

High Molecular Mass Polystannanes *via* Dehydropolymerization of Di(*n*-butyl)stannane

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The dehydropolymerization of $\text{Bu}^n_2\text{SnH}_2$, catalysed by $[\text{Zr}(\text{C}_5\text{H}_5)(\text{C}_5\text{Me}_5)\{\text{Si}(\text{SiMe}_3)_3\}\text{Me}]$, produces cyclic $(\text{SnBu}^n_2)_n$ oligomers and long $\text{H}(\text{SnBu}^n_2)_n\text{H}$ polystannane chains ($M_w/M_n = 17\,500/7800$), which exhibit a long-wavelength electronic absorption ($\lambda_{\text{max}} = 382\text{ nm}$) and emit green light ($\lambda_{\text{max}} = 505\text{ nm}$; 337.1 nm excitation).

The recent discovery and rapid development of polysilane high polymers can be attributed largely to the interesting electronic properties which these materials possess.¹ Polysilanes exhibit a strong near-UV absorption that results from σ -conjugation along the silicon backbone. The radiation-

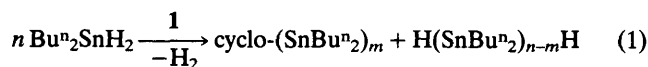
sensitivity associated with excitation of this transition makes these polymers suitable for applications in microlithography. Also, owing to their delocalized electronic structure and relatively narrow band gap (*ca.* 4 eV), polysilanes provide a new class of photoconducting and charge-transporting poly-

mers.¹ In principle, heavier atoms in the polymer backbone should lead to higher photochemical reactivity, and narrower band gaps.² In fact, West³ and Miller⁴ have reported that polygermane derivatives exhibit absorptions that are *ca.* 20 nm red-shifted from the corresponding polysilanes. Unfortunately the Wurtz-coupling method used to prepare polysilanes and polygermanes has not been applicable to polystannanes, so that studies on polystannane properties have been limited to low molecular mass oligomers (≤ 10 Sn atoms).⁵ Recently, however, Zou and Yang have communicated the synthesis of high molecular mass $(\text{SnBu}^n)_n$, accomplished by addition of 15-crown-5 to a mixture of Na and Bu^nSnCl_2 .⁶

An alternative route to polysilanes is based on dehydropolymerization of silanes with titanocene or zirconocene catalysts.⁷ This reaction works best for primary aryl silanes such as PhSiH_3 , for which degrees of polymerization of up to *ca.* 100 ($M_n \approx 5000$ – 7000) have been achieved.^{7b,8} With secondary silanes, the dehydrocoupling reactions are much slower and give only oligomers with up to 8 monomer units.⁹ Harrod has shown that PhGeH_3 is more active towards dehydropolymerization than PhSiH_3 , such that with $(\text{C}_5\text{H}_5)_2\text{TiMe}_2$ as catalyst a three-dimensional gel is obtained.¹⁰ Here we report a dehydrocoupling route to high molecular mass poly(di-*n*-butylstannane diyl), which appears to be the highest molecular mass polystannane yet isolated as judged by its long wavelength absorption.

Addition of neat Bu^nSnH_2 (0.30 g) to the catalyst, $[\text{Zr}(\text{C}_5\text{H}_5)(\text{C}_5\text{Me}_5)\{\text{Si}(\text{SiMe}_3)_3\}\text{Me}]$ **1** (0.02 mol. equiv.), resulted in vigorous evolution of hydrogen and a dark-red mixture, which was protected from room light. The hydrogen evolution slowed after a few min, but continued over the next

5 h, during which the reaction mixture solidified. The solid was dissolved in dry pentane (20 ml), to which dry methanol (20 ml) was added to separate the polymer as a yellow oil. Removal of solvent by decantation, and drying under vacuum resulted in a 93% yield of the polystannanes as a yellow solid. Analysis of the polymer by gel permeation chromatography (GPC; polystyrene standards) revealed [Fig. 1(a)] a sharp peak at *ca.* 1000 (29%), which we tentatively assign to cyclic $(\text{SnBu}^n)_n$ species of as yet undetermined ring size. The predominant, higher molecular mass fraction ($M_w/M_n = 17500/7800$) is attributed to $\text{H}(\text{SnBu}^n)_n\text{H}$ chains, although it is difficult at this point to rule out some degree of branching. A rough estimate for the average degree of polymerization for these chains, made by simply accounting for the differences in size between styrene and SnBu^n_2 monomer units, is *ca.* 80.



