Electrochemical properties of oligothienylene–oligosilanylene block copolymers: Influences of block sizes

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Abstract

The fundamental electrochemical properties of oligothienylene–oligosilanylene block copolymers, especially the influences of the block sizes, were studied in acetonitrile. In electrochemical oxidation, films of the polymers containing Si–Si bonds suffer more or less from decomposition and dissolution due to partial cleavage of the Si–Si bonds in the oligosilanylene units. Decomposition decreases as the oligosilanylene block size decreases, and is not observed with copolymers containing no Si–Si bond, that is, oligothienylene–monosilanylene copolymers. The copolymer films can also be electrochemically anion doped. Cyclic voltammograms obtained at high scan rates generally exhibit a two-step oxidative doping process, though the second-step oxidation is hardly seen for polymers with smaller oligothienylene blocks. The potentials of the oxidative doping peaks show a cathodic shift as the oligosilanylene block size increases because of the σ–π-interaction in the polymer chains and the action of the oligosilanylene block as a spacer, both of which are favourable to the stabilization of the cations and dications generated in the polymer chain.

1. Introduction

Polythiophene, a typical π-conjugated polymer, shows conductivities of up to 10^2 S cm^{-1} after doping, and is stable in air in both anion-doped and undoped states. Unlike polythiophene, polysilanes have only σ-conjugation in the main chains [1]. Although electrochemical oxidation leads to their decomposition [2], polysilanes are able to be doped chemically, giving semiconducting properties [3, 4]. A polymer having π- and σ-conjugation is interesting from both scientific and technological viewpoints. Hence σ–π-conjugated oligothienylene–oligosilanylene copolymers have recently attracted much attention as novel functional materials because of their optoelectronic properties applicable to photoresists [5], conductive materials [6–10] and electroluminescent layers in large-area LEDs [11]. The σ–π-conjugation in the polymer chains originates from π–d_{Si} interaction [12] and/or π–σ_{Si-Si} interaction [13]. These polymers give conductivities of 10^{-5}–10^{-1} S cm^{-1} upon doping chemically or electrochemically [6–10]. Recently, we have reported electrochemical oxidation of some oligothienylene–oligosilanylene block copolymers [10, 14–17], and their photophysical properties in solution [18]. Of these polymers having Si–Si bonds in the main chain are found to be anion dopable electrochemically, accompa-

nied by slow decomposition and dissolution of the films [14–17]. As an extension of the previous work, we have systematically investigated influences of the block sizes on the electrochemical properties of σ–π-conjugated oligothienylene–oligosilanylene copolymers.

2. Experimental details

Three series of polymers (*m*S*n*T), where *m* and *n* represent, respectively, the number of silicon atoms and the number of thiophene rings in a repeating unit of the polymer, were chemically synthesized. Details of the synthesis and characterization can be found elsewhere [9, 19]. Figure 1 gives their chemical structures and abbreviated names (MS*n*T, DS*n*T, and TS*n*T). Other chemicals were reagent grade or better. Special reagent grade acetonitrile (MeCN) was distilled under N$_2$ from P$_2$O$_5$ prior to use.

Films of the polymers of a thickness of about 0.1–0.5 μm were prepared on indium-tin oxide (ITO) electrodes by spinning their chloroform solutions. Electrochemical measurements were carried out at room temperature in a three-compartment cell in MeCN containing 0.1 M electrolyte, with a polymer-coated ITO as the working electrode, a Pt wire as the counter,
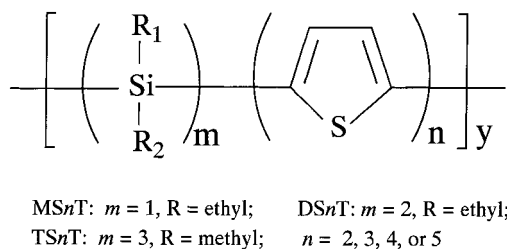
MS*n*T: *m* = 1, R = ethyl;   DS*n*T: *m* = 2, R = ethyl;
TS*n*T: *m* = 3, R = methyl;   *n* = 2, 3, 4, or 5

