Wurtz synthesis of high molecular weight poly(dibutylstannane)

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Dibutyltin polymers with much higher molecular weights (GPC, polystyrene standards: M_n = *ca.* 1 × 10^6) than previously reported are prepared by Wurtz coupling of Bu_2SnCl_2 monomer; the reaction conditions are critical in achieving the maximum chain length, as polymer degradation results from prolonged reaction times.

The successful synthesis of high molecular weight polysilanes[1–3] has consigned to the history books the notion that only carbon of the Group 14 elements is capable of extensive catenation. Recent years have seen intense interest in this class of silicon polymer, fuelled by a wealth of potential applications in the electronic[4–6] and lithographic fields.[7] However, similar polymers centred on the heavier Group 14 elements have remained largely unexplored, presumably as a result of known M–M bond strengths, which decrease rapidly as Group 14 is descended. Polygermanes[8] have received some attention despite their relatively high cost, but until 1992 the longest $(R_2Sn)_n$ chain that had been reported contained only nine metal centres.[9] Zou and Yang[10] were the first to report higher molecular weight linear polymers, when they synthesised $(Bu_2Sn)_{\sim 60}$ by Wurtz coupling of Bu_2SnCl_2 using sodium dispersions in toluene catalysed by the addition of 15-crown-5. More recently, Tilley *et al.* have prepared similar polymers, but with a reported degree of polymerisation of *ca.* 80, by the dehydrogenation of Bu_2SnH_2 catalysed by, for example, $Me_2C(\eta^5\text{-}C_5H_4)_2Zr[Si(SiMe_3)_3]Me$.[11,12] The same study, however, failed to produce polymeric material by the Wurtz coupling route using conditions identical to those reported in 1992.[10]

As part of a synthetic study aimed at understanding the conformational properties of polystannanes, we had cause to optimise the conditions for the generation of $(R_2Sn)_n$ by the Wurtz method, using the commercially available monomer Bu_2SnCl_2 as precursor. Typical experimental conditions are as follows: A rigorously flame-dried Schlenk tube was charged with 15-crown-5 (0.1 mmol) and sodium dispersion (14.1 mmol; 30% mass dispersion in toluene) in freshly distilled Na/benzophenone–dried toluene (17 ml) under a nitrogen atmosphere. The whole vessel was wrapped in foil to exclude ambient light and Bu_2SnCl_2 (6.6 mmol) in toluene (4 ml) added. The resulting mixture was then heated at 60 °C for the appropriate length of time (see Table 1), filtered and the solvent evaporated *in vacuo*. Any traces of residual sodium were quenched by the addition of dry methanol (5 ml). The polymer was then isolated as a sticky brown solid by evaporation of the methanol. Samples for GPC† were taken by dissolving the material in THF or toluene, while ^{119}Sn NMR spectra were recorded in either $[^2H_6]$benzene or $CDCl_3$.

Table 1 Poly(dibutylstannane) synthesis by Wurtz coupling of Bu_2SnCl_2

Conditions	*t*/h	M_n (× 10^6)[a]	M_n/M_w	R[b]
60 °C, toluene	1	1.15	1.3	0.25
	2	1.17	1.3	0.33
	4.2	1.09	1.4	0.80
	5.5	0.91	1.3	0.10
with sonication	1	0.91	1.3	0.8
	2	0.93	1.4	0.3
	4	0.001	2.8	0.0

[a] GPC analysis relative to polystyrene standard; high molecular weight fraction only. [b] Ratio (high M_w/low M_w); low molecular weight refers to cyclic pentamers and hexamers with M_w = *ca.* 1000.

Table 1 shows the crucial dependence of the Wurtz coupling on reaction time. During the first 2 h of the reaction very little polymer is formed, and most of the product is low molecular weight cyclic oligomers which are characterised by sharp ^{119}Sn NMR chemical shifts of δ −203.0 and −204.2,‡ in good agreement with the work of Tilley.[12] The maximum yield of polymer occurs after *ca.* 4 h when remarkably high molecular weight materials‡ are formed (M_n = *ca.* 1 × 10^6) (Fig. 1).The equivalent values for the highest polystannanes previously produced are *ca.* 2 × 10^4,[12] and while more work is needed to define the relationship between polystyrene equivalent and true molecular weights for these novel materials, it is clear that extensive catenation of the metal has occured. Such chains are the longest yet reported and are comparable to the levels of polymerisation routinely observed with silane polymers.[1,2] However, prolonged reaction rapidly leads to chain scission, a phenomenon which has been observed previously in studies of the Wurtz coupling of R_2SiCl_2,[13,14] and the majority of polymer has been reconverted to cyclic oligomer after 5.5 h. We have also briefly examined the use of ultrasound to promote the Wurtz coupling reaction. Our work to date (Table 1) suggests that no improvement in the degree of polymerisation can be achieved by this variation. However, the time required to reach the optimal conditions is approximately halved, and after 4 h any high polymer has been totally degraded to cyclic oligomers.

