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Soluble polymers with constant π-conjugation length: polymers containing thiophene tetramers and hexamers

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Abstract

Soluble polymers (PQE and PSE) with each constant π-conjugation length, containing thiophene tetramers and hexamers in the main chains, were prepared by reductive condensation, respectively. The obtained polymers were soluble in common organic solvents. Cast films could be obtained from their solutions. The PQE and PSE films doped with $FeCl_3$ showed considerable conductivities, $9\text{-}7 \times 10^{-3}$ and 0.4-0.2 S(cm, respectively. The polymer solutions and films were oxidized (doped) by stepwise addition of $FeCl_3$ and characterized by electronic absorption spectra. The spectral change of the PQE solutions and films showed one-step oxidation to produce cation radicals, whereas that of the PSE solutions and films did two-step oxidation to yield cation radicals in the first step and plural-electron-oxidized species such as dications in the second step. In atmosphere, the plural-electron-oxidized species of the PSE films are extremely labile. The spectra of the oxidized PSE films in atmosphere were almost similar to that of doped polythiophene films, indicating that oxidized species existing in doped polythiophenes are mainly cation radicals. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Oligothiophene; Polythiophene; Oxidation

1. Introduction

The electrical and optical properties of π-conjugated polymers have attracted attention of many researchers and then drawn the proposals for their various applications such as batteries, display devices, and molecular electronic devices. Among the polymers, polythiophene and its derivatives have been studied intensively as representative π-conjugated polymers with a non-degenerate ground-state because of their excellent environmental stability in both neutral and oxidized (doped) states [1]. However, it has become apparent that polythiophene includes an observable number of irregular bondings other than 2,5-linkage [2,3], and poly(3-substituted thiophene)s, consist of two different regioregularities, head-to-tail and head-to-head configurations [4-6]. The irregularity of the polymers prevents the satisfactory elucidation of the conduction mechanism containing carrier generation upon their doping. Recently, several researchers prepared oligothiophenes that have well defined structures, and investigated their neutral and oxidized states as model compounds of conductive polythiophenes [7-12]. The oxidation of the oligothiophene yielded cation radicals (polarons) which came to equilibrium with spinless polaron-dimers in the first step, and plural-electron-oxidized species such as dications (bipolarons) in the second step. A comparison between the spectra of oligothiophenes and polythiophenes indicated that oxidized species in polythiophenes were cation radicals. The corroboration of those suggestions would be important and is required to present more exact model compounds of polythiophenes and elucidate the features of oxidized species in film as well as in solution. Polymers containing thiophene tetramers and hexamers were prepared by electrochemical method as more exact model compounds but have not been satisfactorily characterized by comparison with the corresponding oligothiophenes or polythiophenes owing to the insolubility of the obtained polymers [13,14]. Further, we reported on the preparation and fundamental properties of a soluble polymer with a constant π-conjugation length, poly[(3′,3″,4‴,4⁗-tetrahexyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2⁗′-sexithiophene-5,5⁗′-diyl)ethane] (PSE) [15]. In this paper, we report the preparations of polymers with different π-conjugation lengths, PSE and poly[3′,4″-tetrahexyl-2,2′:5′,2″:5″,2‴-quaterthiophene-5,5‴-diyl)ethane] (PQE). The electrical and optical properties of the polymer films and solutions are compared.

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2. Experimental

2.1. Reagents

2-Chlorothiophene (**1**) [16], (3-hexylthiophene-2-yl)magnesium bromide [17], and [1,3-Bis(diphenylphosphino)propane]dichoronickel(II) ($Ni(dppp)Cl_2$) [18] were synthesized using standard literature procedures. The other chemicals were obtained from commercial sources and used without purification. Tetrahydrofuran (THF) and ether were distilled under nitrogen over calcium hydride and lithium aluminum hydride, respectively. *N*,*N*-dimethylacetamide (DMAc) was dried over type 4A molecular sieves and distilled under reduced pressure.

