ELSEVIER

Electrochemical studies of σ–π conjugated organosilicon copolymers

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The electrochemical behaviour of the silylene–phenylene, silylene–thienylene, silylene–diphenylene and silylene–anthranylene copolymers was investigated using cyclic voltammetry. The oxidation potentials of these organosilicon copolymers decreased with increasing dimethylsilylene chain length. The change of the oxidation potential was explained by considering the σ–π conjugation between the dimethylsilylene chain and the π unit. The cyclic voltammograms of the organosilicon copolymers showed the characteristics of an irreversible system. The absorption spectra showed the degradation of the Si–Si chain of the organosilicon copolymers by electrochemical oxidation. The molecular orbitals were calculated to discuss the σ–π conjugation state and to identify the oxidation site in the polymer chain.

INTRODUCTION

Recently, various organosilicon polymers with σ–π conjugation along the polymer chain have attracted considerable interest because they are applicable to semiconducting materials, photoresists and precursors to β-silicon carbide ceramics[1–3]. The electronic structure of σ–π conjugated organosilicon polymers has been discussed on the basis of conductivity, absorption spectra and electrochemical measurements[4–8]. The conductivities of organosilicon polymers are caused by the σ–π conjugation between the σ-conjugated silicon chain and the π electron system[4,5]. The electrochemical oxidation of a variety of polysilane derivatives deposited as thin films on platinum electrodes and dissolved in methylene chloride electrolyte solution has been studied[9,10]. Boberski *et al.* have reported that permethylated oligosilanes (Si_2 through Si_6) have low oxidation potentials (in the range from 1.0 to 2.0 V vs. SCE) and decrease with increased catenation[11]. The electrochemical behaviour of organosilicon polymers consisting of a dimethylsilylene unit and thiophene units in the main chains has been reported[6].

We have reported the synthesis of a series of alternating organosilicon copolymers $-[(SiMe_2)_m-Z]_n-$ ($m = 1, 3, 4$ and 6; Z = phenylene, thienylene, diphenylene and anthranylene) and their optical properties in previous papers[7,8]. More recently, many papers concerning the preparation and properties of alternating organosilicon copolymers $-[(SiMe_2)_m-Z]_n-$ have been published (Z = phenylene, $m = 2$, ref. 12; Z = thienylene, $m = 1, 6$, ref. 3; Z = thienylene, $m = 2$, refs 13, 14; Z = diphenylene, $m = 1, 2$, refs 15, 16).

In this paper, we study the electrochemical behaviour of the silylene–phenylene, silylene–thienylene, silylene–diphenylene and silylene–anthranylene copolymers in comparison with those of the permethylated oligosilanes and α,ω-diphenylpermethylated oligosilanes. The influence of the chain length of the dimethylsilylene sequence in the copolymer backbone on the oxidation potential was investigated. The effect of sweep rate on the electrochemical oxidation reaction was examined. The σ–π conjugation states of organosilicon copolymers were discussed on the basis of the molecular-orbital (MO) calculation using oligomer models.

EXPERIMENTAL

Preparation and characterization

Permethylated oligosilanes $Me-(SiMe_2)_m-Me$ and α, ω-diphenylpermethylated oligosilanes $Ph-(SiMe_2)_m-Ph$ ($m = 3, 4$ and 6) were synthesized according to literature preparations[17].

Silylene–phenylene copolymers **1a–d**, silylene–thienylene copolymers **2a–d**, silylene–diphenylene copolymers **3a–d** and silylene–anthranylene copolymers **4a–d** were prepared by following published procedures[7,8]. The chemical structures of these copolymers are shown in *Figure 1*. The molecular weights of these copolymers were determined by a Toyo Soda HLC-802VR gel permeation chromatograph using monodisperse polystyrene as standard: **1a**, $M_w = 2460$, $M_w/M_n = 1.2$; **1b**, $M_w = 2520$, $M_w/M_n = 1.2$; **1c**, $M_w = 2710$, $M_w/M_n = 1.2$; **1d**, $M_w = 3080$, $M_w/M_n = 1.3$; **2a**, $M_w = 3360$, $M_w/M_n = 1.7$; **2b**, $M_w = 5470$, $M_w/M_n = 1.8$; **2c**, $M_w = 6120$, $M_w/M_n = 2.1$; **2d**, $M_w = 7440$, $M_w/M_n = 2.1$; **3a**, $M_w = 7500$, $M_w/M_n = 1.3$; **3b**, $M_w = 9100$, $M_w/M_n = 1.8$; **3c**, $M_w = 9800$, $M_w/M_n = 1.4$; **3d**, $M_w = 10\,900$, $M_w/M_n = 1.6$; **4a**,

