the reaction mixture within 1 min. After 2.5 h, the reaction mixture contained linear H[(p-^{t}Bu-C_6H_4)$_2$Sn]$_n$H chains (M_w/M_n = 16 000/10 000, 80% by area ratios determined by GPC) and cyclic oligomer ($M_n \approx 1500$). Further heating for an additional 3 h resulted in some depolymerization and a sample containing 24% cyclic oligomer and linear H[(p-^{t}Bu-C_6H_4)$_2$Sn]$_n$H chains with M_w/M_n = 15 000/10 000. A disadvantage to these polymerization conditions is that they produce a large amount of the low molecular weight cyclics (> 20%). As a control experiment, monomer **1** was heated for 3 h at 120 °C under a dynamic vacuum in the absence of a catalyst. Analysis of the final products by GPC indicated that polystannanes were not formed. Instead, the decomposition of **1** under these conditions gave a metallic precipitate (presumably tin metal) and uncharacterized aromatic compounds (by ^{1}H NMR spectroscopy). These results are therefore similar to those obtained for the thermal decomposition of ^{n}Bu$_2$SnH$_2$.[2b]

In general, fractionation procedures may be used to reduce the amount of cyclic species in the polystannane sample. For example, to purify a sample of H[(p-^{t}Bu-C_6H_4)$_2$Sn]$_n$H containing 30% cyclics and linear polystannanes (M_w/M_n = 10 700/6600), the crude polymer was dissolved in THF, and the resulting solution was filtered into a large volume of methanol. Upon standing at room temperature a 50% yield of H[(p-^{t}Bu-C_6H_4)$_2$Sn]$_n$H, which had been significantly enriched in the longer chains (ca. 10% cyclic, M_w/M_n = 20 400/15 100 for the linear fraction), precipitated as an orange solid.

The ^{119}Sn NMR spectra for these samples contain a peak at −197 ppm for the linear H[(p-^{t}Bu-C_6H_4)$_2$Sn]$_n$H chains, and the cyclic oligomer formed in the dehydropolymerization of **1** gives rise to a single ^{119}Sn NMR resonance at −221 ppm (J_{SnSn} = 673, 1003 Hz). The cyclic species was independently synthesized by the reaction of **1** with pyridine[6] (entry 7 of Table 2) and identified by FAB mass spectrometry as the hexamer *cyclo*-[(p-^{t}Bu-C_6H_4)$_2$Sn]$_6$ (λ_{max} = 290 nm; ^{119}Sn NMR: δ −221). It is interesting to note that whereas the dehydrocoupling of **1** gives predominantly the cyclic hexamer, the *cyclo*-pentamer is the major byproduct in the polymerization of dialkylstannanes.[2b]

The influence of hydrocarbon solvents on the polymerization of **1** was examined (entries 2−5, Table 2). At low monomer concentrations ([**1**] = 0.01−0.03 M), dehydrocoupling with CpCp*Zr[Si(SiMe$_3$)$_3$]Me or Cp$_2$ZrMe$_2$ (2−3 mol %; ambient room temperature) gave only low molecular weight oligomers (entry 4 of Table 2). However, at monomer concentrations above 0.09 M, relatively high molecular weight H[(p-^{t}Bu-C_6H_4)$_2$Sn]$_n$H polymers were obtained ($M_n \geq 14\,000$; see entries 2, 3, and 5 of Table 2). These conditions are therefore superior to those involving high temperatures, in that a higher fraction of linear chains, of somewhat higher molecular weight, are produced. Entry 6 of Table 2 describes the polymerization of **1** in *N*,*N*-dibutylaniline solution (0.1 M) by Cp$_2$ZrMe$_2$ (2 mol %), which resulted in slower dehydrocoupling and low molecular weights. This observation indicates that donor solvents inhibit the polymerization, as has been observed previously for the dehydrocoupling of hydrosilanes by group 4 metallocene catalysts.[5a]

Dehydropolymerization of **2** with Cp$_2$ZrMe$_2$ (3 mol %, [**2**] = 0.11 M in pentane, ambient room temperature) over 7 h gave a yellow-orange polystannane as an extremely viscous oil. This polymer sample contains mainly H[(p-^{n}Hex-C_6H_4)$_2$Sn]$_n$H linear chains (M_w/M_n = 34 700/14 300; T_g = −8.1 °C) and a small amount (<5%) of cyclic oligomer (M_w/M_n = 2100/2000). Fractionation of this sample using a mixture of MeOH and THF (10:1 by volume) allowed isolation of a sample enriched in the longer chains (M_w/M_n = 48 200/20 000) but also containing a small amount of cyclics (5%, presumably due to some photodecomposition of the polymer during handling). Analysis of this sample by ^{119}Sn NMR spectroscopy revealed only a resonance at −196 ppm, attributed to the linear chains.

Samples of H[(p-^{t}Bu-C_6H_4)$_2$Sn]$_n$H and H[(p-^{n}Hex-C_6H_4)$_2$Sn]$_n$H exhibit λ_{max} values attributed to $\sigma \rightarrow \sigma^*$ transitions at 432 and 436 nm, respectively (in THF). The half-height widths associated with these transitions (46 and 53 nm, respectively) are quite narrow compared to those observed for poly(dialkyl)stannanes, which vary from ca. 60 to 250 nm depending on the polymer phase.[2c] This suggests the presence of fairly well-defined chromophores and a dominant chain structure. In contrast to related transitions for H(R$_2$Sn)$_n$H (R = ^{n}Hex, ^{n}Oct) polystannanes,[2b] the energies of these absorptions are independent of temperature (−20 to +90 °C; solution or film).

From extensive work on polysilanes, it is known that electronic properties can depend markedly on the conformation of the polymer backbone, and a number of polysilane backbone conformations have been identified.[1,7] In particular, it seems that σ-conjugation is greatest for the planar zigzag conformation. The powder X-ray diffraction pattern for samples of H[(p-^{t}Bu-C_6H_4)$_2$Sn]$_n$H at room temperature contains three peaks at 2θ values of 5.79°, 17.57°, and 40.81°. The low angle peak corresponds to a *d*-spacing of 15.2 Å, which is relatively close to the calculated repeat distance for a 7/3 helical chain structure (15.8 Å), corresponding to a T$_3$GT$_3$G′ (T: trans-, G: gauche-) pattern of conformations about the Sn−Sn bonds.[8] Therefore, this polymer possesses a structure analogous to that for H(^{n}Hex$_2$Sn)$_n$H (λ_{max} 398 nm for the solid film), which also exhibits a *d*-spacing of 15.2 Å).[9] This result suggests that σ-conjugation along the main chain is not optimal in these samples.[7c] Also, based on the assumption that the solid-state samples of H[(p-^{t}Bu-C_6H_4)$_2$Sn]$_n$H and H(^{n}Hex$_2$Sn)$_n$H have the same structure (based on PXRD data), aryl substitution

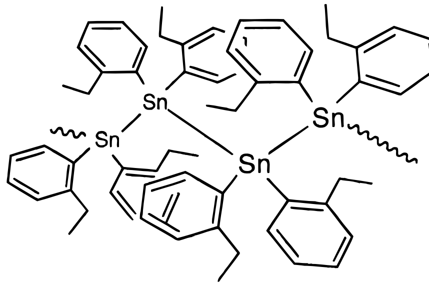
Table 2. Molecular Weight Data for Dehydropolymerizations of $(p\text{-}^t\text{Bu-C}_6\text{H}_4)_2\text{SnH}_2$ (1) as a Function of Monomer Concentration (Polymerizations Involved 2−4 mol % Cp_2ZrMe_2 unless Otherwise Noted)[a]

			entire sample		linear fraction[g]	
reaction conditions	reaction time, h	% cyclic[b]	M_w	M_n	M_w	M_n
1. neat at 120 °C	2.5	20	12 000	5000	16 000	10 000
	5.5	24	10 000	4000	15 000	10 000
	11	50	8 000	2000	7 000	4 000
2. 0.09 M in pentane	24	7	48 000	7000	54 000	15 000
3. 0.13 M in pentane	24[c]	<5			43 000	18 000
4. 0.02 M in benzene[d]	3	>95	4 000	2000		
5. 0.13 M in benzene	3	9	14 000	6000	22 000	14 000
6. 0.10 M in *N*,*N*-dibutylaniline	24	74[e]	800	300	2 700	2 300
7. pyridine[f]	ca. 64	100	1 700	1700		

[a] Ambient room temperature under 1 atm of nitrogen. [b] These values (determined by GPC) probably have large errors associated with them, unless there is good peak separation. [c] The polymer sample was isolated by precipitation with methanol. [d] $\text{CpCp*Zr[Si(SiMe}_3)_3]\text{Me}$ catalyst gave the same results under these conditions. [e] Contains mainly the unreacted monomer (by GPC). [f] This sample was prepared by dissolving **1** in a 2:5 pyridine/benzene-d_6 mixture (see Experimental Section). [g] We assume that the narrow polydispersities observed (those <2) are due to selective precipitation of the polymer under the specific reaction conditions and/or errors associated with sample preparation (for example, during filtration of the sample before injection into the GPC).

appears to correspond to a red shift in the $\sigma-\sigma^*$ transition of 34 nm. For analogous polysilanes systems, it has been observed that aryl substitution results in a similar red shift of 25−35 nm.[1b]

On the basis of models, it appeared that *o*-ethyl substituents might enforce a planar zigzag conformation for the Sn backbone of a poly(diaryl)stannane (structure **A**).[10] To test this possibility, we prepared the monomer $(o\text{-Et-C}_6\text{H}_4)_2\text{SnH}_2$ (**3**). Dehydrocoupling of **3** in hydrocarbon solvents (i.e., pentane, benzene or toluene; [**3**] = 0.15−0.60 M or neat) with Cp_2ZrMe_2 catalyst (2−3 mol %) at ambient room temperature yielded only low molecular weight oligomers ($M_n \leq 1000$, $\lambda_{max} = 414$ nm). However, after heating a mixture of **3** and Cp_2ZrMe_2 at 90 °C for 12 h, poly[bis(*o*-ethylphenyl)]stannane (linear fraction: ca. 60%, M_w/M_n = 22 000/12 000; cyclic fraction: ca. 40%, M_w/M_n = 1000/900)[11] was obtained as a brown solid. Only part of the solid sample could be dissolved in THF, and this part of the product was fractionated in THF/methanol to give a red-orange polystannane in 46% yield. Unfortunately, this polystannane sample could not be redissolved in THF, presumably due to a phase change induced by the precipitation from methanol. Thus, a molecular weight determination on this sample was not possible. Nonetheless, an optical spectrum of the solid pressed between two quartz plates revealed a $\sigma \rightarrow \sigma^*$ transition at 468 nm, which represents a red shift of ca. 30 nm relative to those for samples of $\text{H}[(p\text{-}^t\text{Bu-C}_6\text{H}_4)_2\text{Sn}]_n\text{H}$ and $\text{H}[(p\text{-}^n\text{Hex-C}_6\text{H}_4)_2\text{Sn}]_n\text{H}$. The powder X-ray diffraction pattern of the insoluble $\text{H}[(o\text{-Et-C}_6\text{H}_4)_2\text{Sn}]_n\text{H}$ polymer contained one broad peak corresponding to a *d*-spacing value of 11.5 Å. On the basis of this and the λ_{max} value, it appears that the *o*-ethyl groups on the aryl side chain enforce a different, more conjugated backbone conformation.