2.2. 1,2-Bis(thiophene-2-yl)ethane (2)

To magnesium (13.6 g, 0.56 mol) in THF (350 ml) was added compound **1** (150 g, 1.13 mol) dropwise at room temperature while an ice bath was used occasionally to maintain a mild reflux. The mixture was heated under reflux for 24 h before being poured into 3*N*-ammonium chloride solution. The aqueous layer was extracted with dichloromethane, and the organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by flash chromatography to yield 64 g (58%) of the title compound as a colorless liquid. ^{1}H NMR (60 MHz), δ (ppm): 3.17 (s, 4H), 6.81-7.15 (m, 6H). IR (neat): 3100, 3068, 3039, 2945, 2912, 2846, 1438, 1265, 1238, 1226, 850, 827, 649, 505 cm^{-1}.

2.3. 1,2-Bis(5-bromothiophene-2-yl)ethane (3)

To a solution of compound **2** (6.2 g, 32 mmol) in 180 ml of dichloromethane/acetic acid (1:1) was added in portions *N*-bromosuccinimide (NBS) (10.8 g, 61 mmol). The mixture was heated to reflux for 10 min to complete the bromination. Water was poured into the reaction mixture, and the organic layer was separated, washed with 5% potassium hydroxide and three times, each with water, and then dried over magnesium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by flash chromatography to provide 9.1 g (91%) of the title compound as a colorless liquid having green luminescence. ^{1}H NMR (60 MHz), δ (ppm): 3.05 (s, 4H), 6.52 (d, $J = 3.7$ Hz, 2H), 6.82 (d, $J = 3.7$ Hz, 2H). IR (neat): 3080, 3049, 2925, 2852, 1543, 1444, 1263, 1223, 1047, 964, 793, 739, 702 cm^{-1}.

2.4. 1,2-Bis(3′-hexyl-2,2′-bithiophene-5-yl)ethane (4)

To a two necked round bottom flask which was charged with compound **3** (8.7 g, 22 mmol) $Ni(dppp)Cl_2$ (48 mg, 0.095 mmol), and ether (32 ml) was added dropwise (3-hexylthiophene-2-yl)magnesium bromide (45 mmol) in ether (30 ml) under nitrogen. The mixture was heated to reflux for 19 h and poured into 3*N*-ammonium chloride. The aqueous layer was extracted with benzene, and the organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by flash chromatography to afford 5.2 g (45%) of the title compound as a yellow liquid. ^{1}H NMR (270 MHz), δ (ppm): 0.89 (t, $J = 6.3$ Hz, 6H), 1.17-1.82 (m, 16H), 2.74(t, $J = 7.2$ Hz, 4H), 3.20 (s, 4H), 6.78(d, $J = 4.5$ Hz, 2H), 6.90 (d, $J = 5.4$ Hz, 2H), 6.91 (d, $J = 4.5$ Hz, 2H), 7.13 (d, $J = 5.4$ Hz, 2H).

2.5. 1,2-Bis(5′-bromo-3′-hexyl-2,2″-bithiophene-5-yl)ethane (5)

Analogously to the preparation of **3**, compound **4** in dichloromethane/acetic acid (1:1) were reacted with NBS. Purification by flash chromatography gave the title products as a yellow liquid in a 84% yield. Anal. Calculated for $C_{30}H_{36}S_4Br_2$: C, 52.63; H, 5.30; Br, 23.34. Found: C, 51.70; H, 5.25; Br, 23.58. ^{1}H NMR (270 MHz), δ (ppm): 0.87 (t, $J = 5.6$ Hz, 6H), 1.25-1.80 (m, 16H), 2.65(t, $J = 7.2$ Hz, 4H), 3.18 (s, 4H), 6.74(d, $J = 3.7$ Hz, 2H), 6.86 (d, $J = 3.6$ Hz, 2H), 6.87 (s, 2H).

