Studies on Novel Conducting Polymers Containing Cyclopentadienylidene Moieties

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Contents

Chapter 1 Introduction

Introduction

Recently much attention has been focused on conducting polymers due to the interest as promising candidates for organic batteries, sensors, solar cells, and electronic devices as well as offering virgin territories in science.[1] Two pioneering works ignited this field. One arising in 1977 is the discovery that the conductivity of *trans*-poly(acetylene) (**1**) prepared using Sirakawa's method can be varied by doping (i.e. oxidation or reduction) over 11 orders magnitude (10^{-9}-10^{2} S cm^{-1}).[2] This achievement extremely motivated scientists to research for conducting polymers. Thereafter, poly(acetylene) has been attracting special interest from both theoretical and experimental view points because of the quasi-one dimensional structure and the electrical, optical, and magnetic behaviors which are drastically changed by small amounts of various dopants. Now doped poly(acetylene) is one of the highest conductive material (150 kS cm^{-1}).[3] The other is the oxidative electrolytic polymerization of pyrrole in 1979 which gave the highly conducting (100 S cm^{-1}) and coherent free standing films of poly(pyrrole) (**2**).[4,5] This success has given rise to the electrochemical polymerization for other aromatic compounds, which gave many useful conducting polymers, for example, poly(thiophene) (**3**),[6] poly(aniline) (**4**),[7] poly(*p*-phenylene) (**5**),[8] poly(azulene) (**6**),[9] and poly(pyrene) (**7**).[10]

Conducting polymers such as poly(pyrrole) and poly(thiophene), which can be electrochemically prepared, are the most widely investigated because their properties are electrochemically adjustable and their thin films are easily produced. Especially poly(thiophene) is one of the most widely investigated conducting polymers due to its ready modification and remarkable environmental stability in both undoped and p-doped

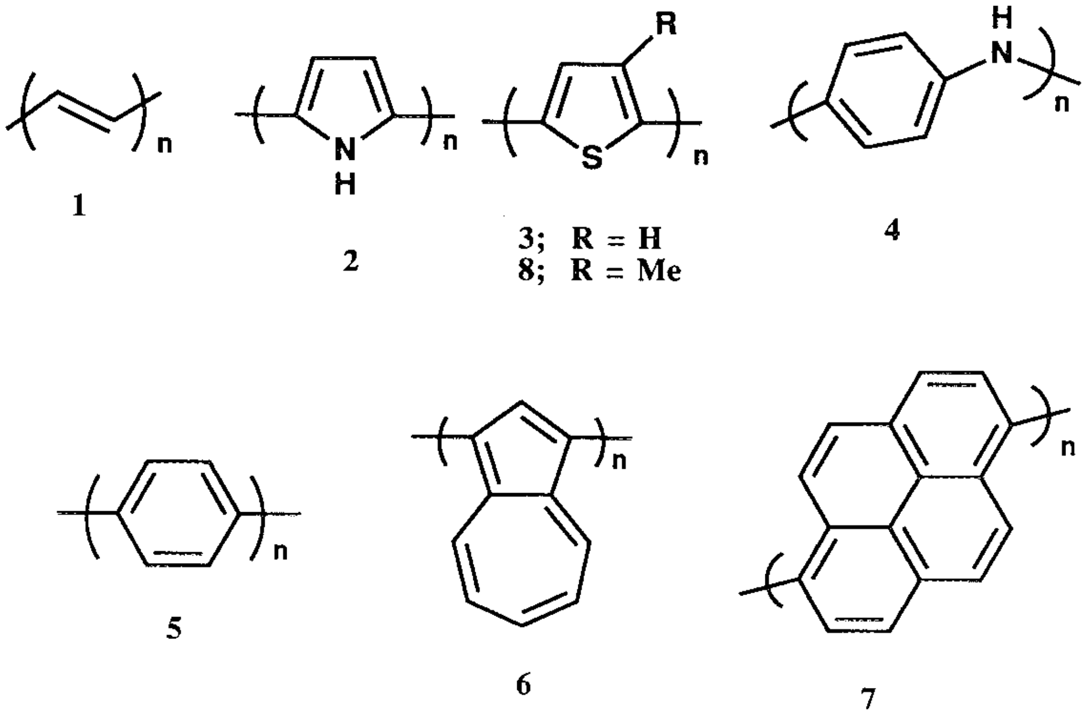


Figure 1. Molecular structures of typical conducting polymers.

Table I. Preparation Methods and Conductivities of Some Polymers

polymer	Preparation method	dopand	conductivity (S cm^{-1})
poly(acetylene) (**1**)	Sirakawa's method	H_2SO_4	4000
	Naarmann's method	I_2	170000 (6-fold extension)
poly(*p*-phenylene) (**5**)	Kovacic method	AsF_5	500 (powder)
	electrochemical polymerization	AsF_6	100 (film)
poly(pyrrole) (**2**)	electrochemical polymerization		1000 (6-fold extension)
poly(thiophene) (**3**)	electrochemical polymerization	ClO_4^-	750 (film)
poly(3-methylthiophene) (**8**)	electrochemical polymerization	ClO_4^-	2000 (film)
poly(aniline) (**4**)	electrochemical polymerization	HCl	5 (film)
poly(azulene) (**6**)	electrochemical polymerization	BF_4^-	0.02-1 (film)
poly(pyrene) (**7**)	electrochemical polymerization	ClO_4^-	1 (film)

states as well as high conductivity.[6] On the other hand, β-substituted pyrroles are difficult to synthesize.[11] Though the introduction of substituents on nitrogen is more accessible than that at the β-position, the N-substituted poly(pyrrole) derivatives have poor conductivities, for example that of poly(N-methylpyrrole) is 0.001 S cm^{-1}.[5]

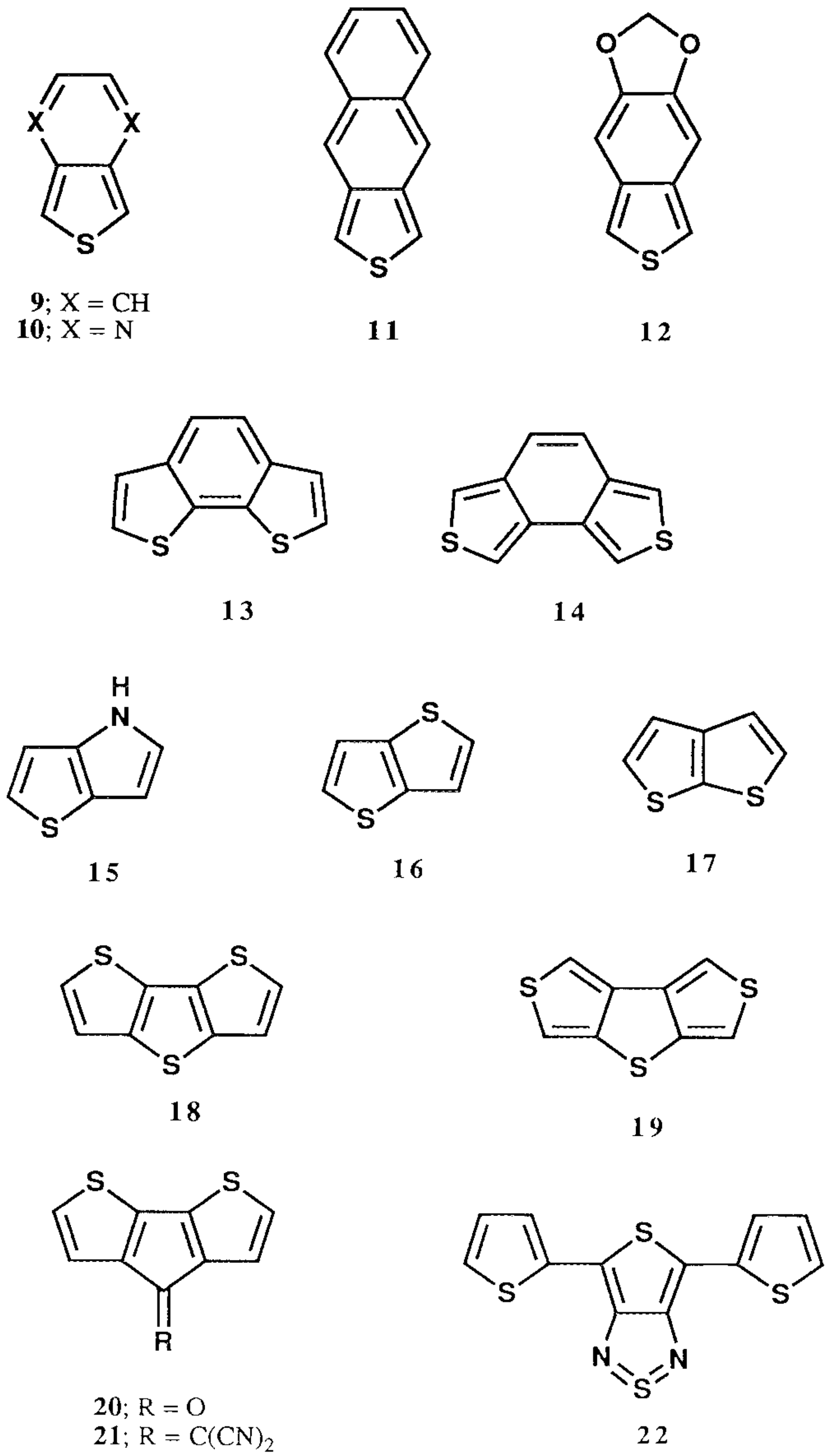
Poly(thiophene) has been prepared by two major approaches that are chemical and electrochemical polymerizations. These methods are characterized by the following fact that the chemical polymerization can provide completely defined chains and the electrochemical method produced the most extensively conjugated and the most conductive poly(thiophene) (370 S cm^{-1}).[12] Some spectroscopic data indicate that poly(thiophene) prepared by the electrochemical method has predominant α-α coupling,[13] but a nonnegligible amount of α-β coupling products is also indicated by IR and XPS data.[14] These physical analyses also show that more regular chains are formed in electrochemically polymerized poly(3-methylthiophene) (**8**) which has an extremely high conductivity (2000 S cm^{-1}).[15] On the other hand, poly(thiophene) prepared by the chemical method has a highly defined structure.[16] Catalyses for the polymerization are some palladium or nickel complexes such as $NiCl_2L_2$, $Ni(cod)_2L_2$, and $PdCl_2L_2$ (L=bipyridine or PPh_3).[17] The conductivity of 14 S cm^{-1} was reported for poly(thiophene) prepared by a nickel catalyzed Grignard coupling of 2,5-diiodothiophene.[18] On the other hand poly(pyrrole) has been generally prepared by the electrochemical method due to the high reactivity of the N-H proton.

There are two important groups in poly(thiophene) derivatives. One is poly(3-alkylthiophenes).[19] Insoluble and inprocessable characters are decisive obstructions for both the detailed characterization and application of conducting polymers, which were overcome by grafting liner alkyl chains onto polymers. Some poly(3-alkylthiophenes) can be dissolved in THF, dichloromethane, chloroform, benzene, toluene, and benzonitrile. The conductivities of these polymers are in high level (10-300 S cm^{-1}) and the polymers show high environmental stability. These additional properties increase the importance of the polymers. Recently poly(3-alkylthiophenes) with completely regioreguler head-to-tail structures were synthesized by three independent chemical polymerizations.[20,21] One of them is the reaction of 2,5-dibromo-3-alkylthiophenes with highly reactive zinc followed by the chemical polymerization with a Ni complex. The resulting poly(3-butylthiophene) shows an extremely high conductivity (1350 S cm^{-1}) by I_2 doping.[21]

The other important group is narrow band gap polymers.[22] Preparation of poly(isothianaphthene) (PITN) (polymer of **9**) in 1984 is the first attempt to get an intrinsic conducting polymer which should have a high conductivity and metallic behavior without doping. PITN shows both a narrow band gap (1.0 eV) in the neutral state and a high conductivity (50 S cm^{-1}) in the doping state.[23] It has become a template model compound for narrow band gap polymers. This work strongly stimulated the investigation of narrow band gap polymers. At first many theoretical studies were devoted to the research for narrow band gap polymers, which proposed some target polymers, for example poly(naphthothiophene) (polymer of **11**)[24] and predicted novel optical properties of narrow band gap polymers.[25] Recently several poly(thiophene) derivatives have been reported as narrow band gap polymers. Among them poly(4-dicyanomemethylen-4H-cyclopenta[2,1-b;3,4-b']dithiophene) (polymer of **21**) has the smallest optical band gap (0.7 eV) which was determined by the absorption spectrum.[26] Nowadays the research for narrow band gap polymers is one of the most active field in this area.

Purpose and Constitution of Present Thesis

Poly(heterocycles) have generated much research interest among chemists and physicists, and many theoretical researchers have designed novel polymers which have interesting electrical, magnetic, and optical properties.[24] There are, however, few studies for the modification of π-systems on the polymers.[1,6] Moreover, most of previously



9; X = CH
10; X = N

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20; R = O
21; R = $C(CN)_2$

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Figure 2. Typical thiophene derivatives which have been polymerized.

reported poly(heterocycles) have very simple structures owing to the hurdle for the modification at the β-positions which are vacant positions for substituents in polymers. On the other hand, in the field of organic conductors with a low molecular weight, many modifications have been performed to basic compounds, such as tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ).[27] These works are making such fields more active. Therefore, the preparation of new conducting polymers with better physical properties is very important for the promotion of the application as well as for the fundamental researches. It is attempted in this thesis to improve the conducting properties of conjugated polymers by the modification of monomers.

The present doctoral thesis consists of three chapters in addition to this one. Each chapter is constructed with a common style. At first preparation and properties of monomers are discussed on the basis of their molecular and crystal structures analyzed

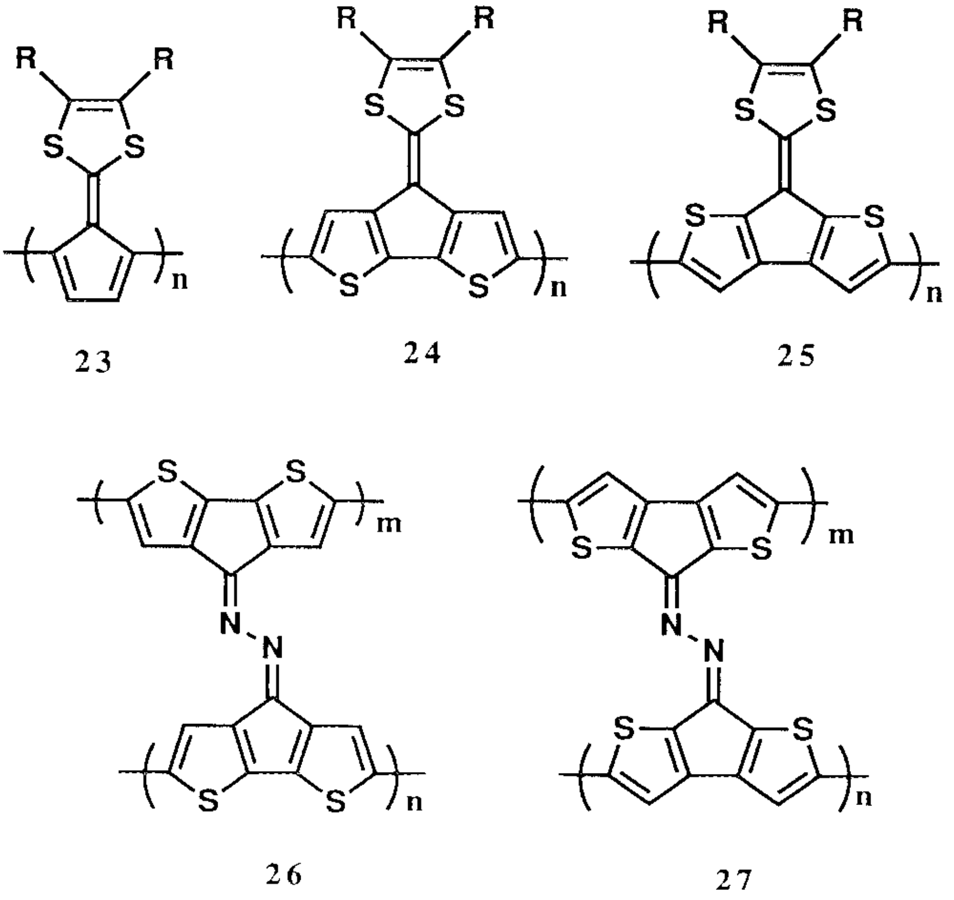

Figure 3. Novel conjugated polymers described in this thesis.

with X-ray diffractions (chapter 3 and 4), cyclic voltammograms, and spectroscopic data. Then the electrochemical polymerizations are described and the resulting polymers are characterized with their cyclic voltammetries, absorption spectra, and so on. Finally, interesting properties and observations are considered in detail with molecular orbital (MO) calculations which are also used for characterizations of molecules.

Chapter 2 deals with poly(2-(2,4-cyclopentadien-1-ylidene)-1,3-dithioles) (**23**) that is the first conducting polymer constructed with carbon five-membered rings except for poly(azulene). This polymer is also characterized by a 1,3-dithiole skeleton and the useful contribution of the 1,3-dithiole skeleton for the conductivity is discussed in this chapter. A novel synthetic route to substituted 2-(2,4-cyclopentadien-1-ylidene)-1,3-dithioles is also proposed. Moreover, the unique behavior of the polymer in their cyclic voltammograms is considered as a main subject for MO calculations.

Chapter 3 describes two groups of novel poly(thiophene) derivatives that are poly(4-(1,3-dithiol-2-ylidene)-4H-cyclopenta[2,1-b;3,4-b']dithiophenes) (**24**) and poly(7-(1,3-dithiol-2-ylidene)-7H-cyclopenta[1,2-b;4,3-b']dithiophenes) (**25**). These polymers are also characterized by 1,3-dithiole skeletons. Some fruitful influences induced by the groups are demonstrated with comparing the properties of both the monomers and polymers with ones of thiophene and poly(thiophene), respectively. In addition, the derivatives with liner alkyl chains are presented as a soluble polymer in order to prove a simple modification arisen from the facile preparation of 1,3-dithiole derivatives. A circumstantial characterization of the soluble polymer was performed by a molecular weight analysis using gel-permeation chromatography (GPC) and a ^{1}H NMR spectrum measurement. Computational investigation is used for the examination of the coplanarity between successive monomer units and the difference of absorption maxima between two groups.

In chapter 4 poly(4H-cyclopenta[2,1-b;3,4-b']dithiophen-4-one azine) (**26**) and poly(7H-cyclopenta[1,2-b;4,3-b']dithiophen-7-one azine) (**27**) are described as a novel poly(thiophene) derivatives with the four positions where the electrochemical polymerization can occur. The polymers can make at least two kinds of network structures in which adjacent chains are linked by azine groups to each other. Favorable contributions of these structures are discussed. On the other hand, electron-accepting properties of azine groups seem to make the band gaps of the polymers smaller. With this in mind, characterizations of both monomers and polymer **26** are performed. Unfortunately polymer **27** was not produced by the electrochemical method. The methyl and thiomethyl derivatives of **26** were also prepared and investigated for the comparison with the other compounds and the interest for the properties of themselves. Band gaps of the polymers are investigated with MO calculations as well as the difference of absorption maxima between two monomers.

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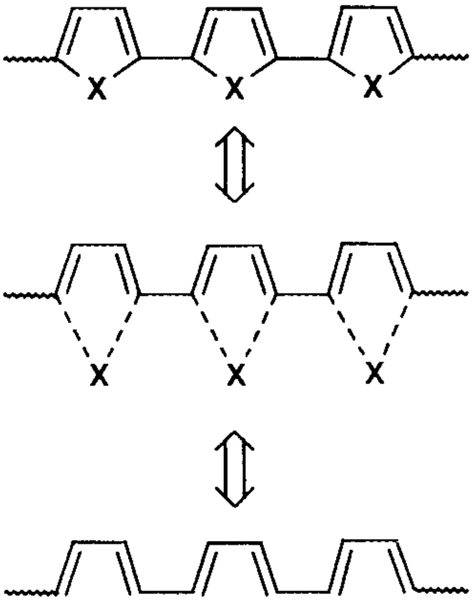
Chapter 2 Preparation and Properties of Poly(2-(2,4-cyclopentadien-1-ylidene)-1,3-dithioles)

Abstract: The author designed poly(2-(2,4-cyclopentadien-1-ylidene)-1,3-dithioles) (**1**) which consist of five-membered carbon skeletons bonded to 1,3-dithiole groups via a cross conjugation. The monomers of **1** have lower oxidation potentials on account of electron-donating properties of 1,3-dithiole skeleton. Parent polymer **1a** and its benzo derivative **1b** prepared by electrochemical polymerization were unstable to oxidation. The stability of polymer was somewhat improved by the introduction of methyl groups at the β-positions of the cyclopentadiene rings, thus the oxidation peak of the polymer was observed at a lower potential in the cyclic voltammogram. This polymer **1c** showed a cathodic peak away from an anodic peak, indicating that the oxidation of **1c** was accompanied by a large conformational change. MNDO-PM3 calculations show that the dihedral angle between the monomers is 93° in the most stable conformation of the dimer derived from **1a**, whereas that for its radical cation is 171°.

