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# Mobilities of charge carriers hopping between π-conjugated polymer chains

**Xiaoqing Jiang,[a] Yutaka Harima,*[a] Lihua Zhu,[a] Yoshihito Kunugi,[a] Kazuo Yamashita,[a] Mune-aki Sakamoto[b] and Masa-aki Sato[b]**

[a]*Faculty of Integrated Arts and Sciences, Hiroshima University, 1-7-1 Kagamiyama, Higashi-Hiroshima 739-8521, Japan. E-mail: harima@mls.ias.hiroshima-u.ac.jp*
[b]*Faculty of Mercantile Marine Science, Kobe University of Mercantile Marine, 5-1-1 Fukae-Minami, Kobe 658-0022, Japan*

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Mobilities of charge carriers in a copolymer film where a possible charge transport is restricted to an interchain path are measured by electrochemical means with doping level as a parameter. The mobility in the low doping regime, corresponding to that of polarons, is $10^{-6}$ cm$^2$ V$^{-1}$ s$^{-1}$, comparable with polaron mobilities in polythiophene films where hopping transports *via* interchain and intrachain routes are both feasible. The coincidence suggests strongly a potential role of the interchain hopping transport in the conduction mechanism of common conducting polymers. As the doping level increases, the mobility falls down to $0.4 \times 10^{-6}$ cm$^2$ V$^{-1}$ s$^{-1}$ and then rises up to $6 \times 10^{-6}$ cm$^2$ V$^{-1}$ s$^{-1}$. Based on spectroelectrochemical measurements of the copolymer film, the decrease of the mobility is interpreted in terms of the generation of cation radical π-dimers that are inactive in charge transport. The mobility increase in a high doping region is ascribed to some structural change of a polymer network, leading to enhancement of the interchain hopping probability.

## Introduction

Organic electrically conducting polymers have attracted much attention in the last two decades, since Heeger and MacDiarmid discovered that polyacetylene, synthesized by the Shirakawa method, underwent a 12 orders of magnitude increase of conductivity upon oxidative doping.[1] Organic polymers had been usually considered as insulating materials until π-electron conjugated polymers such as polyacetylene, polythiophene, polypyrrole, and polyaniline were found to give fairly high conductivities when they were chemically or electrochemically doped *via* an oxidative or a reductive process. These kinds of π-conjugated polymers are referred to as organic conducting polymers and a lot of work has been devoted to understanding of structures and properties of the conducting polymers from academic and technological viewpoints.

Our interest has been directed toward the conduction mechanism in these conducting polymers. A one dimension theory has been proposed, where the generation of one dimensional charge carriers, polarons and bipolarons, is considered to account for conductivities, spectra, and structures of oxidized polythiophene and other conducting polymers.[2,3] In contrast to this early view, recent studies suggested that a cation radical π-dimer is formed in some oligothiophenes by coupling of two polarons on adjacent chains and is a structural alternative to bipolarons in common conducting polymers.[4–7] It was speculated further that the diamagnetic π-dimers may play a crucial role in the conduction mechanism by mediating an interchain hopping of charges, although a possible involvement of π-dimers in the conduction process has not been fully discussed so far. In our previous study aiming to clarify this point, a copolymer film consisting of oligothiophenes bridged by Si atoms (MS5T-OEt, see Fig. 1) was utilized since the intrachain π-electron hopping through a single polymer chain was supposed to be limited by Si atoms and only the interchain hopping may be realized in this copolymer film.[8] With the MS5T-OEt film, however, there still remained a faint doubt that oligothienylene and monosilanylene units interact through a π-$d_{Si}$ conjugation[9] and thus a charge transport through C–Si–C single bondings is unable to be ruled out thoroughly. For this reason, the MS5T-OEt film is replaced in the present work with a poly[(3′,3″,4‴,4⁗-tetrahexyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2′′′′′-sexithiophene-5,5′′′′′-diyl)ethylene] (PSE) film (see Fig. 1 for its chemical structure) where the intrachain hopping may be prohibited by a higher and wider potential barrier due to the aliphatic ethylene unit replacing the monosilanylene unit in MS5T-OEt. Another reason we selected this copolymer for investigation lies in our expectation that the PSE copolymer consisting of oligothiophenes bridged by carbon atoms may be more stable against oxidation than MS5T-OEt and thus may be studied in a wider potential range enabling generations of bipolarons as well as polarons and π-dimers.

The results of the present study will be helpful in understanding the roles of the interchain charge transport and π-dimers in the conduction process of common conducting polymers.

