

# Synthesis of polystannanes in liquid ammonia

**Other Journal Item****Author(s):**

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**Publication date:**

2011-11-23

**Permanent link:**

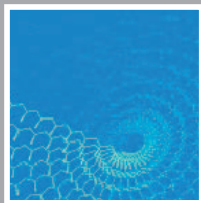
<https://doi.org/10.3929/ethz-b-000564714>

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**Originally published in:**

Chimia 65(11), <https://doi.org/10.2533/chimia.2011.876>



## Polymer and Colloid Highlights

Division of Polymers and Colloids

### Synthesis of Polystannanes in Liquid Ammonia

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**Keywords:** Organometallic polymers · Orientation · Sodium in liquid ammonia · UV-vis spectroscopy

Polystannanes feature a hitherto unique type of backbone: it consists of covalently bonded metal atoms (*cf.* Fig. 1).<sup>[1,2]</sup> Therefore, synthesis and materials properties of polystannanes are of fundamental interest for polymer science. Efficient synthesis of poly(dialkylstannane)s proceeds by polymerization of  $R_2SnH_2$  under the action of the catalyst precursor  $[RhCl(PPh_3)_3]$ .<sup>[3]</sup> This method, however, so far was not successful with aromatic substituents directly bound to the tin atoms. Using compounds of the type  $R_2SnCl_2$ , polymers and copolymers with  $R = \text{phenyl}$  could be synthesized in liquid ammonia comprising dissolved sodium (Fig. 1).<sup>[4]</sup>

Treatment of  $R_2SnCl_2$  ( $R = \text{phenyl}$  or alkyl) with 4 equiv. Na in liquid  $NH_3$  leads to a mixture of  $[Ph_2SnH]^-$  and  $[R_2SnSnR_2]^{2-}$ , but in the case of  $R = \text{alkyl}$  migration of these groups can also occur.<sup>[5]</sup> Exposure of such *in situ* prepared stannides with  $R^1Cl$  yielded  $SnR_2R^1_2$  and with  $R = \text{alkyl}$  also products with alkyl group migration. Accordingly, polystannane homopolymers and copolymers formed in a two-step procedure by *in situ* preparation of stannides that were subsequently converted with  $R_2SnCl_2$  (Fig. 1).<sup>[5]</sup> Alternatively, polystannanes could also be obtained by a one-step route upon treatment of  $R_2SnCl_2$  or  $R_2SnCl_2/R^1_2SnCl_2$  mixtures with 2 equiv. Na per Sn atom (Fig. 1). Thus, poly(dibutylstannane) and poly(diphenylstannane) were synthesized, the latter being insoluble in common solvents. Random  $SnPh_2/SnR_2$  copolymers with  $R = \text{butyl}$ , octyl or dodecyl, however, were partially soluble; typical weight average molar masses amounted to  $\sim 10^4$  g/mol.

Poly(dibutylstannane) featured an absorption maximum ( $\lambda_{max}$ ) at 390 nm in UV-vis spectra, due to delocalization of  $\sigma$ -electrons along the tin atoms in the polymer main chain. For poly(diphenylstannane), however, an absorption edge emerged around 480 nm, which is attributed to delocalization

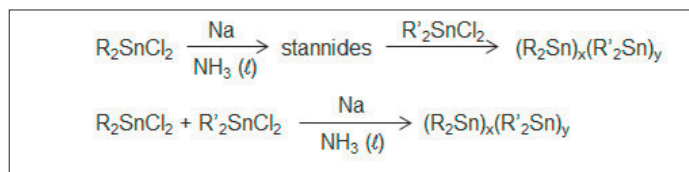


Fig. 1. Two synthetic routes for polystannane homopolymers ( $R = R^1$ ) and random copolymers in liquid  $NH_3$  in presence of Na.

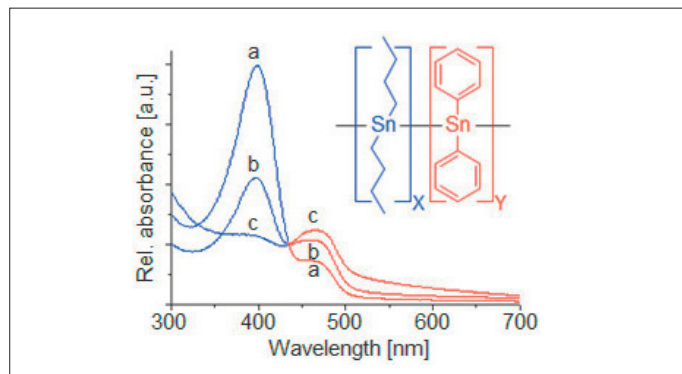


Fig. 2. UV/Vis absorption spectra of random copolymers synthesized in one-step reactions with  $Bu_2SnCl_2/Ph_2SnCl_2$  ratios of 3:1 (a), 1:1 (b) and 1:3 (c), respectively. The absorption maxima of the  $Bu_2Sn$  and  $Ph_2Sn$  units are color coded blue and red, resp.

of the electrons along the backbone and phenyl groups ( $\sigma$ - $\pi$  delocalization). The characteristic absorption wavelengths of the  $Sn(\text{alkyl})_2$  and  $Sn(\text{aryl})_2$  units were reflected in UV-vis spectra of the copolymers (Fig. 2).

The homopolymers and copolymers could be oriented simply by shearing and most of them also by crystallization onto oriented substrates and by drawing of blends with polyethylene. Typically the polystannane main chain oriented preferentially parallel to the direction of the external stimulus. Remarkably, however, the dodecylstannane segments of related copolymers in polyethylene blends oriented perpendicular, thus forcing the main chain to a perpendicular orientation to the direction of deformation.

Received: October 7, 2011

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