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Polystannanes: Polymers of a Molecular, Jacketed Metal–Wire Structure**

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Organometallic polymers comprising a backbone of covalently connected metal atoms can be regarded as molecular metal wires surrounded by a jacket of organic matter. Such polymers are rare and their materials properties are largely unexplored. Here, we report on polystannanes, $(\text{SnR}_2)_n$, that is, polymers with a backbone of tin atoms, which are synthesized by dehydropolymerization of dialkylstannanes (H_2SnR_2) with the catalyst $[\text{RhCl}(\text{PPh}_3)_3]$. The polystannanes feature reversible phase transitions into liquid-crystalline states, remarkably, even below room temperature, and, interestingly, oriented either parallel or perpendicular to external driving forces, depending on the length of the alkyl substituents.

1. Introduction

To our knowledge, tin is the only metallic element that has been reported to form organometallic polymers comprising a backbone of covalently bounded metal atoms, thus representing a molecular metal wire embedded in an organic jacket. Remarkably, the first oligo- or polystannanes were prepared by Löwig already in 1852,^[1] only two years after the first report on the isolation of organotin compounds.^[2] Löwig's compounds were produced by reaction of iodoethane with a Sn/K or a Sn/Na alloy in the presence of quartz sand, which was used to control the reaction rate. After purification and fractionation of the obtained products, compounds with elemental compositions close to those of oligo(diethylstannane) or poly(diethylstannane) were found, referred to as stannic ethyl. Cahours,^[3,4] who produced similar products, attributed their formation to a Wurtz reaction,^[5] which was also later used for the preparation of high-molar-mass poly(dialkylstannane)s.^[6–11] These polystannanes were, however, obtained in low yields and with (cyclic) oligomers as byproducts. Also, high-molar-mass polystannanes synthesized by electrochemical reactions^[12,13] or by catalytic polymerization of dialkylstannanes R_2SnH_2 under release of H_2 ^[11,14–17] typically contained significant

fractions of cyclic oligomers, and frequently the polymers were not isolated. As a consequence, little is known about their actual properties. Hence, the principal objective of our efforts reviewed here was to develop a facile, reproducible route to prepare and isolate polystannanes free of cyclic oligomers at high monomer conversion and to investigate their materials characteristics.

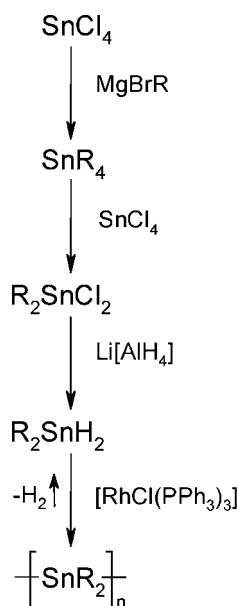
2. Polymerization

In our studies we found that out of approximately 30 tested transition metal complexes, $[\text{RhCl}(\text{PPh}_3)_3]$ (Wilkinson's catalyst) was the most suited catalyst to catalyze the polymerization of dibutylstannane, Bu_2SnH_2 , with virtually 100% monomer conversion without formation of detectable amounts of cyclic byproducts.^[18] More recently, we established that polymerization could be initiated by $[\text{RhCl}(\text{PPh}_3)_3]$ in dichloromethane also with other dialkylstannanes comprising linear alkyl groups ranging from ethyl to dodecyl, according to Scheme 1.^[19] Again, cyclic oligomers were not detected if the samples were well-protected from light during synthesis. When branched dialkylstannanes were used, however, polymerization was found to be highly sensitive to steric hindrance in the proximity of the tin atoms, as summarized in Scheme 2. Polymerization was observed to occur only if the tertiary carbon atom was separated from the tin atom by at least two methylene groups. Also, for monomers comprising only one bulky alkyl group per tin atom, such as $\text{H}_2\text{Sn}(\text{Bu})(\text{Bu})$ (c.f. Table 1),^[20] polymerization did not occur.