Thus, the reaction of eqn. (1) closely resembles the dehydropolymerization of PhSiH_3 , which produces cyclic and linear $(\text{SiHPh})_n$ polysilanes (with compound **1** as catalyst, M_n for the linear species is ≈ 5000 – 6000 ^{7b}). We therefore assume that the reaction described here is mechanistically similar to that proposed for the hydrosilane reaction,^{7b} and proceeds *via* concerted, four-centre transition states that make and break σ bonds. As seen for the dehydropolymerization of silanes, a much higher yield of the lighter cyclic species is obtained under more dilute conditions. Thus, reaction of Bu^nSnH_2 (0.30 g) and catalyst (0.02 mol. equiv.) in toluene (1 ml) for 10 h at room temperature gave principally the cyclic material [Fig. 1(b)].

Whereas the ^1H and ^{13}C NMR spectra for this polymer are relatively uninformative, the cyclic and linear species are well resolved in $^{119}\text{Sn}\{^1\text{H}\}$ spectra. Based on correlations between peak intensities in GPC traces and $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectra (111.9 MHz, $[\text{C}_6\text{H}_6]$ benzene), it is possible to assign a peak at $\delta -189.6$ to the linear species, and a peak at $\delta -200.9$ to the cyclic polystannane(s). We have been unable to detect $-\text{SnHBu}^n_2$ end groups in ^1H or ^{119}Sn NMR spectra, but this is to be expected given the high molecular masses. The above chemical shift assignments differ from those reported by Zou and Yang for $(\text{SnBu}^n)_n$ species obtained by Wurtz-coupling.⁶ However, our data are more consistent with what has been reported earlier for $(\text{SnBu}^n)_n$ oligomers ($n = 3$ – 5).^{5e}

High molecular mass properties for the $\text{H}(\text{SnBu}^n)_n\text{H}$ polystannane are reflected in electronic absorption spectra. For a sample with $M_n = 7800$ (GPC), the λ_{max} value is 382 nm. For comparison, the λ_{max} value for $\text{Et}(\text{SnEt}_2)_6\text{Et}$ is 325 nm,¹¹ and the λ_{max} value for the $(\text{SnBu}^n)_n$ material of Zou and Yang