The high molecular weight polystannanes we observe in these reactions§ are entirely consistent with the materials produced by dehydropolymerisation of R_2SnH_2.[12] δ(^{119}Sn; $CDCl_3$) occurs for the polymer at −178.9† and λ_{max} = 380 nm. The collective data now available for a range of linear diorganotin species (Fig. 2)[12,15] suggests that λ_{max} reaches a plateau value 380 nm [*cf.* 314 nm for $(R_2Si)_n$ and 333 nm for $(R_2Ge)_n$][2,16] though it has recently been shown that in thin film form this can be red-shifted by *ca.* 20 nm due to conformational

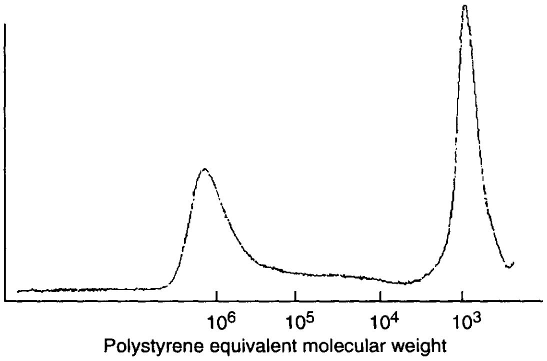

Fig. 1 A representative GPC trace (4 h reaction time) showing the formation of high molecular weight polystannane along with cyclic oligomers

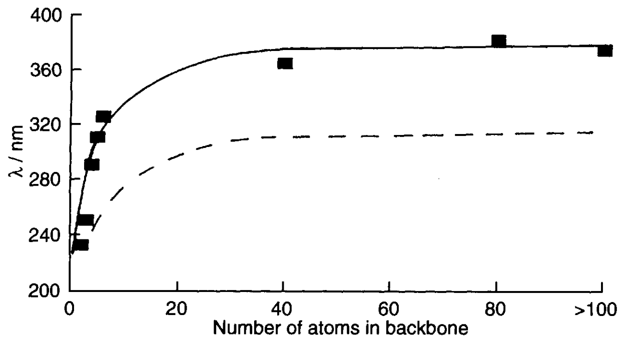

Fig. 2 The relationship between λ_{max} and chain length for $(R_2Sn)_n$ oligomers (n = 2–6)[15] and polymers.[12] Data from this work is shown with an unspecified degree of polymerisation of greater than 100 metal atoms. The broken line shows comparable data for $(R_2Si)_n$.[16]

ordering of the chains,[12] paralleling similar behaviour for polysilanes.[17]

Three points concerning the Wurtz coupling of diorganotin chlorides are worth making. Firstly, as with all polystannane preparations, the exclusion of ambient light is crucial to polymer formation and retention. This is particularly true during workup and spectral sample preparation, and while the polymer is in solution where photobleaching can occur within 1 or 2 min to convert a brown polymer to pale yellow oligomer. Secondly, the workup of the reaction mixtures resulting from Wurtz coupling are more exacting than the dehydropolymerisation route, since residual sodium must be quenched before GPC analysis. This will undoubtedly lead to a less reproducible product. Finally, our work has highlighted why previous studies have failed to observed the very polymeric stannanes that we have shown to exist. Typical Wurtz coupling reactions *e.g.* those carried out by Zou *et al.*,[10] were carried out over 14 h during which time polymer degradation will have become well advanced. The failure of Tilley *et al.* to produce polystannanes under the conditions used by Zou is entirely consistent with this assertion.[12]

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Footnotes

† Gel permeation chromatograms were recorded using THF as the eluent at 1 $cm^3 min^{-1}$ through a 60 cm 'PLGel mixed' column and refractive index detection. Ten polystyrene standards with molecular weights from 1050–2.65 × 10^6 were used as calibrants.

‡ The ^{119}Sn NMR chemical shifts of the cyclic species $(R_2Sn)_n$ in $CDCl_3$ (n = 5, δ −189.7; 6, δ −191.0) are shifted by approximately 10 ppm downfield from the values measured in $[^2H_6]$benzene. The polymer chemical shift in $CDCl_3$ (δ −178.9) is thus comparable with that measured by Tilley in $[^2H_6]$benzene (δ −189.6).

§ Analysis, found (calc. for $C_8H_{18}Sn$): C 39.4(41.2), H 7.55(7.74)%. The Mössbauer spectrum of the polymer (IS: 1.55; QS: 0.00; Γ 1.02 mms^{-1}) contains a small amount of Bu_2SnO (IS: 1.01; QS: 2.25; Γ 0.95 mms^{-1}) which is responsible for the slight discrepancy in the analytical data.

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