



Electrochemical and optical properties of poly[(disilanylene)oligophenylenes], peculiar behavior in the solid state

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Abstract

Electrochemical properties of poly[(disilanylene)oligophenylenes], $[(\text{SiR}^1\text{R}^2\text{SiR}^1\text{R}^2)(\text{C}_6\text{H}_4)_m]_n$ ($\text{R}^1 = \text{R}^2 = \text{Me}$, $\text{R}^1 = \text{R}^2 = \text{Et}$, and $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{Me}$; $m = 1-4$) were investigated. The cyclic voltammograms (CVs) of the polymer films on indium–tin oxide (ITO) display irreversible oxidation peaks. Disilanylene–phenylene polymers ($m = 1$) were oxidized in one step, while polymers with longer oligophenylene groups ($m = 2-4$) underwent multi-step oxidation and the oxidation peaks shifted to lower potentials with the increase of the number of phenylene groups (m) between disilanylene units. Poly[(dimethyldiphenyldisilanylene)phenylene] ($\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{Me}$; $m = 1$) exhibited changes in UV spectrum and CV profile, presumably due to the conformation changes in the polymer chain, on annealing the film at 210°C. We also measured CVs of poly[(dimethylsilylene)biphenylene] and poly[(tetraethyl-disiloxanylene)biphenylene] for comparison and found that the Si–Si orbital plays an important role in the first oxidation step of disilanylene–oligophenylene polymer films. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Organosilicon polymer; Oligophenylene polymer; Electro-oxidation

1. Introduction

Polymers with alternating organosilicon and π -electron units in their backbone represent a new class of conjugated polymers which may be used as functionality materials, such as organic semiconductors, heat-resistant materials, and hole-transporting materials [1–4]. In particular, polymers with disilanylene groups as the organosilicon units exhibit orbital interaction between π -electrons and Si–Si σ -bonds (σ – π conjugation) which originates red-shifted UV absorption bands and highly photoactive properties of the polymers [4]. However, until recently no systematic studies to clarify the relationship between the polymer structures and the electronic properties have been reported.

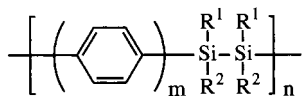
In an effort to understand the σ – π conjugation in the polymers, we have recently synthesized poly[(disilanylene)oligophenylenes] [5] and poly[(disilanylene)oligothienylenes] [6], $[(\text{SiR}_2\text{SiR}_2)(\text{A})_m]_n$ ($\text{A} = p$ -phenylene, $m = 1-4$ or 5; $\text{A} = 2,5$ -thienylene, $m = 1-5$) and investigated their photochemical properties. Interestingly, the photoactivities of these polymers decrease along the number of phenylene and thienylene units (m) in a repeating unit from $m = 1$ to 4 or 5. This is in good agreement with the results of molecular orbital calculations on simplified model polymers ($\text{R} = \text{H}$) using the SCF-CO method, which predict that the nature of both HOCO and LUCO interchanges from σ -type to π -type as the extension of π -conjugated carbon units [5,7]. We also found that the length of the π -electron system affects the thermal properties of poly[(disilanylene)oligophenylenes] and the polymers with biphenylene groups or longer oligophenylene groups

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($m \geq 2$) exhibit higher heat-resistance than the disilanyl-phenylene polymers ($m = 1$) [8].

It is of interest to us to investigate how the structures of the π -electron system of the polymers affect the electrochemical properties of the σ - π conjugated polymers. This would offer important information for designing the polymers with appropriate electron- or hole-transporting properties. Recently, we have demonstrated that poly[(disilanyl)oligothienylenes] are anodically active and their cyclic voltametric (CV) curves reveal oxidation peaks at about 1.0 V versus SCE, which shift to lower potentials with increasing numbers of thienylene units [9]. Matsuda et al. have also studied the anodic behavior of polymers composed of alternating units of an oligosilanyl and π -conjugated system, $[(\text{SiMe}_2)_x\text{-A}]_n$ ($x = 1, 3, 4, 6$; A = phenylene, biphenylene, thienylene, and anthranylene), and found that they reveal irreversible oxidation peaks that shift to lower potentials along the length of the oligosilanyl units (x) [10]. In this paper, we report the electrochemical properties of thin solid films of poly[(disilanyl)oligothienylenes] (**1b**, **c-4a-c**).