A

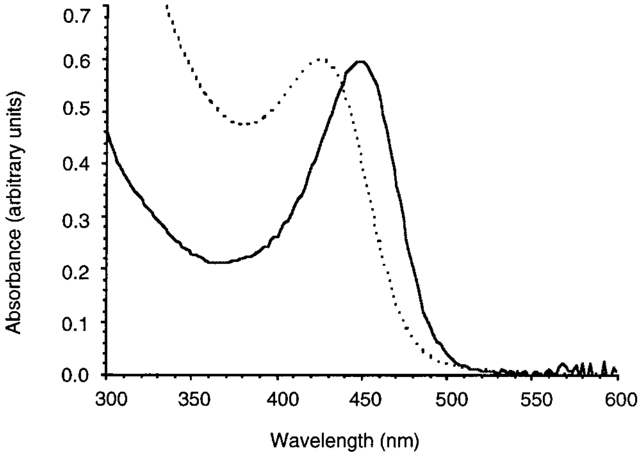
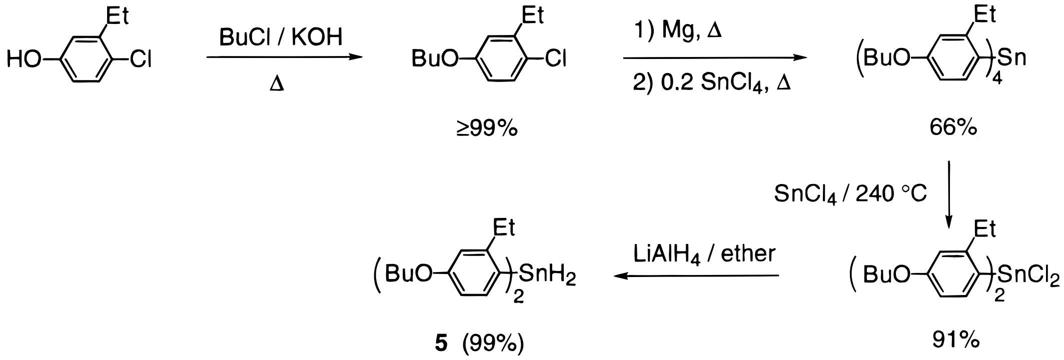


Figure 1. Optical spectra of $\text{H}[(p\text{-}^n\text{BuO}-\text{C}_6\text{H}_4)_2\text{Sn}]_n\text{H}$ in THF: (—) $M_n = 8000$, $\lambda_{max} = 448$ nm; (- - -) $M_n = 3000$, $\lambda_{max} = 424$ nm.

Given the significant $\sigma-\pi$ mixing that appears to exist in the poly(diaryl)stannanes described above, it seemed that further manipulation of the polystannane band gap could result from introduction of donor or acceptor groups onto the aryl substituents. For example, a π-donating group should raise the energy of delocalized bonding levels, thus narrowing the band gap.[1b] We therefore attempted the dehydropolymerization of the alkoxy-containing stannane monomer $(p\text{-}^n\text{BuO-C}_6\text{H}_4)_2\text{SnH}_2$ (**4**), even though Lewis donors are known to inhibit the dehydropolymerization of silanes.[12]

The dehydropolymerization of **4** in pentane solution at concentrations of 0.13−0.48 M with Cp_2ZrMe_2 catalyst (2−3 mol %) at ambient room temperature afforded $\text{H}[(p\text{-}^n\text{BuO-C}_6\text{H}_4)_2\text{Sn}]_n\text{H}$ (M_w/M_n = 12 000/8000, $n \approx 80$, ≤5% cyclics, λ_{max}(THF) = 448 nm).[13] Surprisingly, when aromatic solvents (benzene or toluene) were used, the dehydrocoupling of **4** gave only low molecular weight $\text{H}[(p\text{-}^n\text{BuO-C}_6\text{H}_4)_2\text{Sn}]_n\text{H}$ (M_w/M_n = 4000/3000, $n \approx 30$, λ_{max} (THF) = 424 nm). The different optical properties for these two samples (Figure 1), apparently due to a difference in polymer chain length, is somewhat surprising given what is known about conjugation lengths in polystannane oligomers. On the basis of studies with polystannane oligomers, Sita has shown that λ_{max} values for polystannanes reach a limiting value for chain lengths of not more than ca. 30 monomer units.[14] Introduction of the alkoxy substituent results in a red shift for the $\sigma-\sigma^*$ transition of ca. 12−16 nm relative

Scheme 1



to those for related alkyl-substituted analogues. Similar effects have been seen for aryl-substituted polysilane derivatives (possessing *p*-Me and *p*-MeO groups), but in this case the corresponding red shift in the λ_{max} value is only 6 nm.[1b] This suggests the presence of a significant $\sigma-\pi$ interaction in the poly(diaryl)stannanes.[15]

After observing significant red shifts in the $\sigma-\sigma^*$ transition after introducing *o*-ethyl and *p*-butoxy groups into the diarylstannylene monomer units, it seemed that lower band gaps might be achieved with aryl groups featuring both substituents. Also, the butoxy group was expected to impart greater solubility to the polystannane chain. Thus, we prepared (o-Et-p-^{n}BuO-$C_6H_3)_2$-SnH_2 (**5**), which has a (postulated) polymer backbone directing group (*o*-ethyl) and an electron-donating substituent. Compound **5** was prepared from commercially available 4-chloro-3-ethylphenol in an overall isolated yield of 60% as an air- and temperature-sensitive white solid (Scheme 1). Isolated **5** is analytically and spectroscopically pure and exhibits a ^{1}H NMR resonance at 6.14 ppm (J_{SnH} = 1785, 1868 Hz) assigned to the SnH group, and the ^{119}Sn{^{1}H} NMR spectrum of **5** contained a single resonance at −249.5 ppm.

During studies of the dehydropolymerization of **5**, we encountered problems similar to those we had seen in the polymerization of **3**. For example, the dehydrocoupling of **5** in hydrocarbon solvents at various concentrations (from 0.13 M in pentane or toluene to neat monomer) consistently gave low molecular weight oligomers ($M_w/M_n \approx 2300/1900$). We also varied the ratio of catalyst to monomer (2−10 mol % Cp_2ZrMe_2), the reaction temperature (25−120 °C), and the catalyst structure (Cp_2ZrMe_2, CpCp*Zr[Si(SiMe$_3$)$_3$]Me, Me$_2$C(η^5-$C_5H_4)_2$HfMe$_2$, and Cp$_2$Zr(H)Cl), without success. Unfortunately, it is not clear at this time why higher molecular weights were not produced.

Upon addition of a THF solution of the crude poly[bis(*o*-ethyl-*p*-^{n}butoxylphenyl)]stannane product (obtained with Cp_2ZrMe_2 catalyst) to methanol, a small amount of dark red solid (fraction A, ca. 10%; M_w/M_n = 4400/4000) precipitated after ca. 1.5 weeks. The λ_{max} value for this polystannane, 506 nm (THF solution), is the most red-shifted yet observed for a σ-conjugated polymer. The relatively narrow half-height width for this absorption (57 nm) is comparable to that of the other poly(diaryl)stannanes described above (Table 4). Cooling of the filtrate to −80 °C gave a second fraction (B) of H[(o-Et-p-^{n}BuO−$C_6H_3)_2$Sn]$_n$H as an orange solid (in 30−40% yield), which had a lower molecular weight ($M_w \approx M_n \approx 3000$, λ_{max}(THF) = 472 nm, Figure 2). Thus, the UV−vis data obtained for these polystannanes suggest that even lower band gaps would be observed for higher molecular weight samples. Attempts to study the structure of the solid H[(o-Et-p-^{n}BuO−$C_6H_3)_2$Sn]$_n$H polymer were not successful, as no peaks were observed in the PXRD pattern.

Table 3. Thermal Gravimetric Analysis Data for the Polystannanes

polymer sample	atm	onset temp for decomp (°C)	% yield at 550 °C
H[(p-^{t}Bu−$C_6H_4)_2$Sn]$_n$H	N_2	303	30 (31)[a]
	air	227	39 (39)[b]
H[(p-^{n}Hex−$C_6H_4)_2$Sn]$_n$H	N_2	313	21 (27)[a]
	air	188	40 (34)[b]
H[(o-Et-$C_6H_4)_2$Sn]$_n$H	N_2	203	22 (36)[a]
	O_2	209	46 (46)[b]
H{[p-(Me$_3$Si)$_2$N−$C_6H_4]_2$Sn}$_n$H	N_2	214	38 (20)[a]
	O_2	194	46 (26)[b]
H[(p-^{n}BuO−$C_6H_4)_2$Sn]$_n$H	N_2	327	28 (29)[a]
	O_2	183	43 (36)[b]

[a] Theoretical yield for Sn metal. [b] Theoretical yield for SnO_2.

We also prepared the amino-substituted diarylstannanes **6** and **7** to probe the effect of an NR$_2$ group on the polystannane band gaps.[16] The stannane (p-^{n}Bu$_2$N−$C_6H_4)_2SnH_2$ (**6**) is highly unstable at room temperature and decomposes to give a Sn mirror and *N*,*N*-dibutylaniline (by ^{1}H NMR spectroscopy) as the major identifiable products. This might have been expected, since it is well documented in the literature that secondary hydrostannanes decompose in the presence of amines or pyridines to give *cyclo*-stannanes.[6] However, surprisingly **6** decomposes much more rapidly than other di(aryl)stannanes (such as **1**) dissolved in *N*,*N*-dibutylaniline. Also, the stannane [p-(SiMe$_3$)$_2$N-$C_6H_4]_2SnH_2$ (**7**), isolated as a light brown viscous oil in an overall yield of 61%, is more stable than **6** at room temperature (no decomposition over 8 h in benzene-d_6 by ^{1}H NMR spectroscopy).