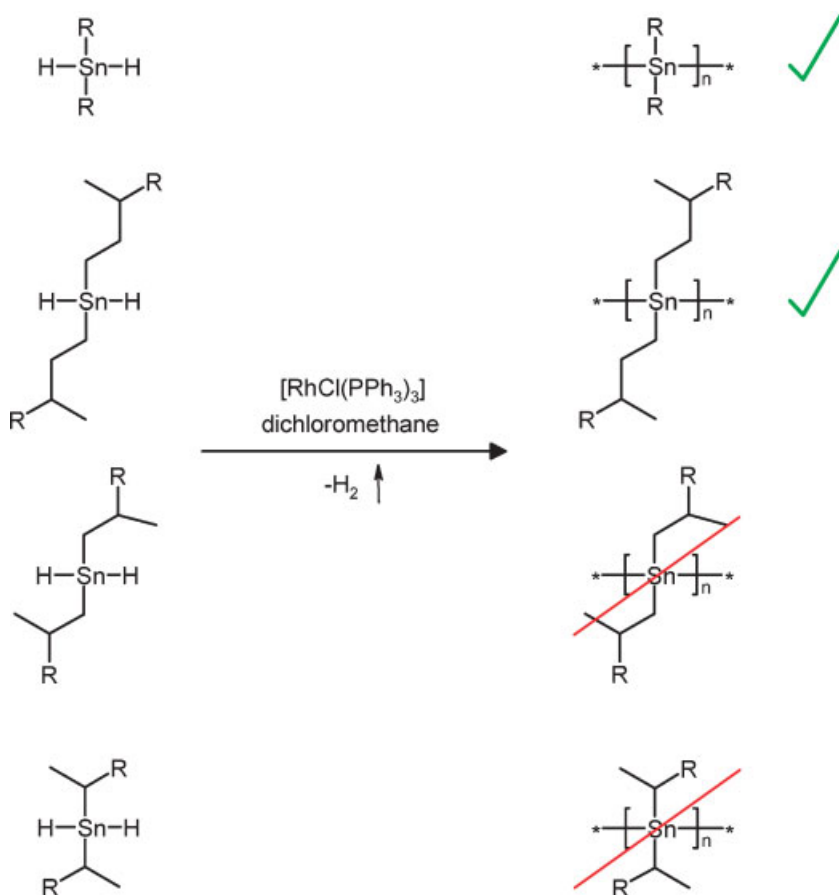
Synthesis of the polymer was conveniently monitored by ^{119}Sn NMR spectroscopy. As is evident from the data in

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Scheme 1. Reaction scheme for the synthesis of poly(dialkylstannane)s.



Scheme 2. Influence of the position of branching sites in dialkylstannanes on polymer formation. R denotes a linear alkyl group.

Table 1, the signals of the polymers were shifted to lower field by 10–15 ppm compared to those of the monomers. The polymers with linear alkyl groups displayed in most cases a chemical shift around -190 ppm, consistent with the literature;^[11,14,18] note that the chemical shifts of the ^{119}Sn peaks were influenced by branching rather than the length of the alkyl groups.

Molar masses of the synthesized polymers were estimated with gel permeation chromatography (GPC) calibrated with poly(styrene) standards, directly from reaction mixtures. The resulting number-average molar masses (M_n) of $10\text{--}40\text{ kg mol}^{-1}$ (Table 1) indicate the formation of polymers which contain ca. 90–300 tin atoms. The polydispersity was typically around 2.5, that is, in the common range of polymers prepared by radical polymerization or polycondensation. The molar mass of poly(dibutylstannane) could be adjusted by addition of tributylstannane (Bu_3SnH). At a $\text{HSnBu}_3/\text{H}_2\text{SnBu}_2$ volume ratio of 1:200–1:4 the molar mass of the polystannanes decreased pronouncedly with increasing tributylstannane fraction. Already a ratio of 1:200 lead to a reduction of the molar mass to 36% of the initial value, and only very short oligomers were found at a $\text{HSnBu}_3/\text{H}_2\text{SnBu}_2$ ratio of 1:4. Hence, tributylstannane either changes the catalytic active species or terminates polymerization by formation of an inactive end group.