Fig. 1. Chemical structures and abbreviated names of *m*S*n*T polymers.

and an Ag/0.1 M AgClO$_4$ electrode as reference. Tetraethylammonium perchlorate (Et$_4$NClO$_4$) was used as supporting electrolyte, unless otherwise specified. *In situ* spectroelectrochemical measurements were conducted in a thin-layer cell (path length 7 mm). All electrochemical experiments were performed with a Hokuto Denko HAB-151 potentiostat–galvanostat with an integrated function generator, in conjunction with a Riken Denshi F-5C X–Y recorder. Absorption and emission spectra were obtained by use of a Shimadzu UV-3101PC scanning spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively. Details of the electrochemical experiments and spectroscopic measurement can be found in previous papers [15, 16].

3. Results and discussion

The copolymers containing Si–Si bonds in the main chain were previously found to be decomposed partially during electrochemical oxidation in MeCN/Et$_4$NBF$_4$ solution due to an electrochemical Si–Si cleavage [14–16]. With the TS5T films, a direct electrochemical Si–Si cleavage was observed at lower potentials, and Si–Si cleavage reaction was promoted by the anion doping at higher potentials [20]; this was referred to as doping-induced Si–Si cleavage. The rate of direct electrochemical Si–Si cleavage was generally low and independent of the type of anions used. The rate of doping-induced Si–Si cleavage was found to be dependent on the type of anions used: the reaction was fast in MeCN/Et$_4$NBF$_4$ solution, but very slow in MeCN/Et$_4$NClO$_4$. Hence, the TS5T film showed better stability in MeCN/Et$_4$NClO$_4$ solution than in MeCN/Et$_4$NBF$_4$ solution. Figure 2 compares the voltammograms of *m*S5T films obtained at 1 mV s^{-1} in MeCN/Et$_4$NClO$_4$ solution. An oxidation peak appears in the potential range 0.5–0.7 V for MS5T, while three oxidation subpeaks occur for DS5T and TS5T. For simplification, these oxidation subpeaks are assigned as peaks A, B, and C, respectively, in order of increasing potential. As in MeCN/Et$_4$NBF$_4$ solution [15, 16], it is speculated that the oxidation subpeak A can be assigned to the electrochemical cleavage of Si–Si bonds in the polymer chains, and the subpeaks B and C are related to electrochemical doping (see below). The subpeak A occurs at 0.52 and 0.45 V for DS5T and TS5T, respectively, indicating that the copolymers become less stable as *m* increases. Cyclic voltammo-
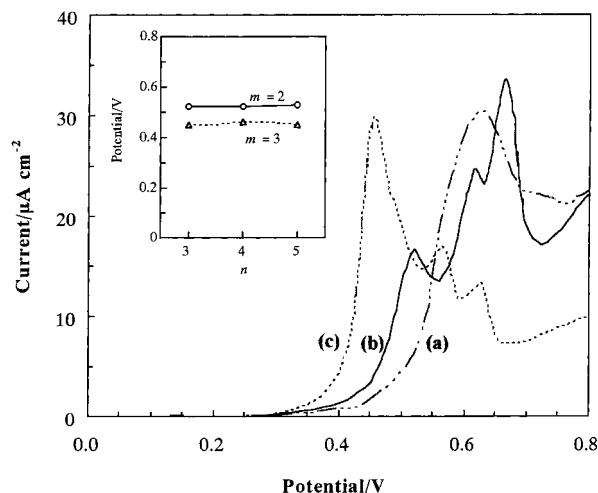

Fig. 2. Voltammograms of (a) MS5T, (b) DS5T and (c) TS5T films in MeCN/perchlorate solution for the first forward scan at 1 mV s^{-1}. Inset gives potential of first oxidation subpeak as a function of *n*.

grams of DS*n*T and TS*n*T films at 1 mV s^{-1} were found to be similar in shape to those of DS5T and TS5T, and the potential of the subpeak A due to the direct electrochemical Si–Si cleavage is plotted against the oligothienylene block size *n* as shown in the inset of Figure 2. It is clear that the potential of the subpeak A is little affected by the number of thiophene rings *n*, while it shifts cathodically by 50–70 mV as *m* is increased from 2 to 3. The lack of dependence of *n* on the potential of the subpeak A strongly supports the suggestion that the Si–Si cleavage is a direct electrochemical one, which is not affected by the oligothienylence block.