The polymerization of **7** with Cp_2ZrMe_2 afforded relatively low molecular weight poly{bis[*p*-(bis-trimethylsilyl)aminophenyl]}stannane (M_w/M_n = 4000/3800, λ_{max} (THF) = 450 nm) after fractionation. Numerous attempts to obtain higher molecular weights were not successful, perhaps due to the presence of the amine functionality. Note that the presence of *N*,*N*-dibutylaniline inhibits chain growth in the dehydropolymerization of (p-^{t}Bu-$C_6H_4)_2SnH_2$ (entry 6 of Table 2). The polymer has very low solubility in common organic solvents (i.e., benzene, toluene, THF, and CH_2Cl_2), thus preventing us from characterizing the polymer fully by NMR spectroscopy. However, it is interesting to note that this low molecular weight H{[p-(SiMe$_3$)$_2$N-$C_6H_4]_2$-Sn}$_n$H exhibits a λ_{max} value (450 nm) that is comparable to those for high molecular weight H[(p-^{n}BuO-$C_6H_4)_2$-

Table 4. Properties for the Poly(diaryl)stannanes

polymer	M_w/M_n (linear)[a]	^{119}Sn (δ)[b]	λ_{max} (nm)[d]	$d_{spacing}$ (Å)[e]
$H[(p\text{-}^tBu\text{-}C_6H_4)_2Sn]_nH$	56 000/16 700	−197.0	432 (THF) (46)	15.2
$H[(p\text{-}^nHex\text{-}C_6H_4)_2Sn]_nH$	48 200/20 000	−196.0	436 (THF) (53)	
$H[(o\text{-}Et\text{-}C_6H_4)_2Sn]_nH$	insoluble[c] (22 000/12 000)		468 (film) (88)	11.5
$H[(p\text{-}^nBuO\text{-}C_6H_4)_2Sn]_nH$	12 000/7000	−183.5	448 (THF) (65)	17.7
$H[(o\text{-}Et\text{-}p\text{-}^nBuO\text{-}C_6H_3)_2Sn]_nH$	4400/4000	−125	506 (THF) (57)	
$H\{[p\text{-}(Me_3Si)_2N\text{-}C_6H_4]_2Sn\}_nH$	4200/3800		450 (THF) (56)	17.6

[a] We assume that the narrow polydispersities observed (those <2) are due to selective precipitation of the polymer under the specific reaction conditions and/or errors associated with sample preparation (for example, during filtration of the sample before injection into the GPC). [b] Benzene-d_6 solvent. [c] The molecular weight determination was performed on the crude reaction mixture. The isolated product is insoluble in THF. [d] Half-height widths are given in parentheses. [e] Derived from the lowest-angle peak in the XRD pattern. These peaks were the most intense ones observed in each pattern.

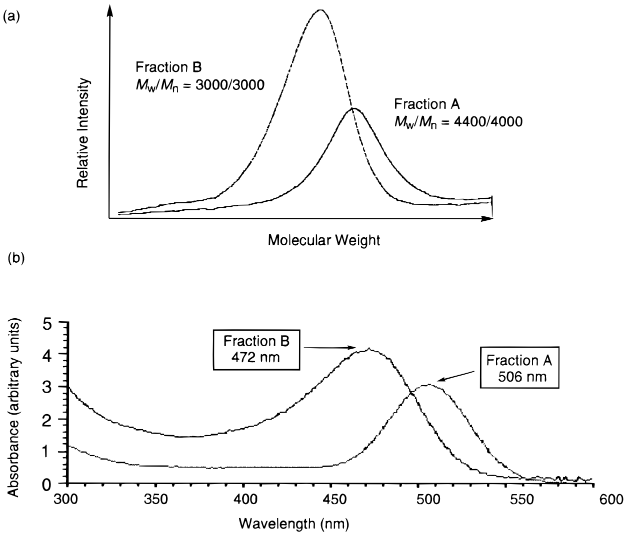


Figure 2. (a) GPC trace for isolated samples of $H[(o\text{-}Et\text{-}p\text{-}^nBuO\text{-}C_6H_3)_2Sn]_nH$. (b) UV−vis absorption spectra for isolated samples of $H[(o\text{-}Et\text{-}p\text{-}^nBuO\text{-}C_6H_3)_2Sn]_nH$.

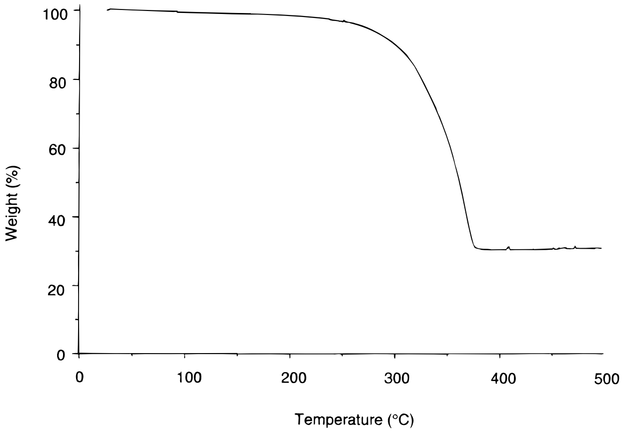


Figure 3. TGA curve for $H[(p\text{-}^tBu\text{-}C_6H_4)_2Sn)_nH$ (under N_2).

$Sn]_nH$. PXRD studies also indicate that $H\{[p\text{-}(Me_3Si)_2N\text{-}C_6H_4]_2Sn\}_nH$ and $H[(p\text{-}^nBuO\text{-}C_6H_4)_2Sn]_nH$ have similar backbone conformations, as suggested by their *d*-spacing values of ca. 17.6 Å.

In general, the poly(diaryl)stannanes described here are air-stable over at least several weeks in the dark and photochemically degrade in solution to give mixtures of cyclic oligomers. Therefore, routine handling of these polymers is best conducted under anaerobic conditions and with low levels of ambient lighting. The photodecomposition of $H[(p\text{-}^tBu\text{-}C_6H_4)_2Sn]_nH$ was studied in most detail. Exposure of a THF solution of $H[(p\text{-}^tBu\text{-}C_6H_4)_2Sn]_nH$ to room light (for 30 min) resulted in depolymerization to a mixture of cyclics, as determined by ^{119}Sn NMR spectroscopy. The major photodecomposition product was *cyclo*-$[(p\text{-}^tBu\text{-}C_6H_4)_2Sn]_6$, and additional products gave rise to ^{119}Sn resonances at δ −214 (J_{SnSn} = 560 Hz, possibly due to *cyclo*-$[(p\text{-}^tBu\text{-}C_6H_4)_2Sn]_5$) and δ −216 (very low intensity; no coupling observed).

Thermal Stabilities of Poly(diaryl)stannanes. Table 3 summarizes the thermal gravimetric analyses (TGAs) for $H(Ar_2Sn)_nH$ polystannanes under various conditions. The TGA traces for $H[(p\text{-}^tBu\text{-}C_6H_4)_2Sn]_nH$ (Figure 3) and $H[(p\text{-}^nBuO\text{-}C_6H_4)_2Sn]_nH$ under nitrogen reveal very little weight loss below 250 °C and then a weight loss of ca. 70% from 310 to 370 °C. The weight losses at 400 °C (70% and 72% for $H[(p\text{-}^tBu\text{-}C_6H_4)_2Sn]_nH$ and $H[(p\text{-}^nBuO\text{-}C_6H_4)_2Sn]_nH$, respectively) are in close agreement with the theoretical yield for Sn metal. A bulk sample of $H[(p\text{-}^tBu\text{-}C_6H_4)_2Sn]_nH$ was heated to 400 °C under flowing nitrogen to yield a black powder (25%) identified (by XRD) as Sn metal (tetragonal) containing a very small amount of SnO (romarchite, presumably resulting from contamination by fortuitous air during experimental manipulations). The polymer $H[(p\text{-}^nHex\text{-}C_6H_4)_2Sn]_nH$ is stable to about 250 °C, after which 79% of the material is lost between 265 and 310 °C. Poly[bis(*o*-ethylphenyl)]stannane is, however, only stable to about 200 °C, and rapid weight loss (78%) occurs between 330 and 390 °C (by TGA). Poly{bis-[*p*-(*N*,*N*-bis-trimethylsilyl)amino]phenyl}stannane exhibits a similar thermal stability. Decomposition of the latter polymer under flowing nitrogen was initiated at ca. 214 °C, and a two-stage process over which 22% of the material was lost occurred between 214 and 270 °C, followed by a second weight loss (40%) between 275 and 400 °C. The weight loss of 62% at 400 °C suggests that the decomposition products contain more than elemental Sn (theoretical yield 20%). Investigation of these decomposition products by PXRD indicated that the main crystalline phase is graphite. This is somewhat surprising since graphite has not been detected in the thermolyses of any other polystannanes.

Thermal analyses of the $H(Ar_2Sn)_nH$ polystannanes also show that these polymers are stable under air or oxygen up to ca. 180 °C. In air, $H[(p\text{-}^tBu\text{-}C_6H_4)_2Sn]_nH$ has an onset temperature for decomposition of 227 °C and exhibits a weight loss at 400 °C of 61% (by TGA), which is the theoretical value for conversion to SnO_2. Conversion to SnO_2 (cassiterite) was confirmed by PXRD. The relatively clean thermal decomposition of $H[(p\text{-}^tBu\text{-}C_6H_4)_2Sn]_nH$ to Sn metal and SnO_2 indicates that poly(diaryl)stannanes, like poly(dialkyl)stannanes, could serve as precursor polymers for the synthesis of tin- and tin oxide-based materials.

Concluding Remarks

The work described here provides synthetic pathways to poly(diaryl)stannanes via the metal-catalyzed dehydrocoupling of secondary stannanes. Unlike poly(dialkyl)stannanes, thin films of poly(diaryl)stannanes do not exhibit thermochromic behavior between −20 and 90 °C. This apparently indicates that phase transitions for these polymers do not occur over the temperature ranges examined. From the limited structural information now available, it appears that conjugation in these chains has not been optimized, in that the all-trans conformation has not yet been identified as a dominant phase.

These polymers appear to exhibit significant $\sigma-\pi$ interactions, which lower their band gaps with respect to those for related poly(dialkyl)stannanes. However, currently it is difficult to fully evaluate the electronic influence of the various aryl substituents, since molecular weights and the solid-state structures for the isolated samples vary. Note that the $H[(o\text{-Et-}p\text{-}^nBuO-C_6H_3)_2Sn]_nH$ sample was obtained with a fractionation procedure that probably biased the sample toward the highest molecular weights present. Nevertheless, the low molecular weight sample isolated for this polymer exhibits the smallest band gap (ca. 2.3 eV) yet reported for a σ-conjugated linear chain, even though the molecular weight is moderate ($M_w < 5000$).

The poly(diaryl)stannanes reported here exhibit λ_{max} values attributed to $\sigma \rightarrow \sigma^*$ transitions in the range 430−506 nm. These values vary according to molecular weights up to values of ca. 8000 (see Figures 1 and 2b). This molecular weight dependence is not too surprising, as it has been well documented in the literature that λ_{max} values increase with molecular weights, up to a limiting value, for polysilanes,[1] polygermanes,[17] and polystannanes.[14,18] Thus, an important remaining question concerns the magnitude of the band gap for high molecular weight poly[bis(*o*-ethyl-*p*-^{n}butoxylphenyl)]-stannane.