2.6. 1,2-Bis(3′,4″-dihexyl-2,2′:5′2″-terthiophene-5-yl)ethane (6)

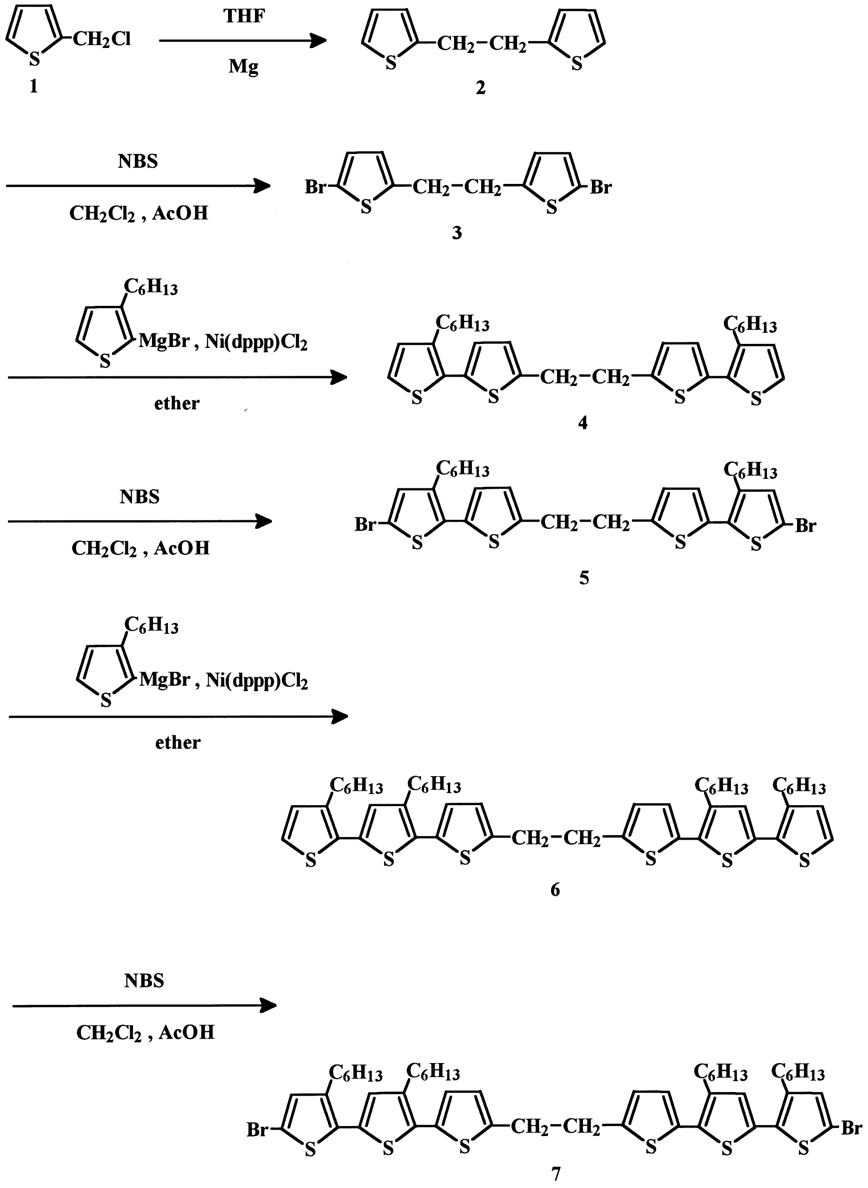
Analogously to the preparation of **4**, compound **6** was obtained from **5**. **6** was purified by flash chromatography giving an orange liquid (64%). ^{1}H NMR (270 MHz), δ (ppm): 0.87 (t, $J = 5.4$ Hz, 12H), 1.18-1.70 (m, 32H), 2.70-2.80(m, 8H), 3.22 (s, 4H), 6.77(d, $J = 5.4$ Hz, 2H), 6.91 (d, $J = 8.1$ Hz, 2H), 6.92 (s, 2H), 6.95 (d, $J = 5.4$ Hz, 2H), 7.15 (d, $J = 8.1$ Hz, 2H).

