



Stability of polystannanes towards light

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ABSTRACT

The influence of pendant side groups on the stability of polystannanes against light 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). Degradation was particularly rapid in tetrahydrofuran (THF) but was markedly retarded in presence of the radical scavenger 2,6-di-*tert*-butyl-4-methylphenol (BHT). Experiments with laser flash photolysis indicated that the superior stability of poly[bis(4-butylphenyl)stannane] was not a result of more stable Sn–Sn bonds but due to recombination of relatively long-living radicals. By contrast there was no evidence for such a process in the case of poly(dibutylstannane). Different reaction pathways of the degradation of polymer molecules themselves were identified by gel permeation chromatography (GPC) analysis of irradiated polymer solutions, leading to the conclusion that two different decomposition mechanisms can occur: i.e. either random scission of polymer chains or unzipping, depending on the polymer architecture and the nature of the solvent.

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1. Introduction

Polystannanes are a unique class of polymers as their backbone consists of covalently bound metal atoms, which, to our knowledge, has not been reported so far with any other metal element. These species were first described by Löwig [1] but gained wide interest in the field of organometallic polymers only in recent years [2–11], often with a view to their thermal, optical and electronic properties [2,5,6]. However, a considerable drawback of these materials is their limited stability towards light, in particular when in solution [4]. The light stability and degradation of linear polystannanes was studied comprehensively only recently [4], exemplary with poly-(dialkylstannane)s, after a facile synthesis method for such polymers was developed (Fig. 1). Results from this study indicated that, depending on the solvent, cyclic oligo(dialkylstannane)s or reaction products with the solvent formed as degradation products.

The stability of poly(diarylstannane)s against light is likely to considerably deviate from that of poly(dialkylstannane)s, as it was reported that the photochemical behaviour of silanes and polysilanes with aryl groups differs significantly from that of related alkyl-substituted compounds [12–15]. Furthermore, replacement

of methyl by phenyl groups in polysiloxanes is known to result in enhanced stability [16–21]. Thus, we devoted this study to a comparison of stability against light of polystannanes with aromatic and aliphatic groups, exemplary for poly[bis-(4-butylphenyl)stannane] and poly(dibutylstannane), and attempted to unveil the mechanism of degradation.

Poly[bis(4-butylphenyl)stannane] was selected since unsubstituted poly(diphenylstannane) – contrary to poly(dibutylstannane) which dissolves in common organic solvents like dichloromethane, toluene, tetrahydrofuran (THF) and hexane – is a rather intractable species that does not dissolve in common solvents even at elevated temperatures, whereas the derivatized version is not, which allows to compare the stability of poly-(dialkylstannane)s and poly-(diarylstannane)s under equivalent conditions.

In addition to irradiation experiments of the polystannanes in different solvents with light of defined wavelengths in a UV/Vis spectrophotometer and under a so-called daylight lamp, also laser flash photolysis was employed. This method was previously used extensively for the characterization of compounds based on elements of the group 14 in the periodic table. In these studies photo-degradation intermediates were investigated ranging from low molar mass alkyl- and aryl-substituted carbon-, silicon-, germanium- and tin-centred compounds [12,13,22] to cyclic and linear oligomeric and polymeric silanes with aryl and alkyl side groups [14,15,23–30].

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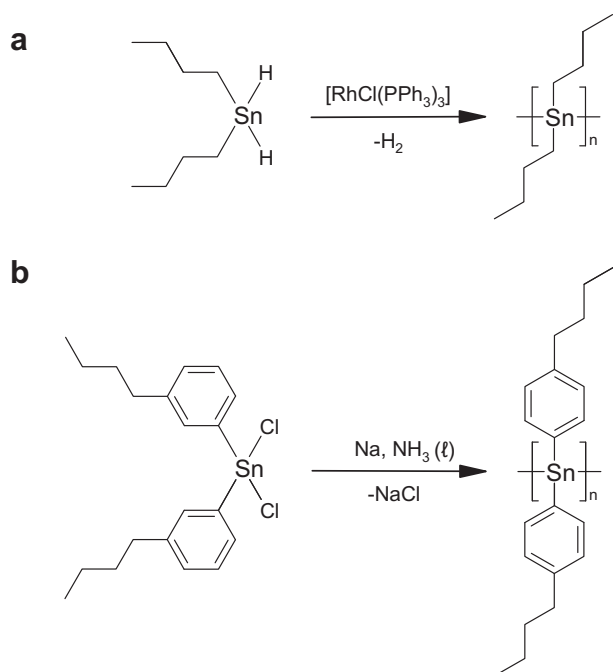


Fig. 1. Schematic representation of the synthesis and structure of (a) poly(dibutylstannane) and (b) poly[bis(4-butylphenyl)stannane].

2. Experimental

2.1. Materials

Ammonia was purchased from PanGas (Dagmarsellen, Switzerland, 99.999%) and dichlorodibutylstannane from ABCR GmbH (Karlsruhe, Germany). The latter compound was recrystallized twice by dissolution in boiling pentane and subsequent precipitation at -20°C . Dichlorobis(4-butylphenyl)stannane was synthesized according to recently published methods [31]. Organic solvents were acquired from Fluka (Buchs, Switzerland), except the inhibitor-free tetrahydrofuran (THF), which was ordered from Sigma-Aldrich (Buchs, Switzerland; typical commercial THF is stabilized with 250 ppm of the radical scavenger 2,6-di-*tert*-butyl-4-methylphenol).

