Studies of conductive poly (3-substituted thiophene) films

佐藤, 正昭

(Degree)
博士（理学）

(Date of Degree)
1989-03-17

(Date of Publication)
2007-09-26

(Resource Type)
doctoral thesis

(Report Number)
乙1270

(URL)
https://hdl.handle.net/20.500.14094/D2001270

神戸大学博士論文

Studies of
Conductive Poly(3-substituted thiophene) Films

(導電性ポリ(3-置換チオフェン)類フィルムの研究)

平成元年1月

Masa-aki Sato

佐　藤　正　昭

CONTENTS

Chapter 1

Introduction

1-1 General introduction

Many organic polymers which are characterized by toughness, plasticity, light weight, and frictional resistance have been developed and replaced conventional metals and inorganic materials in various areas of application. However, until quite recently almost all of the known organic polymers were essentially electrically insulating with electrical conductivities of 10^{-14} S/cm or less, as opposed to the high electrical conductivities (10^{5} - 10^{3} S/cm) shown by metals.

The electrical conductivity σ in a system can be described by the following equation, where n is the total number of carriers, q is the charge on the carriers, and μ is the drift mobility of carriers.

$$\sigma = n\ q\ \mu$$

Charged carriers can be either electrons (negative carriers) or holes (positive carriers). The drift mobility of carriers is defined as the ratio of the drift velocity to the electric field and reflects the ease with which carriers are propagated. The enhancement of the conductivity then requires an increase in the drift mobility and the number of charged carriers. The electrical properties of polymers depend on their chemical and physical structure. The particular importance of the delocalized π-electron to form energy bands of high mobility carriers

was stressed early on[1] and a large number of polymers were considered as having this characteristic[2]. In addition, since conjugated polymers are semiconductors with an energy gap of 1 - 5 eV[3),4] and so do not have intrinsic charged carriers, appropriate charged carriers must be provided by such means as doping. The doping processes involves chemical or electrochemical redox reactions of the polymers. The chemical doping proceeds with the addition of electron acceptors or electron donors into the polymers and the electrochemical one, with the electrolysis on the electrode modified by the polymers. The amount of a dopant or charge consumed for the redox reaction of the polymers is related to the number of charged carriers.

1-2 Preparation of conducting polymers

In 1958, Natta et al. reported that acetylene can be polymerized with a catalyst consisting of triethylaluminium and titanium alcoholates[5]. The electrical conductivity of this type of polyacetylene was studied by Hatano et al. in 1961[6]. Since polyacetylene was obtained only in the form of a powder and not doped in this period, the research did not develop into a large stream. Shirakawa et al. first prepared filmy polyacetylene by an improved method[7),8]. Furthermore, they found that the conductivity of polyacetylene films dramatically increased from an initial value of approximately 10^{-9} S/cm to ap-

proximately 500 S/cm when the films were doped with iodine, bromine, AsF_5 or sodium naphthalide[9),10)]. (At present the highest conductivity reported is of the order of 10^4 S/cm [11)].

The discovery of conductive polyacetylene led to considerable research activity on electrically conducting polymers. In searching for new electrically conducting polymers, it is important to build an understanding of the relationship between the conductive properties and the chemical structure of the polymers. Only very recently, however, different polymer systems exhibiting greatly enhanced electrical conductivity have been reported. These include poly(p-phenylene)[12)-14)], poly(2,6-naphthylene)[15),16)], polypyrrole[17)], polythiophene[18)-24)], polyaniline[25)] poly(p-phenylene vinylene)[26)], poly(p-phenylene sulfide)[27)] (Figure 1,1). Although the number of polymers which can be available for comparative studies is growing, the actual number is still limited and their chemical structures are significantly different. Therefore, it is presently difficult to make useful quantitative generalization.

Poly(p-phenylene), poly(2,6-naphthylene), polypyrrole, polythiophene, and polyaniline have been oxidatively prepared by electrochemical polymerization to yield free-standing films[14),16),17),19)-24),25)]. The electrochemical polymerization is advantageous method to prepare conducting polymer films. The polymer films obtained are in an oxidized form, that

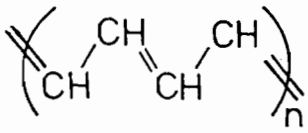
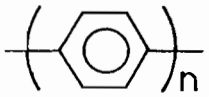
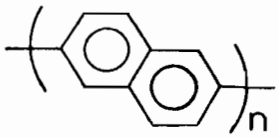
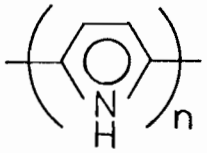
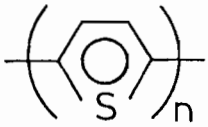
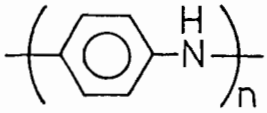
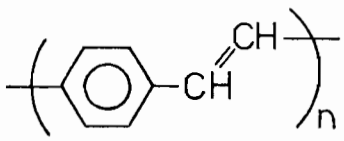
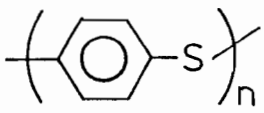
Polymer		Conductivity after doping (S/cm)
Polyacetylene		$200-10^4$
Poly(p-phenylene)		500
Poly(2,6-naphthylene)		0.23
Polypyrrole		40-200
Polythiophene		10-100
Polyaniline		10^{-1}
Poly(p-phenylene vinylene)		1-1000
Poly(p-phenylene sulfide)		3-300

Figure 1,1. Electrically conducting polymers.

is to say, doped one, and hence doping process is not required. The polymerization has electrochemical stoichiometry[28] and the thickness of the films can be controlled by the amount of charge passed during the polymerization. Thin films supported by an electrode surface are electroactive and can be switched between the oxidized and the neutral states[17),29].

Among the conducting polymers, polythiophene and its derivatives are especially stable toward oxygen and moisture in both oxidized and neutral states[30]. The stability would lead to the simplicity of characterization on the conducting polymers. A wide variety of substituted thiophenes is synthetically and commercially available[31] and permits the systematic and electrochemical preparation of the various polythiophene derivatives[32)-35]. The author intends to elucidate the correlation between the chemical structure and the electrical properties of these materials and develop the conducting polymers with the attractive properties such as high conductivity, solubility, and anode-activity attributable to the doping and the undoping with cations.

1-3 Mechanism of charge transfer

In the conducting polymers such as poly(p-phenylene), poly(2,6-naphthylene), polythiophene, and polypyrrole, the resonance structure which can be envisioned is quinoid-like,

the bonds between rings acquiring a strong double-bond character (Figure 1,2). The quinoid resonance structure has a higher total energy than an aromatic-like structure[36),37)]. Therefore, the polymers have a non-degenerate ground state which corresponds to the single aromatic-like structure. However, it was claimed that the quinoid resonance structure is responsible for the high conductivity or the molecular structure of the doped polymers[4),38),39)]. Recently, experimental and theoretical investigations of the evolution of the electronic and the transport properties upon doping were conducted on polythiophene[19),36),40)-46)], poly(p-phenylene)[36),37),40),47)], and polypyrrole[36),40),48)-50)]. Brédas et al. performed theoretical studies of the evolution of the polythiophene electronic band structure as a function of doping level by using a valence effective Hamiltonian technique[36),40)] or an adiabatic Su-Schrieffer-Heeger Hamiltonian technique[41)].

The interaction of a polymer unit cell with all its neighbors lead to the formation of electronic bands. The highest occupied electronic levels constitute the valence band and the lowest unoccupied levels, the conduction band.

The width of the forbidden band, or band gap, between the valence and the conduction bands is about 2.15 eV in the neutral undoped polythiophene (Figure 1,3a). When an electron is removed from the polymer chain, a polaron with spin S=1/2 is formed. The formation of the polaron is associated with

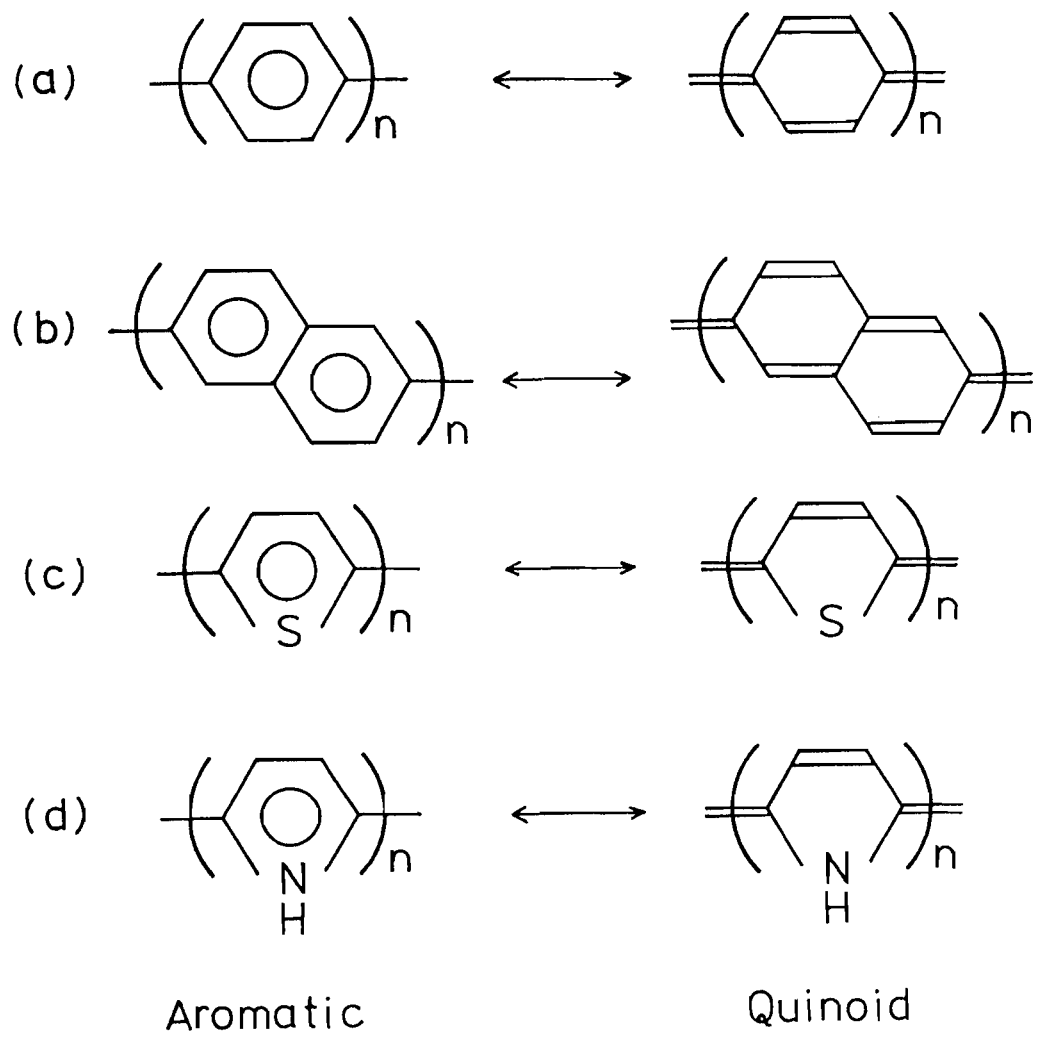


Figure 1,2. Aromatic (ground-state) and quinoid-like geometric structure for (a) poly(p-phenylene), (b) poly(2,6-naphthylene), (c) polythiophene, and (d) polypyrrole.

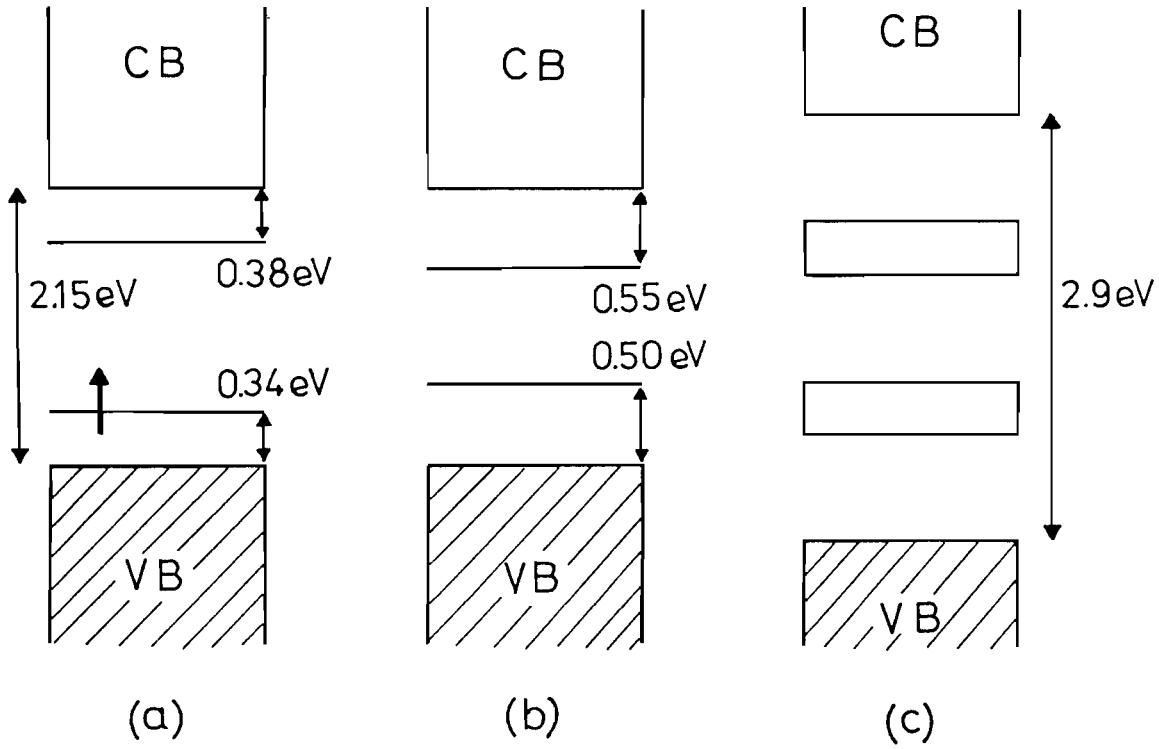
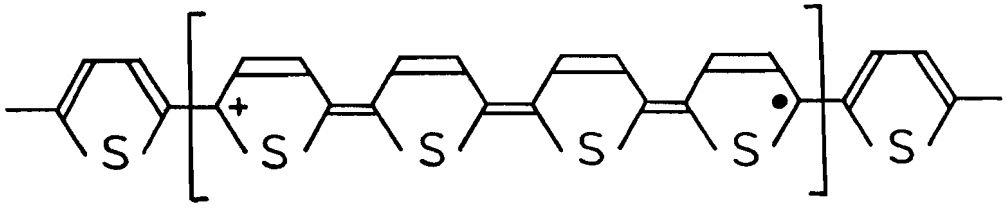


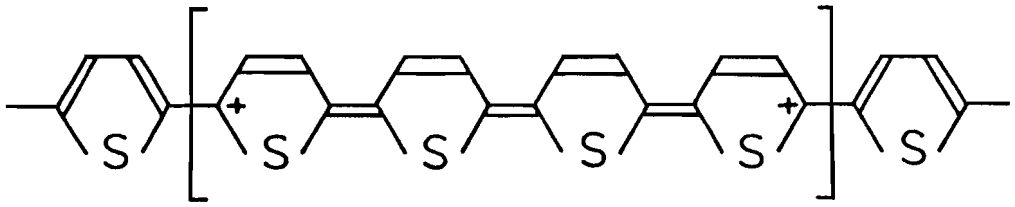
Figure 1,3. Evolution of the polythiophene band structure upon doping: (a) low doping level, polaron formation; (b) moderate doping level, bipolaron formation; (c) high(33 mol%) doping level, formation of bipolaron bands.

quinoid-like geometry relaxation extended over about four thiophene rings.



polaron

The polaron levels are about 0.34 eV away from the band edges (Figure 1,3a). When a second electron is taken out of the chain, a spinless bipolaron that is favored over two polarons is formed. The geometry within the bipolaron is more quinoid-like than within the polaron.



bipolaron

The empty bipolaron electronic levels in the gap are more than 0.50 eV away from the band edges (Figure 1,3b). As doping proceeds, more bipolaron states are formed, eventually producing two bands in the gap. Since the states are derived from valence and conduction band levels, the density of state at the gap edges is decreased and the band gap widens to about 2.9 eV

in the 33 % doped state (Figure 1,3c). This band structure supports the fact which, upon application of an electric field, the spinless bipolarons that carry two charges could become mobile and the transport the current at high doping level. Actually, the evolution of optical[42)-44)] and ESR[44)-46)] data upon doping seems to be consistent with the bipolaron model for polythiophene.

No experimental and theoretical investigations of the electronic and the transport properties for conducting polythiophene derivatives have, so far, been carried out. The author intends to clarify systematically the electronic structure of undoped and doped polythiophene derivatives by optical and electrochemical data.

1-4 Outline of the present work

The poly(3-substituted thiophene)s were prepared systematically by electrochemical polymerization. The polymer films obtained had high conductivities and interesting properties. The relationship between the chemical structure and the electrical or the optical properties of the polymer films were studied.

Chapter 2 describes the preparation and the properties of polythiophene, poly(3-methylthiophene), and poly(3-ethylthiophene) films. The conductivity of poly(3-methylthiophene)

film was the highest among those of the conducting polymer films prepared electrochemically. The cyclic voltammograms and absorption spectra of these three polythiophenes showed that poly(3-methylthiophene) had the highest oxidation potential and a interband π-π^* transition at the lowest energy. These results are discussed in terms of the effects of substituents and the irregularity of polythiophene. The spectral changes of poly(3-methylthiophene) and poly(3-ethylthiophene) films during electrochemical doping were partly inconsistent with the bipolaron theory.

Chapter 3 deals with the preparation and the properties of poly(3-butylthiophene) and poly(3-benzylthiophene) films which have bulkier side-chains than methyl and ethyl groups. These polythiophenes had lower oxidation potential and interband transitions at higher energy than those of poly(3-methylthiophene) and poly(3-ethylthiophene), whereas the positions of the peaks, which are related to the bipolaron levels of the poly(3-alkylthiophene)s and poly(3-benzylthiophene) doped at intermediate stages, are almost the same. The spectral change of poly(3-butylthiophene) was also inconsistent with the bipolaron theory. On the basis of these results, the mechanism of charge transfer is discussed.

Chapter 4 describes the preparation and the properties of poly(3-long alkyl thiophene) films. Poly(3-hexylthiophene), poly(3-octylthiophene), and poly(3-dodecylthiophene) were

soluble conducting polymers. It was possible to determine their molecular weight, and cast films from their solutions. The oxidized poly(3-dodecylthiophene) in solution showed absorption spectra suggesting the presence of bipolaron states.

Chapter 5 describes the preparation and the properties of poly(3-arylthiophene)s. Poly(3-phenylthiophene) was doped with a cation as well as with an anion and had much higher anode-activity than polythiophene which had been reported. The inter-band transition at the lowest energy among the poly(3-substituted thiophene)s suggests that the phenyl group would have an appreciable conjugation effect on the polythiophene main chain. The visible-near i.r. spectra of poly(3-phenyl-thiophene) at slight anion-doping levels showed the formation of the polaron. This is the first example in which polaron is apparently observed in the spectra of polythiophenes.

The author believes that this study will provide clues to prepare more highly conducting polymers and elucidate the mechanisms of doping and conductivity in conducting polymers completely.

1-5. References

1) H. A. Pohl, J. Polym. Sci., **C17**, 13 (1967).

2) H. Miyasaka and S. Kusabayashi, "Kohbunsi-handotai", Kohdan-sha, Tokyo (1977).

3) H. Anzai, U. Itoh, M. Takakusa, and T. Nakajima, Circulars of the Electrotechnical Laboratory, No.157, 1 (1966).

4) R. H. Baughman, J. L. Brėdas, R. R. Chance, R. L. Elsenbaumer, and L. W. Shacklette, Chem. Rev. **82**, 209 (1982).

5) G. Natta, G. Mazzanti, and P. Corradini, Atti. Accad. Naz. Lincei. Cl. Sci. Fis. Mat. Nat. Rend., **25**, 2 (1958).

6) M. Hatano, S. Kambara, S. Okamoto, J. Polym. Sci., **51**, S26 (1961).

7) H. Shirakawa and S. Ikeda, Polym. J., **2**, 231 (1971).

8) T. Ito, H. Shirakawa, S. Ikeda, J. Polym. Sci. Polym. Chem. Ed., **12**, 11 (1974).

9) H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, and A. J. Heeger, J. Chem. Soc., Chem. Commun., **1977**, 578.

10) C. K. Chiang, M. A. Druy, S. C. Gau, A. J. Heeger, E. J. Louis, A. G. MacDiramid, Y. W. Park, and H. Shirakawa, J. Am. Chem. Soc., **100**, 1013 (1978).

11) K. Akagi, S. Katayama, H. Shirakawa, K. Araya, A. Mukoh, and T. Narayama, Synth. Met., **17**, 241 (1987).

12) D. M. Ivory, G. G. Miller, J. M. Sowa, L. W. Schacklette, R. R. Chance, and R. H. Baughman, J. Chem. Phys., **71**, 1506 (1979).

13) L. W. Schacklette, R. R. Chance, D. M. Ivory, G. G. Miller, and R. H. Baughman, Synth. Met., **1**, 307 (1979).

14) M. Satoh, K. Kaneto, and K.Yoshino, J. Chem. Soc., Chem. Commun., **1985**,1629.

15) M. Sato, K. Kaeriyama, and K. Someno, Makromol. Chem., **184**, 2241 (1983).

16) M. Satoh., F. Uesugi, M. Tabata, K. Kaneto, and K. Yoshino, J. Chem. Soc., Chem. Commun., **1986**, 550.

17) K. K. Kanazawa, A. F. Diaz, R. H. Geiss, W. D. Gill, J. F. Kwak, J. A. Logan, J. F. Rabolt, and G. B. Street, J. Chem. Soc., Chem. Commun., **1979**, 854.

18) T. Yamamoto, K. Sanechika, and A. Yamamoto, J. Polm. Sci., Polym. Lett. Ed., **9**, 18 (1980).

19) G. Tourillon and F. Garnier, J. Electroanal. Chem., **135**, 173 (1982).

20) K. Kaneto, K. Yoshino, and Y. Inuishi, Jpn. J. Appl. Phys., **21**, L567 (1982).

21) K. Kaneto, Y. Kohno, K. Yoshino, and Y. Inuishi, J. Chem. Soc., Chem. Commun.,**1983**, 382.

22) S. Hotta, T. Hosaka, and W. Shimotsuma, Synth. Met., **6**, 69 (1983).

23) S. Tanaka, M. Sato, and K. Kaeriyama, Makromol. Chem., **185**, 1295 (1984).

24) M. Sato, S. Tanaka, and K. Kaeriyama, J. Chem. Soc., Chem. Commun., **1985**,713. (Chapter 2)

25) A. F. Diatz and J. A. Logan, J. Electroanal. Chem., **115**, 279 (1980).

26) G. E. Wnek, J. C. W. Chien, F. E. Karasz, and C. P. Lillya, Polymer, **20**, 1441 (1979).

27) J. F. Rabit, T. C. Clark, K. K. Kanazawa, J. R. Reynolds, and G. B. Street, J. Chem. Soc., Chem. Commun., **1980**, 347.

28) A. F. Diaz, J. I. Castillo, J. A. Logan, and W. Lee, J. Electroanal. Chem., **129**, 115 (1981).

29) A. F. Diaz, K. K. Kanazawa, and G. P. Gardini, J. Chem. Soc., Chem. Commun., **1979**, 635.

30) G. Tourillon and F. Garnier, J. Phys. Chem., **87**, 2289 (1983).

31) S. Gronowitz, "Thiophene and its derivatives" Interscience, New York (1985).

32) M. Sato, S. Tanaka, K. Kaeriyama, and F. Tomonaga, Polymer, **28**, 1071 (1987). (Chapter 3)

33) M. Sato, S. Tanaka, and K. Kaeriyama, J. Chem. Soc., Chem. Commun., **1986**, 873. (Chapter 4)

34) M. Sato, S. Tanaka, and K. Kaeriyama, J. Chem. Soc., Chem. Commun., **1987**, 1725. (Chapter 5)

35) S. Tanaka, M. Sato, and K. Kaeriyama, Polym. Commun., **26**, 303 (1985).

36) J. L. Brédas, B. Thémans, J. G. Fripiat, J. M. Andre', and R. R. Chance, Phys. Rev., **B29**, 6761 (1984).

37) J. L. Brédas, R. R. Chance, and R. Silbey, Phys. Rev., **B26**, 5843 (1982).

38) T. Yamamoto, K. Sanechika, and A. Yamamoto, Chem. Lett., **1981**, 1079.

39) M. Sato, S. Tanaka, K. Kaeriyama, H. Kanetsuna, M. Suda, and M. Kato, Sen-i Kohbunshi Zairyoh Kenkyuhsho Kenkyuh Happyohkai Shiryoh, **1982**, 1.

40) J. L. Brédas, B. Themans, J. M. Andre, R. R. Chance, and R. Silbey, Synth. Met., **9**,265 (1984).

41) J. L. Brédas, F. Wudl, and A. J. Heeger, Solid State Commun., **63**, 577 (1987).

42) T. C. Chung, J. H. Kaufman, A. J. Heeger, and F. Wudl, Phys. Rev., **B30**, 702 (1984).

43) M. Sato, S. Tanaka, and K. Kaeriyama, Synth. Met., **14**, 279 (1986). (Chapter 2)

44) K. Kaneto, S. Hayashi, S. Ura, and Y. Yoshino, J. Phys. Soc. Jpn., **54**, 1146 (1985).

45) K. Kaneto, and K. Yoshino, Synth. Met., **18**, 133 (1987).

46) J. Chen, A. J. Heeger, and F. Wudl, Solid State Commun., **58**, 251 (1986).

47) G. Crecelius, M. Stamm, J. Fink, and J. J. Ritsko, Phys. Rev. Lett., **50**, 1498 (1983).

48) J. C. Scott, M. Krounbi, P. Pfluger, and G. B. Street, Phys. Rev., **B28**, 2140 (1983).

49) J. C. Scott, J. L. Brédas, P. Pfluger, and K. Yakushi, and G. B. Street, Synth. Met., **9**, 165 (1984).

50) J. L. Brédas, J. C. Scott, K. Yakushi, and G. B. Street, Phys. Rev., **B30**, 1023 (1984).

Chapter 2

Electrochemical Preparation of Highly Conducting Poly(3-methylthiophene) Films: Comparison with Polythiophene and Poly(3-ethylthiophene) Films.

2-1 Abstract

Optimal conditions for the electrochemical polymerization of 3-methylthiophene were studied. A preferable solvent and electrolyte were propylene carbonate and tetraethylammonium hexafluorophosphate, respectively. The effects of preparation conditions were also examined using this solvent and electrolyte. Electrical and other properties of poly(3-methylthiophene) (PMT) were compared with those of polythiophene (PT) and poly(3-ethylthiophene) (PET) prepared under the same polymerization conditions. The conductivity increased in the order of PT < PET < PMT. The infrared spectra of the neutral polythiophenes indicated that an observable amount of irregular bondings other than the 2,5-linkage are present in PT^0 (the superscript 0 denotes the neutral state), but not in PMT^0 or PET^0. Observations of film surfaces by scanning electron microscope revealed that the surface of PT was granular but those of PMT and PET were rather smooth. Cyclic voltammograms showed that the oxidation potential increased in the order of PMT^0 < PET^0 < PT^0. The visible spectra of the neutral polymers showed that the interband π-π^* transition of PMT^0 occurred at the highest energy among them. These results are discussed in terms of the electronic and steric effect of the substituents and the irregularity of PT^0. Introduction of the irregularity into the polymer chain leads to rough film surface, higher oxidation

potential, and the blue shift of interband transition. The visible-near i.r. spectra of PT at different doping levels were consistent with the bipolaron theory of Brėdas et al. Those of PMT and PET were partly inconsistent.

2-2 Introduction

The electrochemical polymerization of 3-methylthiophene has been reported by two groups[1),2)]. The conductivity measured on a pressed pellet was 100 S/cm[1)], as high as that of polythiophene (PT) films. Usually, films show higher conductivities than pressed pellets, as was observed in doped polyacetylenes[3)]. This is attributable to resistivity at particle boundaries in pressed pellets and differences in chain entanglement. In the case of PT, a film doped with iodine shows a higher conductivity by two orders of magnitude than a pressed pellet[4)]. Higher conductivity would be possible in high-quality films of PMT. Therefore, the author examined the polymerization conditions of 3-methylthiophene in detail and obtained highly conducting films of poly(3-methylthiophene) (PMT).

It should be worthwhile to clarify the properties of higher homologues. For this purpose, the author prepared poly(3-ethylthiophene) (PET). Films of PT, PMT, and PET were prepared under the same polymerization conditions and compared by means of infrared spectroscopy, scanning electron microscopy, cyclic voltammetry, and spectral change during electrochemical doping. The results revealed the effects of substituents and the irregularity of polymer structure on the properties of polythiophenes.

2-3 Experimental

2-3-1 Materials

3-Ethylthiophene was prepared by coupling of ethylmagnesium bromide and 3-bromothiophene according to a similar procedure described for the preparation of 3-butylthiophene[5]. Dichloro[1,3-bis(diphenylphosphino)propane]nickel(II) [Ni(dppp)Cl_2] was used as a catalyst for the coupling. Ni(dppp)Cl_2 was synthesized by reaction of 1,3-bis(diphenylphosphino)propane with nickel(II) chloride[6]. The preparation of 3-ethylthiophene is as follows.

A solution of ethylmagnesium bromide was prepared in a usual manner from 3.65 g (0.15 g-atom) of magnesium and 16.35 g (0.15 mol) of bromoethane in 100 ml of fleshly distilled dry ether.

In a 500-ml three-necked flask, equipped with a stirring bar, a pressure-equalizing dropping funnel, and a reflux condenser to which a nitrogen inlet and outlet are attached, were placed 434 mg (0.87 mmol) of Ni(dppp)Cl_2, 20.38 g (125 mmol) of 3-bromothiophene and 100 ml of fleshly distilled dry ether; the nickel complex was insoluble in the mixture. To the mixture was added dropwise the ethylmagnesium bromide in ether at 0 ^{o}C with stirring under nitrogen over 20 min. After refluxing for 2 hours, the reaction mixture was hydrolyzed with diluted hydrochloric acid under cooling with an ice bath. The organic

layer and ether extracts from the aqueous layer were combined, washed successively with water, a saturated sodium hydrogen carbonate solution, and water, and then dried over magnesium sulfate. After evaporation of the solvent, distillation gave 8.70 g (62 % yield based on the 3-bromothiophene) of 3-ethylthiophene boiling at 136-138 ^{o}C. The structure was confirmed by nuclear magnetic resonance spectroscopy and infrared spectroscopy.

The other thiophenes which were of commercial origin were dried over calcium chloride and distilled. The purified thiophenes were stored under dry nitrogen. Propylene carbonate (PC) was dried over 0.4 nm molecular sieves, distilled and stored under dry nitrogen. The other solvents were dried and purified as usual[7]. The electrolytes were used without further purification.

2-3-2 Electrochemical polymerization

Polythiophenes films were prepared galvanostatically by electroxidation of thiophenes in a one-compartment cell equipped with an indium-tin-oxide conducting glass (ITO) or a platinum anode and a platinum or an aluminum cathode. The oxygen in the solution was swept out with argon prior to the electrochemical polymerization, which was carried out under an argon atmosphere.

2-3-3 Measurements

For measurements of electrical conductivity and scanning electron micrograph, films were prepared by use of a charge density of 2.4 C/cm^2. The films deposited on the surface of anodes were peeled off and washed with n-hexane. The direct current conductivity was measured using a four-point probe method. The thickness of the films was determined with an error of about 100 nm on an Anritsu digital electric micro-meter apparatus. Scanning electron micrographs were obtained with a Hitachi S-500A scanning electron microscope.

For infrared spectroscopy and scanning electron microscopy of neutral films, as-grown films on ITO were reduced by reversing the polarity of electrodes after electrochemical polymerization. The reduction was performed at a constant current density of 1 mA/cm^2 until the voltage between two electrodes increased to 30 V. The films were dried in vacuo at 150 ^oC. Infrared spectra were measured on a JEOL JIR-40 Fourier transform i.r. spectrophotometer.

For visible-near i.r. spectroscopy and cyclic voltammetry, thin films were prepared under the same polymerization conditions as films for conductivity measurement, but the charge density was reduced to 50 and 12 mC/cm^2 for spectroscopy and voltammetry, respectively. The thin films were left on the electrode surface as grown, rinsed with acetonitrile and used for further measurements. The thickness of the thin films

employed for spectroscopy was determined with an error of about 10 nm on a Rank Taylor Hobson Talystep-1. Cyclic voltammograms were recorded for a 0.1 mol/l tetraethylammonium hexafluorophosphate (Et_4NPF_6) solution in acetonitrile at sweep rates of 20, 40, 60, 80, and 100 mV/sec. Platinum plates were used as working and counter electrodes. A reference electrode consisted of an acetonitrile solution containing 0.01 mol/l of silver perchlorate ($AgClO_4$) and 0.1 mol/l of Et_4NPF_6 and a silver wire immersed in it, and connected with an electrochemical cell through a 0.1 mol/l Et_4NPF_6 solution as a salt bridge. The spectral change during electrochemical doping was measured in situ in an acetonitrile solution containing 0.01 mol/l of silver hexafluorophosphate ($AgPF_6$) and 0.1 mol/l of Et_4NPF_6. The working and the counter, reference electrodes were ITO and a silver wire, respectively. Absorption spectra were recorded on a Cary-17D spectrophotometer.