For the polymers described here, ^{119}Sn NMR spectra provide key structural information in that only peaks assigned to linear chains (and not to branching positions) were observed. The soluble linear poly(diaryl)-stannanes exhibit ^{119}Sn resonances in the region of −125 to −197 ppm (Table 4). Such ^{119}Sn shifts are consistent with what has been observed for linear poly(dialkyl)stannanes, which exhibit ^{119}Sn NMR shifts of ca. −190 ppm.[2b] Note that there is an approximately linear correlation between polymer band gap (as indicated by the λ_{max} values) and the ^{119}Sn NMR shifts, with the ^{119}Sn resonance shifting downfield as the polymer band gap is narrowed. A similar trend has been observed by Sita and co-workers for $R(Sn^nBu_2)_nR'$ oligomers, for which the innermost ^{119}Sn resonance shifts downfield and the λ_{max} value red shifts as the chain length increases.[14] For the monomers used in this study, the ^{119}Sn chemical shift range (−227 to −249 ppm) is much less than that observed for the corresponding poly(diaryl)stannanes. Thus, it seems that chemical shifts for the polymers are influenced not only by electronic substituent effects but also by steric factors and the polymer conformation. Similar results have been observed for West and co-workers for polysilanes.[19]

Experimental Section

General. All moisture- or air-sensitive reactions were carried out under nitrogen in a dry solvent. Ether, pentane, and tetrahydrofuran (THF) were distilled under N_2 from sodium benzophenone ketyl. Lithium aluminum hydride (LAH) was recrystallized from ether. Tetrachlorotin ($SnCl_4$) was purchased from Aldrich or Gelest and was used without further purification. 4-Bromohexylbenzene was prepared according to the literature procedure.[20] Alkylations of phenols (in the syntheses of **4** and **5**) were carried out according to the literature procedure reported for similar compounds.[21] Cp_2ZrMe_2,[22] $Cp_2Zr(H)Cl$,[23] $CpCp^*Zr[Si(SiMe_3)_3]Me$,[24] and $Me_2C(\eta^2\text{-}C_5H_4)_2HfMe_2$ [25] were prepared according to literature procedures. Unless otherwise indicated, a 1:1 mixture of air-free $MgSO_4$ and $CaCl_2$ was used as the drying agent for Ar_2SnH_2. In general, the polymerization reactions were initiated in the inert atmosphere drybox. The polystannanes were routinely protected from room light by wrapping the reaction and storage flasks with aluminum foil.

NMR spectra were obtained with Bruker AMX-300, Bruker AMX-400, Bruker AM-400, Bruker AM-500, and Bruker DRX-500 spectrometers. Infrared spectra were recorded on Perkin-Elmer 1330 and Mattson Infinity 60MI spectrometers. UV−vis spectra were obtained with a Hewlett-Packard 8452A UV−vis spectrophotometer. Thermal analyses were performed on a DuPont model 2000 thermal analysis system. Powder X-ray diffraction data were obtained with a Scintag XDS 2000 diffractometer. Elemental analyses was performed by the Microanalytical Laboratory in the College of Chemistry at the University of California, Berkeley. FAB and HREI mass spectrometric analyses were also performed by the Microanalytical Laboratory in the College of Chemistry. The molecular weight distributions for the polymer samples (vs polystyrene standards) were measured with a Water Associates chromatograph equipped with a refractive index detector and a PLgel 5μ mixed-D column using THF as the mobile phase under a nitrogen atmosphere. In general, a polymer sample (ca. 2−3 mg) was dissolved in dry, air-free tetrahydrofuran (ca. 0.3 mL). The resulting solution was filtered through a 1 μm filter. About 20 μL of the solution was then injected into the GPC instrument.

Tetrakis(*p-tert*-butylphenyl)stannane.[26] To a stirred solution of 4-*tert*-butylphenylmagnesium bromide (225 mL, 0.41 M in THF, 91.1 mmol) in a 1 L three-neck, round-bottom flask was added $SnCl_4$ (2.70 mL, 23.1 mmol) via a syringe under a nitrogen counterflow. The reaction mixture turned cloudy, and a white precipitate formed. The solution was heated to reflux for 6 h, stirred at ambient temperature overnight, and filtered into saturated NH_4Cl. The white solid was washed with H_2O (2 × 100 mL) and dried under vacuo at 180 °C for 3 h to afford $(p\text{-}^tBu\text{-}C_6H_4)_4Sn$ (12.5 g, 83.3%, mp 358.5−360.0 °C) as a white powder. ^1H NMR (300.1 MHz, benzene-d_6): δ 1.22 (s, 36 H, CMe_3), 7.31 (d, $J = 8.4$ Hz, 8 H, *meta*- C_6H_5), 7.74 (d, $J = 8.4$ Hz, 8 H, *ortho*-C_6H_5). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene-d_6): δ 31.3 ($C(CH_3)_3$), 34.6 ($C(CH_3)_3$), 126.0 (*meta*-C), 135.2 (*para*-C), 137.7 (*ortho*-C), 151.9 (CSn).

Bis(*p-tert*-butylphenyl)tin Dichloride. Tetrachlorotin (0.55 mL, 4.70 mmol) was added to $(p\text{-}^tBu\text{-}C_6H_4)_4Sn$ (3.07 g, 4.71 mmol) via a syringe. The reaction mixture was degassed, heated at 260 °C in a closed system for 5 h, and extracted with ether (2 × 50 mL). The combined ether extracts were concentrated and cooled (−33 °C) to give $(p\text{-}^tBu\text{-}C_6H_4)_2SnCl_2$ (2.95 g, 68.7%, mp 129−131 °C) as white crystals. ^1H NMR (300.1 MHz, benzene-d_6): δ 1.11 (s, 18 H, CMe_3), 7.17 (d, $J = 8.4$ Hz, 4 H, *meta*-C_6H_5), 7.47 (d, $J = 8.1$ Hz, 4 H, *ortho*-C_6H_5). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene-d_6): δ 31.0 ($C(CH_3)_3$), 34.8 ($C(CH_3)_3$), 126.9 (*meta*-C), 133.9 (*para*-C), 135.2 ($J_{SnC} = 264$ Hz, *ortho*-C), 155.0 (CSn). $^{119}Sn\{^1H)$ NMR (111.9 MHz, benzene-

d_6): δ −18.24. Anal. Calcd for $C_{20}H_{26}Cl_2Sn$: C, 52.68; H, 5.71. Found: C, 52.31; H, 5.73.

Bis(*p*-*tert*-butylphenyl)tin Dihydride (1). An ether solution (ca. 100 mL) of $(p\text{-}{}^t\text{Bu-}C_6H_4)_2SnCl_2$ (1.80 g, 3.94 mmol) was added to a suspension of LAH (0.170 g, 4.48 mmol) in diethyl ether (ca. 100 mL) over a period of 30 min at 0 °C. The resulting white cloudy reaction mixture was stirred for another 2 h at 0 °C. The reaction mixture was then quenched with degassed ice-cold distilled water (ca. 50 mL) at 0 °C and separated. The aqueous layer was washed with ether (3 × 20 mL), and the combined ether layers were dried over $CaCl_2$ for 2 h, filtered, concentrated to dryness, and redissolved in pentane. Cooling (to −78 °C) of the pentane solution gave $(p\text{-}{}^t\text{Bu-}C_6H_4)_2SnH_2$ (1.33 g, 86.9%, mp 73−74 °C) as a white solid. ^1H NMR (300.1 MHz, benzene-d_6): δ 1.19 (s, 18 H, CMe_3), 6.15 (s, J_{SnH} = 1820, 1905 Hz, 2 H, SnH), 7.26 (d, J = 6.0 Hz, 4 H, *meta*-C_6H_5), 7.50 (d, J = 6.0 Hz, 4 H, *ortho*-C_6H_5). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene-d_6): δ 31.3 ($C(CH_3)_3$), 34.6 ($C(CH_3)_3$), 125.9 (*meta*-C), 131.9 (*para*-C), 137.8 (*ortho*-C), 152.0 (CSn). $^{119}Sn\{^1H)$ NMR (111.9 MHz, benzene-d_6): δ −234.1. IR (CH_2Cl_2, cm^{-1}): υ 1871 (SnH). Anal. Calcd for $C_{20}H_{28}Sn$: C, 62.05; H, 7.29. Found: C, 62.04; H, 7.64.

Tetrakis(*p*-^{n}hexylphenyl)stannane. To a THF solution of 4-^{n}hexylphenylmagnesium bromide (400 mL, 0.24 M, 96 mmol) was added $SnCl_4$ (2.58 mL, 22.0 mmol) via a syringe. The reaction mixture turned cloudy, and white precipitate was formed during the initial 30 min. The cloudy solution was stirred at ambient temperature for an additional 30 min while the precipitate dissolved, and it was then heated to reflux for 6 h. It was then allowed to cool to ambient temperature before it was quenched with saturated NH_4Cl (ca. 200 mL). The aqueous layer was separated and was extracted with diethyl ether (2 × 100 mL). The combined organic layers were washed with brine (1 × 100 mL), dried over Na_2SO_4 for 1 h, filtered, and concentrated to give $(p\text{-}{}^n\text{Hex-}C_6H_4)_4Sn$ (16.7 g, 99% based on the amount of $SnCl_4$ used) as a viscous off-white oil. ^1H NMR (500.1 MHz, chloroform-d_1): δ 0.88 (br t, 12 H, CH_3), 1.29−1.35 (m, 24 H, CH_2), 1.60 (quintet, 8 H, CH_2), 2.59 (t, J = 7.8 Hz, 8 H, $PhCH_2$), 7.19 (br d, $^4J_{SnH}$ = 21 Hz, 8 H, *meta*-C_6H_4), 7.50 (br d, $^3J_{SnH}$ = 39, 55 Hz, 8 H, *ortho*-C_6H_4). $^{13}C\{^1H\}$ NMR (100.6 MHz, chloroform-d_1): δ 14.1 (CH_3), 22.6 (CH_2), 29.1 (CH_2), 31.4 (CH_2), 31.7 (CH_2), 36.0 (CH_2), 128.7 (*meta*-C), 134.9 (*para*-C), 137.2 (*ortho*-C), 143.7 (CSn). $^{119}Sn\{^1H)$ NMR (111.9 MHz, chloroform-d_1): δ −127.1. HREIMS, Calcd: 764.43 (M^+). Found: 764.46.

Bis(*p*-^{n}hexylphenyl)tin Dichloride. A mixture of $(p\text{-}{}^n\text{Hex-}C_6H_4)_4Sn$ (5.50 g, 7.20 mmol) and $SnCl_4$ (0.85 mL, 7.26 mmol) was heated gradually to 180 °C, over a period of 3 h in a heavy-wall Schlenk tube under vacuum, and was held at 180 °C for a period of 3 h. It was then cooled, dissolved in pentane (ca. 20 mL), filtered, and concentrated to give $(p\text{-}{}^n\text{Hex-}C_6H_4)_2SnCl_2$ (6.56 g, 89%) as a brown liquid. ^1H NMR (400.1 MHz, benzene-d_6): δ 0.88 (t, 6 H, CH_3), 1.13−1.27 (m, 12 H, CH_2), 1.30−1.46 (m, 4 H, CH_2), 2.36 (t, J = 7.6 Hz, 4 H, $PhCH_2$), 6.99 (d, $^3J_{HH}$ = 8.0 Hz, $^4J_{SnH}$ = 36, 20 Hz, 4 H, *meta*-C_6H_4), 7.46 (d, $^3J_{HH}$ = 8.0 Hz, $^3J_{SnH}$ = 72, 88 Hz, 4 H, *ortho*-C_6H_4). $^{13}C\{^1H\}$ NMR (100.6 MHz, chloroform-d_1): δ 14.3 (CH_3), 22.9 (CH_2), 29.2 (CH_2), 31.5 (CH_2), 32.0 (CH_2), 36.2 (CH_2), 130.0 (*meta*-C), 134.1 (*para*-C), 135.3 (*ortho*-C), 147.1 (CSn). $^{119}Sn\{^1H)$ NMR (111.9 MHz, benzene-d_6): δ −18.6. HREIMS, Calcd: 512.106 (M^+). Found: 512.105.

