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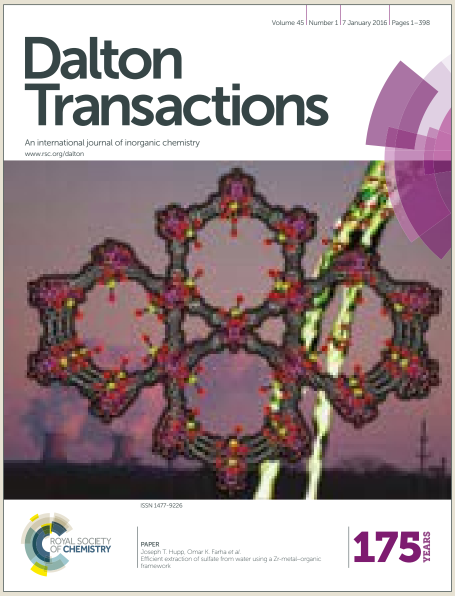

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ARTICLE

"Push-Push and Push-Pull" Polystannanes

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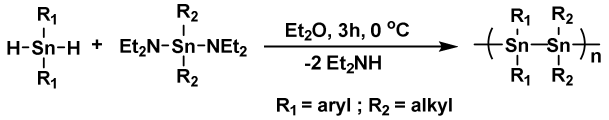
The synthesis and characterization of polystannanes with "push" or "pull" moieties attached to the tin backbone are described. Precursor tetra aryl- (**1**, **2**) stannanes were converted to mono- (**3**) and dichloro- (**4**, **5**) stannanes by either sequential chlorination or by redistribution reactions with $SnCl_4$. Compounds **4** and **5** were transformed to polymerisable tin dihydride monomers **6** and **7** using a large excess (10 x) of $NaBH_4$. Homopolymer **8** with electron donating aryl substituents (p-$MeOC_6H_4$-) was synthesized by dehydrogenative polymerization using Wilkinson's catalyst. Attempts to prepare the homopolymer **9** with electron withdrawing aryl substituents (p-$CF_3C_6H_4$-) from the dehydrocoupling of **7** using similar conditions led only to the formation of low molecular weight oligomeric species. Two alternating polymers, **10** and **11**, were synthesized by condensation polymerization of $(n\text{-Bu})_2Sn(NEt_2)_2$ with monomers **6** or **7**. The first was a "push-push" alternating polymer, **10**, comprised of a repeating unit consisting of two different electron donating groups (p-$MeOC_6H_4$-, n-Bu) at neighboring tin centres. The second was a "push-pull" alternating polymer, **11**, bearing both an electron donating group (n-Bu) and a strongly electron withdrawing substituent (p-$CF_3C_6H_4$-) at neighboring tin atoms. All small molecule stannanes and tin-containing polymers were characterized by NMR (^1H, ^{13}C, ^{119}Sn, and where required ^{19}F) spectroscopy, MS or EA. The absolute molecular weight of tin polymers (**8**, **10**, **11**) were determined by triple detection GPC and in the range of 1.07×10^4 to 1.95×10^4 Da. Rapid photodegradation of polymers was observed by UV-Vis spectroscopy, with a slower degradation observed for the "push-pull" polymer, **11**, compared to the "push-push" polymer, **10**.

Introduction

Organic conducting polymers including polythiophenes and poly (p-phenylenevinylene) continue to draw extensive research interest due to their relative stabilities, low cost and processability for a variety of electronic applications including thin film transistors,[1] photovoltaics,[2] polymeric wires,[3] sensors,[4] and other devices.[5] Less explored are main group containing inorganic polymers, including homopolymers of Ge and Sn. Polystannanes are semi-conductive polymers consisting of a backbone of covalently bonded tin atoms.[6] They possess interesting chemical, thermal, optical and electronic properties as a result of the delocalization of σ-electrons along their backbones.[6,7]

Specialized chain growth syntheses have been employed to obtain polystannanes including Wurtz,[8–14] electrochemical,[15] and dehydrogenative coupling.[10,16–23] Thermally, polystannanes are quite stable (up to 200 °C) under nitrogen atmosphere as well as in air,[12] but show extreme sensitivity towards light and moisture exposure where they rapidly degrade to oligomeric stannanes, cyclic stannanes or stannoxanes.

We have recently detailed the stoichiometric condensation of high purity dialkyl- or diaryl- tin dihydrides and dialkyl- tin diamides in non-polar solvents as a new route to polystannanes (Scheme 1).[24] Herein we describe the step-growth approach to preparing alternating polystannanes with distinct alternating diaryl and dialkyl push/pull substituents attached to the tin backbone.



Scheme 1. Overview of condensation polymerization to produce alternating polymers.