2-4 Results and discussion

2-4-1 Optimization of 3-methylthiophene polymerization

To obtain high-quality films by electrochemical polymerization, the author examined the effects of solvents and electrolytes on the conductivity of PMT films. Solvent selection was important for obtaining high-quality films. PC was

found to be a preferable solvent. Et_4NPF_6 and sodium hexafluoroarsenate ($NaAsF_6$) were good electrolytes. Using PC and Et_4NPF_6, the author examined the electrochemical polymerization of 3-methylthiophene in detail.

The relationship between monomer concentration and electrical conductivity of the films is shown in Figure 2,1. Maximum conductivity was found for the film prepared by using a monomer concentration between 0.175 and 0.20 mol/l. Above this concentration, the conductivity steeply decreased with increasing monomer concentration. The film prepared by using a monomer concentration of 0.125 mol/l was brittle and heterogeneous. Below this concentration no films were obtained. High-quality films could be obtained in a small range of monomer concentrations. The dependence of electrical conductivity of the films on electrolyte concentration is shown in Figure 2,2. The film prepared in a solution containing 0.03 mol/l of the electrolyte had the highest conductivity.

Figure 2,3 shows the electrical conductivity of the films as a function of polymerization temperature. The conductivity hardly changed in the temperature range -15 to 5 ^{o}C. However, the conductivity decreased linearly at higher temperatures. At -20 ^{o}C, homogeneous films were not deposited on the anode surface.

The electrical conductivity of the films is plotted versus applied current densities during polymerization in Figure 2,4.

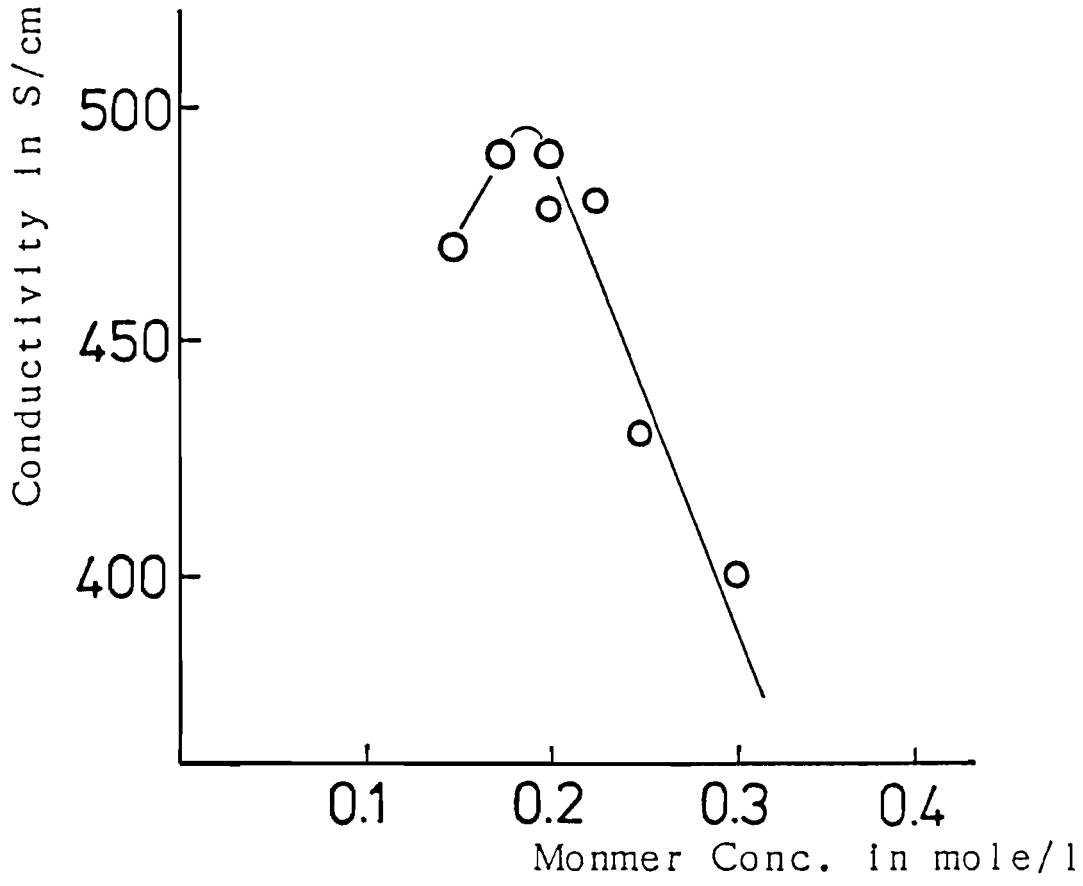


Figure 2,1. Effect of monomer concentration on conductivity of PMT. Concentration of Et_4NPF_6, temperature and current density were 0.03 mol/l, 5 ^{o}C and 10 mA/cm^2, respectively.

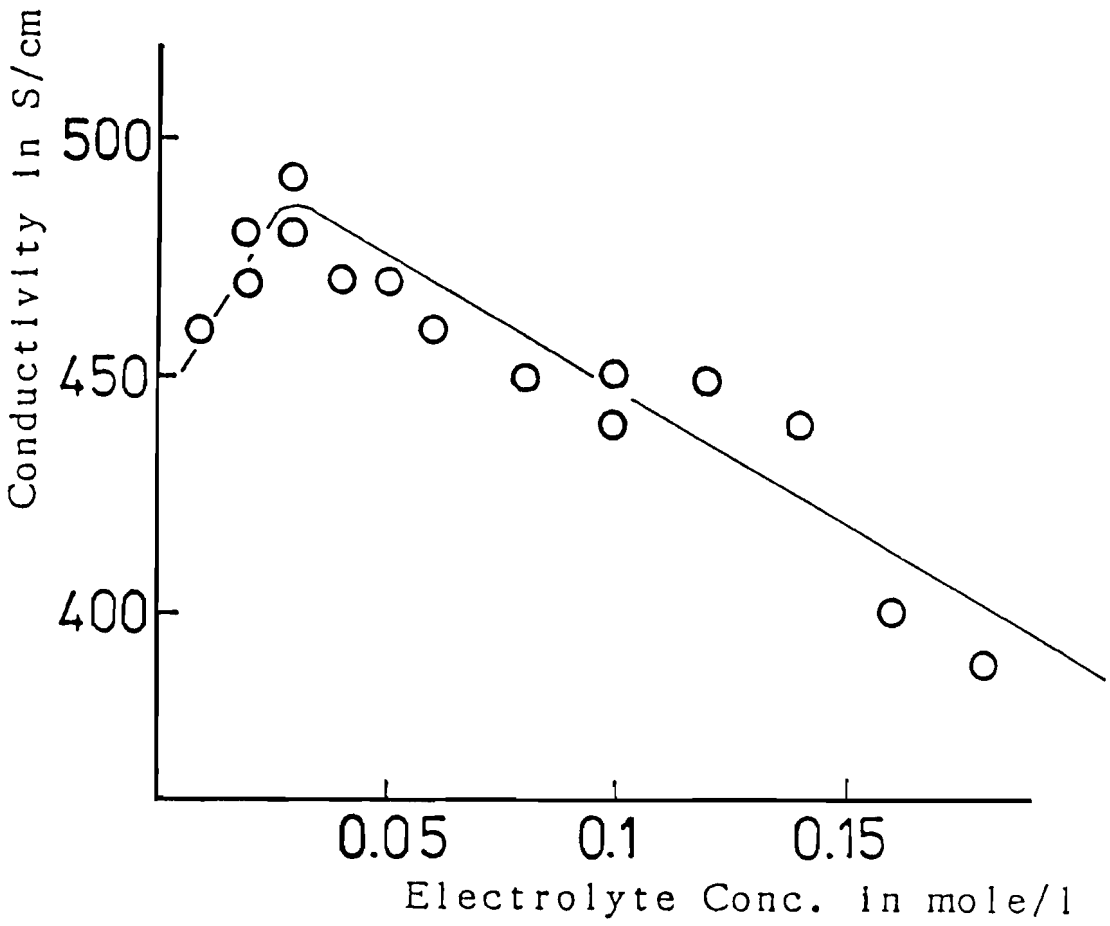


Figure 2,2. Effect of electrolyte concentration on conductivity of PMT. Monomer concentration, temperature and current density were 0.2 mol/l , 5°C and 10 mA/cm², respectively.

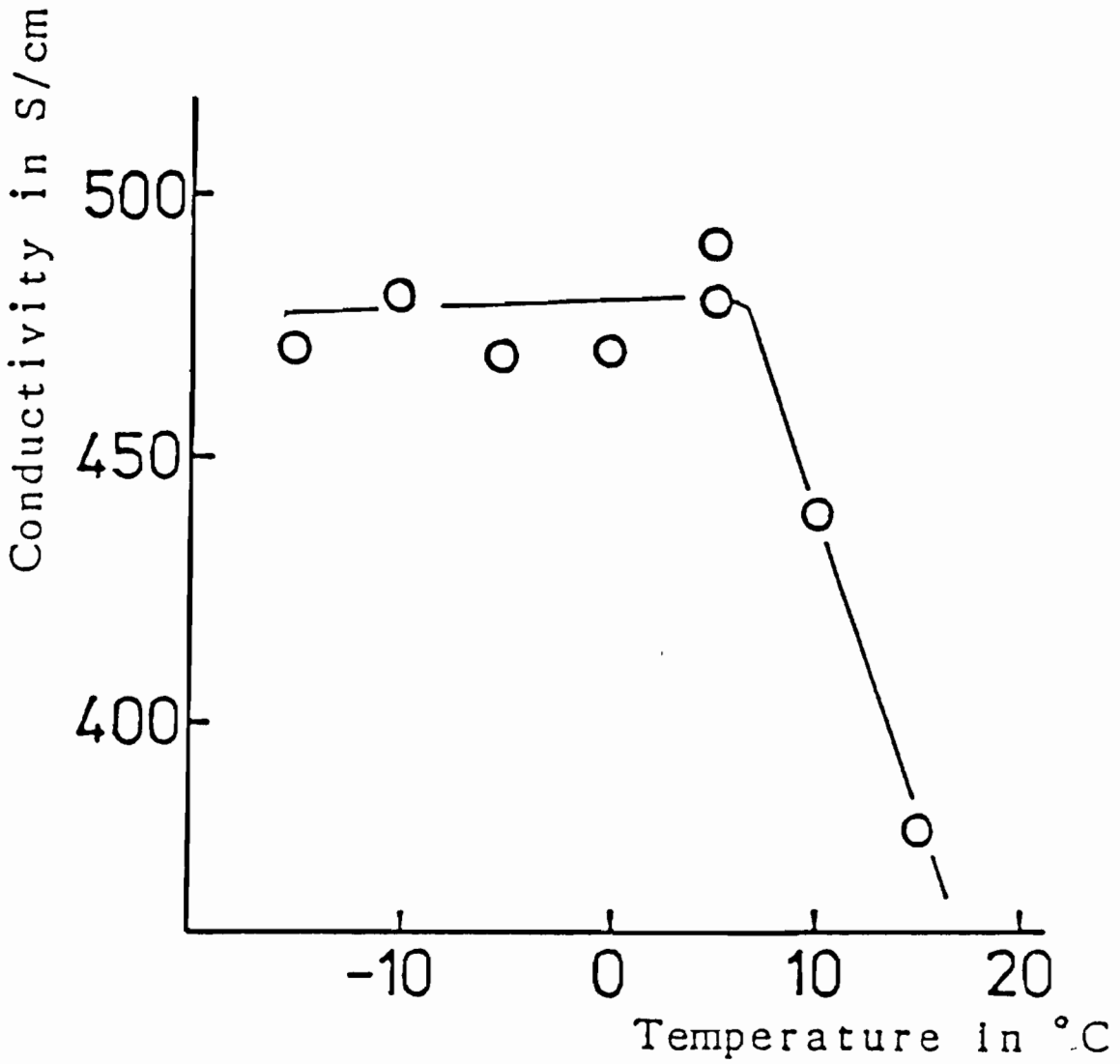


Figure 2,3. Effect of polymerization temperature on conductivity of PMT. Concentrations of Et_4NPF_6 and monomer were 0.03 and 0.2 mol/l, respectively. Current density was 10 mA/cm^2.

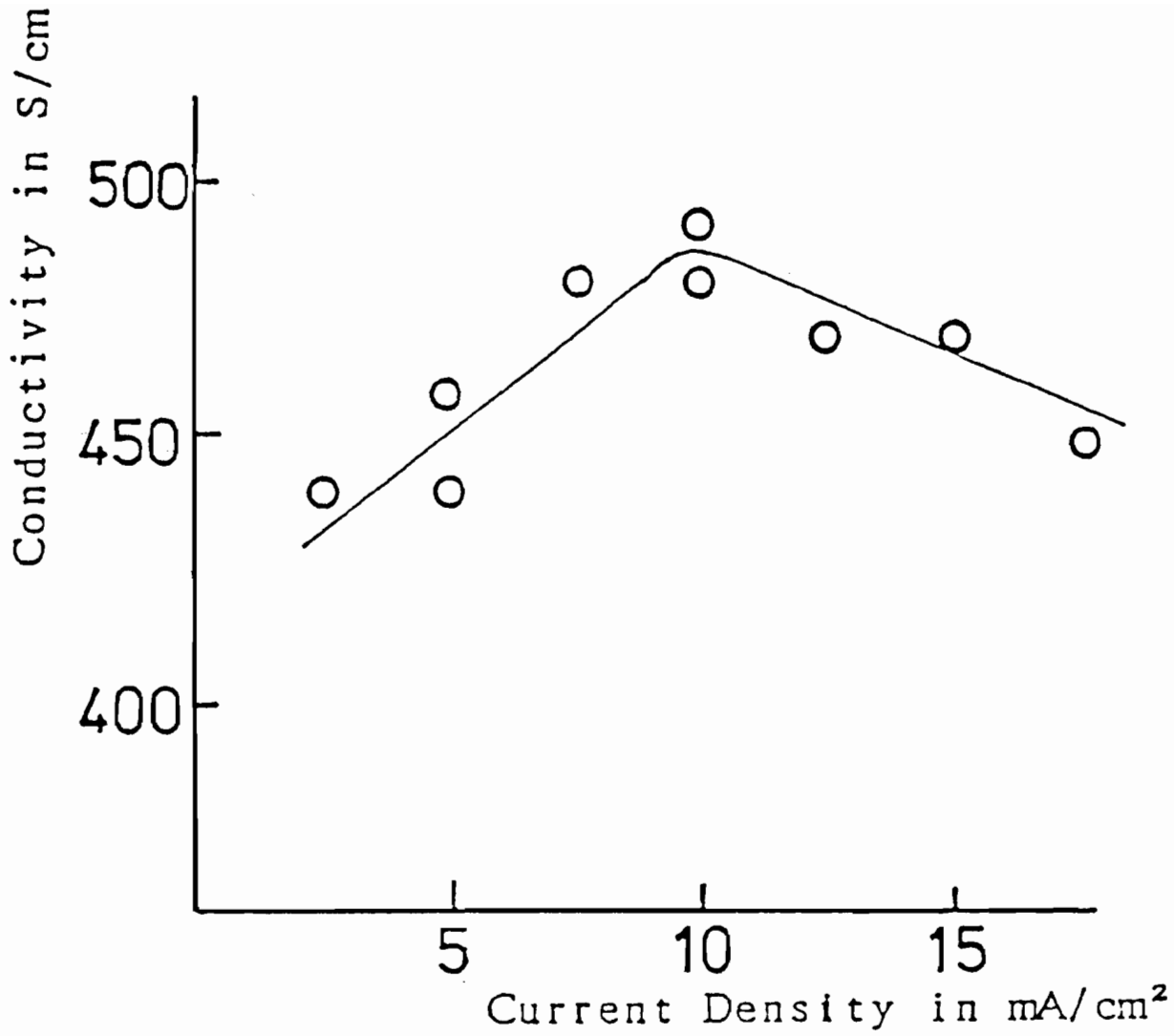


Figure 2,4. Effect of current density on conductivity of PMT. Concentrations of Et_4NPF_6 and monomer were 0.03 and 0.2 mol/l, respectively. Temperature was 5°C.

The maximum conductivity was observed for a film prepared at a current density of 10 mA/cm^2. Although coherent film were obtained, the conductivity decreased gradually on both sides of the maximum. As for the polymerization of 3-methylthiophene, the optimum concentrations of the monomer and the electrolyte were 0.2 and 0.03 mol/l, respectively, and the optimum current density was 10 mA/cm^2. Polymerization temperature between -15 and 5 ^oC was best. Under these conditions, the voltage between the two electrodes was about 10 V and did not change during polymerization. The PMT films obtained here were the most conductive of as-grown films prepared by electrochemical polymerization of heterocyclic compounds. An as-grown films of PMT was black and had luster.

2-4-2 Polymerization of other monomers

The results of polymerization of thiophene, 3-methylthiophene and 3-ethylthiophene are summarized in Table 2,1. Thiophene and 3-ethylthiophene were electrochemically polymerized under the same conditions as 3-methylthiophene, but the current density was lowered to 5 mA/cm^2 for $NaAsF_6$ as an electrolyte, since ITO had been oxidized to an insulating substance at the overpotential for oxidation of the thiophenes. An aluminum plate was used as a cathode for $NaAsF_6$. Aluminum forms an alloy with sodium and thus the cathode reaction should cause no contamination by decomposition products. Highly conducting

Table 2,1. Results of electrochemical polymerization[a)]

Run	Monomer[b)]	Electrolyte	Solvent[c)]	Anode	Cathode	Conductivity (S/cm)	Dopant[d)] content
1	T	Et_4NPF_6	PC	ITO	Pt	190	0.17
2	T	$NaAsF_6$	PC	ITO	Al	170	--
3	MT	Et_4NPF_6	PC	ITO	Pt	510	0.18
4	MT	Et_4NPF_6	PC	Pt	Pt	490	--
5	MT	$NaAsF_6$	PC	ITO	Al	500	--
6	MT	Et_4NBF_4	PC	ITO	Pt	450	--
7	MT	Et_4NClO_4	PC	ITO	Pt	150	--
8	MT	Et_4NPF_6	BN	ITO	Pt	190	--
9	MT	Et_4NPF_6	NB	ITO	Pt	100	--
10	MT	Et_4NPF_6	AN	ITO	Pt	-[e)]	--
11	ET	Et_4NPF_6	PC	ITO	Pt	240	0.17
12	ET	$NaAsF_6$	PC	ITO	Al	270	--

a) The current density was 10 mA/cm^2 except for runs 2 and 12, where it was 5 mA/cm^2. The polymerization temperature was 5 ^{o}C. [monomer] = 0.2 mol/l; [electrolyte] = 0.03 mol/l.

b) T:thiophene; MT:3-methylthiophene; ET:3-ethylthiophene.

c) PC:propylene carbonate; BN:benzonitrile; NB:nitrobenzene; AN:acetonitrile.

d) Dopant per monomer unit determined from elemental analysis of sulphur and phosphorus.

e) The film was heterogeneous.

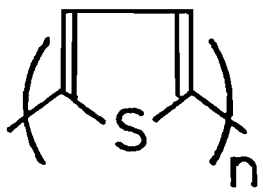
and tough films of PT and PET were obtained.

The dopant content per monomer unit was calculated from the elemental analysis of sulfur and phosphorus. Despite the large difference in the conductivity, the polythiophenes films contained almost the same amount of the dopant.

2-4-3 Infrared spectra

The Fourier transform i.r. spectra of the neutral polythiophenes are shown in Figure 2,5. The spectrum of PT^0 exhibited a band at 3064 cm^{-1} which is characteristic of C-H stretching vibrations in β-position relative to the sulfur atom. A very strong band appeared at 789 cm^{-1}, attributable to a 2,5-disubstituted thiophene ring, and two weak bands at 739 and 837 cm^{-1}, possibly attributable to a small amount of irregular substitution such as 2,4-di- and 2,3,5-tri-substitutions[8),9)]. The PT^0 which was prepared in the reaction solution employed repeatedly absorbed at 839 cm^{-1} with more strong intensity.

There were weak bands at 700 cm^{-1} in common in the spectra of PT^0, PMT^0, and PET^0. The bands were assigned to the terminal 2-monosubstituted thiophene ring[8),9)].



Poly(2,5-thiophenediyl)

The spectrum of PMT^0 showed bands at 3057 and 2968-2860 cm^{-1} which were

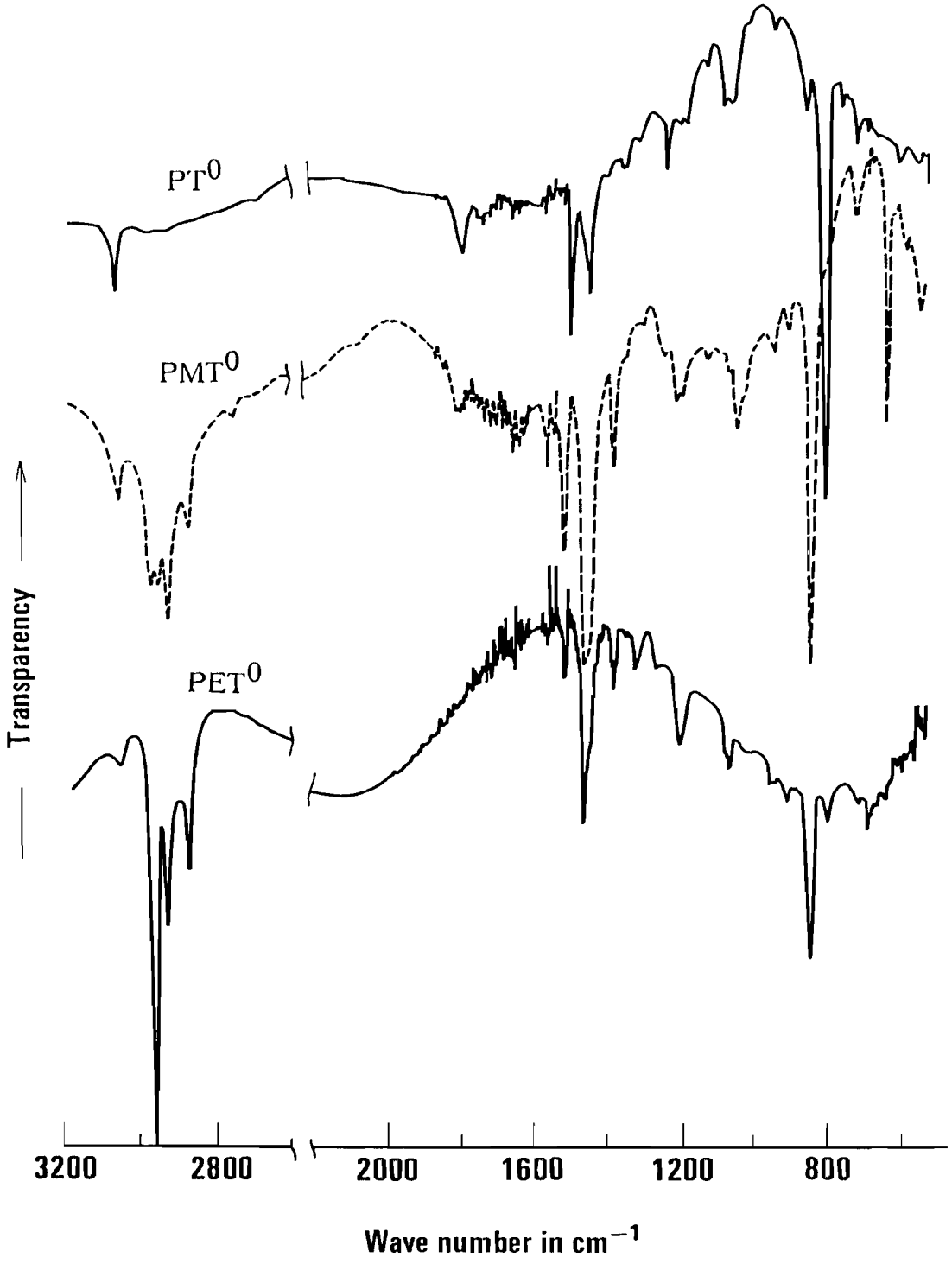
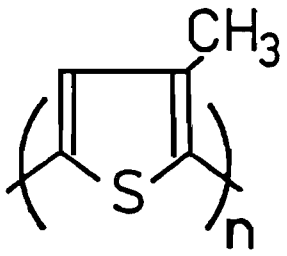
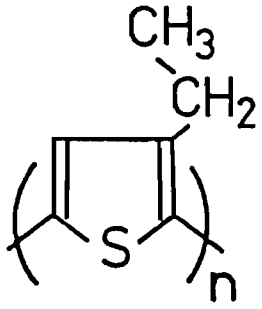


Figure 2,5. Infrared spectra of PT^0, PMT^0, and PET^0.

assigned to the aromatic and the aliphatic C-H stretching vibrations, respectively. There was a band at 822 cm^{-1} assigned to the C-H deformation vibration of a 2,3,5-trisubstituted thiophene ring[10]. There were no bands showing other modes of substitution on the thiophene rings. The spectrum of PET^0 was very similar to that of PMT^0, but had stronger aliphatic bands at 2966-2871 cm^{-1} and a weak band at 785 cm^{-1} assigned to the rocking vibration of a methylene group[11]. These spectra show that PMT^0 and PET^0 have a regular structure, which can be denoted as poly(3-alkyl-2,5-thiophenediyl), but PT^0 contains considerable irregular structures such as reticulation.



PMT^0



PET^0

2-4-4 Scanning electron micrographs

Figure 2,6 shows the scanning electron micrographs of the surface of PT, PMT, and PET films. The films were 5-8 μm thick. Both sides of the polythiophenes films exhibit different aspects. Side (a) was in contact with the electrolyte solution and side (b) was in contact with the electrode.

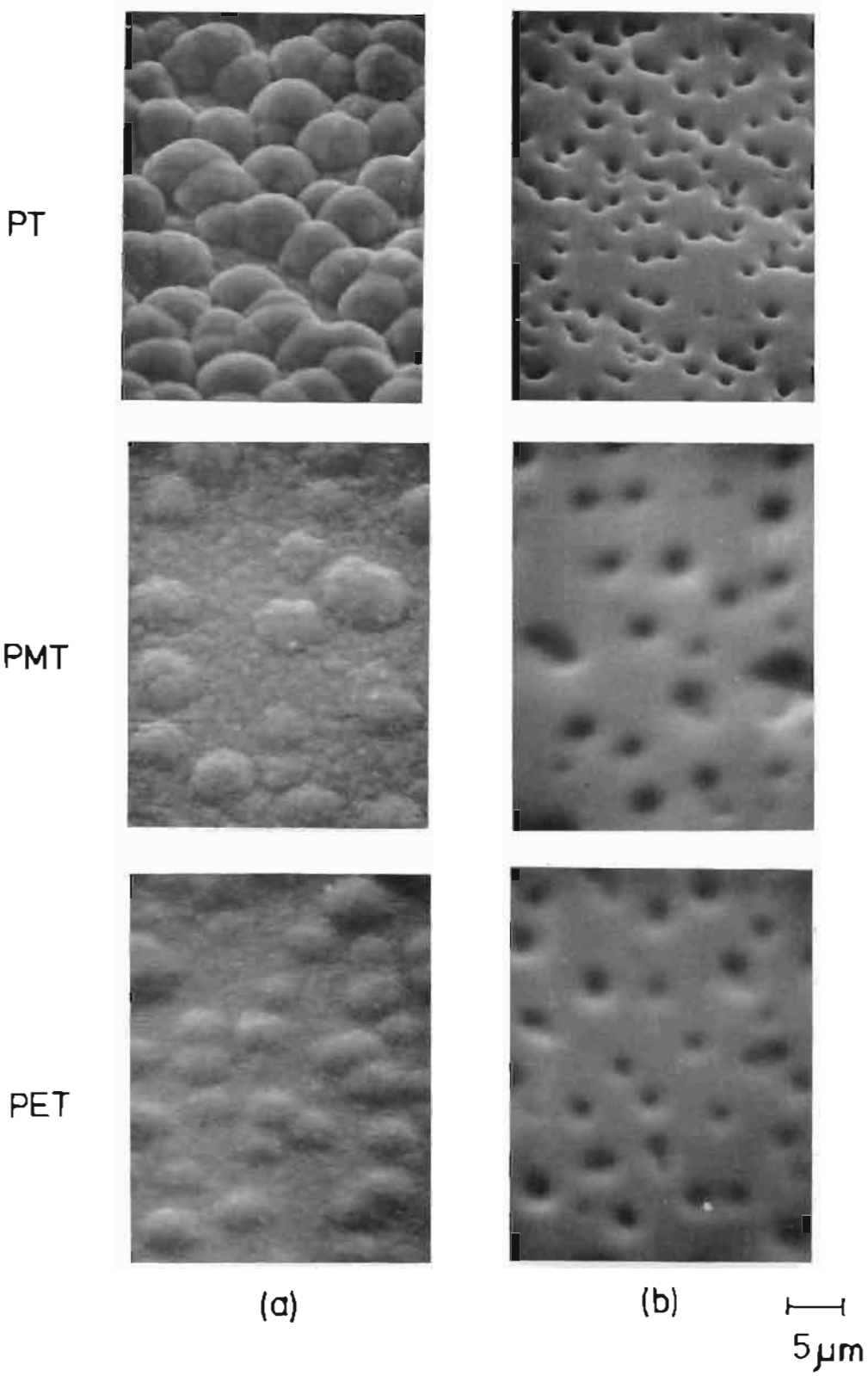


Figure 2,6. SEM of the surface of PT, PMT, and PET films.

As for PT, the side (a) is granular and the side (b) has many voids. The pictures of the present films are different from those of PT films which were prepared in acetonitrile with tetrabutylammonium hexafluorophosphate as an electrolyte[12] or in nitrobenzene with tetrabutylammonium tetrafluoroborate[4]. This result shows that the morphology of PT films, as well as the conductivity of them, is influenced by conditions used in electrochemical preparation of the films. The morphology of PMT films is similar to that of PET films. The sides (a) are not so granular as the side (a) of PT films and the sides (b) have dimples. These results would be related to the difference of the regularity of the polymer structure which was confirmed by the i.r. spectra of the neutral polythiophenes.

The scanning electron micrographs of the neutral PT^0, PMT^0, and PET^0 films are shown in Figure 2,7. The films were 4-6 mm thick. The neutral polythiophenes films had extremely low conductivity. Accordingly, the films were sputtered with gold to prevent them from charging by electron-ray.