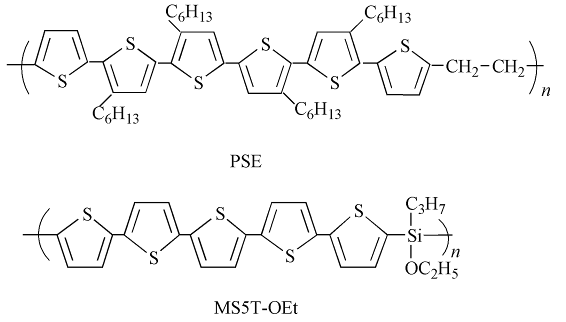

**Fig. 1** Chemical structures of PSE and MS5T-OEt.

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## Experimental

The synthesis and characterization of PSE have been reported earlier.[10] All other chemicals were of reagent grade or better. Tetraethylammonium perchlorate ($Et_4NClO_4$) from Katayama Chemicals was used as a supporting electrolyte after being purified by recrystallization from ethanol and dried under vacuum at 70 °C. Acetonitrile (MeCN) from Tokyo Kasei was refluxed over $P_2O_5$ for several hours under $N_2$ atmosphere and then distilled just before use. Copolymer films for electrochemical measurements were prepared on an indium–tin oxide (ITO) electrode or a microarray electrode by spin coating from a chloroform solution of PSE. The film thickness measured by UV-vis absorption spectroscopy was about 0.2 μm. Electrochemical measurements were made in an air-tight glass cell with two subsidiary compartments: one was for the reference electrode ($Ag/AgClO_4$ (0.1 M), $Et_4NClO_4$ (0.1 M)) and the other for the Pt counter electrode.

Apparent mobilities ($\mu$) of charge carriers in the PSE film were evaluated from the equation $\mu = \sigma/ne$ for a single carrier model where $\sigma$ is the conductivity and $n$ is the density of charge carriers. Here, $e$ denotes a unit charge. Conductivities of the copolymer film were measured *in situ* by use of the two-probe method with a microarray electrode of a 20 μm channel spacing.[8] The voltage between two Pt bands of the microarray electrode was swept between $\pm 2$ mV with one of the Pt bands being fixed at a desired potential. The potential scan rate was changed from 0.048 mV $s^{-1}$ to 2 mV $s^{-1}$ in order to observe a possible influence of the scan rate on the conductivities. The degree of oxidation of the PSE film was also controlled by an applied potential and the amount of charge in the PSE film at a given potential ($Q$) was determined from the plot of the amount of electricity *vs.* time in potential-step chronocoulometry as described earlier.[11] The measurements were made with the same PSE-deposited microarray electrode simultaneously with the conductivity measurement. The carrier density $n$ was evaluated from $n = \rho Q/eW$ with the data of $Q$, the film density ($\rho$), and the weight of the copolymer film ($W$). The $\rho$ value of the PSE film was assumed as 1.0 g $cm^{-3}$ and $W$ was estimated by measuring an absorption spectrum of a PSE film dissolved in chloroform. Doping levels, defined as the number of unit charges per thiophene ring, were obtained from $Q$ and $W$.[12] The above electrochemical measurements, including cyclic voltammetry, were made with Hokuto Denko HAB-151 potentiostat/galvanostats integrated with a function generator, in conjunction with a Riken Denshi F5C *x–y* recorder. *In situ* absorption spectra were taken on a Shimadzu UV-3101 spectrophotometer, where an air-tight thin layer cell (5 mm in optical pathlength) with ITO as the counter electrode and the $Ag/Ag^+$ reference electrode in a separate compartment was employed. Sample solutions were transferred into the cell with a syringe.

Prior to electrochemical or spectroelectrochemical measurements, the copolymer film was activated as described later. All the measurements were made at room temperature unless otherwise stated.

## Results

Curve 1 of Fig. 2 depicts a typical cyclic voltammogram of a PSE film in MeCN, where the potential is cycled between −0.2 and 0.52 V at 100 mV $s^{-1}$. The voltammogram exhibits a pair of redox waves with oxidation/reduction peak potentials at 0.49/0.37 V. The oxidation and reduction peak currents increased by 2–5% per cycle during the initial several scans and reached a maximum in about the 40th scan. Further repeated scans up to 200 times resulted in a slight decrease of the oxidation peak current with a negative shift of the peak potential. A similar trend has already been reported for the MS5T-OEt film and explained by a highly insulating nature of the pristine film of the copolymer which is likely to prevent a uniform oxidation of the film.[13] This may also be the case for the PSE film. In contrast to the MS5T-OEt film[13] however, no clear oxidation peak corresponding to the second oxidation step is seen in curves 2–7 obtained by cycling the potential between −0.2 and 0.8 V. Furthermore, anodic currents at higher potentials decrease with repeated potential scans. This finding suggests that dications (bipolarons) in the PSE film are less stable than in the MS5T-OEt film, which is different from our expectation for stabilities of the two copolymers. Indeed, after the potential-cycling experiment between −0.2 and 0.8 V, the PSE film was found to become insoluble in chloroform, indicative of a further polymerization of the copolymer. On these bases, prior to electrochemical and spectroelectrochemical measurements pristine PSE films were treated by cycling the potential between −0.2 and 0.5 V at 100 mV $s^{-1}$ for more than several tens of times. This activation process of the PSE film was completed sooner as the switching potential was higher, but the switching potential of 0.5 V was selected to avoid possible degradation of the PSE film.