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$M_w = 6100$; $M_w/M_n = 1.4$; **4b**, $M_w = 8500$, $M_w/M_n = 1.4$; **4c**, $M_w = 9700$, $M_w/M_n = 1.5$; **4d**, $M_w = 10\,100$, $M_w/M_n = 1.6$.

Measurements

Cyclic voltammetry was carried out in a 20 ml single-compartment cell using a potentiostat/galvanostat HAB-151 with a function generator (Hokuto Denko Ltd). The oligosilanes and copolymers were dissolved in dry tetrahydrofuran (THF) containing the electrolyte 0.1 M tetra-n-butylammonium perchlorate (TBAP). The platinum electrode of 0.02 cm² geometric area was polished with Al_2O_3 paste and used as a working electrode. A platinum wire was used as a counter-electrode. The reference electrode was Ag/Ag^+ (0.01 M $AgNO_3$ in 0.1 M TBAP acetonitrile). All systems were bubbled with nitrogen for 5 min.

Absorption spectra were measured in a quartz cell with electrolyte solutions by a spectrometer (Hitachi U-3400).

RESULTS AND DISCUSSION

Electrochemical behaviour of oligosilanes and organosilicon copolymers

The electrochemical oxidation reactions of permethylated oligosilanes $Me–(SiMe_2)_m–Me$, α,ω-diphenylpermethylated oligosilanes $Ph–(SiMe_2)_m–Ph$ ($m = 3, 4$ and 6) and organosilicon copolymers dissolved in THF containing 0.1 M TBAP were observed using cyclic voltammetry. The effect of the σ–π conjugation induced by incorporating the π unit into the dimethylsilylene chain on the electrochemical behaviour was studied. The chemical structures of alternating organosilicon copolymers, silylene–phenylene copolymers **1a–d**, silylene–thienylene copolymers **2a–d**, silylene–diphenylene copolymers **3a–d** and silylene–anthranylene copolymers **4a–d**, are summarized in *Figure 1*.

The electrochemical behaviour of the dimethylsilylene chain without the π unit was investigated using the permethylated oligosilanes $Me–(SiMe_2)_m–Me$ ($m = 3, 4$ and 6). *Figure 2* shows cyclic voltammograms for permethylated oligosilanes in THF containing 0.1 M TBAP. The anodic waves in the cyclic voltammograms are attributed to the oxidation of the Si–Si chain of permethylated oligosilanes. The oxidation potential decreases with increasing dimethylsilylene chain length.
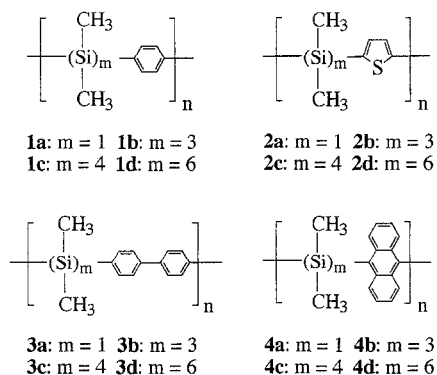
Permethylated trisilane, tetrasilane and hexasilane show anodic current peaks at 2.20, 1.97 and 1.68 V vs. Ag/Ag^+, respectively. This result suggests that the σ conjugation of the Si–Si chain is enhanced by the increasing dimethylsilylene chain length. The order of the ease of oxidation agrees with the order of ionization potentials (*IPs*) of permethylated oligosilanes $Me–(SiMe_2)_m–Me$: 8.19, 7.98 and 7.70 eV for $m = 3$, 4 and 6, respectively[18,19].