Electrochemical Si–Si cleavage was reported by Fang et al. [21] for thienylene–oligosilanylene and other σ–π-conjugated copolymers. These authors found that Si–Si cleavage occurs at lower oxidation potential as the number of silicon atoms in the oligosilanylene blocks increases. This is consistent with our finding about the influence of *m* on the Si–Si cleavage. Because the Si–Si cleavage is a direct one, its reaction potential is little influenced by the π-blocks. Thus, the potential of the subpeak A is affected only by *m*, but not by *n*. When *m* = 1, there is no Si–Si bond in polymer chains, thus no oxidation subpeak for the Si–Si cleavage process is found in the voltammogram of MS5T in Figure 2. Indeed, MS5T films are electrochemically stable. We scanned the potential successively at 100 mV s^{-1} between 0 and 0.75 V, the current of the oxidation peak at about 0.64 V in the 400th cycle was found to be almost the same as that in the second cycle for the MS5T film.

The electrochemical Si–Si cleavage in the polymer film results in dissolution of some fluorescent products into the solution. To compare the decomposition rates of the copolymer films at different potentials, we oxidized the polymer film at given potentials for 2 min, and measured the fluorescence intensity of the resulting solution at the fluorescence maximum of the decomposition product with excitation at its absorption maximum. The change in the fluorescence intensity is considered to be

equivalent to the average decomposition rate of the polymer film over the initial 2 min. A freshly prepared film was used for each measurement. Figure 3 shows the dependence of the fluorescence intensity on potential for mS5T films. In perchlorate solution, little dissolution of MS5T films is observed, while the dissolution rates of both DS5T and TS5T films increase initially with potential. It is observed that the onset potential of the dissolution of the DS5T film is more positive than that of the TS5T film, indicating again that the latter is less stable than the former. Although the dissolution rates of both DS5T and TS5T films in perchlorate solution become almost constant at potentials where doping occurs, their dissolution rates in tetrafluoroborate solution increase further when the films are doped as shown in the inset of Figure 3. This difference demonstrates that for both DSnT and TSnT films, the reaction of the doping-induced Si–Si cleavage is fast in tetrafluoroborate solution, but is very slow in perchlorate solution. This finding is consistent with out previous observation with the TS5T film [20].

After being isolated from the electrolytic solution, the generated soluble decomposition products of the DSnT and TSnT films were characterized using u.v.–vis. absorption, fluorescence, FTIR, and GPC measurements [14–16]. Their absorption and fluorescence spectra in dioxane were similar to those of their corresponding oligothiophenes (nTs). The decomposed products exhibited molecular weights close to that of a repeat unit of the corresponding copolymers. Along with the FTIR measurements [14–16], these results demonstrate that the partial dissolution of these polymer films is due to the electrochemical cleavage of Si–Si bonds in the polymer chains, and that the structures of the generated soluble decomposition products of DSnT and TSnT polymers are very close to those of their corresponding nTs. This basic structure of the soluble

decomposition products is found to be generally independent of the applied potentials.

As described above, the electrochemical oxidation of the σ-block in the copolymers leads to the Si–Si cleavage and the partial decomposition of the DSnT and TSnT films. In addition, the π-block in the copolymers can be also electrochemically oxidized. For example, Figure 4 shows the u.v.–vis. near infrared absorption spectra of a MS5T film *in situ* measured at various potentials. The neutral film looks light yellowish-green, and its π–π* transition band appears at around 423 nm. As the potential increased, the film changes colour from light yellowish-green to deep blue and several new bands occur and increase in intensity. The electrochromic change and the occurrence of the new absorption bands at about 600, 1030 and 1350 nm are typical of anion-doped polythiophene films. Therefore, the oxidation of the π-block results in the anion doping of the copolymer film.