Introduction

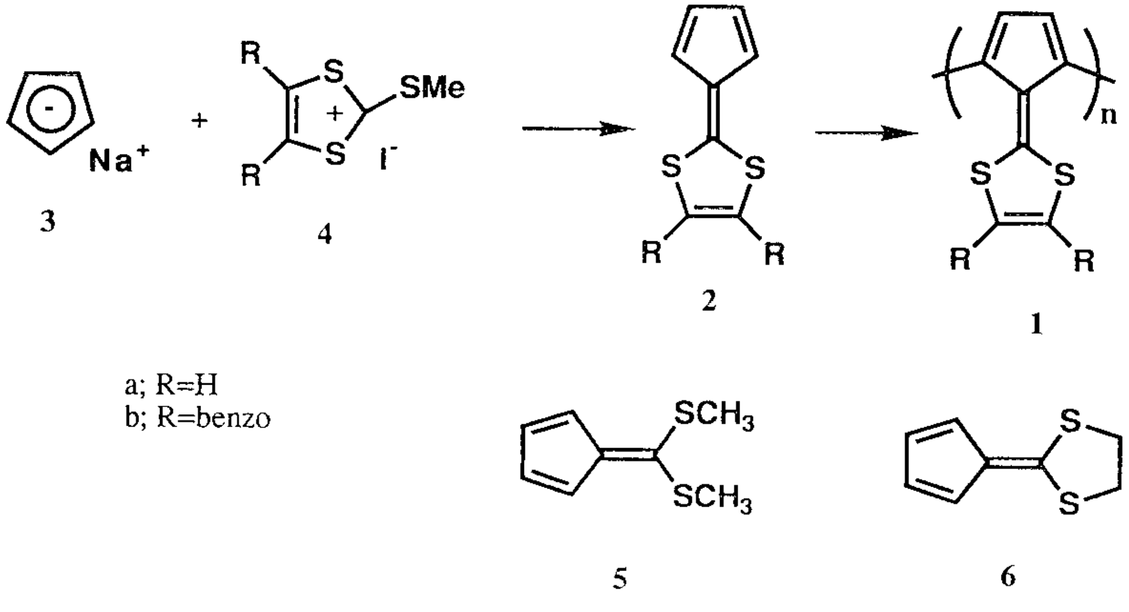
Though doped *trans*-poly(acetylene) is the highest conductive polymer (150 kS cm^{-1}),[1] its high environmental instability limits the application of the polymer.[2] Many derivatives such as poly(heptadiine)[3] have been synthesized in order to overcome this problem. On the other hand, polymers consisting of five-membered heterocyclic compounds are considered as poly(acetylene) analogues, because their backbones consist of the structure of *cis*-poly(acetylene). The heteroatoms are expected to give a perturbation to this structure and its properties. These polymers such as poly(pyrrole) and poly(thiophene) have been found to show high conductivities in the doping states as well as high environmental stability of both its doped and undoped states.[2a,4] Therefore it seems very interesting to introduce a cross-conjugation system instead of a heteroatom. Recently, valence effective Hamiltonian (VHF) calculations performed for poly(fulvene) (PF) predicted that PF should have unusual properties compared with poly(pyrrole) and poly(thiophene), for example the band gap (E_g) of PF is smaller than that of poly(thiophene).[5] In this connection, the author designed poly(2-(2,4-cyclopentadien-1-ylidene)-1,3-dithioles) (**1**) which consist of carbon five-membered rings attached to 1,3-dithiole skeletons through cross conjugations. Introduction of 1,3-dithiole groups into a conducting polymer brings some advantages for four reasons.[6] (i) They induce strong intermolecular interactions through chalcogen-atom contacts as observed in the tetrathiafulvalene (TTF) series.[7] This may result in strong interchain interactions which are useful for the enhancement of charge transport between adjacent chains as well as for the control of structural order.[8] (ii) The extended π-conjugation and polarization inherent to 1,3-dithiole groups may lead to smaller bandgaps which are favorable for intramolecular electron movement.[9] (iii) The p-doping, conducting states may be stabilized by aromatic 1,3-dithiolium ions formed by oxidation, which is important for preservation of conductivities. (iv) Substituents can be easily introduced to 1,3-dithiole rings in order to modify the characters of polymers.[10] Preparation and properties of **1** and their monomers **2** are described here.



Results and Discussion

Preparation of Poly(2-(2,4-cyclopentadien-1-ylidene)-1,3-dithioles)

2-(2,4-Cyclopentadien-1-ylidene)-1,3-dithioles (**2a,b**) were synthesized by a reported method[11] (Scheme 1). In the paper it was also reported that the introduction of a 1,3-dithiole ring increases the dipole moment, which was shown by a comparison of their absorption spectra with those of analogous compounds (Table I). Cyclic voltammograms of **2a,b** were measured using a Pt disk and SCE as a working and reference electrode, respectively, in MeCN containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte, and with a scanning rate of 100 mV s^{-1}. They showed irreversible oxidation waves at remarkably lower potentials than that of thiophene (1.95 V vs SCE)[12] due to the 1,3-dithiole skeleton. Their anodic peak potentials (E_{pa}) are summarized in Table I.



Scheme 1

Table I. Absorption maxima and oxidation potentials of 2-(2,4-cyclopentadien-1-ylidene)-1,3-dithioles and analogous compounds

Compd	$\lambda_{max}(\log \varepsilon)^a$	E_{pa}^b
5	353 (-)	-
6	367 (4.07)	-
2a	405 (4.47)	1.13
2b	418 (4.39)	1.12
2c	392 (4.45)	0.85

[a] In $CHCl_3$. [b] 0.1 mol dm^{-3} n-Bu_4NClO_4 in MeCN, Pt electrode, V vs SCE, scan rate 100 mV s^{-1}.

Polymerizations of **1a,b** were performed by the electrolytic oxidation of the corresponding monomers **2a,b** using a Pt disk or indium-tin oxide (ITO), and SCE as a working and reference electrode, respectively, in 0.1 mol dm^{-3} TBAP/MeCN solution, and with a scanning rate of 100 mV s^{-1}. No polymerization occurred under these conditions. The polymerization was also tried using other supporting electrolytes such as n-Bu_4NBF_4, n-Bu_4NPF_6, or n-Et_4NOTs. When CF_3CO_2Na and ITO were used as a supporting electrolyte and working electrode, respectively, an increase in both the anodic and cathodic current values was observed in a low potential region with the repetition of the scan as shown in Figure 1. However, the current value of the oxidation wave of the monomer **2a,b** decreased in the successive cycles. These results can be explained by considering that electrochemically low active species deposited on the surface of the electrode. After several cycles the current value of the new peak also decreased and a small amount of black film was formed on the electrode. In the voltammograms of the polymers **1a,b** measured in a monomer free electrolyte, a clear redox peak was not observed. The resulting polymers may be so unstable to oxidation that they decomposed during their polymerization.

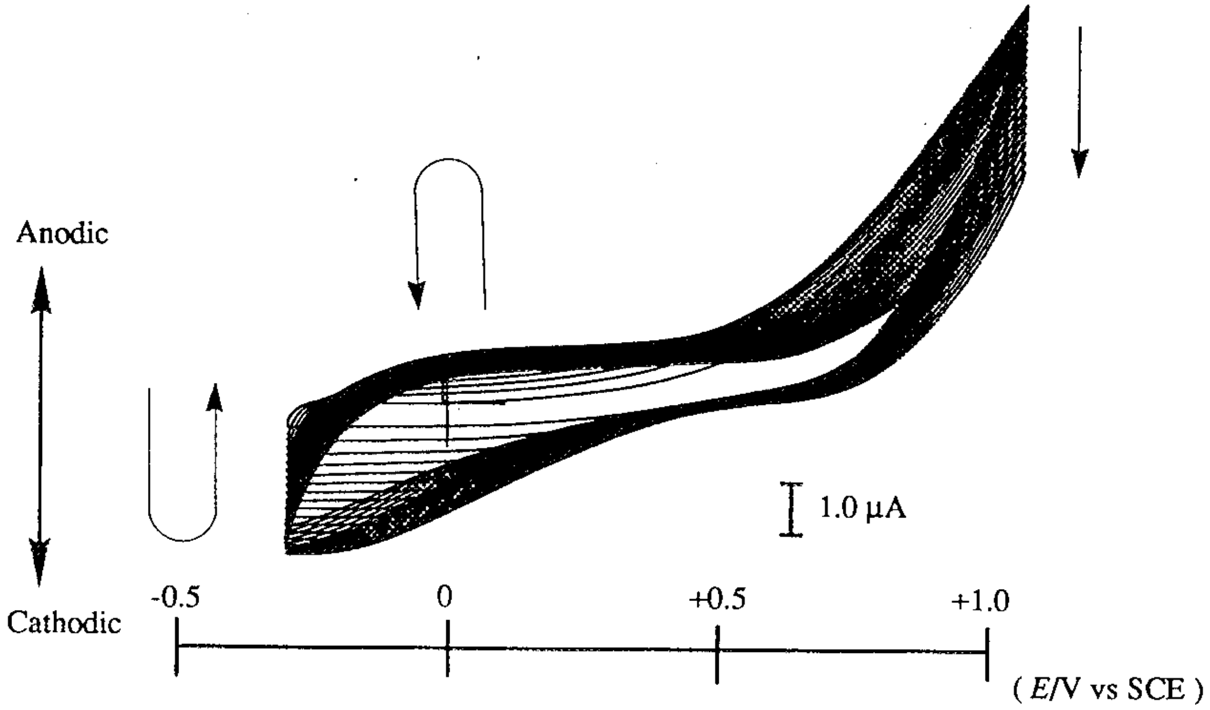
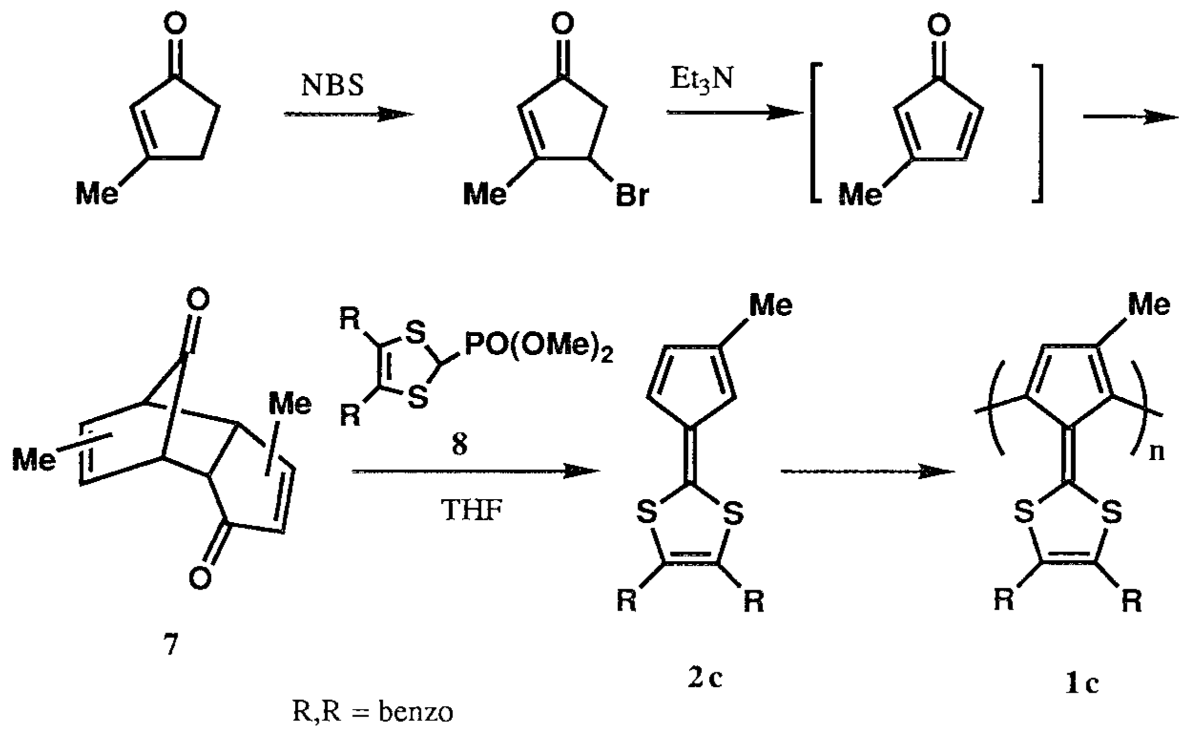


Figure 1. Successive cyclic voltammograms of **2a** in MeCN containing 0.1 mol dm^{-3} CF_3CO_2Na, scan rate 100 mV s^{-1}. ITO and SCE were used as a working and a reference electrode, respectively.

Preparation and Properties of Poly(2-(3-methyl-2,4-cyclopentadien-1-ylidene)-1,3-benzodithiole)

In order to stabilize the radical cation of **1a** and obtain the polymer with more regular structure like poly(3-methylthiophene),[13] methyl derivative **2c** was prepared by the Wittig-Hornor reaction of 3-methyl-2,4-cyclopentadiene-1-one dimer (**7**)[14] with the carbanion derived from **8**[15] in THF followed by a spontaneous retro-Diels-Alder reaction in 88% yield (Scheme 2). Derivative **2c** has an absorption maximum at 392 nm in the UV spectrum, which corresponds to a red-shift of 26 nm compared to **2b** due to a reduced polarization (Table I). Cyclic voltammograms of **2c** were recorded under the condition as described for **2a,b** (Figure 2). The oxidation potential of **2c** (0.85 V vs SCE) was lower than that of **2b** by 0.27 V due to the electron donating property of the



Scheme 2

methyl group. Electrochemical polymerization of **2c** was performed under the conditions as described above. In this case, the peak current increased in the successive cycles and a new peak appeared at a lower potential. This indicates a deposition and the growth of an electrochemically active polymer on the surface of the electrode. It is very interesting that the cathodic peak appeared away from the anodic peak. This observation indicates that a large structural change occurred with the oxidation of the polymer. Though the cyclic voltammogram of the polymer measured in a monomer free electrolyte showed an anodic and a cathodic peaks at +0.65 and -0.14 V vs SCE, respectively, at the first scan, both the anodic and the cathodic peak currents decreased in the successive scans (Figure 3(a)). After several cycles both peaks disappeared and a new anodic peak appeared at +0.83 V vs SCE (Figure 3(b)). These facts indicate that an oxidation process of **1c** is accompanied by a structural change. The current value of this new peak gradually decreased due to the instability of the polymer to oxidation. The oxidation potentials of

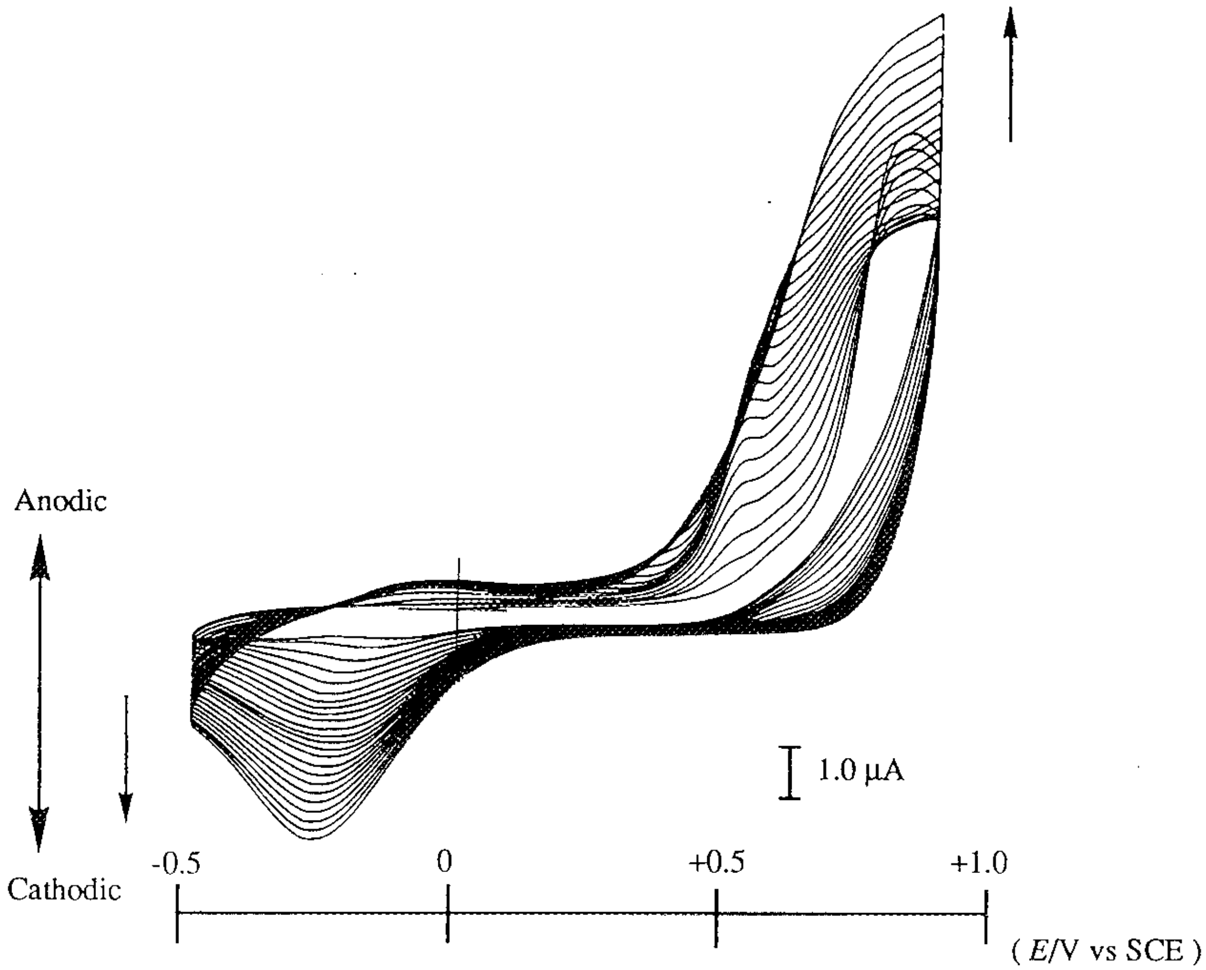


Figure 2. Successive cyclic voltammograms of **2a** in MeCN containing 0.1 mol dm^{-3} TBAP, scan rate 100 mV s^{-1}. A platinum disk and SCE were used as a working and a reference electrode, respectively.

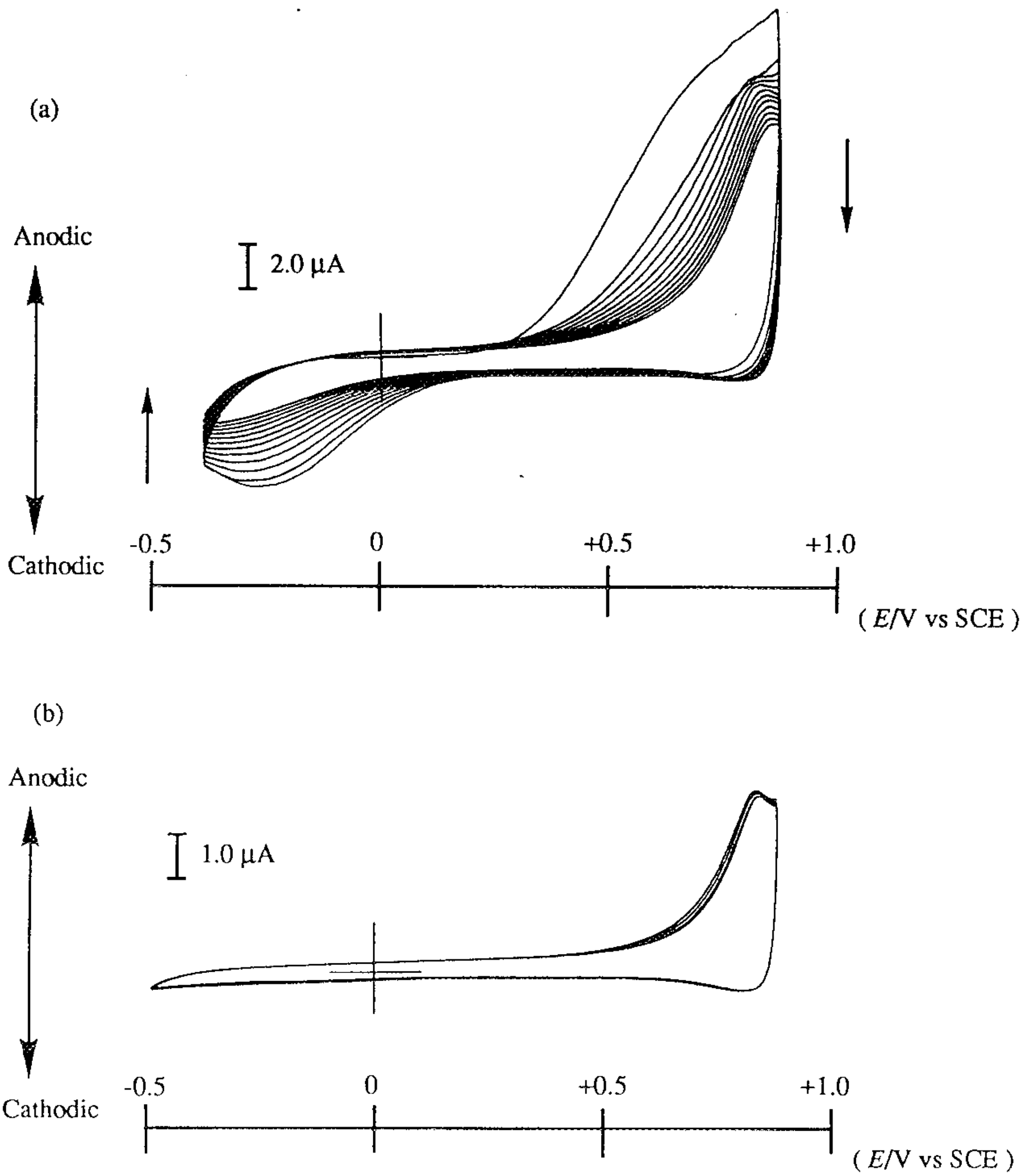
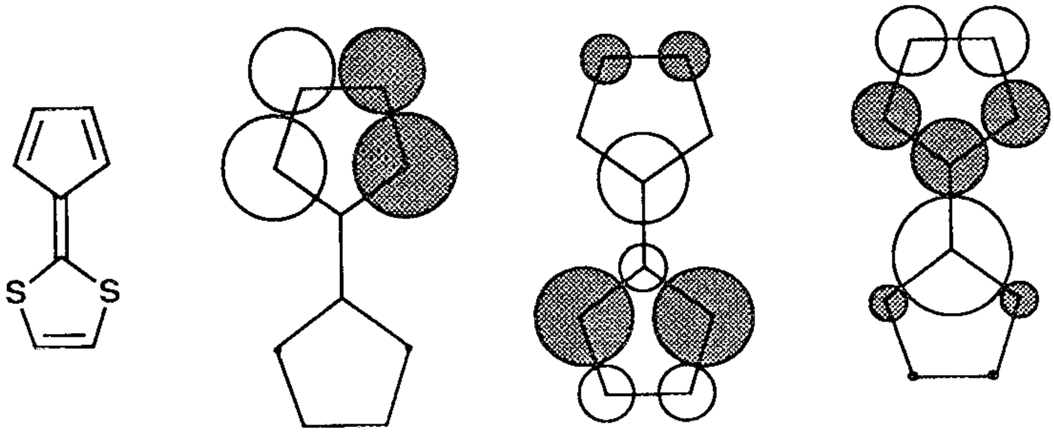


Figure 3. Successive cyclic voltammograms of **1c** measured in a monomer-free MeCN / 0.1 mol dm^{-3} TBAP under an argon atmosphere. A platinum disk and SCE were used as a working and a reference electrode, respectively. (a) From the first scan. (b) After several scans.

