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Alternating Polystannanes: Syntheses and Properties

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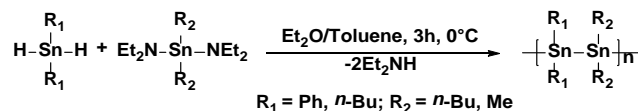**A new condensation polymerization route leading to alternating polystannanes is presented. The stoichiometric reaction of tin dihydrides and tin diamides in diethyl ether or toluene under mild reaction conditions afforded three new moderate molecular weight alternating polystannanes, –[Ph₂Sn-*alt*-Sn(*n*-Bu)₂]ₙ–, –[Ph₂Sn-*alt*-SnMe₂]ₙ–, –[Me₂Sn-*alt*-Sn(*n*-Bu)₂]ₙ–, in addition to a known homopolymer, –[(*n*-Bu)₂]ₙ–.**

For more than 20 years, dialkyl and diaryl homopolystannanes have been prepared by reductive coupling of either tin dichlorides[1-8] or tin dihydrides.[9-23] These intriguing polymers possess a backbone of σ-σ delocalized[1-3,6-13,15,16] organotins envisioned for use as processable intrinsic semiconductors[1-4,7,13,15,22] or printable polymeric wires.[2-6,12] Along with the considerable synthetic challenges in preparing later Group 14 polymeric materials is their profound sensitivity to moisture and light[1,2,7-13,15,18,24-27], increasing down the period. In the case of polystannanes, the Lewis acidic nature of formally Sn(IV) centers results in weak σ-σ overlap between neighbouring tin centers and a likely cause of their inherent susceptibility.[11,13,15-20,22,25] Despite the original promise of these materials, a relatively limited number of researchers have continued to pursue improved alternative synthetic methods and stabilization strategies with polystannanes. Dialkylpolystannanes, –[R₂Sn]ₙ–, (R = Et[8-13,15-20,22,24], Pr[8-13,18-20,22], *n*-Bu[2,8-13,15-20], hexyl[2,13,14-17], etc.) are soluble in most organic solvents where as diarylpolystannanes (R = Ph[22] etc.) are often considerably less soluble but demonstrate a dramatic red shift of the σ-σ* transititon in the UV-visible range in addition to their increased stability. Random dialkyl (*n*-Bu, octyl, dodecyl) and diphenyl polystannanes were recently prepared by Caseri *et al.* via a two-step Na Wurtz coupling in liquid ammonia. The recovered polymers are only partially THF soluble and of moderate molecular weight.[25] Polystannanes with improved light stability

were afforded by utilizing ethyl spacers directly attached to tin were also described by Caseri *et al.*[18-20,26] This was done in part to facilitate dehydrocoupling with a bulky Rh catalyst as a minimum of an ethyl spacer unit must be present separating the tin atoms from an aryl carbon.[26]

Our approach to preparing polystannanes employs condensation polymerization where both diaryl and dialkyl substituents can be introduced alternatively into the backbone to ensure increased solubility[27] and, surprisingly, an improved degree of light stability. Toluene or Et₂O solutions of equimolar quantities of high purity tin dihydrides and tin diamides (NMR) were added together at 0ºC to facilitate optimal polycondensation conditions.[28,29] This condensation (Scheme 1) produces volatile diethyl amine, which along with the reaction solvent, is removed *in vacuo* resulting in the recovery of a relatively pure polymer.

$$\underset{R_1}{\overset{R_1}{H-Sn-H}} + \underset{R_2}{\overset{R_2}{Et_2N-Sn-NEt_2}} \xrightarrow[-2Et_2NH]{Et_2O/Toluene,\ 3h,\ 0°C} \underset{R_1\ R_2}{\overset{R_1\ R_2}{+Sn-Sn+_n}}$$

R₁ = Ph, *n*-Bu; R₂ = *n*-Bu, Me

Scheme 1 Preparation of alternating polystannanes.