Bis(*p*-^{n}hexylphenyl)tin Dihydride (2). Following the procedure for **1**, 2.04 g (80%) of $(p\text{-}{}^n\text{Hex-}C_6H_4)_2SnH_2$ was obtained as an off-white solid which melted upon warming to room temperature. ^1H NMR (400.1 MHz, benzene-d_6): δ 0.86 (br t, 6 H, CH_3), 1.17−1.25 (m, 12 H, CH_2), 1.47−1.53 (m, 4 H, CH_2), 2.45 (t, J = 7.7 Hz, 4 H, $PhCH_2$), 6.14 (s, J_{SnH} = 1821, 1906 Hz, SnH) 7.07 (d, $^3J_{HH}$ = 7.8 Hz, 4 H, *meta*-C_6H_4), 7.47 (d, $^3J_{HH}$ = 7.8 Hz, $^3J_{SnH}$ = 45, 62 Hz, 4 H, *ortho*-C_6H_4). $^{13}C\{^1H\}$ NMR (100.6 MHz, benzene-d_6): δ 14.3 (CH_3), 22.9 (CH_2), 29.3 (CH_2), 31.7 (CH_2), 32.0 (CH_2), 36.2 (CH_2), 129.2 (*meta*-C), 132.1 (*para*-C), 137.9 (J_{SnC} = 42.7 Hz, *ortho*-C), 144.0 (CSn). $^{119}Sn\{^1H)$ NMR (111.9 MHz, benzene-d_6): δ −232.1. IR (CH_2Cl_2, cm^{-1}): υ 1860 (SnH). Anal. Calcd for $C_{24}H_{36}Sn$: C, 65.04; H, 8.19. Found: C, 65.26; H, 8.27.

Tetrakis(*o*-ethylphenyl)stannane. Tetrachlorotin (3.00 mL, 0.0256 mol) was added to a THF solution of 2-ethylphenylmagnesium bromide (200 mL, 0.765 M) via a syringe at ambient room temperature. White precipitate formed initially, but it then redissolved. The gold-colored reaction mixture was heated to reflux overnight before saturated NH_4Cl (ca. 800 mL) was added to separate the layers. The aqueous layer was extracted with ether (4 × 200 mL), and the combined organic layers were dried over $MgSO_4$ for ca. 30 min, filtered, concentrated (ca. 400 mL), and cooled (−80 °C) to give $(o\text{-Et-}C_6H_4)_4Sn$ (12.14 g, 88%, mp 160−161 °C) as a white solid. ^1H NMR (400.1 MHz, benzene-d_6): δ 0.71 (t, J = 7.5 Hz, 12 H, CH_3), 2.68−2.73 (m, 8 H, CH_2), 7.04−7.10 (m, 4 H), 7.17−7.24 (m, 8 H), 7.71 (dd, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.2 Hz, J_{SnH} = 46, 61 Hz, 4 H). $^{13}C\{^1H\}$ NMR (100.6 MHz, benzene-d_6): δ 15.5 (CH_3), 33.0 (CH_2), 126.5 (CH), 128.4 (CH), 129.8 (CH), 137.8 (CH), 140.2 (C_{ipso}), 151.5 (CSn). $^{119}Sn\{^1H\}$ NMR (111.9 MHz, benzene-d_6): δ −116.1. Anal. Calcd for $C_{32}H_{36}Sn$: C, 71.3; H, 6.73. Found: C, 71.6; H, 6.91.

Bis(*o*-ethylphenyl)tin Dichloride. A mixture of $(o\text{-Et-}C_6H_4)_4Sn$ (2.00 g, 3.71 mmol) and $SnCl_4$ (0.45 mL, 3.85 mmol) was degassed, heated at 250 °C in a closed system for 16 h, extracted with ether (ca. 40 mL), filtered, and cooled (−80 °C) to give $(o\text{-Et-}C_6H_4)_2SnCl_2$ (2.41 g, 81%) as a yellowish solid which melted upon warming to room temperature to yield a pale yellow liquid. ^1H NMR (500.1 MHz, benzene-d_6): δ 0.92 (t, J = 7.5 Hz, 6 H, CH_3), 2.52−2.57 (m, 4 H, CH_2), 6.91 (d, J_{HH} = 7.8 Hz, J_{SnH} = 36, 52 Hz, 2 H), 6.94−7.02 (m, 2 H), 7.05−7.11 (m, 2 H), 7.90 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.2 Hz, J_{SnH} = 80, 95 Hz, 2 H). $^{13}C\{^1H\}$ NMR (100.6 MHz, benzene-d_6): δ 16.1 (CH_3), 32.7 (CH_2), 127.3 (CH), 129.3 (CH), 132.1 (CH), 135.4 (CH), 138.8 (C_{ipso}), 149.9 (CSn). $^{119}Sn\{^1H\}$ NMR (111.9 MHz, benzene-d_6): δ −15.8. HREIMS, Calcd: 399.981 (M^+). Found: 399.980.

Bis(*o*-ethylphenyl)tin Dihydride (3). Following the procedure for **1**, 1.80 g of $(o\text{-Et-}C_6H_4)_2SnH_2$ was obtained as off-white crystals (73%, mp < −40 °C). ^1H NMR (400.1 MHz, benzene-d_6): δ 1.05 (t, J = 7.6 Hz, 6 H, CH_3), 2.55−2.62 (m, 4 H, CH_2), 6.13 (s, J_{SnH} = 1802, 1885 Hz, 2 H, SnH), 6.96−7.03 (m, 2 H), 7.04−7.11 (m, 2 H), 7.13−7.20 (m, 2 H), 7.50 (dd, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.3 Hz, J_{SnH} = 53, 67 Hz, 2 H). $^{13}C\{^1H\}$ NMR (100.6 MHz, benzene-d_6): δ 16.3 (CH_3), 33.1 (CH_2), 126.3 (J_{SnC} = 56 Hz, CH), 128.1 (J_{SnC} = 42 Hz, CH), 130.0 (J_{SnC} = 10 Hz, CH), 136.5 (C_{ipso}), 138.8 (J_{SnC} = 44 Hz), 151.2 (J_{SnC} = 33 Hz, CSn). $^{119}Sn\{^1H\}$ NMR (111.9 MHz, benzene-d_6): δ −249.3. IR (THF, cm^{-1}): υ 1852 (SnH). Anal. Calcd for $C_{16}H_{20}Sn$: C, 58.1; H, 6.09. Found: C, 58.0; H, 6.13.

Tetrakis(*p*-^{n}butoxylphenyl)stannane. To an ether solution (ca. 225 mL) of *p*-^{n}butoxylphenylmagnesium bromide, prepared from *p*-bromophenyl-^{n}butyl ether (20.65 g, 0.0901 mol) and Mg powder (6.00 g, 0.247 mol) in ether solution (ca. 225 mL), was added $SnCl_4$ (2.20 mL, 0.0188 mol) via a syringe. After the reaction mixture was heated to reflux for 10 h, it was allowed to cool to room temperature before saturated NH_4Cl (ca. 500 mL) was added to give two layers. The aqueous layer was separated and extracted with ether (2 × 200 mL), and the combined organic layers were dried over $MgSO_4$ for 1 h, filtered, concentrated (to ca. 100 mL) and cooled (−40 °C) to afford $(p\text{-}{}^n\text{BuO}-C_6H_4)_4Sn$ as white crystals (7.42 g, 55%, mp 62−65 °C). ^1H NMR (500.1 MHz, benzene-d_6): δ 0.80 (t, J = 7.4 Hz, 12 H, CH_3), 1.29−1.34 (m, 8 H, γ-CH_2), 1.53−1.56 (m, 8 H, β-CH_2), 3.64 (t, J = 6.4 Hz, 8 H, OCH_2), 6.98 (d, $^3J_{HH}$ = 8.4 Hz, 8 H), 7.72 (d, $^3J_{HH}$ = 8.4 Hz, 8 H). $^{13}C\{^1H\}$ NMR (100.6 MHz, benzene-d_6): δ 13.9 (CH_3), 19.5 ($CH_3\mathit{C}H_2CH_2CH_2O$), 31.5 ($CH_3CH_2\mathit{C}H_2CH_2O$), 57.3 ($OCH_2$), 115.6 (*meta*-C), 129.2 (*para*-C), 138.9 (*ortho*-C), 160.8 (CSn). $^{119}Sn\{^1H\}$ NMR (111.9 MHz, benzene-d_6): δ −112.0. Anal. Calcd for $C_{40}H_{52}O_4Sn$: C, 67.1; H, 7.32. Found: C, 67.2; H, 7.45.

Bis(*p*-^{n}butoxylphenyl)tin Dichloride. A reaction mixture of $(p\text{-}{}^n\text{BuO}-C_6H_4)_4Sn$ (1.00 g, 1.30 mmol) and $SnCl_4$ (0.17 mL, 1.41 mmol) was degassed and heated gradually to 220 °C, over a period of 1 h, and was held at 220 °C for a period of 10.5 h. It was then cooled, dissolved in pentane (ca. 30 mL), and filtered. Cooling of the pentane solution at −20 °C yielded two crops of $(p\text{-}{}^n\text{BuO}-C_6H_4)_2SnCl_2$ (0.84 g, 62%, mp 55−56 °C) as an off-white solid. ^{1}H NMR (400.1 MHz, benzene-d_6): δ 0.81 (t, $J = 7.4$ Hz, 6 H, $\mathrm{CH_3}$), 1.29 (sextet, $J = 7.7$ Hz, 4 H, γ-$\mathrm{CH_2}$), 1.50 (quintet, $J = 6.6$ Hz, 4 H, β-$\mathrm{CH_2}$), 3.50 (t, $J = 6.4$ Hz, 4 H, $\mathrm{OCH_2}$), 6.75 (d, $J_{\mathrm{HH}} = 8.6$ Hz, $J_{\mathrm{SnH}} = 32, 175, 192$ Hz, 4 H), 7.44 (d, $^3J_{\mathrm{HH}} = 8.6$ Hz, $^4J_{\mathrm{HH}} = 2.3$ Hz, $J_{\mathrm{SnH}} = 68, 85$ Hz, 4 H). ^{13}C{^{1}H} NMR (100.6 MHz, benzene-d_6): δ 13.9 ($\mathrm{CH_3}$), 19.4 ($\mathrm{CH_3\mathit{C}H_2CH_2CH_2O}$), 31.3 ($\mathrm{CH_3CH_2\mathit{C}H_2CH_2O}$), 67.5 ($\mathrm{OCH_2}$), 116.1 (*meta*-C), 127.6 (*para*-C), 136.8 (*ortho*-C), 162.3 (CSn). ^{119}Sn{^{1}H} NMR (111.9 MHz, benzene-d_6): δ −11.52. Anal. Calcd for $\mathrm{C_{20}H_{26}Cl_2O_2Sn}$: C, 49.2; H, 5.37. Found: C, 48.5; H, 5.54. HREIMS Calcd: 488.033 ($\mathrm{M^+}$). Found: 488.032.