In addition, the electrochemical behaviour of α,ω-diphenylpermethylated oligosilanes $Ph–(SiMe_2)_m–Ph$ has been determined. Cyclic voltammograms for α,ω-diphenylpermethylated oligosilanes are shown in *Figure 3*. The α,ω-diphenylpermethylated trisilane, tetrasilane and hexasilane show anodic current peaks at 1.95, 1.82 and 1.50 V vs. Ag/Ag^+, respectively. In a similar manner, the oxidation potentials of the α,ω-diphenylpermethylated oligosilanes increase with increasing dimethylsilylene chain length. Moreover, the $Ph–(SiMe_2)_m–Ph$ series show lower oxidation potentials than those of the corresponding $Me–(SiMe_2)_m–Me$ series. This result suggests that an intense interaction between the phenylene and the Si–Si chain affects the oxidation potential.

Figures 4–7 show cyclic voltammograms of σ–π organosilicon copolymers. It should be noted that the cyclic voltammograms of silylene–phenylene copolymer
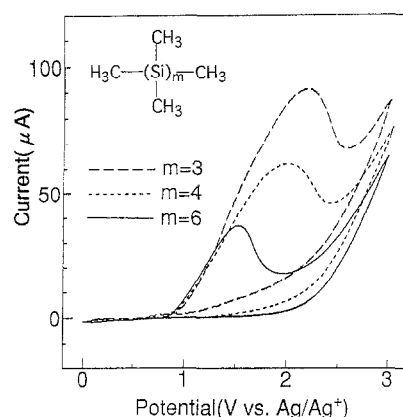

Figure 2 Cyclic voltammograms for 0.05 M permethylated oligosilanes in THF containing 0.1 M TBAP using a 0.02 cm² platinum electrode vs. Ag/Ag^+ (0.01 M $AgNO_3$ in 0.1 M TBAP acetonitrile) at 20 mV s⁻¹ sweep rate

Figure 1 Skeletons of silylene–phenylene copolymers **1a–d**, silylene–thienylene copolymers **2a–d**, silylene–diphenylene copolymers **3a–d** and silylene–anthranylene copolymers **4a–d**
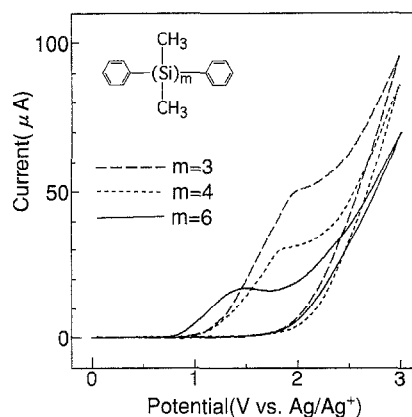

Figure 3 Cyclic voltammograms for 0.05 M α,ω-diphenylpermethylated oligosilanes in THF containing 0.1 M TBAP using a 0.02 cm² platinum electrode vs. Ag/Ag^+ at 20 mV s⁻¹ sweep rate

1a, silylene–thienylene copolymer 2a, silylene–diphenylene copolymer 3a and silylene–anthranylene copolymer 4a do not show any redox peak. There are two possible assignments for the electrochemical oxidation of organosilicon copolymers. The first one is the oxidation of the π unit and the other is the oxidation of the Si–Si chain. If the anodic wave could be attributed to the oxidation of the π unit, the anodic peak current should be observed for organosilicon copolymers with a dimethylsilylene unit ($m = 1$). However, organosilicon copolymers 1a, 2a, 3a and 4a ($m = 1$) show no anodic current peak as shown in *Figures 4–7*. Therefore, the anodic wave can be assigned to the oxidation of the Si–Si chain. The oxidation potentials for permethylated oligosilanes, α,ω-diphenylpermethylated oligosilanes and σ–π organosilicon copolymers are summarized in *Table 1*. The oxidation potentials of copolymers are lower than those of permethylated oligosilanes. For example, the first oxidation potentials of organosilicon copolymers 1d, 2d, 3d and 4d ($m = 6$) are 1.41, 1.60, 1.38 and 1.29 V, respectively, which are lower than that of permethylated hexasilane (1.68 V). Further, silylene–phenylene copolymers 1b–d show slightly lower oxidation potential in comparison with those of the corresponding α,ω-diphenylpermethylated oligosilanes. The decrease of the oxidation potential must be caused by

the σ–π conjugation between the dimethylsilylene chain and the π unit along the polymer chain.

