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Low-Band-Gap, σ-Conjugated Polymers: Poly(diarylstannanes)

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The discovery of polysilanes in the early 1980s introduced a new class of charge-transporting materials and focused considerable attention on polymers that possess σ-delocalization in one dimension.[1] Such polymers, which have until recently been available only as catenated silicon and germanium chains, are of interest as soluble, one-dimensional semiconductors or quantum wires. Given the strong interest in the fundamental properties of these materials, we recently developed a route to linear polystannanes which possess inherently lower band gaps.[2] Thus, we have observed that poly(dialkylstannanes) display a strong σ−σ* transition at ca. 390−400 nm, which represents a red shift with respect to analogous polysilanes of ca. 70 nm.[1b] One aspect of our investigations of this new polymer system concerns exploring the limits of semiconductor behavior for σ-conjugated polymers, by examining structural parameters which allow manipulation of the polystannane band gap. Based on previous studies with polysilanes, it seemed that more narrow band gaps might be achieved with aryl substituents, which should increase conjugation via σ−π delocalization.[1b] In addition, lower band gaps may be achieved by enforcing a planar zigzag conformation for the polystannane chain.[1b,3]

Our synthesis of poly(dialkylstannanes) is based on the metal-catalyzed dehydropolymerization of a secondary stannane R_2SnH_2. An initial attempt to synthesize a poly(diarylstannane) via dehydrocoupling of Ph_2SnH_2 gave relatively low molecular weight material (M_w/M_n = 6700/5000), apparently because of limited solubility for the polystannane products. Nonetheless, this $H(SnPh_2)_nH$ sample exhibited a λ_{max} value of 402 nm, which suggested that the phenyl groups might be involved in σ/π conjugation with the polystannane chain.[2b] To examine this possibility further, we modified the aryl groups by incorporation of a solubilizing alkyl substituent in the *para* position, which allows for homogeneous reaction mixtures and therefore significantly higher molecular weights.[4] The resulting poly(diarylstannanes) reported here possess the most red-shifted σ−σ* transitions yet observed for a σ-conjugated system.

The diarylstannane monomers chosen for this study, $(p\text{-}^tBu\text{-}C_6H_4)_2SnH_2$ (**1**) and $(p\text{-}^nHex\text{-}C_6H_4)_2SnH_2$ (**2**), were prepared in reasonable yields (80%) via $LiAlH_4$ reduction of the corresponding Ar_2SnCl_2, which were obtained by comproportionation of $SnAr_4$ and $SnCl_4$.[5] Both monomers are air- and temperature-sensitive, and whereas **1** is a solid at room temperature, **2** is a colorless, viscous oil.[6]

Dehydrocoupling of **1** in hydrocarbon solvents at low concentrations ([**1**] = 0.01−0.03 M), with $CpCp^*Zr[Si(SiMe_3)_3]Me$ or Cp_2ZrMe_2 catalyst (2−3 mol %; room temperature), gave only low molecular weight polystannane oligomers (by gel permeation chromatography (GPC); polystyrene standards). However, at monomer concentrations above 0.09 M, relatively high molecular weight polystannanes were obtained. At a monomer concentration of 0.09 M in pentane, the dehydropolymerization of **1** by Cp_2ZrMe_2 yielded the polystannane as an orange solid (M_n = 14 700, PDI = 3.7, 7% cyclic hexamer). In an attempt to lower the cyclic content of the polymer sample, a polymerization with neat, melted monomer was conducted.[4] However, this approach required relatively high temperatures (ca. 120 °C; under vacuum; 2.5 h; Cp_2ZrMe_2 catalyst), which gave more of the cyclic hexamer (20%, M_w/M_n = 1500/1400) and linear $H[(p\text{-}^tBu\text{-}C_6H_4)_2Sn]_nH$ chains with M_w/M_n = 16 000/10 000 (eq 1).

$$(p\text{-}RC_6H_4)_2SnH_2 \xrightarrow[-H_2]{Cp_2ZrMe_2} \quad R = {}^tBu,\ {}^nHex \quad cyclo\text{-}[(p\text{-}RC_6H_4)_2Sn]_6 = H[(p\text{-}RC_6H_4)_2Sn]_nH \qquad (1)$$

Further heating for an additional 3 h resulted in some depolymerization, and a sample containing 24% cyclic and linear $H[(p\text{-}^tBu\text{-}C_6H_4)_2Sn]_nH$ chains with M_w/M_n = 14 800/9900 (by GPC). Fractionation of a low molecular weight sample (30% cyclics, M_w/M_n = 10 700/6600 for the linear fraction), by addition of a THF solution to methanol, resulted in 50% recovery of polystannane which had been significantly enriched in the longer chains (ca. 10% cyclics, M_w/M_n = 20 400/15 100 for the linear fraction). The ^{119}Sn NMR spectra for these samples contain a peak at −197 ppm for the linear polystannane chains and a resonance at −221 ppm attributed to *cyclo*-$[(p\text{-}^tBu\text{-}C_6H_4)_2Sn]_6$.