Polymer	m	R^1	R^2	M_w	M_n
1b	1	Et	Et	11 000	5800
1c		Ph	Me	8900	3800
2a	2	Me	Me	17 000	6000
2b		Et	Et	27 000	10 000
2c		Ph	Me	14 000	5800
3a	3	Me	Me	9500	4900
3b		Et	Et	8500	4000
3c		Ph	Me	7000	3600
4a	4	Me	Me	5800	4000
4b		Et	Et	7000	4500
4c		Ph	Me	6900	3400

2. Results and discussion

Firstly, we investigated the influence of the film thickness on the CV profile, using the polymer **2b** as an example. Fig. 1 shows the CV curves for the films prepared on indium–tin oxide (ITO) by spin-coating of solutions of polymer **2b** in CHCl_3 with different concentrations which relate to the film thickness. As can be seen in Fig. 1, when the concentration is higher than 3.2 g l^{-1} , the oxidation peaks of the films become broad and shift to slightly higher potentials, while films pre-

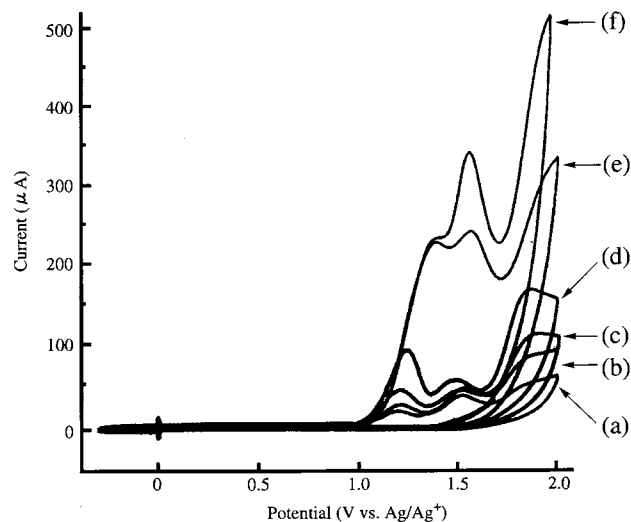


Fig. 1. CV curves of solid films on ITO, prepared by the spin-coating of CHCl_3 solutions of polymer **2b** with different concentrations of (a) 0.8; (b) 1.6; (c) 2.4; (d) 3.2; (e) 6.4, and (f) 9.6 g l^{-1} .

pared from solutions with a concentration of 3.2 g l^{-1} or less exhibit almost the same CV profile.

Fig. 2 displays the oxidation peak potentials for the films of polymer **2b** with different film thicknesses, as a function of scan rate. The peaks shift to higher potentials with increasing scan rate. The degree of the shifts for the thinner film is, however, smaller than that for the thicker film, and the scan rate does not significantly affect the peak potentials of the thinner film in the range of $50\text{--}200 \text{ mV s}^{-1}$.

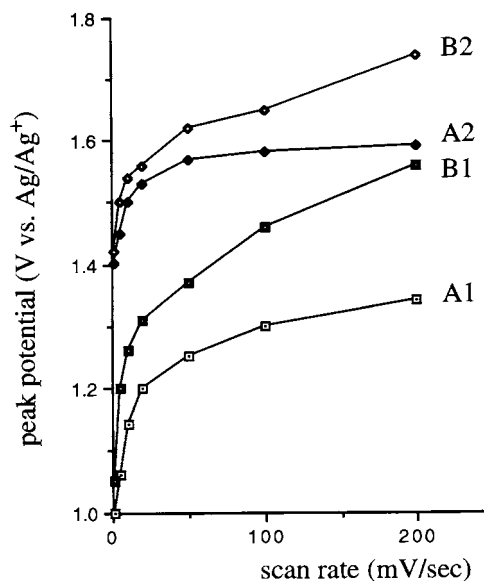


Fig. 2. Plots of scan rates versus potentials for the first (A1) and the second oxidation peaks (A2) of solid films on ITO prepared by the spin-coating of a polymer **2b** solution of 2.0 g l^{-1} in CHCl_3 , and first (B1) and the second oxidation peak (B2) of the solid film prepared from the solution of 10.0 g l^{-1} in CHCl_3 .

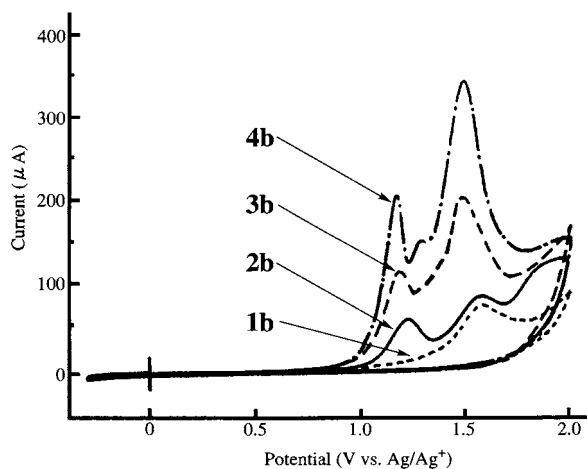


Fig. 3. CV curves for the solid films of polymers **1b–4b** on ITO.