The dependence of the first oxidation potentials upon the dimethylsilylene chain length are shown in *Figure 8* for permethylated oligosilanes, α,ω-diphenylpermethylated oligosilanes and copolymers 1a–d, 2a–d, 3a–d and 4a–d. The first oxidation potentials for these copolymers are lower than those for the corresponding permethylated oligosilanes in all cases. The order of oxidation potentials is consistent with the order of *IPs* of the incorporated π unit into the polymer chain except for silylene–anthranylene copolymers[20,21]: benzene (9.25 eV), thiophene (8.86 eV), diphenyl (8.27 eV) and anthracene (7.43 eV). The silylene–anthranylene copolymers show some deviation from the order of the *IPs* in *Figure 8*. There may be additional factors having an influence on the oxidation potential of copolymers. For example, the bulkiness of the large anthracene group may prevent the approach of the dimethylsilylene chain to the electrode. This effect may be significant in the case of the copolymer with a short silylene chain ($m = 3$ and 4).

The diffusion process of the redox species also influences the oxidation potential in the case of an irreversible system. The peak potential of the cyclic
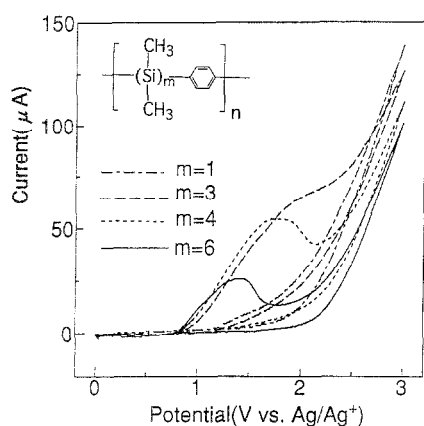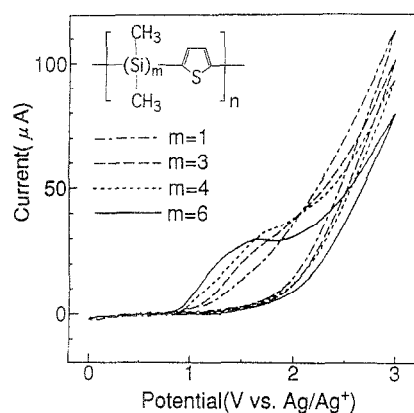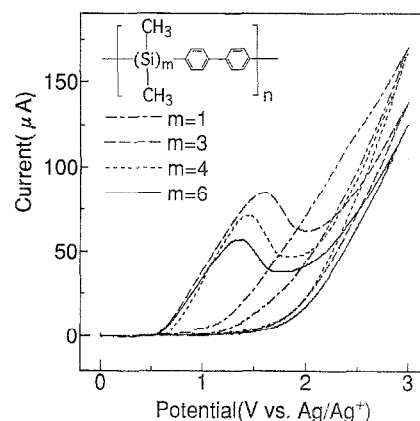

Figure 4 Cyclic voltammograms for 0.05 M repeat unit concentration silylene–phenylene copolymers 1a–d in THF containing 0.1 M TBAP using a 0.02 cm² platinum electrode vs. Ag/Ag⁺ at 20 mV s⁻¹ sweep rate

Figure 6 Cyclic voltammograms for 0.05 M repeat unit concentration silylene–diphenylene copolymers 3a–d in THF containing 0.1 M TBAP using a 0.02 cm² platinum electrode vs. Ag/Ag⁺ at 20 mV s⁻¹ sweep rate
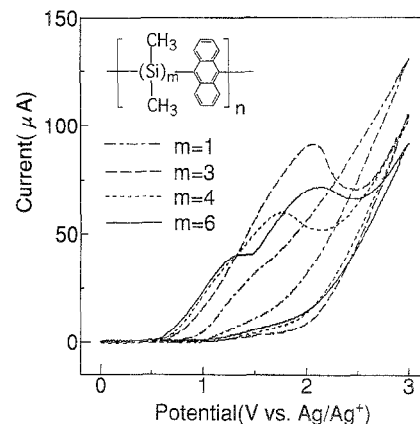