The oxidation/reduction of the π-block was further investigated by cyclic voltammetry. It is necessary to eliminate the possible influence of the Si–Si cleavage on the cyclic voltammograms. As discussed above, this may be realized by using two measures. First, higher scan rates are used in consideration that the direct electrochemical Si–Si cleavage is a slow process. Secondly, the measurements were conducted in perchlorate solutions, where the rate of the doping-induced Si–Si cleavage is very slow. Thus, the cyclic voltammograms should clearly demonstrate the redox behaviour of the π-blocks, that is, the doping–dedoping behaviour of the copolymer films.

Voltammograms of the DS5T and TS5T films were obtained at various scan rates. As the scan rate increased up to 100 mV s^{-1}, the oxidation subpeaks in Figure 2 appeared as a single oxidation peak, indicating that the polymer decomposition is relatively depressed at a fast scan rate. When the switching potential was increased, a second main oxidation peak was observed. Therefore, the cyclic voltammetric behaviour of the
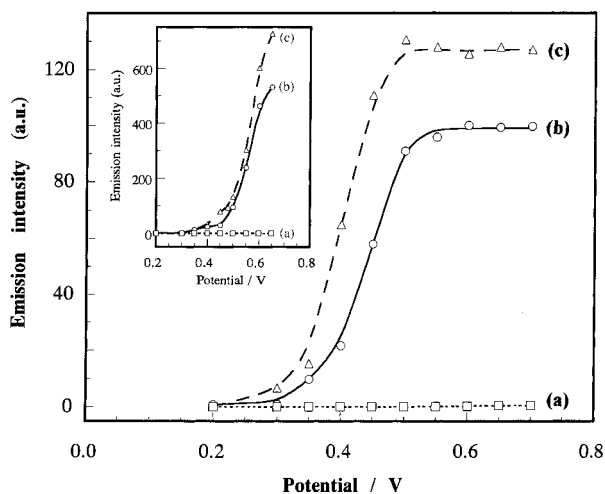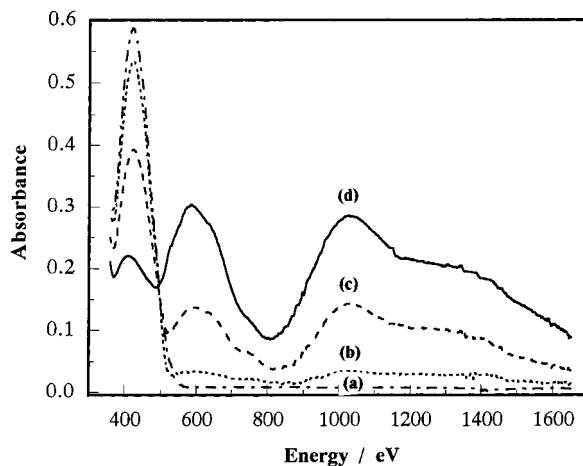

Fig. 3. Potential dependence of the fluorescence intensity of MeCN/perchlorate solution in which the freshly prepared (a) MS5T, (b) DS5T and (c) TS5T films were oxidized at given potentials for 2 min for each measurement. Inset gives data obtained in MeCN/tetrafluoroborate solution.

Fig. 4. In situ absorption spectra of a MS5T film in MeCN/perchlorate solution at (a) 0.35, (b) 0.50, (c) 0.55 and (d) 0.65 V.