Regarding the polymerization mechanisms, two basic concepts can be considered. The complex $[\text{RhCl}(\text{PPh}_3)_3]$ might assist random condensation of dialkylstannanes, as proposed for polymerization with Zr catalysts.^[11] Hereby, dimers are formed first, which subsequently grow step-wise to polymers. The characteristic attribute of this mechanism is that polymers of considerable mass (ca. 2000 g mol^{-1}) form only at high monomer conversion ($>90\%$). Alternatively, the polymer chain might grow at a single rhodium atom by continuous addition of monomer to that rhodium atom, followed by insertion of the added monomer into the growing polymer chain (c.f. Fig. 1). In this case, high molar masses are obtained already from the beginning of polymerization. Clearly, these mechanisms can be distinguished by determination of the molar mass at different monomer conversion, which was followed by measurement of H_2 released during polymerization. As the molar mass of the poly(dibutylstannane) did not strikingly change during monomer consumption, a mechanism with a chain growth at the catalyst appears more likely, for example, by stannylene insertion analogous to dehydropolymerization of germanes to polygermanes with a Ru catalyst.^[21]

Table 1. ^{119}Sn NMR data of monomers and polymers recorded in (a) toluene- d^8 or (b) dichloromethane- d^2 [a].

R ¹	R ²	^{119}Sn NMR [ppm]		GPC [kg mol ⁻¹]	DSC [°C]	
		H ₂ SnR ¹ R ²	(SnR ¹ R ²) _n		T ₁	T ₂
Et	Et	−182 (a)	−172 (b)	31/13	15	–
Pr	Pr	−208 (a)	−195 (a)	27/10	93	–
Bu	Bu	−204 (a)	−191 (a)	91/36	1	–
Pe	Pe	−204 (a)	−192 (a)	48/19	6	57
Hex	Hex	−204 (a)	−193 (b)	76/31	34	68
Oc	Oc	−204 (a)	−192 (b)	97/40	29	74
Dod	Dod	−204 (a)	−189 (a)	28/19	55	91
^t Bu	^t Bu	−117 (a)	no polymer	–	–	–
^t Bu	Bu	−153 (a)	no polymer	–	–	–
Bu-2-Me	Bu-2-Me	−232 (b)	no polymer	–	–	–
Bu-3-Me	Bu-3-Me	−197 (a)	−187 (a)	27/13	16	37

[a] Molar masses of the polymers were measured with gel permeation chromatography (GPC) and endothermic transition temperatures were obtained from the second run in differential scanning calorimetry (DSC) thermograms. M_w : weight-average molar mass. M_n : number-average molar mass. Et = ethyl, Pr = propyl, Bu = butyl, Pe = pentyl, Hex = hexyl, Oc = octyl, Dod = dodecyl, ^tBu = *tert*-butyl, Bu-2-Me = 2-methylbutyl, Bu-3-Me = 3-methylbutyl.

3. Thermal Properties and Blends

The polystannanes could simply be isolated from the reaction mixtures by precipitation after cooling the reaction solutions to -78°C (yields 65%–90%). The polymers featured a characteristic yellow color which might be attributed to the σ -conjugation of the Sn atoms in the polymer backbone. Accordingly, the absorption maxima of the polystannanes were located at around 380 nm. The polystannanes were thermally stable under nitrogen atmosphere. Mass loss was detected by thermogravimetric analysis (TGA) only after ca. 250°C .

Differential scanning calorimetry (DSC) of the polystannanes in the range between -50°C and 120°C revealed reversible phase transitions for all polymers (Table 1). Their phase behavior strongly depended on the side chains. More specific, polystannanes with side groups comprising less than

five carbon atoms showed only one, and those with more carbon atoms two, phase transitions. Below the (first) transition temperature T_1 , all polystannanes displayed strong birefringence when observed between crossed polarizers, which implies that the polymer molecules are present at least partially in an ordered state. Upon heating above T_1 (see Table 1) the materials became soft due to an increase in mobility of the polymer chains. In the case of polystannanes with six or more carbon atoms per side group the birefringence became significantly weaker after T_1 and vanished after T_2 (upon cooling the birefringence reappeared at low temperatures). For the polystannanes with shorter alkyl chains, however, no change in birefringence was visible upon heating above T_1 . These observations lead to the conclusion that the polymers with shorter side chains are present in a liquid-crystalline state at room temperature.^[18] Remarkably, the phase transition of poly(dibutylstannane) at 1°C was also reflected in electrical charge mobility measurements.^[22] Upon heating from -50°C , the charge mobility dropped around 0°C from approximately $0.1\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ to $0.03\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$. The latter value is in the range of polysilanes and polygermanes mesophases.