1c is lower than one of poly(thiophene) (+1.03 V vs SCE)[11] but higher than poly(3-methylthiophene) (ca. +0.55 V vs SCE).[16] The introduction of methyl group at the β-position did not prevent the polymerization, which show that the polymerization predominantly took place at the α-positions.

Results of Molecular Orbital Calculations

MNDO-PM3 calculations[17] for **2a** show that there are no atomic orbital (AO) coefficients at the α-positions and moderate ones at the β-positions in the HOMO (Figure 4). These results are consistent with the observation that the introduction of a methyl group at the β-position causes a large decrease in the oxidation potential. On the other hand, there are large AO coefficients at the α-positions besides the β-positions in the



next HOMO -9.29

HOMO -8.39

LUMO -1.17

(kcal mol^{-1})

Figure 4. AO coefficients in the next-HOMO, HOMO, and LUMO of **2a** calculated by MNDO-PM3 method. The radii of circles are approximately proportional to the magnitude of the coefficients.

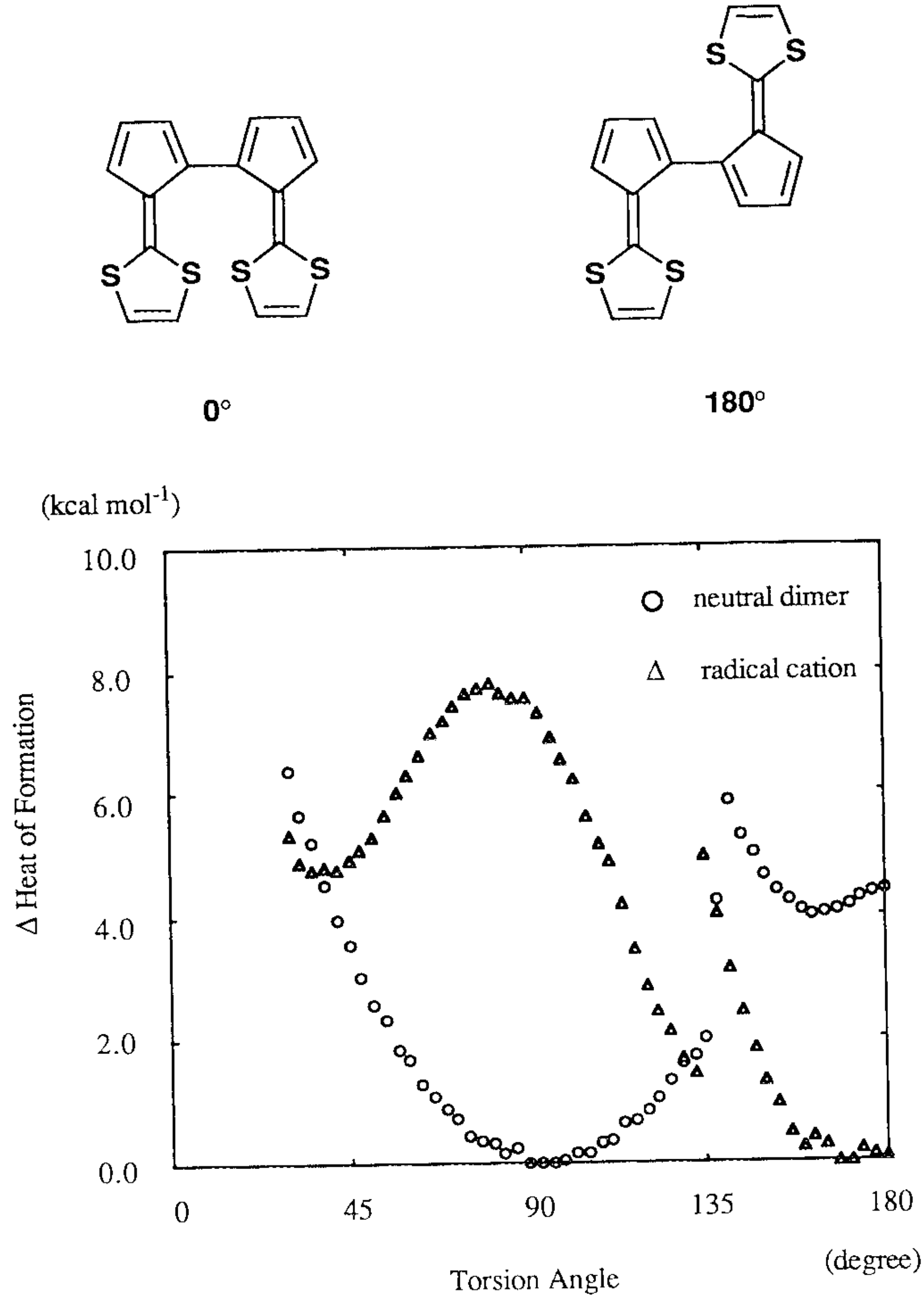
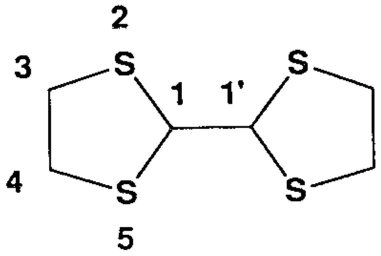


Figure 5. MNDO-PM3 torsional potential diagram of the neutral dimer derived from 2a and its radical cation.

next-HOMO. Methyl group at the β-position did not prevent the polymerization, namely the polymerization predominantly took place at the α-position. Therefore the next-HOMO of **2a** extremely contributes to the SOMO of the radical cation of **2a** which is a intermediate of the polymerization.

A coplanarity between monomer units is important for the delocalization of polarons and bipolarons.[4b,18] The reaction path calculations for the rotation of the intermonomer C-C bond were performed on the dimer derived from **2a** and their radical cation (Figure 5). The MNDO-PM3 calculations were carried out every 3° from 30° to 180° with optimization. The calculations indicate that there is an energy minimum at 93° for the neutral dimer. The energy gradually rises toward the coplanar conformation except for the range 135°-165°. In contrast, the calculations on the radical cation of the dimer denote a potential maximum at 84°. The most stable conformation was found around the torsion angle of 180° where the rings are alternate. The exceptionally drastic changes of the energy exist between 135° and 165° in both the neutral dimer and its radical cation, since there exists a contact which is shorter than the sum of the van der Waals radii. The same contact was found around 0° between other atoms. These results support that the conformation of the polymer remarkably changes at the oxidation. The energy of about 7.8 kcal mol^{-1} (0.08 eV mol^{-1}) is gained by the variation of the conformation in the radical cation. On the other hand, the same calculations on bithiophene indicated a shallow potential minimum at 30° with the energy barrier height of only 0.65 kcal mol^{-1}. These results suggest that polymers **1** have more steric hindrance between the monomer units than poly(thiophene) and it is difficult to take a planar conformation in the neutral states. These calculation results are in good agreement with the X-ray diffraction data which indicate that 4-(1,3-dithiol-2-ylidene)-2,5-cyclopentadiene-1,2-dicarbonitrile) dimer have large dihedral angle between two monomer units.[19] In this paper it was also reported that the S2-C1 and C1-C1' distance are charge dependance in TTF. The charged species have longer C1-C1' and shorter C1-S2 bonds than ones of neutral TTF. The similar change seems to act in **2a** and corresponding polymer. Therefore the charged polymer derived from **2a** has a smaller steric congestion than one of neutral polymer.

Table II. Bond Length (Å) for various TTF compounds[a]



	1-1'	1-2	2-3	3-4	
neutral	1.349	1.757	1.726	1.314	Exptl.
$HgCl_3$	1.41	1.72	1.71	1.31	Exptl.
$Cl_{0.67}$	1.38	1.72	1.719	1.32	Calc.
dication	1.45	1.701	1.755	1.328	Exptl.

[a] ref. 19.

Conclusion

Novel conducting polymers poly(2-(2,4-cyclopentadien-1-ylidene)-1,3-dithioles), were electrochemically prepared. The formed polymer had a low stability to oxidation so that it could not be characterized in detail. In order to improve the stability of the polymer, a methyl group was introduced onto the cyclopentadiene ring. The resulting polymer was somewhat stable to oxidation so that the oxidation peak was obviously observed in the cyclic voltammetry. The large separation between anodic and cathodic peak potentials show that a large conformational change occurred in the redox process of the polymer. On the other hand, investigation of the properties of the monomers revealed that the introduction of a 1,3-dithiole group leads to a low oxidation potential and a high polarization. MO calculations indicate a large steric interaction between monomer units in the neutral dimer and such interaction is not found in the corresponding radical cation. These results support that the conformational change occurs in the transformation to the radical cation state from the neutral one.

Experimental

General. Melting points are uncorrected. Infrared spectra were taken in KBr pellets. ^{1}H NMR spectra were recorded at 400 MHz. Chemical shifts are reported in ppm from TMS as an internal standard and are given in δ units. Mass spectra were obtained in the EI mode at 70 eV unless indicated otherwise.

2-(3-Methyl-2,4-cyclopentadien-1-ylidene)-1,3-dithiole. To the carbanion prepared from **8** (524 mg, 2.0 mmol) and n-BuLi in hexane (1.2 mmol) in dry THF (10 ml) at -78 °C under argon was added **7** (94 mg, 0.5 mmol). This solution was stirred for 15 min at -78 °C. After a cooling bath was removed, the solution was further stirred for 20 min. The solvent was evaporated in vacuo. The resulting residue was diluted with water and extracted with CH_2Cl_2. The extract was washed with brine and water and then dried over anhydrous $MgSO_4$. After evaporation of the solvent, the resulting solid was purified by recrystallization from EtOAc to give **2c** (101 mg) as orange crystals in 88 % yield.

2c: orange crystals, mp 164 °C; ^{1}H NMR ($CDCl_3$) δ 2.04 (bs, 3 H, Me), 6.01 (m, 1 H), 6.18 (dd, J = 1.5, 4.9 Hz, 1 H), 6.31 (dd, J = 2.1, 4.9 Hz, 1 H), 7.19 (m, 2 H), 7.33 (m, 2 H); IR (KBr) 2919, 1572, 1546, 784, 739 cm^{-1}; UV ($CHCl_3$) λ_{max} 244 nm (log ε 4.22), 328 (3.67, sh), 392 (4.45); MS m/z (relative intensity) 230 (M^+, 79), 229 (100), 197 (11), 121 (11). Anal. Calcd. for $C_{13}H_{10}S_2$: C, 67.82; H, 4.38. Found: C, 67.71; H, 4.54.

Electrochemical Measurements. All cyclic voltammetries were carried out with a three-component cell in distilled MeCN containing 0.1 mol dm^{-3} TBAP at a scan rate of 100 mV s^{-1}. The solution was degassed by argon bubbling before an electrochemical measurement which was performed under an argon atmosphere. A Pt disk, Pt wire, and SCE electrode were used as a working, counter, and reference electrode, respectively. ITO electrode was also used as a working electrode.

The polymers for the measurement of cyclic voltammetries were prepared by a cyclic potential-sweep technique using the above conditions. The resulting polymers on the electrode were thoroughly washed with MeCN. Cyclic voltammograms of polymers were then recorded in monomer free electrolytes under the same conditions.

Computational Studies. MNDO-PM3 calculations were performed by using version 6.10 of the MOPAC program.[20] These calculations were carried out using the Sony-Tektronix CAChe system.

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Chapter 3 Preparation and Properties of Novel Poly(thiophenes) Containing 1,3-Dithiol-2-ylidene Moieties

Abstract: 4-(1,3-Dithiol-2-ylidene)-4H-cyclopenta[2,1-b;3,4-b']dithiophenes (**1**) and 7-(1,3-dithiol-2-ylidene)-7H-cyclopenta[1,2-b;4,3-b']dithiophenes (**2**) were prepared by Wittig-Horner or Wittig reactions. The X-ray structural analyses of the parent compounds **1a** and **2a** reveal that both molecules have planar structures with short intermolecular S···S contacts and **2a** additionally has short intramolecular S···S contacts. They have low oxidation potentials and absorptions in a long wavelength region due to the 1,3-dithiole skeleton. Electrochemical oxidation of **1** and **2** afforded the corresponding polymers **3** and **4**, which have low oxidation potentials. Electrochemically dedoped films of **3** and **4** have interband absorptions at 610-690 nm and 420-590 nm, respectively, in their electronic spectra. Some films of **3** and **4** exhibited high electrical conductivities with doping, for instance **3c**$\cdot(PF_6^-)_x$, 33 S cm^{-1} and **3e**$\cdot(BF_4^-)_x$, 52 S cm^{-1}. Derivatives **3f-h**, containing linear alkyl chains, were synthesized in order to enhance solubilities in organic solvents and were found to be somewhat soluble in THF and chloroform. Dedoped **3g** showed broad peaks in the ^{1}H NMR spectrum, assigned to the alkyl protons. MNDO-PM3 calculations showed that the torsion angles between the neighbor monomer fragments in the dimers and trimers of **1a** and **2a** are about 30°. However, the oligomers derived from **1a** have more extended conjugated systems than those from **2a**, which was indicated by INDO/1 calculations.

Introduction

Recently, much work has been devoted to the development of conducting polymers on account of their novel electrical, electrochemical, and optical properties.[1,2] Poly(thiophene) is one of the most widely investigated conducting polymers due to its ready modification and stability in both undoped and doped states.[2,3,4] Many poly(thiophene) derivatives have been prepared[4] although their conductivities are rather low compared to that of the parent poly(thiophene), except for a few derivatives such as poly(isothianaphthene) (PITN) reported by Wudl et al.[5] Two strategies have been considered to improve the conducting properties. One is to make the polymer structure more defined,[3] and the other is to modify the structure of the monomer.[4] In this connection, we decided to introduce 1,3-dithiole groups into a conductive polymer for four reasons which are explained in Chapter 2. In Chapter 2 the advantage of the introduction of 1,3-dithiole skeletons was experimentally proved, but the polymer, poly(2-(2,4-cyclopentadien-1-ylidene)-1,3-dithiole), was unstable. The extension of conjugation system seems to overcome this problem. Therefore, we have designed 4-(1,3-dithiol-2-ylidene)-4H-cyclopenta[2,1-b;3,4-b']dithiophenes (**1**) and 7-(1,3-dithiol-2-ylidene)-7H-cyclopenta [1,2-b;4,3-b']dithiophenes (**2**) and prepared the corresponding conducting polymers **3** and **4** by an electrochemical method. In these polymers, the 1,3-dithiole rings are located such that no significant steric interactions occur. It is important to prevent steric congestion between contiguous monomer units.[6] Furthermore, the intramolecular short S···S contacts expected in **2** and **4** may be useful for the delocalization of electrons. We report here the preparation and properties of the monomers and their polymers.

Results and Discussion

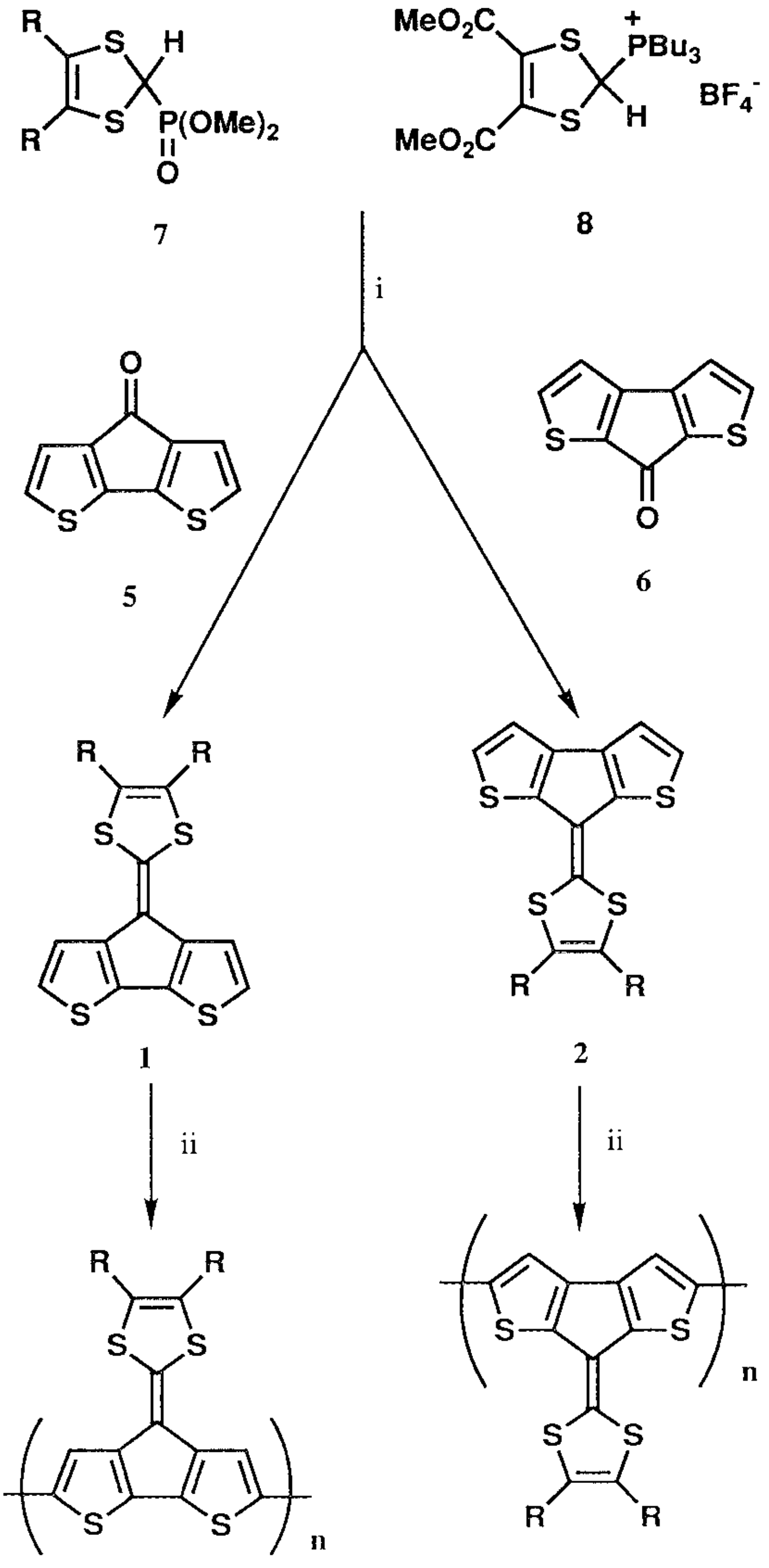
Preparation and Properties of the Monomers

Ketones **5** and **6**,[7] phosphonate esters **7**,[8] and the Wittig reagent **8**[9] were synthesized by reported methods. 1,3-Dithiole compounds **1a-d** were prepared in 64-95% yields by a Wittig-Horner reaction of **5** with carbanions derived from **7**. Similarly, compounds **2a-d** were prepared from the corresponding ketone **6** in 72-80% yields (Scheme I). Dicarbomethoxy derivatives **1e** and **2e** were obtained by a Wittig reaction of

Table I. Properties of 1,3-Dithiole Compounds **1** and **2**

compd	R	yield/%	mp/°C	λ_{max}/nm[a]	E_{pa}/V vs SCE[b]
1a	H	65	171-173	411	+0.87
1b	Me	71	223-224	419	+0.83 (+0.78[c])
1c	benzo	89	212-213	400	+0.92
1d	SMe	98	167-168	411	+0.87
1e[d]	CO_2Me	41	223-225	389	+1.02
1f	$S(CH_2)_3CH_3$	78	71-72	412	+0.88 (+0.91[c])
1g	$S(CH_2)_5CH_3$	96	oil	412	+0.87 (+0.97[c])
1h	$S(CH_2)_9CH_3$	64	54-56	412	+0.86 (+0.91[c])
2a	H	75	137	420	+0.83
2b	Me	80	277	430	+0.78
2c	benzo	80	215-217	414	+0.97
2d	SMe	72	155-156	427	+0.90
2e[d]	CO_2Me	38	213-215	407	+1.09

[a] Measured in EtOH (**1a-f**), n-hexane (**1g,h**), and CH_2Cl_2 (**2a-e**). [b] Measured by cyclic voltammetry in PhCN, 0.1 mol dm^{-3} TBAP, scan rate 100 mV s^{-1}, Pt electrode. [c] Measured in EtCN. [d] Irreversible reduction waves with peak potentials (E_{pc}) of -1.32 V (**1e**) and -1.33 V (**2e**) vs SCE.



a: R=H
b: R=Me
c: R=benzo
d: R=SMe
e: R=CO_2Me
f: R=$S(CH_2)_3CH_3$
g: R=$S(CH_2)_5CH_3$
h: R=$S(CH_2)_9CH_3$

Scheme I *Reagents* : i, n-BuLi, THF; ii, electrochemical polymerization

8 with **5** and **6** in 41 and 38% yields, respectively. Their properties are summarized in Table I. Their absorption maxima are observed at longer wavelengths than that of TTF,[10] and introduction of electron donating groups makes the absorptions red-shifted, suggesting that some polarization exists in **1** and **2**.