2.2. Methods

2.2.1. Synthesis of poly[bis(4-butylphenyl)stannane]

Sodium (8 mmol) was dissolved in 90 mL of liquid ammonia at -78°C by stirring for 15 min. To this solution, a quantity of dichlorobis(4-butylphenyl)stannane (2 mmol) dissolved in 10 mL THF was added through a septum and stirred for 30 min. Subsequently, the flask was completely wrapped with white soft tissue and surrounded by aluminum foil; another portion of dichlorobis(4-butylphenyl)stannane (2 mmol) dissolved in 10 mL THF was added through a septum. The polymer precipitated after about 10 s–15 s. After two minutes, the ammonia was evaporated by warming the reaction solution to room temperature under a nitrogen stream, and the THF was removed at room temperature *in vacuo* (about 0.1 mbar, 12 h). The resulting solid was dissolved in dichloromethane, insoluble residues were filtered off, the solvent was removed and the residue dried again (0.1 mbar, 24 h). The polymer (dissolved in THF) possessed a molar mass at the peak maximum of gel permeation chromatography (GPC) diagrams M_p of 8.5 kg/mol, employing a PL gel 5 μm Mixed-D column from Polymer Laboratories Ltd. (Shropshire, United Kingdom) with THF

as eluent. The calibration was performed with atactic-poly(styrene) standards.

2.2.2. Synthesis of poly(dibutylstannane)

Poly(dibutylstannane) was synthesized according to previously reported procedures [3,5] by dehydropolymerization starting from dihydrodibutylstannane with Wilkinson's catalyst. It possessed a molar mass M_p of about 15 kg/mol according to GPC analysis in THF.

2.2.3. UV/Vis exposure

Solutions of ca. 0.01 mg/mL poly[bis(4-butylphenyl)stannane] or poly(dibutylstannane) in THF (stabilized and unstabilized) or dichloromethane, respectively, were prepared at room temperature in the air and protected from light prior to the exposure experiments. UV/Vis absorption measurements were performed with a Perkin Elmer Lambda 900 (Schwerzenbach, Switzerland) spectrophotometer. The experiments were conducted by means of scans between 500 nm and 300 nm at a constant scan speed of 214.29 nm/min, a 5 nm slit, an integration time of 0.24 s and a data interval of 1 nm. All spectra shown in this report stem from a series which was analyzed within the same week to ensure constant conditions since the intensity of the lamp is also depending on the lamp's lifetime.

2.2.4. "Daylight-lamp" irradiation; GPC analysis

Solutions of 2 mg/mL of poly[bis(4-butylphenyl)stannane] and poly(dibutylstannane), respectively, were prepared in the dark in stabilized THF in the air and directly measured with gel permeation chromatography. Subsequently the GPC vial with the polymer solution was irradiated with an Osram Dulux S Luminux 7 W/860 (Daylight) lamp (Jeker Leuchten AG, Zurich, Switzerland) in a closed irradiation box with a distance of 13 cm between sample and lamp, as also described previously [4]. Irradiation times are indicated in the corresponding figures. Measurements in CH_2Cl_2 were performed by irradiation of polystannanes solutions (~ 20 mg/mL) in a Schlenk tube and subsequent dilution of 0.2 mL in 2 mL THF in the GPC vial.

2.2.5. Laser flash photolysis

Polymer solutions of a concentration of ca. 0.01 mg/mL in THF (stabilized) and dichloromethane were used in the air and thoroughly protected from light. 2 mL of the solutions were transferred into quartz glass cuvettes and UV/Vis absorption spectra were recorded. Subsequently, laser flash photolysis was carried out with the third harmonic (355 nm) of a Brilliant B YAG laser (Quantel, Les Ulis, France) coupled to an Applied Photophysics LKS 50 (Leatherhead UK) instrument. Briefly, in this technique a sample is irradiated by a laser pulse while a single beam UV/Vis spectrometer records time-resolved spectral information, in our case with sampling rates up to 100 MHz (setup see Fig. 2). The 5 ns laser

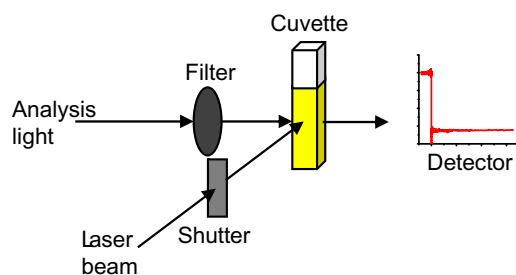


Fig. 2. Setup for flash photolysis experiments with a laser pulse energy of 60 mJ/pulse at 355 nm. The intensity of the analysis light beam was reduced with a cut-off filter at 370 nm and grey filter with 5% transmission to avoid degradation of the sample upon irradiation of the analysis light. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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