Figure 5 Cyclic voltammograms for 0.05 M repeat unit concentration silylene–thienylene copolymers 2a–d in THF containing 0.1 M TBAP using a 0.02 cm² platinum electrode vs. Ag/Ag⁺ at 20 mV s⁻¹ sweep rate
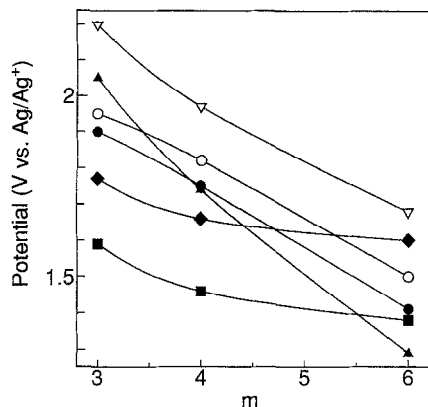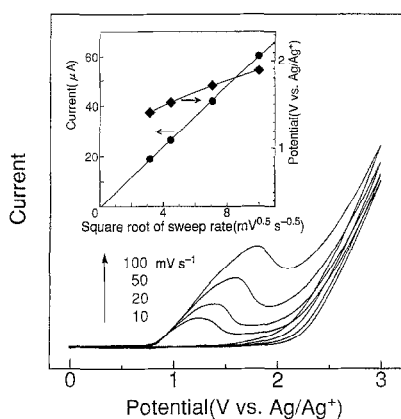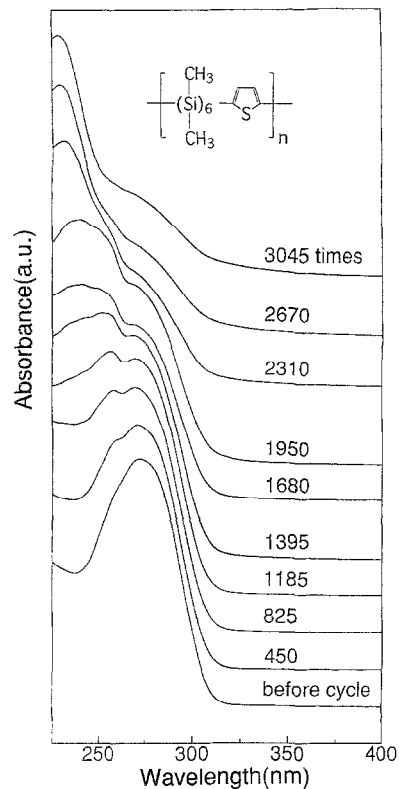

Figure 7 Cyclic voltammograms for 0.05 M repeat unit concentration silylene–anthranylene copolymers 4a–d in THF containing 0.1 M TBAP using a 0.02 cm² platinum electrode vs. Ag/Ag⁺ at 20 mV s⁻¹ sweep rate

Table 1 Summary of oxidation potentials (V) for 0.05 M permethylated oligosilanes, α,ω-diphenylpermethylated oligosilanes, silylene–phenylene copolymers **1a–d**, silylene–thienylene copolymers **2a–d**, silylene–diphenylene copolymers **3a–d** and silylene–anthranylene copolymers **4a–d** measured in 0.1 M TBAP/THF using Pt vs. Ag/Ag$^+$ at 20 mV s^{-1} sweep rate

Si chain length, m	Me–(SiMe$_2$)$_m$–Me	Ph–(SiMe$_2$)$_m$–Ph	Organosilicon copolymers			
			1a–d	**2a–d**	**3a–d**	**4a–d**
1			–^{a}	–	–	–
3	2.20	1.95	1.90	1.77	1.59	2.05
4	1.97	1.82	1.75	1.66	1.46	1.75
6	1.68	1.50	1.41	1.60	1.38	1.29, 2.09

^{a} Neither peak nor shoulder is observed

Figure 8 The plot of the first oxidation potential (V vs. Ag/Ag$^+$) vs. the dimethylsilylene chain length m for permethylated oligosilanes (▽), α,ω-diphenylpermethylated oligosilanes (○), silylene–phenylene copolymers **1a–d** (●), silylene–thienylene copolymers **2a–d** (◆), silylene–diphenylene copolymers **3a–d** (■) and silylene–anthranylene copolymers **4a–d** (▲) in THF electrolyte

Figure 9 Cyclic voltammograms for 0.05 M copolymer repeat unit concentration of silylene–phenylene copolymer **1d** in THF containing 0.1 M TBAP using a 0.02 cm^2 platinum electrode vs. Ag/Ag$^+$ at various sweep rates between 10 and 100 mV s^{-1}. Inset: plot of peak current and potential against square root of sweep rate