Results and discussion

Synthesis of tin monomers 6 and 7

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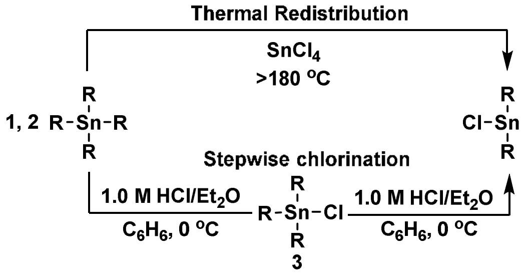
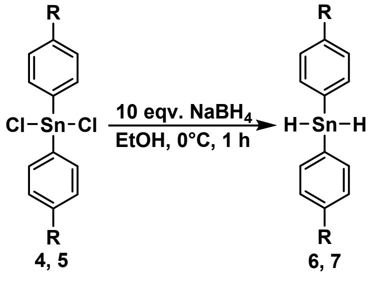
Tetraarylstannanes **1** and **2** were previously synthesized by Wharf *et al.*[25] and King *et al.*[26] by Grignard reactions of a bromobenzenes with $SnCl_4$. In this study, **1** and **2** were readily prepared via lithium-halogen exchange[13] of the aryl bromide with *n*-BuLi, followed by the reaction with $SnCl_4$ to obtain **1** and **2** in 77 % and 94 % yields, respectively. Compounds **3** and **4** (Scheme 2) were isolated in 86 % and 51 % yields from sequential 2h exchange reactions with 1.0 M HCl (1:1 ratio) in under 2 h. A similar stepwise exchange reaction with HCl was also attempted with CF_3- containing tetrastannane **2**, which resulted in only the recovery of the starting material. Dichlorostannane **5** was successfully synthesized in a 61 % yield as previously demonstrated,[13] *via* a more traditional and longer redistribution reaction of **2** with $SnCl_4$ under static vacuum for 5 days at 180 °C.



Scheme 2. Reaction scheme for synthesis of chlorinated aryltin compounds; **1**, **3** and **4**: R = −OMe, and **2** and **5**: $-CF_3$.[13]



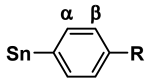
Scheme 3. Reaction scheme for synthesis of aryltin dihydride compounds; **4**, **6**: R = −OMe, and **5**, **7**: $-CF_3$.

Tin dichlorides (**4** and **5**) were reacted with a large excess of $NaBH_4$ (10 ×) in EtOH for 1 h to obtain **6** and **7** in 77 % and 97 % yields respectively (Scheme 3). These dihydrides were observed to be extremely sensitive to heat and moisture, and therefore polymerization attempts were carried out on the same day.

Characterization of monomers

The ^{119}Sn NMR spectra of **1** to **7** (Table 1) reveal significant downfield resonances for the mono- (**3**) or dichlorinated (**4** and **5**) stannanes compared to their parent tetraarylstannanes (**1** and **2**)**.** Upfield resonances for the tin dihydrides **6** and **7** (Table 1) was observed, which is typical for other reported diarylstannanes. ^{1}H NMR shifts of the aromatic protons of the chlorinated tin compounds (**3**, **4** and **5**) were also characteristically deshielded from their parent tetraaryltin compounds (**1** and **2**). The aromatic protons (α and β) in **2** are chemically distinct, but are magnetically equivalent (Table 1). The hydride protons in **6** and **7** display strong $^{119/117}$Sn-H couplings (**6**: $J_{119Sn-H}$ = 954 Hz, $J_{117Sn-H}$ = 912 Hz; **7**: $J_{119Sn-H}$ = 1012 Hz, $J_{117Sn-H}$ = 963 Hz).

Table 1. ^{119}Sn, ^{1}H NMR spectroscopic data for compounds **1** to **7**



Compounds	^{119}Sn NMR δ (ppm)	^{1}H NMR δ (ppm) (α, β)
1*	−116.2	6.96, 7.50
2*	−130.9	7.69
3*	−27.5	7.02, 7.59
4*	−14.5	7.06, 7.63
5*	−32.6	7.83, 7.84
6**	−229.5	6.81, 7.40
7**	−235.5	7.13, 7.32

* = $CDCl_3$; ** = C_6D_6

Recrystallization of **4** with CH_2Cl_2/hexanes at −20 °C afforded small white crystals which were appropriate for single-crystal X-ray diffraction (Figure 1). The bond length and angles observed for **4** are similar to other tin diaryl dichlorides reported in literature.[13]

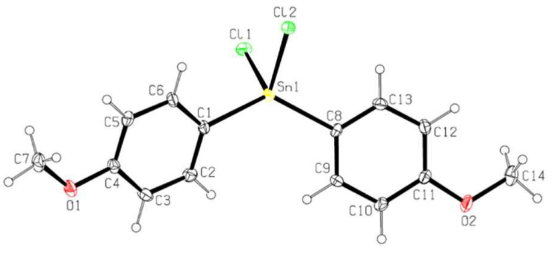


Figure 1. ORTEP structure of **4**. Selected bond lengths [Å] and angles [°]: Sn(1)-C(1) 2.104(6), Sn(1)-C(8) 2.107(6), Sn(1)-Cl(1) 2.3694(16), Sn(1)-Cl(2) 2.3532(16), C(1)-Sn(1)-C(8) 127.1(2), C(1)-Sn(1)-Cl(1) 105.73(18), C(1)-Sn(1)-Cl(2) 106.65(18), C(8)-Sn(1)-Cl(2) 107.08(18), C(8)-Sn(1)-Cl(1) 107.73(18), Cl(2)-Sn(1)-Cl(1) 99.13(6).