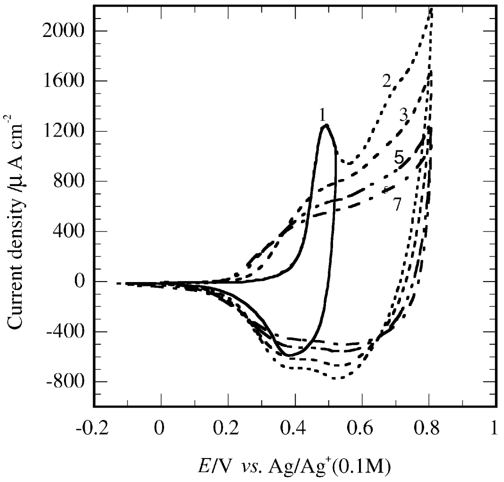

**Fig. 2** Cyclic voltammograms of a PSE film in MeCN–$Et_4NClO_4$ (0.1 M) at 100 mV $s^{-1}$. The switching potential was 0.52 V for curve 1, and 0.8 V for curves 2–7. Numerals denote the cycle number. The film thickness is around 0.2 μm.

Cyclic voltammograms of the PSE film were also measured at −20 °C. They exhibited two oxidation peaks at 0.7 V and 1.2 V, but one reduction peak at 0.55 V. On the other hand, two pairs of redox waves were observed in cyclic voltammograms of PSE dissolved in dichloroethane with oxidation/reduction peak potentials at 0.40/0.29 V and 0.58/0.51 V with respect to $Ag/Ag^+$(0.1 M) in the same solvent. Similarly to the voltammograms for the PSE film, the shape of the first pair of redox peaks for PSE in solution remained almost unchanged in successive cycles when the switching potential was below 0.5 V. When the switching potential was raised to 0.65 V, however, the current increased and the voltammograms changed significantly with repeated scans.

As in our previous doping-level measurements,[11,13] doping and dedoping charges coincided well with each other when the doping potential was not so high, suggesting a reversible nature of the doping/dedoping process at the PSE film in the limited potential range. As the doping potential was increased beyond 0.55 V, however, the doping charge became slightly greater than the dedoping charge. For this reason, doping-level measurements for the PSE film were carried out up to a potential of 0.525 V. Fig. 3 depicts a plot of doping level *vs.* potential. It is seen that the logarithm of the doping level increases almost linearly with potential in the range of 0.30–0.35 V and levels off at higher potentials. The slope of the linear portion is 40 mV $decade^{-1}$ of doping level, almost half of the slope value for the MS5T-OEt[8] and close to a theoretical slope for a

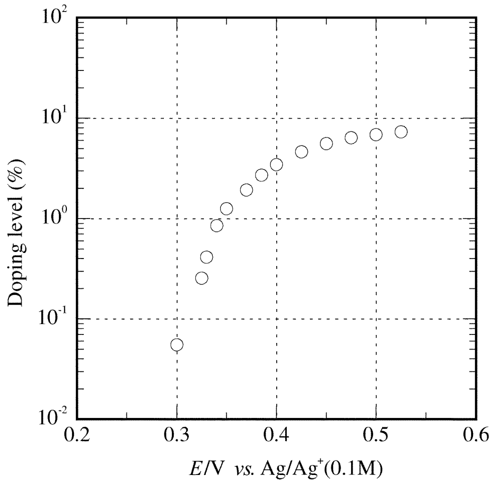

**Fig. 3** Logarithmic plot of doping level *vs.* potential for the PSE film.

reversible two-electron transfer process (30 mV decade$^{-1}$). The maximum doping level of 7% at 0.525 V is smaller than a theoretical value for a one-electron oxidation of a sexithienylene unit of PSE (17%).