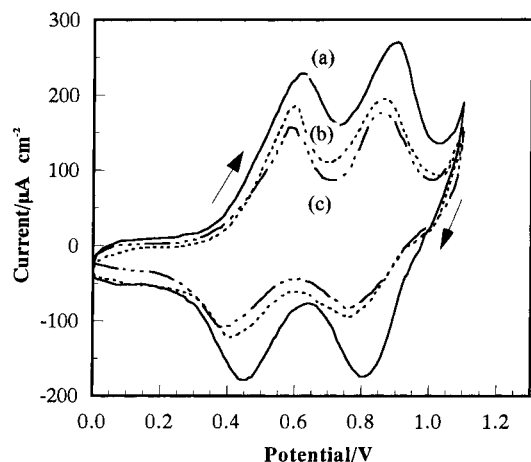*Fig. 5.* Voltammograms of (a) MS5T, (b) DS5T and (c) TS5T films in MeCN/perchlorate solution for the third scan at 100 mV s^{-1}.
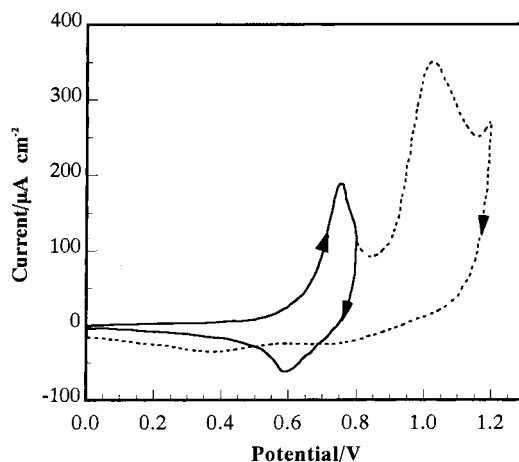

Fig. 6. Cyclic voltammograms of MS4T films at 100 mV s^{-1} in MeCN/perchlorate solution. Switching potential is 0.8 V (solid) and 1.2 V (dotted).

polymer films at such a high scan rate is mainly dependent on the doping process. Cyclic voltammograms of the *m*S5T films in the third scan during a successive scanning at 100 mV s^{-1} are given in Figure 5. The two pairs of redox peaks in each of these voltammograms indicate that the electrochemical oxidation of these polymers is a two-step process. The repeat unit of the polymer chain is oxidized to a cation in the first step, and to a dication in the second step (see below). The oxidation–reduction peaks occur at 0.65/0.46 and 0.94/0.81 V for MS5T, 0.61/0.40 and 0.88/0.76 V for DS5T, and 0.60/0.39 and 0.86/0.75 V for TS5T.

A two-step oxidation process is also observed in cyclic voltammograms of the *m*S4T films at 100 mV s^{-1}. The first oxidation process of *m*S4T is fairly reversible, whereas the second oxidation process for *m*S4T is irreversible. As shown in Figure 6, the cyclic voltammogram of the MS4T film exhibits a pair of reversible redox peaks when the potential in swept between 0 and 0.8 V. When the switching potential is increased to 1.2 V, two oxidation peaks and their ill-shaped cathodic partners are observed for the first potential scan, which are difficult to recognize in the second scan. This is because the dication generated in the second-step oxidation is unstable. The cyclic voltammetric behaviour of DS4T and TS4T is similar to that of MS4T, but the DS4T and TS4T films are less stable because of partial decomposition of DS4T and TS4T. The oxidation peaks for the *m*S4T films appear at more positive potentials relative to the *m*S5T films. The first pair of oxidation–reduction peaks and the second oxidation peak were observed at 0.74/0.59 and 1.02 V for MS4T, 0.67/0.54 and 0.97 V for DS4T, and 0.66/0.53 and 0.95 V for TS4T.

The cyclic voltammetric behaviour of the *m*S2T and *m*S3T films is rather different from that of *m*S4T and *m*S5T films: the second-step oxidation process is hardly seen for *m*S2T and *m*S3T in a potential range from 0 to 1.3 V. For *m*S3T, an oxidation peak was observed at about 0.76–0.96 V in the first scan, and its cathodic partner was ill shaped. In MeCN/Et$_4$NBF$_4$ solution,

Yi et al. [7] investigated the cyclic voltammetric behaviour of cast films of poly(2,5″-terthienylene silylene)s with different substitution groups of such as methyl, phenyl and/or methoxyphenyl groups, which are structurally similar to MS3T in the present work. These MS3T-like polymers were found to show only one couple of redox peaks with the oxidation peak at about 1.06 V, which is close to 0.96 V observed for MS3T. For *m*S2T films, the oxidation peak shifted to about 1.05 V without a corresponding reduction peak. As the cycle number increased, the oxidation peak currents for both *m*S2T and *m*S3T film decreased due to overoxidation.