The pictures of the neutral films and the corresponding as-grown films account for the expulsion process of the dopant, which takes place between the oxidized and the neutral, undoped, states. By the neutralization, the granular projections and voids observed on the surface of the PT films became smaller and the PMT and PET films swelled at the dimples. However, the change of the morphology of the polythiophenes

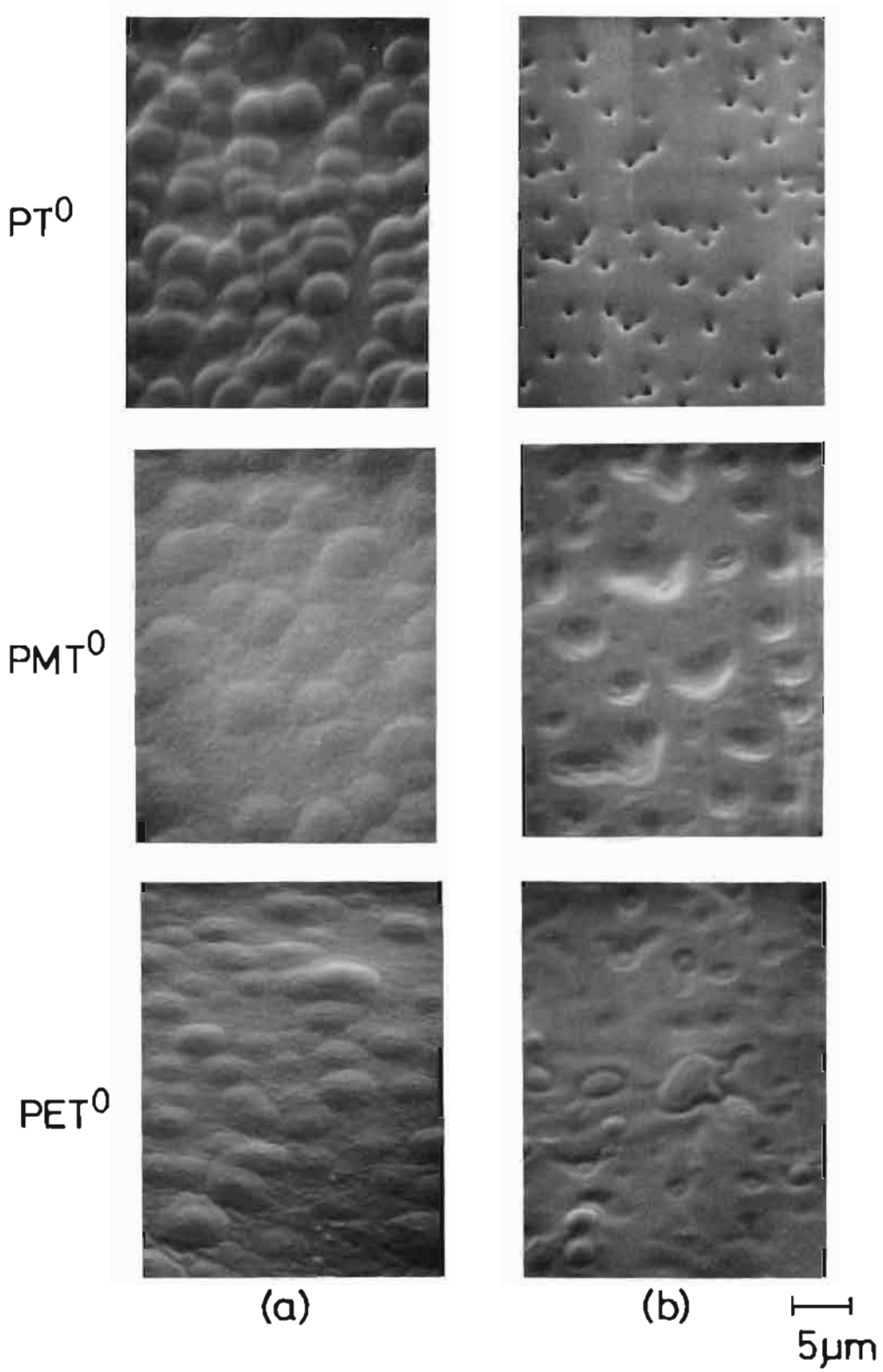


Figure 2,7. SEM of the surface of PT^0, PMT^0, and PET^0 films.

films is slight, indicating no deterioration to take place during the neutralization.

2-4-5 Cyclic voltammograms

The cyclic voltammograms of polythiophenes films grafted on Pt are presented in Figures 2,8-2,10. The films could change repeatedly between oxidized and neutral states with no appreciable decomposition of material. The oxidation, doping, of the polymer films corresponds to the transfer of electrons from the films to the Pt electrodes, producing holes, and then to the formation of ion-pairs consisted of holes and anions derived from the supporting electrolyte. The redox reaction was accompanied by reversible color change.

The cyclic voltammograms of PT (Figure 2,8) showed one oxidation peak at 0.67-0.69 V (vs. Ag^+/Ag) and two reduction peaks about 0.6 and 0.3 V. The shapes of voltammograms were quite similar to those of polythiophene prepared from 2,2'-bithiophene, although a different electrolyte was used[13]. The cyclic voltammograms of PMT (Figure 2,9) showed two oxidation peaks at 0.25-0.28 V and around 0.53 V and two reduction peaks at 0.45 and -0.12 V. In the cyclic voltammograms reported previously, only one peak was observed in the oxidation waves, and the first reduction peak was located at a lower voltage than the oxidation peak[14]. The cyclic voltammograms of PET (Figure 2,10) showed one oxidation peak at 0.44-0.47 V, one

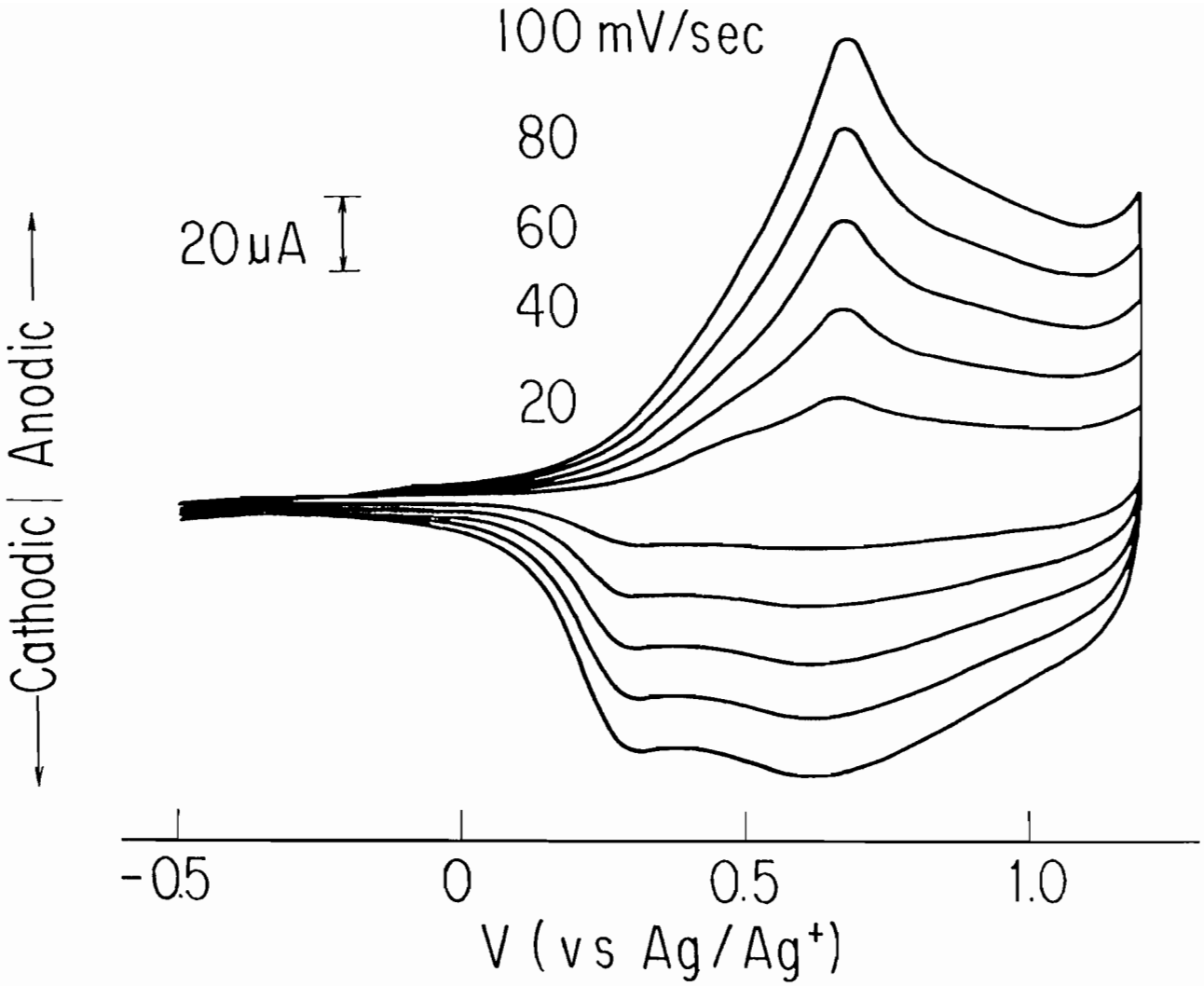


Figure 2,8. Cyclic voltammograms of a PT film.

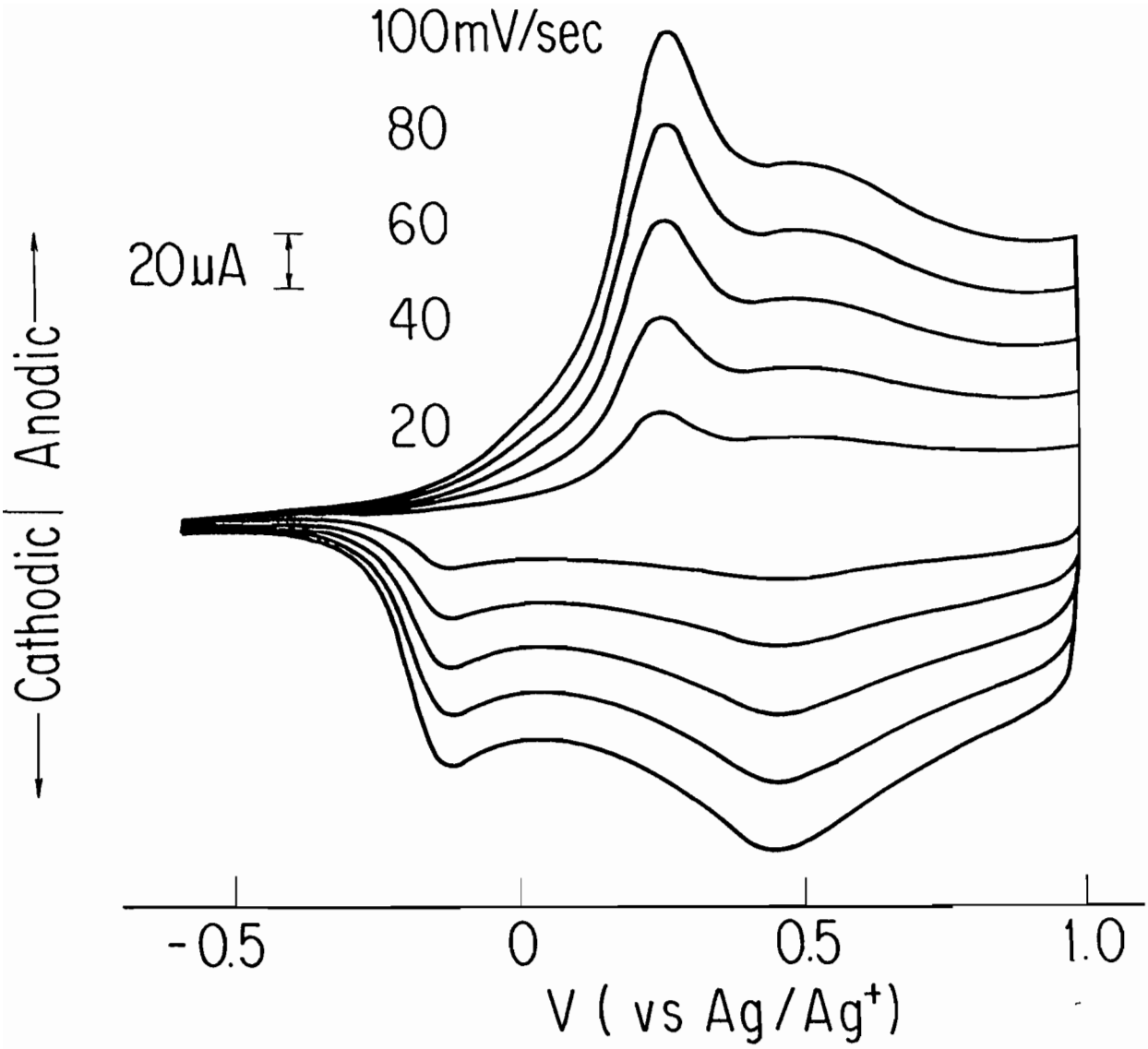


Figure 2,9. Cyclic voltammograms of a PMT film.

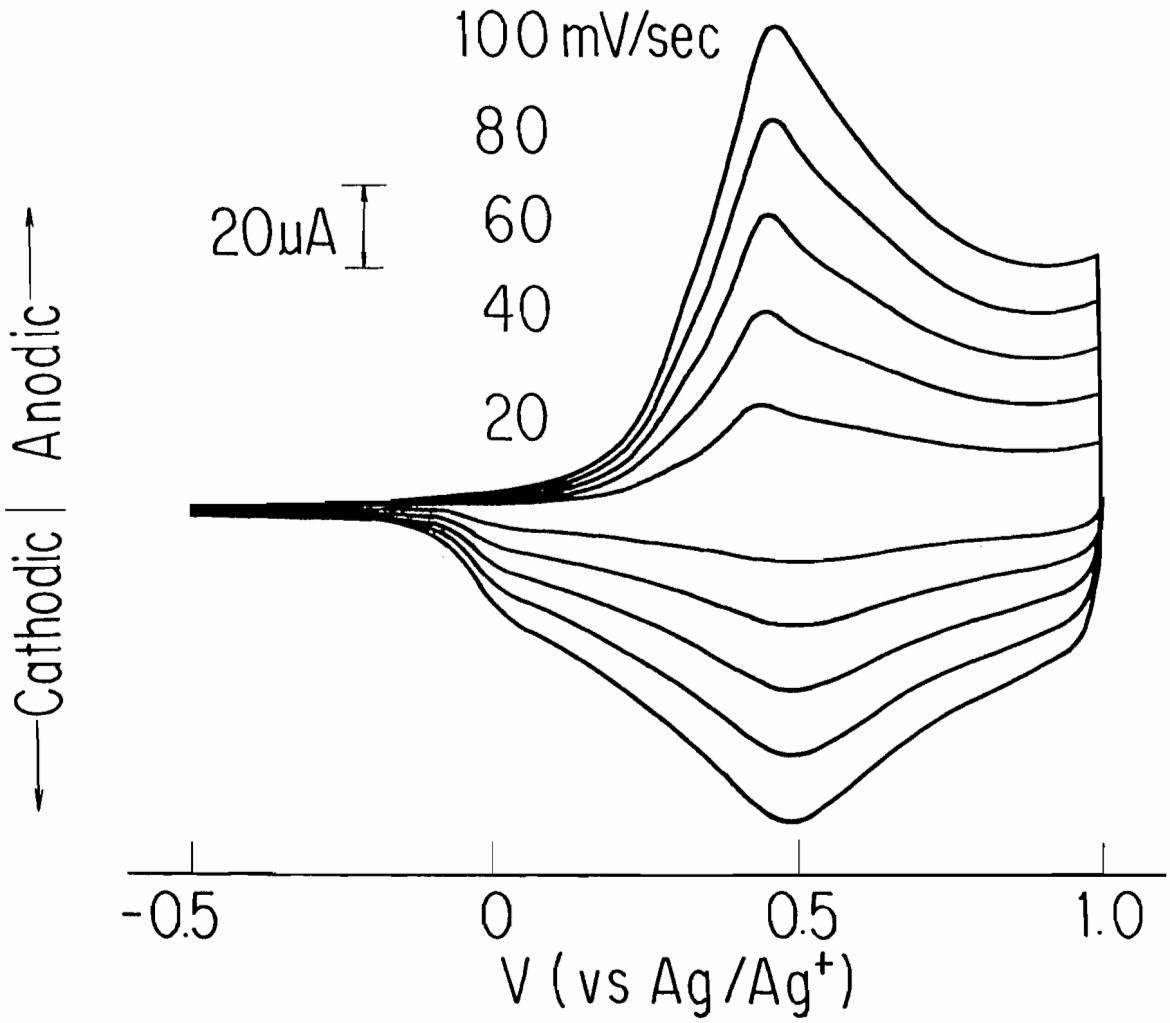


Figure 2,10. Cyclic voltammograms of a PET film.

reduction peak at 0.50-0.48 V.

The peak heights of the oxidation and the reduction peaks were proportional to the sweep rate. The voltammograms did not change when the solutions were stirred. These observations indicate that the electroactive material is not dispersed in a solution but localized on the electrode surface and diffusion process is not involved in the rate-determining step of the redox reactions. This behavior is characteristic of an electroactive film grafted on an electrode. The voltammograms showed the presence of large residual currents in the potential regions beyond the oxidation peaks. These currents were attributed to capacitive charging currents, similar to the behavior of a porous metal[15),16)].

As shown in Figures 2,8 and 2,9, the reduction process was more complex to analyse and displayed at least two components. As the attribution of these waves was not straightforward, the author carried out further discussion by considering the feature of the positive sweep of the voltammograms.

Oxidation peaks of PMT^0 were located about 0.4 V lower than those for PT^0. PMT^0 was oxidized more easily than PT^0. The theoretical investigations of the electronic structure of polythiophenes had mentioned that poly(2,5-thiophenediyl) has 0.05 eV higher ionization potential than poly(3-methyl-2,5-thiophenediyl)[17)] and the irregularity in PT^0 leads to increase of the ionization potential[18)]. The present results would be

interpreted by the electronic effect of the substituent and the irregularity of PT^0. The oxidation peaks of PET^0 were located midway between PT^0 and PMT^0. This would not arise from differences in the electron donating effects between the methyl and the ethyl groups, in that the Hammett constants of the methyl group are very close to those of the ethyl group and an approximately liner relationship is present between the benzene and thiophene series[19),20)]. It could be explained as being due to a steric effect. Since the 3-ethyl group hinders successive rings from taking coplanar conformation, the conformation along the polymer chains become less effective, causing an increase in polymer oxidation potential.

2-4-6 Spectral change during doping

Neutral polythiophenes films which were obtained by the reduction of as-grown films in a three-electrode system were electrochemically oxidized, doped, at different applied voltages. The change in visible-near i.r. spectra of polythiophenes during doping is shown in Figures 2,11-2,13. The voltage across the cell was set at the desired value, and the cell was allowed to come to an equilibrium.

At 0.0 V, π-π^* transitions were observed. PT, PMT, and PET had absorption peaks at 2.5, 2.45, and 2.70 eV, respectively. These peak positions would be associated with the band gaps of the corresponding polythiophenes. The electronic structure cal-

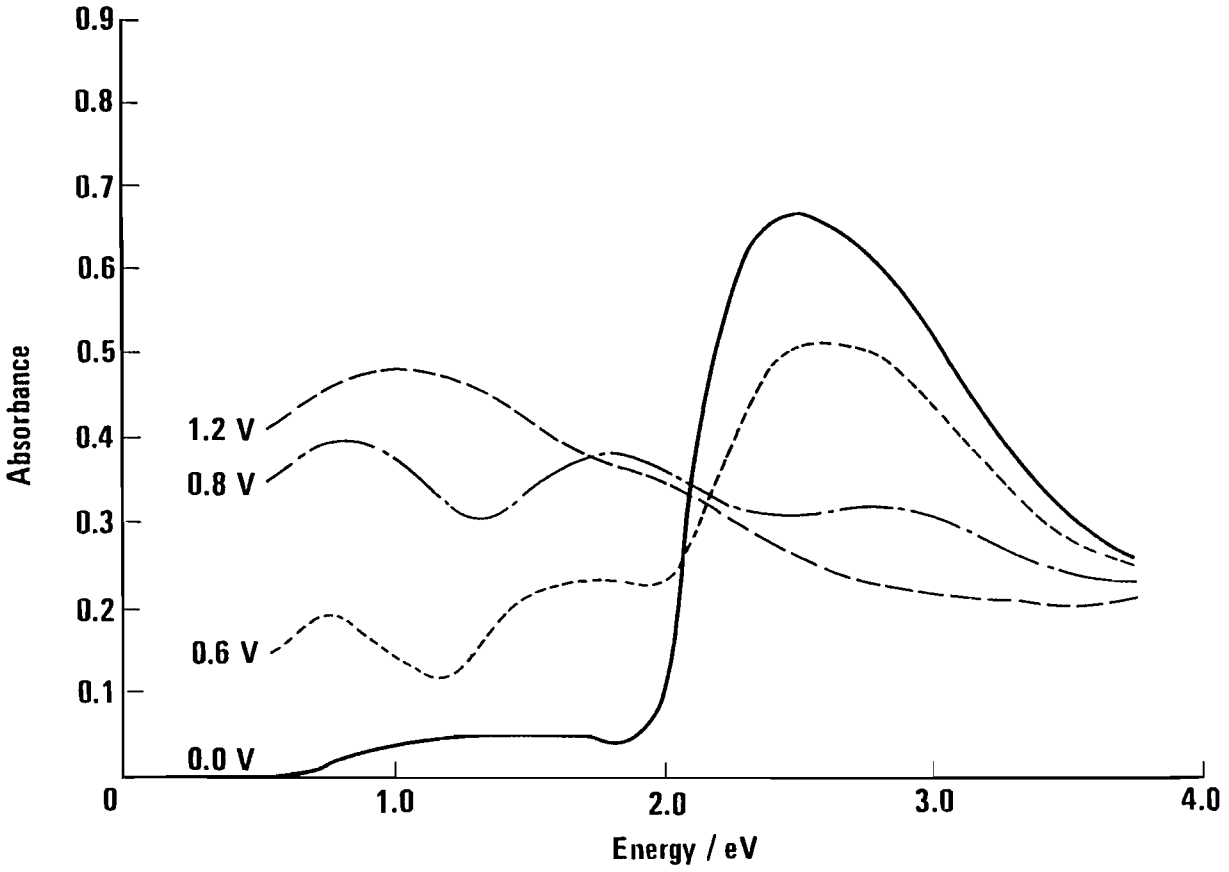


Figure 2,11. Spectral change of a PT film during electrochemical doping. Applied voltage is shown on the left.

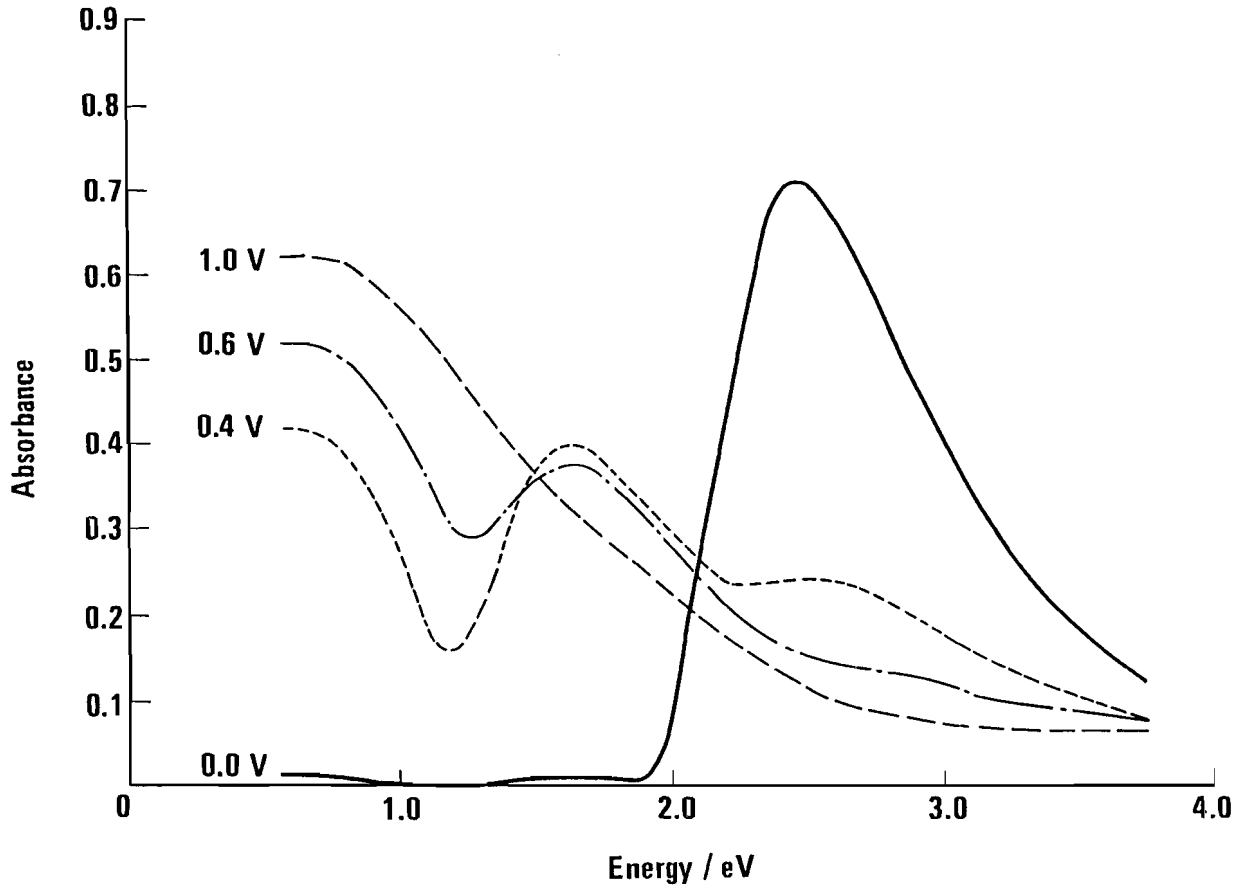


Figure 2,12. Spectral change of a PMT film during electrochemical doping. Applied voltage is shown on the left.

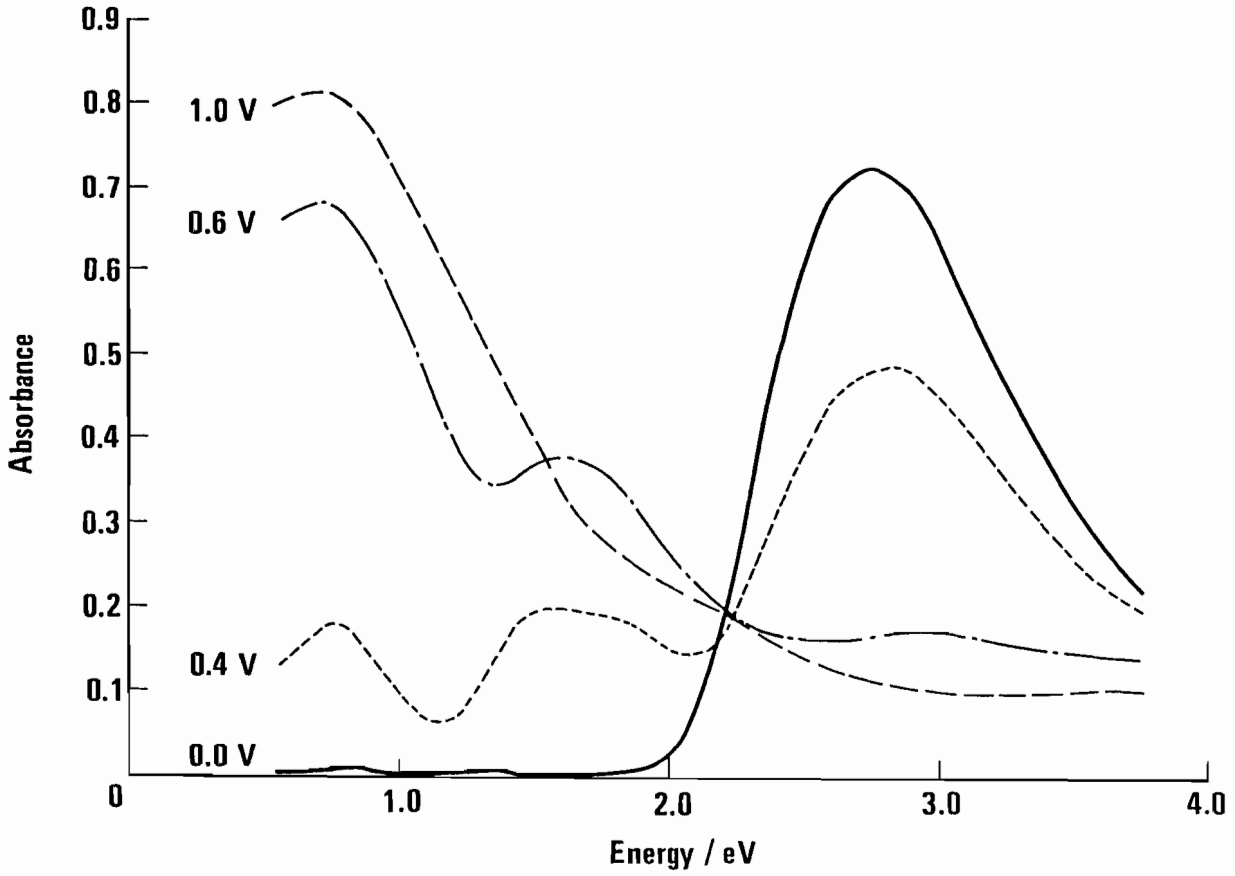


Figure 2,13. Spectral change of a PET film during electrochemical doping. Applied voltage is shown on the left.

culations on polythiophenes had demonstrated that the introduction of a 3-methyl or ethyl group and the irregularity in poly(2,5-thiophenediyl) cause its band gap to widen[17),18)]. The absorption of PT at higher energy than that of PMT would be explained by the irregularity of PT^0. The absorption of PET at the highest energy could be interpreted by the steric hindrance of the bulky ethyl group to successive rings taking coplanar conformation. The spectrum of PT shows weak and broad features below 2 eV. This would be attributed to incomplete neutralization owing to the irregularity of PT^0.

When a PT film was electrochemically doped, two additional peaks appeared in the gap region and the peak height of the π-π^* transition decreased. These three peaks shifted to the high energy side as the doping level increased. At 1.2 V, two peaks disappeared and a broad one remained at 1.0 eV. Brédas et al. predicted electronic structure modifications from theoretical studies as follows[21)]. Two bipolaron states appear in the gap between the valence and the conduction bands on doping. The gaps between the valence band and the bipolaron bands and between the valence band and the conduction band become larger as doping proceeds. The present results are clearly explained by the appearance of two bipolaron bands and increase in the gaps. Chung et al. also reported similar spectral changes during doping with perchlorate anions[22)].

In doped states, the spectra of PET showed almost the same

frequency dependence as those of PMT. At intermediate stages of doping, two absorption peaks appeared about 0.7 and 1.6 eV. These peaks possibly correspond to transitions from the valence band to the two bipolaron bands, but they do not show blue shifts with increase in the doping levels. The peak of the π-π^* transition showed apparent blue shifts. This is inconsistent with results of theoretical study by Brèdas et al.[21]. At 1.0 V, only one peak was observed at 0.7 eV. These changes show that the band structure of PMT is quite similar to that of PET in doped states. This may imply that successive thiophene rings take on coplanar conformation. The differences in spectral change between PT and PMT or PET would be ascribed to the irregularity of PT^0.

2-5 Conclusions

For the electrochemical polymerization of 3-methylthiophene, PC and Et_4NPF_6 were found to be a appropriate as the solvent and electrolyte, respectively. Using these, optimal conditions for obtaining high-quality films were found. The PMT film was tough and had a conductivity of 510 S/cm. The PT and the PET films prepared under the same polymerization conditions showed conductivities of 190 and 270 S/cm, respectively. These three films were compared by infrared spectroscopy, cyclic vol-

tammetry and visible-near i.r. spectroscopy. Infrared spectra indicated the presence of an observable number of irregular bondings other than the 2,5-linkage in PT^0, but not in either PMT^0 or PET^0. The scanning electron micrographs of the surface of as-grown and neutral films represented that the surface of PT was rougher than those of PMT and PET.

The cyclic voltammograms suggested that the oxidation potential increases in the order of $PMT^0 < PET^0 < PT^0$. The visible spectra of neutral films showed that the peak of the π-π^* transition shifted to high energy side in the order of $PMT^0 < PT^0 < PET^0$. The frequency dependence of spectral change implied that the band structure of PMT was similar to that of PET in doped states. These results were explained by assuming that both the effects of the substituents and the irregularity of PT^0 are important in neutral states, but that the effect of the irregularity is dominant in doped states. The spectral changes of PT at different doping levels were consistent with the bipolaron theory of Brėdas et al. Those of PMT and PET were partly inconsistent.

Further study will be necessary for a more detailed clarification of the substituent effects.

2-6. References

1) G. Tourillon and F. Garnier, J, Phys. Chem., **87**, 2289 (1983).

2) S. Hotta, T. Hosaka, and W. Shimotsuma, Synth. Met., **6** 317 (1983).

3) K. Soga, M. Nakamaru, Y. Kobayashi, and S. Ikeda, Synth. Met.,**6**, 275 (1983)

4) S. Tanaka, M. Sato, and K. Kaeriyama, Makromol. Chem., **185**, 1295 (1984).

5) K. Tamao, S. Kodama, I. Nakajima, and M. Kumada, Tetrahedron, **22**, 3347(1982).

6) G. R. V. Hecke and W. D. Horrocks Jr., Inorganic Chemistry, **5**, 1968 (1966).

7) J. A. Riddick and W. B. Bunger, "Organic Solvents", Willey, New York (1970).

8) S. Hotta, T. Hosaka, M. Soga, and W. Shimotsuma, Synth. Met., **10** 95 (1984/1985).

9) M. Akiyama, J. Mol. Spectrosc., **43**, 226 (1972).

10) S. Hotta, W. Shimotsuma, M. Taketani, and S. Kohiki, Synth. Met., **11** 139 (1985).

11) R. M. Silverstein, G. C. Basser, and T. C. Morrill, "Spectrometric Identification of Organic Compounds", Wiley, New York, p.86 (1974).

12) G. Tourillon and F. Garnier, J. Polym. Sci., Polym. Phys. Ed., **22**, 33 (1984).

13) R. J. Waltman, J. Bargon, and A. F. Diaz, J. Phys. Chem., **87** 1459 (1983).

14) G. Tourillon and F. Garnier, J. Electroanal. Chem., **161** 51 (1984).

15) S. W. Feldbelg, J. Am. Chem. Soc., **106**, 4671 (1984).

16) N. Mermilliod, J. Tanguy, and F. Petiot, J. Electrochem. Soc., **129**, 4671 (1986).

17) B. Thémans, J. M. Andrė, and J. L. Brėdas, Synth. Met., **21**, 149 (1987).