The X-ray structural analysis of **1a** reveals that there are two crystallographically independent molecules (Molecule I and Molecule II) which are almost planar (Figure 1). The crystal structure is shown in Figure 2, where three intermolecular S···S contacts (3.43, 3.43, and 3.51 Å), which are shorter than the sum of the van der Waals radii (3.70 Å), are observed between the thiophene rings of Molecules II. In the crystal, both Molecules I and II are uniformly stacked along the c axis in a dimeric structure as shown in Figure 2. Distances between the molecular planes in Molecules II are 3.63 Å in the dimer and 3.97 Å between the dimers. On the other hand, the X-ray structural analysis of **2a** reveals that the molecule is almost planar and there are two intramolecular S···S contacts (3.39 Å and 3.38 Å) which are shorter than the sum of the van der Waals radii, as shown in Figure 3. Such short contacts may facilitate the delocalization of electrons. The crystal structure is shown in Figure 4, wherein a short intermolecular S···S contact (3.60 Å) is observed between the 1,3-dithiole rings. The molecules of **2a** are uniformly stacked along the b axis with good overlap as shown in Figure 3. The distance between the molecular planes is 3.57 Å.

Cyclic voltammograms for **1a**-**e** and **2** were measured using a Pt disk as a working electrode, in PhCN containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte, and with a scanning rate of 100 mV s^{-1}. They revealed irreversible oxidation waves (Figures 5 and 7). Their anodic peak potentials of these compounds (E_{pa}) are summarized in Table I. The compounds **1** have similar E_{pa} values to the corresponding **2**. These values are significantly lower than that of bithiophene (+1.44 V vs SCE).[11] This fact can be attributed to the electron donating ability of the 1,3-dithiole rings. In both **1** and **2**, the E_{pa} are strongly dependent on the substituents, indicating that HOMOs in each molecule have large atomic orbital (AO) coefficients at the carbon atoms bearing the substituents. This shows that the electronic

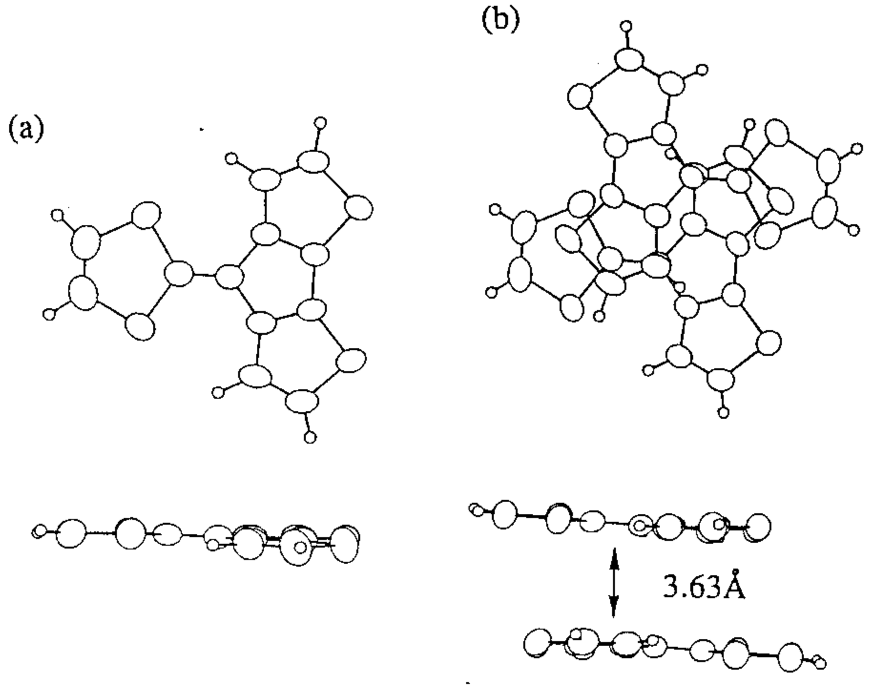


Figure 1. Molecular structures and overlap mode of **1a**. (a) Molecule I, (b) Molecule II.

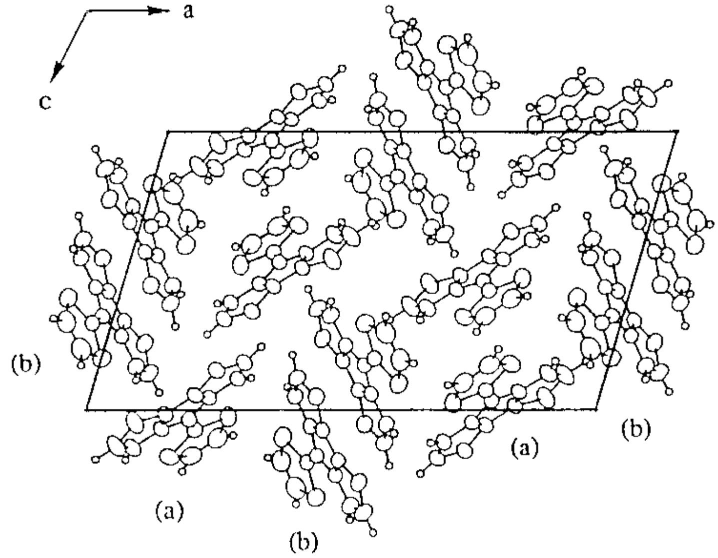


Figure 2. Crystal structure of **1a**. (a) Molecule I, (b) Molecule II.

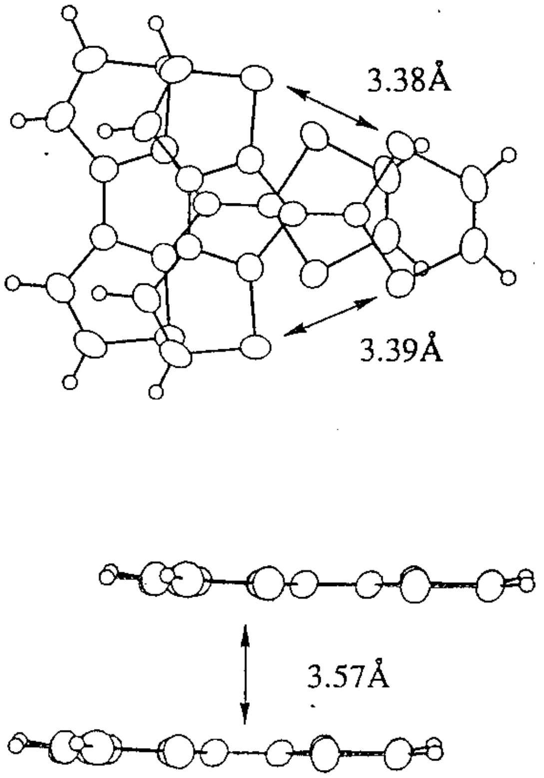


Figure 3. Molecular structure and overlap mode of **2a**.

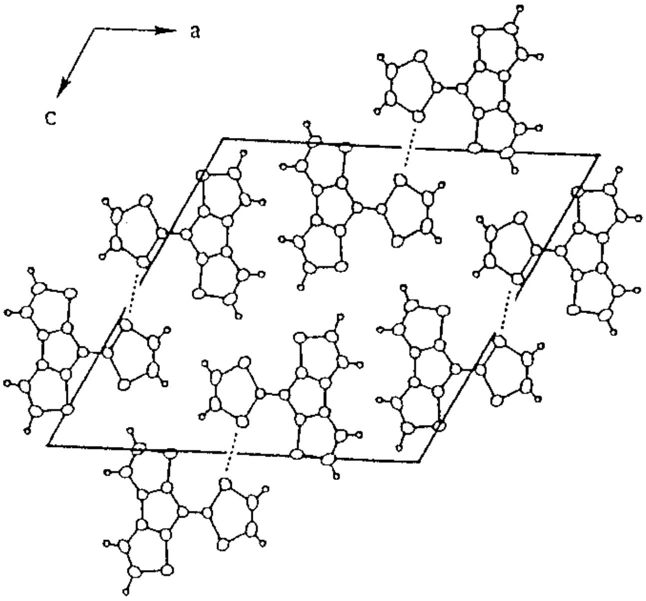


Figure 4. Crystal structure of **2a**. Broken lines; S···S interactions [3.603 (2) Å].

state can be easily modified by the introduction of substituents onto the 1,3-dithiole ring. Moreover, dicarbomethoxy derivatives **1e** and **2e** showed irreversible reduction waves with peak potentials (E_{pc}) of -1.32 V and -1.33 V vs SCE, respectively.

Preparation and Properties of Polymers

Polymers **3a**, **c-e** and **4** were prepared by the electrolytic oxidation of the corresponding monomers **1** and **2** using a Pt disk or indium-tin oxide (ITO) as a working electrode in 0.1 mol dm^{-3} TBAP/PhCN solution (Figures 5 and 7). For **3b**, EtCN was used as a solvent since PhCN yielded none. The peak current increased in the successive cycles and a new peak appeared at lower potentials as shown in Figures 5 and 7, indicating the deposition and growth of polymers on the surface of the electrode. The E_{pa} values shifted gradually to higher potentials as the thickness of the polymer film increased. This is attributable to the IR drop across the film. The oxidation potentials of polymers **3a**-**e** and **4**, summarized in Table II, were measured in monomer free electrolytes. They are remarkably lower than that of poly(thiophene) (+1.03 V vs SCE).[11] Cyclic voltammograms of **3a** and **4a** measured at various scan rates are shown in Figures 6 and 8. They showed reversible peaks due to the p-doping. The anodic peak current (i_{pa}) in **3a** is proportional to the scan rate in the potential range of -1.0 V to +1.0 V vs SCE as shown in Figure 6, indicating that the electrode reactions of the films are phenomenologically equivalent to that of a surface-attached redox species.[12] On the other hand, the dependence of the i_{pa} of **4a** on the scan rate is somewhere between linear and second order, in the potential range of -1.0 V to +1.0 V vs SCE. After several repeated scans, the i_{pa} of **3a** was unchanged, but that of **4a** was slightly decreased, indicating that polymer **4a** is somewhat sensitive to oxidation.

The FT-IR spectra of the electrochemically dedoped film, and doped films of **3** and **4** showed the characteristic peaks of monomers such as those around 1500 cm^{-1} due

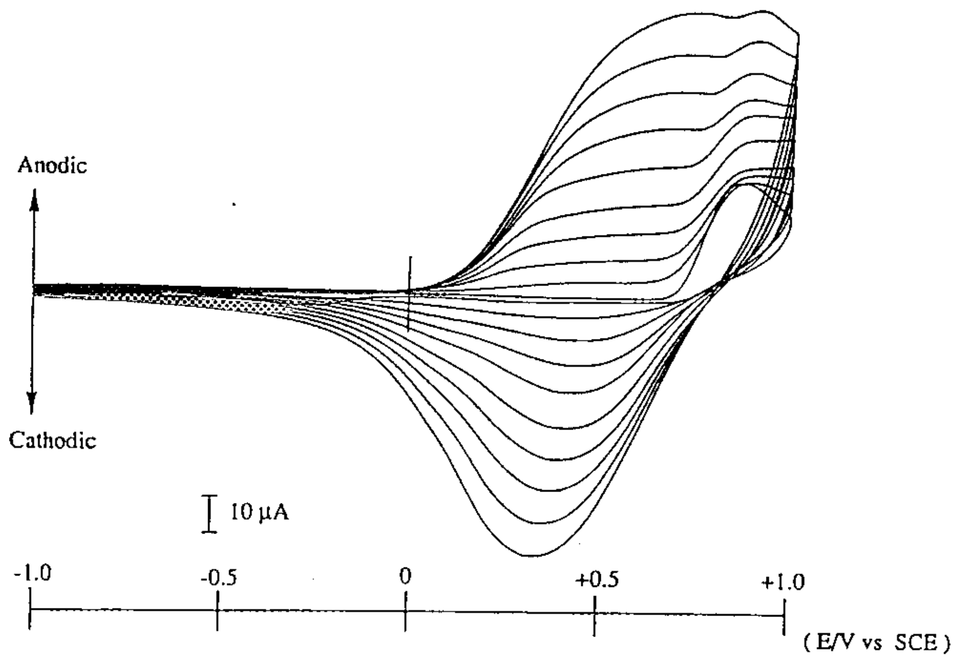


Figure 5. Successive cyclic voltammograms of **1a** in PhCN containing 0.1 mol dm^{-3} TBAP, scan rate 100 mV s^{-1}. They were recorded every five cycles. A platinum disk and SCE were used as a working and a reference electrode, respectively.

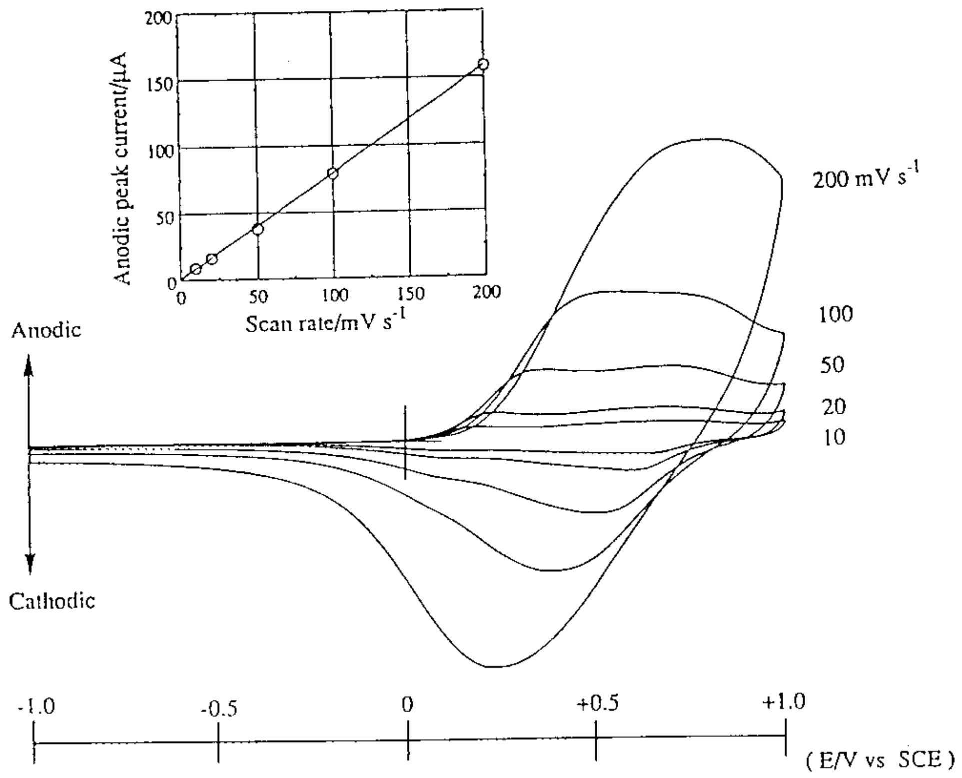


Figure 6. Cyclic voltammograms of **3a** measured in a monomer-free PhCN / 0.1 mol dm^{-3} TBAP at various scan rates under an argon atmosphere. A platinum disk and SCE were used as a working and a reference electrode, respectively. The insert shows the dependence of *i*pa on scan rate.

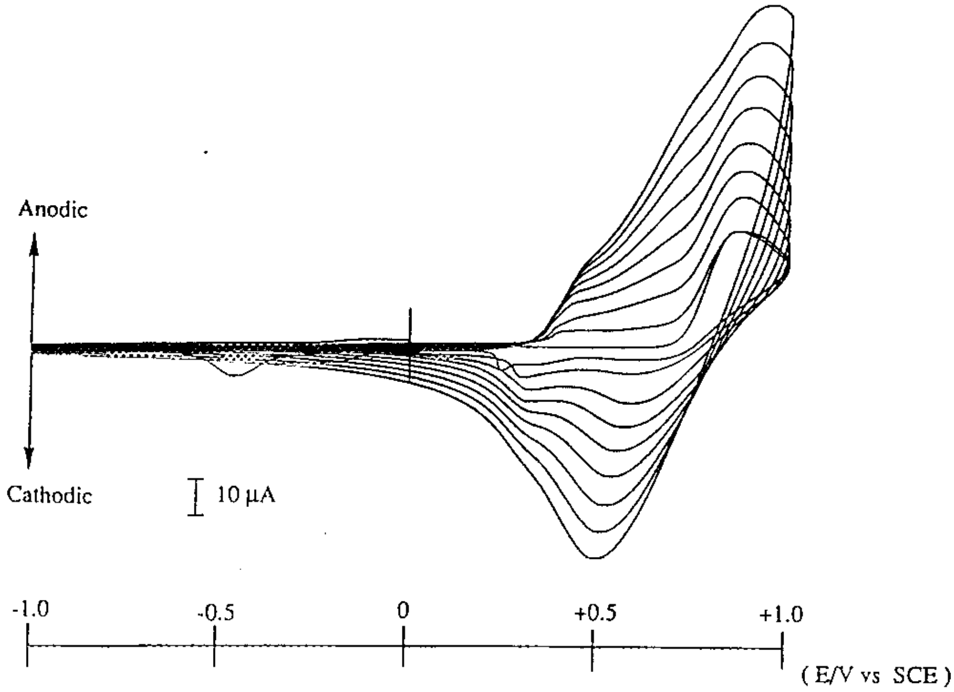


Figure 7. Successive cyclic voltammograms of **2a** in PhCN containing 0.1 mol dm^{-3} TBAP, scan rate 100 mV s^{-1}. They were recorded every five cycles. A platinum disk and SCE were used as a working and a reference electrode, respectively.

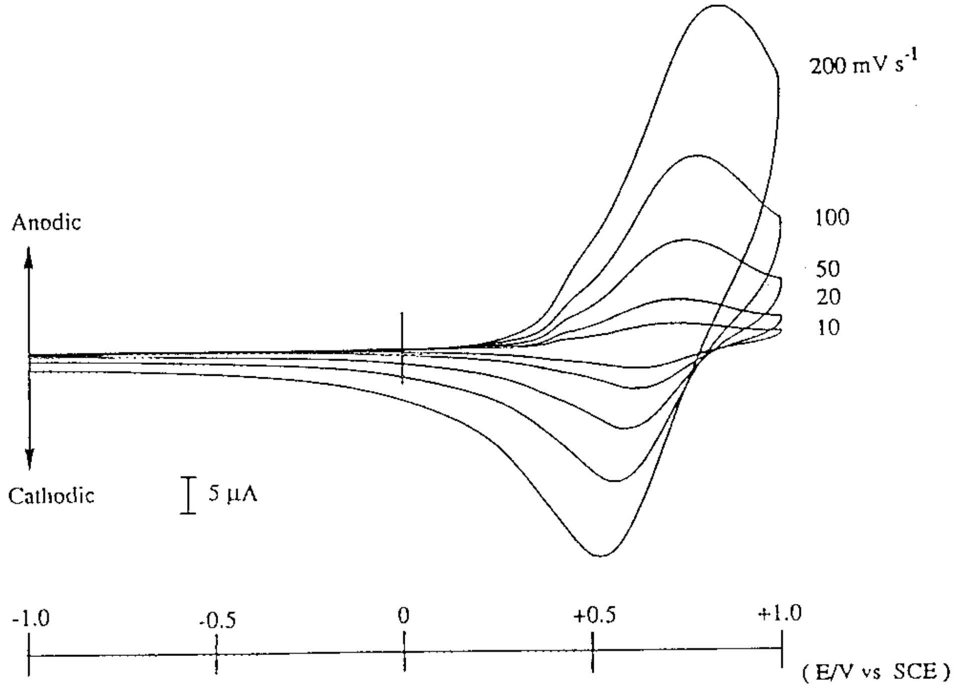


Figure 8. Cyclic voltammograms of **4a** measured in a monomer-free PhCN / 0.1 mol dm^{-3} TBAP at various scan rates under an argon atmosphere. A platinum disk and SCE were used as a working and a reference electrode, respectively.

