Electrochemical synthesis of dialkylsubstituted polystannanes and their properties

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Poly(dibutylstannane) and poly(dioctylstannane) were obtained by electrochemical polymerization of dibutyldichlorostannane and dioctyldichlorostannane, respectively, in a one-compartment cell equipped with a platinum cathode and a silver anode, using tetrabutylammonium perchlorate and DME as the supporting electrolyte and the solvent, respectively.

Polystannanes have attracted the attention of many researchers,[1–4] because heavier atoms in the backbone of σ-conjugated polymers are expected to give larger σ-conjugation, narrower band gaps, and more metallic character.[5–10]

The most frequently employed synthetic pathways to polysilanes and polygermanes, which have been more extensively studied as σ-conjugated polymers, are Wurtz coupling with alkali metals,[11] electrochemical reduction,[12–15] and dehydrogenative coupling.[16] Among these, electrochemical reduction has been said to be the most important pathway as an industrial method. However, for polystannanes, Wurtz coupling[4,17] and dehydrogenative coupling[1,2] reactions, but no electrochemical reduction, have been reported.

The purpose of this communication is to report the electrochemical syntheses of poly(dibutylstannane), $(Bu_2Sn)_n$, and poly(dioctylstannane), $(Oct_2Sn)_n$, and their basic properties.

Dibutyldichlorostannane and dioctyldichlorostannane were purchased from Tokyo Kasei Kogyo and Gelest, Inc., respectively, and vacuum distilled before use. Electrosynthesis was carried out according to the method reported previously,[12] using a Pt cathode, an Ag anode, and a one-compartment cell equipped with a syringe port. Tetrabutylammonium perchlorate (TBAP), precipitated from ethyl acetate–pentane solution and vacuum dried, was the supporting electrolyte and dry DME was the solvent. A constant voltage of 20 V was applied between the two electrodes. The charge passing through the circuit was monitored by a coulometer. Electrolysis was terminated when the charge reached a previously calculated value based on eqn. (1) and the amount of monomer used. Typically, 95% of the theoretically required charge was passed because it was known from previous work[12] that complete electrolysis (electrolysis with 100% of the theoretically calculated charge) tends to give a lower yield and lower molecular weight as a result of back-biting reactions.

$$n\mathrm{R_2SnCl_2} \xrightarrow{+\,2ne} (\mathrm{R_2Sn})_n + 2n\mathrm{Cl^-} \qquad (1)$$

$$\mathrm{R = Bu,\ Oct}$$

Isolation of the dialkyl-substituted polystannane was carried out as follows. As described in detail below, the polystannanes are extremely sensitive to moisture in air. Therefore, all the isolation procedures were carried out under nitrogen atmosphere and using syringe techniques. After electrolysis, most of the polymer was obtained as a precipitate and the rest of the polymer was dissolved in the electrolyte solution. Firstly, all the contents of the electrolysis cell were transferred to a two-necked flask connected to a vacuum line and equipped with a rubber septum. The supernatant solution in the electrolysis cell was transferred to the two-necked flask by a syringe technique. Then, pentane (50 ml) was introduced into the electrolysis cell and the remaining precipitated polymer was dissolved whilst being stirred magnetically. The polymer solution thus obtained was transferred and added to the previously collected supernatant solution in the two-necked flask. Then, all the solvent was removed from the two-necked flask under reduced pressure. Next, the polymer was separated from the supporting electrolyte and low molecular weight compounds as follows. Pentane (30 ml) was introduced into the two-necked flask to redissolve all the polymer. In order to precipitate polystannane and to dissolve the supporting electrolyte and low molecular weight compounds, dry methanol (100 ml) was added. The polymer was obtained by discarding the supernatant solution. The above procedure for the separation of supporting electrolyte and low molecular weight compounds was repeated. Then, the remaining solvent was removed under reduced pressure to obtain the polymer sample. A pure sample was obtained by Soxhlet extraction using pentane as the solvent. Finally, the collected polymer was dried in vacuum. The resulting polymer was a slightly sticky yellow solid regardless of the substituent groups (butyl or octyl).

Typical synthetic data are summarized in Table 1. Yields were 40–60% for $(Bu_2Sn)_n$ and 30–50% for $(Oct_2Sn)_n$. Syntheses were also successful in tetrahydrofuran. Absorption spectra were measured in pentane because pentane dissolves polystannanes well and also because polystannanes were found to be stable in pentane in the dark. Absorption maxima varied from 378 to 381 nm for $(Bu_2Sn)_n$, and were at slightly shorter wavelengths for $(Oct_2Sn)_n$. Devylder *et al.* reported that λ_{max} of $(Bu_2Sn)_n$ reaches a plateau value of 380 nm as its molecular weight increases.[4] Therefore, electrochemically obtained $(Bu_2Sn)_n$ had λ_{max} values as long as those of $(Bu_2Sn)_n$. Molecular weight values should be handled with care for they were measured using tetrahydrofuran as the eluent, in which the polystannanes degraded slowly because of the moisture remaining in THF. Significant amounts of polystannanes may have decomposed during the analysis. However, the molecular weight values seem reasonable. Molecular weights of *ca.* 10000 are as good as electrochemically synthesized σ-conjugated polymers since under the same electrolysis conditions, the authors obtained a M_w of 10 000–25 000 for $(Bu_2Ge)_n$ and 15 000–35 000 for $(Bu_2Si)_n$.