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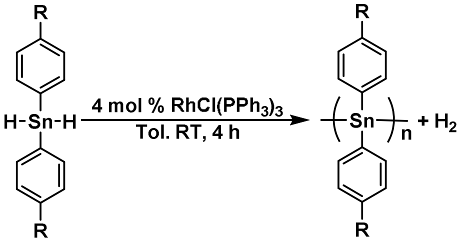
Polystannanes 8 and 9

Previous research by Caseri *et al.*[27] reported that high molecular weight diaryl polymers could not be prepared by dehydrogenative coupling using Wilkinson's catalyst. In the attempted dehydrocoupling of Ph_2SnH_2 with Wilkinson's catalyst, a poor yield of oligomeric $-[Sn(Ph)_2)]_n-$ ($M_w < 5 \times 10^4$ Da) was obtained when the reaction was performed at 70 °C.[27] By contrast, asymmetric dihydrides with alkyl and aryl substituents have been shown to readily polymerize at RT with Wilkinson's catalyst.[27] Interestingly, homopolymer, **8**, was readily synthesized by dehydrocoupling of **6** using the Wilkinson's catalyst in toluene at R.T. to yield an orange coloured waxy product (Scheme 4). Polymer **8** was purified by dissolving the crude in minimum amount of THF (~ 10 mL) and recovery by precipitation from a 6 × excess of cold hexanes at −20 °C and recovered as an orange powder in 83 % yield. A GPC analysis indicated that a moderate molecular weight polymer ($M_w = 1.07 \times 10^4$ Da) was obtained (Table 2). The ^{119}Sn NMR spectra of **8** shows a surprisingly well resolved resonance at -229.6 ppm, with extensive ^{119}Sn and ^{117}Sn couplings present. Polymer **9** was previously synthesized[13] via a Wurtz coupling using Na, but was found to be extremely light sensitive. An attempted dehydrocoupling of **7** using $RhCl(PPh_3)_3$ to synthesize **9** resulted in recovery of only oligomeric material.

According to Caseri *et al.*,[27] attaching two phenyl groups onto one tin impairs the efficiency of Wilkinson's catalyst presumably due to steric considerations. Additionally, the efficiency of the Wilkinson's catalyst may be dependent on the Lewis nature of the tin monomer. In our case, the highly electron donating groups (–OMe) of **8** increase the Lewis basicity of the tin metal center, thereby increasing its reactivity. By contrast, Wilkinson's catalyst is presumed to be less effective for highly electron withdrawing groups such as ($-CF_3$) which render the tin centers more Lewis acidic. Therefore, the electronics of the moieties of the tin monomers likely impacts the degree of polymerization.



6, 7

8, 9

Scheme 4. Reaction scheme for the synthesis of **8** and **9** *via* dehydrocoupling of **6** (R = –OMe) and **7** (R = $-CF_3$).

Alternating polystannanes, 10, 11 and 12

We previously described a condensation polymerization route which led to the first example of an alternating polystannane, **12**.[24] This condensation route involves the polymerization of 1:1 ratio of dihydride monomer with $(n\text{-Bu})_2Sn(NEt_2)_2$ in Et_2O which produces a volatile $HNEt_2$ byproduct (Scheme 5). Polymers, **10** and **11** were recovered as yellow coloured solids. By design, polymer **10** was constructed as a "push-push" system comprising two different electron donating groups (*p*-$MeOC_6H_4$ and *n*-Bu) at neighboring tin atoms. Polymer **11** was synthesized with an electron donating group (*n*-Bu) and a strongly electron withdrawing substituent (*p*-$CF_3C_6H_4$) at neighboring tin atoms to make it a "push-pull" system.

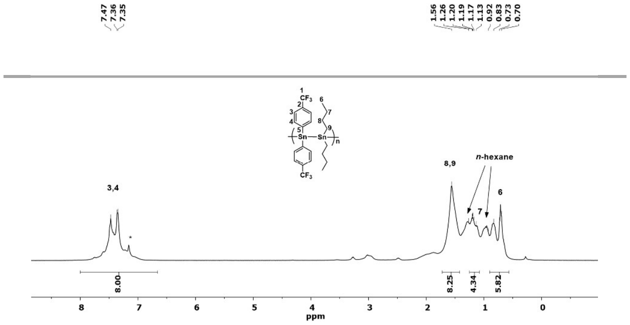
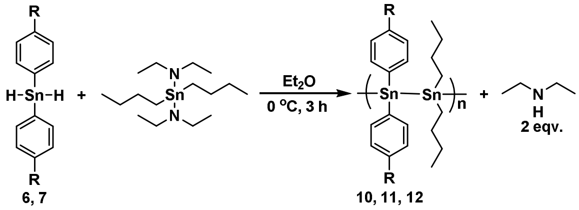


Figure 2. ^1H NMR (C_6D_6) of **11**.



6, 7

10, 11, 12

Scheme 5. Reaction scheme for the synthesis of alternating polystannanes; **10**: R = –OMe, **11**: R = $-CF_3$ and **12**: R = –H.[24]

The ^1H NMR spectrum of **11** shows a broad doublet in aromatic region between δ = 7.35 − 7.45 ppm corresponding to H3 and H4 (Figure 2). It also shows a plethora of peaks corresponding to *n*-butyl chain between δ = 0.69 − 1.59 ppm (H6–H9). Despite extensive efforts to dry the polymer, trace *n*-hexanes was detected in the alkyl region of the ^1H NMR spectra of **11**.