Table II. Oxidation Potentials and Absorption Maxima of Polymers

polymer	R	E_{pa}/V vs SCE[a]	λ_{max}/nm[b]
3a	H	+0.65	629
3b	Me	+0.65	614
3c	benzo	+0.70	626
3d	SMe	+0.61	662
3e	CO_2Me	+0.59	689
3f	$S(CH_2)_3CH_3$	+0.62	660
3g	$S(CH_2)_5CH_3$	+0.58	653
3h	$S(CH_2)_9CH_3$	+0.56	650
4a	H	+0.72	448
4b	Me	+0.63	584
4c	benzo	+0.76	562
4d	SMe	+0.77	457
4e	CO_2Me	+0.84	424

[a] Measured by cyclic voltammetry in PhCN for **3a**, **c**-**e**, and **4**, and EtCN for **3b**, **f**-**g**, 0.1 mol dm^{-3} TBAP, scan rate 10 mV s^{-1}, Pt electrode. [b] Measured on ITO.

to the 1,3-dithiol-2-ylidene moiety (Table VII), indicating that the skeleton is intact in the polymers. On the other hand, a considerable decrease in the intensity of the peaks around 650 cm^{-1}, assigned to the C-H out-of-plane vibration, was observed after polymerization (Figure 9, 10). The UV-vis-NIR spectra of the electrochemically dedoped films on ITO showed peaks at λ_{max} = 614-689 nm for **3a**-**e** and 444-584 nm for **4** (Table II), indicating that **3a**-**e** and **4** have extended conjugated systems. Additional absorptions in longer wavelength regions were observed in the doped films due to the formation of polarons and/or bipolarons. Electrochemical cycles between the doping and dedoping

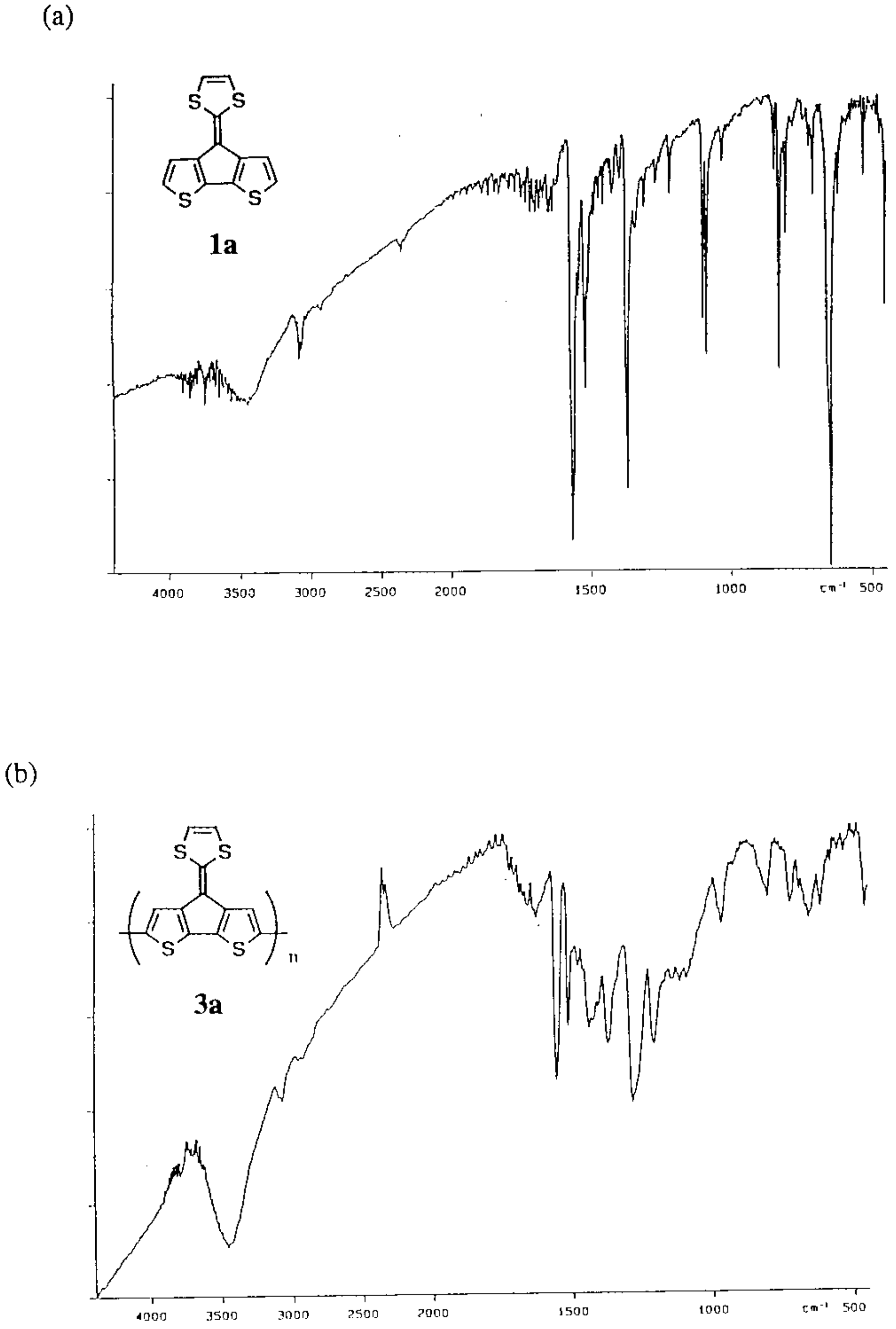


Figure 9. FT-IR spectra of (a) **1a** and (b) **3a**.

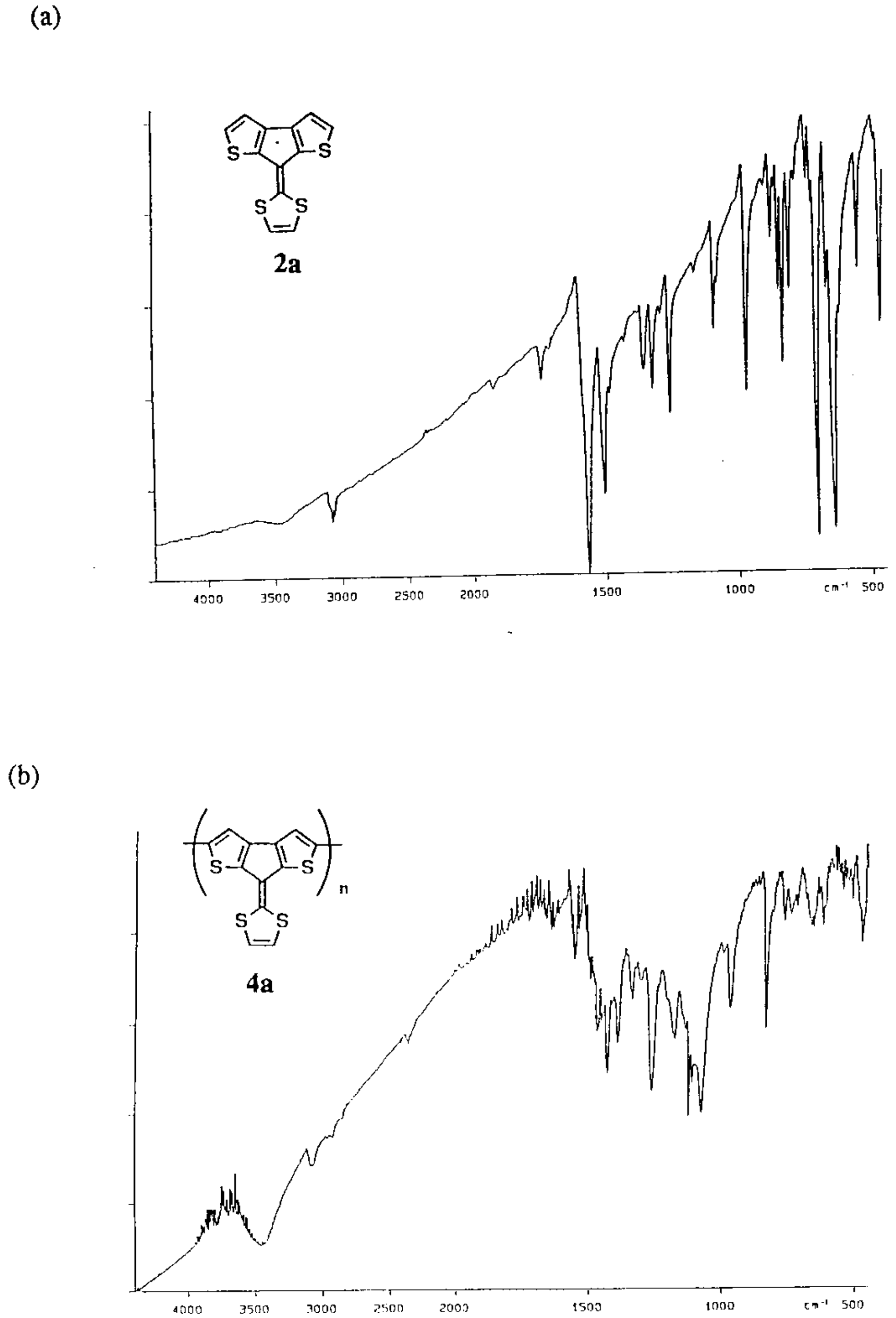


Figure 10. FT-IR spectra of (a) **2a** and (b) **4a**.

Table III. Conductivities of Oxidized Polymers

polymer	R	X	Potential/V vs SCE[a]	σ/S cm^{-1} [b]
3a	H	ClO_4^-	0.70	4.1x10^{-1}
		BF_4^-	1.10	1.1x10^{-3}
		OTs^-	0.70	2.7x10^{-3}
3b	Me	ClO_4^-	0.75	4.4x10^{-1}
3c	benzo	ClO_4^-	0.75	4.4x10^{-1}
		BF_4^-	1.20	3.2x10^{-1}
		PF_6^-	0.85	33
		OTs^-	0.90	3.3x10^{-1}
3d	SMe	ClO_4^-	0.70	1.7
3e	CO_2Me	ClO_4^-	0.85	41
		BF_4^-	1.20	52
		PF_6^-	0.90	46
3f	$S(CH_2)_3CH_3$	ClO_4^-	0.80	1.5x10^{-4} [c]
3g	$S(CH_2)_5CH_3$	ClO_4^-	0.80	3.7x10^{-4} [c]
3h	$S(CH_2)_9CH_3$	ClO_4^-	0.80	3.5x10^{-4} [c]
4a	H	ClO_4^-	0.75	2.5x10^{-2} [d]
		BF_4^-	0.85	2.0x10^{-3} [d]
		OTs^-	0.70	5.9x10^{-3}
4b	Me	ClO_4^-	0.80	3.0x10^{-3} [d]
		BF_4^-	0.80	5.8x10^{-4} [d]
		OTs^-	0.75	<10^{-6} [d]
4c	benzo	ClO_4^-	0.90	2.0x10^{-2}
		PF_6^-	0.85	2.0x10^{-1}
		OTs^-	0.95	1.9x10^{-3} [d]
4d	SMe	ClO_4^-	0.90	1.0x10^{-3} [d]

[a] Potentials for polymer synthesis. See experimental section. [b] Measured by a four-probe method. [c] Measured on compressed pellets by a two-probe method. [d] Measured by a two-probe method.

states were accompanied by reversible color changes (typically from green (dedoping) to blue (doping)).

In order to investigate a dependence of the conducting properties of the polymers on anions contained in the supporting electrolytes, polymerizations were carried out by the constant potential method using an ITO electrode in PhCN containing TBAP, tetrabutylammonium tetrafluoroborate ($TBABF_4$), tetrabutylammonium hexafluorophosphate ($TBAPF_6$), or tetraethylammonium *p*-toluenesulfonate (TEAOTs) as supporting electrolytes. The potentials for the polymerizations were set somewhat lower than the E_{pa} of the monomers. The conductivities of the films so grown were measured by a four- or two-probe method. The typical thicknesses of the films measured by a scanning electron microscope (SEM) were 1-30 μm. All combinations of the monomers and anions shown in Table III gave free standing films tough enough for measurements of conductivities. It is notable that some films such as **3c**$\cdot(PF_6^-)_x$, **3e**$\cdot(ClO_4^-)_x$, and **3e**$\cdot(BF_4^-)_x$ showed conductivities as high as the doped film of PITN (50 S cm^{-1}).[5b] The conductivities of other films such as **3a**$\cdot(ClO_4^-)_x$, **3d**$\cdot(ClO_4^-)_x$, and **4c**$\cdot(PF_6^-)x$ were also higher than those of heterocycle-fused poly(thiophenes) such as poly(dithieno[3,2-b; 2',3'-d]thiophene) (0.4 S cm^{-1})[4a] and poly(2,3-dihexylthieno[3,4-b] pyrazine) (3×10^{-2} S cm^{-1}).[4e] The doping states of **3a**-**e** and **4** are stable and the conductivities didn't change after storage under air for a month. On the other hand, **3a**$\cdot(OTs^-)_x$, **3a**$\cdot(BF_4^-)_x$, and **4a**$\cdot(OTs^-)_x$ gave physically strong films, but their conductivities were lower. Polymers **3a**-**e** generally have a tendency to give films with better conductivities than **4**. Most of the superficial morphologies of the films of **3a**-**e** and **4** observed by SEM show a granular appearance similar to that of poly(thiophene),[13] whereas **3a**$\cdot(OTs^-)_x$ and **4a**$\cdot(OTs^-)_x$ have very smooth, flat surfaces. Moreover, these films were very thick (20-30 μm).

For doped films of **3** and **4**, elemental analyses were performed to learn about the polymer structures and doping levels. At first, films so grown were washed with acetonitrile using a soxhlet with a glass filter to remove monomer and the supporting electrode. Then, washed films were dried at 60 °C in vacuo. Some films such as

Table IV. Data for Elemental Analyses

polymer	X	molecular formula	analysis[a]
3a	ClO_4^-	$(C_{12}H_4S_4)(ClO_4^-)_{0.31}$	calc. C, 46.97; H, 1.31
			found C, 46.90; H, 1.70
	BF_4^-	$(C_{12}H_4S_4)(BF_4^-)_{0.17}$	calc. C, 49.50; H, 1.39
			found C, 49.65; H, 1.98
3c	ClO_4^-	$(C_{16}H_6S_4)(ClO_4^-)_{0.43}$	calc. C, 52.05; H, 1.64
			found C, 51.98; H, 2.05
	BF_4^-	$(C_{16}H_6S_4)(BF_4^-)_{0.46}$	calc. C, 52.45; H, 1.65
			found C, 52.45; H, 2.11
	PF_6^-	$(C_{16}H_6S_4)(PF_6^-)_{0.24}$	calc. C, 53.20; H, 1.67
			found C, 53.30; H, 2.17
3e	ClO_4^-	$(C_{16}H_8O_4S_4)(ClO_4^-)_{0.28}$	calc. C, 45.75; H, 1.92
			found C, 45.76; H, 2.07
	PF_6^-	$(C_{16}H_8O_4S_4)(PF_6^-)_{0.18}$	calc. C, 45.91; H, 1.93
			found C, 46.19; H, 2.07

[a] Inclusion of nitrogen on all samples were 0.00%.

3b$\cdot(ClO_4^-)_x$, **4a**$\cdot(PF_6^-)_x$, and **4b**$\cdot(BF_4^-)_x$, which were prepared as physically weak ones, became powder and passed through the glass filter during washing. Therefore it was impossible to perform their elemental analyses. As described in the discussion about the conductivity measurements, polymers **4** tended to give very weak films. On the other hand, the polymers containing OTs^- were so hygroscopic that the elemental analyses could not be carried out. The results of elemental analyses are shown in Table IV.

Preparation and Properties of Alkyl-Substituted Polymers

The introduction of linear alkyl chains into polymers increases their solubility in solvents and lends structural control.[15] With this in mind, compounds **1f**-**h**, containing linear alkyl chains, were synthesized in 64-96% yields using a method similar to that described above. In **1f**-**h**, introduction of linear alkyl chains dramatically lowered their melting points, and in particular, that of **1g** was below room temperature (Table I). On the other hand, the alkyl chain length had no effect on the electronic spectrum and E_{pa}. Electrochemical polymerizations performed under the conditions described above, except for varying solvent, gave the corresponding polymers **3f**-**h**. For electrochemical polymerizations of **1f**-**h**, EtCN was used as solvent since no polymer formed in PhCN. This can be explained by the notion that reaction intermediates that would otherwise lead to polymers dissolved in PhCN and thus diffused away from the electrode surface.[16] This is supported by the observation that during the polymerizations, the color of the solution around the surface of the electrode changed to green. After polymerization, the films were washed with EtCN to remove the supporting electrolytes and the monomers. Although **3f**-**h** were obtained as good free standing films, the structures of these films were like sponge and the thicknesses of the films could not be estimated. Thus the electrical conductivities were measured on compressed pellets by a two-probe method (Table III). The values were three or four orders of magnitude lower than those of other films of **3**. In the FT-IR spectra of electrochemically dedoped **3f**-**h**, absorption bands corresponding to the C-H vibrations of the alkyl groups were observed around 2950 cm^{-1} (Table VII and Figure 11). Both the electrochemically dedoped and doped films were partially soluble in organic solvents such as THF, chloroform, and carbon disulfide. The solubilities of the dedoped polymers were generally higher than those of the doped ones.[17] Dedoped **3g** showed the best solubility although there was still an insoluble component which probably consists of the polymer with a higher molecular weight. The soluble portion of **3g** was treated with hydrazine hydrate to give completely dedoped films and used for measurements of the ^{1}H NMR (Figure 12) and electronic spectra

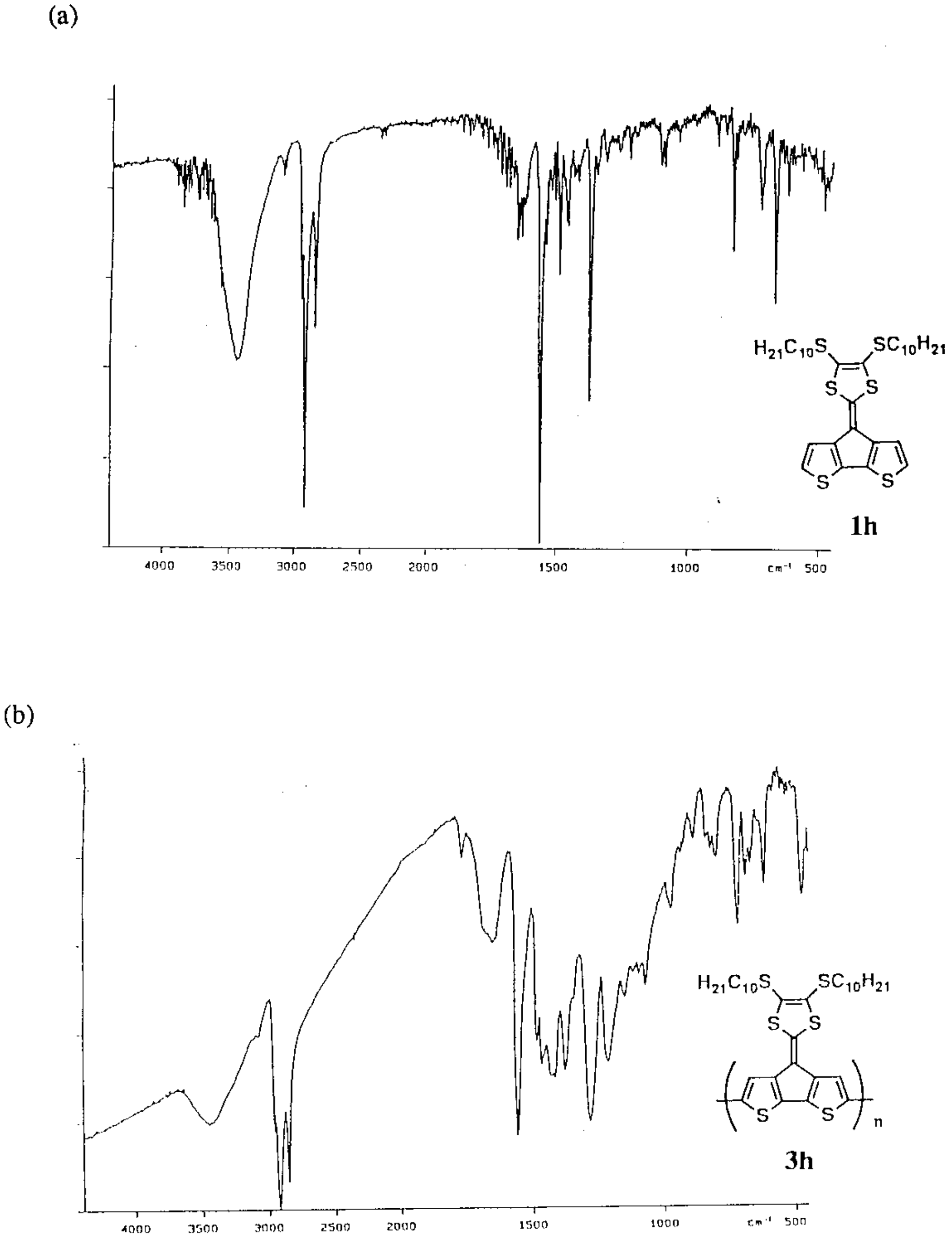


Figure 11. FT-IR spectra of (a) **1h** and (b) **3h**.

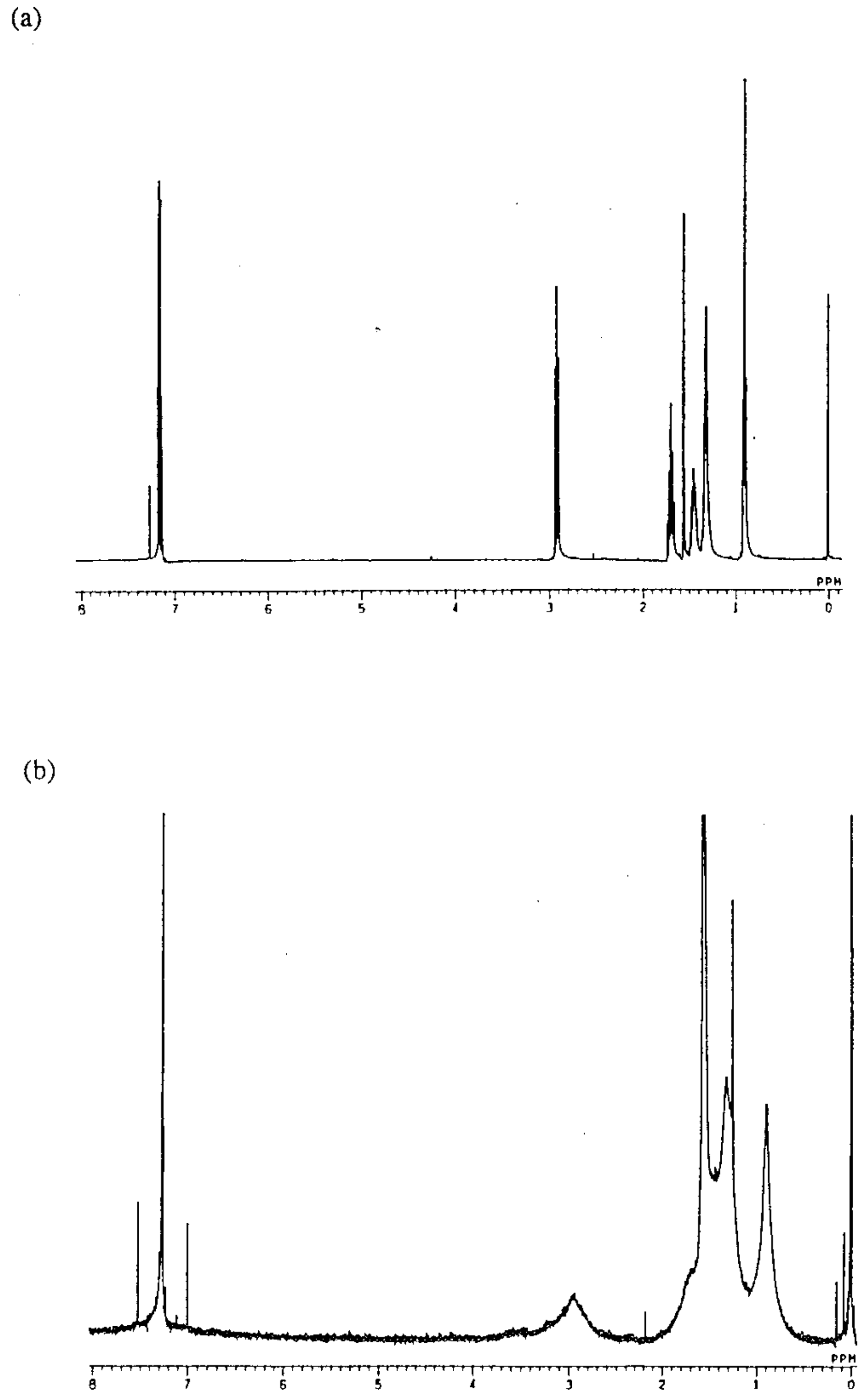


Figure 12. ^{1}H NMR spectra of (a) **1g** and (b) **3g**.