2.7. 1,2-Bis(2′-bromo-3′,4″-dihexyl-2,2′:5′2″-terthiophene-5-yl)ethane (7)

Analogously to the preparation of **3**, compound **6** in dichloromethane/acetic acid (1:1) were reacted with NBS. Purification by flash chromatography gave the title products as an orange liquid in a 41% yield. Anal. Calculated for $C_{50}H_{64}S_6Br_2$: C, 59.04; H, 6.34; Br, 15.71. Found: C, 58.53; H, 6.46; Br, 15.12. ^{1}H NMR (270 MHz), δ (ppm): 0.88 (t, $J = 5.2$ Hz, 12H), 1.10-1.75 (m, 32H), 2.65-2.75 (m, 8H), 3.20 (s, 4H), 6.75(d, $J = 4.5$ Hz, 2H), 6.85 (s, 4H), 6.93 (d, $J = 4.5$ Hz, 2H).

2.8. Poly[3′,4″-tetrahexyl-2,2′:5′,2″:5″,2‴-quaterthiophene-5,5‴-diyl)ethane] (PQE)

In two-necked flask were placed nickel chloride (9.0 mg, 69 mmol), triphenylphosphine (370 mg, 1.4 mmol), bipyridine (11 mg, 0.74 mmol), zinc (280 mg, 4.3 mmol), compound **5** (1.7 g, 5.0 mmol), DMAc (12 ml). The mixture was heated at 90°C for 3 h under nitrogen. The resulting mixture was poured into 5% hydrochloric acid in methanol to precipitate the crude polymer. The polymer was dissolved



Scheme 1.

in chloroform and reprecipitated by addition of the solution to acetone. The yield of purified PQE, a red solid, was 820 mg (85%).

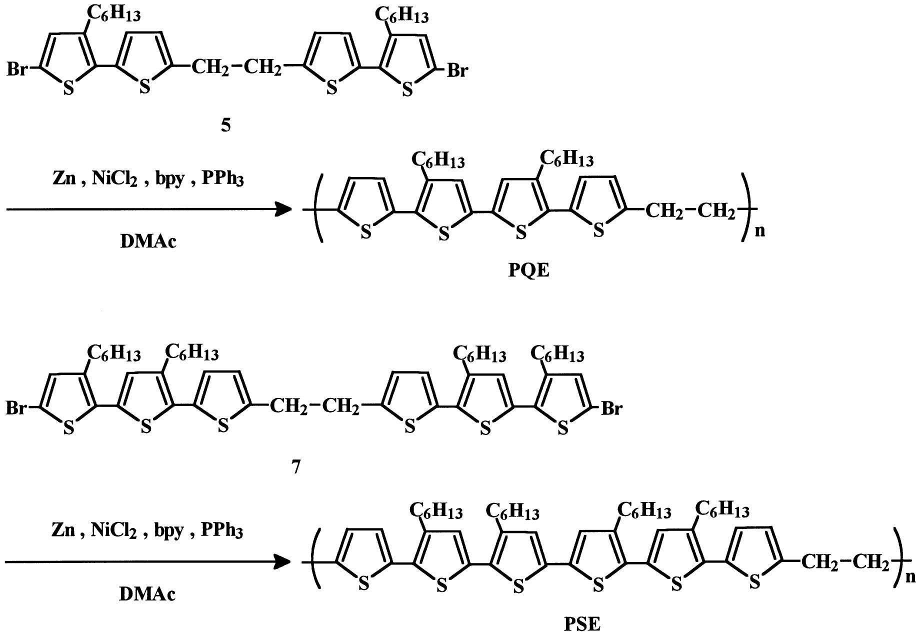
Anal. Calculated for $(C_{30}H_{64}S_4)n$: C, 68.65; H, 6.91. Found: C, 68.59; H, 6.96; Br, 0.42.