Because well-shaped oxidation peaks are observed only in the first potential scan for some polymers, as discussed above, the first-cycle voltammograms of the polymers were used to evaluate qualitatively the influences of both *m* and *n* on their electrochemical behaviour. Very thin films were used to minimize the difference between the peak potentials observed in the first scan and in successive scans. This ensures that the difference will not seriously affect the following discussion about the influences of *m* and *n* on the oxidation behaviour of the films. Figure 7 shows the first-cycle voltammograms of MS*n*T films at 100 mV s^{-1}. The potentials of the oxidation peaks for these polymers observed at 100 mV s^{-1} in the first potential scan are plotted against *n* in Figure 8. It is clearly seen from Figures 7 and 8 that the first (or the second) oxidation peak shifts to more positive potentials as *n* decreases.

The cyclic voltammetric behaviour of these polymers is similar to that of oligothiophenes and their derivatives. Noma and coworkers [22] have reported that the voltammogram of α-ethyldisubstituted quinquethiophene dissolved in dichloromethane shows two pairs of oxidation–reduction peaks at 0.56/0.48 and 0.82/0.75 V, while that of α-ethyl-disubstituted quaterthiophene gives a pair of oxidation–reduction peaks around 0.62/0.52 V and a second oxidation peak at about 1.01 V. Hapiot et al. [23] have found α-trimethylsilyl-disubstituted
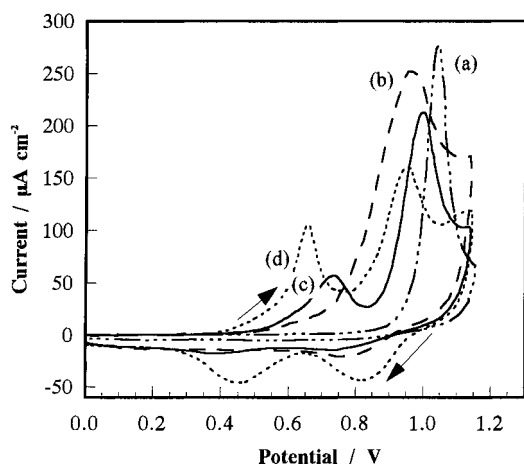
Fig. 7. Voltammograms of (a) MS2T, (b) MS3T, (c) MS4T, and (d) MS5T films in MeCN/perchlorate solution for the first scan at 100 mV s^{-1}.
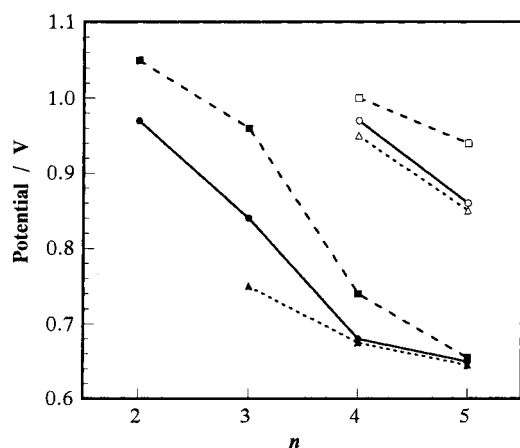

Fig. 8. Influence of n on potentials of the (solid) first and (open) second oxidation peaks for (square) MSnT, (circle) DSnT and (triangle) TSnT films in MeCN/perchlorate solution. Scan rate 100 mV s^{-1}.

oligothiophenes (Me$_3$Si-nT-SiMe$_3$) dissolved in MeCN show the formal oxidation potential for the first-step oxidation at about 0.74 V for $n = 3$ and 0.64 V for $n = 4$. Furthermore, the n dependence of the oxidation peak potentials for mSnT films is similar to that observed for nTs [24] and their derivatives [25]. In dichloromethane, for example, the oligothiphenes end-capped by cyclohexane caps exhibit redox potentials of 0.95, 0.79, 0.73 and 0.67 V for the first-step oxidation, 1.6, 1.2, 1.1 and 0.96 V for the second-step oxidation for $n = 2$, 3, 4 and 5, respectively [25]. These comparisons demonstrate that the electrochemical redox processes of mSnT polymers are mainly dependent on the oligothiophene parts separated by the silanylene parts in the polymer chains. That is, the repeat units of the polymers are oxidized to radical cations in the first step and then to dications in the second step. A repeat unit of larger n has longer π-conjugation length, being favourable to the stability of the generated radical cations and dications. Thus, the

potentials of the oxidation peaks for the mSnT films shift cathodically as n increases (Figure 8).