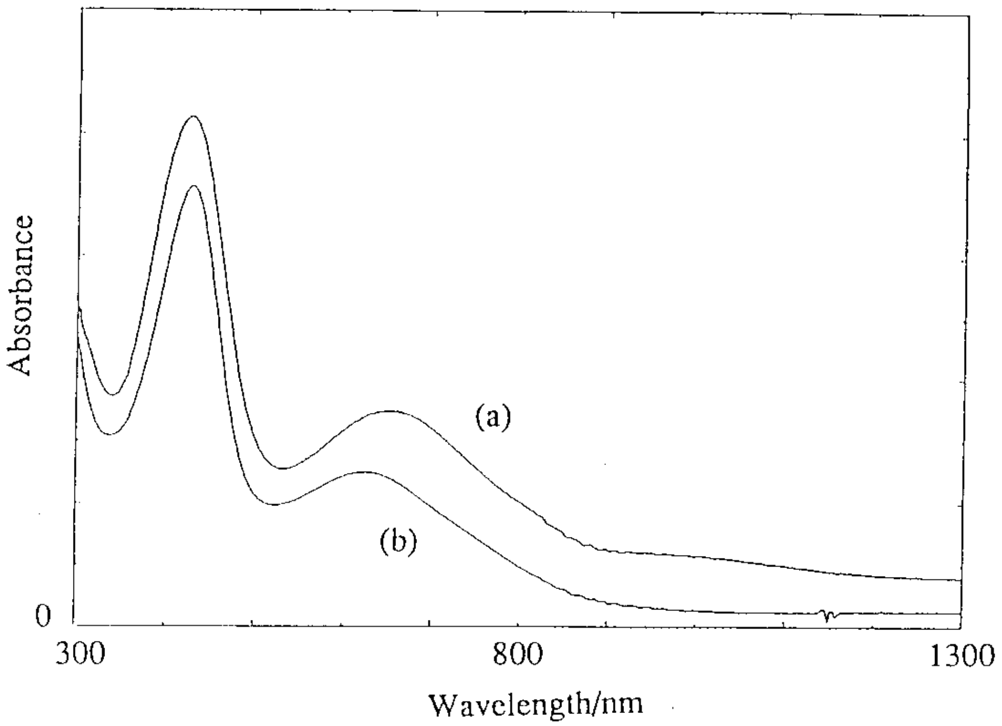


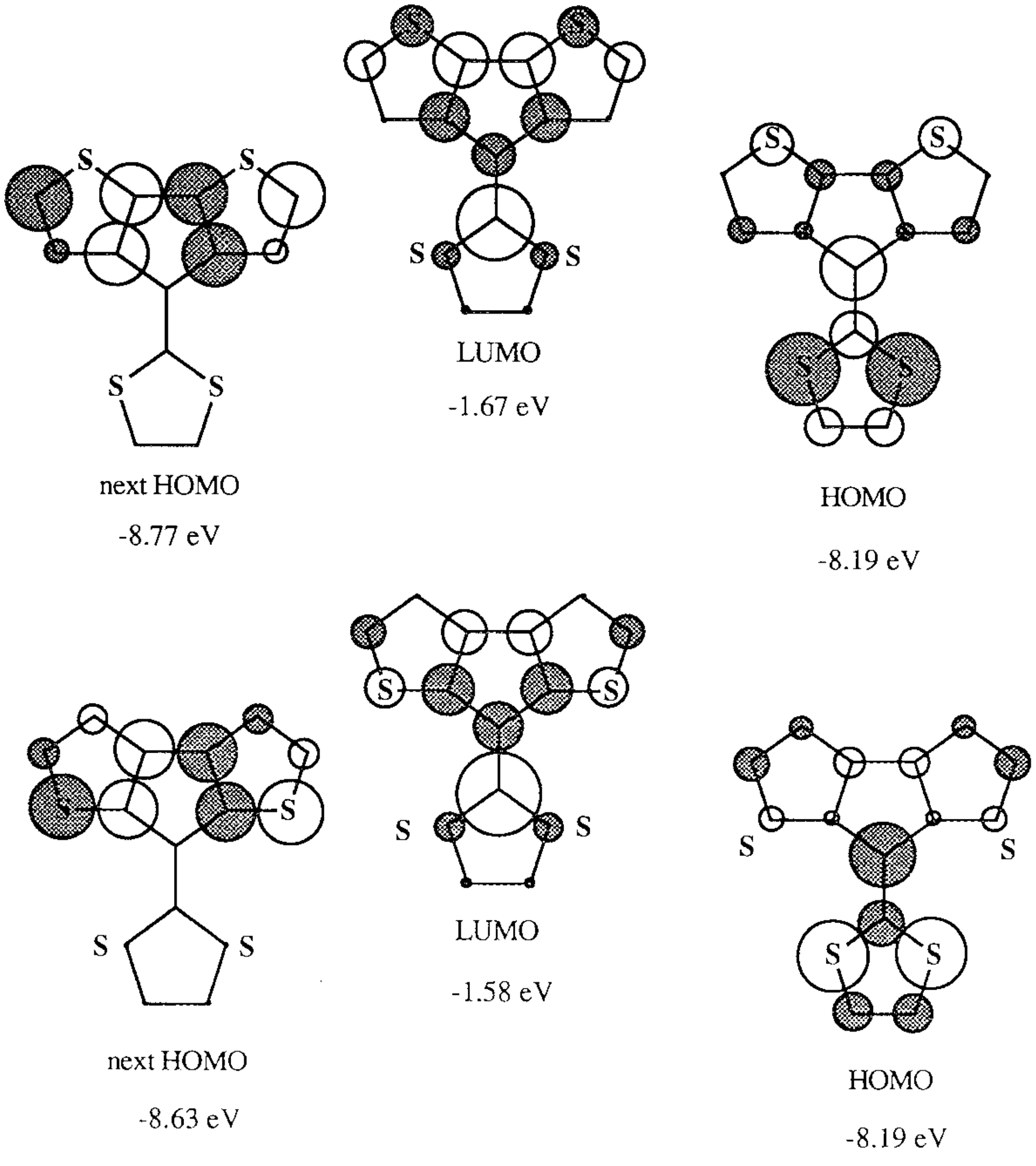
Figure 13. Absorption spectra of (a) electrochemically dedoped thin film of **3g** on ITO and (b) hydrazin-treated **3g** in $CHCl_3$.

(Figure 13). The ^{1}H NMR spectrum of **3g** showed some broad peaks, assigned to the hexyl protons, which appear at the same chemical shifts as those of **1g**. However, the peaks of the ring protons were not clearly discernible because of their broad signals. The electronic spectrum of **3g** in $CHCl_3$ showed an absorption maximum at 626 nm which is red-shifted by 27 nm relative to that of the film on ITO. This spectrum showed a clear base line and an absorption edge, as shown in Figure 13. This fact indicates that charges still remain in the electrochemically dedoped films. The optical band gap of **3g**, estimated from the absorption edge, is around 1.4 eV which is much narrower than that of poly(thiophene) (2.1 eV).[14c,18] The GPC analysis of **3g** in THF indicated a weight-average molecular weight (M_w) of 5456 (polystyrene standard) with a polydispersity of 2.0, which corresponds to about 11 monomer units.

Molecular Orbital Calculation Results

MNDO-PM3 calculations[19] show that **1a** has very large AO coefficients at the carbon atoms at the α-positions of the thiophene rings in the next-HOMO, while the AO coefficients at the α- and β-carbon atoms at the thiophene rings are smaller in the HOMO as shown in Figure 14. On the other hand, **2a** has larger AO coefficients at the α-positions than at the β-positions in the HOMO. These facts suggest that the electropolymerizations proceed predominantly at the α-positions. The HOMOs of **1a** and **2a** also have large AO coefficients at the 3- and 4-positions of the 1,3-dithiole ring. This fact is consistent with the observation that the electronic properties of **1** and **2** were greatly affected by the introduction of substituents at these positions.

The difference in the absorption spectra of **3** and **4** (Table II) indicates that more delocalization of π-electrons takes place in **3** than in **4**. This may be attributable to the torsion between the monomer units or the intrinsic electronic character of each molecule. We have investigated this possibility with MO calculations.[1a, 20] First, to obtain



next HOMO
-8.77 eV

LUMO
-1.67 eV

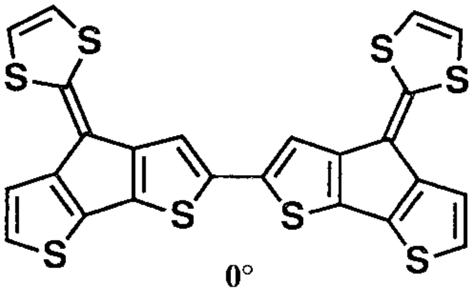
HOMO
-8.19 eV

next HOMO
-8.63 eV

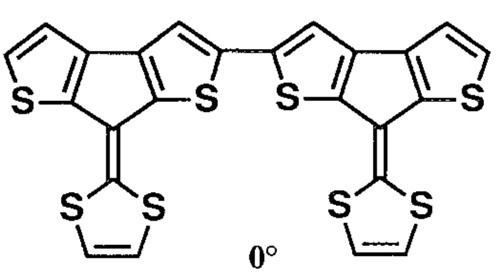
LUMO
-1.58 eV

HOMO
-8.19 eV

Figure 14. AO coefficients in next HOMOs, HOMOs, and LUMOs of **1a** (upper) and **2a** (lower) calculated by the MNDO-PM3 method. The radii of circles are approximately proportional to the magnitude of the coefficients.



9a



10a

Table V. The MNDO-PM3 Calculation Results of Reaction Path Calculations for Inter-monomer Rotation

compd	dihedral angle at energy minimum (deg)	energy barrier heights (kcal mol^{-1})
9a	30	0.89
10a	30	0.83
bithiophene	28	0.65

information about the energy barrier for rotation around the inter-ring C-C single bonds, reaction path calculations for this rotation were performed on the dimers **9a** and **10a** derived from **1a** and **2a**, respectively (Table V). The calculations were carried out every 10° from 0° to 180° with optimization and showed very shallow energy minima at dihedral angles of about 30° (S-C-C-S) for both dimers, where the energy barrier heights are 0.89 kcal mol^{-1} for **9a** and 0.83 kcal mol^{-1} for **10a**. On the other hand, the calculations on bithiophene indicated a shallow potential minimum at 30° with an energy barrier height of 0.65 kcal mol^{-1}. These results suggest that polymers **3a** and **4a** have steric interactions between the monomer units that are comparable to those in poly(thiophene). Since terthiophene has a coplaner conformation in the crystal,[21] these results suggest that **3a** and **4a** also have coplanar conformations in the solid state.

Absorption maxima of the structure-optimized oligomers shown in Table VI were calculated by the INDO/1-CI method using Zener's parameters.[22] The author performed

Table VI. Absorption Maxima of the Oligomers Derived from **1a** and **2a** Calculated by the INDO/1-CI Method

compd		λ_{max}/nm (log ε)	$\Delta\lambda_{max}$[a]
1a	monomer	510 (3.92)	-
	dimer	594 (4.58)	84
	trimer	647 (4.80)	137
	tetramer	671 (4.95)	161
2a	monomer	361 (4.54)b	-
	dimer	475 (4.03)	114
	trimer	482 (4.26)	121
	tetramer	484 (4.46)	123
bithiophene	monomer	323 (4.63)	-

[a] $\Delta\lambda$max = λmax(monomer) - λmax(oligomer). [b] There is a forbidden transition at 447 nm.

the configuration interaction (CI) calculations up to 100 configuration functions. The calculations show that each oligomer derived from **1a** has absorptions with larger molar decadic absorption coefficients (ε) at longer wavelengths than those derived from **2a**. In addition, as the oligomerization proceeds, the absorption maxima are more blue-shifted in **1a** than in **2a**. Therefore it was deduced that polymer **3a** has the absorption in longer wavelength region than **4a**. These results are in agreement with the physical observations and indicate that the difference in the absorption maxima of **3a** and **4a** can not be attributed to the torsion between the monomer units but the intrinsic π-electronic character of each molecule.

Conclusion

Two types of novel poly(thiophene) derivatives containing 1,3-dithiole moieties were electrochemically prepared. The polymers showing low oxidation potentials were very stable. Some polymers exhibited high conductivities which can be attributed to the 1,3-dithiole groups. The polymers **3** showed higher conductivities than isomers **4**. Investigation of the properties of the monomers revealed that the introduction of 1,3-dithiole groups leads to an increase in the intermolecular interactions, stability of radical cations, and polarization of molecules. The polymers **3** have the absorptions at longer wavelength region than one of **4** in their electronic spectra. This result was explained by differences in the conjugation across the monomer units, which were investigated by MO calculations. Effective conjugation across monomer units proves to be important. MO calculations also indicated little steric hindrance between the monomer units, in both polymers. Finally, the introduction of long alkyl chains improved the solubility of the polymers, and simple methods for the preparation of 1,3-dithiole derivatives made these modifications simple.

Experimental Section

General. Melting points are uncorrected. Infrared spectra were taken in KBr pellets. Mass spectra were obtained in the EI mode at 70 eV unless indicated otherwise.

General Procedure for Wittig Horner and Wittig Reactions. To the carbanions prepared from **7** or **8** (2.0-4.0 mmol) and n-BuLi in hexane (1.8-3.6 mmol) in dry THF (10 ml) at -78 °C under argon was added **5** or **6** (1.0 mmol). This solution was stirred for 15 min at -78 °C. After a cooling bath was removed, the solution was further stirred for 20 min. The solvent was evaporated in vacuo. The resulting residue was diluted with water and extracted with CH_2Cl_2. The solution was washed with brine and water, and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the resulting solid was purified by recrystallization.

1a: orange crystals, mp 171-173 °C (from CCl_4); ^1H NMR ($CDCl_3$) δ 6.66 (s, 2 H), 7.14 (d, J = 5.0 Hz, 2 H), 7.21 (d, J = 5.0 Hz, 2 H); IR (KBr) 1567, 1520, 1373, 831, 652 cm^{-1}; UV (EtOH) λ_{max} 264 nm (log ε 4.33), 397 (4.39, sh), 411 (4.45); MS m/z (relative intensity) 278 (M^+, 100), 220 (23), 176 (12). Anal. Calcd. for $C_{12}H_6S_4$: C, 51.81; H, 2.18. Found: C, 51.67; H, 2.33.

1b: yellow crystals, mp 223-224 °C (from EtOAc); ^1H NMR ($CDCl_3$) δ 2.07 (s, 6 H), 7.11 (d, J = 4.9 Hz, 2 H), 7.18 (d, J = 4.9 Hz, 2 H); IR (KBr) 1540, 1374, 828, 659 cm^{-1}; UV (EtOH) λ_{max} 265 nm (log ε 4.20), 403 (4.26, sh), 408 (4.33); MS m/z (relative intensity) 306 (M^+, 100), 220 (9), 176 (8). Anal. Calcd. for $C_{14}H_{10}S_4$: C, 54.91; H, 3.29. Found: C, 54.81; H, 3.37.

1c: orange crystals, mp 212-213 °C (from $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.15 (d, J = 4.9 Hz, 2 H), 7.23 (dd, J = 3.2, 6.0 Hz, 2 H), 7.29 (d, J = 4.9 Hz, 2 H), 7.42 (dd, J = 3.2, 6.0 Hz, 2 H); IR (KBr) 1575, 1553, 830, 672 cm^{-1}; UV (EtOH) λ_{max} 252 nm (log ε 4.36), 263 (4.38), 382 (4.46), 400 (4.52); MS m/z (relative intensity) 328 (M^+, 100), 296 (11), 164 (16). Anal. Calcd. for $C_{16}H_8S_4$: C, 58.55; H, 2.46. Found: C, 58.26; H, 2.49.

1d: orange crystals, mp 167-168 °C (from Acetone); ^1H NMR ($CDCl_3$) δ 2.52 (s, 6 H), 7.13 (d, J = 4.9 Hz, 2 H), 7.15 (d, J = 4.9 Hz, 2 H); IR (KBr) 1560, 1488, 1368, 670 cm^{-1}; UV (EtOH) λ_{max} 266 nm (log ε 4.56), 411 (4.61); MS m/z (relative intensity) 370 (M^+, 100), 322 (36), 220 (88). Anal. Calcd. for $C_{14}H_{10}S_6$: C, 45.42; H, 2.72. Found: C, 45.22; H, 2.68.

1e: orange crystals, mp 223-225 °C (from EtOAc); ^1H NMR ($CDCl_3$) δ 3.92 (s, 6 H), 7.14 (s, 4 H); (C_6D_6) δ 3.29 (s, 6 H), 6.64 (d, J = 5.0 Hz, 2 H), 6.88 (d, J = 5.0 Hz, 2 H); IR (KBr) 1750, 1709, 1579, 1272, 1236, 661 cm^{-1}; UV (EtOH) λ_{max} 263 nm (log ε 4.21), 389 (4.29); MS m/z (relative intensity) 394 (M^+, 100), 220 (39), 176 (12). Anal. Calcd. for $C_{16}H_{10}O_4S_4$: C, 48.74; H, 2.56. Found: C, 48.59; H, 2.74.

1f: orange crystals, mp 71-72 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ 0.95 (t, *J* = 7.5 Hz, 6 H), 1.48 (m, 4 H), 1.68 (tt, *J* = 7.3, 7.3 Hz, 4 H), 2.92 (t, *J* = 7.3 Hz, 4 H), 7.13 (d, *J* = 5.2 Hz, 2 H), 7.16 (d, *J* = 5.2 Hz, 2 H); IR (KBr) 2956, 1561, 1374, 660 cm^{-1}; UV (EtOH) λ_{max} 266 nm (log ε 4.33), 412 (4.44); MS m/z (relative intensity) 454 (M^+, 100), 364 (42), 341 (20), 220 (56). Anal. Calcd. for $C_{20}H_{22}S_6$: C, 52.86; H, 4.88. Found: C, 53.02; H, 5.03.

1g: orange oil, ^{1}H NMR ($CDCl_3$) δ 0.90 (t, *J* = 6.9 Hz, 6 H), 1.31 (m, 8 H), 1.45 (m, 4 H), 1.69 (tt, *J* = 7.4, 7.5 Hz, 4 H), 2.90 (t, *J* = 7.4 Hz, 4 H), 7.13 (d, *J* = 5.0 Hz, 2 H), 7.16 (d, *J* = 5.0 Hz, 2 H); IR (NaCl) 2922, 1678, 1565, 1371 cm^{-1}; UV (Hexane) λ_{max} 266 nm (log ε 4.31), 396 (4.38), 411 (4.46); MS m/z (relative intensity) 510 (M^+, 100), 392 (21), 341 (13), 220 (27). Anal. Calcd. for $C_{24}H_{30}S_6$: C, 56.46; H, 5.93. Found: C, 56.05; H, 5.79.

1h: yellow crystals, mp 54-56 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ 0.87 (t, *J* = 6.9 Hz, 6 H), 1.29 (m, 24 H), 1.44 (m, 4 H), 1.69 (tt, *J* = 7.4, 7.4 Hz, 4 H), 2.91 (t, *J* = 7.4 Hz, 4 H), 7.13 (d, *J* = 5.0 Hz, 2 H), 7.16 (d, *J* = 5.0 Hz, 2 H); IR (KBr) 2922, 1561, 1373, 670 cm^{-1}; UV (Hexane) λ_{max} 266 nm (log ε 4.36), 396 (4.44), 411 (4.53); MS m/z (relative intensity) 622 (M^+, 100), 488 (16), 341 (17), 220 (48). Anal. Calcd. for $C_{32}H_{46}S_6$: C, 61.72; H, 7.45. Found: C, 61.74; H, 7.28.

2a: yellow crystals, mp 143-144 °C (from benzene); ^{1}H NMR ($CDCl_3$) δ 6.81 (s, 2 H), 7.21 (d, *J* = 4.9 Hz, 2 H), 7.35 (d, *J* = 4.9 Hz, 2 H); IR (KBr) 1569, 705, 641 cm^{-1}; UV (CH_2Cl_2) λ_{max} 253 nm (log ε 4.26), 281 (4.04), 405 (4.33), 420 (4.37); MS m/z (relative intensity) 278 (M^+, 100), 220 (18), 176 (14). Anal. Calcd. for $C_{12}H_6S_4$: C, 51.81; H, 2.18. Found: C, 51.60; H, 2.37.

2b: yellow crystals, mp 277 °C (from EtOAc); ^{1}H NMR ($CDCl_3$) δ 2.16 (s, 6 H), 7.20 (d, *J* = 4.9 Hz, 2 H), 7.32 (d, *J* = 4.9 Hz, 2 H); IR (KBr) 1543, 1507, 708, 641 cm^{-1}; UV (CH_2Cl_2) λ_{max} 253 nm (log ε 4.26), 281 (4.04), 405 (4.33), 420 (4.37); MS m/z (relative intensity) 306 (M^+, 100), 220 (18), 176 (19). Anal. Calcd. for $C_{14}H_{10}S_4$: C, 54.90; H, 3.28. Found: C, 54.97; H, 3.48.

2c: yellow crystals, mp 215-217 °C (from EtOAc); ^{1}H NMR ($CDCl_3$) δ 7.20 (d, *J* = 4.9 Hz, 2 H), 7.29 (dd, *J* = 3.2, 6.0 Hz, 2 H), 7.38 (d, *J* = 4.9 Hz, 2 H), 7.53 (dd, *J* = 3.2, 6.0 Hz, 2 H); IR (KBr) 1576, 1554, 744, 709, 646 cm^{-1}; UV (CH_2Cl_2) λ_{max} 252 nm (log ε 4.41), 276 (4.11, sh), 309 (3.56, sh), 402 (4.46, sh), 414 (4.50); MS m/z (relative intensity) 328 (M^+, 100), 164 (9), 93 (12). Anal. Calcd. for $C_{12}H_6S_4$: C, 58.55; H, 2.46. Found: C, 58.35; H, 2.45.