Related examples of oligostannanes prepared by transmetalation or condensation were described independently by both Dräger and Sita. Dräger *et al.*[30,31] prepared a series of oligostannanes with one to four (*t*-Bu)₂Sn moieties as the central core capped on each end with a Ph₃Sn unit. Sita *et al*[12] carried out a careful, stepwise condensation of (*n*-Bu)₂SnH₂ with (*n*-Bu)₂Sn(OCH₂CH₂OEt)(NMe₂) in the presence of a strong base to produce linear oligostannanes containing 3-15 tin atoms. For both the Dräger and Sita oligomers, a red shift of the σ-σ* transition was observed with increasing catenation.

Alternating polystannanes prepared by polycondensation of tin hydrides with tin amides are listed in Table 1. Four starting materials,

(*n*-Bu)₂SnH₂ (**1**), Ph₂SnH₂ (**2**), (*n*-Bu)₂Sn(NEt₂)₂ (**3**) and Me₂Sn(NEt₂)₂ (**4**) were prepared in good yield following literature methods.[19,32] The choice of these starting materials was based on ease and safety. Dimethyltin dihydride, Me₂SnH₂, is a gas at room temperature and is extremely toxic.[33] All possible combinations of polymers were then made incorporating the four compounds listed above.

The polystannane (–[(*n*-Bu)₂Sn]ₙ–), **5**, was chosen in order to validate the condensation polymerization process, as extensive characterization of this homopolymer has been previously carried out. Under an inert atmosphere in the absence of light, an ethereal solution of **1** was added slowly at 0°C to a Schlenk flask containing **3** in Et₂O and the mixture allowed to react for 3 hours at 0°C. The solvent and diethylamine co-product were then removed *in vacuo*. Condensations were carried out at 0°C in an effort to avoid thermally promoted self-polymerization of the heat sensitive alkyl or aryl stannyl dihydrides, as well as to limit possible termination reactions. Polymer **5** was recovered as a brightly yellow coloured solid and characterized by NMR (¹¹⁹Sn, ¹H, ¹³C), GPC, UV-Vis spectroscopy and DSC. GPC analysis showed the polymer to be of modest molecular weight (Table 1). Three new alternating polymers, **6** (–[Ph₂Sn-*alt*-Sn(*n*-Bu)₂]ₙ–), **7** (–[Ph₂Sn-*alt*-SnMe₂]ₙ–), and **8** (–[Me₂Sn-*alt*-Sn(*n*-Bu)₂]ₙ–) were also synthesized using the same methodology. Their data is listed in Table 1. The calculated elemental analysis was based on the relative degree of polymerization of the sample and accounts for the uncertainty in the process. For more details on the methodology used for this estimation, see supplementary (S1).

Cmpd.	¹¹⁹Sn NMR δ (C₆D₆) ppm	T_g (°C)	Mw (KDa), PDI	EA
5[19]	-191	1	91, 2.53	$C_{calc/found}$: 40.76/41.25 $H_{calc/found}$: 7.79/7.61
5	-191	1	18.1, 2.27	$C_{calc/found}$: 40.76/39.81 $H_{calc/found}$: 7.79/7.13
6	-187, -208	117	18.8 2.86	$C_{calc/found}$: 47.30/46.56 $H_{calc/found}$: 5.95/5.39
7	-60, -201	118	242.5, 2.03	$C_{calc/found}$: 34.81/33.72 $H_{calc/found}$: 5.50/5.63
8	-186, -235	-6	82.1, 2.86	$C_{calc/found}$: 31.30/29.26 $H_{calc/found}$: 6.28/6.37

Table 1 Data for tin-containing condensation polymers.

A hydrostannolysis[34] reaction of the two difunctional monomers results in the release of HNEt₂ and formation of Sn-Sn bonds; thus promoting a facile condensation polymerization. This type of condensation has previously been demonstrated in part by others for tin systems, including oligostannanes,[12] but to our knowledge has not been used exclusively for the preparation of polystannanes. This methodology allows for the reaction to be carried out in a single vessel, at modest temperature, with short polymerization period(s) and proceeds without the aid of an external catalyst.

The phenyl-containing polymer derivatives **6** and **7** (Figure 1) showed increased chemical stability to light and moisture in the

solid state with exposure up to 5 days with no apparent loss of colour or change in the ¹¹⁹Sn NMR spectroscopic profile. Similar stability of homopolystannanes bearing phenyl derivatives as side groups was reported by Tilley.[10] Under these same conditions, the alkylated polymer **8** experienced a more rapid degradation with a noticeable colour change from a yellow semisolid texture to a white powder; possibly this represents formation of a stannoxane. Polymer **5** degraded to a similar white powder in much the same way as previously described by Tilley and others.[7-10,13,15,25,35]

6 **7**

Fig. 1 Polystannanes **6** and **7** after exposure to ambient light for 7 days.