18) K. Tanaka, T. Shichiri, and T. Yamabe, Synth. Met,. **14**, 271 (1986).

19) P. Zumman and R. Patel, "Techniques in Organic Reaction Kinetics", Wiley, New york, p.228 (1984).

20) S. Alunni, S. Clemnti, C. Ebert, P. Linda, M. Sjostrom, and S. Wold, J. Chem. Soc., Perkin Trans., **2**, 485 (1985).

21) J. L. Brėdas, B. Thémans, J. G. Fripiat, J. M. Andrė and R. R. Chance, Phys. Rev., **B29**, 6761 (1984).

22) T. C. Chung, J. H. Kaufman, A. J. Heeger, and F. Wudl, Phys. Rev., **B30**, 702 (1984).

Chapter 3

Poly(3-butylthiophene) and Poly(3-benzylthiophene) Films: Effect of Substituents and Electronic Structure for Electronic and Optical properties.

3-1 Abstract

Poly(3-butylthiophene) (PBUT) and poly(3-benzylthiophene) (PBZT) films were electrochemically prepared and their properties were examined. The conductivities of PBUT and PBZT were 110 and 13 S/cm, respectively. Cyclic voltammograms of PBUT were similar to those of poly(3-ethylthiophene). Cyclic voltammograms of PBZT were sharp and well defined. Spectral change of PBZT during electrochemical doping showed that the positions of the peak of π-π^* transition did not shift until heavily doping level. From these results, it was assumed that the bandwidths of the valence and the conduction bands of $PBZT^0$ (the superscript 0 denotes the neutral state) are smaller and the bipolaron levels caused by doping are derived from the whole of the valence and the conduction bands evenly. The conductivities and the electrochemical and the optical data of PBUT and PBZT were compared with those of poly(3-methylthiophene) and poly(3-ethylthiophene). The bulkier substituent group decreased the conductivity of the doped polymer and increased the oxidation potential of the neutral polymer. The optical data indicated that the bipolaron states at intermediate stages of doping are localized in the polymer chains.

3-2 Introduction

The properties of the polymers depend primarily on their chemical structures, but the relation between structure and conductivities has not been studied intensively. This might be due to the fact that chemical modification of polymers usually has undesirable effects on their conductivities. For example, although the conductivity of polyacetylene is higher than 10^4 S/cm[1], substituted polyacetylenes show conductivities less than 10^{-3} S/cm[2]. Polythiophenes were shown to be an exception to this. Poly(3-methylthiophene) (PMT) and poly(3-ethylthiophene) (PET) were more conducting than polythiophene (PT)[3]. Infrared spectra of the neutral polymers indicated that PT^0 contained an observable amount of irregular bondings other than the 2,5-linkage, but PMT^0 and PET^0 had a regular structure. In cyclic voltammetry, scanning electron spectroscopy, and visible-near i.r. spectroscopy, it was elucidated that the irregularity of polymer structure affected the morphology and the electronic structure of the neutral and the doped polymer which were associated with the electrical conductivity[4].

In this chapter, the preparation, the cyclic voltammograms, and the spectral changes of PBUT and PBZT are described. These results are discussed in terms of the steric effect of the substituents and the electronic structure of the

polymers. The property of PBUT was on the extrapolation of that of PET, but PBZT showed interesting properties different from poly(3-alkylthiophene)s.

The conductivities and the electrochemical and the optical data of PBUT and PBZT were compared with those of PMT and PET.

3-3 Experimental

3-3-1 Materials

3-Butylthiophene (BUT) was prepared according to the previously reported method (b.p. 85-86 ^{o}C at 28 mmHg)[5].

3-Benzylthiophene (BZT) was synthesized by coupling of benzylmagnesium chloride with 3-bromothiophene in the presence of dichloro[1,3-bis(diphenylphosphino)propane]nickel(II) [Ni(dppp)Cl_2] which was prepared from 1,3-bis(diphenylphosphino)propane and nickel(II) chloride[6]. The procedure of the coupling reaction is as follows. To a mixture of 3-bromothiophene (10,0 g; 61.3 mmol), Ni(dppp)Cl_2 (60 mg; 0.1 mmol), and fleshly distilled dry ether (50 ml) was added a solution of benzylmagnesium chloride, which was prepared from magnesium (1.94 g; 79.8 mg-atom) and benzyl chloride (10.1 g; 79.8 mmol) in freshly distilled dry ether (60 ml), at 0 ^{o}C with stirring under nitrogen over 10 min. The resulting black homogeneous mixture was stirred overnight at room temperature

and hydrolyzed with 10 % ammonium chloride solution under cooling with an ice bath. The organic layer and ether extracts from the aqueous layer were combined, washed successively with water, a saturated sodium hydrogen carbonate solution, and water, and then dried over magnesium sulfate. After evaporation of the solvent, distillation under reduced pressure gave 8.15 g (77% yield based on the 3-bromothiophene) of 3-benzylthiophene: b.p. 87-89 ^{o}C at 1 mmHg.

When dichlorobis(triphenylphosphine)nickel(II) [$Ni(PPh_3)Cl_2$] was used in the place of $Ni(dppp)Cl_2$, 3-benzylthiophene was obtained in a 44 % yield.

The distilled thiophenes were stored under dry nitrogen. The structures of these monomers were confirmed by nuclear magnetic resonance spectroscopy and infrared spectroscopy.

The solvents used were propylene carbonate (PC), benzonitrile (BN), acetonitrile (AN) and nitrobenzene (NB). PC was dried over 0.4 nm molecular sieves, distilled below 100 ^{o}C under reduced pressure and stored under dry nitrogen. The other solvents were dried and purified as usual[7]. The electrolytes were used without further purification.

3-3-2 Electrochemical polymerization

PBUT and PBZT films were prepared galvanostatically by oxidative polymerization of the corresponding monomers according to a similar procedure described for the preparation of PT,

PMT and PET. The reaction vessel was a one-compartment cell equipped with an indium tin oxide conducting glass (ITO) anode and a platinum cathode. The concentration of the monomers and the electrolytes was 0.2 mol/l and 0.03 mol/l, respectively. Prior to polymerization argon was bubbled through the solution to sweep the oxygen in it, and argon had been blowing it up to the end of the polymerization. The electrochemical polymerization was carried out at 5 ^{o}C in a propylene carbonate solution and continued until the charge density reached 2.4 C/cm^{2}. In a typical case the current density was 10 mA/cm^{2}. The films deposited on the surface of the anode were peeled off and washed with n-hexane. Since PBZT films were seem to be swollen with the solvent, the solvent was sufficiently sucked out from the film by a tissue paper.

A neutral film was obtained by reversing the direction of current after an oxidized film was formed. The current density was 1 mA/cm^{2} until the voltage between two electrodes increased to 30 V. The obtained free-standing film was soaked with methanol for 24 hours in order to get a highly neutral film.

3-3-3 Measurements

The direct current conductivity was measured using a four-point probe method. Infrared spectra were measured on a JEOL JIR-40 Fourier transform i.r. spectrophotometer.

Cyclic voltammograms were measured by a method similar to

that described in the previous paper[4]. A platinum plate was used as a working electrode and an ITO sputtered with platinum used as a counter electrode. The charge density for the preparation of films was 25 mC/cm^2. The thin films were left on the working electrode surface for cyclic voltammetry. In cyclic voltammograms, the potential swept with rates of 20, 60, and 100 mV/s.

Spectral change during hexafluorophosphate anion (PF_6^-) doping was measured by a method similar to that previously reported[8]. The films were prepared on ITO, a working electrode, by using a charge density of 100 mC/cm^2. Spectral change during perchlorate anion (ClO_4^-) doping of a neutral film was measured in situ in an acetonitrile solution containing 0.01 mol/l of silver perchlorate ($AgClO_4$) and 0.1 mol/l of tetraethylammonium perchlorate (Et_4NClO_4). The counter electrode was a silver wire which was employed as a reference electrode, as well. Visible-near i.r. spectra were recorded on a Hitachi U-3400 spectrophotometer.

3-4 Results and discussion

3-4-1 Electrochemical polymerization

The results of electrochemical polymerization of BUT and BZT are summarized in Table 3,1.

Table 3,1. Results of electrochemical polymerization[a)]

Run	Monomer	Solvent	Electrolyte	Current density (mA/cm^2)	Conductivity[b)] (S/cm)	Dopant[c)] content
1	BUT	PC	Et_4NPF_6	10	110	0.18
2	BUT	BN	Et_4NPF_6	10	58	--
3	BUT	NB	Et_4NPF_6	10	--[d)]	--
4	BUT	AN	Et_4NPF_6	10	--[d)]	--
5	BUT	PC	Et_4NBF_4	10	51	--
6	BZT	PC	Et_4NPF_6	10	--[e)]	--
7	BZT	PC	Et_4NPF_6	5	13	0.37

a) [Monomer]=0.2 mol/l, [Electrolyte]=0.03 mol/l, Charge=2.4 C/cm^2, at 5 ^oC.

b) At room temperature.

c) Dopant per monomer unit determined from elemental analysis of sulphur and phosphorus.

d) The film was heterogeneous.

e) The polymerization could not continue owing to raise of voltage.

The electrochemical polymerization of 3-butylthiophene was carried out in five kinds of solutions. PC and tetraethylammonium hexafluorophosphate (Et_4NPF_6) were a preferred solvent and electrolyte, respectively. Benzonitrile (BN) and tetraethylammonium tetrafluoroborate (Et_4NBF_4) were also effective as a solvent and an electrolyte, respectively. When nitrobenzene or acetonitrile were used, the films were heterogeneous and thereby could not be peeled from an anode. Using PC and Et_4NPF_6, tough films having high conductivity of 110 S/cm were obtained. This optimum combination of PC and Et_4NPF_6 was the same as that found for the electrochemical polymerization of 3-methylthiophene. In Run 6, the voltage between the anode and the cathode increased without deposition of a film as the electrolysis proceeded and it was impossible to continue the polymerization until the charge density of 2.4 C/cm^2. By lowering the current density to 5 mA/cm^2, PBZT films were obtained on the surface of ITO. The conductivity of the films was 13 S/cm.

Recently, Hirooka et al. compared the conductivity of the various conjugated polymers, such as polyacetylene[8),9)], poly(3-methylthiophene)[10)], poly(p-phenylene vinylene)[11),12)], polypyrrole[13)], and poly(p-phenylene sulfide)[14)], with wide range of dopants. They concluded that the conductivity of conjugated polymers only depends on the dopant concentration which is expressed as the concentration of dopant per π-electron of

the conjugated polymer chain, irrespective of the kinds of polymers and dopants[15].

The dopant content per monomer unit was calculated from the elemental analysis of sulfur and phosphorus. The dopant content of PBUT film was nearly equal to those of PT, PMT, and PET films which were 0.17, 0.18, and 0.17 per thiophenes unit, respectively[4]. As compared with poly(3-alkylthiophene) films, PBZT films contained a large amount of dopant but had low conductivity. These results are inconsistent with the conclusion drawn by Hirooka et al., indicating that these substituents, the alkyl and benzyl groups that are not conjugated with the main chains, do not directly participate in transmission of carriers. Further, the conductivities of PBZT are too low even if the bulkiness of the substituent is taking into account. The dopant content is related to the number of carriers which transport the charge on itself in an electric field as described in Chapter 1. Consequently, the lower conductivity of PBZT films, which contained a larger amount of dopant, results from the lower drift mobility of carriers. As mentioned in Chapter 1, the drift mobility of carriers is defined as the ratio of the drift velocity to the electric field and reflects the ease with which carriers are propagated in materials.

3-4-2 Infrared spectra

Figure 3,1 shows the Fourier transform i.r. spectra of $PBUT^0$ and $PBZT^0$.

The spectrum of $PBUT^0$ was similar to that of PMT^0 and PET^0. A weak band appeared at 3062 cm^{-1}, assignable to the aromatic C-H stretching vibrations in the β-position relative to the sulfur atom. The strong bands in the 2956-2858 cm^{-1} region were ascribable to the aliphatic C-H stretching vibrations. The medium bands at 1458 and 1377 cm^{-1} were assigned to the asymmetric and the symmetric bending vibrations of the butyl group, respectively. In the region of the out-of-plane C-H bending vibrations, there was a medium band at 829 cm^{-1} which was attributable to a 2,3,5-trisubstituted thiophene ring[16].

The spectrum of $PBZT^0$ showed medium bands in the 3103-3026 cm^{-1} and the 2914-2843 cm^{-1} regions, assignable to the aromatic and the methylene C-H stretching vibrations, respectively. The bands in the 1602-1433 cm^{-1} region were assigned to the skeletal vibrations, involving carbon to carbon and carbon to sulfur stretchings within the aromatic rings[17]. The weak bands in the 1178-1074 cm^{-1} region were ascribed to the in-plane C-H bending vibrations. In the region of the out-of-plane C-H bending vibrations, there were a weak band at 843 cm^{-1} attributable to a 2,3,5-trisubstituted thiophene ring[16] and a strong band at 698 cm^{-1} and a shoulder near 760 cm^{-1} attributable to a

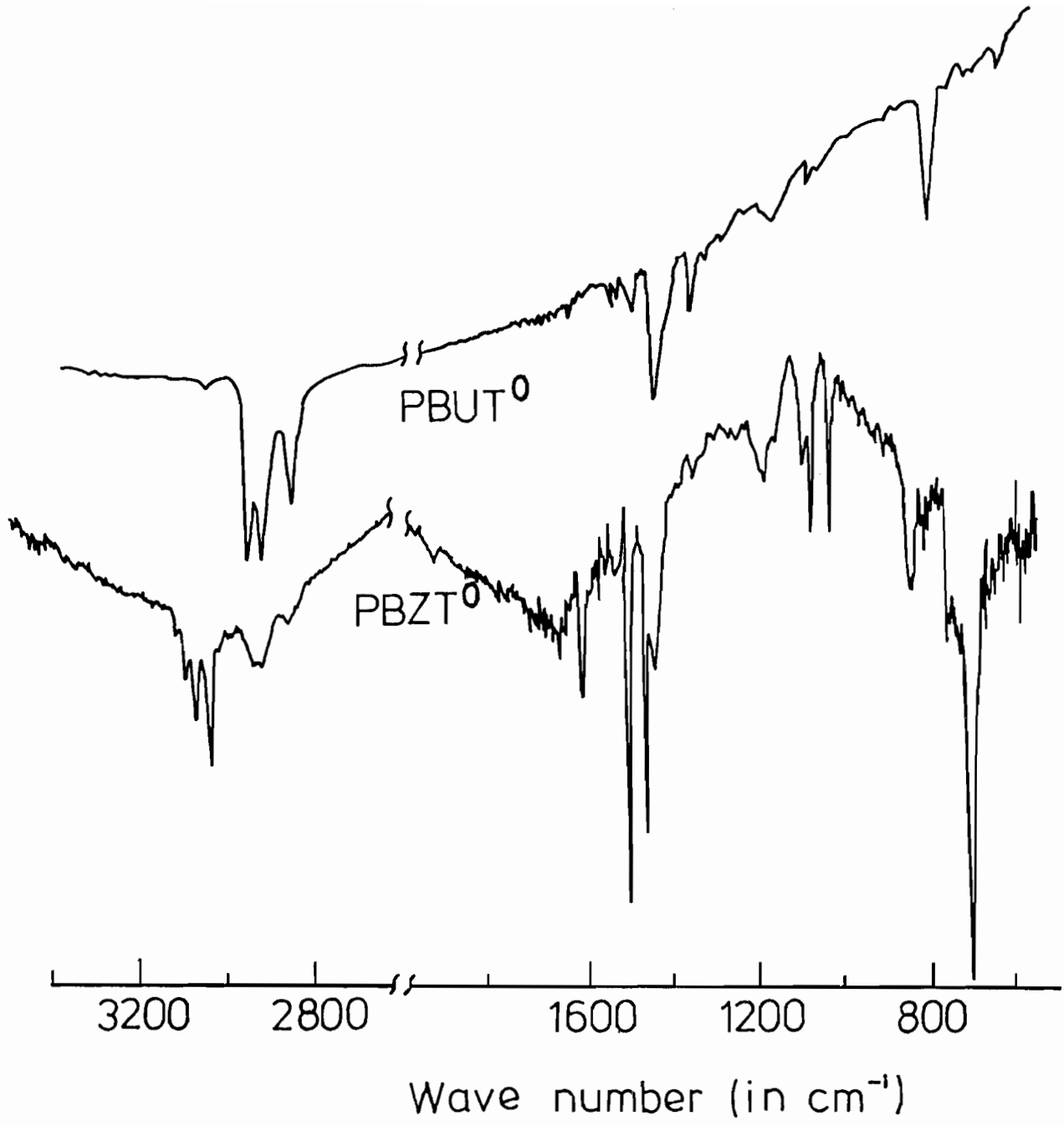
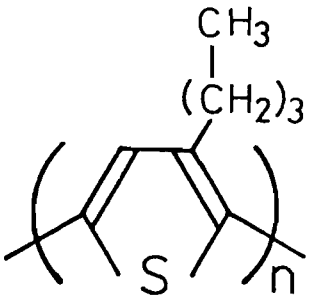
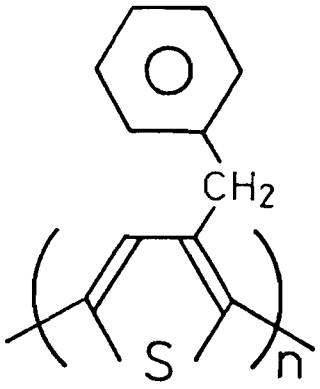


Figure 3,1. Infrared spectra of $PBUT^0$ and $PBZT^0$.

monosubstituted benzene ring[18]. These i.r. spectra show that $PBUT^0$ and $PBZT^0$ have the same regular structure, which can be denoted as poly(3-butyl and benzyl-2,5-thiophenediyl), respectively.



$PBUT^0$



$PBZT^0$

3-4-3 Cyclic voltammograms

The cyclic voltammograms of PBUT and PBZT films are presented in Figures 3,2 and 3,3, respectively. The films could changed repeatedly between oxidized and neutral states without loss of their electrochemical activity. The redox reaction was accompanied by reversible color change. The oxidized films were blue and the neutral ones red.

The cyclic voltammograms of PBUT (Figure 3,2) showed an anodic peak at 0.49-0.52 V, a shoulder about 0.65 V, and a

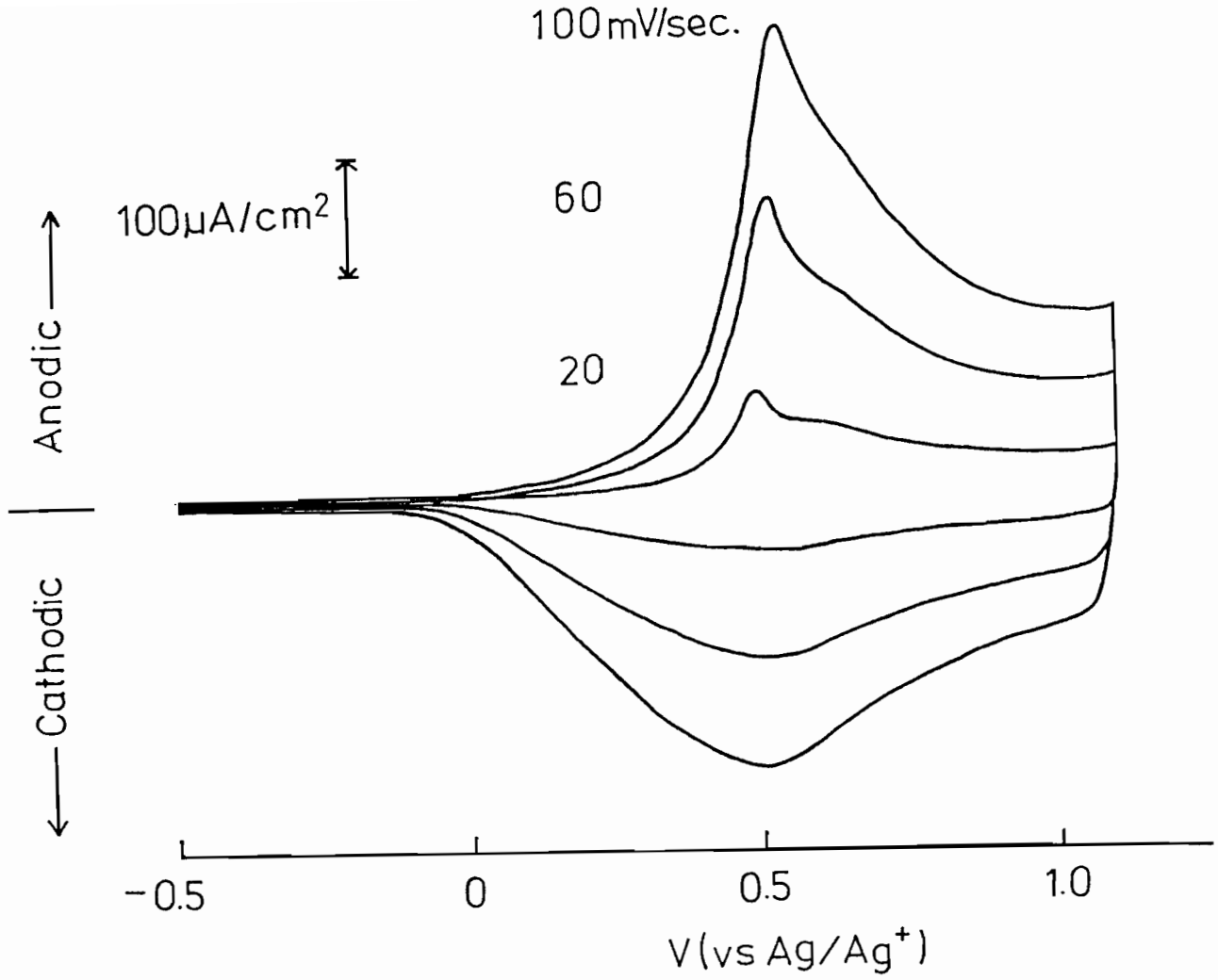


Figure 3,2. Cyclic voltammograms of a PBUT film.

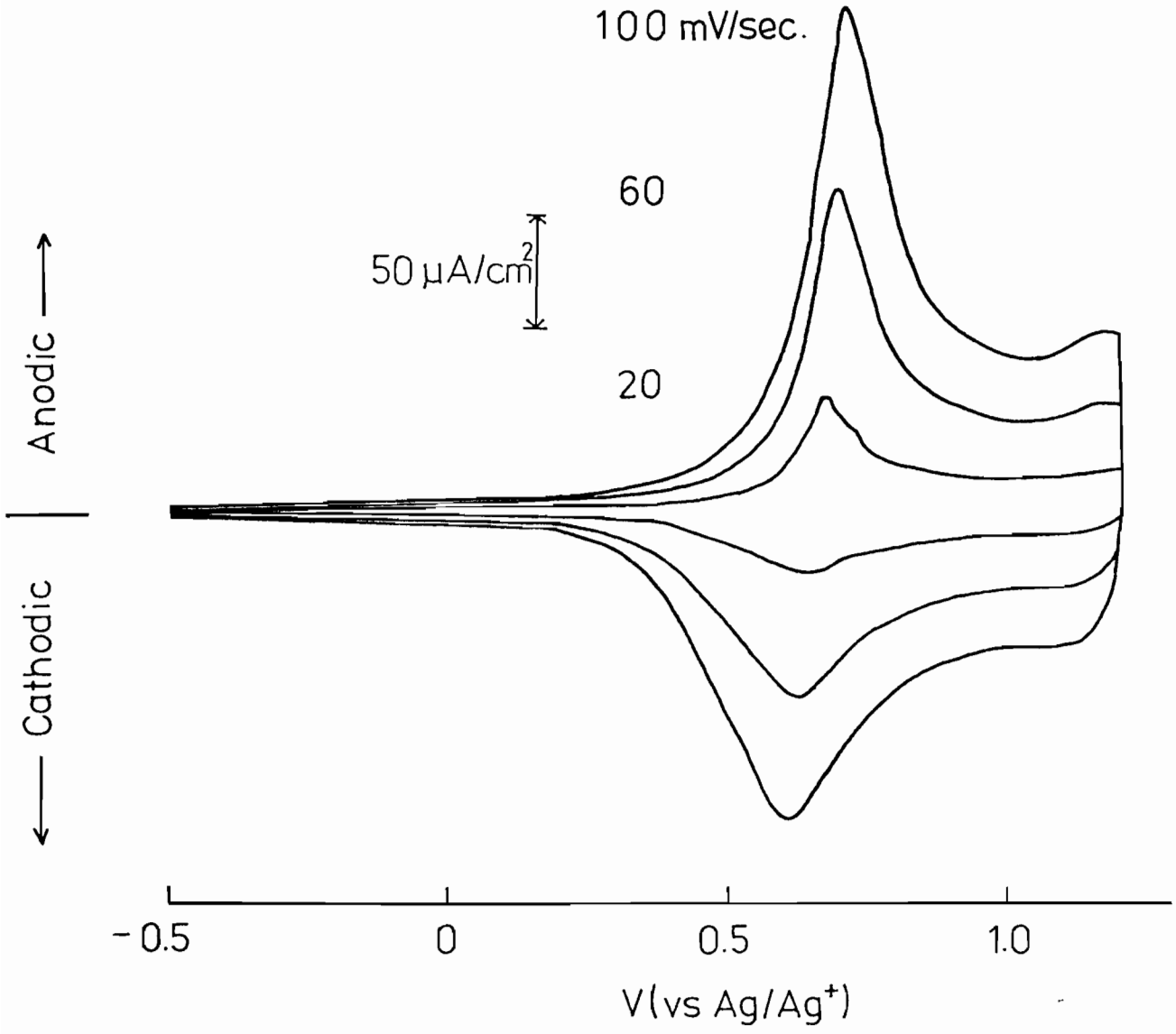


Figure 3,3. Cyclic voltammograms of a PBZT film.

cathodic peak at 0.52-0.50 V. The shapes of the voltammograms were similar to those of PET. The cyclic voltammograms of PBZT (Figure 3,3) had an anodic peak at 0.67-0.70 V, a small shoulder around 0.75 V and a cathodic peak at 0.63-0.61 V. The peak heights of the oxidation and the reduction peaks varied linearly with the sweep rate between 20 and 100 mV/s, as expected for a surface attached species. In the potential regions beyond the oxidation peaks, the voltammograms showed the presence of large residual currents arising from the capacitance charging similar to the case of PT, PMT and PET[4].

The shapes of the voltammograms of PBZT were considerably different from those of the poly(3-alkylthiophene)s. The oxidation and the reduction waves were sharp and well defined. These would be due to the smaller bandwidth of the highest occupied band, valence band, of $PBZT^0$.

The oxidation potential of $PBZT^0$ and neutral poly(3-alkylthiophene)s increased in the order of PMT^0 < PET^0 < $PBUT^0$ < $PBZT^0$. This shows the effect of the substituents on the ease of the doping with anion. Since the bulky benzyl group hinders successive thiophene rings from taking on a coplanar conformation, the conjugation along the polymer chains becomes less effective, causing an increase in the oxidation potential of $PBZT^0$.

3-4-4 Spectral change during doping

The visible-near i.r. spectra of PT during the electrochemical doping process, oxidizing process, were reported by several groups[4),19),20)].

Spectral change during electrochemical doping with PF_6^- was measured in situ in acetonitrile solutions[4)]. In neutral states, a peak corresponding to the transition between the valence and the conduction bands was observed. When the films were electrochemically doped, two additional peaks appeared in the gap region and these three peaks shifted to higher energy with increasing the level of doping. At higher levels of doping, two peaks disappeared and a broad one remained. These spectral changes are consistent with results of the theoretical study by Brédas et al.[21)]., which predicted that the two bipolaron bands were derived from the edge of the valence and the conduction bands, and the band gap increased.

The spectral change of PBUT during electrochemical doping is presented in Figure 3,4. The peak of the transition between the valence and the conduction bands shifted to higher energy and its height decreased as the doping level increased. Two additional peaks appeared in the gap region and their height increased as doping proceeded. The position of the middle peak related to an upper bipolaron level was independent of the doping level. The same trends were observed in PMT and PET[4)]. In these poly(3-alkylthiophene)s, the bipolaron level are

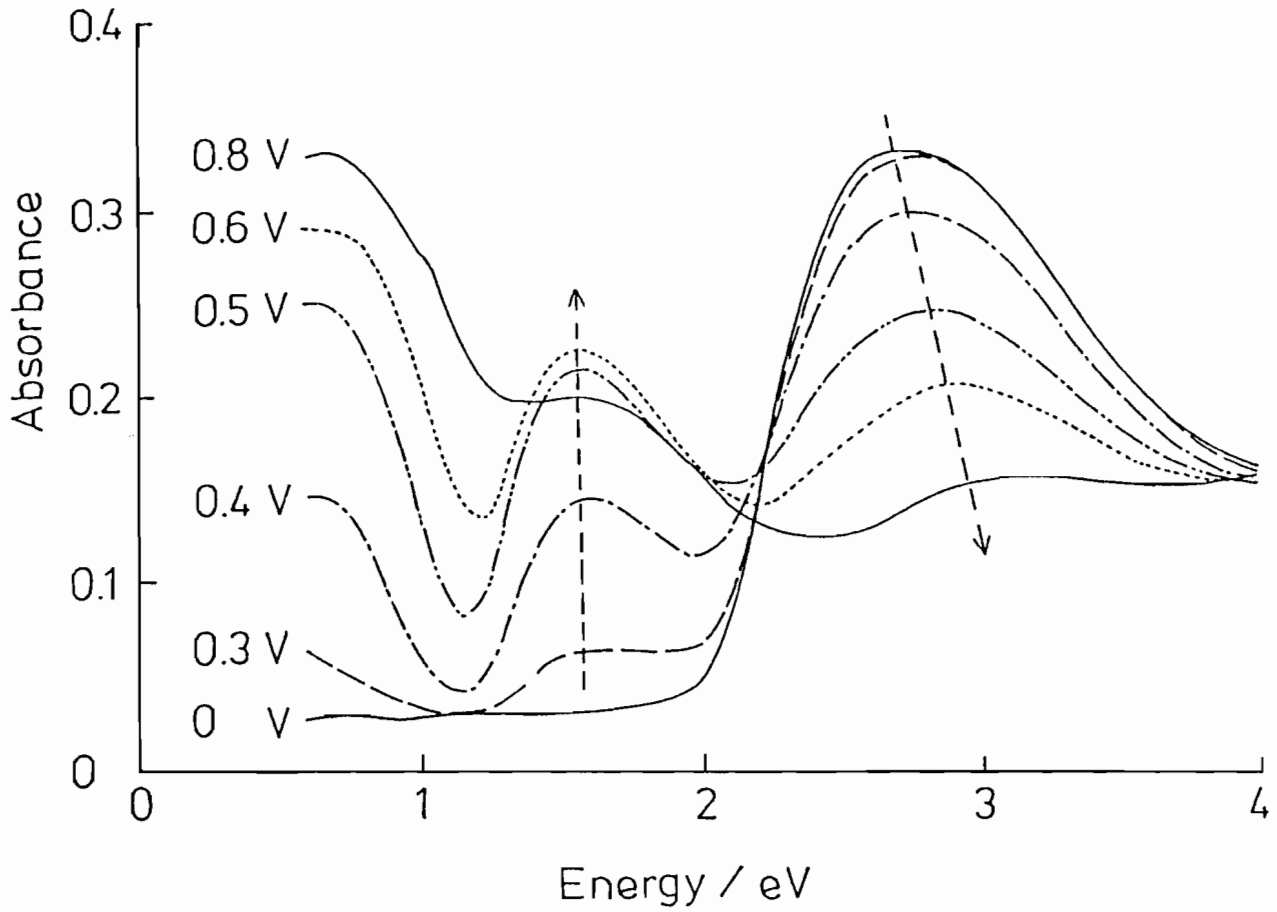


Figure 3,4. Spectral change of a PBUT film during electrochemical doping. Electrolyte: Et_4NPF_6.
(Applied voltage is shown on the left.)

derived from the edges of the valence and the conduction bands.

Visible-near i.r. spectra of PBZT are shown in Figure 3,5. The two additional absorption bands were clearly evolved, but the positions of the peaks related to π-π^* transition and an upper bipolaron level were independent of the applied voltage until the latter peak attributable to the bipolaron level began to decline at 0.7 V, then abruptly shifted to higher energy. Brédas et al. predicted from their theoretical study that two bipolaron bands would be derived from the edge of the valence and the conduction bands and the band gap would increase as a result[21]. The change in spectra of PBZT is inconsistent with this prediction. The explanation for this is to assume that the bipolaron levels are not derived from the band edges, but from the whole of the valence and the conduction bands evenly. Since the π-π^* transition peak of PBZT was sharper than that of PBUT, the bandwidths of the highest occupied (valence) band and the lowest occupied (conduction) band of PBZT would be smaller. This would corroborate the above explanation.