2d: yellow crystals, mp 155-156 °C (from EtOAc); ^{1}H NMR ($CDCl_3$) δ 2.56 (s, 6 H), 7.19 (d, *J* = 4.7 Hz, 2 H), 7.35 (d, *J* = 4.7 Hz, 2 H); IR (KBr) 1560, 1484, 712 cm^{-1}; UV (CH_2Cl_2) λ_{max} 253 nm (log ε 4.26), 281 (4.04), 405 (4.33), 420 (4.37); MS m/z (relative intensity) 370 (M^+, 88), 220 (100), 176 (32). Anal. Calcd. for $C_{14}H_{10}S_6$: C, 45.42; H, 2.72. Found: C, 45.39; H, 2.89.

2e: yellow crystals, mp 226 °C (from EtOAc); ^{1}H NMR ($CDCl_3$); δ 3.94 (s, 6 H), 7.17 (d, *J* = 4.9 Hz, 2 H), 7.38 (d, *J* = 4.9 Hz, 2 H); IR (KBr) 1744, 1726, 1585, 1248, 721, 650 cm^{-1}; UV (CH_2Cl_2) λ_{max} 253 nm (log ε 4.26), 281 (4.04), 405 (4.33), 420 (4.37); MS m/z (relative intensity) 394 (M^+, 100), 220 (48), 176 (15). Anal. Calcd. for $C_{16}H_{10}O_4S_4$: C, 48.74; H, 2.56. Found: C, 48.89; H, 2.62.

X-ray Structural Analyses. The crystals for the data collections were prepared by slow evaporation of the solvents used for recrystallizations. An Enraf-Nonius CAD4 diffractometer was used with graphite-monochromated Cu Kα radiation; $\theta / 2\theta$ scan technique. The atomic and thermal parameters and bond lengths and angles are presented in appendix at the end of this thesis. The crystal data are summarized in Table VII. Cell parameters were determined from least-squares procedures on 25 reflections (44° $< 2\theta <$ 50°). No significant variation was observed in intensities of three standards monitored every 7200 s. The structures were solved by the direct method using the MULTAN78 program[23] and refined by the block-diagonal least squares analysis based on *F* values using UNICS III program package.[24] All the non-hydrogen atoms of the molecule were refined with anisotropic temperature factors. The positions of hydrogen atoms were determined by a difference Fourier synthesis. At the final stage, hydrogen atoms were included in the refinement with isotropic temperature factors.

These calculations were carried out in the Computer Center of Institute for Molecular Science.

Electrochemical Measurements. All cyclic voltammetries were carried out with a three-component cell in distilled PhCN or EtCN containing 0.1 mol dm^{-3} TBAP at scan rate of 100 mV s^{-1}. The solution was degassed by argon bubbling before an electrochemical measurement which was performed under an argon atmosphere. A Pt

Table VII. Crystal Data for 1,3-Dithiole Compounds **1a** and **2a**

compd	**1a**	**2a**
formula	$C_{12}H_6S_4$	$C_{12}H_6S_4$
f_w	278.42	278.42
space group	*P*21/*n*	*P*21/*n*
a (Å)	21.093 (18)	18.297 (5)
b (Å)	9.404 (1)	4.006 (0)
c (Å)	12.185 (1)	17.220 (0)
α (deg)	90.0	90.0
β (deg)	105.95 (1)	118.05 (1)
γ (deg)	90.0	90.0
V (Å3)	2315.9 (4)	1113.9 (4)
Z	8	4
ρ_{calcd} (g cm^{-3})	1.60	1.96
cryst size (mm)	0.05 × 0.11 × 0.34	0.13 × 0.18 × 0.49
radiation	Cu Kα	Cu Kα
$2\theta_{max}$ (deg)	1, 70	1, 70
total data measd	4403	2458
obsd unique data	3794 (3σ)	1897 (3σ)
R	0.0673	0.0776

disk, Pt wire, and SCE electrode were used as a working, counter, and reference electrode, respectively.

The polymers for cyclic voltammetries were prepared by a cyclic potential-sweep technique using the above conditions. The resulting polymers on the electrode were thoroughly washed with PhCN or EtCN. Cyclic voltammograms of the polymers were then recorded in monomer free electrolytes under the same conditions as above except for a scan rate. In order to avoid shifts of the E_{pa} arising from the IR drop across the films, cyclic voltammograms of the polymers were measured at a scan rate of 10 mV s^{-1}.

General Procedure for Electrochemical Polymerizations. The polymers for the conductivity measurements were prepared by a constant potential method using an ITO, Pt wire, and SCE as a working, counter, and reference electrode, respectively, in distilled PhCN (EtCN for **3b**) containing 0.01-0.03 mol dm^{-3} monomer and 0.1 mol dm^{-3} supporting electrolytes. The potentials are shown in Table III. After degassed by argon, the polymerizations were performed under an argon atmosphere until a current became slight. The films so grown were peeled off from the electrode in MeCN, rinsed with MeCN, and dried. The polymers were yielded as black films. The conductivity measurements were carried out by a four- or two-probe method. The thicknesses of the films were measured by SEM which was also used for the observation of a superficial morphology of the films.

The polymers for elemental analyses were prepared by a constant potential technique under the same conditions as above. After the polymerizations, the resulting films were peeled off from ITO and thoroughly washed with MeCN. The films were further washed with MeCN using a soxhlet with a glass filter for 24 hours and dried under vacuum at 60 °C for 24 hours. Elemental analyses were performed twice for the each sample to check homogeneities and these two values agreed in 0.30 %. Inclusion of nitrogen on all these samples were 0.00%.

The polymers for the measurements of absorption spectra were prepared by a cyclic potential-sweep technique under the conditions as described above except for using 2.0-6.0 mmol dm^{-3} monomer solutions. After the polymerizations, the resulting dark

Table VIII. Spectroscopic Properties of Electrochemically Dedoped Polymers

polymer	IR/cm^{-1}	UV-vis (λ_{max})/nm
3a	1555, 1515, 1286, 1210, 662	422, 629
3b	1532, 1437, 1265, 1122, 668	323, 433, 614
3c	1572, 1546, 1202, 1102, 666	413, 626
3d	1553, 1485, 1414, 1269, 968	317, 436, 662
3e	1714, 1567, 1433, 1252, 728	324, 423, 689
3f	2953, 1553, 1269, 1208, 728	432, 660
3g	2923, 1557, 1374, 1281, 720	425, 653
3h	2922, 1557, 1414, 1280, 721	429, 650
4a	1552, 1423, 1261, 1074, 834	326, 448
4b	1542, 1420, 1263, 1081, 836	378, 584
4c	1573, 1552, 1122, 834, 739	432, 562
4d	1540, 1429, 1264, 1075, 836	359, 457
4e	1734, 1579, 1433, 1260, 835	316, 424

green films were thoroughly washed with PhCN (EtCN for **3b**). Then, electrochemical dedopings were carried out in monomer free electrolytes at the most negative potentials which do no serious damage to the films and ITO. Before the measurements of electronic spectra, the dedoped films were rinsed with MeCN. On the other hand, for FT-IR measurements the dedoped films were peeled off from ITO, washed with MeCN, and dried. Spectroscopic properties of the electrochemically dedoped polymers are displayed in Table VIII.

In the case of **3f-h**, the electrochemically dedoped films prepared in EtCN were washed with EtCN, and then dissolved in $CHCl_3$. After filtration, the filtrates were further treated with a hydrazine solution. The solutions were washed with water, and dried. After evaporation, dark green solids were obtained. The solid of **3g** was used for the measurement of electronic and ^{1}H NMR spectrum without a further treatment. ^{1}H NMR ($CDCl_3$) δ 0.88, 1.26, 1.58, 2.97; UV ($CHCl_3$) λ_{max} (relative intensity) 626 nm (100), 428 (40). For GPC analysis the solid of **3g** was washed with acetone to remove oligomers. GPC analysis performed by using a Tosoh TSK-GEL G3000HHR column (7.8 mm × 30 cm) and THF as a solvent indicated $M_w = 5647$ based on polystyrene calibration with a polydispersity of 2.0.

Computational Studies. MNDO-PM3 calculations were performed by using version 6.10 of the MOPAC program.[25] INDO/1-CI calculations were performed by the ZINDO program.[22] These calculations were carried out using the Sony-Tektronix CAChe system.

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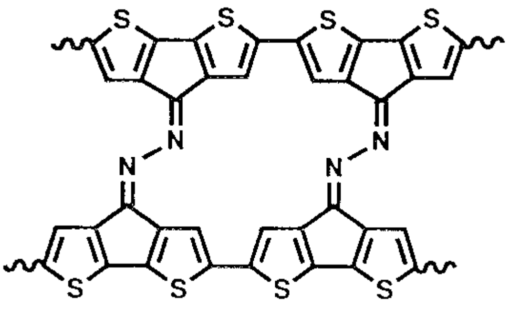
Chapter 4 Preparation and Properties of Poly(thiophenes) Connected by Azine Groups

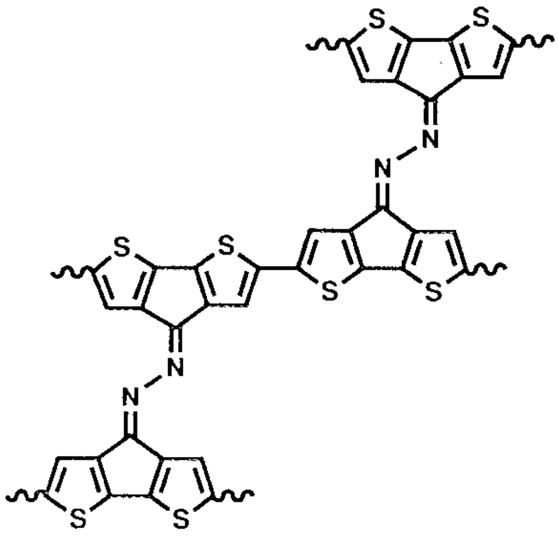
Abstract: 4H-Cyclopenta[2,1-b;3,4-b']dithiophen-4-one azines (**1**) and 7H-cyclopenta[1,2-b;4,3-b']dithiophen-7-one azine (**2**) were prepared by the dehydrating condensation reactions of the corresponding ketones with hydrazine. The X-ray structural analysis of the parent compound **1a** shows that the molecule is planar. Their absorptions were observed in a long wavelength region. The introduction of electron donating groups into α-positions made the absorption shift to longer wavelength region. The cyclic voltammograms of **1** and **2** showed one irreversible two-electron oxidation wave and two quasi-reversible one-electron reduction ones corresponding to the formation of their dications, anions, and dianions, respectively. Especially thiomethyl derivatives **1c** have the lowest oxidation and reduction potentials. Polymer **3** was prepared by an electrochemical oxidation as a free standing film. On the other hand, **4** could not be obtained by an electrochemical method. Cyclic voltammograms of **3** showed both oxidation and reduction waves. Electrochemically dedoped **3** has an absorption edge at 1.4 eV. The doped film of **3** shows a low conductivity and the inclusion of dopant anion is 0.6 for a monomer. MNDO-PM3 calculations demonstrate that **1a** and **2** have three almost degenerated orbitals as HOMOs. The calculations showing a large AO coefficient at the α-positions in HOMOs predict that polymerization would proceed at these positions. This prediction was proved by the fact that the polymerization was prevented by the introduction of methyl groups on the α-positions of **1a**. MO calculations estimate the small HOMO-LUMO gaps for **1a** and **2** than these of analogous compounds.

Introduction

Many modifications have been performed for poly(pyrrole) and poly(thiophene) in order to improve their physical properties owing to their high environmental stabilities and good conductivities.[1,2] In particular the structural versatility of poly(thiophene) have promoted such investigation.[2] However there are a few reports about the polymers with branched chains,[3] because such structures are considered to give a defect which decreases conductivities. The polymers reported previously as branched ones have unfavorable structures for conductivities for example bad coplanarities[3a-c,f] and substituents on unsuitable positions.[3d,e] Therefore it seems that intrinsic properties have not been precisely estimated for the branched polymers. The branched chains can facilitate a charge transport between adjacent chains and give better mechanical properties for the polymers. From these viewpoints, the author designed poly(4H-cyclopenta[2,1-b;3,4-b']dithiophen-4-one azine) (**3**) and poly(7H-cyclopenta[1,2-b;4,3-b']dithiophen-7-one azine) (**4**), which are constituted of two cyclopentadithiophene parts linked with the electron-accepting azine group.



Type I



Type II

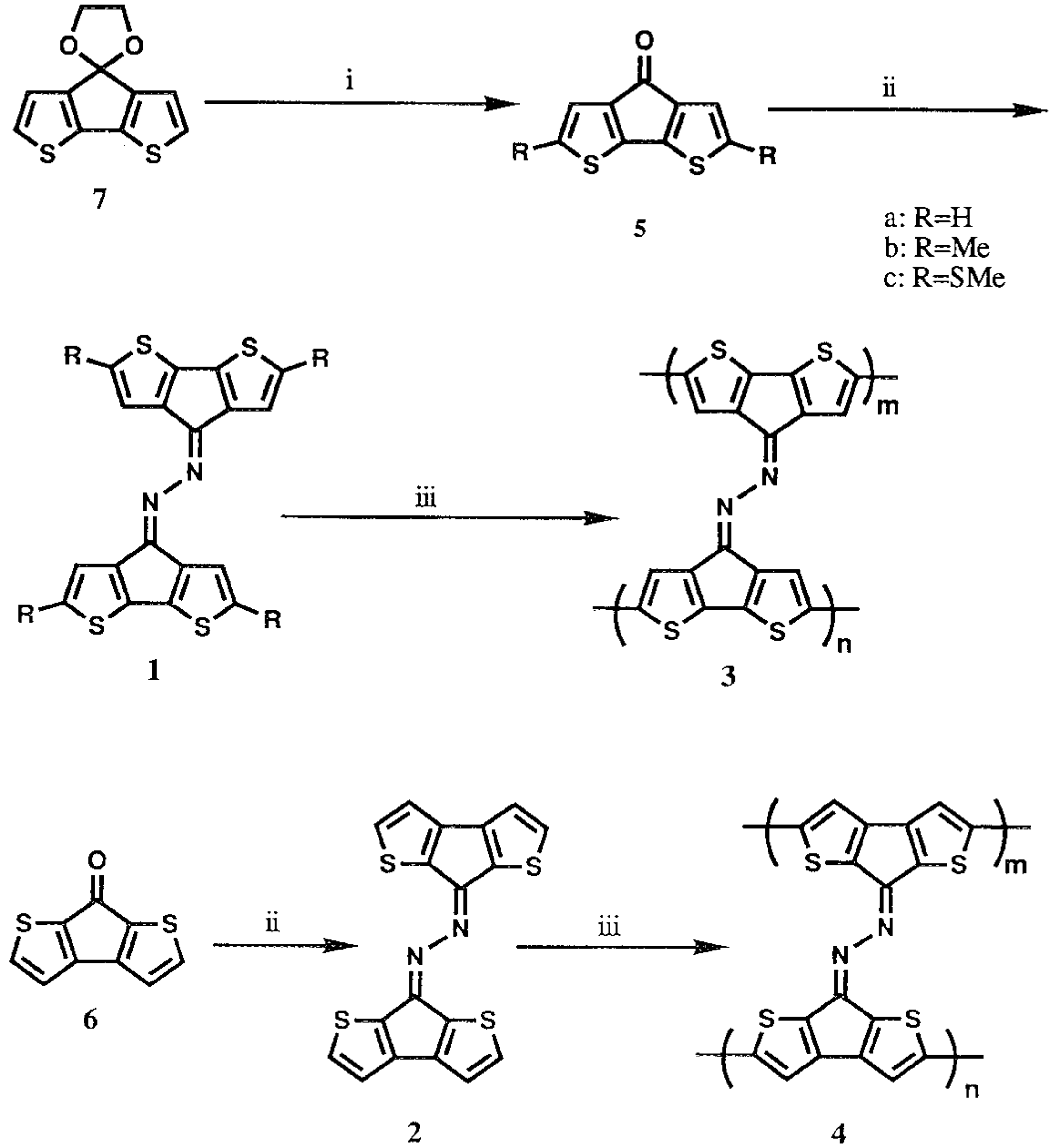
The polymers **3** and **4** may have two structures (Type I and Type II) in their film. The Type I structure is able to construct paired chains which make interactions between these two chains stronger and the conformation between successive monomer units completely planar. The Type II structure can join some pairs of chains, which is favorable for a charge transfer between polymer chains in addition to mechanical properties of the films. Moreover, the cyclopentadithiophene skeleton is very fruitful for a modification of poly(thiophene) in terms of steric congestion as indicated in the previous section.

Recently, it was reported that cyclopentadithiophene derivatives containing electron-withdrawing groups show small HOMO-LUMO gaps and the polymers prepared from such molecules have narrow band gaps.[4] Therefore, it seems that **3** and **4** should have narrow band gaps on account of the electron-accepting character of azine group. Narrow band gap polymers attract special attention owing to their novel electronic and optical properties which are predicted by much theoretical works.[5]

Results and Discussion

Preparation and properties of the Monomers and Derivatives

Ketones **5a** and **6** were synthesized according to previously reported methods.[6] Ketones **5b** and **5c** were obtained by the reactions of 4H-cyclopenta[2,1-b;3,4-b']dithiophen-4-one ethylene acetal (**7**) with a large excess of n-BuLi in THF at -78 °C followed by the treatment with the corresponding nucleophiles, iodomethane for **5b** and dimethyl sulfide for **5c**, and then hydrogen chloride in 85 and 59 % yields, respectively.[7] 4H-Cyclopenta[2,1-b;3,4-b']dithiophen-4-one azines (**1**) and 7H-cyclopenta[1,2-b;4,3-b']dithiophen-7-one azine (**2**) were prepared by the dehydrating condensation reactions of the corresponding ketones **5** and **6** with hydrazine in the presence of *p*-toluenesulfonic



Scheme I *Reagents* : i, n-BuLi, MeI or MeSSMe; ii, H_2NNH_2, EtOH; iii, electrochemical polymerization

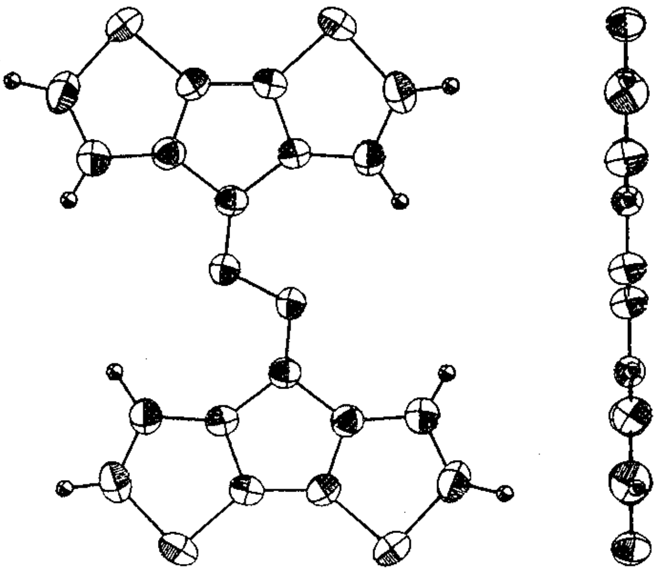


Figure 1. The top view of the X-ray molecular structure of **1a**. The side view results from 90° rotation around the perpendicular axis.

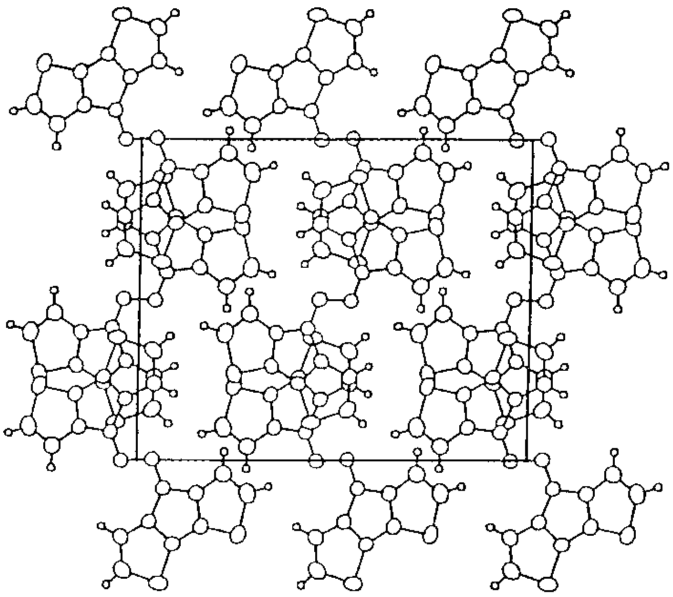


Figure 2. X-ray crystal structure of **1a**.

Table I. Properties of **1** and **2**

compd	λ_{max}/nm (log ε)[a]	E_{pa}[b]	E_{pc1}[b]	E_{pc2}[b]
1a	467 (3.32)	+1.25	-1.01	-1.33
1b	528 (3.18)	+1.20	-1.03	-1.34
1c	527 (3.36)	+0.86	-0.78	-1.06
2	445 (4.02)	+1.47	-0.96	-1.39

[a] Measured in CH_2Cl_2. [b] Measured by cyclic voltammetry in PhCN, 0.1 mol dm^{-3} TBAP, scan rate 100 mV s^{-1}, Pt electrode, V vs SCE.

acid in 85-89 % yields (Scheme 1).[8] All azines are air-stable purple crystals. The X-ray structural analysis of **1a** shows that the molecule is planar and is located on a symmetry center in the crystal (Figure 1). The molecules are stacked along the b axis with making a two dimensional structure shown in Figure 2.