It has been reported that polystannanes are somewhat sensitive to the air.[2] The authors wished to clarify whether

Table 1 Synthetic results

Polymer	Yield/g (%)	C.E.[b]	λ_{max}[c]/nm	M_w (× 10^4)	M_w/M_n
$(Bu_2Sn)_n$	2.22 (56.1)	59.1	381	1.09	2.6
$(Bu_2Sn)_n$	1.83 (46.6)	49.1	379	1.17	2.1
$(Bu_2Sn)_n$[a]	2.01 (50.8)	53.5	378	0.64	1.3
$(Oct_2Sn)_n$	1.20 (27.9)	29.4	378	0.59	1.7

[a] Synthesized in THF. [b] Current efficiency. [c] Measured in pentane. [d] Measured by GPC using THF as the eluent.

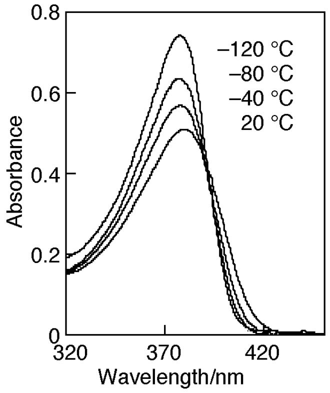

Fig. 1 Absorption spectra of $(Bu_2Sn)_n$ as a function of temperature.

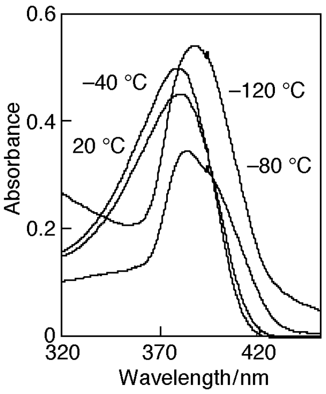

Fig. 2 Absorption spectra of $(Oct_2Sn)_n$ as a function of temperature.

polystannanes are sensitive to oxygen or sensitive to moisture in the air. In order to determine the stability of $(Bu_2Sn)_n$ toward oxygen, oxygen gas was bubbled into the pentane solution of $(Bu_2Sn)_n$. No decomposition was observed. In contrast, it was very difficult to obtain a stable tetrahydrofuran solution of $(Bu_2Sn)_n$. Even in freshly distilled CaH-dried tetrahydrofuran, a $(Bu_2Sn)_n$ solution of a concentration suitable for UV absorption measurements was not stable. Therefore, it was concluded that $(Bu_2Sn)_n$ is stable toward oxygen but extremely reactive to moisture.

The thermochromic behavior of $(Bu_2Sn)_n$ was examined because thermochromic behavior is most frequently discussed as a typical property of σ-conjugated polymers. Polysilanes and polygermanes, which have dialkyl substituent groups larger than butyl, are well known to exhibit so-called discontinuous thermochromic changes. However, $(Bu_2Sn)_n$ did not exhibit discontinuous thermochromic changes in pentane between −120 °C and room temperature (see Fig. 1). It has been said that the thermochromic behavior of σ-conjugated polymers is attributable to conformation changes in the main chains, and that such conformation changes are controlled by side chain interactions. Considering the fact that Sn–Sn bonds are much longer than Si–Si and Ge–Ge bonds, the above-mentioned lack of discontinuous thermochromic changes in $(Bu_2Sn)_n$ is attributable to weak side chain interactions. In contrast to $(Bu_2Sn)_n$, $(Oct_2Sn)_n$ showed discontinuous thermochromic changes (see Fig. 2). The absorption shift was much smaller than those observed for $(Oct_2Ge)_n$ and $(Oct_2Si)_n$. The absorption shift, which can be regarded as a manifestation of changes in effective conjugation length induced by conformation changes, decreased from $(Oct_2Si)_n$ to $(Oct_2Sn)_n$. For further discussions concerning these phenomena, it should be confirmed that the conformation changes of the polymers are of the same kind, *i.e.* all-*trans* and helical-*gauche* conformations.

To conclude, two dialkyl-substituted polystannanes were successfully synthesized by an electrochemical method. Considering the results obtained in the electrochemical syntheses of various polysilanes and polygermanes,[12] syntheses of all kinds of dialkyl-substituted polystannanes are expected to be successful as well. Syntheses of phenyl-substituted polystannanes are the authors' next challenge in this field because syntheses of phenyl-substituted polysilanes and polygermanes are more difficult than the dialkyl-substituted polymers.[12]

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