The spectral change of PBZT was measured using another electrolyte. The PBZT film was prepared and undoped in the same procedure as the film used in Figure 3,5. Then the electrolyte solution was thoroughly replaced with an acetonitrile solution of Et_4NClO_4. The results are shown in Figure 3,6. The spectra changed in a similar way as seen in Figure 3,5, indicating the evolution of the electronic structure during doping to be inde-

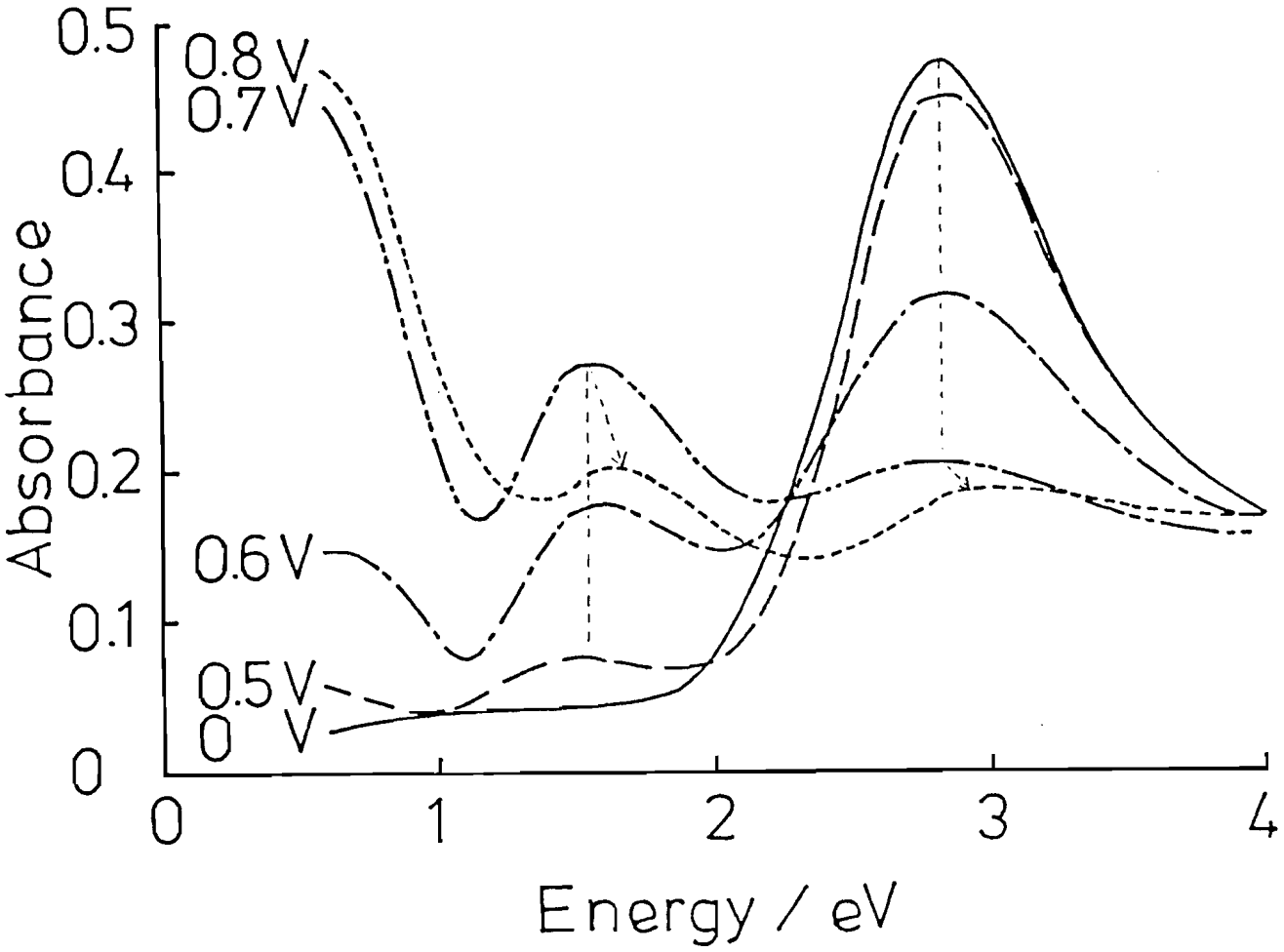


Figure 3,5. Spectral change of a PBZT film during electrochemical doping. Electrolyte: Et_4NPF_6.
(Applied voltage is shown on the left.)

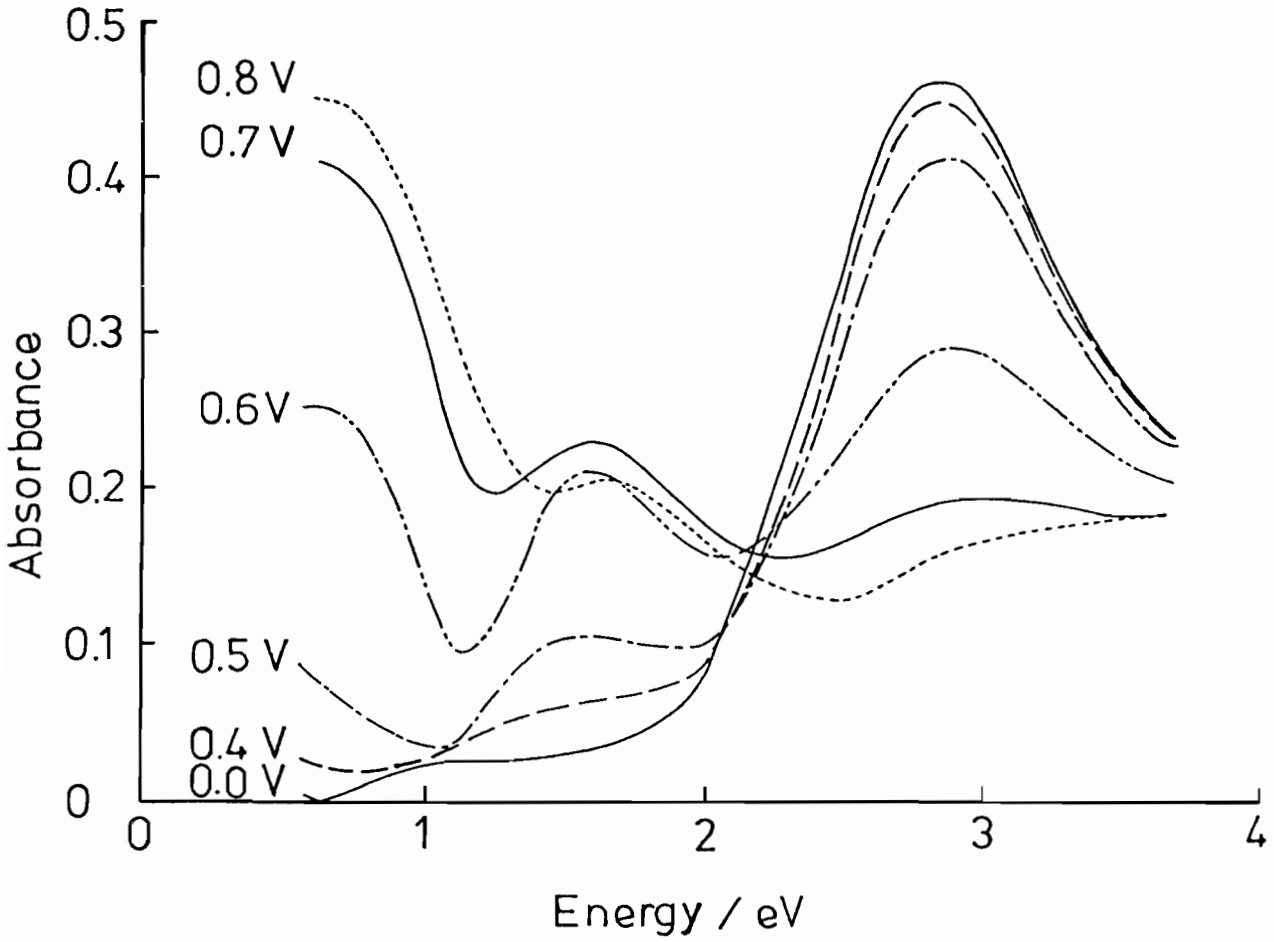


Figure 3,6. Spectral change of a PBZT film during electrochemical doping. Electrolyte: Et_4NClO_4.
(Applied voltage is shown on the left.)

pendent of the kind of the dopant, arising from electrolyte, but dependent on the kind of polymer.

3-4-5 Comparison with other thiophenes

The properties of poly(3-alkylthiophene)s[4] and PBZT prepared under the same polymerization conditions are summarized in Table 3,2. The bulkier the substituent of the polymer, the lower was the conductivity of the doped polymer and the higher was the oxidation potential of the neutral polymer.

In the results of visible-near i.r. spectra, the energy of π-π^* transition increases in the order of PMT^0 < PET^0 = $PBUT^0$ < $PBZT^0$. On the other hand, the peak positions, which are related to the bipolaron levels of the polymers doped at intermediate stages, are almost the same. It is concluded that the electronic structure of the bipolaron states in poly(3-alkylthiophene)s and PBZT doped at intermediate stages is scarcely influenced by their substituents as described in Chapter 2. Moreover, in the spectral changes of poly(3-alkylthiophene)s during PF_6^- doping, the peaks of the π-π^* transition showed apparent blue shifts but the peaks related to the bipolaron levels showed no shift with an increase in the doping levels[4]. These observations show that the peak positions ascribed to bipolaron levels are independent of the peak positions corresponding to the π-π^* transition. For PT, Brédas

Table 3,2. Properties of poly(3-alkylthiophene)s

Polymer	Conductivity (S/cm)	Electrochemical data Anodic peak[a] (V)	Optical data π-π^* Addit. peaks[b] (eV)
PMT	510	0.28	2.45
			0.7
			1.6
PET	240	0.47	2.7
			0.7
			1.6
PBUT	110	0.52	2.7
			0.6
			1.6
PBZT	13	0.70	2.8
			<0.6
			1.6

a) At scan rate of 100 mV/s.

b) The peaks were related to the bipolaron levels formed at intermediate stages of doping.

et al. predicted that the bipolaron state formed upon doping were delocalized along the polymer chain even at intermediate stages of doping, and interpreted the evolution of PT absorption spectra as a function of doping levels[21]. However, the results obtained for poly(3-alkylthiophene)s and PBZT are inconsistent with the bipolaron theory proposed by Brédas et al.. This rather suggests that bipolaron states at intermediate stages of doping are localized in the polymer chain.

3-5 Conclusions

PBUT and PBZT films were prepared by electrochemical polymerization and showed the conductivities of 110 and 13 S/cm, respectively. PBZT contained a high dopant per monomer unit ratio than poly(3-alkylthiophene)s, but had a lower conductivity. This was interpreted in terms of the lower drift mobility of carriers in PBZT films. The infrared spectra of these neutral polymers indicated that $PBUT^0$ and $PBZT^0$ have a highly defined structure, with dominance of poly(3-butyl and benzyl-2,5-thiophenediyl) structures. The cyclic voltammograms of PBZT were sharp and well defined. The spectral change of PBZT during electrochemical doping was different from those of poly(3-alkylthiophene)s. These results can be explained by assuming that the bandwidths of the valence and the conduction

bands in the electronic structure of $PBZT^0$ are smaller. Electrical and optical properties of PBUT and PBZT films were compared with those of poly(3-alkylthiophene) films. The poly(3-alkylthiophene) having a bulkier group showed a lower conductivity in doped states and higher oxidation potential, and the peak of the π-π^* transition at higher energy in neutral states. The spectra of poly(3-alkylthiophene)s and PBZT at different doping levels were inconsistent with the bipolaron theory. The inconsistency is attributed to localization of the bipolaron states in the polymer chain at intermediate stages of doping. Polythiophenes had a considerable conductivity at dilute doping levels[22)-24)]. The author concludes that the charge transfer is not due to the propagation of carriers in bands, which predicted by Brédas et al.[21)], but the hopping of carriers between bipolaron levels.

3-6 References

1) K. Akagi, S. Katayama, H. Shirakawa, K. Araya, A. Mukoh, and T. Narayama, Synth. Met., **17**, 241 (1987).

2) A. C. Chiang, P. F. Waters, and M. J. Aldridge, J. Polym. Sci., Polym. Chem. Ed., **20**, 1807 (1982).

3) M. Sato, S. Tanaka, and K. Kaeriyama, J. Chem. Soc., Chem. Commun., 713 (1985). (Chapter 2)

4) M. Sato, S. Tanaka, and K. Kaeriyama, Synth. Met., **14**, 279 (1986). (Chapter 2)

5) K. Tamao, S. Kodama, I. Nakajima, M. Kumada, A. Minato, and K. Suzuki, Tetrahedron., **38**, 3347 (1982).

6) G. R. V. Hecke and W. D. Horrocks Jr., Inorg. Chem., **5**, 1968 (1966).

7) J. A. Riddick and W. B. Bunger, "Organic Solvents", Willey, New York (1970).

8) H. Shirakawa and H. Nemoto, Polymer Preprints, **31**, 372 (1982).

9) H. Shirakawa and T. Kobayashi, Polymer Preprints, **31**, 373 (1982).

10) S. Hotta, W. Shimotsuma, M. Taketani, and S. Kohiki, Synth. Met., **11**, 139 (1985).

11) I. Murase, T. Ohnishi, T. Noguchi, and M. Hirooka, Polymer, Commun., **25**, 327 (1984).

12) I. Murase, T. Ohnishi, T. Noguchi, and M. Hirooka, Polymer, Commun., **26** , 362 (1985).

13) M. Ogasawara, K. Funahashi, and K. Iwata, Mol. Cryst. Liq. Cryst., **118**, 159 (1985).

14) J. E. Frommer, R. L. Elsenbaumer, and R. R. Chance, Org. Appl. Polym. Sci., **48**, 552 (1983).

15) M. Hirooka and T. Doi, Synth. Met., **17**, 209 (1987).

16) M. Akiyama, J. Mol. Spectrosc., **43**, 226 (1972).

17) T. Shimauchi, Y. Mashiko, and K. Nakanishi, "Sekigaisen-Kyusyu-Supekutoru", Nankohdoh, p123 (1964).

18) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", Champman and Hall, London, p86 (1975).

19) T. C. Chung, J. H. Kaufman, A. J. Heeger, and F. Wudl, Phys. Rev., **B30**, 702 (1984).

20) K. Yoshino, S. Hayashi, and R. Sugimoto, Jpn. J. Appl. Phys., **23**, L899 (1984).

21) J. L. Brédas, B. Thémans, J. G. Fripiat, J. M. André, and R. R. Chance, Phys. Rev., **B29**, 6761 (1984).

22) S. Hotta, T. Hosaka, M. Soga, and W. Shimotsuma, Synth. Met., **9**, 381 (1984).

23) K. Kaneto, S. Hayashi, S. Ura, and Y. Yoshino, J. Phys. Soc. Jpn., **54**, 1146 (1987).

24) S. Hotta, W. Shimotsuma, M. Taketani, and S. Kohiki, Synth. Met., **11**, 139 (1985).

Chapter 4

Poly(3-long alkyl-thiophene) Films: Soluble Conducting Polymers.

4-1 Abstract

Poly(3-hexylthiophene) (PHT), poly(3-octylthiophene) (POT), poly(3-dodecylthiophene) (PDDT), poly(3-octadecylthiophene), and poly(3-eicosylthiophene) were electrochemically prepared. Their conductivities were 95 to 11 S/cm. PHT^0, POT^0, and $PDDT^0$ (the superscript 0 denotes the neutral state) were soluble in chloroform, their degrees of polymerization being $2.3x10^2$, $1.4x10^2$, and 9x10, respectively. An as-grown PDDT film and films cast from an oxidized and a neutral PDDT solution in tetrahydronaphthalene were found to be electrochemically active. In cyclic voltammograms of the as-grown film, two anodic peaks and cathodic peaks were observed. The two peaks were attributed to the doping of two parts of the polymer having different conjugation lengths. Change in visible-near infrared spectra of the as-grown PDDT film during doping indicated that the bipolaron states are localized in the polymer chain at intermediate stages of doping. The oxidized PDDT in a chloroform solution showed ultraviolet-visible-near infrared spectra suggesting the presence of bipolaron. The absorption spectra of the oxidized and the neutral PDDT in chloroform solutions were compared with those of the as-grown PDDT films. The results indicated that oxidized PDDT is composed of a rigid charged part and a flexible neutral part in chloroform and does not aggregate in the solvent.

4-2 Introduction

Synthesis of π-conjugated polymers with high electrical conductivities and elucidation of the mechanism of the electric conduction are subjects of recent interest. Several polymers including polyacetylene[1)-3)], poly(p-phenylene)[4)], poly(2,6-naphthylene)[5),6)], and polypyrrole[7)] have been found to have high electrical conductivities when they are doped chemically or electrochemically.

In the preceding papers[8)-10)], the author reported the electrochemical preparation of polythiophene (PT), poly(3-alkylthiophene)s, and poly(3-benzylthiophene) and discussed the relation between the properties and the chemical structure of them. The polythiophenes films prepared were heavily doped from in situ doping with anions of a supporting electrolyte during electrochemical polymerization. The as-grown films have considerable electrical conductivities. The conductivity of poly(3-methylthiophene) (PMT) film, 510 S/cm, was the highest among those of the conducting polymer films prepared electrochemically. The poly(3-alkylthiophene) having a bulkier group showed a lower conductivity in doped states, higher oxidation potential, and the peak of the π-π^* transition at higher energy in a neutral state.

However, the characteristics of the conducting polymers have not completely been clarified. For example, such a fun-

damental quality as the degree of polymerization is still uncertain. Difficulties arise from the infusibility and the insolubility of the conducting polymers, because of the stiffness of the main chains consisting of conjugated bonds.

In this chapter, the author presents the results of study of the soluble conducting polymers, namely poly(3-hexylthiophene) (PHT), poly(3-octylthiophene) (POT), and poly(3-dodecylthiophene) (PDDT). It was possible to determine their degrees of polymerization and to cast films from their solutions. The polymers were investigated by infrared spectroscopy, cyclic voltammetry, and ultraviolet-visible-near infrared spectroscopy. Poly(3-octadecylthiophene) (PODT) and poly(3-eicosylthiophene) (PEIT) were also prepared by the electrochemical method and were compared with the soluble conducting polymers.

4-3 Experimental

4-3-1 Materials

Monomeric alkylthiophenes were prepared by coupling of alkylmagnesium bromides with 3-bromothiophene in the presence of a nickel catalyst[11]. 3-Dodecylthiophene, for example, was prepared as follows. To a mixture of 3-bromothiophene (20.38 g; 25 mmol), dichloro[1,3-bis(diphenylphosphino)propane]

nickel(II)[12], and fleshly distilled dry ether (95 ml) was added dropwise a solution of dodecylmagnesium bromide, which was prepared from magnesium (3.77 g; 155 mg-atom) and dodecyl bromide (25 g; 100 mmol) in freshly distilled dry ether (60 ml), at 0 ^{o}C with stirring under nitrogen over 20 minutes The resulting black homogeneous mixture was refluxed for 3 hours to complete the coupling. The mixture was hydrolyzed with diluted hydrochloric acid under cooling with an ice bath, and then extracted with benzene and ether. The organic layer was washed successively with water, a saturated sodium hydrogen carbonate solution, and water, and then dried over magnesium sulfate. After evaporation of the solvent, distillation under reduced pressure gave 19.0 g (60 % yield based on the 3-bromothiophene) of 3-dodecylthiophene: b.p. 128-130 ^{o}C at 2 mmHg.

NMR (360 MHz, $CDCl_3$): δ = 0.88 (t; J = 6.8 Hz, 3H), 1.26-1.30 (m; 18H), 1.57-1.63 (m; 2H), 2.61 (t; J = 7.7 Hz, 2H), 6.89-6.92 (m; 2H), 7.21 (dd; J = 3 and 5 Hz, 1H).

Calc. for $C_{16}H_{28}S$: C, 76.12; H, 11.18; S, 12.70 %.

Found : C, 76.03; H, 11.30; S, 12.87 %.

3-Hexylthiophene and 3-octylthiophene boiled at 105.0-105.5 ^{o}C/ 25 mmHg and 72-73 ^{o}C/ 2 mmHg, respectively. 3-Octadecylthiophene and 3-eicosylthiophene were recrystallized from ethanol and melted at 37.0-38.2 and 45.0-45.5 ^{o}C, respectively. The purified thiophenes were stored under dry

nitrogen.

Nitrobenzene was distilled over phosphorus pentoxide under reduced pressure and stored under dry nitrogen. The other solvents were dried and purified as usual[13]. The electrolytes were used without further purification.

4-3-2 Electrochemical polymerization

Poly(3-alkylthiophene) films were prepared by electrochemical polymerization of the corresponding monomers in nitrobenzene[14),15)]. The polymerization vessel was a one-compartment cell equipped with an indium tin oxide conducting glass (ITO) as an anode and a platinum plate as a cathode. The polymerization was carried out at 5 ^{o}C at a constant current density of 2 mA/cm^2 under an argon atmosphere and was continued until the charge density reached 0.96 C/cm^2. Tetraethylammonium hexafluorophosphate (Et_4NPF_6) was used as an electrolyte. The concentration of the monomer and the electrolyte were 0.2 and 0.025 mol/l, respectively. The films, deposited on the anode surface, were peeled off and washed with hexane.

Neutral films were obtained by reversing the polarity of the electrodes after the as-grown films were deposited on the anodes. The current density for the neutralization of the as-grown films was 1 mA/cm^2 and the electrolysis was continued until the voltage between both electrodes reached 4 V. The obtained free-standing films were soaked with methanol for 24

hours in order to get highly neutral films.

4-3-3 Measurements

Cyclic voltammograms were measured by the same method as described in Chapter 3. The charge density for the preparation of films was 12 mC/cm^2. The thin films were left on the working electrode surface for cyclic voltammetry. In cyclic voltammograms, the potential swept with rates of 20, 40, 60, 80 and 100 mV/s.

Visible-near i.r. spectra were recorded on a Hitachi U-3400 spectrophotometer. Spectral change during hexafluorophosphate anion (PF_6^-) doping was measured in the same way as previously reported[9]. The film was prepared on ITO, a working electrode, by using a charge density of 90 mC/cm^2.

The direct current conductivity was measured using a four-point probe method. Molecular weight was measured on a vapor pressure osmometer (Hitachi 117) in chloroform. N.m.r. spectra and i.r. spectra were recorded on a Nicolet NT-360 spectrometer and JEOL JIR-40 Fourier transform i.r. spectrometer, respectively.

4-4 Results and discussion

4-4-1 Electrical conductivity

In the electrochemical polymerization of alkylthiophenes, propylene carbonate was a preferred solvent and highly conducting films were obtained[8-10], but alkylthiophenes with more than 8 carbon atoms in the alkyl group is immiscible with propylene carbonate. Thus, the author used nitrobenzene as a solvent for alkylthiophenes with more than 6 carbon atoms in alkyl group. It must be noticed that the polymerization solvent has a large effect on the properties of polythiophenes films produced, when the properties of the polymers are compared.

The conductivities and the dopant content of PHT, POT, PDDT, PODT, and PEIT films are summarized in Table 4,1.

The films deposited on the anode were in an oxidized, doped, form and had good conductivity. The poly(3-alkylthiophene) having longer alkyl chains showed a lower conductivity in a doped state.

The dopant content per monomer unit was calculated from the elemental analysis of sulfur and phosphorus. For example, the elemental analysis of PDDT films was as follows:

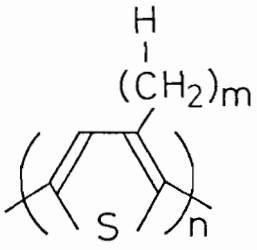
Calc.for $[(C_{16}H_{26}S)_4PF_6]$: C,67.03; H,9.14; S,11.19;
P,2.70; F,9.94 %.

Found : C,66.70; H,9.54; S,11.06;
P,2.67; F,7.24 %.

Table 4,1. Conductivity of poly(3-alkylthiophene) films

	PHT	POT	PDDT	PODT	PEIT
Conductivity (S/cm)	95	78	67	17	11
Dopant[a]	0.27	0.27	0.25	0.34	0.38

[a] Mole ratio of dopant per thiophene ring were calculated from the elemental analysis of sulfur and phosphorus.



m = 6	PHT
8	POT
12	PDDT
18	PODT
20	PEIT

The ratio of sulfur to phosphorus showed that the PDDT films contained 0.25 counterions per monomer unit. The content of fluorine was lower than calculated if $(PF_6)^{-1}$ was assumed to act as the counterion. The poly(3-alkylthiophene) films prepared in nitrobenzene contained a larger amount of dopant than PT, PMT, poly(3-ethylthiophene), and poly(3-butylthiophene) films prepared in propylene carbonate. The conductivities of PHT, POT, PDDT, and PEIT films seem to be independent of the dopant content in the films. These results are similar to that showed in Chapter 3 and inconsistent with the conclusion drown by Hirooka et al.[16].

4-4-2 Infrared spectra

Figure 4,1 presents the Fourier transform i.r. spectra of PHT^0, $PDDT^0$, and $PEIT^0$ films.

The spectra were simple and resemble each other. The spectrum of PHT^0 showed a weak band at 3057 cm^{-1}, assignable to the C-H stretching vibrations in the β-position on the thiophene rings. The spectra of all the polymers showed strong bands in the 2956-2852 cm^{-1} region, assignable to the aliphatic C-H stretching vibrations. The bands in the 1512-1377 cm^{-1} region were explained by overlap of bands which were ascribable to the skeletal vibrations[17] and the aliphatic C-H bending vibrations. The common primary bands near 830 cm^{-1} were clearly attributable to the C-H out-of-plane vibrations which are

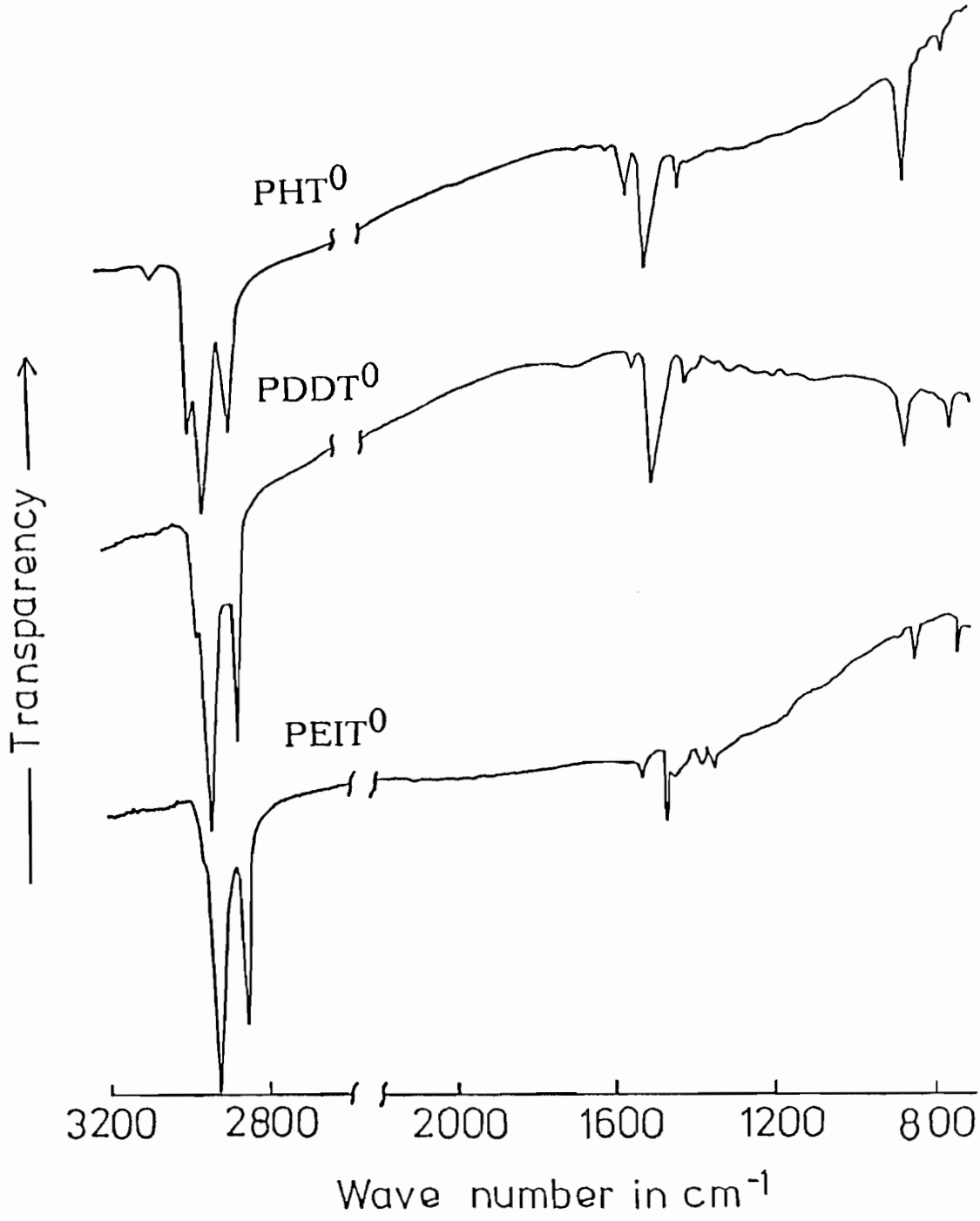
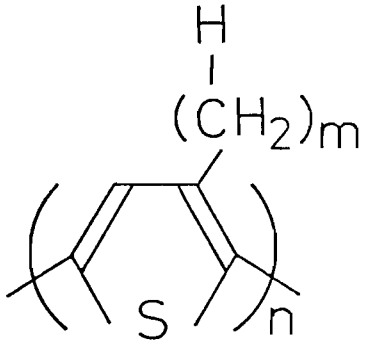


Figure 4,1. Infrared spectra of PHT^0, $PDDT^0$, and $PEIT^0$.

characteristic of 2,3,5-trisubstituted thiophene[18]. The bands near 720 cm^{-1} were assignable to the rocking vibrations of methylene groups. The i.r. spectra of POT^0 and $PODT^0$ were almost the same as shown in Figure 4,1. These spectra indicate that the poly(3-alkylthiophene)s would be denoted as poly(3-alkyl-2,5-thiophenediyl).



m =	6	PHT^0
	8	POT^0
	12	$PDDT^0$
	18	$PODT^0$
	20	$PEIT^0$

4-4-3 Solubility

The solubility of oxidized and neutral polymers is summarized in Table 4,2. The solubility was determined by weight loss of the oxidized and the neutral polymer films placed in hot solvents.

Tetrahydronaphthalene was the most preferable among the solvents examined. Chloroform, benzene, n-hexane, and toluene were also effective as solvents, but propylene carbonate, nitrobenzene, ethyl acetate, N-methyl-2-pyrrolidone, and sulfuric acid were not. PDDT was the most easily soluble, while PODT and PEIT, having longer alkyl chains, were less so.

Table 4,2. Solubility of poly(3-alkylthiophene)s[a]

Solvent	PHT		POT		PDDT		PODT		PEIT	
	Ox	Ne	Ox	Ne	Ox	Ne	Ox	Ne	Ox	Ne
Chloroform	△	○	X	○	△	○	△	△	△	△
Benzene	△	○	△	○	△	○	△	△	△	△
Tetrahydronaphthalene	△	○	△	○	○	○	△	△	△	△
Degrees[b]	--	230	--	140	--	90	--	--	--	--

[a] Ox:in oxidized states; Ne:in neutral states.
○ :soluble; △ :partly soluble; X :insoluble.

[b] Dgrees of polymerizations.

Since PHT^0, POT^0, and $PDDT^0$ were soluble in chloroform, the degrees of polymerization of the neutral polymers were determined by vapor-phase osmometry using chloroform and shown in Table 4,2. The degrees of polymerization of PHT^0, POT^0, and $PDDT^0$ prepared electrochemically were higher than 90. The shorter the alkyl chain of the polymer, the higher was its degree of polymerization. Lin et al. prepared PT^0 from 2,5-dibromothiophene with magnesium in the presence of bis(acetylacetonato)nickel(II)[19),20)] and presumed the degree of polymerization of the PT^0 to be about 14 on the basis of the elemental analysis of the polymer[20)]. The present results show that electrochemical polymerization is an advantageous method to prepare the conjugated polymer with a high degree of polymerization compared with the polycondensation of the thienyl Grignard reagent.

Films were cast from tetrahydronaphthalene solutions of oxidized and neutral PDDT and washed with acetonitrile in order to remove an electrolyte and products resulting from the dopant. They showed the same i.r. spectra as those of neutral films obtained by electrochemical reduction of an as-grown film, indicating no deterioration to take place during dissolution and casting.

4-4-4 Cyclic voltammograms

Figures 4,2-4,5 present cyclic voltammograms of PDDT films

under various conditions. Figure 4,2 shows the cyclic voltammograms of an as-grown film. There were two anodic peaks at 0.48 and 0.76 V as well as a cathodic peak at 0.65 V and a shoulder around 0.27 V at a scan rate of 100 mV/s. This film was dissolved in tetrahydronaphthalene, cast on a working electrode, and dried under vacuum. Figure 4,3 shows the cyclic voltammograms of a film thus obtained. There were only one anodic peak at 0.72 V and one cathodic peak at 0.64 V. Two peaks observed at lower voltages for the as-grown film disappeared. After an as-grown film was electrochemically reduced, a film was cast on a working electrode according to the above described procedure. Figure 4,4 shows the cyclic voltammograms of the film. There were two anodic peaks at 0.42 and 0.79 V, a cathodic peak at 0.57 V and a slight shoulder around 0.18 V. These features are clearly different from Figure 4,3. It is an interesting problem that the cyclic voltammograms of the film prepared from an oxidized PDDT solution is different from those of the as-grown film and the film from a neutral PDDT solution.