2.9. Poly[(3′,3″,4‴,4⁗′-tetrahexyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2⁗′-sexithiophene-5,5⁗′-diyl)ethane] (PSE)

Analogously to the preparation of PQE, 1.1 g of compound **7** was polymerized with an active nickel(0) reagent. Purification by reprecipitation of the crude product gave 750 mg (87%) of purified PSE as a red solid. Anal. Calculated for $(C_{50}H_{64}S_6)n$: C, 70.04; H, 7.52. Found: C, 69.94; H, 7.56; Br, 0.18.

2.10. Characterization

The polymer was characterized by gel permeation chromatography (GPC) in $CHCl_3$ using a Shimazu FCV-1008 instrument equipped with a Shodex K-803 column. Infrared spectra were obtained by a JASCO FT-IR-230 and UV-visible-near IR spectra were recorded on a JASCO V-570. ^1H NMR experiments were performed on a JEOL GSX 270 spectrometer or Hitachi FT-60 R-1500 spectrometer with trimethylsilane as internal standard and d-chloroform.



Scheme 2.

Conductivity measurements were performed on polymer films by the four-probe method.

3. Results and discussion

3.1. Preparation

The synthetic routes of the monomers, 1,2-bis(5′-bromo-3′-hexyl-2,2′-bithiophene-5-yl)ethane **5** and 1,2-bis(2″-bromo-3′,4″-dihexyl-2,2′:5′,2″-terthiophene-5-yl)ethane **7** are depicted in Scheme 1. 2-Chloromethylthiophene **1** was treated with magnesium in tetrahydrofuran (THF) to give 1,2-dithienylethane **2**. Compound **2** was brominated with *N*-bromosuccinimide (NBS) in a mixture of dichloromethane(CH_2Cl_2) and acetic acid (AcOH) to give the corresponding dibromide **3**, which was coupled with (3-hexylthiophene-2-yl)magnesium bromide in the presence of dichloro[1,3-bis(diphenylphosphino)propane] nickel (II) (Ni(dppp)Cl_2) in ether to give **4** as a pale yellow viscous liquid. This compound was then brominated with NBS under the same conditions used for the synthesis of **3** to yield compound **5**, the monomer for PQE. The other monomer, compound **7**, was prepared by repetition of this sequence of coupling reaction with the Grignard reagents and bromination steps.

Each of the obtained **5** and **7** were polymerized in the presence of nickel(II) chloride ($NiCl_2$), zinc, triphenylphosphine (PPh_3), and bipyridine (bpy) in *N*,*N*-dimethylacetamide (DMAc) according to a similar procedure described for the preparation of octithiophenes [19], as shown in Scheme 2. The crude polymers were reprecipitated from chloroform-acetone to give red solids.

3.2. Structure

The IR spectrum of PQE was compared with those of the bis(bithienyl)ethane derivative **4** and bis(bromobithienyl)ethane derivative **5**, and the IR spectrum of PSE those of the bis(terthienyl)ethane derivative **6** and bis(bromoterthienyl)ethane derivative **7**. The pattern of the spectra of PQE and PSE are similar to those of the bromides (**5** and **7**) but are different from those of the derivative non-substituted at terminal positions (**4** and **6**). **4** and **6** showed a band at 3100 cm^{-1} assignable to the C-H stretching vibration in the 2-position of the thiophene rings, while the polymers and the bromide (**5** and **7**) showed no band. In spectra of **4** and **6**, there were strong bands in the region 690-600 cm^{-1}, which would be primarily assigned to the terminal 2,3-disubstituted thiophene ring [20]. However, there were only weak bands in the range in the spectra of bromides (**5** and **7**) PQE, and PSE. In addition, elemental analyses for PQE and PSE showed that the contents of bromine which could be attributed to a terminal group were negligible, less than 0.5%. These results indicate that PQE and PSE are linear structures, denoted in Scheme 2.