Conductivities of the PSE film were found to depend considerably on the scan rate of potential in the two-probe method especially when the doping potential was less positive. The dependencies are shown in Fig. 4 as plots of $\sigma$ *vs.* scan rate at different doping potentials. Fig. 4a for lower doping potentials shows that the conductivity of the PSE film increases linearly with the scan rate between 0.048 and 0.4 mV s$^{-1}$, although the data points tended to fit straight lines in the $\sigma$ *vs.* (scan rate)$^{1/2}$ plots at higher scan rates (not shown). The slope decreases and tends to become zero at higher potentials as shown in Fig. 4b. We suppose that the scan-rate dependence of $\sigma$ originates from the difference between the currents flowing normal to the two Pt band electrodes from the counter electrode. In *in-situ* conductivity measurements, the potential of one electrode is fixed, and that of the other is varied linearly with respect to the former electrode. Under these conditions the currents flowing to the two electrodes from the counter electrode are likely to be different in magnitude. This current difference should be included in the measured current and affect the evaluation of the conductivity of the polymer film itself. It is reported in the literature that in the case where diffusion phenomena are not involved in the redox process the redox peak current of a conducting polymer film grafted on an electrode varies linearly with the potential scan rate.[14] If this applies to the PSE film, the influence of the current difference in the intermediate doping region may be reasonably eliminated by extrapolating each straight line to the zero scan rate as shown by dotted lines in Fig. 4a. Details of the scan-rate dependence of conductivity will be discussed in a separate paper.[15] Fig. 5 depicts corrected values of $\sigma$ plotted against potential, where the potential is controlled below 0.525 V to ensure the stability of the PSE film. The conductivity increases by about three orders of magnitude from $4.1 \times 10^{-7}$ S cm$^{-1}$ at 0.3 V to $2.5 \times 10^{-4}$ S cm$^{-1}$ at 0.525 V. When the potential was raised beyond 0.55 V, the conductivity decreased with time, indicative of degradation of the PSE film at higher potentials.

Apparent mobilities $\mu$ calculated from corrected $\sigma$ values and carrier densities $n$ obtained from $Q$ are plotted in Fig. 6 as a function of the doping level, together with three similar plots for poly(3-methylthiophene) (PMT),[16] polythiophene (PT)[12] and MS5T-OEt. The plot for the MS5T-OEt film is replaced with a new one which was obtained by taking into account a scan rate dependence of conductivities. The mobility of the PSE film is $10^{-6}$ cm$^2$ V$^{-1}$ s$^{-1}$ in the low doping regime, and starts to decrease at a doping level of 0.3%, and then increases sharply to reach $6 \times 10^{-6}$ cm$^2$ V$^{-1}$ s$^{-1}$ at a 7% doping level. Here, the doping range 0.3–7% corresponds to the potential range 0.325–0.525 V. The mobility measurements were repeated several times and a similar trend was observed for the $\mu$ *vs.* doping level plot. Especially, it was confirmed that mobilities in the doping range 0.02–0.3% were constant at *ca.* $10^{-6}$ cm$^2$ V$^{-1}$ s$^{-1}$.

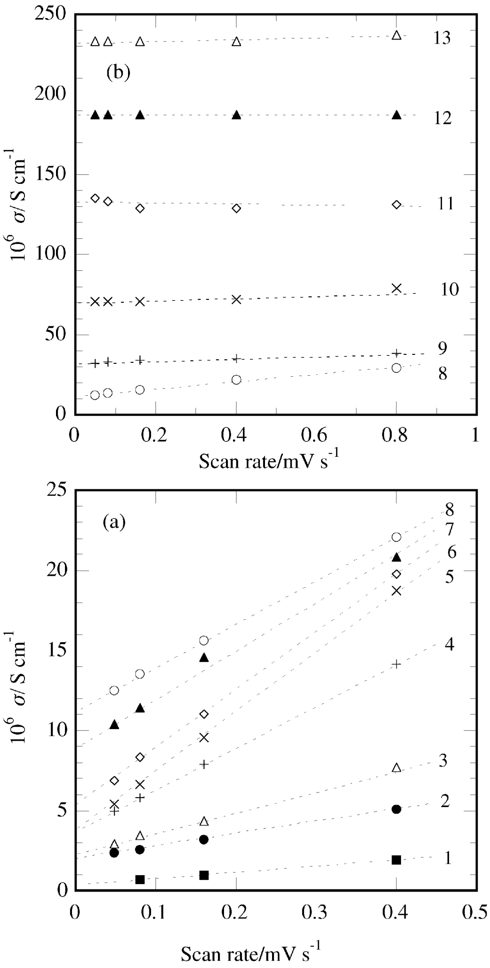

**Fig. 4** Scan rate dependence of conductivity of the PSE film at different doping potentials of 1) 0.30, 2) 0.325, 3) 0.33, 4) 0.34, 5) 0.35, 6) 0.37, 7) 0.385, 8) 0.40, 9) 0.425, 10) 0.45, 11) 0.475 , 12) 0.50, and 13) 0.525 V.