NMR (¹H, ¹³C, ¹¹⁹Sn) analysis of the new alternating polymers (**6**, **7**, and **8**) revealed resonances corresponding to both attached R groups as well as two well separated ¹¹⁹Sn NMR resonances. ¹H NMR spectroscopy for polymers **6-8** support the integration of both monomer units at an approximately 1:1 ratio (**6**, 1:0.98 SnPh₂ to Sn(*n*-Bu)₂, **7**, 1:0.99 SnPh₂ to SnMe₂, **8**, 1:0.96 of SnMe₂ to Sn(*n*-Bu)₂). The alternating polymers **7** and **8** showed a distinct downfield ¹¹⁹Sn resonance (-60 and -186 ppm) for the Me substituents, whereas the Ph (-200 ppm) and *n*-Bu (-235 ppm) substituents are found in the region more typical of known cyclic stannanes and polystannanes. Evidence of strong Sn-Sn coupling (Figure 2) was also observed for methylated tin center of **7** (¹¹⁹/¹¹⁷J = 4421 Hz) and is similar to reported ¹J couplings for methylated stannanes[32] and a polyferrocenyldistannane.[36] Polymers **5**, **6** and **8** are found in a region more typical of most polystannanes (δ = -190 to -210 ppm) with one exception.[1,2,8-11,13,15,18-20,22,24] The Sn(*n*-Bu)₂ chemical shift of **8** (δ = **-235 ppm**) was displaced upfield by a further 45 ppm relative to **5** (δ = **-190 ppm**).
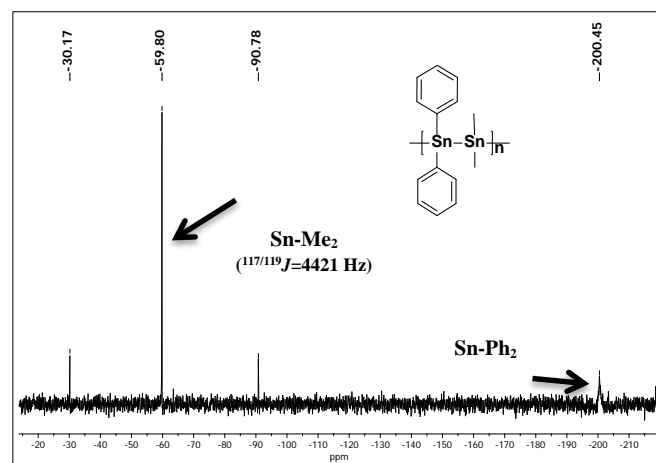

Fig. 2 ¹¹⁹Sn NMR (C₆D₆) of **7**.

There is no evidence (NMR) for either end group in any of the polymers prepared by condensation. As all efforts were made to keep samples away from reactive solvents or moisture, it is presumed that one of the terminal ends contains a Sn-H bond and, the other a Sn-NEt$_2$ containing unit. Alternatively, termination maybe the result of macrocyclic cyclization and an absence of end groups.