Dehydropolymerization of **2** by Cp_2ZrMe_2 (3 mol %, [**2**] = 0.11 M in pentane, room temperature) over 7 h gave a yellow-orange polystannane as an extremely viscous oil. This polymer contained primarily $H[(p\text{-}^nHexC_6H_4)_2Sn]_nH$ chains (M_w/M_n = 34 700/14 300; T_g = −8.1 °C), and a small amount of cyclic oligomer (M_w/M_n = 2100/2000) was detected by GPC.[6] After fractionation with methanol, a sample was obtained for which M_w/M_n = 48 200/20 000 for the linear fraction (ca. 5% cyclic material was present also). The ^{119}Sn NMR spectrum of this sample revealed only a resonance at −196 ppm attributed to the linear polymer.

The cyclic oligomer formed in the polymerization of $(p\text{-}^tBu\text{-}C_6H_4)_2SnH_2$ gives rise to a single ^{119}Sn NMR resonance at −221 ppm (J_{SnSn} = 1003 Hz; 673 Hz). This cyclic species was independently synthesized by the reaction of $(p\text{-}^tBu\text{-}C_6H_4)_2SnH_2$ with pyridine[7] and was identified by FAB mass spectrometry as the hexamer *cyclo*-$[(p\text{-}^tBuC_6H_4)_2Sn]_6$. Exposure of a THF solution of $H[(p\text{-}^tBu\text{-}C_6H_4)_2Sn]_nH$ to room light 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 resonances at δ −214 (J_{SnSn} = 560 Hz, possibly due to *cyclo*-$[(p\text{-}^tBu\text{-}C_6H_4)_2Sn]_5$[2b]) and δ −216 (low intensity; no coupling observed).

The $H[Ar_2Sn]_nH$ polystannane polymers exhibit λ_{max} values attributed to $\sigma \rightarrow \sigma^*$ transitions at 432 nm ($H[(p\text{-}^tBu\text{-}C_6H_4)_2Sn]_nH$) and 436 nm ($H[p\text{-}^nHex\text{-}C_6H_4)_2Sn]_nH$). In contrast to the related transitions for $H[SnR_2]_nH$ (R = ^{n}Hex, ^{n}Oct) polystannanes,[2b] the energies of these absorptions are independent of temperature (−20 to +90 °C) and the polymer phase (solution vs solid). Since these transitions are 30−40 nm red shifted with respect to the poly(dialkylstannanes), we conclude that significant σ−π conjugation exists between the polystannane backbone and the aryl substituents.

The poly(diarylstannanes) reported here are only slightly air- and light-sensitive in the solid state, but

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much more sensitive in solution. Thermal gravimetric analysis (TGA) of $\mathrm{H}[(p\text{-}{}^{t}\mathrm{Bu}\text{-}\mathrm{C}_6\mathrm{H}_4)_2\mathrm{Sn}]_n\mathrm{H}$ under nitrogen reveals no weight loss to 300 °C, and then a 70% weight loss from 310 to 370 °C. The ceramic yield (30% at 400 °C) is very close to the theoretical yield for conversion to Sn metal. A bulk sample of $\mathrm{H}[(p\text{-}{}^{t}\mathrm{Bu}\text{-}\mathrm{C}_6\mathrm{H}_4)_2\mathrm{Sn}]_n\mathrm{H}$ 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). In air, this polymer has an onset temperature for decomposition at 227 °C and gives a ceramic yield at 400 °C of 39% (by TGA), which is the theoretical yield for conversion to SnO_2. The product of air oxidation was shown by XRD to be SnO_2 (cassiterite). The relatively clean thermal decomposition of $\mathrm{H}[(p\text{-}{}^{t}\mathrm{Bu}\text{-}\mathrm{C}_6\mathrm{H}_4)_2\mathrm{Sn}]_n\mathrm{H}$ to Sn or SnO_2 indicates that poly(diarylstannanes), like poly(dialkylstannanes),[2b] might be used as preceramic polymers for the preparation of semiconductor thin films.

It has been observed that the electronic structures of polysilanes depend markedly on the conformation of the polymer backbone, and a number of backbone conformations in polysilanes have been identified.[1b,3] The degree of σ-conjugation is greatest for the planar zigzag structures. The powder X-ray diffraction pattern for samples of $\mathrm{H}[(p\text{-}{}^{t}\mathrm{Bu}\text{-}\mathrm{C}_6\mathrm{H}_4)_2\mathrm{Sn}]_n\mathrm{H}$ 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 (15.8 Å) for a 7/3 helical chain structure involving a $\mathrm{T_3GT_3G'}$ (T, trans; G, gauche) pattern of conformations about the Sn−Sn bonds.[8,9] Therefore this polymer exhibits a structure analogous to that for $\mathrm{H}[{}^{n}\mathrm{Hex}_2\mathrm{Sn}]_n\mathrm{H}$, which also exhibits a d-spacing of 15.2 Å.[10]

In conclusion, we have prepared the first examples of high molecular weight poly(diarylstannane) polymers, which possess low band gaps (the lowest yet observed for a σ-conjugated linear chain). These polymers appear to possess a helical structure, which indicates that σ-conjugation along the main chain is far from optimal. Encouraged by these results, we are attempting to prepare poly(diarylstannane) polymers that adopt a planar zigzag conformation, and therefore even lower band gaps.