UV-vis-NIR spectroelectrochemistry of the PSE film on ITO was conducted to identify chemical species that are generated at various oxidation stages of the copolymer film. When the

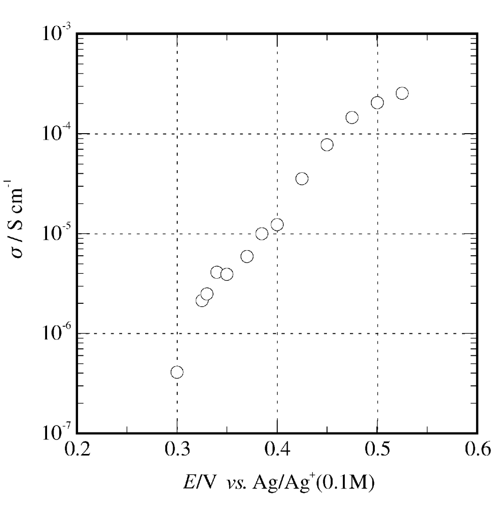

**Fig. 5** Logarithmic plot of *in situ* conductivity *vs.* potential for the PSE film.

applied potential was less positive than about 0.5 V, absorption spectra of the PSE film changed reversibly. However, once the copolymer film was oxidized at potentials beyond 0.5 V, its spectrum did not recover to the initial one any longer and the PSE film became insoluble in chloroform. These observations correspond well to an irreversible nature observed in the doping-level and conductivity measurements at high potentials. The neutral film was yellow and its bandgap absorption appeared at 2.93 eV. As the potential was increased, the film changed its color from yellow to deep-blue. Fig. 7 depicts difference absorption spectra of the PSE film in the potential range 0.20–0.50 V, where the spectrum at 0 V is used as reference. At potentials below 0.3 V, weak absorption bands are seen at 0.85 and 1.65 eV. When the potential is increased to 0.325 V, two absorption bands at 0.90 and 1.80 eV become dominating. As the potential increases further to 0.50 V, we note a hypsochromic shift of the 0.90 eV band and a bathochromic shift of the 1.80 eV band.

Oxidation of PSE was also performed in dichloroethane by a stepwise addition of a concentrated $FeCl_3$ solution and absorption spectra of PSE at various oxidation stages were taken. Fig. 8 depicts difference absorption spectra of the PSE solution, where the spectrum of a neutral solution was used as reference. Upon oxidation, two absorption bands appear at 0.78 and 1.58 eV each with a shoulder on the high-energy side. Up to the addition of one equivalent of $FeCl_3$, the two bands increase their intensities whilst keeping the shapes almost unchanged. Further oxidation up to about two equivalents of $FeCl_3$, corresponding to a complete one-electron oxidation of a sexithienylene unit in PSE, leads to new bands at 0.93 and 1.78 eV. By oxidizing the PSE solution further, two new

