Synthesis and Photochemical Reactions of Polystannanes

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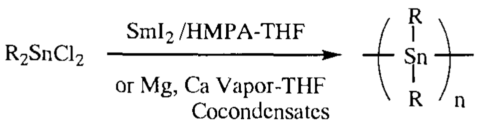
Several polystannanes were synthesized by the reaction of dichlorostannanes with samarium (II) diiodide and alkali earth metal (Mg, Ca) vapor-solvent cocondensates. Laser flash photolysis of the polystannane involved Sn-Sn bond homolysis to yield mainly polystannyl radicals.

σ-Conjugated polymers such as polysilanes, polygermanes, and polystannanes have attracted considerable interest in recent years because of their unique chemical, physical, and optical properties, and potential applications.[1-3] Much attention is therefore being directed towards the development of synthetic routes and the study of their properties. However, the study of polystannanes is very much limited compared with those of polysilanes and polygermanes.[4] In this paper, we describe new synthetic procedures of polystannanes under mild conditions, and their photodegradation probed by laser flash photolysis and trapping experiments.

The most practical method for synthesizing polystannanes is a Wurtz-type coupling polymerization of tin dihalides with alkali metal (Kipping method). These reactions are usually carried out under harsh conditions and often lead to low yields of the polymers. Sodium metal often leads to the degradation of high molecular weight of the polystannanes due to the weak Sn-Sn bond. Moreover, such reactions, in which moisture-sensitive alkali metals are used, can be hazardous. To circumvent these problems, we tried new synthetic procedures for the formation of polystannanes using SmI_2 and alkali earth metal (Mg, Ca) vapor-solvent cocondensates under mild conditions (eq. 1). Their results are summarized in Table 1.



$$R_2SnCl_2 \xrightarrow[\text{or Mg, Ca Vapor-THF Cocondensates}]{SmI_2/\text{HMPA-THF}} \left(\begin{array}{c} R \\ | \\ Sn \\ | \\ R \end{array} \right)_n \qquad (1)$$

R=alkyl

SmI_2 has been applied in a wide variety of carbon-carbon bond formation reactions as a mild one-electron reducing agent. In Table 1, SmI_2 is a useful agent for the polycondensation of tin dichlorides under mild conditions (entries 1, 2, and 5).[5] The resulting polystannanes had a narrow molecular weight distribution (M_w/M_n=1.2-1.5) that included molecular weights (M_w > 10^3). In particular, poly(diethylstannylene), $(Et_2Sn)_n$, (**2**) was obtained in good yield and high molecular weight (entry 2). Mg and Ca vapors when cocondensed with THF at 77 K are also effective agents[6] for the synthesis of polystannanes, although yields are relatively low (entries 3 and 4) in Table 1. Reaction conditions are mild and manipulations are simple. The difference of UV absorption bands of **2** may be mainly ascribed their molecular weights (entries 2-4). The UV spectrum of **2** in THF is shown in Figure 1.

Table 1. Polymerization of R_2SnCl_2

Entry	R_2SnCl_2	Conditions	λ_{max}/nm[a]	M_w[b]	M_w/M_n	Yield/%[c]
1	Me_2SnCl_2 (**1**)	SmI_2[d]	285	1120	1.49	19.1
2	Et_2SnCl_2 (**2**)	SmI_2[d]	368	4820	1.21	74.4
3	Et_2SnCl_2 (**2**)	Mg[e]	350	4100	1.25	5.0[f]
4	Et_2SnCl_2 (**2**)	Ca[e]	340	3700	1.15	5.0[f]
5	Hex_2SnCl_2 (**3**)	SmI_2[g]	305	2770	1.18	5.8

[a] in THF. [b] Determined by GPC based on polystyrene standard. [c] Isolated yields. [d] SmI_2 (2 equiv.) in HMPA-THF, r.t., 24 h. [e] in THF, r.t., 1 h. [f] Based on amount of metal used. [g] SmI_2 (2 equiv.) in HMPA-THF, r.t., 120 h.

The polystannanes prepared in this study showed characteristic electronic absorption bands at 285-368 nm. As expected, the polymers were quite light sensitive. Upon irradiation of cyclohexane solutions of **2**, M_w=4200, with a 110-W low-pressure Hg arc lamp (λ=254 nm) at room temperature, lower molecular weight chain fragments (M_w=1190) were obtained by chain scission. These phenomena were verified by GPC examination and UV spectroscopy of irradiated samples. To obtain information regarding intermediates of photodegradation of polystan-

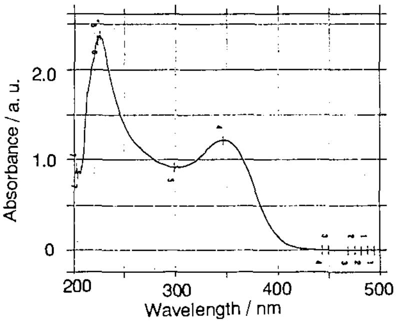


Fig. 1. UV spectrum of $(Et_2Sn)_n$ in THF.

nanes, laser flash photolysis was carried out.

Laser flash photolysis (λ=266 nm, pulse width 5 ns, power 10 mJ/pulse)[7] of poly(dimethylstannylene), $(Me_2Sn)_n$, (**1**) and **2** (ca. 10^{-3} M) in cyclohexane at 293 K gave transient absorption bands at 400 nm. The transient absorption spectrum of **2** is shown in Figure 2. The transient peak at 400 nm may be assigned to that of a polystannyl radical from comparison of its spectral characteristics with those of similar stannyl radicals generated by abstraction of hydrogen of stannane with *tert*-butoxyl radical.[8,9] This assignment was further substantiated by quenching experiments with the stannyl radical trapping agents oxygen and alkyl halides. The transient in the presence of oxygen decayed with pseudo-first-order kinetics (k=7.6 x 10^9 and 2.0 x 10^9 $s^{-1}M^{-1}$ for **1** and **2**, respectively). Addition of hexyl bromide quenched very slowly the transient absorption (k=1.4 x 10^5 and < 10^5 $s^{-1}M^{-1}$ for **1** and **2**, respectively).

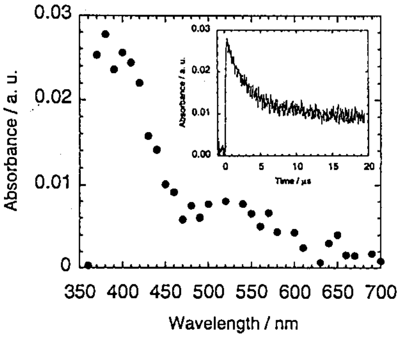


Fig. 2. Transient absorption spectra observed at 1 μs after excitation of the THF solution of $(Et_2Sn)_n$. Insert: Absorption-time profiles at 400 nm.

Along with laser flash photolysis, product studies were carried out by photolyzing **1**, (ca. 5.0 x 10^{-4} M) in cyclohexane with a 110-W low-pressure Hg arc lamp at room temperature for cyclohexane solutions of **1** containing chloroform were similarly irradiated. Tetrachloroethane was obtained 30 min under argon. To trap possible intermediates, as the main product (29.4%). The presence of tetrachloroethane is consistent with the intermediacy of polystannyl radicals generated by Sn-Sn bond homolysis. Photogenerated polystannyl radicals abstract a chlorine from chloroform to give polystannyl chlorides and dichloromethyl radical. The dichloromethyl radical dimerizes to form tetrachloroethane. The formation of polystannyl chlorides could not be detected.

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