The i.r. spectra of the films that were cast from an oxidized and a neutral PDDT solution and washed with acetonitrile was accurately identical to that of an electrochemical reduced film as mentioned in Chapter 4-4-3. This indicates that the difference in the cyclic voltammograms were not attributable to chemical deterioration. In addition,

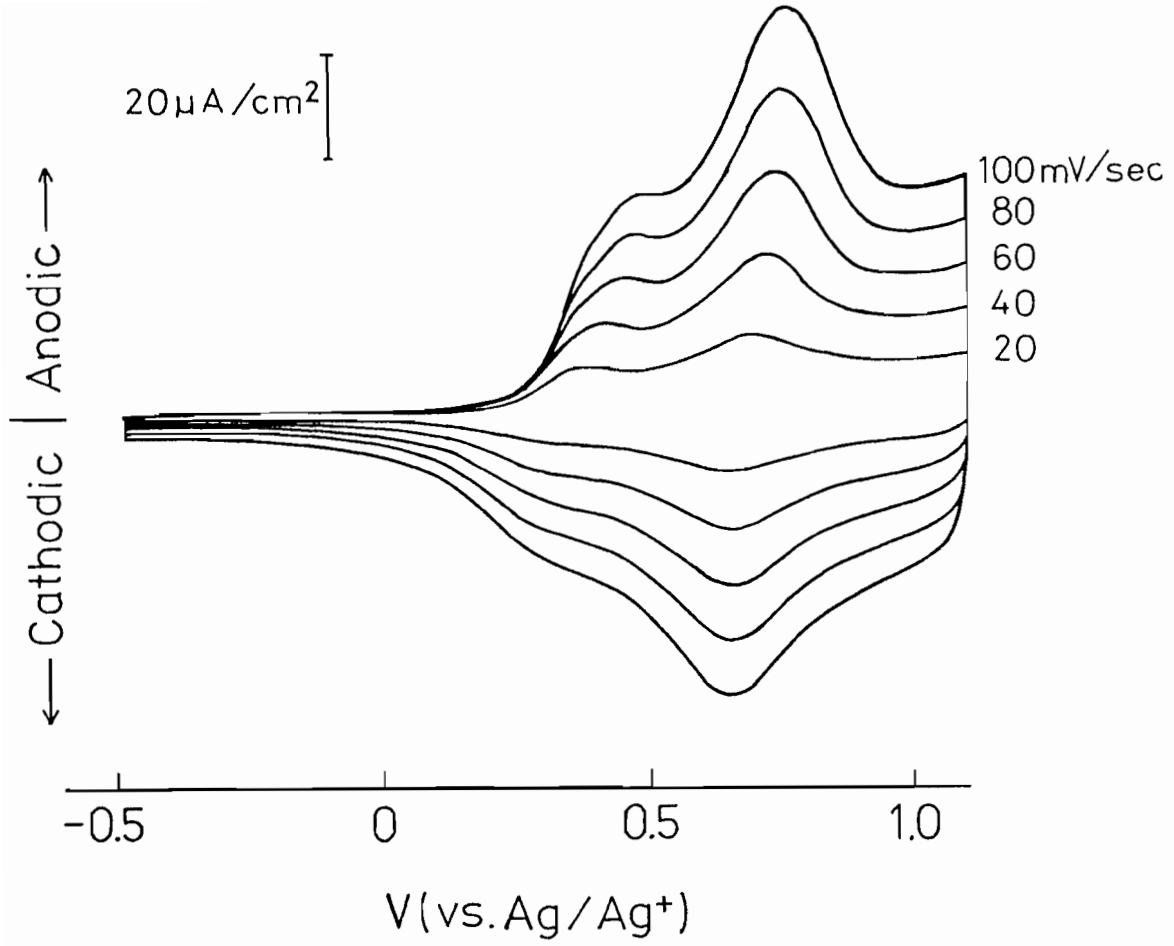


Figure 4,2. Cyclic voltammograms of an as-grown PDDT film.

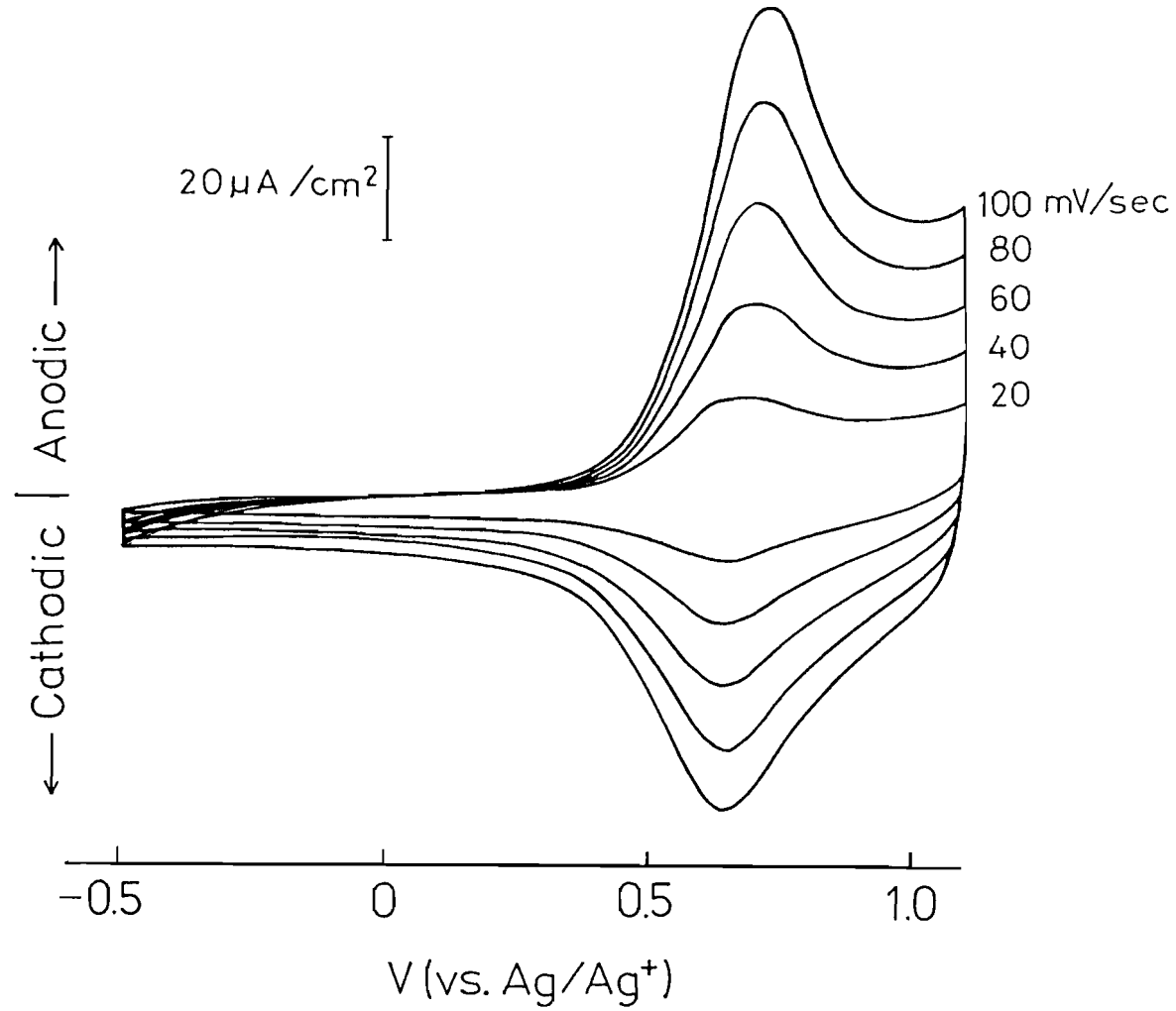


Figure 4,3. Cyclic voltammograms of a film prepared from a tetrahydronaphthalene solution of oxidized PDDT.

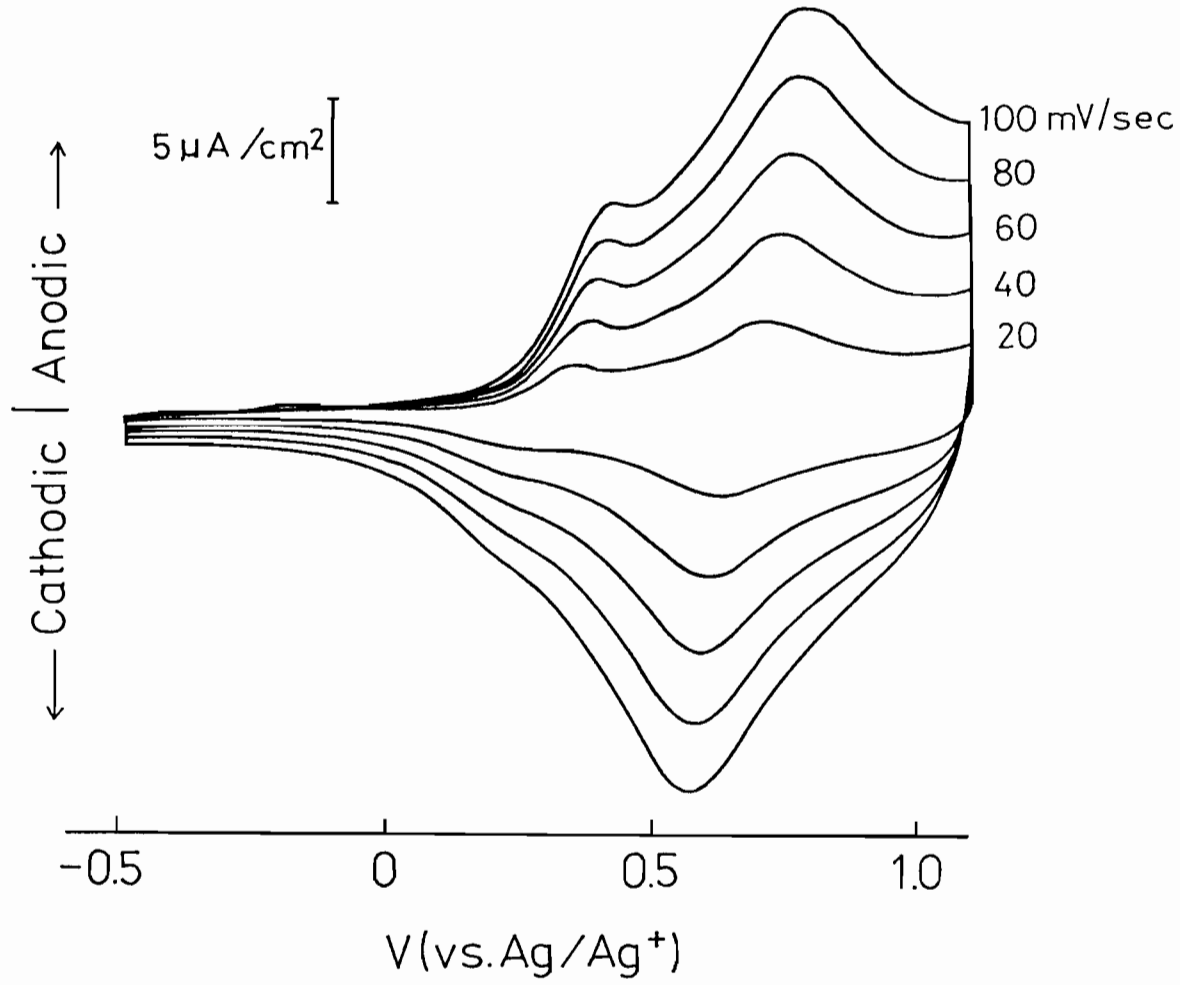


Figure 4,4. Cyclic voltammograms of a film prepared from a tetrahydronaphthalene solution of neutral PDDT.

since these two polymers gave two different types of cyclic voltammograms, the difference is not due to a difference in such chemical structures, as linking mode of adjacent thiophene rings.

Although the absorption spectra of an oxidized PDDT solution in tetrahydronaphthalene and a neutral PDDT solution were equal, there was still a possibility that PF_6^- was included in the most labile parts of the film employed in Figure 4,3, and that the peaks at lower voltages in Figure 4,2 were due to these parts. The author applied -0.5 V for 30 minutes to the film employed in Figure 4,3, then measured cyclic voltammograms. No new peaks appeared.

Therefore, a reasonable answer to this is to assume that the two peaks correspond to two different conjugation lengths. Longer conjugation is assigned to the peak at a lower voltage and shorter conjugation to that at a higher voltage. Tetrahydronaphthalene is a poor solvent for oxidized PDDT. In this solvent, the polymer chain takes a shrinked conformation. Since this conformation is retained in a cast film, the conjugated π-electron system along the polymer chain is short. Since tetrahydronaphthalene is a better solvent for neutral PDDT than for oxidized PDDT, a part of the neutral polymer chains would take a more stretched conformation. The peak at a lower voltage is ascribed to this part.

The cyclic voltammograms of an as-grown film were measured

using another electrolyte. The as-grown film was previously reduced in an acetonitrile solution of Et_4NPF_6 and the electrolyte solution was replaced with an acetonitrile solution of tetraethylammonium perchlorate. As shown in Figure 4,5, there were two anodic peaks at 0.28 V and 0.76 V as well as a cathodic peak at 0.62 V and a shoulder around 0.19 V. These features are similar to those of the as-grown film in a Et_4NPF_6 solution. Therefore, the appearance of the two anodic peaks can not be ascribed to the behavior of the dopant arising from an electrolyte. This corroborates the above mentioned.

4-4-5 Optical properties

The redox reaction was accompanied by reversible color change. Oxidized PDDT films were blue and neutral ones red. A neutral PDDT film on an ITO conducting glass was electrochemically oxidized at different applied voltages. Figure 4,6 shows a series of absorption spectra measured during the oxidation process.

At 0.0 V, only a π-π^* transition was observed. At intermediate stages of oxidation, additional absorption bands appeared below 1.0 eV and about 1.5 eV. This observation of two additional absorption bands suggests the presence of bipolarons. As oxidation level increased, the peak of the π-π^* transition showed an apparent blue shift but the absorption peak about 1.5 eV related to the upper bipolaron level showed a

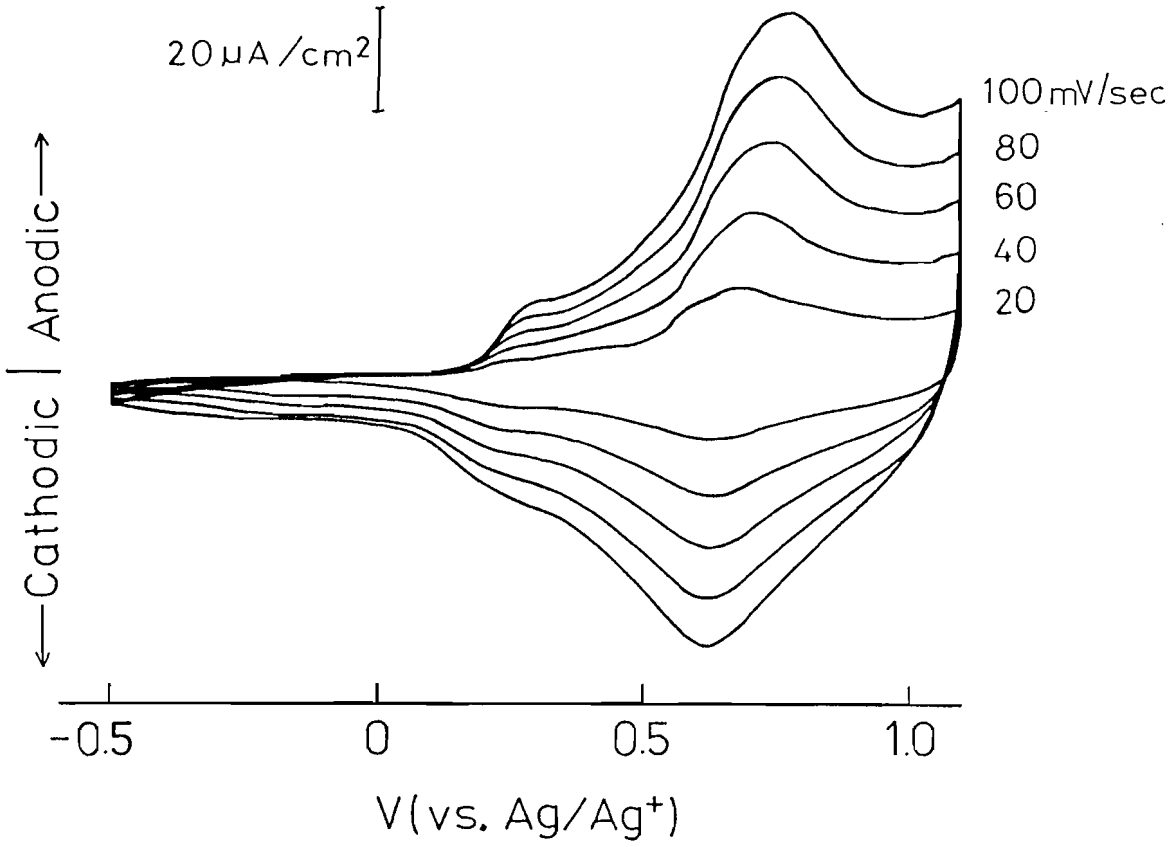


Figure 4,5. Cyclic voltammograms of an as-grown PDDT film with use of tetraethylammonium perchlorate as electrolyte.

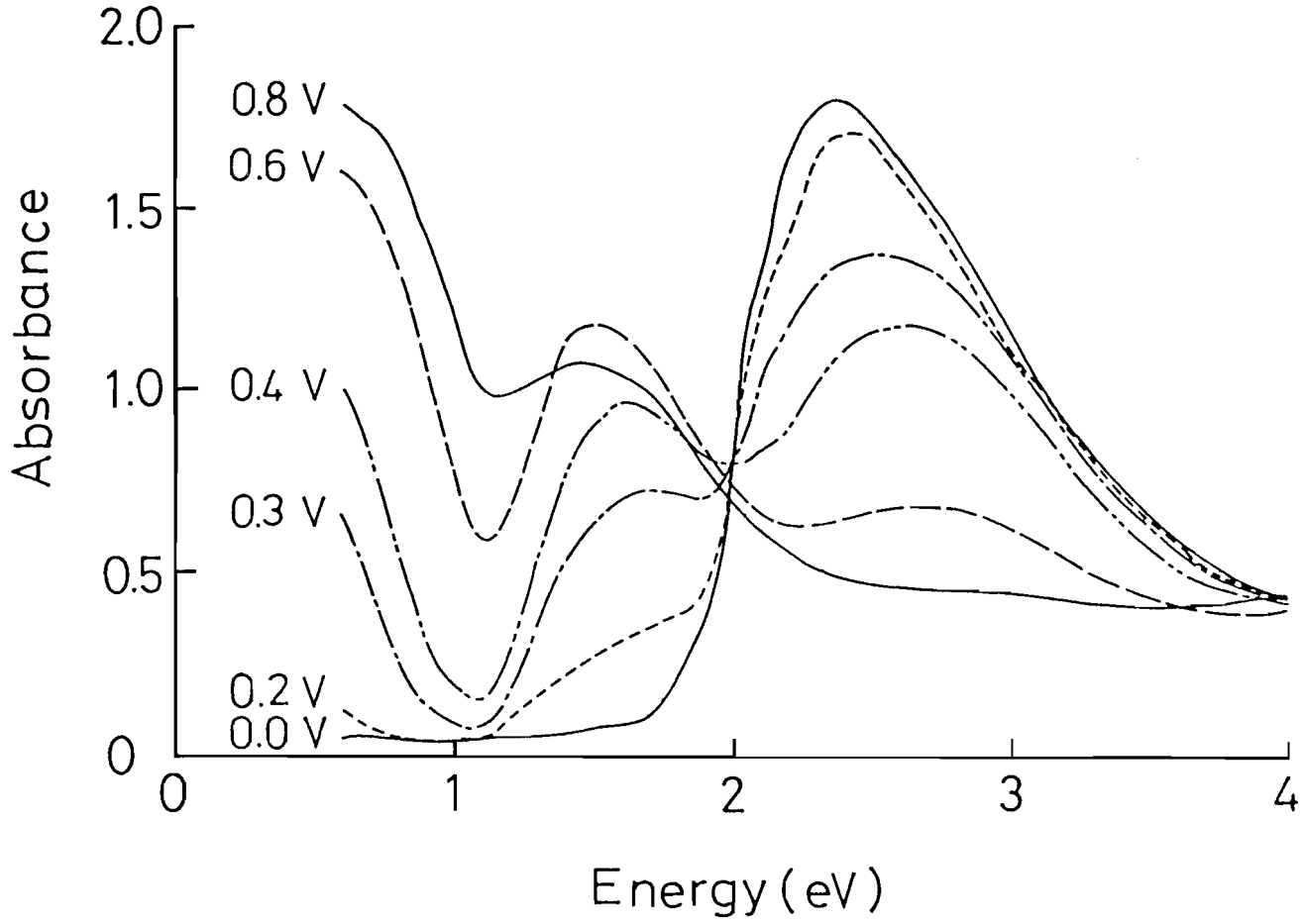


Figure 4,6. Spectral change of a PDDT film during electrochemical doping.
(Applied voltage is shown on the left.)

red shift. The present finding is inconsistent with the results of a theoretical study by Brédas et al[21]. and optical data of polythiophene[9),22),23)]. As mentioned in Chapter 3, these results suggest that bipolaron states at intermediate stages of doping are localized in the polymer chain.

Figure 4,7 shows the absorption spectra of PDDT films and an oxidized and a neutral PDDT solution. The spectrum of the neutral PDDT solution in chloroform had a peak at 2.83 eV, corresponding to the interband transition between the valence and the conduction bands. The spectrum of the oxidized PDDT solution showed peaks at 2.93 and 1.49 eV and an absorption band below 1.0 eV, indicating PDDT to be in oxidized states in solution. These spectra were compared with those of the films. The spectrum of the neutral film obtained by electrochemical reduction of an as-grown film had one peak at 2.38 eV. When the film was electrochemically oxidized at 0.3 V, there were two peaks at 2.55 and 1.68 eV and an absorption band below 1.0 eV. The interband transition in the solution shifted extraordinarily to higher energy compared with that in the film. Difference in the positions of the middle peaks was small. These results would show that there is a rigid charged part causing the middle peak and a flexible neutral part causing the interband peak in one polymer chain. While the charged part retains a coplanar conformation, the neutral part takes a more winding conformation such as a random coil or a helix. Thus, only the

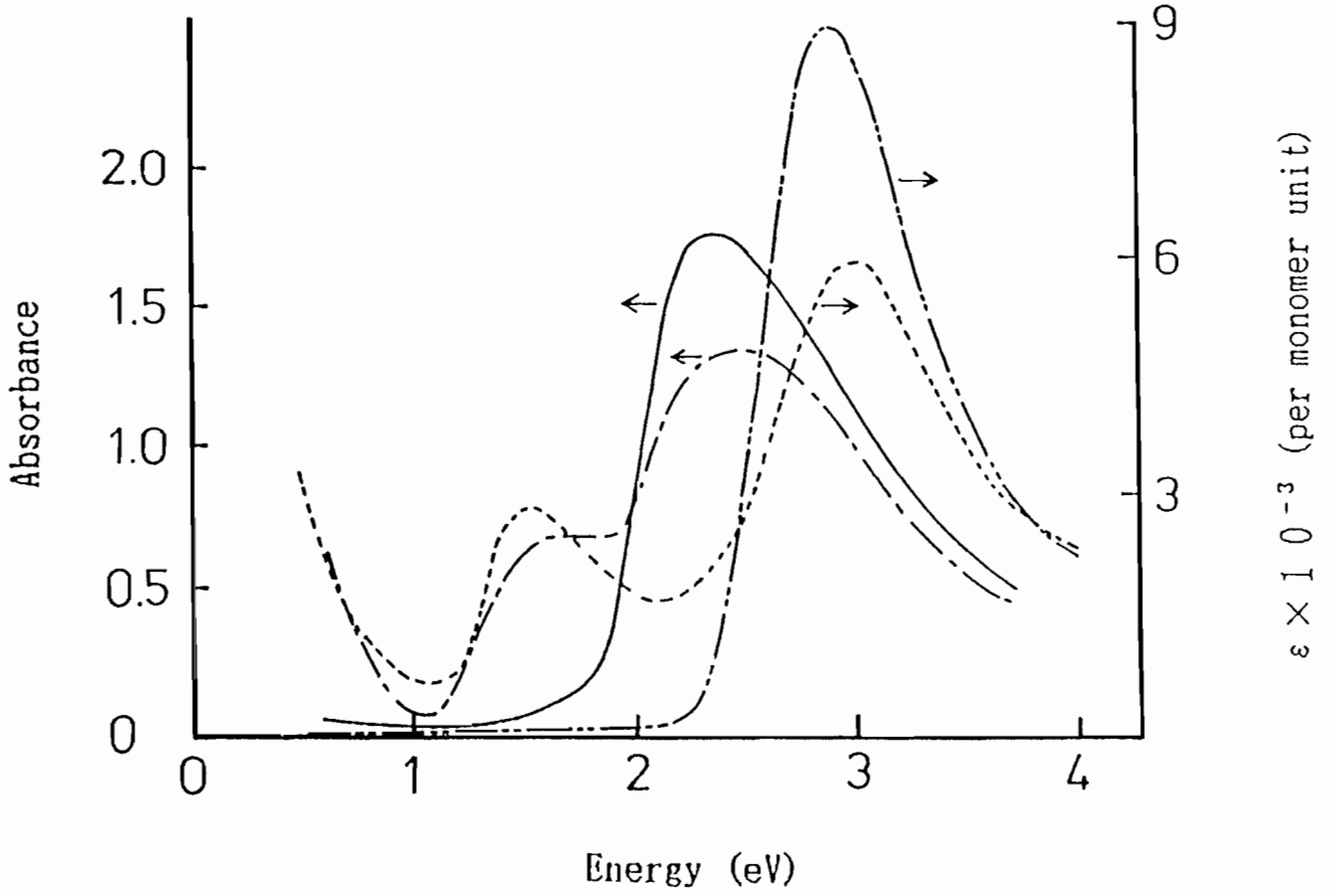


Figure 4,7. Absorption spectra of PDDT. ——— : neutral film, — — — : film oxidized at 0.3 V, — · — · — : neutral PDDT solution in chloroform, - - - - - : oxidized PDDT solution in chloroform.

interband transition largely shifts to higher energy.

Figure 4,8 shows the concentration dependence of the peak positions of the interband transition peak and the middle peak of the spectra in the chloroform solution. The positions were almost independent of the PDDT concentration in the range examined but nevertheless shifted from those of the film oxidized at 0.3 V.

Figure 4,9 shows dependence of absorbance on the polymer concentration. The absorbance was approximately proportional to the concentration. These results indicate that the molecules of the oxidized polymer were dispersed in solution without interaction with other polymer molecules. The oxidation of conjugated polymers is not a collective phenomenon, but a reaction between a molecule of the conjugated polymer and a molecule of the oxidizing agent. In Figure 4,9, small deviation from the origin would be due to gradual decay of oxidized states into neutral states during dilution and spectral measurement. This is compatible with the direction of the deviation.

4-5 Conclusions

The first example of a soluble conducting polymer has been demonstrated by the introduction of a long alkyl chain at 3 position of the thiophene ring.

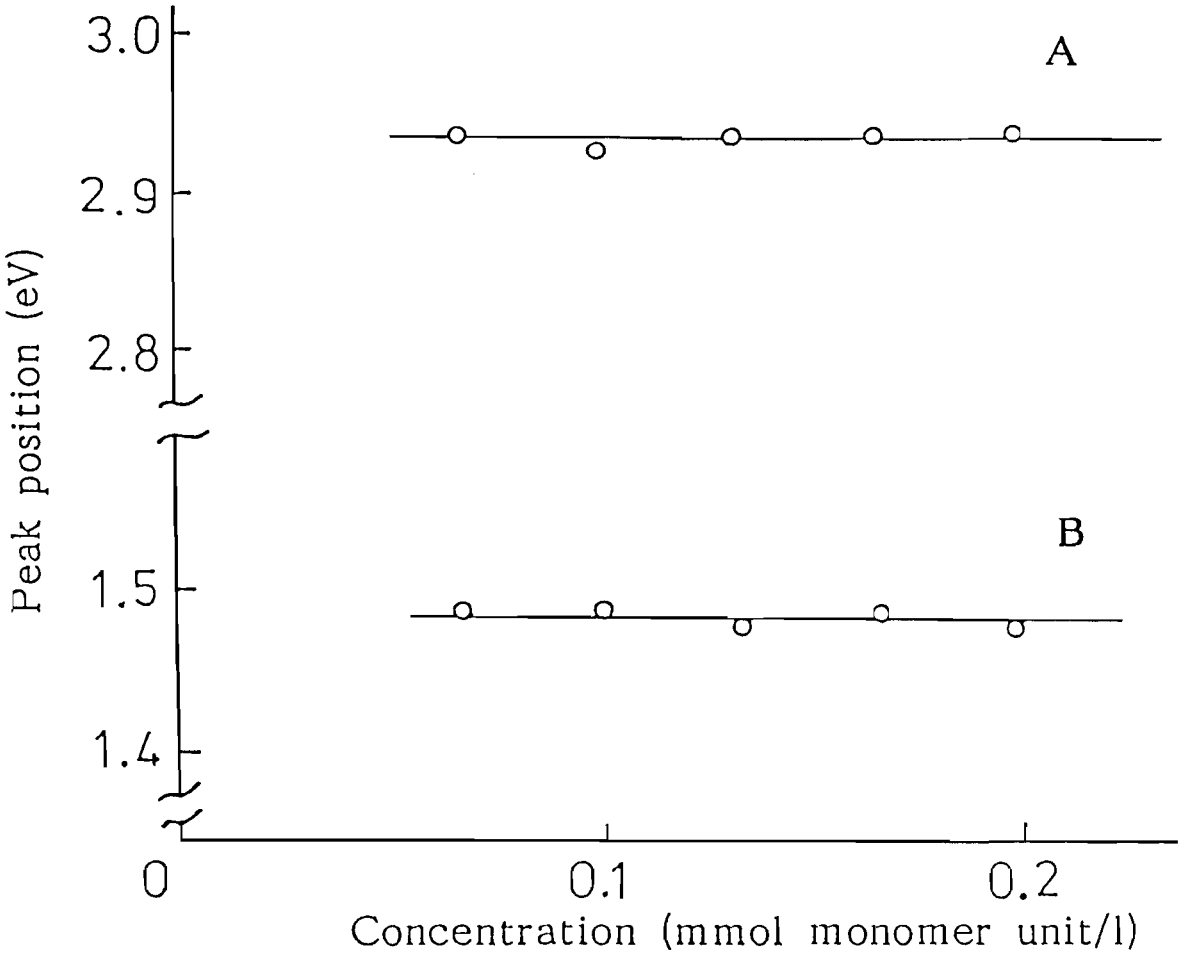


Figure 4,8. Dependence of the peak position on the concentration for the PDDT spectra in chloroform solutions.
A: interband transition. B: middle peak.