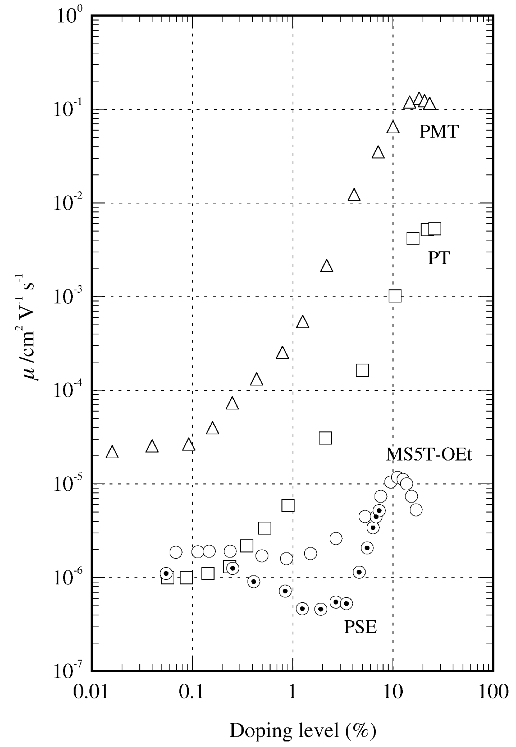

**Fig. 6** Apparent mobilities of positive charge carriers in the (⊙) PSE, (○) MS5T-OEt, (△) PMT, and (□) PT films.

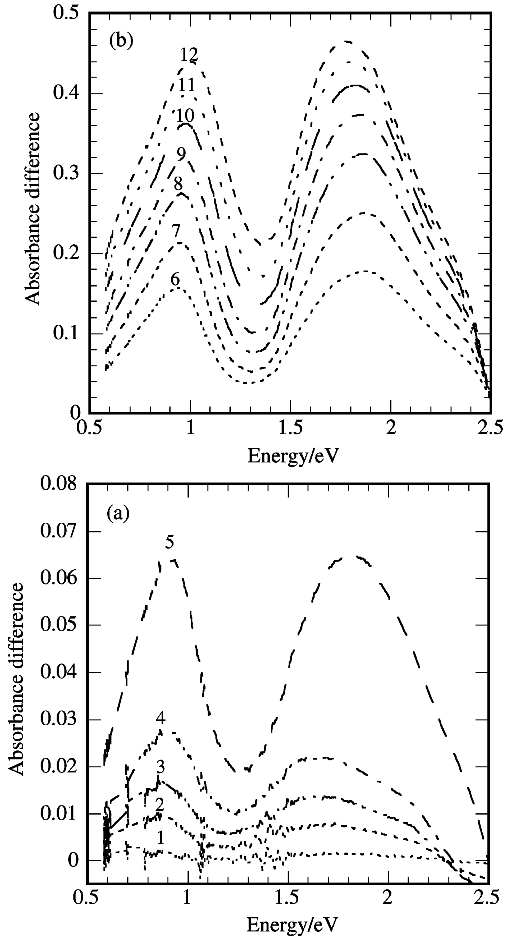

**Fig. 7** Difference absorption spectra of a PSE film on ITO electrode at potentials of 1) 0.225, 2) 0.25, 3) 0.275, 4) 0.30, 5) 0.325, 6) 0.35, 7) 0.375, 8) 0.40, 9) 0.425, 10) 0.45, 11) 0.475, and 12) 0.50 V in MeCN–$Et_4NClO_4$ (0.1 M).

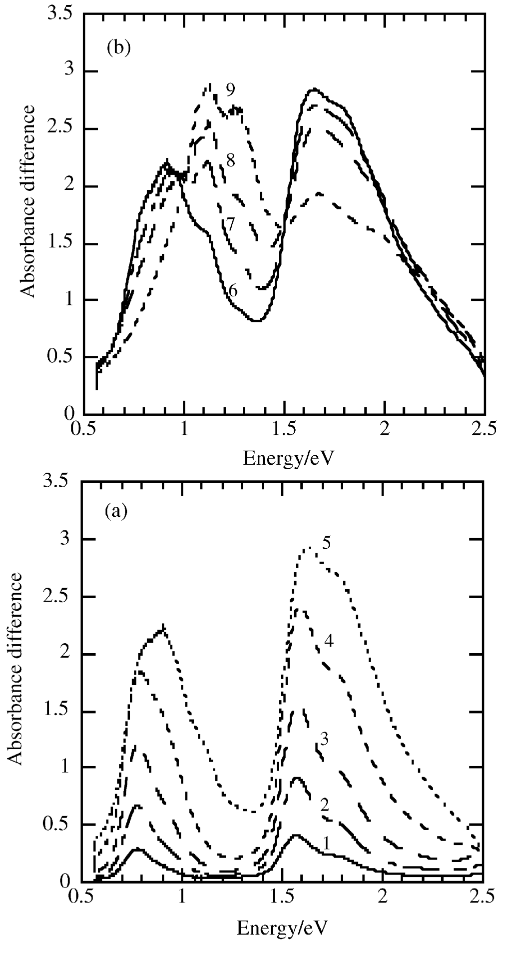

**Fig. 8** Difference absorption spectra of a 0.1 mM solution of PSE in dichloroethane after oxidation with 1) 0.16, 2) 0.32, 3) 0.56, 4) 1.04, 5) 2.0, 6) 2.5, 7) 3.2, 8) 4.4, and 9) 8.8 equivalents of $FeCl_3$.

absorption bands appear at 1.12 and 1.26 eV with a simultaneous extinction of other absorption bands, although the intensities of the two bands decreased with time.