Figure 10 Absorption spectra of 0.15 mM repeat unit concentration of silylene–thienylene copolymer **2d** in THF containing 0.1 M TBAP using a 0.02 cm^2 platinum electrode and at 100 mV s^{-1} sweep rate in the 0.00 to +3.00 V range before and after repeated cycles on the cyclic voltammograms

voltammogram for an irreversible system is a function of the diffusion constant of the redox species and the potential sweep rate. *Figure 9* shows the dependence of cyclic voltammograms on the potential sweep rate for silylene–phenylene copolymer **1d**. The anodic peak shifts to higher potential with increasing sweep rate. The anodic peak current of the voltammograms is proportional to the square root of the sweep rate. This dependence is shown in the figure inserted in *Figure 9*.
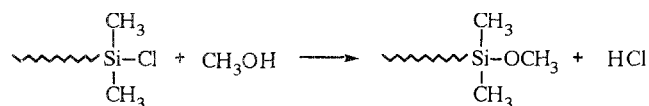
Degradation of organosilicon copolymers by electrochemical oxidation

The cyclic voltammograms of organosilicon copolymers showed significant irreversibility in *Figures 4–7*. These copolymers show only anodic waves without any cathodic waves. This suggests that the degradation of organosilicon copolymers by electrochemical oxidation. Absorption spectroscopy is an effective technique to study the degradation of organosilicon copolymers[22]. In the case of photodegradation, cleavage of the Si–Si chain reduces the σ conjugation along the polymer chain and the absorption spectrum shows a blue shift. The absorption spectra of silylene–thienylene copolymers **2a–d** were measured after a repetitive sweep between 0.00 and 3.00 V to investigate the degradation of the Si–Si chain. *Figure 10* shows the absorption spectra of 0.15 mM repeat unit concentration silylene–thienylene copolymer **2d** in THF during potential sweep cycles. On

increasing the number of repetitive potential sweep cycles, the absorbance at longer wavelength decreases and the absorption maximum gradually shifts towards lower wavelength. This result suggests the degradation of the Si–Si chain by electrochemical oxidation. The Si–Si bond must be cleaved via the radical cation state of silylene–thienylene copolymer **2d**. However, the absorption spectra of the silylene–thienylene copolymer **2a** showed only a decrease of the absorbance and did not show a blue shift as shown in *Figure 11*. The silylene–thienylene copolymer **2a** has no sequence of dimethyl-silylene units and no σ conjugation; therefore, the spectral change must be attributed to the degradation of the thienylene unit. Similar results were obtained for the other organosilicon copolymers. The degradation is caused by the oxidation of the Si–Si chain and the formation of the Si–O–Si bond.

Fti.r. spectra of organosilicon copolymers show the signals attributed to stretching vibrations of the Si–O linkage even before the electrochemical oxidation. The Si–O bond was formed as the end-group SiOCH₃ of organosilicon copolymers through the precipitation step in methanol, according to the following reaction:

$$\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\text{wwwSi–Cl}}} + CH_3OH \longrightarrow \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\text{wwwSi–OCH}_3}} + HCl$$

Since Okawara has assigned the band of ethoxy- and methylethoxy-oligosiloxanes near $1080\,cm^{-1}$ to the Si–O–C linkage[23], the bands near $1000\,cm^{-1}$ of silylene–phenylene copolymers in our previous paper[7] can be attributed to the Si–O–C linkage in methoxy end-groups. Moreover, di- and trimethoxysilanes show intense bands around $1050–1100\,cm^{-1}$ attributable to stretching vibrations of the Si–O band[24]. The signals of the SiOCH₃ group were also detected in the ¹H n.m.r. spectra near 3.5 ppm (multiplet).