On the basis of the above-mentioned observations, we carried out the following CV measurements for the disilanyl-oligophenylene polymers, using the solid films prepared by spin-coating 2.0 g l^{-1} polymer solutions with a scan rate of 50 mV s^{-1} , in order to minimize the deviation of peak potentials depending on the conditions. The thicknesses of the films prepared from 2.0 g l^{-1} of polymer solutions were determined to be $0.02\text{--}0.04 \text{ }\mu\text{m}$.

The CV curves for the solid films of disilanyl-oligophenylene polymers **1b–4b** on ITO glass plates are illustrated in Fig. 3. Table 1 summarizes the oxidation peak potentials and UV absorption maxima for the disilanyl-oligophenylene polymers. As can be seen in Fig. 3 and Table 1, disilanyl-phenylene polymers **1b** and **1c** were oxidized in one step, while disilanyl-oligophenylene polymers underwent electrochemical oxidation in multi-steps. This is in contrast to the CV curves of biphenylene polymers $[(\text{SiMe}_2)_x(\text{C}_6\text{H}_4)_2]_n$ ($x = 1, 3, 4, 6$) in solution reported by Matsuda et al., which show a single oxidation peak [10]. The first oxidation peaks of the polymers shift to lower potentials with increasing numbers of phenylene groups between the disilanyl units, from $m = 1$ to 4, compatible with the red-shifted UV absorptions for the polymers along the increasing m . The other peaks also tend to shift in the same direction with increasing m .

The oxidation occurred irreversibly and no cathodic counterparts were observed in the CV curves, in marked contrast to those of poly[(disilanyl-ene)oligothienylenes], which reveal a couple of anodic and cathodic peaks [9]. After sweeping in the potential range of $0.0\text{--}1.7 \text{ V}$ versus $\text{Ag}|\text{Ag}^+$, almost all of the polymers were dissolved into the solution. GPC analysis of the organic products in the solution after one cycle of CV scanning of polymer **4a** ($M_w = 4400$; $M_w/M_n = 1.63$), showed the existence of oligomers with a molecular weight of $M_w = 670$, indicating that cleavage

of polymer main chain occurred during the CV measurement. The UV spectrum of the oligomers reveals an absorption maximum at 292 nm , which is blue-shifted by 12 nm from that of the starting polymer **4a** and near to that of quarterphenylene ($\lambda_{\text{max}} = 300 \text{ nm}$ in cyclohexane) [11]. These results suggest that the cleavage of Si–Si and/or Si–phenylene bonds rather than phenylene–phenylene bonds is involved in the electrolysis of the film of polymer **4a**.

Comparing peak potentials of the polymers with the same number of phenylene groups in a repeating unit (m), no apparent influence of the nature of substituents attached to the silicon atoms on the CV profiles could be seen, with one exception for disilanyl-phenylene polymers **1b** and **1c**. The oxidation peak of polymer **1b** with peralkylated disilanyl units appeared at higher potential by 0.28 V than that of **1c** having a phenyl group on the disilanyl silicon atom. To elucidate the origin of the difference in the oxidation potentials for polymers **1b** and **1c**, we examined optical properties of the polymers in the solid state. Interestingly, polymer **1c** exhibits an absorption band in the solid state at 277 nm , lower in energy by 23 nm than that in a THF solution [5], this in contrast to the other disilanyl-oligophenylene polymers including polymer **1b** whose UV spectra in the solid state are almost the same as those in solution. It seems likely that the conformation of polymer **1c** in the solid state is frozen to favor the $\sigma\text{--}\pi$ conjugation in the solid state, leading to a higher-lying HOMO than in solution. In fact, when the film of polymer **1c** was heated at 210°C for 20 h in vacuo and then cooled to room temperature, the UV absorption maximum of the film shifted to higher energy (269 nm) and the oxidation peak in its CV curves moved to higher potential (1.38 V vs. $\text{Ag}|\text{Ag}^+$). Dissolving the polymer film in THF after heating at 210°C for 20 h reproduced the original UV spectrum of the polymer in solution, indicating that no structure changes were involved in this process. TGA analysis of **1c** in a nitrogen atmosphere also suggests thermal stability of the polymer up to 210°C [8]. Similar treatment of the film of polymer **1b** led to no changes in the UV spectra and CV curves before and after annealing the polymer film at the same temperature.