Polystannanes are extremely sensitive to light and moisture and thermodynamically favour the formation of low molecular weight oligomers and cyclic oligomers. Purification of these sensitive polystannanes is tedious, and this polymerization was conducted several times in attempts to optimize methods of purification. In earlier attempts, **10** was purified by dissolving the crude in a minimum amount of dry THF (~10 mL) and precipitation in a 6 × excess of cold hexanes at −20 °C. This purification method was repeated 4 – 5 times in attempts to obtain clean ^{119}Sn and ^1H NMR spectrum. Unfortunately, repeated purification led to further degradation of the polymer despite using dry solvents and taking precautions to avoid ambient light. Therefore, a different and more effective

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method of purification was needed. Crude **10** was dissolved in a minimum amount of toluene (~10 mL) and layered with 6× excess of hexanes. The flask was then slowly cooled to −50 °C to precipitate out **10**. Solvents were then decanted via cannula to recover **10** with the removal of majority of the oligomer species. The ^{119}Sn NMR spectrum of **10** shows two main polymer peaks at $\delta = -188.8$ ($(n\text{-Bu})_2$Sn) and −208.6 ($(\text{MeOC}_6\text{H}_4)_2$Sn) ppm indicative of the formation of an alternating polymer (Supplementary Figure A26, Table 2). These resonances are downfield from their respective homopolymers, $((n\text{-Bu})_2\text{Sn})_n$ (δ = -190.1 ppm)[20] and **8** (δ = -229.6 ppm) in the same solvent (C_6D_6). The ^{119}Sn NMR spectrum of **11** shows two polymer peaks at $\delta = -180.7$ ($(n\text{-Bu})_2$Sn) and −213.9 ($(\text{CF}_3\text{C}_6\text{H}_4)_2$Sn) ppm characteristic of the formation of an alternating polymer (Supplementary Figure A30, Table 2). In the case of **11**, the ($(n\text{-Bu})_2$Sn) half is found 10 ppm further downfield from the homopolymer, $((n\text{-Bu})_2\text{Sn})_n$, whereas the fluoro-containing half is found 163 ppm further upfield from **9**. The resonances for **10** and **11** are similar to the previously reported values for other alternating polystannanes.[24] Additionally, a number of small tin impurities were also detected in the ^{119}Sn NMR spectra of **10** and **11** which were not assigned. As a result of the extreme light and moisture sensitivity of polymers **10** and **11**, reliable elemental analysis could not be obtained despite repeated attempts.

Table 2. Characterization data for **8**, **9**, **10**, **11** and **12**.

Polymer	^{119}Sn NMR ppm (C_6D_6)	M_w (Da) × 10^4	PDI
8	−229.6	1.07	1.07
9*[13]	−56.7	292	4.40
10	−189, −209	1.95	2.08
11	−181, −214	1.17	2.95
12[24]	−187, −208	1.88	2.86

* = Previously synthesized *via.* Wurtz coupling.

The GPC data for the tin-containing polymers **8**, **10** and **11** is provided in Table 2 and their GPC chromatograms shown in Figure 3. Alternating polymer, **10** was first prepared by the dropwise addition of dihydride monomer, **6** to $(n\text{-Bu})_2\text{Sn}(\text{NEt}_2)_2$ which resulted in the formation of low molecular weight oligomeric species (M_W: 9.9 × 10^3 Da). Higher molecular weight **10** (Table 2) was observed when polymerization was carried out with the rapid addition of dihydride, **6**, to $(n\text{-Bu})_2\text{Sn}(\text{NEt}_2)_2$.

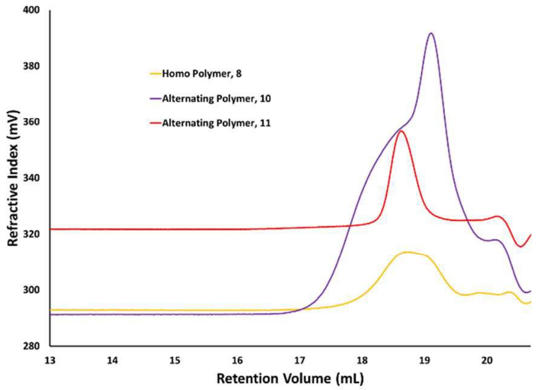

Figure 3. GPC chromatogram of polymers, **8**, **10** and **11**.

UV-Vis spectroscopy and Polymer stability

UV-Vis spectroscopy of **8**, **10**, and **11** in C_6H_6 was performed. The absorption characteristics of all polymers were similar. Five consecutive scans of homopolymer, **8** revealed no evidence of degradation in solution or photoscission upon exposure to light in solution (SI B1A). In contrast to **8**, alternating polymers, **10** (SI B1B) and **11**, showed rapid degradation after five consecutive scans. Complete disappearance of σ-σ* absorption of **11** was observed in 90 minutes (Figure 4). A loss of the characteristic yellow colour upon purification was visually observed to be faster for the "push-push" alternating polymer, **10**, compared to "push-pull" alternating polymer, **11**. This may indicate that **11** possesses marginally better light stability as a result of incorporating the alternating electron donating and electron withdrawing moieties along the tin backbone. Whereas in alternating polymer, **10**, the electron density is focused onto the tin backbone, making it more susceptible to photolytic cleavage.