Molecular-orbital calculations

Correlations have been reported between calculated highest occupied molecular orbital (HOMO) energies
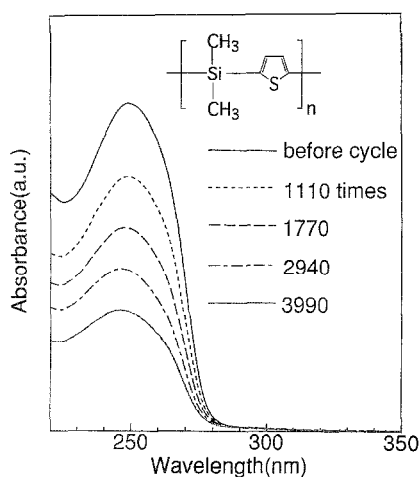
and experimental oxidation potentials[25–27]. The molecular orbitals (MOs) of organosilicon copolymers were calculated using the MNDO (modified neglect of differential overlap) method[28] to discuss the σ–π conjugation state and to identify the oxidation site in the polymer chain. The MNDO procedure, developed by Dewar and his collaborators[29], is known to be effective in predicting the orbital sequence in large molecules. The MO calculations were carried out for oligomer models as shown in *Figure 12*. The geometries of all the oligomer models were optimized by using the energy gradient method before MO calculations.

Figure 13 shows the MOs of the HOMO and lowest unoccupied molecular orbital (LUMO) level for the oligomer models of silylene–phenylene copolymers. The HOMO and LUMO energies were calculated for the optimized geometries. It is found that the possible oxidation site is in the HOMO level of the Si–Si chain except for the dimethylsilylene chain length $m = 1$. This result is consistent with the cyclic voltammograms of silylene–phenylene copolymer. Organosilicon copolymer **1a** $(m = 1)$ shows no anodic current peak of the dimethylsilylene unit as shown in *Figure 4*. On the other hand, the main orbitals of the HOMO level are distributed on the Si–Si chain. This result is also consistent with the assignment of the oxidation site to the Si–Si chain. The LUMO patterns show that the σ–π conjugation along the polymer chain becomes stronger with an increase in the dimethylsilylene chain length.

The *IPs* from the HOMO energies are plotted against the dimethylsilylene chain length m for the oligomer models in *Figure 14*. The σ–π conjugation between the Si–Si chain orbitals and the π unit orbitals increases the HOMO energy and results in a decrease in the first ionization potential with increasing dimethylsilylene chain length.
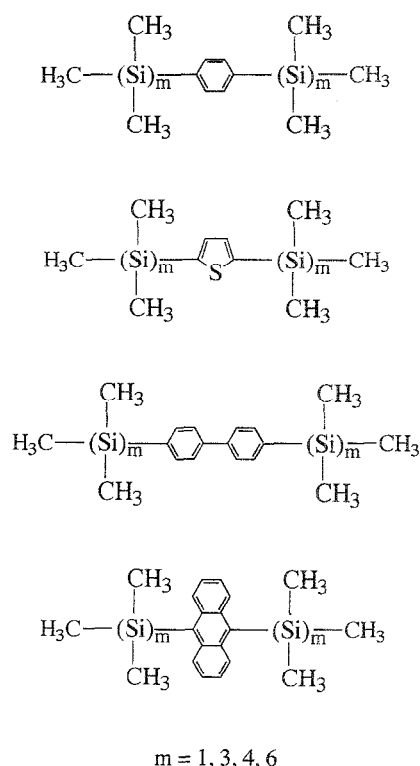

Figure 11 Absorption spectra of 0.15 mM repeat unit concentration of silylene–thienylene copolymer **2a** in THF containing 0.1 M TBAP using a 0.02 cm² platinum electrode and at 100 mV s⁻¹ sweep rate in the 0.00 to +3.00 V range before and after repeated cycles on the cyclic voltammograms

$m = 1, 3, 4, 6$

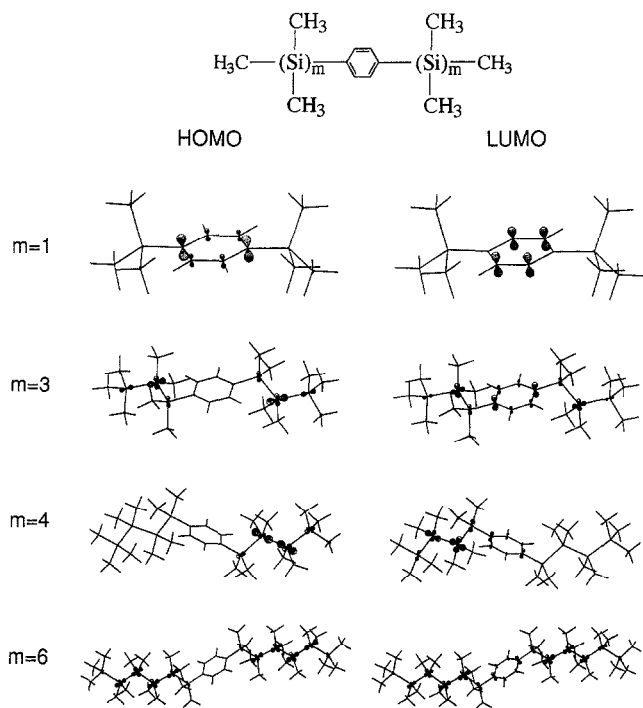**Figure 12** The oligomer models of σ–π organosilicon copolymers