Molecular weights of the polymers do not significantly affect the oxidation potentials. No obvious changes in CV curves of polymer **2b** depending on the molecular weight were observed, as shown in Fig. 4.

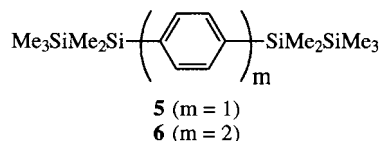
The first oxidation potentials for the present polymers are higher than those for poly[(disilanyl-ene)oligothienylenes] (ca. $1.0\text{--}1.2 \text{ V}$ vs. SCE, the potential of SCE is -0.33 V vs. $\text{Ag}|\text{Ag}^+$) [9]. However, they are at lower potentials than those reported for the corresponding p -oligophenylenes, $\text{H}(\text{C}_6\text{H}_4)_m\text{H}$ in solution (2.4 V vs. $\text{Ag}|\text{Ag}^+$ for $m = 1$, 1.85 V for $m = 2$, 1.60 V for $m = 3$, 1.47 V for $m = 4$) [12], and

Table 1
Oxidation potentials of polymer films

Polymer	Potential (V) ^a	λ_{\max} in THF	Polymer	Potential (V) ^a	λ_{\max} in THF
1b	1.58	260	3a	1.16, (1.35), 1.57	204, 294
1c	1.30	254	3b	1.20, (1.39), 1.53	205, 294
2a	1.21, 1.56	222, 282	3c	(1.18), 1.22, 1.54	292
2b	1.25, 1.58	204, 284	4a	1.16, (1.30), 1.36, 1.58	208, 304
2c	1.24, 1.56	283	4b	1.18, 1.30, 1.53	204, 305
2d	1.65	210, 266	4c	1.18, 1.54	305
2e	1.49	205, 275			

^a Peak potential versus Ag|Ag⁺, numbers in parentheses indicate potentials for shoulders.

those observed for 1,4-bis(pentamethyldisilanyl)benzene (**5**, 2.22 V) and 4,4'-bis(pentamethyldisilanyl)biphenyl (**6**, 1.60 V) in CH₃CN. These facts indicate the existence of enhanced σ - π conjugation in the polymers **1b**, **c**-**4a**-**c**, which would elevate the HOMO energy levels of these polymers and thus lower oxidation potentials. However, as can be seen in Fig. 5, the degree of potential shifts for the polymers relative to oligophenylenes decreases along the length of oligophenylene chain, indicating the less favorable σ - π conjugation for polymers with extended π -electron systems, as has been previously suggested by optical studies of the polymers [5] (Fig. 6).



In order to determine more about the electrochemical behavior of disilanyl-oligophenylene polymers, we prepared the corresponding siloxane polymer (**2d**) by the reaction of **2b** with trimethylamine oxide and measured its CV under the same conditions. The results of CV analysis of **2d** are also summarized in Table 1. The CV of **2d** film reveals only one oxidation peak at 1.65 V versus Ag|Ag⁺. No peaks around the first oxidation

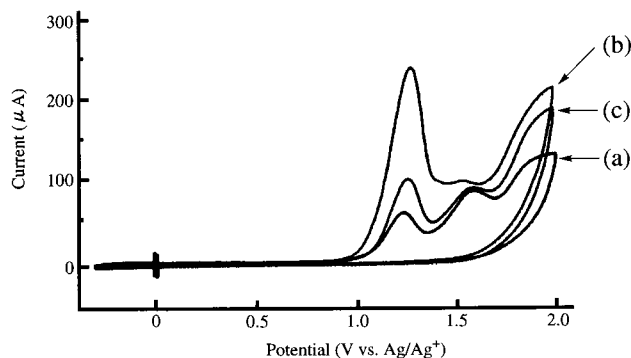
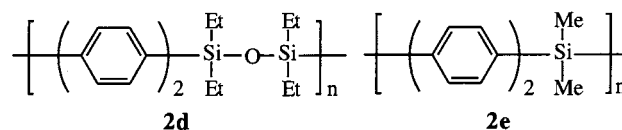


Fig. 4. CV curves of solid films of polymer **2b** with different molecular weights of M_w (M_n) = (a) 27 000 (10 000); (b) 15 000 (8000), and (c) 5300 (3400).

potential of **2b** (1.25 V vs. Ag|Ag⁺) are observed. Similarly, the CV of the film of poly[(dimethylsilylene)biphenylene] (**2e**) shows a single oxidation peak at 1.49 V versus Ag|Ag⁺. These facts clearly suggest that the Si-Si orbital plays an important role in the first oxidation step of the disilanyl-oligophenylene polymer films.