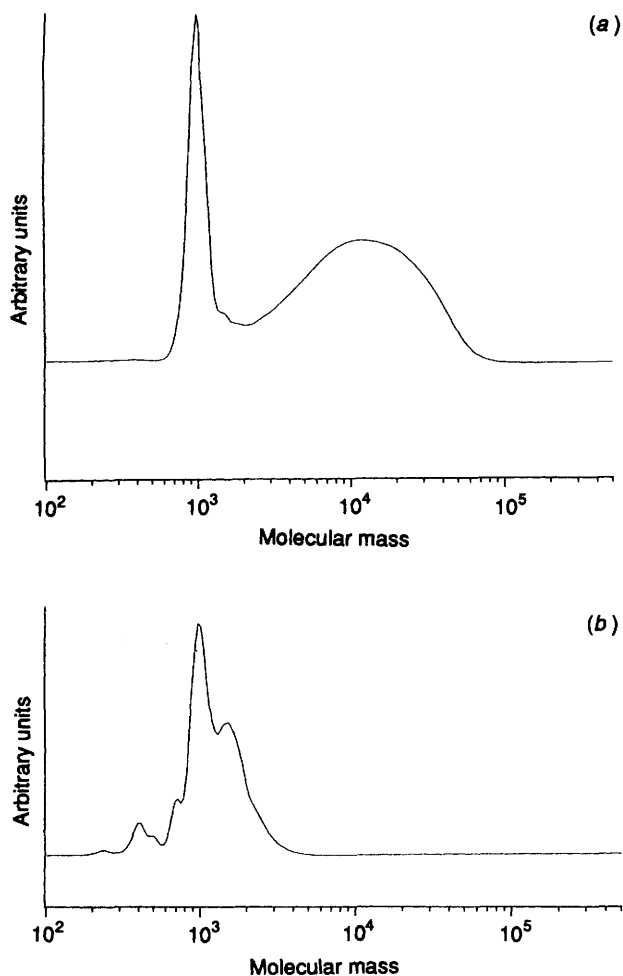


Fig. 1 Gel permeation chromatograms for polystannane samples obtained under conditions of (a) no solvent, and (b) in toluene solution ($M_w/M_n = 1400/1200$)

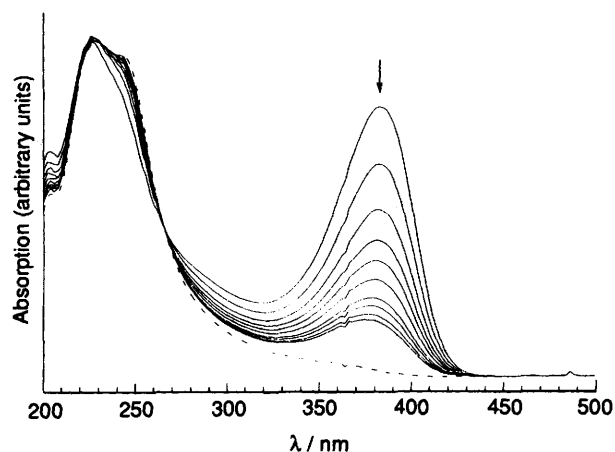


Fig. 2 The UV-VIS spectrum for $\text{H}(\text{SnBu}^n)_n\text{H}$ ($M_n = 7800$), showing the photobleaching behaviour in pentane solution upon irradiation by room light. Measurements were taken every 30 s; final spectrum is given by the dotted line.

is 365 nm. It has been established that the λ_{max} values increase with molecular mass, up to a limiting value, for polysilanes,¹ polygermanes,^{3,4} and polystannanes.^{5a-c} In addition, the corresponding $(\text{SiBu}^n_2)_n$ polysilane and $(\text{GeBu}^n_2)_n$ polygermane having limiting λ_{max} values of 314¹ and 333 nm,³ respectively. Thus, the polystannane reported here appears to possess relatively long, σ -conjugated chromophores. As might be expected these polystannanes are photosensitive, and photodegradation occurs upon exposure of the polymer to fluorescent room light (Fig. 2). Such photobleaching behaviour has been previously reported for polysilanes and polygermanes, and is of interest with respect to photoresist technology.¹ Whereas no emission (337.1 nm excitation; N₂ laser) was observed for the cyclic $(\text{SnBu}^n_2)_n$ oligomer, the higher molecular mass chains give rise to an emission band centred at 505 nm (solid state). By comparison, high molecular mass polysilanes are known to exhibit 20–30 nm Stokes-shifted emissions.¹

The results reported here are significant in that they show: (i) that high molecular mass polystannanes are available via a straightforward synthetic method, and (ii) that a metal-catalysed dehydropolymerization reaction can be useful in providing a polymer that is not readily obtained by other methods. Also, it appears that polystannanes may in general give rise to electronic absorptions that are significantly more red-shifted than their polysilane and polygermane counterparts.

We thank the Divisions of Chemistry and Materials Research at the National Science Foundation and Nikko Kyodo Co., Ltd., for their support of this research. We also thank Professor Michael Sailor for help in obtaining emission spectra.

Received, 14th June 1993; Com. 3/03423B

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