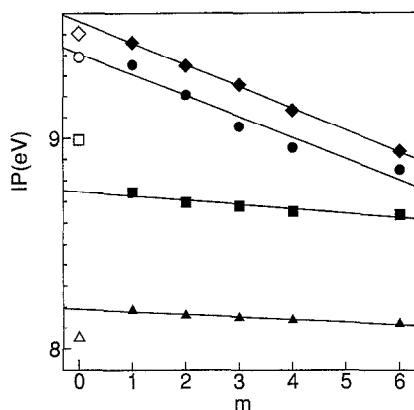Figure 13 Molecular-orbital patterns of the HOMO and LUMO for silylene–phenylene oligomer models

Figure 16 The changes of the *IP*s depending on the degree of polymerization *n* of $-[SiMe_2-Ph]_n-$ (◇), $-[(SiMe_2)_3-Ph]_n-$ (△), $-[(SiMe_2)_4-Ph]_n-$ (□) and $-[(SiMe_2)_6-Ph]_n-$ (○) by using MO calculations

The dependence of the degree of polymerization on the *IP* is estimated by MO calculations. *Figures 15* and *16* show the calculated *IP*s for permethylated oligosilanes and silylene–phenylene copolymers, respectively. It is shown that there is a decrease in *IP*s with increased degree of polymerization. The calculated *IP*s in the present study are in reasonable agreement with the experimental values for permethylated oligosilanes[30]. Decreases in *IP*s due to the σ conjugation and σ–π conjugation were found for permethylated oligosilanes and silylene–phenylene copolymers, respectively.

CONCLUSIONS

The oxidation potentials of silylene–phenylene, silylene–thienylene, silylene–diphenylene and silylene–anthranylene copolymers decreased with increasing dimethylsilylene chain length. In comparison with the electrochemical behaviour of the permethylated oligosilanes and α,ω-diphenylpermethylated oligosilanes, the decrease of the oxidation potential was explained by the σ–π conjugation between the dimethylsilylene chain and the π unit. The MO calculation demonstrated the enhancement of the σ–π conjugation with increasing dimethylsilylene chain length.

Figure 14 The changes of the *IP*s depending on the dimethylsilylene chain length *m* for silylene–phenylene (●), silylene–thienylene (◆), silylene–diphenylene (■) and silylene–anthranylene (▲) oligomer models, benzene (○), thiophene (◇), diphenyl (□) and anthracene (△)
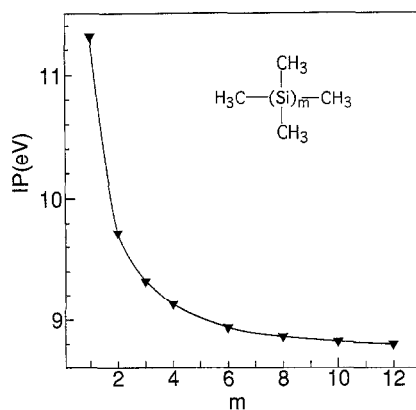
Figure 15 The changes of the *IP*s depending on the degree of polymerization *m* of permethylated oligosilanes by using MO calculations
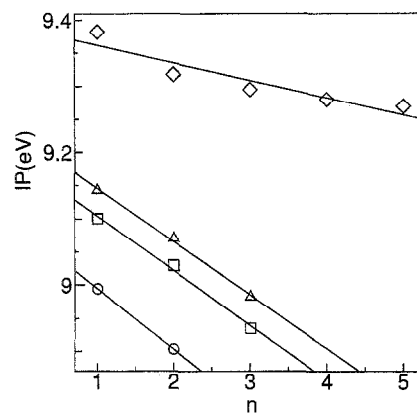
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