Bis(*p*-^{n}butoxylphenyl)tin Dihydride (4). Following the procedure for **1**, 1.41 g of (p-$^n\mathrm{BuO{-}C_6H_4)_2SnH_2}$ (82%, mp 38−40 °C) was obtained as an off-white solid. ^{1}H NMR (500.1 MHz, benzene-d_6): δ 0.80 (t, $J = 7.4$ Hz, 6 H, $\mathrm{CH_3}$), 1.31 (sextet, $J = 7.7$ Hz, 4 H, γ-$\mathrm{CH_2}$), 1.51−1.56 (m, 4 H, β-$\mathrm{CH_2}$), 3.59 (t, $J = 6.4$ Hz, 4 H, $\mathrm{OCH_2}$), 6.14 (s, $J_{\mathrm{SnH}} = 1820, 1905$ Hz, 2 H, SnH), 6.87 (d, $J_{\mathrm{HH}} = 8.4$ Hz, $J_{\mathrm{SnH}} = 18$ Hz, 4 H), 7.44 (d, $J_{\mathrm{HH}} = 8.4$ Hz, $J_{\mathrm{SnH}} = 43, 59$ Hz, 4 H). ^{13}C{^{1}H} NMR (100.6 MHz, benzene-d_6): δ 13.9 ($\mathrm{CH_3}$), 19.5 ($\mathrm{CH_3\mathit{C}H_2CH_2CH_2O}$), 31.5 ($\mathrm{CH_3CH_2\mathit{C}H_2CH_2O}$), 67.3 ($\mathrm{OCH_2}$), 115.5 (*meta*-C), 125.6 (*para*-C), 139.0 (*ortho*-C), 160.7 (CSn). ^{119}Sn{^{1}H} NMR (111.9 MHz, benzene-d_6): δ −228.6. IR (KBr, cm^{-1}): υ 1846 (SnH). Anal. Calcd for $\mathrm{C_{20}H_{28}O_2Sn}$: C, 57.3; H, 6.73. Found: C, 57.3; H, 6.71.

Tetrakis(*p*-^{n}butoxyl-*ortho*-ethylphenyl)stannane. Following the procedure for tetrakis(*o*-ethylphenyl)stannane, 16.1 g of (o-Et-p-$^n\mathrm{BuO{-}C_6H_3)_4Sn}$ (66%, mp 125.0−125.5 °C) as a white solid was crystallized from pentane at −20 °C. ^{1}H NMR (300.1 MHz, benzene-d_6): δ 0.81 (t, $J = 7.4$ Hz, 12 H), 0.90 (t, $J = 7.5$ Hz, 12 H), 1.28−1.40 (m), 1.53−1.62 (m), 2.80−2.90 (m, 8 H, $\mathrm{CH_3C\mathit{H}_2}$), 3.69 (t, $J = 6.4$ Hz, 8 H, $\mathrm{OCH_2}$), 6.88 (dd, $^3J_{\mathrm{HH}} = 8.2$ Hz, $^4J_{\mathrm{HH}} = 2.6$ Hz, 4 H), 7.05 (d, $J_{\mathrm{HH}} = 25$ Hz, $J_{\mathrm{SnH}} = 14, 19$ Hz, 4 H), 7.76 (d, $J_{\mathrm{HH}} = 8.2$ Hz, $J_{\mathrm{SnH}} = 45, 61$ Hz, 4 H). ^{13}C{^{1}H} NMR (100.6 MHz, benzene-d_6): δ 14.0 ($\mathrm{\mathit{C}H_3CH_2CH_2CH_2O}$), 15.7 ($\mathrm{\mathit{C}H_3CH_2}$), 19.5 ($\mathrm{CH_3\mathit{C}H_2CH_2CH_2O}$), 31.7 ($\mathrm{CH_3CH_2\mathit{C}H_2CH_2O}$), 32.9 ($\mathrm{CH_3\mathit{C}H_2}$), 67.2 ($\mathrm{OCH_2}$), 112.8 (CH), 115.1 (CH), 128.2 ($\mathrm{C_{ipso}}$), 138.9 (CH), 153.2 ($\mathrm{C_{ipso}}$), 161.3 (CSn). ^{119}Sn{^{1}H} NMR (111.9 MHz, benzene-d_6): δ −110.6. Anal. Calcd for $\mathrm{C_{48}H_{68}O_4Sn}$: C, 69.7; H, 8.28. Found: C, 69.8; H, 8.13.

Bis(*p*-^{n}butoxyl-*o*-ethylphenyl)tin Dichloride. A mixture of (o-Et-p-$^n\mathrm{BuO{-}C_6H_3)_4Sn}$ (5.00 g, 6.04 mmol) and $\mathrm{SnCl_4}$ (0.71 mL, 6.07 mmol) was placed in a sealed heavy-wall Schlenk tube and was heated at 240 °C for 2 days. The solid mixture was then extracted with hexanes (ca. 150 mL), and cooling of the hexanes solution at −80 °C gave (o-Et-p-$^n\mathrm{BuO{-}C_6H_3)_2SnCl_2}$ (5.95 g, 91%, mp 31−32 °C) as a yellow solid. ^{1}H NMR (300.1 MHz, benzene-d_6): δ 0.83 (t, $J = 7.2$ Hz, 6 H), 1.01 (t, $J = 7.5$ Hz, 6 H), 1.27−1.37 (m), 1.48−1.55 (m), 2.64 (q, $J = 7.5$ Hz, 4 H, $\mathrm{CH_3C\mathit{H}_2}$), 3.55 (t, $J = 6.3$ Hz, 4 H, $\mathrm{OCH_2}$), 6.66 (dd, $^3J_{\mathrm{HH}} = 8.4$ Hz, $^4J_{\mathrm{HH}} = 2.7$ Hz, $J_{\mathrm{SnH}} = 24, 30$ Hz, 2 H), 6.77 (d, $J_{\mathrm{HH}} = 2.4$ Hz, $J_{\mathrm{SnH}} = 34, 39$ Hz, 2 H), 7.93 (d, $J_{\mathrm{HH}} = 8.4$ Hz, $J_{\mathrm{SnH}} = 38, 46$ Hz, 2 H). ^{13}C{^{1}H} NMR (100.6 MHz, benzene-d_6): δ 13.9 ($\mathrm{\mathit{C}H_3CH_2CH_2CH_2O}$), 16.0 ($\mathrm{\mathit{C}H_3CH_2}$), 19.4 ($\mathrm{CH_3\mathit{C}H_2CH_2CH_2O}$), 31.4 ($\mathrm{CH_3CH_2\mathit{C}H_2CH_2O}$), 32.5 ($\mathrm{CH_3\mathit{C}H_2}$), 67.5 ($\mathrm{OCH_2}$), 113.0 (CH), 116.6 (CH), 129.5 ($\mathrm{C_{ipso}}$), 137.0 (CH), 151.8 ($\mathrm{C_{ipso}}$), 162.8 (CSn). ^{119}Sn{^{1}H} NMR (111.9 MHz, benzene-d_6): δ −5.7. Anal. Calcd for $\mathrm{C_{24}H_{34}Cl_2O_2Sn}$: C, 53.0; H, 6.30. Found: C, 52.6; H, 6.18.

Bis(*p*-^{n}butoxyl-*o*-ethylphenyl)tin Dihydride (5). Following the procedure for **1**, 3.54 g of (o-Et-$p$$^n\mathrm{BuO{-}C_6H_4)_2SnH_2}$ was obtained as a white solid (99%, mp 23−24 °C). ^{1}H NMR (500.1 MHz, benzene-d_6): δ 0.82 (t, $J = 7.4$ Hz, 6 H), 1.12 (t, $J = 7.6$ Hz, 6 H), 1.34 (sextet, $J = 7.4$ Hz, 4 H, $\mathrm{CH_2}$), 1.54−1.59 (m, 4 H), 2.62−2.67 (m, 4 H, $\mathrm{CH_3C\mathit{H}_2}$), 3.64 (t, $J = 6.4$ Hz, 4 H, $\mathrm{OCH_2}$), 6.14 (s, $J_{\mathrm{SnH}} = 1785, 1868$ Hz, 2 H, SnH), 6.71 (dd, $^3J_{\mathrm{HH}} = 8.1$, $^4J_{\mathrm{HH}} = 2.6$ Hz, $J_{\mathrm{SnH}} = 18$ Hz, 2 H), 6.92 (d, $J_{\mathrm{HH}} = 2.5$ Hz, $J_{\mathrm{SnH}} = 18$ Hz, 2 H), 7.51 (d, $J_{\mathrm{HH}} = 8.1$ Hz, $J_{\mathrm{SnH}} = 34, 51$ Hz, 2 H). ^{13}C{^{1}H} NMR (100.6 MHz, benzene-d_6): δ 13.9 ($\mathrm{\mathit{C}H_3CH_2CH_2CH_2O}$), 16.2 ($\mathrm{\mathit{C}H_3CH_2}$), 19.5 ($\mathrm{CH_3\mathit{C}H_2CH_2CH_2O}$), 31.6 ($\mathrm{CH_3CH_2\mathit{C}H_2CH_2O}$), 33.2 ($\mathrm{CH_3\mathit{C}H_2}$), 67.2 ($\mathrm{OCH_2}$), 112.3 (CH), 115.3 (CH), 126.6 ($\mathrm{C_{ipso}}$), 139.8 (CH), 152.9 ($\mathrm{C_{ipso}}$), 161.4 (CSn). ^{119}Sn{^{1}H} NMR (111.9 MHz, benzene-d_6): δ −246.5. IR (KBr, cm^{-1}): υ 1863 (SnH). Anal. Calcd for $\mathrm{C_{24}H_{36}O_2Sn}$: C, 60.7; H, 7.64. Found: C, 60.6; H, 7.82.