DSC analysis of **5** produced by our condensation polymerization shows a nearly identical glass transition (T_g = 1°C) to polymers of **5** produced by reductive coupling.[11] Polymer **5** recovered from the catalyst free condensation polymerization described earlier is a yellow coloured solid absent of 5- and 6-membered cyclic stannanes (GPC, NMR).[4,9,18] The alternating polystannanes **6** and **7** (Table 1) display higher glass transitions (**6** T_g = 117°C, **7** T_g = 118°C) compared to the homopolymer (**5** T_g = 1°C), while a slightly lower glass transition (T_g = -6°C) was detected for the mixed dialkyl polystannane **8**. Like **5**, polymers **6**, **7** and **8** appear to be amorphous with no detectable melt transition in the scan range (-50 to 225°C).
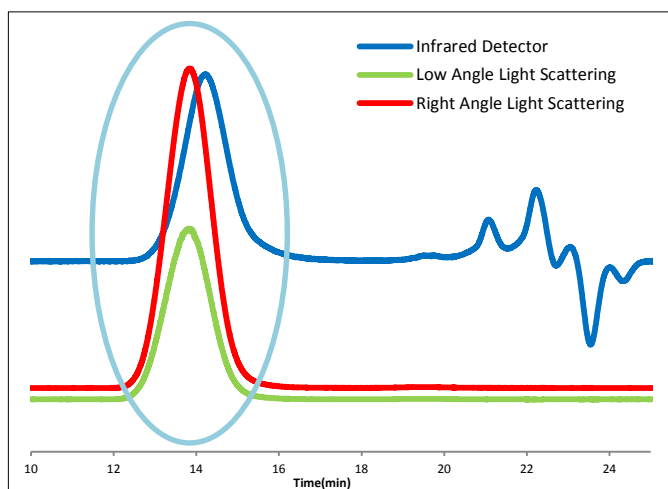

Fig. 3 GPC of polymer **7** in THF.

The GPC analysis (Table 1) for the condensation polymers (**5-8**) show PDI's between 2 and 3 with the value expected for an ideal condensation polymerization to be closer to 2. With the exception of the **7**, the molecular weights of polymers prepared by condensation are lower than polystannanes prepared by dehydrocoupling reactions. The triple detection GPC traces of polymers (Figure 3) appear to be monomodal for the most part.

Dräger *et al.*[30,31], Sita *et al.*[12], and others[7-13,14-20,22-27] have observed a red shift of the σ-σ* λ_{max} transition with increasing catenation. What differs in the previous studies with this work is that two of the polymers (**6,7**) have two phenyl rings near each Sn-Sn bond with one tin possessing a direct Sn-C$_{aromatic}$ bond. The aromatic rings are themselves capable of σ+π orbital mixing with Sn, but can also act as a chromophore to absorb light energy that might damage Sn-Sn bonds. As the repeat unit consists of at least two dialkyl substituents (Me or *n*-Bu), the polymer remains reasonable soluble in solution. Figure 4 shows the UV-Vis spectra of the alternating polymers as well as for the homopolymer **5** prepared

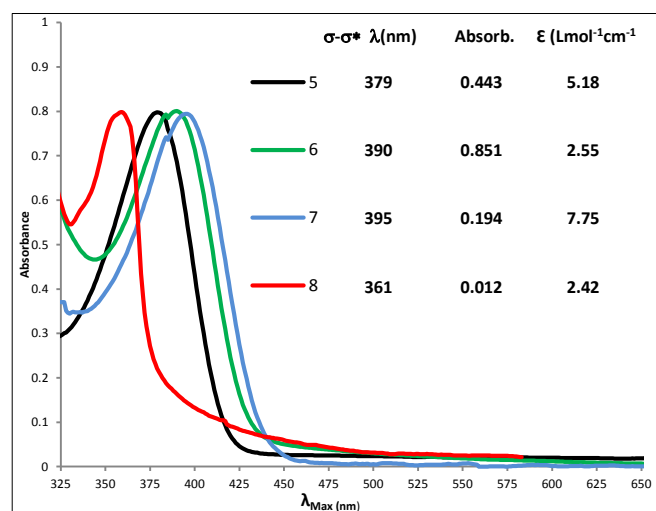by condensation, which is in good agreement with literature values.[19]

Fig. 4 UV-Vis (normalized) of **6-8** alternating polymers compared to the homopolymer **5** in THF.

Polystannanes **6** and **7** comprised of alternating alkyl and aryl substituents display a small redshift (10-15 nm) of their σ−σ* transition relative to **5** (λ_{max} = 379 nm) while a blue shift of similar magnitude (16 nm) was observed for the mixed alkyl polymer **8**. The redshift of polymers **6** and **7** is likely a consequence of σ+π conjugation from the Ph substituents attached to Sn.[27]

Conclusions

A new condensation route to homopolystannanes and previously unknown alternating polystannanes has been demonstrated. This thermally favourable condensation reaction offers a relatively straightforward process and enables design features that could lead to even more light and moisture stable polystannanes.

Support

Notes and references

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† Electronic Supplementary Information (ESI) available: [Experimental details, NMR characterization etc.]

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