Blends of ultra-high-molar-mass polyethylene and polystannanes (up to 70% w/w) were prepared by mixing both components in *p*-xylene at 130°C followed by casting and drying. Blends with polystannane contents $\leq 40\%$ w/w could be drawn on a hot stage at ca. 110°C to 7–40 times the original length. The resulting tapes were rather transparent and suitable for polarized UV-vis spectroscopy. A pronounced dichroism is manifested in the wavelength region of polystannane absorption (see Fig. 2). The dichroic ratios at the maximum absorption wavelength were in the range of 10–35, indicating that the polystannane chains were highly oriented. For poly(dibutylstannane) the absorbance was highest parallel to the drawing direction and lowest perpendicular to it, while – most remarkably – the opposite was observed for poly(didodecylstannane). Thus, the poly(dibutylstannane) back-

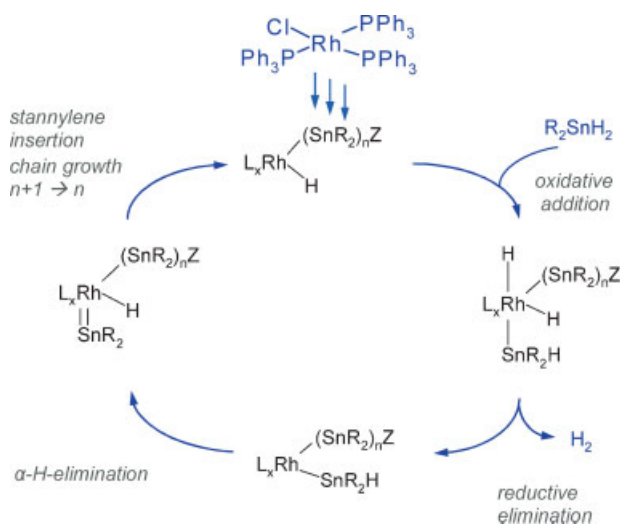


Figure 1. Schematic of a possible reaction path of the polymerization of dialkylstannanes catalyzed by $[\text{RhCl}(\text{PPh}_3)_3]$.