Bromination of *N*,*N*-Dibutylaniline. *N*,*N*-Dibutylaniline (14.7 g, 0.072 mol) was dissolved in $\mathrm{CCl_4}$ (ca. 100 mL), and ca. 2 g of iron powder was added. The reaction mixture was cooled to −15 °C before $\mathrm{Br_2}$ (3.8 mL, 0.072 mol) was added rather quickly. After it was stirred overnight at ambient temperature, deionized $\mathrm{H_2O}$ (ca. 200 mL), NaOH (300 mL, 1 N), and ether (ca. 300 mL) were added. The organic layer was separated, dried over $\mathrm{MgSO_4}$, and concentrated. The crude reaction mixture was then subjected to column chromatography using hexanes as the eluent. The first fraction was concentrated to yield 4-bromo-*N*,*N*-dibutylaniline (15 g, 73%) as a brown liquid. ^{1}H NMR (500.1 MHz, chloroform-d_1): δ 0.93 (t, $J = 7.4$ Hz, 6 H, $\mathrm{CH_3}$), 1.32 (sextet, $J = 7.6$ Hz, 4 H, γ-$\mathrm{CH_2}$), 1.49−1.55 (m, 4 H, β-$\mathrm{CH_2}$), 3.21 (t, $J = 7.7$ Hz, 4 H, $\mathrm{NCH_2}$), 6.48 (d, $J = 9.0$ Hz, 2 H), 7.23 (d, $J = 9.0$ H, 2 H).

Tetrakis(*p*-di^{n}butylaminophenyl)stannane. Following the procedure for tetrakis(*o*-ethylphenyl)stannane, 10.2 g of (p-$^n\mathrm{Bu_2N{-}C_6H_4)_4Sn}$ was obtained as a light brown solid (99% based on the amount of $\mathrm{SnCl_4}$ used, mp 91−92 °C). ^{1}H NMR (400.1 MHz, benzene-d_6): δ 0.82 (t, $J = 7.3$ Hz, 24 H, $\mathrm{CH_3}$), 1.15 (sextet, $J = 7.6$ Hz, 16 H, $\mathrm{CH_2}$), 1.43 (quintet, $J = 7.4$ Hz, 16 H, $\mathrm{CH_2}$), 3.06 (t, $J = 7.4$ Hz, 16 H, $\mathrm{NCH_2}$), 6.73 (d, $J = 8.6$ Hz, 8 H), 7.90 (d, $J = 8.6$ Hz, $J_{\mathrm{SnH}} = 37, 53$ Hz, 8 H). ^{13}C{^{1}H} NMR (100.6 MHz, benzene-d_6): δ 14.1 ($\mathrm{CH_3}$), 20.6 ($\mathrm{CH_3\mathit{C}H_2CH_2CH_2N}$), 29.8 ($\mathrm{CH_3CH_2\mathit{C}H_2CH_2N}$), 50.9 ($\mathrm{NCH_2}$), 113.0 (CH), 124.2 (*para*-C), 138.9 (CH), 148.8 (CSn). ^{119}Sn{^{1}H} NMR (186.5, benzene-d_6): δ −106.2. Anal. Calcd for $\mathrm{C_{56}H_{88}N_4Sn}$: C, 71.86; H, 9.46. Found: C, 71.50; H, 9.52.

Bis(*p*-di^{n}butylaminophenyl)tin Dichloride. A reaction mixture of (p-$^n\mathrm{Bu_2N{-}C_6H_4)_4Sn}$ and $\mathrm{SnCl_4}$ was degassed, heated at 80−90 °C for 8 h (^{1}H NMR spectroscopic analysis showed quantitative conversion), extracted with ether (1 × 100 mL), and filtered. Removal of the volatile material from the filtrate gave a brown oil which appeared to be the corresponding dichloride based on NMR spectroscopic analysis, and it was used for the next step without further purification. ^{1}H NMR (500.1 MHz, benzene-d_6): δ 0.82 (t, $J = 7.5$ Hz, 12 H), 1.10 (sextet, $J = 7.5$ Hz, 8 H), 1.33 (quintet, $J = 7.5$ Hz, 8 H), 2.93 (t, $J = 8.0$ Hz, 8 H), 6.52 (d, $J = 9.0$ Hz, 4 H), 7.58 (d, $J = 9.0$ Hz, 4 H). ^{13}C{^{1}H} NMR (100.6 MHz, benzene-d_6): δ 14.1 ($\mathrm{CH_3}$), 20.4 ($\mathrm{CH_3\mathit{C}H_2CH_2CH_2N}$), 29.5 ($\mathrm{CH_3CH_2\mathit{C}H_2CH_2N}$), 50.6 ($\mathrm{NCH_2}$), 112.8 (CH), 121.5 (*para*-C), 136.7 (CH), 150.4 (CSn). ^{119}Sn{^{1}H} NMR (111.9 MHz, benzene-d_6): δ −1.19.

Bis(*p*-di^{n}butylaminophenyl)tin Dihydride (6). Following the procedure for **1**, 1.72 g (76%) of (p-$^n\mathrm{Bu_2N{-}C_6H_4)_2SnH_2}$ was obtained as a light yellow liquid, which decomposed rapidly to give a dark brown liquid containing a tin mirror. ^{1}H NMR (400.1 MHz, benzene-d_6): δ 0.81 (t, $J = 7.2$ Hz, 12 H), 1.13 (sextet, $J = 7.6$ Hz, 8 H), 1.40 (quintet, $J = 7.2$ Hz, 8 H), 3.02 (t, $J = 7.6$ Hz, 8 H), 6.26 (s, $J_{\mathrm{SnH}} = 1766, 1847$ Hz, 2 H, SnH), 6.68 (d, $J_{\mathrm{HH}} = 8.8$ Hz, 4 H), 7.59 (d, $J_{\mathrm{HH}} = 8.4$ Hz, $J_{\mathrm{SnH}} = 44, 59$ Hz, 4 H). ^{13}C{^{1}H} NMR (75.5 MHz, benzene-d_6): δ 14.2 ($\mathrm{CH_3}$), 20.6 ($\mathrm{CH_3\mathit{C}H_2CH_2CH_2N}$), 29.8 ($\mathrm{CH_3CH_2\mathit{C}H_2CH_2N}$), 50.8 ($\mathrm{NCH_2}$), 112.9 (CH), 119.2 (*para*-C), 138.9 (CH), 149.0 (CSn). ^{119}Sn{^{1}H} NMR (111.9 MHz, benzene-d_6): δ −226.7.

Tetrakis[*p*-bis(trimethylsilyl)aminophenyl]stannane. To an ether solution (ca. 500 mL) of *p*-bis(trimethylsilyl)aminophenyllithium ether adduct (10.62 g, 33.4 mmol), prepared from p-$\mathrm{(Me_3Si)_2NC_6H_4Br}$ and ^{n}BuLi in ether, was added $\mathrm{SnCl_4}$ (0.98 mL, 8.37 mmol). The colorless reaction mixture containing a white solid was heated to reflux for 5 h before it was allowed to cool to ambient room temperature. The resulting clear yellow solution was filtered, and the volatile material was removed to give a yellow solid. Recrystallization of [p-$\mathrm{(Me_3Si)_2N{-}C_6H_4]_4Sn}$ from hexanes at −80 °C gave an off-white solid (7.35 g, 83%, mp 260 dec). ^{1}H NMR (500.1 MHz, benzene-d_6): δ 0.092 (s, 72 H, $\mathrm{SiMe_3}$), 6.94 (d, $J_{\mathrm{HH}} = 6.0$ Hz, 8H), 7.62 (d, $J_{\mathrm{HH}} = 6.5$, $J_{\mathrm{SnH}} = 38$ Hz, 8 H). ^{13}C{^{1}H} NMR (125.8 MHz, benzene-d_6): δ 2.25 ($\mathrm{Si(\mathit{C}H_3)_3}$), 130.9 ($J_{\mathrm{SnC}} = 54$ Hz, CH), 133.2 ($\mathrm{C_{ipso}}$), 137.9 ($J_{\mathrm{SnC}} = 40$ Hz, CH), 149.4 ($\mathrm{C_{ipso}}$). ^{119}Sn{^{1}H} NMR (186.5 MHz, benzene-d_6): δ −115.2. Anal. Calcd for $\mathrm{C_{48}H_{88}N_4Si_8Sn}$: C, 54.2; H, 8.33; N, 5.26. Found: C, 51.6; H, 8.30; N, 4.86. HREIMS, Calcd: 1064.63 ($\mathrm{M^+}$). Found: 1064.42.

Bis(*p*-bis(trimethylsilyl)aminophenyl)tin Dichloride. A mixture of $[p\text{-}(Me_3Si)_2N-C_6H_4]_4Sn$ (1.688 g, 1.58 mmol) and $SnCl_4$ (0.186 mL, 1.59 mmol) was degassed, heated at 110 °C in a closed system for 2.5 h, extracted with pentane (ca. 40 mL), filtered, and cooled (−80 °C) to yield $[p\text{-}(Me_3Si)_2NC_6H_4]_2SnCl_2$ as an off-white solid (1.67 g, 80%, mp 76−80 °C). ^1H NMR (500.1 MHz, benzene-d_6): δ 0.049 (s, 36 H, SiMe$_3$), 6.83 (d, J_{HH} = 8.0 Hz, J_{SnH} = 34, 146, 154 Hz, 4 H), 7.39 (d, J_{HH} = 8.3, J_{SnH} = 72, 86 Hz, 4 H). $^{13}C\{^1H\}$ NMR (125.8 MHz, benzene-d_6): δ 2.15 (Si(CH$_3$)$_3$), 131.5 (CH), 131.6 (C$_{ipso}$), 135.7 (CH), 152.4 (C$_{ipso}$). $^{119}Sn\{^1H\}$ NMR (186.5 MHz, benzene-d_6): δ −14.4. Anal. Calcd for $C_{24}H_{44}Cl_2N_2Si_4Sn$: C, 43.5; H. 6.09; N, 4.23. Found: C, 42.8; H, 6.95; N, 3.95.

Bis(*p*-bis(trimethylsilyl)aminophenyl)tin Dihydride (7). This compound was prepared in a manner similar to that for $(p\text{-}^nBuO-C_6H_4)_2SnH_2$, except that the reaction mixture was not quenched with H_2O during the workup. After ether and the other volatile materials were removed under reduced pressure, the reaction mixture was extracted with pentane (ca. 100 mL). Removal of pentane gave $[p\text{-}(Me_3Si)_2N-C_6H_4]_2SnH_2$ (5.56 g, 92%) as a light brown oil. ^1H NMR (500.1 MHz, benzene-d_6): δ 0.094 (s, 36 H, SiMe$_3$), 6.09 (s, J_{SnH} = 1823, 1908 Hz, 2 H, SnH), 6.88 (d, J_{HH} = 7.5 Hz, 4 H), 7.37 (d, J_{HH} = 7.5, J_{SnH} = 45, 60 Hz, 4 H). $^{13}C\{^1H\}$ NMR (125.8 MHz, benzene-d_6): δ 2.23 (Si(CH$_3$)$_3$), 129.8 (C$_{ipso}$), 130.9 (CH), 138.2 (CH), 149.3 (C$_{ipso}$). $^{119}Sn\{^1H\}$ NMR (186.5 MHz, benzene-d_6): δ −230.2. IR (pentane, cm^{-1}): υ 1858 (SnH). Anal. Calcd for $C_{24}H_{46}N_2Si_4Sn$: C, 48.6; H. 7.81; N, 4.72. Found: C, 47.4; H, 7.83; N, 4.06.