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Supporting Information Available: Experimental procedures and characterization data for compounds (5 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) West, R. *J. Organomet. Chem.* **1986**, *300*, 327. (b) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359. (c) Ziegler, J. M. *Mol. Cryst. Liq. Cryst.* **1990**, *190*, 265. (d) Matyjaszewski, K.; Cypryk, M.; Frey, H.; Hrkach, J.; Kim, H. K.; Moeller, M.; Ruehl, K.; White, M. *J. Macromol. Sci., Chem.* **1991**, *A28*, 1151.

(2) (a) Imori, T.; Tilley, T. D. *J. Chem. Soc., Chem. Commun.* **1993**, 1607. (b) Imori, T.; Lu, V.; Cai, H.; Tilley, T. D. *J. Am. Chem. Soc.* **1995**, *117*, 9931. (c) Imori, T.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L. *J. Organomet. Chem.* **1995**, *493*, 83.

(3) (a) Tachibana, H.; Matsumoto, M.; Moritomo, Y. T.; Yamaguchi, A.; Koshihara, S.; Miller, R. D.; Abe, S. *Phys. Rev.* **1993**, *47*, 4363. (b) Takeda, K.; Shiraishi, K. *Chem. Phys. Lett.* **1992**, *195*, 121.

(4) Tilley, T. D. *Acc. Chem. Res.* **1993**, *26*, 22.

(5) Van der Kerk, G. J. M.; Luijten, J. G. A. *J. Appl. Chem.* **1957**, *7*, 369.

(6) For **1**: (mp 73−74 °C) ^{1}H NMR (300 MHz, benzene-d_6) δ 1.19 (s, 18 H, $\mathrm{CMe_3}$), 6.15 (s, 2 H, $\mathrm{SnH_2}$, $J_{\mathrm{SnH}} = 1905$, 1820 Hz), 7.26 (d, $J = 6$ Hz, 4 H, m-$\mathrm{C_6H_4}$), 7.50 (d, $J = 6$ Hz, 4 H, o-$\mathrm{C_6H_4}$). Anal. Calcd for $\mathrm{C_{20}H_{28}Sn}$: C, 62.05; H, 7.29. Found: C, 62.04; H, 7.64. For **2**: ^{1}H NMR (400 MHz, benzene-d_6) δ 0.86 (br t, 6 H, $\mathrm{CH_3}$), 1.17−1.25 (m, 12 H, $\mathrm{CH_2}$), 1.47−1.53 (m, 4 H, $\mathrm{CH_2}$), 2.45 (t, $J = 8$ Hz, 4 H, $\mathrm{C}H_2\mathrm{C_6H_4}$), 6.14 (s, 2 H, $\mathrm{SnH_2}$, $J_{\mathrm{SnH}} = 1906$, 1821 Hz), 7.07 (d, $^3J_{\mathrm{HH}} = 7.8$ Hz, 4 H, m-$\mathrm{C_6H_4}$), 7.47 (d, $^3J_{\mathrm{HH}} = 7.8$ Hz, $^3J_{\mathrm{SnH}} = 45$, 62 Hz, 4 H, o-$\mathrm{C_6H_4}$). Anal. Calcd for $\mathrm{C_{24}H_{36}Sn}$: C, 65.04; H, 8.19. Found: C, 65.26; H, 8.27. For $[(p\text{-}{}^{t}\mathrm{Bu}\text{-}\mathrm{C_6H_4})_2\mathrm{Sn}]_n$: Anal. Calcd for $\mathrm{C_{20}H_{26}Sn}$: C, 62.38; H, 6.80. Found: C, 62.10; H, 6.82. For $[(p\text{-}\mathrm{Hex}\text{-}\mathrm{C_6H_4})_2\mathrm{Sn}]_n$: Anal. Calcd for $\mathrm{C_{24}H_{34}Sn}$: C, 65.33; H, 7.77. Found: C, 64.98; H, 7.78.

(7) Neumann, W. P.; König, K. *Angew. Chem.* **1962**, *74*, 212.

(8) Karikari, E. K.; Greso, A. J.; Farmer, B. L.; Miller, R. D.; Rabolt, J. F. *Macromolecules*, **1993**, *26*, 3937.

(9) For this calculation, a Sn−Sn bond length of 2.787 Å and a Sn−Sn−Sn bond angle of 111.5° were assumed, based on published crystallographic data: Puff, H.; Bach, C.; Reuter, H.; Schuh, W. *J. Organomet. Chem.* **1984**, *277*, 17.

(10) Lu, V. Y.; Tilley, T. D., unpublished results.

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