The weight-average molecular weight (M_w) and polydispersity relative to the polystyrene standard were 42 000 and 2.4 for PQE, 58 000 and 3.1 for PSE, respectively. The degree of polymerization of PQE and PSE was about 80-70, calculated from its M_w values. In spite of high molecular weights of chemically synthesized PQE and PSE, the polymers were soluble in common organic solvents, such as dichloromethane, benzene, tetrahydrofuran, and 1-methyl-2-pyrrolidinone. In contrast, polymers containing non-substituted thiophene tetramers and hexamers had been prepared by electrochemical method and they were

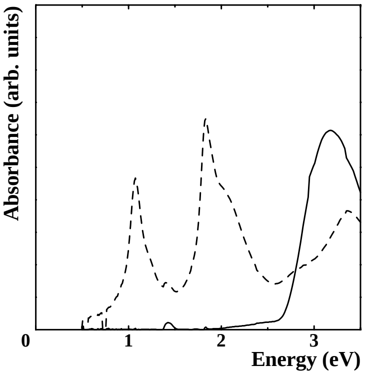


Fig. 1. Electronic absorption spectra of PQE in dichloromethane. The concentration of the monomer unit is 1×10^{-4} M: neutral PQE (solid line), oxidized PQE (dashed line).

insoluble, as described in some papers [13,14]. The alkyl groups in PQE and PSE lead to enhance the solubility of the polymers.

3.3. Conductivity

The PQE and PSE films (ca. 2-μm-thick) cast from chloroform solutions were $FeCl_3$-doped in nitromethane solutions of 0.1 M $FeCl_3$ for one night and then rinsed in nitromethane to remove excess $FeCl_3$ in the atmosphere. The PQE and PSE films changed from orange and orange red to blue immediately after immersion in the $FeCl_3$ solution and finally had a glossy black color, respectively. The conductivities of the doped PQE film were $9\text{-}7 \times 10^{-3}$ S/cm at an ambient temperature in the atmosphere and those of the doped PSE film were 0.4-0.2 S/cm. The conductivities were ohmic at current densities applied below 6 A/cm^2. These conductivities are comparable to those of all-conjugated copolymers composed of thiophene and ethylene units, 10^{-1}-10^{-6} S/cm [21,22], and higher than polymers containing thiophene oligomers as pendant groups, 10^{-5}-10^{-8} S/cm [23]. The conductivities of the doped PQE and PSE films retained the same order during one day in the atmosphere. The dopant contents per repeating thiophene tetramer unit or hexamer unit were estimated from the increase in weight of the film during doping, based on the assumption that $FeCl_4^-$ molecules are the dopant. The dopant content of PQE was 0.44, ca. half, and that of PSE was 0.98, ca. 1. These results suggest that the thiophene tetramer units in the PQE chain would be partially doped and the thiophene hexamer units in the PSE chain would be in one-electron-oxidized states.

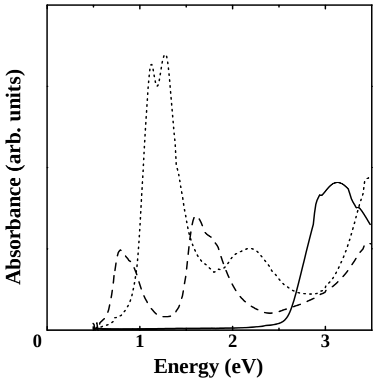


Fig. 2. Electronic absorption spectra of PSE in dichloromethane. The concentration of the monomer unit is 1×10^{-4} M: neutral PSE (solid line), PSE oxidized in the first step (dashed line), heavily oxidized PSE (dotted line).

3.4. Neutral state of the polymer solutions

The absorption spectra of the neutral PQE and PSE in dichloromethane showed π-π^* transition bands at 3.19 and 3.04 eV, respectively. The band of PSE is at the lower energy than that of PQE. The peak position in PQE is very close to that in α-quaterthiophene, 391 nm (3.17 eV) [24], and that in PSE is also close to that in alkyl-substituted α-sexithiophene, 3.02 eV [25,26]. The peak positions imply that the obtained PQE and PSE contain thiophene tetramers or hexamers as units possessed constant conjugation lengths in the polymers, respectively.