In conclusion, we have studied the electrochemical properties of poly[(disilanyl)oligophenylenes] and found that the oxidation peak potentials in CV curves reflect the existence of sufficient σ - π conjugation and move to lower energy as increasing the number of phenylenes in a polymer unit. This is in good agreement with our recent findings in the optical properties of the polymers [5]. Interestingly, polymer **1c** exhibited changes in UV spectrum and CV profiles in the solid state on annealing the film at 210°C. Matsuda et al. have previously reported that the UV absorption maxima of alternating polymers composed of oligo-

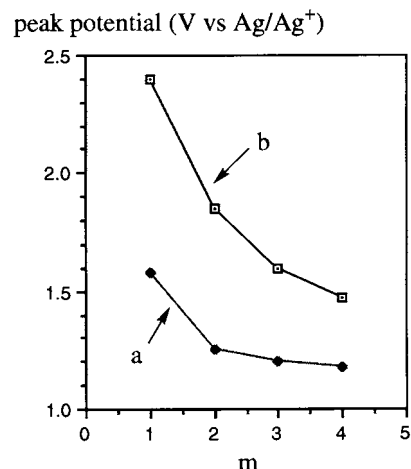


Fig. 5. Plots of first oxidation peak potentials for (a) polymers **1b**-**4b** and (b) oligophenylenes versus the number of phenylene groups in a unit (m).

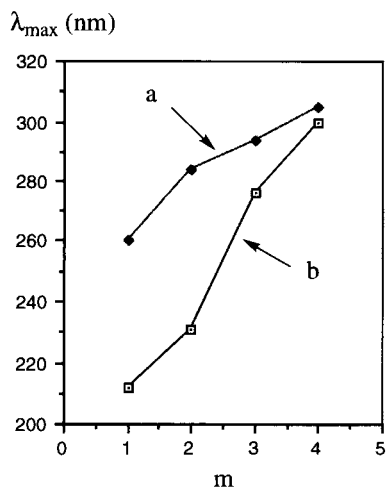


Fig. 6. Plots of UV λ_{\max} for (a) polymers **1b–4b** and (b) oligophenylenes versus the number of phenylene groups in a unit (m).

lanylene and π -conjugated carbon units in solutions shift slightly depending on the temperature [13,14]. In the present case of polymer **1c**, we observed the first example of changes of optical and electrochemical behaviors in the solid state for a σ - π conjugated polymer.

3. Experimental

3.1. General

Poly[(disilanylene)-*p*-oligophenylenes] (**1b**, **c–4a–c**), polymer **2e** [5,8], and compounds **5** [15] and **6** [5] were synthesized as reported in the literature. The film thicknesses were determined by a Taylor–Hobson Talystep equipment. CV measurements for the disilanylene–oligophenylene polymers were carried out using a three electrode system in an acetonitrile solution containing 100 mM of tetraethylammonium tetrafluoroborate as the supporting electrolyte. Thin solid films of the polymers were prepared by spin coating the polymer solution in chloroform on ITO working electrodes. An Ag/0.1 M AgClO₄ electrode and a Pt plate were used as the reference and counter electrode, respectively. The peak potential was determined in a sweep rate of 50 mV s⁻¹. The current–voltage curve was recorded on a Hokuto Denko HAB-151 potentiostat/galvanostat.

3.2. Preparation of polymer **2d**

Into a 30 ml two-necked flask fitted with a magnetic stirrer and reflux condenser was placed a mixture of

0.102 g (0.315 mmol, $M_w = 27\,000$, $M_n = 10\,000$) of poly[(tetraethylsilylanylene)biphenylene] and 0.029 g (0.386 mmol) of trimethylamine oxide in 4 ml of dry benzene. The mixture was heated to reflux for 56 h. After evaporation of the solvent, the residue was reprecipitated from benzene–ethanol to give 0.096 g (90% yield) of **2d**: $M_w = 19\,000$ ($M_n = 9200$). IR: 1077 cm⁻¹ ($\nu_{\text{O-Si}}$): ¹H-NMR (CDCl₃): $\delta = 0.94$ (t, 12H, CH₃, $J = 6.75$ Hz), 1.06 (m, 8H, CH₂Si), 7.62–7.74 (br. s, 8H, ring H). ¹³C-NMR (CDCl₃): $\delta = 6.88$, 7.22, 126.3, 134.1, 136.7, 141.7. ²⁹Si-NMR (CDCl₃) $\delta = 0.083$.

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