Interestingly, homopolymer **8** showed the lowest loss in colour after UV exposure, indicating that bulky aromatic moieties[17] are likely required for the improved stability of the polystannanes.

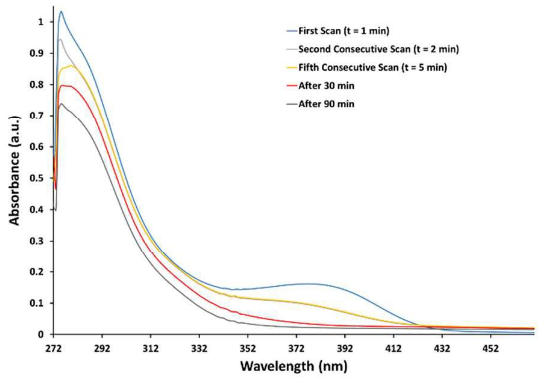

Figure 4. UV-Vis (C_6H_6) spectroscopy of polymer **11** showing the degradation.

Conclusions

A series of tetraaryl (**1** and **2**), chlorinated (**3**, **4** and **5**) and dihydride (**6** and **7**) tin small molecules were successfully synthesized. Homopolymer **8** was synthesized by a catalytic dehydrogenative coupling reaction of dihydride monomer, **6**. Alternating polymers, **10**, and **11** were successfully prepared by the condensation polymerization of the dihydride and the diamide monomers. It was expected that the use of bulky aromatic moieties onto the tin backbone will improve the light and moisture stability of the polystannanes. However, alternating polymers **10** and **11** demonstrated extreme sensitivity towards the light and moisture, and experienced a rapid degradation in solution while purification. Despite the initial promise of improved stability from the incorporation of the alternating electron donating and the electron

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withdrawing moieties along the tin backbone, further design features are needed to achieve complete light and moisture stable polystannanes. We are actively exploring the incorporation of both light absorbing groups[28] onto the polymer backbone along with hypercoordinate architecture[29] to achieve this goal.

Experimental

Materials and methods

All reagents and solvents were obtained from Sigma-Aldrich and used as received, unless otherwise indicated. Solvents were dried either through an MBraun solvent drying system, or through vacuum distillation and stored under an inert nitrogen atmosphere. All reactions were carried out under nitrogen atmosphere using Schlenk techniques unless otherwise noted. Nuclear magnetic resonance (NMR) spectroscopic experiments were carried out on a Bruker 400 MHz Avance spectrometer using $CDCl_3$ or C_6D_6 as the solvent. ^{1}H NMR (400 MHz) and ^{13}C NMR (100.6 MHz) spectra were referenced to the residual proton and central carbon peak of the solvent. The ^{19}F NMR (376 MHz) and ^{119}Sn NMR (149 MHz) were referenced to $CFCl_3$ and $SnMe_4$, respectively as internal standards. All the chemical shifts are given in δ (ppm) relative to the solvent and assigned to atoms. All NMR spectra were analyzed on MestReNova v6.0.2 software. High-resolution mass spectrometry was performed using an accuTOF DART-MS at the University of Toronto. Molecular weights of polymers were determined by gel permeation chromatography (GPC) using a Viscotek Triple Model 302 Detector system equipped with a Refractive Index Detector (RI), a four capillary differential viscometer (VISC), a right angle (90°) laser light scattering detector. GPC columns were calibrated versus polystyrene standards (American Polymer Standards). A flow rate of 1.0 mL min^{-1} was used with ACS grade THF as eluent. GPC sample were prepared using 10-15 mg of polymers per mL THF, and filtered using a 0.45 μm filter. UV-Vis spectroscopy was carried out using Cary 5000 UV-Vis-NIR spectrophotometer by Agilent technologies. Samples were prepared by dissolving the polymer in benzene. Elemental analysis of polymers and dichloride compound was performed by Atlantic Microlab of Norcross Georgia.

Note: Elemental analysis of polymers **8** and **10** were unsuccessful despite repeated attempts (3 ×). This was due to decomposition of the samples during transport or analysis. Only low resolution mass spectrometry were successfully carried out on compounds **6** and **7** due to the rapid dehydrogenation that would occur before samples could be detected, despite taking all necessary precautions. All polymers and monomers were found to be sufficiently stable to conduct extensive NMR analysis (^{119}Sn, ^{1}H, and ^{13}C) and 2D NMR to make all chemical shift assignments (see SI material).