## Discussion

In Table 1 are summarized spectroscopic data of sexithiophene and related compounds in the literature.[17–25] Peak positions of the first set of absorption bands for PSE in dichloroethane (0.78 and 1.58 eV) compare well with those for cation radicals (polarons) of sexithiophene and its derivatives, while energies of the second set (0.93 and 1.78 eV) are in good agreement with those for cation radical π-dimers. As is also seen from Table 1, absorption bands observed temporarily for heavily oxidized PSE solutions (1.12 and 1.26 eV) are ascribable to dications (bipolarons). In view of the assignment and by comparing Figs. 7 and 8, one can interpret absorption spectra of the PSE film at various potentials as follows: Major chemical species are polarons in the PSE film at potentials below 0.3 V which corresponds to the lowest doping level of 0.06% in Fig. 3. At a potential of 0.325 V, π-dimer bands at 0.90 and 1.80 eV appear and become dominating. As the potential is increased beyond 0.4 V (3% doping level), peak positions of the π-dimer bands shift gradually. Because of the energy shifts and extensive overlap of polaron and π-dimer bands, a quantitative estimation of an equilibrium constant for π-dimerization ($K$) in PSE film was not made, whereas the $K$ value for the MS5T-OEt film is estimated as 10 $\mathrm{M}^{-1}$.[26] It is found that longer π-conjugated oligomers dimerize more and the $K$ value increases by a factor of $10^3$ on going from terthiophene to quinquethiophene.[22] Thus, it is reasonable to presume that the $K$ value for the PSE film is greater than that for the MS5T-OEt film since they are copolymers of sexithiophene and quinquethiophene, respectively. Ease of the generation of π-dimers in the PSE film is readily seen from a comparison of Fig. 7 and Fig. 6 of ref. 26 for the MS5T-OEt film. Based on the above spectroscopic findings, we will discuss the mobility of charge carriers in the PSE film and its dependence on the doping level below.

It is now evident that the majority of charge carriers in the PSE film of doping levels below 0.3% are polarons and thus the mobility of polarons is determined from Fig. 6 as $10^{-6}$ cm$^2$ V$^{-1}$ s$^{-1}$. In view of the fact that the electrical conduction in the PSE film is limited to the interchain path, the mobility reflects the rate of a hopping transport of polarons between adjacent sexithienylene units in separate chains. If two sexithienylene units in the same copolymer chain are overlapped, a charge transport from one oligomeric unit to another not through the ethylene unit is feasible. According to the definition of the term, this is also an interchain hopping process though not explicitly stated in this and previous papers.[8,12,16] Its rate may not differ much from that for the interchain hopping transport because a charge hopping in both transport processes takes place *via* a π–π interaction between two neighboring π-conjugated units. Because of a mechanistic similarity, our mobility measurements will be discussed below by classifying formally this type of an intrachain process into the interchain hopping transport. The mobility value of $10^{-6}$ cm$^2$ V$^{-1}$ s$^{-1}$ is in close agreement with those of polarons in MS5T-OEt and PT films. The agreement of mobilities in PSE and MS5T-OEt films indicates that a hopping transport of charges in the latter film is blocked effectively by a Si atom bridging two quinquethienylene units just like a non-conjugated ethylene unit in the former film. Moreover, the mobility coincidence between PSE and PT films suggests that a possible intrachain hopping of charges in the PT film may contribute little to macroscopically observed conductivities and the rate of the interchain hopping path determines the mobility. The conclusion suggests that high mobility molecular materials will be realized not by extending a π-conjugation length of a polymer, but by enhancing a π–π interaction between π-conjugated units. π-Conjugated polymers and oligomers with high mobilities reported so far meet this condition.[27–30] The current electrochemical technique has been applied to a polymer film consisting of regioregular poly(3-octylthiophene) (POT) for determining mobilities.[31] POT is known to form a well-defined highly stacked film. This stacked polymer film in the low doping regime gives a mobility value close to $10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$, in good agreement with those for similar polymers evaluated by the field-effect-transistor technique.[29]

Absorption spectra of the PSE film shows that cation radical π-dimers start to be created at doping levels beyond 0.3%. It is seen from Fig. 6 that the mobility starts to decrease at almost the same doping level. On this basis, it is reasonable to assume that π-dimers are immobile and their generation in the doping range above 0.3% is responsible for the decrease of apparent mobilities calculated from the single carrier model. Zotti has obtained a similar conclusion that polarons are pinned by π-dimerization.[32] The mobility decrease for the PSE film is more evident than the case of the MS5T-OEt film. The difference may be accounted for in terms of the difference in the $K$ value between the two copolymer films. Similar mobility decrease is reported for the POT film and is explained in part by increased molar fractions of π-dimers at higher doping levels. This is confirmed by measuring EPR spectra of the POT film at various potentials because polarons are paramagnetic while π-dimers are diamagnetic.[31] In contrast, we have considered diamagnetic species in the PMT and PT films as bipolarons in place of π-dimers.[12,16] Mobilities of charges in these polymer films increase drastically with the increase of the doping level or with the increase of the molar fraction of diamagnetic species,