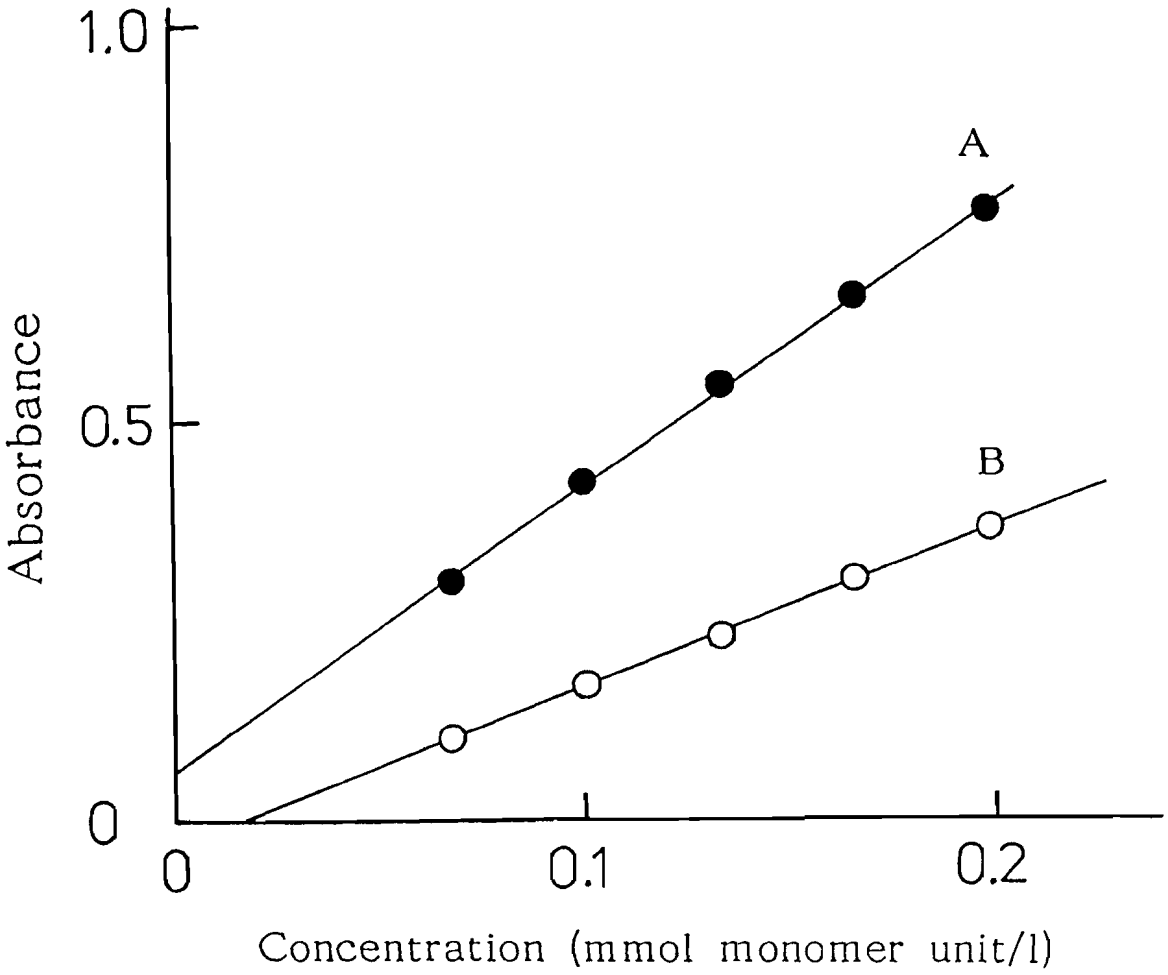


Figure 4,9. Dependence of the absorbance on the concentration. A: interband transition. B: middle peak.

PHT, POT, PDDT, PODT, and PEIT were prepared by electrochemical polymerization and showed the conductivity of 95 to 11 S/cm. Analysis of the infrared spectra demonstrated that these polymers have a well-defined molecular structure, the available data are completely consistent with liner chain of poly(3-alkyl-2,5-thiophenediyl). The solubility of the polymers was examined with various solvents. Tetrahydronaphthalene was the most preferable among the solvents examined. Chloroform, benzene, n-hexane, and toluene were also effective. PDDT was the most easily soluble. PHT^0, POT^0, and $PDDT^0$ were soluble in chloroform, their degrees of polymerization being $2.3x10^2$, $1.4x10^2$ and 9x10, respectively. These degrees were higher than the degree of polymerization of PT^0 prepared chemically.

While the cyclic voltammograms of an as-grown PDDT film had two anodic peaks and two cathodic peaks, those of a film cast from an oxidized PDDT solution had one anodic peak and one cathodic peak. The two peaks would correspond to two conjugation lengths. Visible-near i.r. spectra of the PDDT film as a function of oxidation potential were inconsistent with the bipolaron theory. The inconsistency is attributed to localization of bipolaron states in the polymer chain at intermediate stages of doping. U.v-visible-near i.r. spectra of the PDDT solutions in chloroform were compared with the spectra of the PDDT films. The energy of the interband transition was found to

be much higher in the solutions than in the films. Difference in the positions of the middle peaks, attributable to the bipolaron levels, was small. The results indicate the presence of a rigid oxidized part and a flexible neutral part in the polymer chain. The concentration dependence of the spectra indicates that oxidized PDDT does not aggregate in solution.

The present results also suggest that any conducting polymers can be transformed into soluble type by reducing the inter-chain interaction and cross-linking through introduction of an appropriate spacer group in the molecular structure.

4-6 References

1) H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, and A. J. Heeger, J. Chem. Soc., Chem. Commun., **1977**, 578.

2) C. K. Chiang, M. A. Druy, S. C. Gau, A. J. Heeger, E. J. Louis, A. G. MacDiarmid, Y. W. Park, and H. Shirakawa, J. Am. Chem. Soc., **100**, 1013 (1978).

3) K. Akagi, S. Katayama, H. Shirakawa, K. Araya, A. Mukoh, and T. Narayama, Synth. Met., **17**, 241 (1987).

4) L. W. Schacklette, R. R. Chance, D. M. Ivory, G. G. Miller, and R. H. Baughman, Synth. Met., **1**, 307 (1979).

5) M. Sato, K. Kaeriyama, and K. Someno, Makromol. Chem., **184**, 2241 (1983).

6) M. Satoh, F. Uesugi, M. Tabata, K. Kaneto, and K. Yoshino, J. Chem. Soc., Chem. Commun., **1986**, 550.

7) K. K. Kanazawa, A. F. Diaz, R. H. Geiss, W. D. Gill, J. F. Kwak, J. A. Logan, J. F. Rabolt, and G. B. Street, J. Chem. Soc., Chem. Commun.,**1979**, 854.

8) M. Sato, S. Tanaka, and K. Kaeriyama, J. Chem. Soc., Chem. Commun., **1985**, 713. (Chapter 2)

9) M. Sato, S. Tanaka, and K. Kaeriyama, Synth. Met., **14**, 279 (1986). (Chapter 2)

10) M. Sato, S. Tanaka, K. Kaeriyama, and F. Tomonaga, Polymer, **28**,1071 (1987). (Chapter 3)

11) K. Tamao, S. Kodama, I. Nakajima, M Kumada, A. Minato, and K. Suzuki, K. Tetrahedron., **38**, 3347 (1982).

12) G. R. V. Hecke and W. D. Horrocks Jr., Inorg. Chem., 5, 1968 (1966).

13) J. A. Riddick and W. B. Bunger, "Organic Solvents", Willey, New York (1970).

14) S. Hotta, T. Hosaka, and W. Shimotsuma, Synth. Met., **6**, 317 (1983).

15) S. Tanaka, M. Sato, and K. Kaeriyama, Makromol. Chem., **185**, 1295 (1984).

16) M. Hirooka and T. Doi, Synth. Met., **17**, 209 (1987).

17) T. Shimauchi, Y. Mashiko, and K. Nakanishi, "Sekigaisen-Kyusyu-Supekutoru", Nankohdoh, Tokyo, p123 (1964).

18) M. Akiyama, J. Mol Spectrosc., **43**, 226 (1972).

19) T. Yamamoto, K. Sanechika, and A. Yamamoto, J. Polym. Sci., Polym. Lett. Ed., **18**, 9 (1980).

20) J. W. P. Lin and L. P. Dadek, J. Polym. Sci., Polym. Lett. Ed., **18**, 2869 (1980).

21) J. L. Brédas, B. Thémans, J. G. Fripiat, J. M. André, and R. R. Chance, Phys. Rev.,**B29**, 6761 (1984).

22) T. C. Chung, J. H. Kaufman, A. J. Heeger, and F. Wudl, Phys. Rev., **B30**, 702 (1984).

23) K. Yoshino, S. Hayashi, and R. Sugimoto, Jpn. J. Appl. Phys., **23**, L899 (1984).

Chapter 5

A Poly(3-phenylthiophene) Film: Highly Anode-Active Polymer.

5-1 Abstract

Poly(3-phenylthiophene) (PPT), poly[3-(4'-methoxyphenyl)-thiophene] (PMPT), and poly[3-(4'-trifluoromethylphenyl)-thiophene] (PFPT) films were electrochemically prepared. The conductivities of PPT, PMPT, and PFPT were 140, 40, and 1.8 X 10^{-3} S/cm, respectively. The infrared spectra of the neutral polymers showed that PPT^0, $PMPT^0$, and $PFPT^0$ (the superscript 0 denotes the neutral state) have the same regular structure, which can be denoted as poly(3-aryl-2,5-thiophenediyl). Cyclic voltammograms showed that the oxidation potential increased in the order of $PMPT^0$ < PPT^0 < $PFPT^0$. The results are discussed in terms of the electronic effect of the substituents. PPT was highly anode-active. The activity was three times as high as that of polythiophene. The visible spectra of PPT^0 showed that the π-π^* transition occurred at the lowest energy among those of poly(3-substituted thiophene)s. This indicated that the pendant phenyl group is apparently conjugated with the main chain. The spectral change of PPT during PF_6^- doping showed the formation of polarons at low doping levels. The spectral change of PPT during Et_4N^+ doping showed that the absorption peak of the π-π^* transition shifted to the low energy side as the doping level increased.

5-2 Introduction

Electrically conducting polymers have attracted considerable attention, owing to various electronic properties such as electrochromism, energy storage and rectification[1)-4)]. Electrochemical polymerization has been found to be a convenient technique for obtaining conducting polymers from five-membered heterocycles. Among the polyheterocycles, polythiophenes are of increasing interest owing to their enhanced stability in both oxidized and neutral states. The author reported the electrochemical preparation of polythiophene (PT), poly(3-alkylthiophene)s, and poly(3-benzylthiophene) and clarified the relation between the properties and the chemical structure of them. A poly(3-methylthiophene) (PMT) film had the highest conductivity, 510 S/cm, among the conducting polymer films prepared electrochemically[5),6)]. Poly(3-hexylthiophene), poly(3-octylthiophene), and poly(3-dodecylthiophene) were soluble conducting polymers and had the degrees of polymerization of 9 X 10 to 2.3 X 10^2 [7),8),9)]. Optical data of these polymers indicated that bipolaron states are formed by doping but, in opposition to bipolaron theory, the states are localized in a polymer chain at the intermediate stage of doping.

Poly(3-aryl thiophene)s for which one can expect π-conjugation between the polymer backbones and the substituent would have different properties from poly(3-alkylthiophene)s

or PT.

In this paper, the author will report on the electrical properties of poly(3-phenylthiophene) (PPT), poly[3-(4'-methoxyphenyl)thiophene] (PMPT), and poly[3-(4'-trifluoromethylphenyl)thiophene] (PFPT) films prepared by electrochemical polymerization of the corresponding monomers. The electrochemical and the optical properties of PPT will be discussed in comparison with those of PT.

5-3 Experimental

5-3-1 Materials

3-phenylthiophene (3-PT) 3-(4'-methoxyphenyl)thiophene (3-MPT), and 3-(4'-trifluoromethylphenyl)thiophene (3-FPT) were obtained by coupling of phenylmagnesium bromide, 4-methoxyphenylmagnesium bromide, and 4-trifluoromethylphenylmagnesium bromide with 3-bromothiophene in the presence of a nickel catalyst, respectively, according to a procedure similar to that described for the preparation of 3-butylthiophene [10]. 3-PT, for example, was synthesized as follows. A solution of phenylmagnesium bromide was prepared in a usual manner from 3.77 g (155 mg-atom) of magnesium activated by iodine and 24.34 g (155 mmol) of bromobenzene in 40 ml of fleshly distilled dry ether. The Grignard solution was then added dropwise

to a mixture composed of 24.46 g (150 mmol) of 3-bromothiophene, 434 mg 0.87 mmol) of [1,3-bis(diphenylphosphino)propane]nickel(II)[11], and 95 ml of fleshly distilled dry ether, at 0 °C with stirring under nitrogen over 20 min. After refluxing for 2 hours, the reaction mixture was hydrolyzed with diluted hydrochloric acid under cooling with an ice bath, and then extracted with dichloromethane. The organic layer was washed successively with water, a saturated sodium hydrogen carbonate solution, and water, and then dried over magnesium sulfate. After evaporation of the solvent, the residue was crystallized from ethanol to afford 19.9 g (83 % yield based on the 3-bromothiophene) of 3-PT, m.p. 92.3-93.6 °C (lit 92 °C)[12].

3-MPT and 3-FPT melted at 129.7-130.4 °C and 120.1-121.7 °C, respectively. The structure was confirmed by nuclear magnetic resonance spectroscopy and infrared spectroscopy.

Propylene carbonate was dried over 0.4 nm molecular sieves, distilled and stored under dry nitrogen. The other solvents were dried and purified as usual[13]. The electrolytes were used without further purification.

5-3-2 Electrochemical polymerization and measurements.

The electrochemical vessel consisted of a one-compartment cell equipped with a platinum plate as a cathode and an indium tin oxide conducting glass (ITO) plate for electrochemical

polymerization and spectroscopic measurements or a polished platinum disk electrode (s = 0.024 cm^2) for cyclic voltammetry as an anode.

The films were prepared in a propylene carbonate solution containing a 0.1 mol/l monomer and 0.03 mol/l tetraethylammonium hexafluorophosphate (Et_4NPF_6) as an electrolyte. The oxygen in the solution was swept out with argon gas prior to the electrolysis. The electrochemical polymerization was performed at a constant current density of 1 mA/cm^2 at 5 ^oC and continued until the charge density reached 1.8 C/cm^2. The direct current conductivities of as-grown films were measured using a four-point probe method.

For infrared spectroscopy, as-grown films on ITO were neutralized by reversing the polarity of the electrodes after polymerization. The neutralization was carried out at conditions that described previously[6),9)]. The films neutralized electrochemically were soaked with methanol for 24 hours in order to get a highly neutral film. Infrared spectra were measured on a JEOL JIR-40 Fourier transform i.r. spectrophotometer.

For visible-near i.r. spectroscopy and cyclic voltammetry, thin films were prepared under the same polymerization conditions as noted above, but the charge density was reduced 27 and 24 mC/cm^2 for spectroscopy and voltammetry, respectively. The thin films were left on the electrode surface as grown, rinsed

with acetonitrile and used for further measurements. Cyclic voltammograms were recorded for a 0.1 mol/l Et_4NPF_6 solution in acetonitrile at sweep rates of 20, 40, 60, 80, and 100 mV/sec. The spectral change during electrochemical doping was measured in situ in an acetonitrile solution containing 0.1 mol/l Et_4NPF_6. All potentials refer to a Ag/Ag^+ reference electrode. Absorption spectra were recorded on a Hitachi U-3400 spectrophotometer.

5-4 Results and discussion

5-4-1 Electrical conductivity

The conductivities and the dopant content of PPT, PMPT, and PFPT are summarized in Table 5,1.

The films deposited on an anode were in an oxidized, doped, form. The conductivity increased in the order of PFPT << PMPT < PPT. The introduction of methoxy or trifluoromethyl groups in PPT caused its conductivity to decrease. Especially, the oxidized PFPT films were unstable when allowed to stand in the atmosphere. The PFPT films changed from blue to red-purple in the atmosphere for several hours. The change in color indicates the neutralization of the as-grown PFPT films.

The dopant content per monomer unit was calculated from the elemental analysis of sulfur and phosphorus. The dopant

Table 5,1. Conductivity of poly(3-arylthiophene) films

	PPT	PMPT	PFPT
Conductivity (S/cm)	140	40	$1.8X10^{-3}$
Dopant[a)]	0.19	0.35	0.22

a) Mole ratio of dopant per thiophene ring were caluculated from the elemental analysis of sulfur and phosphorus.

content of PPT films was nearly equal to those of PT, PMT, poly(3-ethylthiophene), and poly(3-butylthiophene) films which were 0.17, 0.18, 0.17, and 0.18 per thiophene unit, respectively[6),14)]. These polythiophenes films had conductivities higher than 10^2 S/cm. On the other band, PMPT, PFPT, and PBZT[14)] films contained a larger amount of dopant but had conductivities lower than 10^2 S/cm. From these results, the dopant content of polythiophenes necessary for high electrically conduction seems to be 0.17-0.19 per monomer unit.

5-4-2 Infrared spectra

The Fourier transform i.r. spectra of neutral poly(3-arylthiophene)s are shown in Figure 5,1. These neutral polythiophenes films were attached on the surface of potassium bromide pellets, because the free-standing films were brittle to handle.

The spectrum of PPT^0 exhibited bands in 3100-3000 cm^{-1} which are characteristic of the aromatic C-H stretching vibrations. The bands in the 1445-1601 cm^{-1} region were assigned to the skeletal vibrations, involving carbon to carbon and carbon to sulfur stretchings within the aromatic rings[15)]. The weak bands at 1070 and 1028 cm^{-1} were ascribed to the in-plane C-H bending vibrations. In the region of the out-of-plane C-H bending vibrations, there were a medium band at 839 cm^{-1} which was attributable to a 2,3,5-trisubstituted thiophene

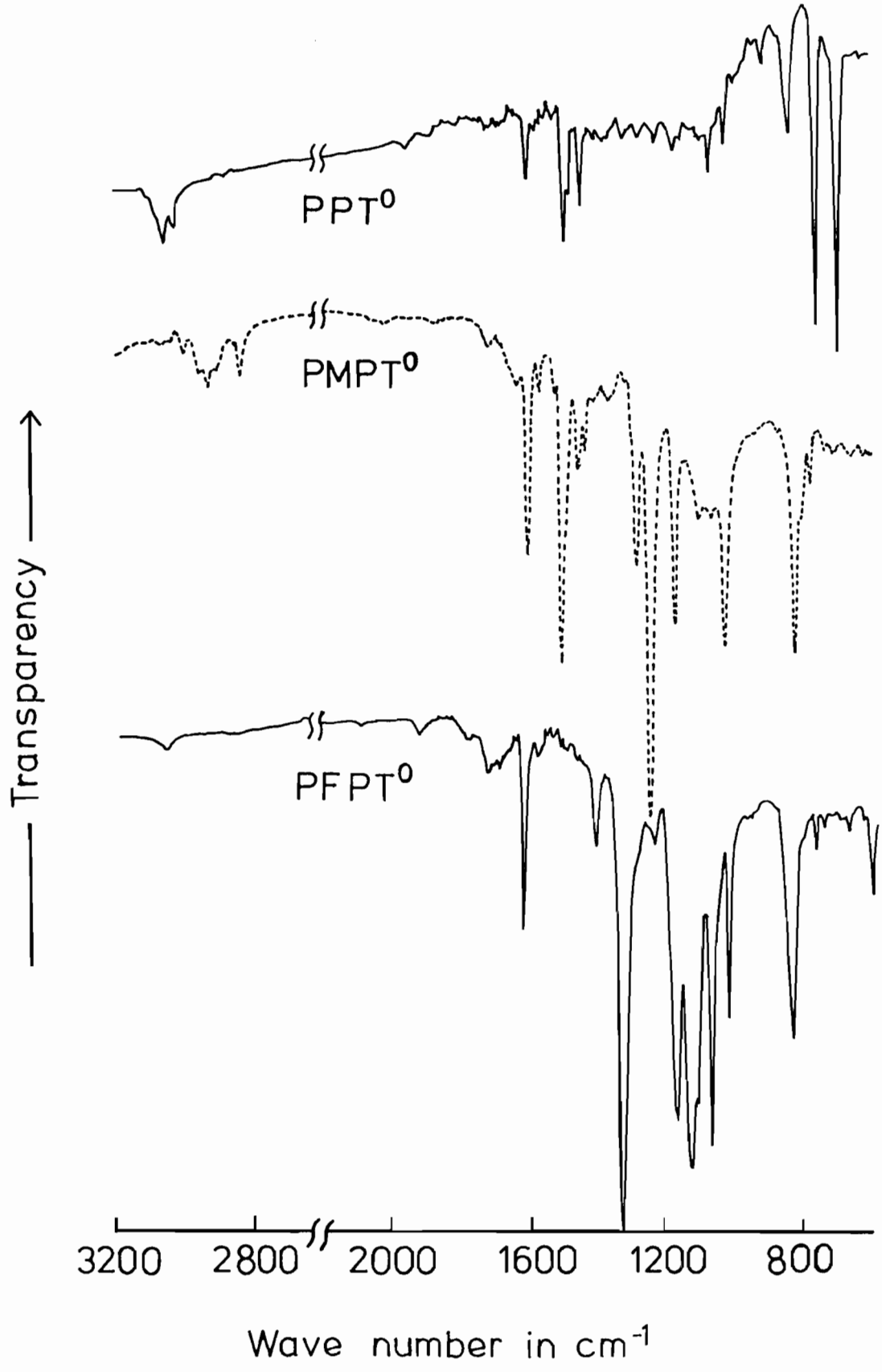
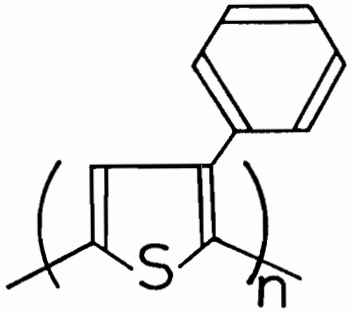


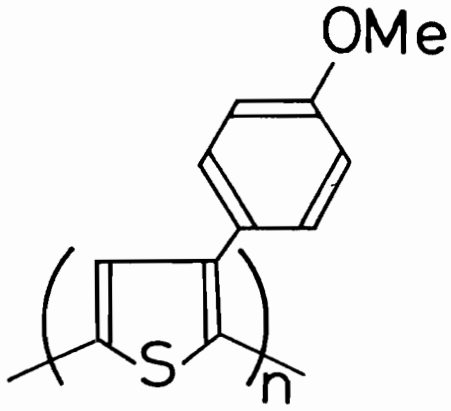
Figure 5,1. Infrared spectra of neutral poly(3-arylthiophene)s.

ring[16] and two strong bands at 760 and 698 cm^{-1} which were ascribed to a monosubstituted benzene ring of PPT^0 [17].

The spectrum of $PMPT^0$ showed bands in 3066-3035 and 2953-2833 cm^{-1} which were assigned to the aromatic and the aliphatic C-H stretching vibrations, respectively. The bands in the 1439-1608 cm^{-1} region were assigned to the skeletal vibrations. The strong band at 1248 cm^{-1} was obviously attributable to the asymmetrical C-O-C stretching vibration and the medium band at 1032 cm^{-1}, attributable to the symmetrical one. There was a medium band at 825 cm^{-1}, assigned to the C-H deformation vibrations of a 2,3,5-trisubstituted thiophene and a 1,4-disubstituted benzene ring[17]. $PFPT^0$ had the broad band near 3060 cm^{-1} assignable to the aromatic C-H stretching vibrations and the band at 1618 cm^{-1} assignable to the skeletal vibration. The multiple strong bands in 1325-1065 cm^{-1} were ascribable to the C-F stretching mode of CF_3 group. There was a medium band at 833 cm^{-1} due to a 2,3,5-trisubstituted thiophene and a 1,4-disubstituted

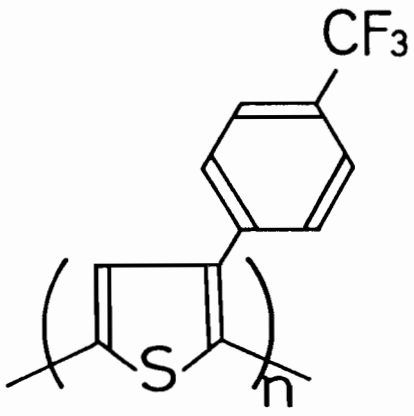


PPT^0



$PMPT^0$

benzene ring. Therefore, in the electrochemical polymerization of 3-phenylthiophene, 3-(4'-methoxyphenyl)thiophene, and 3-(4'-trifluoromethylphenyl)thiophene, the C-C bonds are formed at the carbon atoms adjacent to the sulfur atom. The structures of these polymers can be denoted poly(3-aryl-2,5-thiophenediyl).



PFPT^0

5-4-3 Cyclic voltammograms

Figure 5,2 shows the cyclic voltammograms of a PPT film grafted on a platinum disk in the potential ranges of -0.5 to +1.1 V and -0.5 to -2.3 V vs. Ag/Ag^+.

In the range of -0.5 to +1.1 V, there were an anodic peak at +0.76 - +0.72 V, two shoulders about 0.9 and 0.4 V, and a cathodic peak at +0.62 - +0.58 V, a shoulder about +0.35 V. The anodic peak and shoulders were ascribed to the doping with PF_6^-. The cathodic peak and shoulder were attributed to the un-doping with PF_6^-. The oxidized film was blue and the neutral one red-purple. The charge which was reversibly exchanged during the redox cycles was determined by integrating the absolute value of the current in the range of -0.5 to +1.1 V with

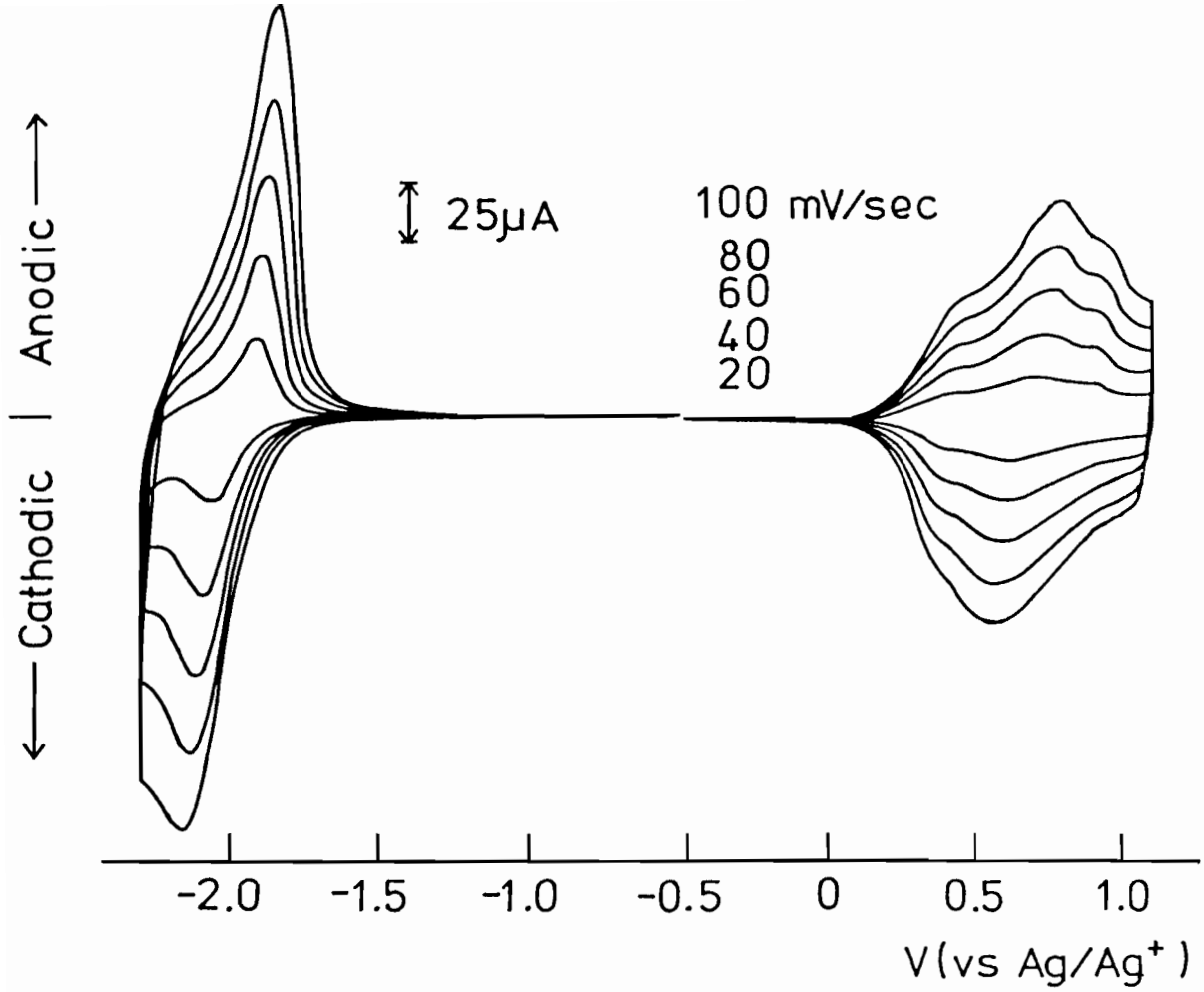


Figure 5,2. Cyclic voltammograms of a PPT film.

respect to sweep time. The amount of charge Q was obtained by dividing the charge by polymer weight on the electrode. The Q value for PF_6^- doping and undoping was 0.78 electron per monomer unit.

In the range of -0.5 to -2.3 V, the cathodic peak at -1.99 - -2.13 V and the anodic peak at -1.90 - -1.85 V would be ascribed to the doping and the undoping with Et_4N^+, respectively. These redox peaks for Et_4N^+ doping and undoping were sharper than those for PF_6^- doping and undoping. The difference in the shapes of the peaks would arise from the electronic structure of doped or neutral PPT. The reduced film was blue-purple and the neutral one red-purple. The amount charge Q for Et_4N^+ doping and undoping was determined just as described above. The Q value for Et_4N^+ doping and undoping was 0.72 electron per monomer unit.

PT had been electrochemically doped not only with anions but also with cations[18),19)]. However, those results had been reported only briefly without quantitative experimental results. Figure 5,3 shows the cyclic voltammograms of a PT film on a platinum disk in the potential ranges of -0.5 to +1.15 V and -0.5 to -2.4 V vs. Ag/Ag^+. The PT film was prepared just as described in Chapter 2.

In the range of -0.5 to +1.15 V, there were an anodic peak at +0.69 - +0.72 V and two cathodic peaks about +0.6 and +0.3 V. The shapes of the voltammograms in the range were identical

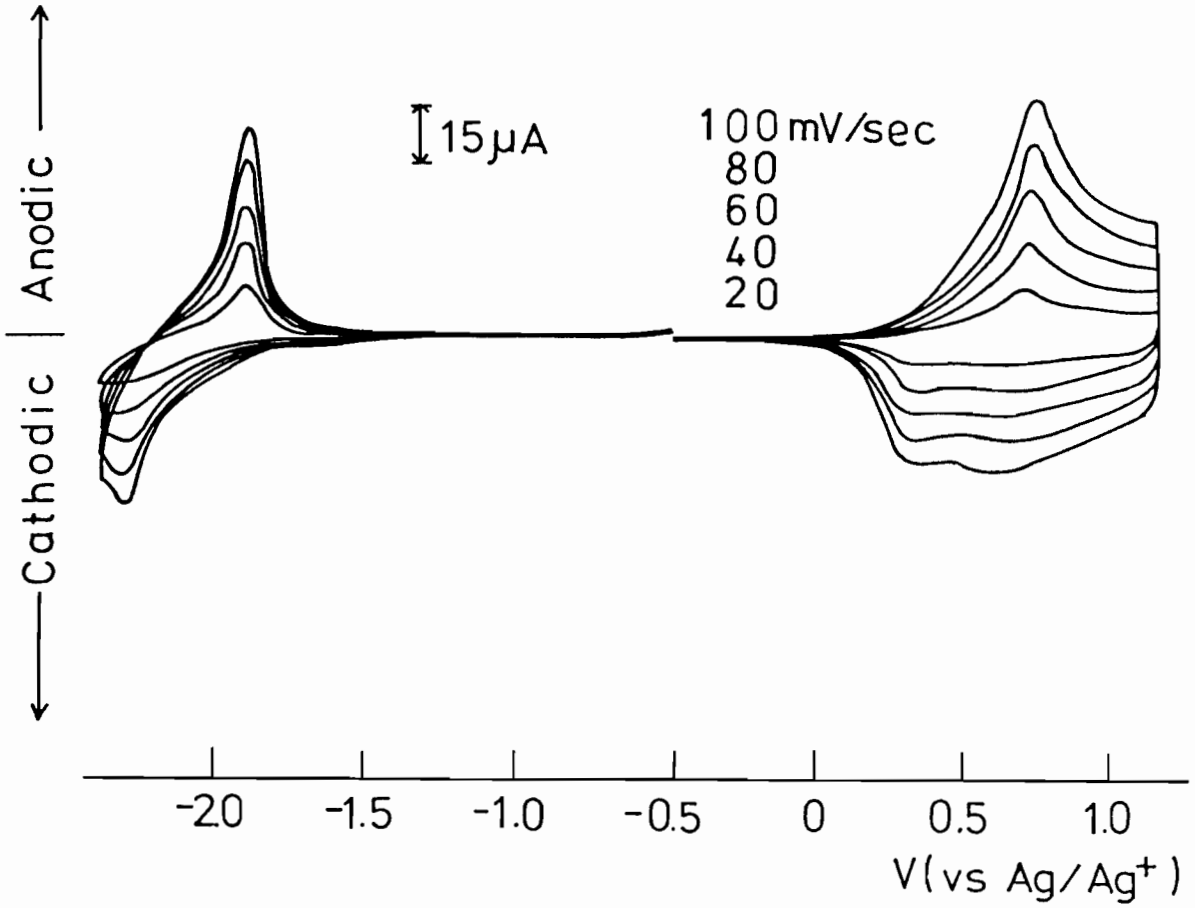


Figure 5,3. Cyclic voltammograms of a PT film.

with those of polythiophene shown in Chapter 2. These peaks were attributed to the doping and the undoping with PF_6^-. The oxidized film was blue and the neutral one red. The amount of charge Q for PF_6^- doping and undoping was estimated to be 0.69 electron per monomer unit. In the range of -0.5 to -2.4 V, the cathodic peak at -2.30 - -2.31 V and the anodic peak at -1.91 - -1.90 V would be ascribed to the doping and the undoping with Et_4N^+, respectively. The reduced film was blue and the neutral one red. The Q value for Et_4N^+ doping and undoping was 0.24 electron per monomer unit.