Synthesis of tetraarylstannanes

Tetra(4-methoxyphenyl)stannane (**1**): In a 250 mL Schlenk flask charged with 100 mL of Et_2O, 1-bromo-4-methoxybenzene (3.8 mL, 30.35 mmol) was added. The solution was cooled to -94 °C before the addition of a 1.6 M solution of *n*-BuLi (19.92 mL, 31.87 mmol) dropwise and the mixture was allowed to stir for 2 h at this temperature. The reaction mixture was allowed to warm to R.T. before $SnCl_4$ (0.89 mL, 7.59 mmol) was added dropwise to the solution. The clear reaction mixture turned milky white and was allowed to stir for 4 h at R.T., and subsequent quenched with *t*-BuOH (~1 mL). The reaction mixture was filtered using a Schlenk filter funnel and solvent was removed in *vacuo* to produce a white coloured solid. Crude **1** was dissolved in hot toluene (10 mL) and precipitated in cold EtOH (40 mL) at −20 °C, resulting in a pure white solid, mp 132–133 °C (lit 133–134 °C[25]). Analysis by ^{119}Sn, ^{1}H, and ^{13}C NMR agreed with literature values reported by Lehmler *et al.*[30] Yield 77 % (3.18 g).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.50 (d, 8H, J = 8.5 Hz, $^3J_{119Sn-H}$ = 27 Hz, $^3J_{117Sn-H}$ = 19 Hz), 6.96 (d, 8H, J = 8.5 Hz, $^4J_{Sn-H}$ = 9.3 Hz), 3.82 (s, 12H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$, δ): 160.52, 138.28 ($^2J_{C-Sn}$ = 21.5 Hz), 128.81 ($^1J_{C-Sn}$ = 264 Hz), 114.48 ($^3J_{C-Sn}$ = 27.5 Hz), 55.03 ppm. **^{119}Sn NMR** (149 MHz, $CDCl_3$, δ): −116.1 ppm.

Tetra(4-benzotrifluoride)stannane (**2**) was prepared by the previously described synthesis by King *et al.*[26] and Foucher *et al.*[13] Organolithium route was used instead of Grignard route due to the higher yield compared to Grignard reaction.

Synthesis of chlorinated arylstannanes

Compounds **3** and **4** were prepared according to the method previously described by Munguia *et al.*[31]

Mono-chloro-tri-(4-methoxyphenyl)stannane (**3**): In a 100 mL Schlenk flask, compound **1** (2.17 g, 3.97 mmol) was added and dissolved in C_6H_6 (~ 50 mL). The solution was then placed in an ice bath and allowed to cool down for 15 min before the addition of a solution of 1.0 M HCl in Et_2O (3.97 mL, 3.97 mmol) dropwise. The reaction mixture was allowed to stir at 0 °C for 30 min before removing the ice bath and stirring for additional 60 min. Next, the solvent was removed in *vacuo*, resulting in the formation of a white viscous liquid. Crude **3** was dissolved in hot DCM (10 mL) and precipitated out from cold hexanes (40 mL) at -20 °C. The top solvent layer was decanted and removed in *vacuo* to obtain a viscous white liquid, **3**. Yield 86.0 % (1.62 g).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.59 (d, 6H, J = 8.5 Hz), 7.02 (d, 6H J = 8.5 Hz), 3.84 (s, 9H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$, δ): 161.40, 137.41, 128.10, 114.92, 55.03 ppm. **^{119}Sn NMR** (149 MHz, $CDCl_3$, δ): −27.8 ppm.

Di-chloro-di-(4-methoxyphenyl)stannane (**4**): In a 100 mL Schlenk flask, compound **3** (1.62 g, 3.41 mmol) was added and dissolved in C_6H_6 (~ 25 mL). The solution was then placed in an ice bath and allowed to cool down for 15 min before the addition of a solution of 1.0 M HCl in Et_2O (3.41 mL, 3.41 mmol) dropwise. The reaction mixture was allowed to stir at 0 °C for 30 min before removing the ice bath and stirring for additional 60 min. Next, the solvent was removed in *vacuo*, resulting in the formation of a pinkish white colour solid. Crude

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4 was washed with hexanes (3 × 10 mL) resulted in a formation of a white powder. It was then allowed to recrystallize from hexanes at -20 °C, which resulted in the formation of white needle like crystals of **4**, mp 74–75 °C (lit 75.5–76.5 °C[32]) Yield 51.1 % (0.71 g).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.63 (d, 4H, *J* = 8.5 Hz, $^{3}J_{119Sn\text{-}H}$ = 42 Hz, $^{3}J_{117Sn\text{-}H}$ = 35 Hz), 7.06 (d, 4H, *J* = 8.5Hz, $^{4}J_{Sn\text{-}H}$ = 15.5 Hz), 3.85 (s, 6H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$, δ): 162.37, 136.46 ($^{2}J_{C\text{-}Sn}$ = 36.8 Hz), 127.63, 115.41 ($^{3}J_{C\text{-}Sn}$ = 47 Hz), 55.31 ppm. **^{119}Sn NMR** (149 MHz, $CDCl_3$, δ): −14.5 ppm. EA: Anal. Calc. C,41.64; H, 3.49; Found. C, 41.56; H, 3.73.

Di-chloro-di-(4-(trifluoromethyl)phenylstannane (**5**) was prepared by the previously described synthesis by Foucher *et al*.[13]

Synthesis of dihydride arylstannanes

Di-hydride-di-(4-methoxyphenyl)stannane (**6**): In a 100 mL Schlenk flask, compound **4** (0.71 g, 1.74 mmol) was added and dissolved in 8 mL of EtOH and placed into an ice bath. In another 50 mL Schlenk flask, excess $NaBH_4$ (0.66 g, 17.41 mmol) was added and dissolved in 18 mL of EtOH and placed into an ice bath. In a separate 50 mL round bottom, 25 mL distilled water was degassed at 0 °C while the hydride was prepared. The solution of $NaBH_4$ was added dropwise *via* cannula to the Schlenk flask containing compound **4**, which resulted in the clear white reaction mixture turning yellow. The reaction mixture was allowed to stir for 45 min at 0 °C, after which 30 mL of hexanes were added. Then, 10 mL of distilled degassed water was added dropwise. The reaction mixture was extracted in a 250 mL separatory funnel. After extraction, the aqueous layer was discarded and the organic layer was transferred to a 50 mL Schlenk flask and hexanes removed in *vacuo*, which resulted in the formation of white coloured powder. Yield = 77.0 % (0.45 g).

