POLYSTANNANES – Reaction Mechanism and Products

A dissertation submitted to

ETH ZURICH

for the degree of

Doctor of Sciences

presented by

MARKUS TRUMMER

DI

22.03.1980

citizen of Austria

accepted on the recommendation of

Prof. Paul Smith, examiner

Prof. Walter Caseri, co-examiner

Prof. Frank Uhlig, co-examiner

PD Dr. Wolfram Uhlig, co-examiner

2011
Summary

Polystannanes are specified by a polymer main chain consisting of covalently interconnected tin atoms, which is to our knowledge unprecedented for other metals and therefore of fundamental interest. Due to the delocalization of the electrons in the polymer backbone (σ-delocalization), polystannanes are potentially appealing materials concerning their chemical, optical, thermal and electrical properties.

The first synthesis providing pure high molar mass polystannanes was based on dehydropolymerization of dialkylstannanes (H₂SnR₂) with the catalyst [RhCl(PPh₃)₃] (Wilkinson’s catalyst). This route allows to obtain and isolate pure linear poly(dialkylstannane)s without cyclic oligomers; but on the other hand, has some substantial drawbacks. In particular, this method has so far not been suited to synthesize poly(diarylstannane)s. Hence, to create such materials a new synthetic route is required, for instance reaction of dichlorodiorganostannanes in liquid ammonia.

It has frequently been proposed that diorganostannide dianions, SnR₂²⁻, form during reactions of dihalodiorganostannanes with sodium in liquid ammonia. The formation of this intermediate has been advanced to be an important step in the synthesis of polystannanes. However, our investigations conducted with ¹¹⁹Sn NMR spectroscopy in liquid NH₃ of reaction intermediates formed in-situ during the exposure of dichlorodiphenylstannane, dichlorodibutylstannane and dichlorodioctylstannane to a stoichiometric amount of sodium (i.e. 4 molar equivalents sodium per tin atom) unveiled that the proposed SnR₂²⁻ dianion was not present. Tetraorganodistannides, (R₂Sn-SnR₂)²⁻, and hydrodiorganostannides (tin hydri-
des), R₂SnH⁻, were detected instead. Also, products resulting from mixtures of R₂SnCl₂/Na ratios of 1:3 to 1:10 were soluble and, hence, could be studied in-situ in liquid ammonia with ¹¹⁹Sn NMR spectroscopy. The composition of the respective compounds was found to be essentially independent of the R₂SnCl₂/Na ratio. Our experiments showed that the chemical structure of the in-situ generated species did not permit to draw conclusions about the composition of the corresponding reaction products with bromoethane and vice versa – a practice commonly employed. Furthermore, we observed migration of butyl groups both in-situ during the reaction of dichlorodibutylstannane with sodium in liquid ammonia, as well as in the final reaction products. By contrast, in the case of phenyl substituents, migration was not detected in liquid ammonia, unless a large excess of sodium was present. These observations imply a different mechanism for butyl and phenyl group migration.

At a molar ratio of R₂SnCl₂/Na of 1:2, polystannanes precipitated from the reaction mixture, in some cases accompanied by cyclic oligostannanes. Therefore, in the case of dichlorodibutylstannane, Bu₂SnCl₂, and dichlorodiphenylstannane, Ph₂SnCl₂, two different reaction pathways could be applied: the monomers were either directly treated with 2 molar equivalents of sodium, or the reactive organostannides formed in-situ were further converted with the respective R₂SnCl₂. The polymers obtained with the new synthesis route were compared to the products obtained in polymerization with Wilkinson’s catalyst and tetramethylethylenediamin (TMEDA). The route employing Wilkinson’s catalyst was most beneficial for preparation of poly(dibutylstannane) and TMEDA for polystannanes containing at least one aromatic group per Sn atom, whereas synthesis in Na/NH₃ yielded best results for polystannanes comprising two aromatic groups per Sn atom – poly(diarylstannane)s.
To expand the range of polystannanes, poly(diarylstannane)s and copolymers of dialkylstannanes (butyl, octyl and dodecyl) and diarylstannanes were synthesized and characterized. UV/Vis absorption spectroscopy unveiled the presence of σ-delocalization and σ-π-delocalization in the copolymers with the σ-π-delocalization originating from the SnPh_2 moieties in the polymer. The copolymers were mainly soluble, dichroic materials which could easily be oriented. Depending on the length of the alkyl side chain, the orientation was parallel or perpendicular to the direction of external stimuli.

Finally, the influence of pendant side groups on the stability towards light of polystannanes in solution was studied; more specifically poly[bis(4-butylphenyl)stannane] and poly(dibutylstannane) in solutions of tetrahydrofuran and dichloromethane. In both solvents, the poly(diarylstannane) was found to be more resistant towards light than the poly(dialkylstannane). Experiments with laser flash photolysis and gel permeation chromatography (GPC) analysis of irradiated polymer solutions resulted in the conclusion that two different decomposition mechanisms can occur: either random scission of polymer chains or unzipping, depending on the polymer architecture and the nature of the solvent.


Generell wurde bis anhin in der Literatur davon ausgegangen, dass die Umsetzung von Dichlordiorganostannanen mit Natrium in flüssigem Ammoniak zur Bildung des Dianions R₂Sn²⁻ führt. Die entstehenden Produkte sind ein wichtiger Schritt bei der Umsetzung zu Polymeren und wurde deswegen mittels \textit{in-situ} \textsuperscript{119}Sn NMR Messungen in flüssigem Ammoniak genauer untersucht. Dabei zeigte sich, dass bei einer stöchiometrischen Umsatz (4 molare Äquivalente Natrium pro Zinn-Atom) das Dianion R₂Sn²⁻ nicht gebildet wird. In der Lösung detektiert wurden Tetraorganodistannide (R₂Sn-SnR₂)²⁻ und Diorganohydrostannide R₂SnH⁻. Auch durch die Veränderung des Stannan : Natrium

Durch die Herstellung von Poly(diarylstannan)en und Copolymeren zwischen Dialkylstannanen (Butyl, Octyl, und Dodecyl) und Diarylstannanen wurde der Bereich der zugänglichen Materialien deutlich erweitert. Mittels UV/Vis Spektroskopie wurde die $\sigma$-Delokalisierung des aliphatischen- und die $\sigma$-$\pi$-Delokalisierung des aromatischen Anteils in den Polymeren verdeutlicht. Die Copolymere sind größtenteils lösliche, dichroitische Materialien, die leicht orientierbar sind. Je nach Länge der Alkyl-Seitenkette orientiert sich die Sn-Sn Hauptkette parallel oder senkrecht zur Orientierungsrichtung.