Polymerization of 1 with Dimethylzirconocene. A solid mixture of $(p\text{-}^tBu\text{-}C_6H_4)_2SnH_2$ (200 mg) and Cp_2ZrMe_2 (3.8 mg, 3 mol %) was heated for 5.5 h at 120 °C under vacuum. The solid residue (ca. 30% cyclics by GPC, M_w/M_n = 10 700/6600; ^{119}Sn NMR (186.5 MHz, benzene-d_6), −197 (linear), −221 (*cyclo*-$[(p\text{-}^tBu\text{-}C_6H_4)_2Sn]_6$)) as a brown solid was dissolved in THF (ca. 30 mL), and the THF solution was filtered into MeOH (ca. 150 mL). $H(p\text{-}^tBu\text{-}C_6H_4)_2Sn]_nH$ (100 mg, 50%) as an orange solid (ca. 10% cyclics with M_w/M_n = 1500/1400) precipitated. The sample was filtered and dried under vacuum for 12 h. GPC (THF): M_w/M_n = 20 400/15 100; UV−vis (THF): λ_{max} = 432 nm; ^1H NMR (300.1 MHz, benzene-d_6): δ 1.13−1.46 (br s, C(CH$_3$), 6.72−7.34 (m, C$_6$H$_4$); $^{119}Sn\{^1H)$ NMR (186.5 MHz, benzene-d_6): δ −197 (linear), −221 (*cyclo*- $(Sn^tBuPh_2)_6$). Anal. Calcd for $C_{20}H_{26}Sn$: C, 62.38; H, 6.80. Found: C, 62.10; H, 6.82.

Photodecomposition of $H[(p\text{-}^tBu\text{-}C_6H_4)_2Sn]_nH$. Exposure of a THF solution (ca. 20 mL) of $H[(p\text{-}^tBu\text{-}C_6H_4)_2Sn]_nH$ (30 mg, M_w/M_n = 20 400/15 100) to ambient room light for 30 min resulted in depolymerization to give a mixture of cyclics. GPC (THF): M_w/M_n = 1500/1400; $^{119}Sn\{^1H)$ NMR (186.5 MHz, benzene-d_6): δ −214 (J_{SnSn} = 560 Hz, possibly due to *cyclo*-$[(p\text{-}^tBu\text{-}C_6H_4)_2Sn]_5$), −216 (low intensity), −221 (J_{SnSn} = 1003, 673 Hz, *cyclo*-$[(p\text{-}^tBu\text{-}C_6H_4)_2Sn]_6$).

Reaction of $(p\text{-}^tBu\text{-}C_6H_4)_2SnH_2$ with Pyridine. To a benzene-d_6 solution (ca. 0.5 mL) of **1** (37 mg) was added pyridine (ca. 2 mL). The reaction mixture was allowed to stand at ambient room temperature for 2 days before it was filtered and concentrated to give *cyclo*-$[(p\text{-}^tBu\text{-}C_6H_4)_2Sn]_6$). GPC (THF): M_w/M_n = 1700/1700; ^1H NMR (300.1 MHz, benzene-d_6): δ 1.17 (s, 9 H, C(CH$_3$)$_3$), 7.10 (d, J = 8 Hz, 2 H), 7.72 (d, J = 8 Hz, 2 H). $^{119}Sn\{^1H\}$ NMR (111.9 MHz, benzene-d_6): δ −221. UV−vis (THF): λ_{max} = 290 nm). FABMS, Calcd: 2317 [M$^+$]. Found: 2316.

Polymerization of 2 with Dimethylzirconocene. Addition of Cp_2ZrMe_2 (1.7 mg, 3 mol %) to $(p\text{-}^nHex\text{-}C_6H_4)_2SnH_2$ (100 mg, 0.11 M in pentane) resulted in vigorous gas evolution. After ca. 7 h, the volatile material was removed, the brown solid (GPC: M_w/M_n = 34 700/14 300), was dissolved in THF (ca. 20 mL), and the resulting solution was filtered into MeOH (ca. 100 mL). After ca. 24 h, $H[(p\text{-}^nHex\text{-}C_6H_4)_2Sn]_nH$ (ca. 50%) precipitated as a yellow-orange viscous oil. GPC (THF): linear fraction M_w/M_n = 48 200/20 000, cyclics (ca. 5%) M_n = 2000; UV−vis (THF): λ_{max} = 436 nm; ^1H NMR (300.1 MHz, benzene-d_6): δ 0.85−1.17 (br s), 1.20−1.80 (br s), 2.40−2.80 (br s), 6.60−7.40 (br m). $^{13}C\{^1H\}$ NMR (100.6 MHz, benzene-d_6): δ 14.4 (CH$_3$), 23.1 (CH$_2$), 29.9 (CH$_2$), 32.3 (two overlapping peaks, CH$_2$), 36.6 (CH$_2$), 128.7 (CH), 138.2 (*para*-C), 138.9 (CH), 142.0 (CSn). $^{119}Sn\{^1H)$ NMR (111.9 MHz, benzene-d_6): δ −196. Anal. Calcd for $C_{24}H_{34}Sn$: C, 65.3 H, 7.82. Found: C, 65.0; H, 7.78.

Polymerization of 3 with Dimethylzirconocene. To neat $(o\text{-}Et\text{-}C_6H_4)_2SnH_2$ (100 mg) was added Cp_2ZrMe_2 (1.5 mg, 2 mol %). Vigorous gas evolution was observed while the reaction mixture solidified rather quickly to give a brown solid. The reaction mixture was then heated at 90 °C under dynamic vacuum for 12 h to give a dark brown solid. GPC (THF) M_w/M_n = 22 000/12 000 (linear fraction, ca. 60%), M_w/M_n = 1000/900 (cyclic fraction, ca. 40%). The solid was then dissolved in THF (only ca. 50% of the reaction mixture was soluble) and filtered into dry MeOH (100 mL). A red-orange solid precipitated. The sample was very insoluble in THF and benzene, which prevented a molecular weight determination. UV−vis (solid film, nm): λ_{max} = 468.

Polymerization of 4 with Dimethylzirconocene. To a pentane solution of $(p\text{-}^nBuO-C_6H_4)_2SnH_2$ (120 mg, 0.286 mmol) was added Cp_2ZrMe_2 (1.5 mg, 5.98 μmol, 2 mol %). The reaction mixture turned from colorless to dark brown, and a precipitate formed. After 47 h, removal of the volatile material gave a brown solid (GPC (THF): M_w/M_n = 10 000/5000) which was then dissolved in THF and filtered into MeOH (100 mL). $H[(p\text{-}^nBuO-C_6H_4)_2Sn]_nH$, as an orange solid (100 mg, 83%), precipitated out. GPC (THF): M_w/M_n = 12 000/7000; UV−vis (THF): λ_{max} = 448 nm; ^1H NMR (500.1 MHz, benzene-d_6): δ 0.75−1.25 (br s, CH$_3$), 1.27−2.05 (br m, CH$_2$), 3.40−4.10 (br s, OCH$_2$), 6.00−7.70 (br m, Aryl-H). $^{13}C\{^1H\}$ NMR (125.8 MHz, benzene-d_6): δ 14.1 (CH$_3$), 19.7 ($CH_3\mathit{C}H_2CH_2CH_2O$), 31.9 ($CH_3CH_2\mathit{C}H_2CH_2O$), 67.3 (OCH$_2$), 115.3 (C$_6H_4$), 139.2 (C$_6H_4$), 140.0 (C$_6H_4$), 159.8 (CSn). $^{119}Sn\{^1H)$ NMR (111.9 MHz, benzene-d_6): δ −183.5. Anal. Calcd for $C_{20}H_{26}O_2Sn$: C, 57.59; H, 6.28. Found: C, 58.60; H, 6.30. PXRD: 2θ (deg) 5.17, 11.89, 20.97, 44.23.

Polymerization of 5 with Dimethylzirconocene. A solid mixture of $(o\text{-}Et\text{-}p\text{-}^nBuO-C_6H_3)_2SnH_2$ (100 mg) and Cp_2ZrMe_2 (1.6 mg, 3 mol %) was heated under vacuum at 50 °C for 1 h and then at 90 °C for another 3 h. The resulting solid mixture was dissolved in THF (ca. 10 mL) and transferred into MeOH (ca. 50 mL). The solution was allowed to stand at ambient temperature for about 1.5 weeks, during which time a small amount of dark red solid (ca. 10%) precipitated out and was collected. GPC (THF): M_w/M_n = 4400/4000; UV−vis (THF): λ_{max} = 506 nm; ^1H NMR (500.1 MHz, benzene-d_6): δ 0.50−1.15 (br m, CH$_3$), 1.15−1.48 (m, CH$_2$), 1.48−1.82 (m, CH$_2$), 2.15−3.00 (m, CH$_2$), 6.22−6.64 (m, CH), 6.77−7.10 (m, CH), 7.20−8.00 (m, CH). $^{13}C\{^1H\}$ NMR (125.8 MHz, benzene-d_6): δ 14.0 (br s, $\mathit{C}H_3CH_2CH_2CH_2O$), 14.1−15.1 (br m, $\mathit{C}H_3CH_2$), 19.6 (br s, $CH_3\mathit{C}H_2CH_2CH_2O$), 31.7 (br s, $CH_3CH_2\mathit{C}H_2CH_2O$), 33.0−34.2 (br m, CH$_3CH_2$), 67.2 (br s, OCH$_2$), 111.2−112.0 (br m), 114.5−115.0 (br m), 139.0−140.2 (br m), 152.0−153.5 (br m), 161.0 (br m, CSn). $^{119}Sn\{^1H\}$ NMR (186.5 MHz, benzene-d_6): δ −125 (br m). A much weaker resonance at −180 ppm (br m) may be due to the presence of some cyclic oligomer. Anal. Calcd for $C_{24}H_{34}O_2Sn$: C, 60.92; H, 7.95. Found: C, 61.85; H, 7.95.

Polymerization of 7 with Dimethylzirconocene. The polymerization was carried out in a manner similar to those described above. The resulting $H\{[p\text{-}(Me_3Si)_2N-C_6H_4]_2Sn\}_nH$ was isolated as a green solid (75%) after fractionation from THF/methanol. The green color is presumably due to impurities in the sample. GPC (THF): M_w/M_n = 4200/3800; UV−vis (THF): λ_{max} = 450 nm; ^1H NMR (500.1 MHz, benzene-d_6): δ 0.10−0.40 (br m, SiMe$_3$), 6.72−7.40 (br m, C$_6$H$_4$). IR (KBr, cm^{-1}): υ 525, 679 756 (SiC or CH$_3$), 836 (SiN), 905, 972, 1063, 1179, 1220 (CH$_3$), 1251 (CH$_3$), 1486 (CN), 1576 (CN), 2808, 2899, 2955, 3039. PXRD: 2θ (°) 5.02, 13.3, 30.4, 31.7, 43.7, 44.8.

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