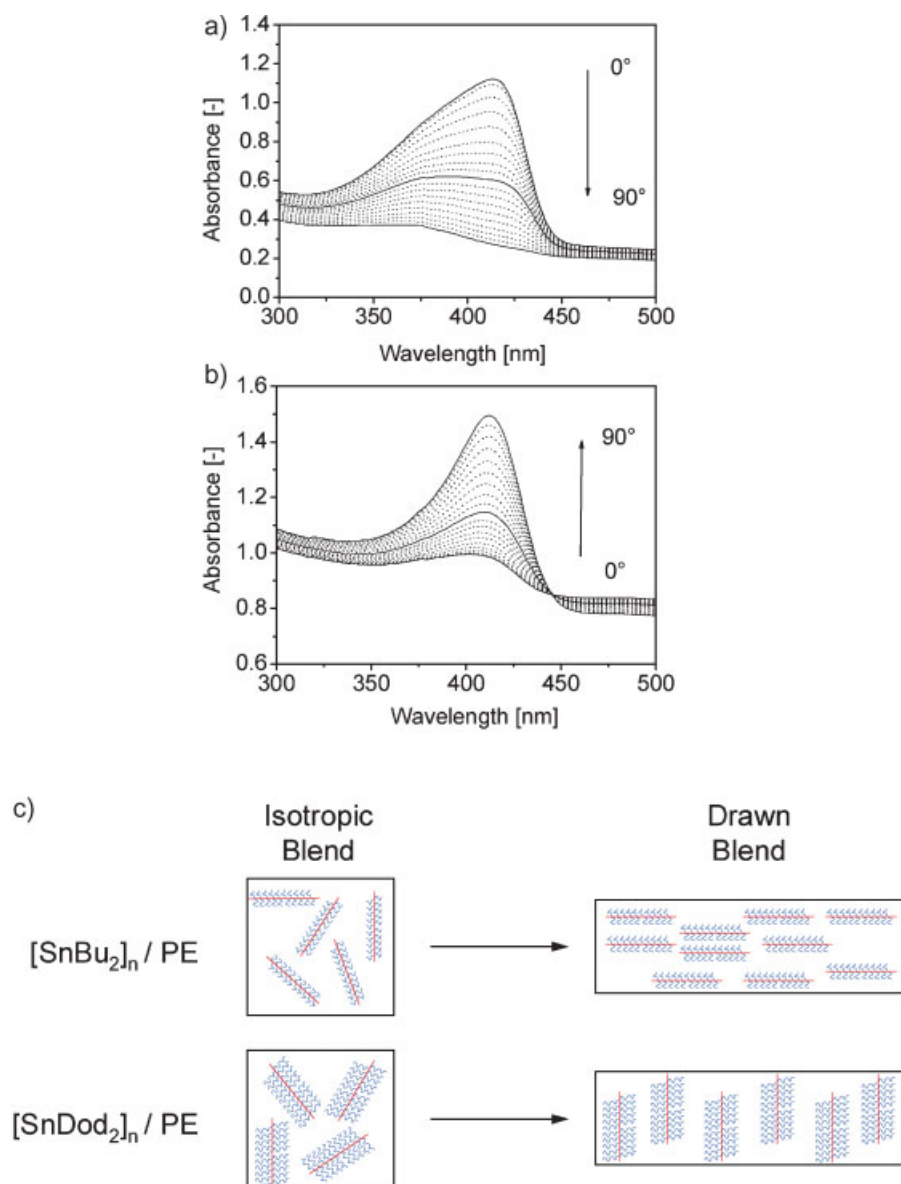


Figure 2. Optical absorption spectra of drawn blends comprising polyethylene and 25% w/w polystannane, recorded with polarized light at different angles φ between the polarization plane of the light and the drawing direction. a) poly(dibutylstannane), b) poly(didodecylstannane). Note the opposite angle dependence for both polymers, indicative of orientation of the polymers, resp., parallel and perpendicular to the direction of drawing (c).

bone oriented *parallel*, but the poly(didodecylstannane) backbone *perpendicular* to the direction of drawing. It appears therefore that in the case of poly(didodecylstannane) the long dodecyl side groups and not the polystannane backbone align in the drawing direction and, therewith, force the backbone to adopt a perpendicular orientation to it (Fig. 2c).

4. Perspectives

As polystannanes can readily be prepared with a variety of side groups, including mixtures thereof, their thermal transi-

tions can be adjusted to specific demands, which might be of interest in the context of electrical conductivity.^[22] Because the polystannanes can be oriented with simple techniques, anisotropic electrical conductivity could result, in particular after enhancement of the electrical conductivity by treatment with chemical agents such as SbF_5 .^[11] However, it has to be noted that the poly(dialkylstannane)s prepared so far are sensitive to light. Thus, stabilization of polystannanes, for example by incorporation of light-absorbing side groups, is an important challenge for future studies.

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- [19] SnR_4 was prepared by Grignard reaction of an alkylmagnesium bromide with SnCl_4 . The resulting compounds were thereafter converted at high temperatures with an equimolar amount of SnCl_4 to

R_2SnCl_2 . The dialkyltin dichlorides were subsequently reduced with $Li[AlH_4]$ to R_2SnH_2 .

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product of $BuSnCl_3$ with iBuMgBr (in diethylether); yield 24%; ^{119}Sn NMR: $\delta = 99$ ppm. $H_2Sn(^iBu)(Bu)$ was prepared by reduction of $Cl_2Sn(^iBu)(Bu)$ with $Li[AlH_4]$.

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