The peak heights of all the anodic and the cathodic waves were proportional to the sweep rate, suggesting that the electroactive material is located on the surface of the electrodes. Increasing the upper positive and decreasing the lower negative potential limits, +1.1 V and -2.3 V for PPT and +1.15 V and -2.4 V for PT, led to the destruction of the polymers.

Table 5,2 lists the amount of charges Q of PPT and PT described above. The Q values of PT and PPT films for PF_6^- doping and undoping were quite similar. However, a PPT film showed a Q value for Et_4N^+ doping and undoping three times as high as a PT film did. These results indicate that PPT have not only high cathode-activity but also high anode-activity. It is clear that phenyl group has a favorable effect on the cation doping of polythiophene.

Table 5,2. The amount of charges exchanged during redox cycles

	PF_6^-	Et_4N^+
PPT	0.78	0.72
PT	0.69	0.24

PF_6^-:The charges for PF_6^- doping and undoping.
Et_4N^+: Those for Et_4N^+ doping and undoping.

The cyclic voltammograms of PMPT and PFPT showed that the redox process related to PF_6^- doping and undoping recurred reversibly but that related to Et_4N^+ doping and undoping did not owing to the deterioration of the polymers. In the former redox process, the anodic peaks of PMPT and PFPT were located at +0.64 - +0.65 V and +0.98 - +1.00 V, respectively. The oxidation potential of poly(3-arylthiophene)s increased in the order of $PMPT^0$ < PPT^0 < $PFPT^0$. The present result is explained in terms of the electronic effect of the substituents. The unstability of the oxidized PFPT film, presented in "5-4-1 Electrical Conductivity", results from the highest oxidation potential of PFPT among that of poly(3-arylthiophene)s.

5-4-4 Spectral change during doping

The change in visible-near i.r. spectra of PT during PF_6^- doping is shown in Figure 5,4[6),20)]. The PT film was prepared just as described in Chapter 2.

At 0.0 V, there was an absorption peak at 2.5 eV, associated with the transition between the valence and the conduction bands, the π-π^* transition. When a film was electrochemically doped with PF_6^-, two additional peaks appeared at 1.8-1.5 eV and 0.6-0.7 eV and the peak height of the π-π^* transition decreased. These three peaks shifted to the high energy side as the doping level increased. The spectral

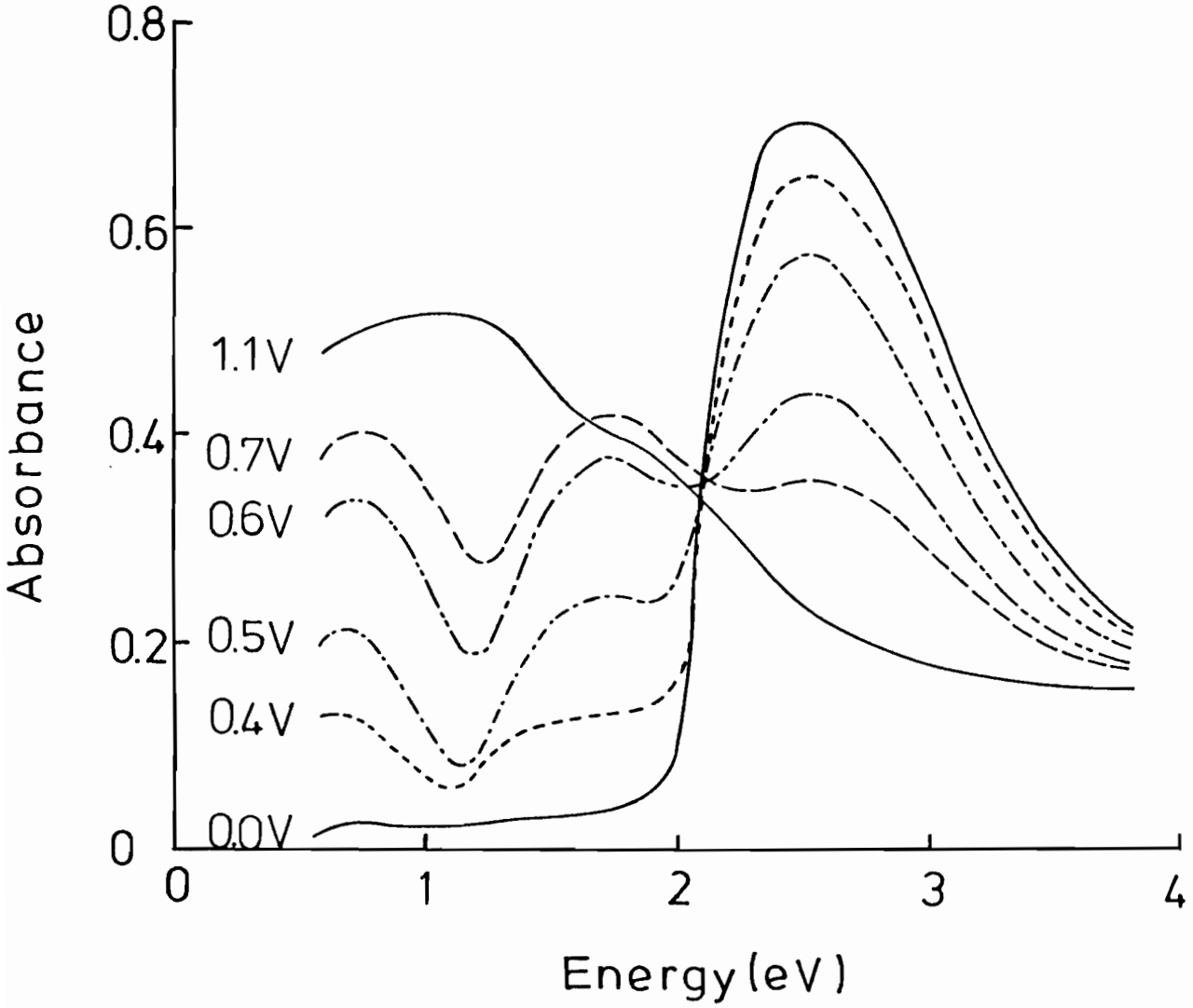


Figure 5,4. Spectral change of a PT film during electrochemical PF_6^- doping.
(Applied voltage is shown on the left.)

change was similar to that shown in Chapter 2.

The spectral change of PT during electrochemical Et_4N^+ doping is presented in Figure 5,5. PT was in a neutral state from 0.00 V to -1.80 V. The evolution of the absorption spectrum for Et_4N^+ doping is essentially the same as that for PF_6^- doping. These spectra shows that bipolarons which consist of dianions are caused in polymer chains by Et_4N^+ doping as well and the electronic structure of the bipolaron states is similar to that of bipolaron states caused by PF_6^- doping. Moreover, both bipolaron levels are derived from the edges of the valence and the conduction bands.

The change in visible-near i.r. spectra of PPT during PF_6^- doping is shown in Figure 5,6.

At 0.0 V, PPT was in a neutral state. The absorption peak corresponding to the interband π-π^* transition was observed at 2.21 eV. There was the absorption onset at 1.74 eV. These values were the smallest among poly(3-substituted thiophene)s[6)-9),14),21)]. It is apparent that the substituent, phenyl group, is conjugated with the main chain. At low doping levels, 0.4 and 0.5 V, three additional absorption bands appeared at 1.48 and 1.21 eV and below 1.0 eV. These three additional absorption bands suggest that there would be polaron states described in Chapter 1 on the polymer chains, in analogy with polypyrrole[22)]. The absorption band at 1.21 eV would be associated with the transition between the two polaron levels

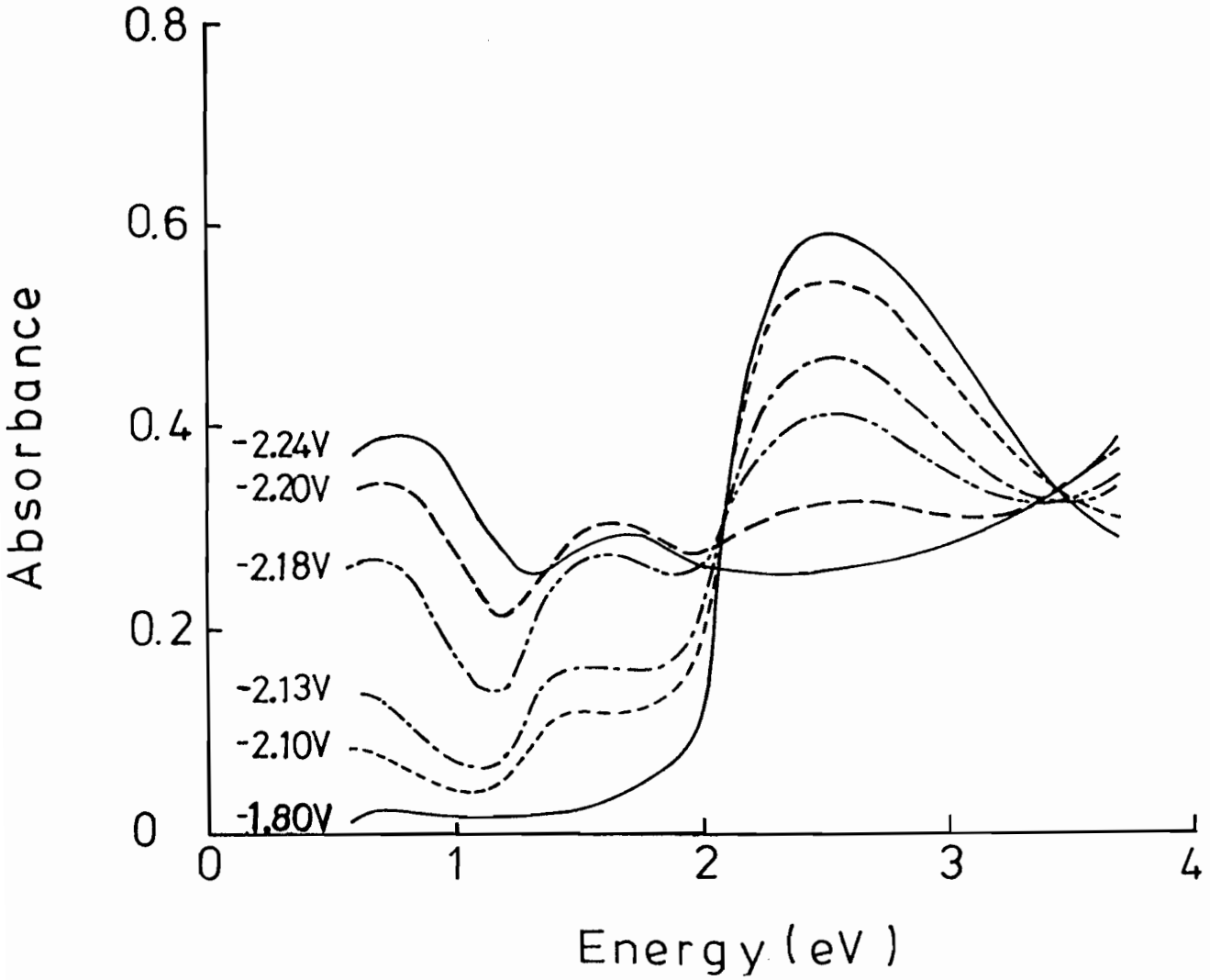


Figure 5,5. Spectral change of a PT film during electrochemical Et_4N^+ doping.
(Applied voltage is shown on the left.)

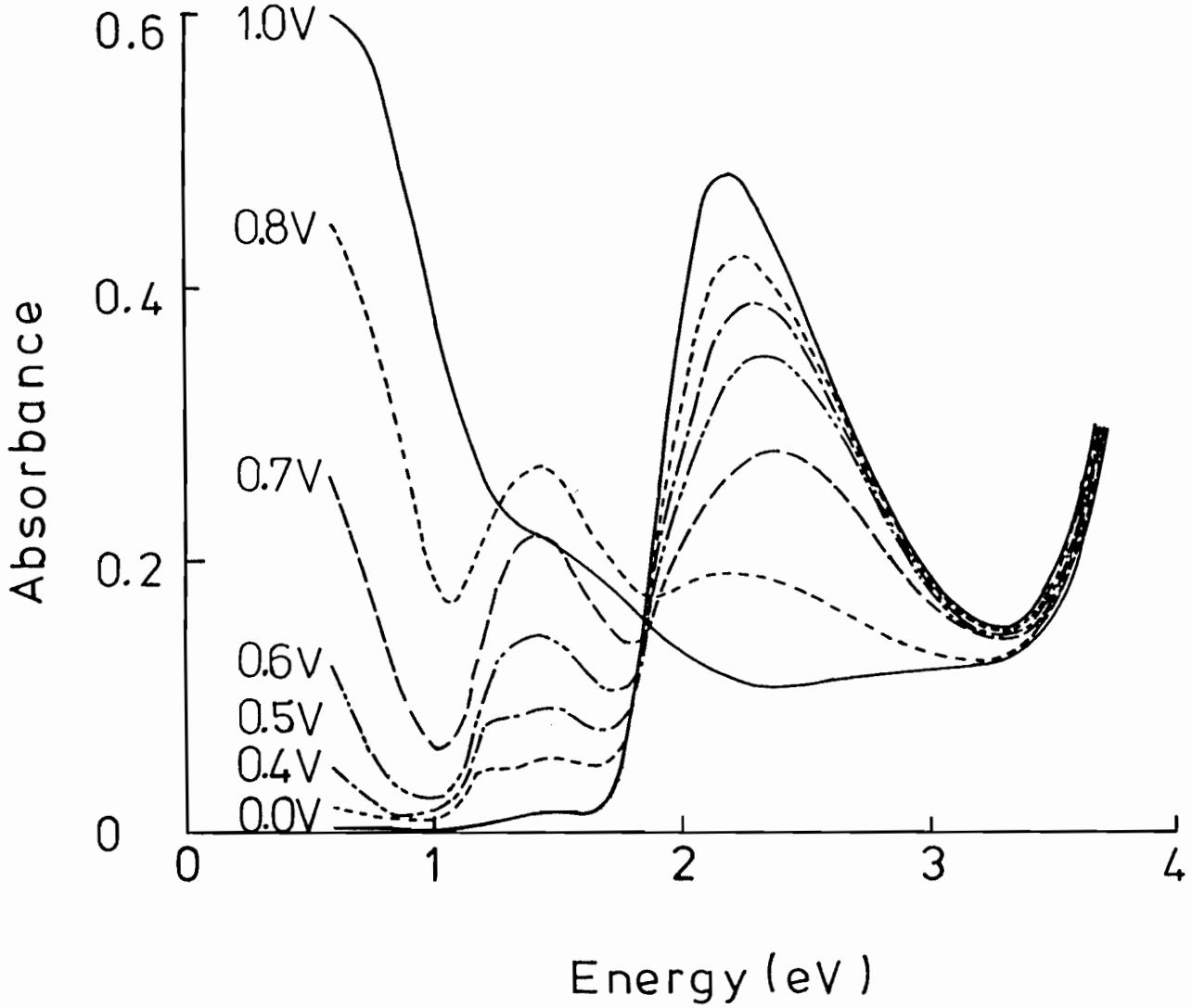


Figure 5,6. Spectral change of a PPT film during electrochemical PF_6^- doping.
(Applied voltage is shown on the left.)

which had not hitherto been observed explicitly in the spectra of polythiophenes. At higher doping levels, the two absorption bands due to bipolaron levels were observed at 1.43 and below 1.0 eV. The disappearance of the absorption band at 1.21 eV is consistent with the recombination of polarons to form bipolarons. The position of the middle peak related to an upper bipolaron level was independent of the doping level in analogy with poly(3-methyl, 3-ethyl, or 3-butylthiophene)[6),14)].

The spectral change of PPT during electrochemical Et_4N^+ doping is presented in Figure 5,7. When a PPT film was electrochemically doped with Et_4N^+, two absorption bands about 1.5 and below 1.2 eV appeared in addition to the interband transition peak at 2.21 eV. The interband transition peak shifted to the low energy side as the doping level increased. These spectra indicate that the electronic states like polarons or bipolarons formed by Et_4N^+ doping are not derived from the edges of the valence and the conduction bands.

Neutral PMPT and PFPT films had the absorption peaks of the π-π^* transition at 2.26 and 2.30 eV, respectively. The effect of substituents on the peak positions of the π-π^* transition of poly(3-arylthiophene)s is hardly discernible.

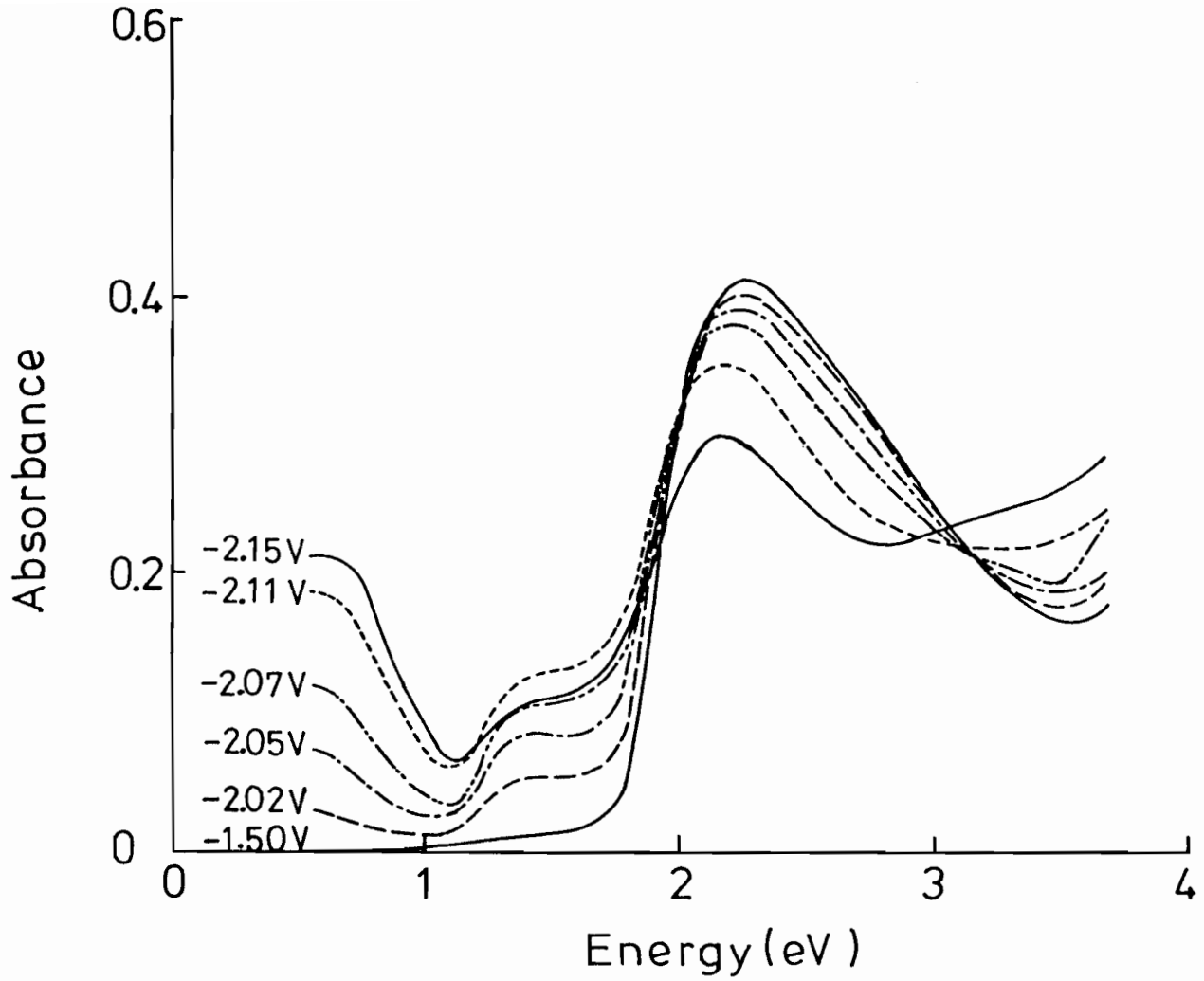


Figure 5,7. Spectral change of a PPT film during electrochemical Et_4N^+ doping.
(Applied voltage is shown on the left.)

5-5 Conclusions

PPT, PMPT, and PFPT films were prepared by electrochemical polymerization and showed the conductivities of 140, 40 and 1.8 X 10^{-3} S/cm, respectively. PPT contained 0.19 dopant per monomer unit. From the relationship between the conductivities and the dopant contents of poly(3-substituted thiophene)s, the dopant content of polythiophenes necessary for high electrically conduction seem to be 0.17-0.19 per monomer unit. The infrared spectra of PPT^0, $PMPT^0$, and $PFPT^0$ were consistent with the regular structure denoted as poly(3-aryl-2,5-thiophenediyl). The cyclic voltammograms of PPT showed that the polymer had not only high cathode-activity but also high anode-activity. The anode-activity of PPT was three times as high as that of PT which had been reported previously. The oxidation potential of poly(3-arylthiophene)s increased in the order of $PMPT^0$ < PPT^0 < $PFPT^0$. The high oxidation potential of $PFPT^0$ is responsible for the unstability of the oxidized PFPT film. The visible spectra of PPT^0 films showed the absorption peak of the π-π^* transition at 2.21 eV. The value was the smallest among poly(3-substituted thiophene)s, suggesting that the substituent, phenyl group, is conjugated with the main chain. The visible-near i.r. spectra of PPT at slight PF_6^- doping levels showed the formation of polarons. This is the first ex-

ample in which polarons are apparently detected by the spectra of polythiophenes. The spectral change of PPT during Et_4N^+ doping showed that the absorption peak of the π-π^* transition shifted to the low energy side as the doping level increased. The shift indicates that the electronic states like polarons or bipolarons formed by Et_4N^+ doping are not derived from the edges of the valence and the conduction bands.

5-6 References

1) F. Garnier and G. Tourillon, J. Electroanal. Chem., **148**, 299 (1983).

2) G. Tourillon and F. Garnier, J. Electroanal. Chem., **135**, 173 (1982).

3) K. Kaneto, K. Yoshino, and Y. Inuishi, Jpn. J. Appl.Phys., **22**, L567 (1983).

4) M. Aizawa, T. Yamada, H. Shinohara, K. Akagi, and H. Shirakawa, J. Chem. Soc., Chem. Commun., **1986**, 1315.

5) M. Sato, S. Tanaka, and K. Kaeriyama, J. Chem. Soc., Chem. Commun., **1985**, 713. (Chapter 2)

6) M. Sato, S. Tanaka, and K. Kaeriyama, Synth. Met., **14**, 279 (1986). (Chapter 2)

7) M. Sato, S. Tanaka, and K. Kaeriyama, J. Chem. Soc., Chem. Commun., **1986**, 873. (Chapter 4)

8) M. Sato, S. Tanaka, and K. Kaeriyama, Synth. Met., **18**, 229 (1987). (Chapter 4)

9) M. Sato, S. Tanaka, and K. Kaeriyama, Makromol. Chem., **188**, 1763 (1987). (Chapter 4)

10) K. Tamao, S. Kodama, I. Nakajima, M. Kumada, A. Minato, and K. Suzuki, Tetrahedron, **38**, 3347 (1982).

11) G. R. V. Hecke and W. D. Horrocks Jr., Inorg. Chem., **5**, 1968 (1966).

12) J. Buckingham, "Dictionary of Organic Compounds", 5th edn., vol. 5, Chapman and Hall, New York, p. 4684 (1982).

13) J. A. Riddick and W. B. Bunger, "Organic Solvents", Willey, New York (1970).

14) M. Sato, S. Tanaka, K. Kaeriyama, and F. Tomonaga, Polymer, **28**, 1071 (1987). (Chapter 3)

15) T. Shimauchi, Y. Mashiko, and K. Nakanishi, "Sekigaisen-Kyusyu-Supekutoru", Nankohdoh, p123 (1964).

16) M. Akiyama, J. Mol. Spectrosc., **43**, 226 (1972).

17) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", Champman and Hall, London, p86 (1975).

18) K. Kaneto, S. Ura, K. Yoshino, and Y. Inuishi, Jpn. J. Appl. Phys., **23**, L189 (1984).

19) M. Aizawa, S. Watanabe, H. Shinohara, and H. Shirakawa, J. Chem. Soc., Chem., Commun., **1985**, 264.

20) T. C. Chung, J. H. Kaufman, A. J. Heeger, and F. Wudl, Phys. Rev., **B30**, 702 (1984).

21) S. Tanaka, M. Sato, and K. Kaeriyama, Polymer, Commun., **26**, 303 (1985).

22) J. C. Scott, J. L. Brėdas, K. Yakushi, P. Pfluger, and G. B. Street, Synth. Met., **9**, 165 (1984).

Chapter 6

Conclusions

6-1. Electrical conductivity and other properties

6-2. Oxidation potential

6-3. Mechanism of charge transfer

6-4. Future scope of the present study

6-1 Electrical conductivity and other properties

Conductive polythiophene (PT) and poly(3-methylthiophene) (PMT) films had been prepared in acetonitrile, nitrobenzene, or benzonitrile by electrochemical methods. However, the study of those polymerization conditions and the preparation of other polythiophenes films had not hitherto been reported.

Optimal conditions for the electrochemical polymerization of 3-methylthiophene were established. A good solvent and electrolyte were propylene carbonate (PC) and tetraethylammonium hexafluorophosphate (Et_4NPF_6), respectively. This optimum combinations of PC and Et_4NPF_6 was the same as that found for the electrochemical polymerization of 3-butylthiophene. The PMT film prepared under the optimal conditions showed a conductivity of 510 S/cm. The conductivity was the highest among those of the conducting polymer films prepared electrochemically.

A PT, a poly(3-long alkyl-thiophene)s, a poly(3-benzylthiophene) (PBZT), and a poly(3-phenylthiophene) (PPT) film synthesized electrochemically had lower conductivities than the PMT film. However, poly(3-hexylthiophene), poly(3-octylthiophene), and poly(3-dodecylthiophene) films were soluble in common organic solvents. It was possible to determine their degrees of polymerization, and cast films from their solutions. Further, the PPT films had not only high cathode-activity but also high anode-activity. The anode-activity of PPT was three times as high as that of PT which had been reported previously. Thus we can obtain

the conductive polythiophenes with the attractive properties by the introduction of long alkyl or phenyl group at 3 position of the thiophene ring.

The as-grown polythiophenes films were in an oxidized form and contained a certain amount of dopant, anion released from the supporting electrolyte. The polythiophenes films having the conductivities higher than 10^2 S/cm contained 0.17-0.19 dopant per monomer unit, whereas those having the conductivities lower than 10^2 S/cm contained a larger amount of dopant. From these results, the dopant content of polythiophenes necessary for high conduction seems to be 0.17-0.19 per monomer unit.

6-2 Oxidation potential

Oxidation potential of polymers having π-conjugation systems along the polymer chains is a reliable indication of the ease with which the polymers are doped, oxidized, and the stability of the doped polymers in the atmosphere. The effects of substituents and the irregularity of polymer structure on the oxidation potential of polythiophenes were revealed by cyclic voltammetry.

The oxidation potential of PT having an observable number of irregular bondings other than 2,5-linkage was considerably higher than that of PMT having a regular structure. The bulkier the substituent group of polythiophenes, the higher was its oxidation potential. Furthermore, the order of the oxidation potential of

poly(3-arylthiophene)s was explained by the electron-withdrawing effects of the substituents. These results indicate that the electronic and the steric effects of substituents and the effect of the irregularity of polymer structure are important in the oxidation potential of polythiophenes. Therefore, we can control the oxidation potential of poly(3-substituted thiophene)s by the choice of the substituent.

6-3 Mechanism of charge transfer

Brédas et al. had presented the results of band-structure calculations on a polythiophene chain, as a function of doping. At low doping level, polarons are formed on the polymer chains, and then polarons combine to form spinless bipolarons at higher doping levels. As doping proceeds, two bipolaron bands occurs in the gap and the band gap widens. Bipolarons could become mobile and transport the current at high doping level.

The electronic structures of doped and neutral polythiophenes were investigated by means of visible-near infrared spectroscopy. The mechanism of charge transfer was discussed on the basis of these electronic structures.

The spectra of PPT at slight PF_6^- doping levels showed the three absorption bands related to polarons. Those of PPT, PT, PBZT, and poly(3-alkylthiophene)s at moderate doping levels showed the two absorption bands ascribed to bipolarons. These

results are consistent with the bipolaron model proposed by Brédas et al. and show that polaron or bipolaron states are present on doped polythiophenes chains and polarons combine to form bipolarons which are the current carriers.

In the spectral changes of poly(3-alkylthiophene)s and PPT during PF_6^- doping, the peaks of the interband transition showed apparent blue shifts with an increase in doping level, whereas the peaks related to the bipolaron levels showed no shift or red shifts. The spectra of doped and neutral poly(3-alkylthiophene)s and PBZT prepared in PC showed that the energy of the interband transition of the neutral ones was influenced by their substituents, but the peak positions which are related to the bipolaron levels of the doped ones were not. Moreover, the peaks of the interband transition in doped and neutral PDDT solutions shifted extraordinarily to the higher energy side compared with that in the oxidized and neutral films, but difference in the positions of the peaks attributable to the upper bipolaron level was small.

These results shows that the peak positions ascribed to bipolaron levels are independent of the peak positions corresponding to the interband transition, suggesting the localization of bipolaron states in polymer chains at the intermediate stages of doping. When a considerable conductivity of polythiophenes at dilute doping levels is taking into accounts, we can conclude that the charge transfer is not due to the propaga-

tion of carriers in bands, which predicted by Brédas et al., but the hopping of carriers between bipolaron levels.

6-4 Future scope of the present study

The present thesis revealed that the introduction of substituents in poly(2,5-thiophenediyl) caused the attractive properties of the obtained polymers, e.g., high conductivity, solubility, and anode-activity, and elucidated the effects of the substituents and the polymer structure on the electrical properties of the polymers. Furthermore, it made the conduction mechanism for polythiophenes clearer.

These results obtained for polythiophenes are applicable to other conducting polymers having a non-degenerate ground state, for example, poly(p-phenylene), poly(2,6-naphthylene), and polypyrrole. Therefore, they give a valuable guide to the design of a highly conductive polymer and conducting polymers with desirable properties.

In conclusion, it is clear that the present study is useful for a more understanding of conducting polymers. The author hopes that theoretical studies are carried out on basis of the present data and the discussion and then present a more accurate electronic structure of conducting polymers.

List of Publication

1. "Electrochemical Preparation of Highly Conducting Polythiophene Films"
   J. Chem. Soc., Chem. Commun., **1985**, 713.
   M. Sato, S. Tanaka, and K. Kaeriyama (Chapter 2)

2. "Electrochemical Preparation of Conducting Poly(3-methylthiophene): Comparison with Polythiophene and Poly(3-ethylthiophene)"
   Synth. Met., **14**, 279 (1986).
   M. Sato, S. Tanaka, and K. Kaeriyama (Chapter 2)

3. "Soluble Conducting Polythiophenes"
   J. Chem. Soc., Chem. Commun., **1986**, 873.
   M. Sato, S. Tanaka, and K. Kaeriyama (Chapter 4)

4. "Soluble Conducting Polymers by Electrochemical Polymerization of Thiophenes Having a Long Alkyl Substituent"
   Synth. Met., **18**, 229 (1987).
   M. Sato, S. Tanaka, and K. Kaeriyama (Chapter 4)

5. "Poly-3-butylthiophene and Poly-3-benzylthiophene Films"
   Polymer, **28**, 1071 (1987).
   M. Sato, S. Tanaka, K. Kaeriyama, and F. Tomonaga (Chapter 3)

6. "Poly(3-dodecyl-2,5-thiophenediyl): Soluble and Conducting Polythiophene"
Makromol. Chem., **188**, 1763 (1987).
M. Sato, S. Tanaka, and K. Kaeriyama (Chapter 4)

7. "Electrochemical Preparation of Highly Anode-Active Poly(3-phenylthiophene)"
J. Chem. Soc., Chem. Commun., **1987**, 1725.
M. Sato, S. Tanaka, and K. Kaeriyama (Chapter 5)

Acknowledgments

I would like to express my sincere gratitude to Professor Akira Sera (Kobe University) for his continuing guidance and encouragement throughout the present study. I am also grateful to Professor Michio Ashida and Professor Katsuhiko Nakamae (Kobe University) for their useful discussion. I am indebted to Associate Professor Hiroaki Yamada and Dr. Kuniaki Itoh for their useful advice.

I wish to thank Drs. Yoshio Suda, Aizoh Yamauchi, Masao Kato, Kyoji Kaeriyama, Hachiro Nakanishi, Susumu Tanaka (Research Institute for Polymers and Textiles), and Mr. Fumiaki Tomonaga (Yamaguchi Prefectural Center for Commerce and Industry) for their continuous encouragement in accomplishing this thesis. Thanks are also due to the colleague in RIPT for their helpful discussion and assistance.

Finally, I wish to thank to my family for their hearty encouragement during the course of studies.