3.5. Oxidized state of the polymer solutions

PQE and PSE were oxidized with stoichiometric amounts of $FeCl_3$ in dichloromethane. The oxidation was achieved by stepwise addition of a $FeCl_3$ solution to polymer solutions.

The electronic absorption spectra of neutral and oxidized PQE are shown in Fig. 1. The spectrum of the neutral PQE had a π-π^* transition band at 3.19 eV. The oxidation of PQE resulted in the disappearance of the π-π^* transition band and the appearance of two strong bands at 1.83 and 1.07 eV with a shoulder on the high-energy side. The intensities of the two bands attained maximum values when about two equivalents of $FeCl_3$ per repeating thiophene tetramer unit were added. It is generally admitted that two equivalents of $FeCl_3$ are necessary for one-electron oxidation of a substrate. These spectral changes are similar to those of quaterthiophene derivative reported previously [7,9], indicating that PQE was oxidized to produce cation radicals and their π-dimers on thiophene tetramer units. The two strong bands and shoulders in the spectra would be attributed to the cation radicals and their π-dimers, respectively. Further addition of $FeCl_3$ increased the intensity of the bands attributable to $FeCl_3$ alone and led no additional peak to appear. These results suggest that PQE in dichloromethane undergoes only one-oxidation step and does not undergo further oxidation steps with $FeCl_3$ as an oxidant.

The electronic absorption spectra of neutral and oxidized PSE are shown in Fig. 2. The spectrum of the neutral PSE had a π-π^* transition band at 3.04 eV. When two equivalents of $FeCl_3$ per repeating thiophene hexamer unit were added to the PSE solution, the π-π^* transition band disappeared and two strong bands with a shoulder on the high-energy side appeared at 1.59 and 0.78 eV. Further oxidation

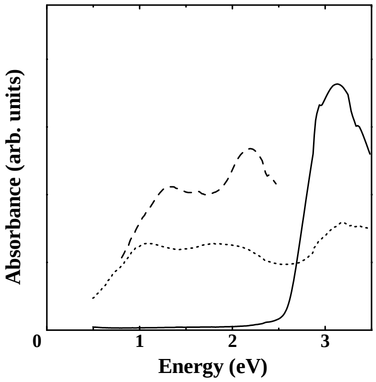


Fig. 3. Electronic absorption spectra of PQE films: a neutral film (solid line), a doped film in a $FeCl_3$ solution (dashed line), a doped film in the atmosphere (dotted line).

of the oxidized solution caused two strong bands at 1.26 and 1.12 eV and a weak band at about 2.2 eV. These spectral changes during $FeCl_3$-oxidizing closely resemble those of sexithiophenes reported previously [7,9-11]. These observations indicate that the thiophene hexamer units in PSE undergo a two-step oxidation to produce cation radicals and their π-dimers in the first step and plural-electron-oxidized species such as dications in the successive second step.