The electrochemical redox behaviour is further influenced by the σ–π-interaction. The interaction between σ- and π-energy levels of the individual σ- and π-units results in the formation of new hybrid energy levels [26]. A stronger σ–π-conjugation is expected to occur when the σ-level in the oligosilanylene block approaches the π-level in the π-conjugated block, hence depending on the sizes (m and n) of the individual blocks. For the copolymers studied here, the variation of the σ-block size (m) is small, thus the σ–π-interaction is generally stronger for small values of n and decreases as n increases. It is easily seen from Figure 8 that the difference between the potential of the first oxidation peak considerably increases with the decreases on n. When n is up to 5, the σ–π-interaction becomes much weak, which is observed in the previous photophysical study of these polymers in dioxane solution [18]. Therefore, almost the same potential of the first oxidation peak occurs for MS5T, DS5T and TS5T films. For smaller n values, the σ–π-interaction becomes stronger and the first oxidation peak shows a cathodic shift as m increases. These findings can be accounted for by that the σ–π-conjugation is favourable to stabilization of the cations generated in the π-blocks.

Furthermore, the cations and dications generated in the polymer chains, especially for the copolymers of smaller n values, become more stable when separated by larger spacers, that is, oligosilanylene blocks of larger m. This may also partly explain the decreased potentials of the first oxidation peaks observed with decrease in n. Moreover, for the mS5T films, the second oxidation peak shifts in the cathodic direction as m increases, although these films give the almost same potential of the first oxidation peak. This is possibly related to the greater separation between the two adjacent π-blocks due to the larger bridging σ-block.

4. Conclusions

The copolymers of $m = 1$ (MSnT) are found to be relatively stable. In the cyclic voltammograms, two pairs of redox peaks generally occur, though the second oxidation peak is hardly seen for MS2T and MS3T due to the instability of the radical cations generated in their main chains. *In situ* measurements of the absorption spectra indicate that the polymer films can be electrochemically doped. It is found that the redox behaviour of the polymers is mainly dependent on n, and the oxidation peaks shift considerably in the cathodic direction as n increases. The copolymers of $m = 2$ (DSnT) and $m = 3$ (TSnT) are possibly partially decomposed and dissolved by electrochemical oxidation because of the Si–Si cleavage. The voltammetric behaviour of the DSnT and TSnT films is similar to

that of the MSnT films, but is affected by the Si–Si cleavage process. An oxidation subpeak due to the direct electrochemical Si–Si cleavage occurs in the voltammograms of the films obtained at slow scan rates. The onset potential of this cleavage reaction decreases as m increases. In the voltammograms obtained at fast scan rates in perchlorate solutions, the doping process dominates over the possible Si–Si cleavage reaction (both the direct and the doping-induced). This permits a comparison between the potentials of the oxidation peaks of mSnT films. It is found that for a given n, the oxidation peak shifts cathodically as m increases, especially for smaller values of n. This is possibly related to the effects of the σ–π-conjugation and of the oligosilanylene block as a spacer.

Among the copolymers used, those containing Si–Si bonds are limited in some applications because of their poor stability related to electrochemical Si–Si cleavage. However, these copolymers combine at least partly the properties of polysilanes and of π-conjugated conductive polymers. It is the Si–Si cleavage that brings about some very interesting new applications for polysilanes. The oligothienylene–monosilanylene copolymers, containing no Si–Si bond, are relatively stable, and may be used as conductive materials. These copolymers are also useful for studying the conduction mechanism in conductive polythiophenes as model compounds for polythiophene. The ease of control of the oxidation potential by adjustment of the oligothienylene block size also permits their application as hole-transport materials in organic electroluminescence devices. Related investigations are ongoing.

Acknowledgement

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