**Table 1** Summary of spectroscopic data for sexithiophene and its derivatives in organic solvents

| | UV-vis-NIR data/in eV | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Neutral | Polaron | | π-Dimer | | Bipolaron | | | | |
| Compound | | 1 | 2 | 1 | 2 | 1 | 2 | 3 | Solvent | Ref. |
| Unsubstituted sexithiophene | 2.87 | 0.84 | 1.59 | 0.98 | 1.81 | 1.24 | 1.36 | | $CH_2Cl_2$ | 17 |
| | 2.85 | 0.86 | 1.60 | | | 1.24 | | 2.07 | | 18 |
| Dialkylsexithiophene | 2.97 | 0.87 | 1.60 | 1.12 | 1.81 | 1.31 | 1.47 | | $CH_2Cl_2$ | 19 |
| β-Didecylsexithiophene | 2.92 | 0.84 | 1.59 | (1.0)[a] | (1.72)[a] | 1.26 | | 2.34 | $CH_2Cl_2$ | 20 |
| α-Dihexylsexithiophene | 2.80 | 0.78 | 1.53 | | | 1.17 | | 2.26 | $CH_2Cl_2$ | 20 |
| α-Bis(trimethylsilyl)sexithiophene | 2.94 | 0.79 | 1.59 | 0.97 | 1.78 | 1.14 | 1.30 | | $CH_2Cl_2$ | 21 |
| Methyl-terminated tetramethoxysexithiophene | 2.55 | 0.73[b] | 1.44[b] | 0.98[c] | 1.75[c] | 1.2[b] | | | $CH_2Cl_2$[b]<br>$CH_3CN$[c] | 22 |
| Didodecylsexithiophene | 2.92 | 0.84 | 1.59 | 1.0 | 1.81 | 1.28 | 1.42 | | $CH_2Cl_2$ | 23 |
| β-Tetrahexylsexithiophene | 3.0 | 0.80 | 1.55 | 1.0 | 1.8 | 1.22 | 1.35 | | $CH_2Cl_2$ | 24 25 |

[a] Values in parentheses are obtained from spectra in ref. 18. These transitions were previously assigned to vibronic coupling. [b] $CH_2Cl_2$ as solvent. [c] $CH_3CN$ as solvent.

indicative of entirely different contributions of the two diamagnetic species, bipolarons and π-dimers, to apparent mobilities. The second stage of the mobility increase at doping levels higher than *ca.* 1% is explained by the transition of a transport mechanism from a hopping transport to a metallic conduction.[33] We should point out, however, the conclusion that the mobility decrease observed for PSE film is caused by the formation of π-dimers is not conclusive at present when EPR data for PSE are not available. The mobility decrease might be explained alternatively by the conformation change of the polymer.

A final feature to be discussed on the mobility change observed for the PSE film is the increase in the high doping region beyond 3%. As shown in Fig. 6, the mobility increases from $5 \times 10^{-6}$ cm$^2$ V$^{-1}$ s$^{-1}$ at *ca.* 2% doping level to $5 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$ at the highest doping level of 7%. The observed mobility change is quite similar to the case of MS5T-OEt. We note further that the onset doping level of the mobility increase for these copolymers corresponds well to those for the second stage of the mobility increase observed clearly with the PMT film and less clearly with the PT film. Similarly, a three orders-of-magnitude increase of the mobility is found to set in at a doping level of 2% for the POT film.[31] Compared with the large mobility increase for these polymer films having long π-conjugation lengths, PSE and MS5T-OEt films whose π-conjugation extends only over six and five thiophene units give a relatively small increase of mobilities. Despite the difference, the common onset doping level of a few percent observed with these polymers and copolymers all based on thiophene hints that the mobility increase may be caused by the same origin. Involvement of bipolarons is highly unlikely to account for the mobility enhancement because they are so unstable to be present in the PSE film. So far as the PSE film is concerned, a hypsochromic shift of the 0.95 eV band and a bathochromic shift of the 1.86 eV band are observed in the doping region of current interest. The mobility increase for the PSE film might be related to some structural change of the copolymer film associated with shifts of these absorption bands. More elaborate studies will be required to clarify the cause for the mobility enhancement in the relatively high doping region, although evolution of the metallic conduction is still an important candidate for it.

## Conclusion

According to the results of cyclic voltammetry and UV-vis-NIR spectroscopy, cation radicals (polarons) and their π-dimers are stable in the PSE film while dications (bipolarons) are found to be less stable, which is different from our expectation. Apparent mobilities in the PSE film at low doping levels are constant and are of the same order of magnitude as those for the PT and MS5T-OEt films. The coincidence of mobility values between π-conjugated polymers with and without high potential barriers in the polymer chain suggests strongly that the interchain hopping transport of polarons is a dominating path of the electrical conduction in lightly doped polymer films. The decrease of apparent mobilities with the increase of doping level supports our previous conclusion that π-dimers are almost immobile and a hopping transport of charges is unlikely to be mediated by π-dimers. The increase of mobilities at doping levels higher than 3% seems to be related to some structural change of the copolymer film, speculated from the continuous shifts of absorption peaks of the film in the corresponding doping region.

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