3.6. Oxidation of the film

The doping (oxidation) of PQE and PSE films (ca. 0.4-μm-thick) was accomplished by immersing them in a nitromethane solution of 0.1 M $FeCl_3$ for one day. Fig. 3 shows the electronic absorption spectra of the neutral and doped PQE films. The π-π^* transition band of the neutral film was observed at 3.12 eV. The band appeared at slightly higher energy than that of neutral PQE in dichloromethane, 3.19 eV. The spectrum of the doped PQE film soaked in the $FeCl_3$ solution showed two strong bands at 2.18 and 1.31 eV. The spectrum of the film in the $FeCl_3$ solution higher than 2.3 eV was not satisfactorily detected due to the intense absorbance of $FeCl_3$. The positions of the two bands are nearly in agreement with those of each shoulders accompanied by two bands that were observed in PQE oxidized in dichloromethane. The doped films were taken out of the $FeCl_3$ solution, rinsed with nitromethane, and immediately used for spectroscopy. The spectrum of the doped PQE film on the atmosphere showed two broad bands at 1.84 and 1.08 eV. The positions of the two bands are not close to those of the shoulders observed in PQE oxidized in dichloromethane but the two strong bands observed at 1.83 and 1.07 eV in it. In spectrum of PQE oxidized in dichloromethane, the two bands and the shoulders would be attributed to cation radicals and their π-dimers, respectively, as already described. The comparison between the spectra of doped PQE in film and in solution shows that the film oxidized in the $FeCl_3$ solution chiefly forms π-dimers of cation radicals and the oxidized film on the atmosphere principally possesses isolated cation radicals in the main chain. This implies that taking out of the $FeCl_3$ solution to the atmosphere leads to decay oxidized (doped) states and isolate each cation radical in the film. These are consistent with the conclusion that thiophene tetramer units in the PQE chain would be partially doped in the atmosphere, as it was elucidated from the dopant contents of the doped PQE films.

Fig. 4 shows the electronic absorption spectra of the neutral and doped PSE films. The π-π^* transition band of the neutral film was observed at 2.87 eV. The spectrum of the doped PSE film soaked in the $FeCl_3$ solution had a strong band at 1.25 eV and a shoulder around 1.1 eV. The positions of the band and the shoulder are close to those of the two strong bands observed in PSE oxidized heavily in dichloromethane, suggesting that plural-electron-oxidized species is mainly present in the doped PSE film soaked in the $FeCl_3$ solution. The spectrum of the doped PSE film that was taken out of the $FeCl_3$ solution to the atmosphere showed two bands at 1.64 and 0.83 eV. These two bands would be assigned to cation radicals of thiophene hexamer units in PSE from analogy with the spectrum of PSE oxidized in the first step in dichloromethane. The bands ascribed to the plural-electron-oxidized species reduced rapidly on exposure to air. The spectrum of the doped PSE film in the atmosphere showed hardly any alteration after one day. These observations lead us to conclude that in the atmosphere, the plural-electron-oxidized species is unstable and the cation radicals are predominantly present in the doped PSE films. These conclusions are supported by the results of the dopant content of the doped PSE film, the thiophene hexamer units in the PSE chain would be one-electron-oxidized states. Moreover, these conclusions corroborate the speculation that oxidized species existing in doped polythiophenes are cation radicals, derived by comparison of the spectra of the doped polythiophenes with those of the doped oligothiophene in some papers [24-26].

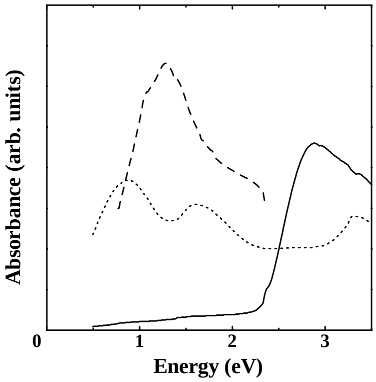


Fig. 4. Electronic absorption spectra of PSE films: a neutral film (solid line), a doped film in a $FeCl_3$ solution (dashed line), a doped film in the atmosphere (dotted line).

4. Conclusions

We prepared soluble PQE and PSE in which the π-conjugation length were limited to a thiophene tetramer and hexamer, respectively. The polymers possessed a high degree of polymerization. The cast films had conductivities of the order from 10^{-3} to 10^{-1} S/cm in the atmosphere after doping with $FeCl_3$. Oxidizing (doping) the PQE solution and film by use of $FeCl_3$ produced one-electron-oxidized species, cation radicals (polarons). On the contrary, the oxidation of the PSE film yielded plural-electron-oxidized species in a $FeCl_3$ solution. The plural-electron-oxidized species decayed on exposure of the doped films to air, and one-electron-oxidized species was predominantly present in the doped film in the atmosphere.

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