^{1}H NMR (400 MHz, C_6D_6, δ): 7.40 (d, 4H, *J* = 8.5 Hz, $^{3}J_{119Sn\text{-}H}$ = 29 Hz, $^{3}J_{117Sn\text{-}H}$ = 21.5 Hz), 6.81 (d, 4H, *J* = 8.5Hz), 6.12 (s, 2H, $J_{119Sn\text{-}H}$ = 954 Hz, $J_{117Sn\text{-}H}$ = 912 Hz), 3.29 (s, 6H) ppm. **^{13}C {^{1}H} NMR** (100 MHz, C_6D_6, δ): 160.76, 138.65 ($^{2}J_{C\text{-}Sn}$ = 23.7 Hz), 125.40, 114.65 ($^{3}J_{C\text{-}Sn}$ = 29.3 Hz), 54.20 ppm. **^{119}Sn NMR** (149 MHz, C_6D_6, δ): −229.6 ($J_{119Sn\text{-}117Sn}$ = 696 Hz) ppm. **LRMS-DART (m/z):** [M^+]+H. Calc 337.01; Found 337.0.

Di-hydride-di-(4-(trifluoromethyl)phenylstannane (**7**): In a 100 mL Schlenk flask, compound **5** (0.34 g, 1.74 mmol) was added and dissolved in 5 mL of EtOH and placed into an ice bath. In another 50 mL Schlenk flask, excess $NaBH_4$ (0.27 g, 17.41 mmol) was added and dissolved in 12 mL of EtOH and placed into an ice bath. In a separate 50 mL round bottom, 25 mL of distilled water was degassed at 0 °C while the hydride was prepared. The solution of $NaBH_4$ was added dropwise *via* cannula to the Schlenk flask containing compound **5**, which resulted in the clear white reaction mixture turning yellow. The reaction mixture was allowed to stir for 1 h at 0 °C, after which 20 mL of hexanes were added. Then, 10 mL of distilled degassed water was added dropwise. The reaction mixture was extracted in a 250 mL separatory funnel. After extraction, the aqueous layer was discarded and the organic layer was transferred to a 50 mL Schlenk flask and hexanes removed in *vacuo*, which resulted in the formation of yellow coloured powder. Analysis by ^{119}Sn, ^{1}H, ^{13}C NMR showed the presence of pure compound **7**. Yield = 96.9 % (0.28 g).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.32 (d, 4H, *J* = 7.3 Hz), 7.13 (d, 4H, *J* = 7.3 Hz), 5.93 (s, 2H, $J_{119Sn\text{-}H}$ = 1012 Hz, $J_{117Sn\text{-}H}$ = 963 Hz) ppm. **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$, δ): 139.60, 137.48 ($^{2}J_{C\text{-}Sn}$ = 21.1 Hz), 131.14 ($^{2}J_{C\text{-}F}$ = 32.4 Hz, $^{4}J_{C\text{-}Sn}$ = 5.9 Hz), 124.79 ($^{3}J_{C\text{-}F}$ = 3.8 Hz, $^{3}J_{C\text{-}119Sn}$ = 28.8 Hz, $^{3}J_{C\text{-}117Sn}$ = 24.7 Hz), 124.44 ($^{1}J_{C\text{-}F}$ = 272.1 Hz) ppm. **^{119}Sn NMR** (149 MHz, $CDCl_3$, δ): −235.5 ppm. **^{19}F NMR** ($CDCl_3$, δ): −62.8 (s, CF_3) ppm. **LRMS-DART (m/z)**: [M^+] + H_2O. Calc 428.95; Found 428.9.

Synthesis of Polystannanes

Poly-(di-(4-methoxyphenyl)stannane) (**8**): In a 50 mL Schlenk flask wrapped with aluminum foil, Wilkinson's catalyst (0.034 g, 0.036 mmol) was added and dissolved in 10 mL of dry toluene and stirred for 20 minutes. In a separate 50 mL Schlenk flask, compound **6** (0.31 g, 0.91 mmol) was added and dissolved in 5 mL of dry toluene. It was then added by syringe to a solution of Wilkinson's catalyst dropwise and the reaction mixture was allowed to stir at R.T. for 4 h, after which the solvent was removed in *vacuo* to produce an orange coloured waxy product. The crude product was dissolved in 10 mL THF and precipitated out from 60 mL of cold hexanes to obtain an orange powder, **8**. Yield = 83.0 % (0.30 g).

^{1}H NMR (400 MHz, C_6D_6, δ): 7.65 – 7.37 (bm, 4H, H4), 7.05 – 6.63 (bm, 4H, H3), 3.28 (s, 6H, H1) ppm. **^{13}C {^{1}H} NMR** (100 MHz, C_6D_6, δ): 160.17 (C2), 139.48 (C4), 133.70 (C5), 114.32 (C3), 54.04 (C1) ppm. **^{119}Sn NMR** (149 MHz, C_6D_6, δ): −229.6 ppm, ($^{1}J_{119Sn\text{-}117Sn}$ = 3703 Hz). Note: additional Sn couplings not assigned. **EA:** Anal. Calc. C, 50.50; H, 4.24; Found. C, 45.31; H, 4.09.

Poly-(di-*n*-butyl-*alt*-di-(4-methoxyphenyl)stannane (**10**): In a 100 mL Schlenk flask, compound **6** (0.35 g, 1.05 mmol) was added and dissolved in 15 mL Et_2O. In a separate 100 mL Schlenk flask wrapped with aluminum foil, $(n\text{-Bu})_2Sn(NEt_2)_2$ (0.40 g, 1.05 mmol) was added and dissolved in 10 mL Et_2O. Both of the solutions were cooled down to 0 °C for 20 min before the rapid addition of dihydride solution to the amine solution using a syringe. The reaction mixture was allowed to stir for 3 h at 0 °C, after which the solvent was removed in *vacuo* to produce a yellow coloured waxy product. The crude product was dissolved in 10 mL THF and precipitated out from 60 mL cold hexanes to obtain a yellow powder, **10**. Yield = 75.0 % (0.44 g).

^{1}H NMR (400 MHz, C_6D_6, δ): 7.66 – 7.50 (bm, 4H, H4), 6.87 – 6.68 (bm, 4H, H3), 3.34 (s, 6H, H1), 1.63 – 1.62 (bm, 8H, H8, H9), 1.44 – 1.42 (bm, 4H, H7), 0.95 – 0.88 (bm, 6H, H6) ppm. **^{13}C {^{1}H} NMR** (100 MHz, C_6D_6, δ): 160.06 (C2), 139.29 (C4), 130.70 (C5), 114.56 (C3), 54.05 (C1), 32.84 (C8), 27.61 (C7), 13.55 (C9), 8.74 (C6) ppm. **^{119}Sn NMR** (149 MHz, C_6D_6, δ):

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−188.8 ((*n*-Bu)$_2$Sn), −208.6 ((OMeC$_6$H$_4$)$_2$Sn) ppm. **EA:** Anal. Calc. C, 46.69; H, 5.70; Found. C, 41.64; H, 5,34.

Poly-(di-*n*-butyl-*alt*-di-(4-(trifluoromethyl)phenyl)stannane (**11**): In a 100 mL Schlenk flask, compound **7** (0.27 g, 0.66 mmol) was added and dissolved in 15 mL Et$_2$O. In a separate 100 mL Schlenk flask wrapped with aluminum foil, (*n*-Bu)$_2$Sn(NEt$_2$)$_2$ (0.25 g, 0.66 mmol) was added and dissolved in 3 mL Et$_2$O. Both of the solutions were cooled to 0 °C for 20 min before the rapid addition of dihydride solution to the amine solution using a syringe. The reaction mixture was allowed to stir for 3 h at 0 °C. After the elapsed time, solvent was removed in *vacuo* to produce a yellow coloured waxy product. The crude product was dissolved in 10 mL THF and precipitated out from 60 mL cold hexanes to obtain yellow powder, **11**. Yield = 43 % (0.18 g).

^{1}H NMR (400 MHz, C$_6$D$_6$, δ): 7.39 (bd, 8H, H3 and H4, *J* = 46.8 Hz), 1.59 – 1.46 (bm, 8H, H8, H9), 1.30 – 1.15 (bm, 8H, H7), 0.86 – 0.69 (bm, 6H, H6) ppm. **^{13}C {^{1}H} NMR** (100 MHz, C$_6$D$_6$, δ): 145.0.3 (C5), 138.09 (C4), 130.96 (C2, $^2J_{C\text{-}F}$ = 32.6 Hz), 125.04 (C3), 124.31 (C1, $^1J_{C\text{-}F}$ = 272.6 Hz), 32.50 (C8), 27.34 (C7), 13.16 (C6), 11.80 (C9) ppm. **^{119}Sn NMR** (149 MHz, C$_6$D$_6$, δ): −180.7 ((*n*-Bu)$_2$Sn), −213.9 ((CF$_3$C$_6$H$_4$)$_2$Sn) ppm. **^{19}F NMR** (C$_6$D$_6$, δ): −62.9 (s, CF$_3$) ppm. **EA:** Anal. Calc. C, 41.17; H, 4.08; Found. C, 43.08; H, 4.33.

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Notes and references

‡ Additional data is found in the SI material associated with this work. The crystallographic data for compound 4 was deposited with Cambridge structural database (CCDC 1858149).

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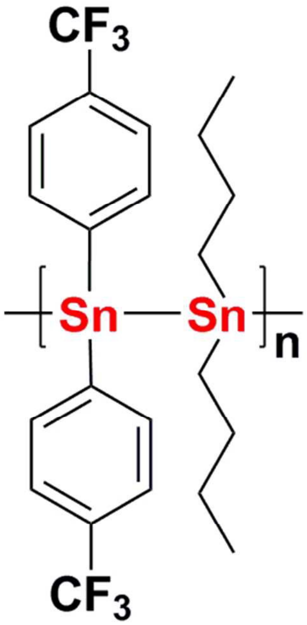

Alternating "Push-Pull" and "Push-Push" polystannanes pre[ared by condensation of tin diamides and tin dihydrides are described.

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