The cyclic voltammograms of **1** and **2** were measured in PhCN containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate (TBAP) at a scan rate of 100 mV s^{-1}, and using a Pt electrode and SCE as a working and reference electrode, respectively. The redox potentials are listed in Table I and the cyclic voltammograms of **1a** and **2** are shown in Figure 3. All azines showed one irreversible two-electron oxidation wave and two quasi-reversible one-electron reduction ones corresponding to the formation of their dications, anions, and dianions, respectively. The similar electrochemical properties are reported for other analogous compounds with azine-bridges such as fluorenone azine.[9] The simultaneous oxidations reflect small on-site Coulombic repulsion in these molecules. Therefore, in the polymer there may be small interactions between polarons on paired chains, which allow two polarons to exist on paired chains at the same time. Methylthio groups decrease both oxidation and reduction potentials. Only **1c** showed the cathodic peak corresponding to the reduction of its dication at +0.73 V vs SCE. These special effects of methylthio group are reported in other systems.[8,10]

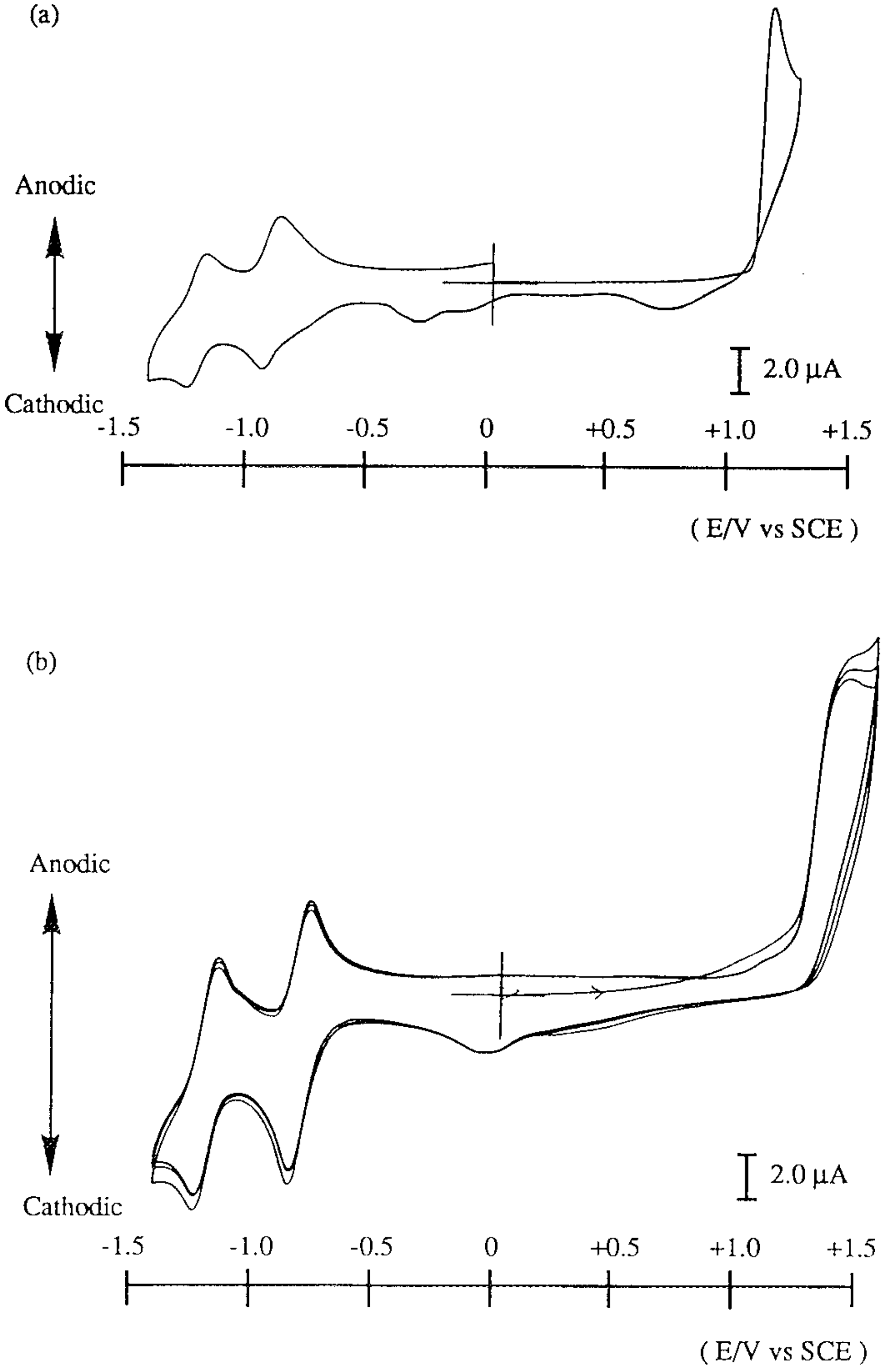


Figure 3. Cyclic voltammograms of (a) **1** and (b) **2** measured in PhCN containing 0.1 mol dm^{-3} TBAPF$_6$, scan rate 100 mV s^{-1}, and under an argon atmosphere. A platinum disk and SCE were used as a working and a reference electrode, respectively.

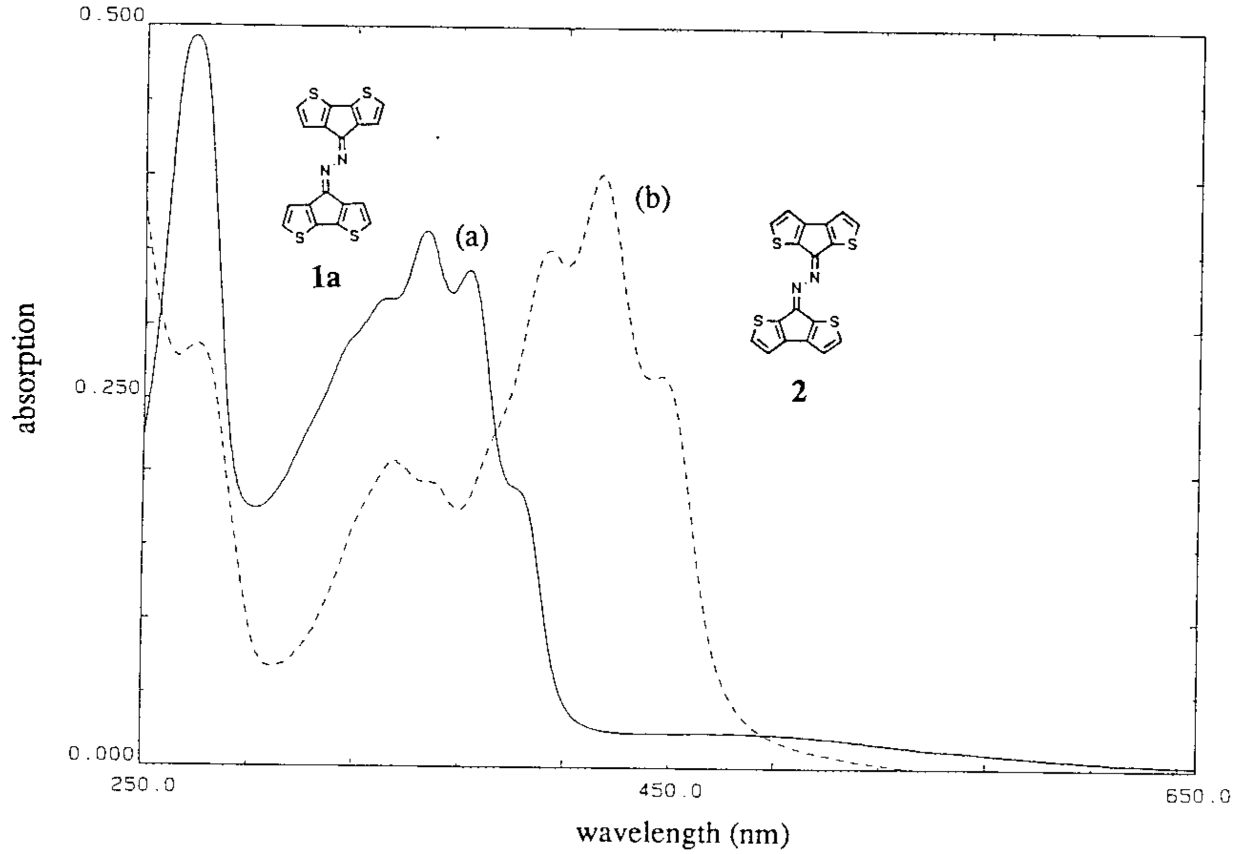


Figure 4. Electronic absorption spectra of (a) **1a** and (b) **2**.

Absorption maxima of **1** and **2** in UV-vis spectra are summarized in Table I. Weak absorptions (log ε = 3.1-3.4) were observed in a long wavelength region in addition to the strong ones in the spectra of **1**. Especially, **1b** and **1c** bearing electron-donating groups have absorptions at longer wavelengths than that of **1a** due to their higher polarization. The absorption maxima shift by about 60 nm compared with that of **1a**. Similar bathochromatic shifts are observed in ketones **5**. Azine **2** also has the absorption in the longer wavelength region. But there is no additional weak absorption like the observed for **1**.

Preparation and Properties of Polymers

The polymer **3** was prepared by the electrochemical oxidation of **1a** using a Pt disk or indium-tin oxide (ITO) as a working electrode in PhCN solution containing 0.1 mol dm^{-3} tetrabutylammonium hexafluorophosphate (TBAPF$_6$). The polymerization was performed by a cyclic potential-sweep technique in the potential range of -0.5 to +1.5 V vs SCE (Figure 5). The cyclic voltammograms recorded during the polymerization have typical characters for the growth and deposition of electrochemically active polymers on the electrode, such as an increase in the current and appearance of new peaks at lower potentials. The thick film of **3** was prepared for the measurement of the conductivity using a constant potential method at +1.2 V vs SCE. It is noteworthy that the strong free standing film could be yielded even in a dilute solution of the monomer (3.0 mmol dm^{-3}). This high ability for forming the thin film may be attributed to the two dimensional network structures. The observation with scanning electron microscope (SEM) indicates that the thickness of the film is 4.0 μm and the film has very smooth, flat surfaces.[11] On the other hand, **4** could not be prepared by an electrochemical method.

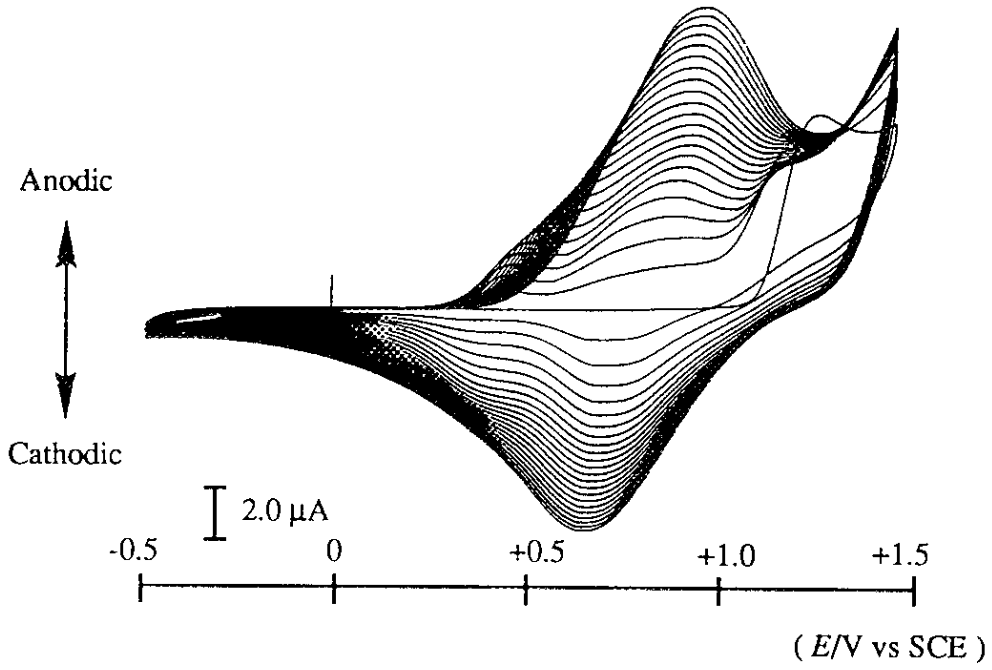


Figure 5. Cyclic voltammograms recorded during the polymerization of **1** in PhCN containing 0.1 mol dm^{-3} $TBAPF_6$, scan rate 100 mV s^{-1}, and under an argon atmosphere. A platinum disk and SCE were used as a working and a reference electrode, respectively.

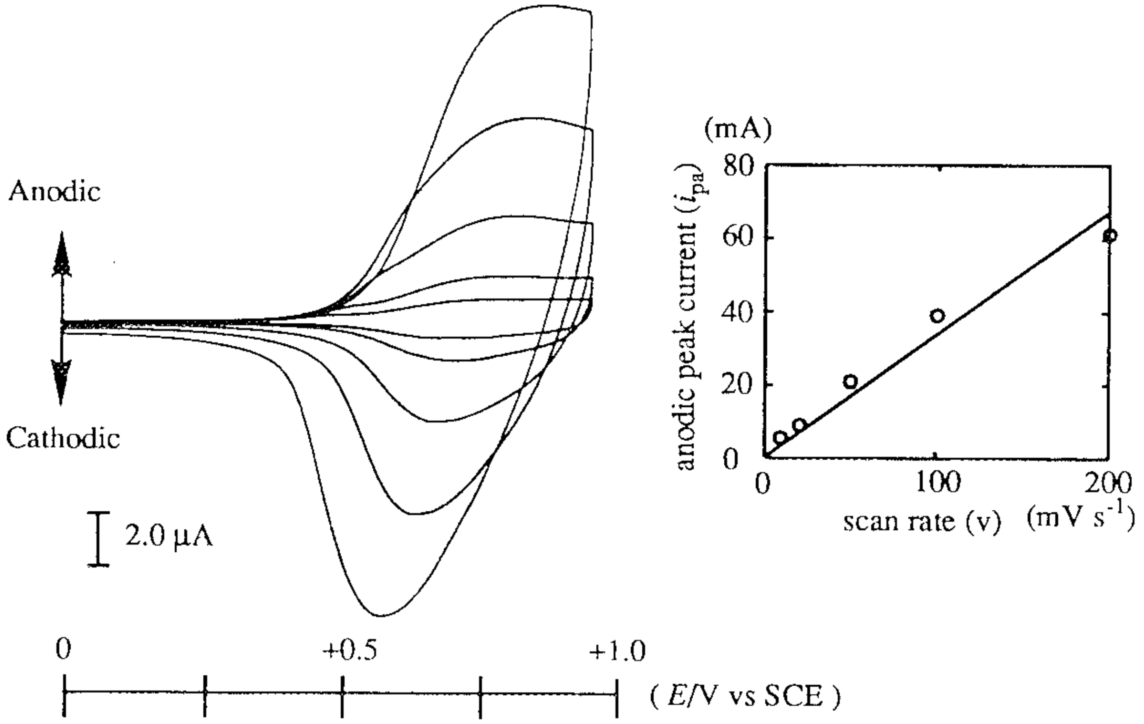


Figure 6. Cyclic voltammograms of **3** measured in a monomer-free PhCN / 0.1 mol dm^{-3} $TBAPF_6$ at various scan rates under an argon atmosphere. A platinum disk and SCE were used as a working and a reference electrode, respectively. The insert shows the dependence of i_{pa} on scan rate.

Figure 6 shows the cyclic voltammograms of **3** measured in a monomer free medium, in the potential range of 0.0 to +1.0 V vs SCE, and at various scan rates. Polymer **3** has the oxidation peak at +0.75 V vs SCE at a scan rate of 10 mV s^{-1} and the current value of the peak almost unchanged during the repeat of the redox cycles in this region. The height of anodic peak current (i_{pa}) was proportional to the scan rate (v) in the range of 10-200 mV s^{-1} (the insert in Figure 6). This linear correlation is characteristic of an electroactive polymer film grafted on an electrode.[12] The current is not diffusion controlled and the behavior of the cyclic voltammogram is attributed to the electroactive species on the electrode surface. When the scan range was expanded from -0.9 to +1.0 V vs SCE, the reduction wave was observed around -1.0 V vs SCE besides the oxidation peak (Figure 7). However, the reduction peak was not discernible and the current value of the anodic and reduction peak decreased in the successive cycles, which shows that the n-doping state is sensitive to the oxidation and the polymer decomposes as found in polyisothianaphthene (PITN).[13] The polymerization also proceeded using other supporting electrolytes such as $LiClO_4$ and TBAP.

In the infrared spectrum of electrochemically dedoped **3**, two peaks assigned to the azine group were observed at 1699 and 1622 cm^{-1}, whereas **1a** showed only a peak at 1620 cm^{-1} (Figure 9). These facts show that there are at least two configurations which involve different bridge-types. A remarkable decrease in the intensity of the peak at 687 cm^{-1}, assigned to the C-H out-of-plane vibration, was observed after polymerization. In the UV-vis-NIR spectrum, electrochemically dedoped **3** shows an absorption maximum at 379 nm with an absorption edge at about 900 nm (Figure 8). An additional absorption appears at a lower energy region in the p-doping of **3**. The optical band gap of neutral **3** is estimated to be 1.4 eV from the absorption edge which is extremely lower than that of polythiophene (2.1 eV).[13] However, the film of **3**$\cdot(ClO_4^-)_x$ has only poor conductivity (< 10^{-3} S cm^{-1}). The elemental analysis of this doped film showed that the dopant concentration is 0.6 for a monomer unit, namely 0.3 for a cyclopentadithiophene part.

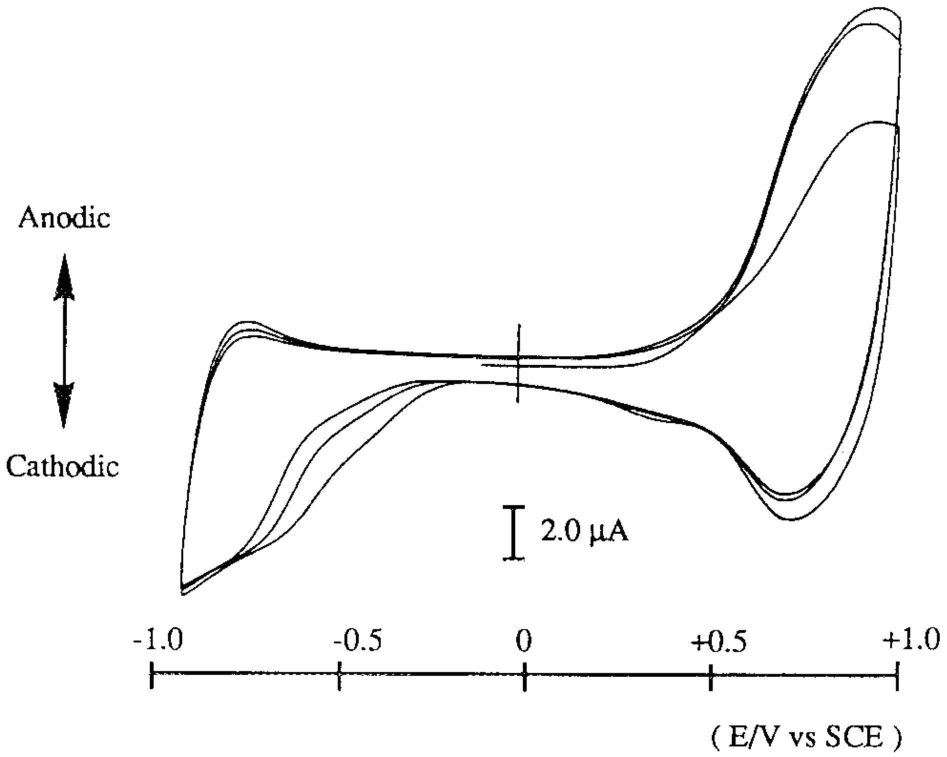


Figure 7. Cyclic voltammograms of **3** measured in a monomer-free PhCN / 0.1 mol dm^{-3} TBAPF$_6$ at a scan rate 100 mV s^{-1} under an argon atmosphere. A platinum disk and SCE were used as a working and a reference electrode, respectively.

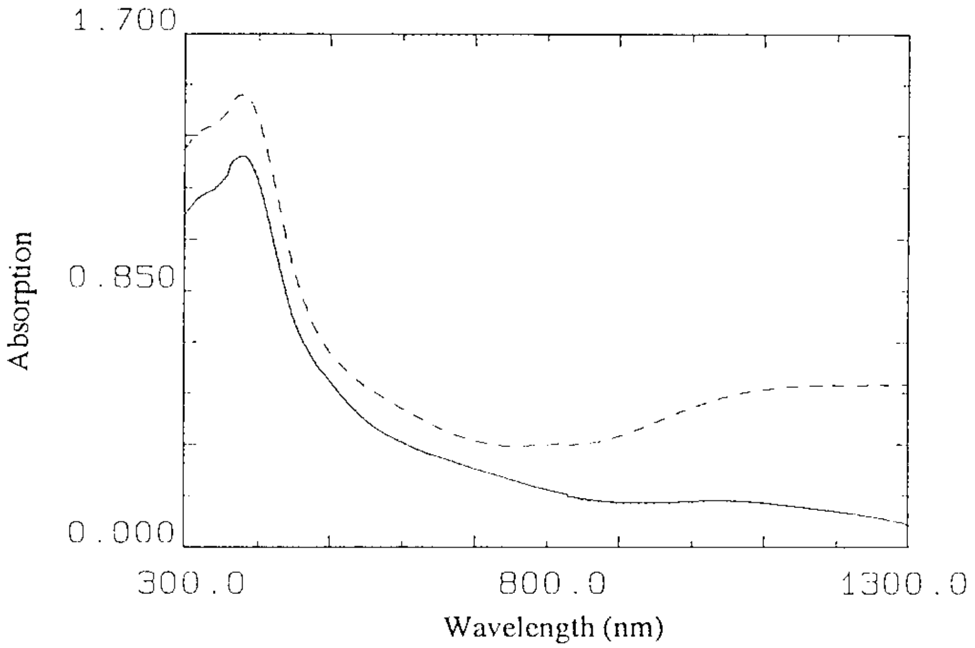


Figure 8. Electronic absorption spectra of electrochemically dedoped (solid line) and doped (broken line) polymer 3.

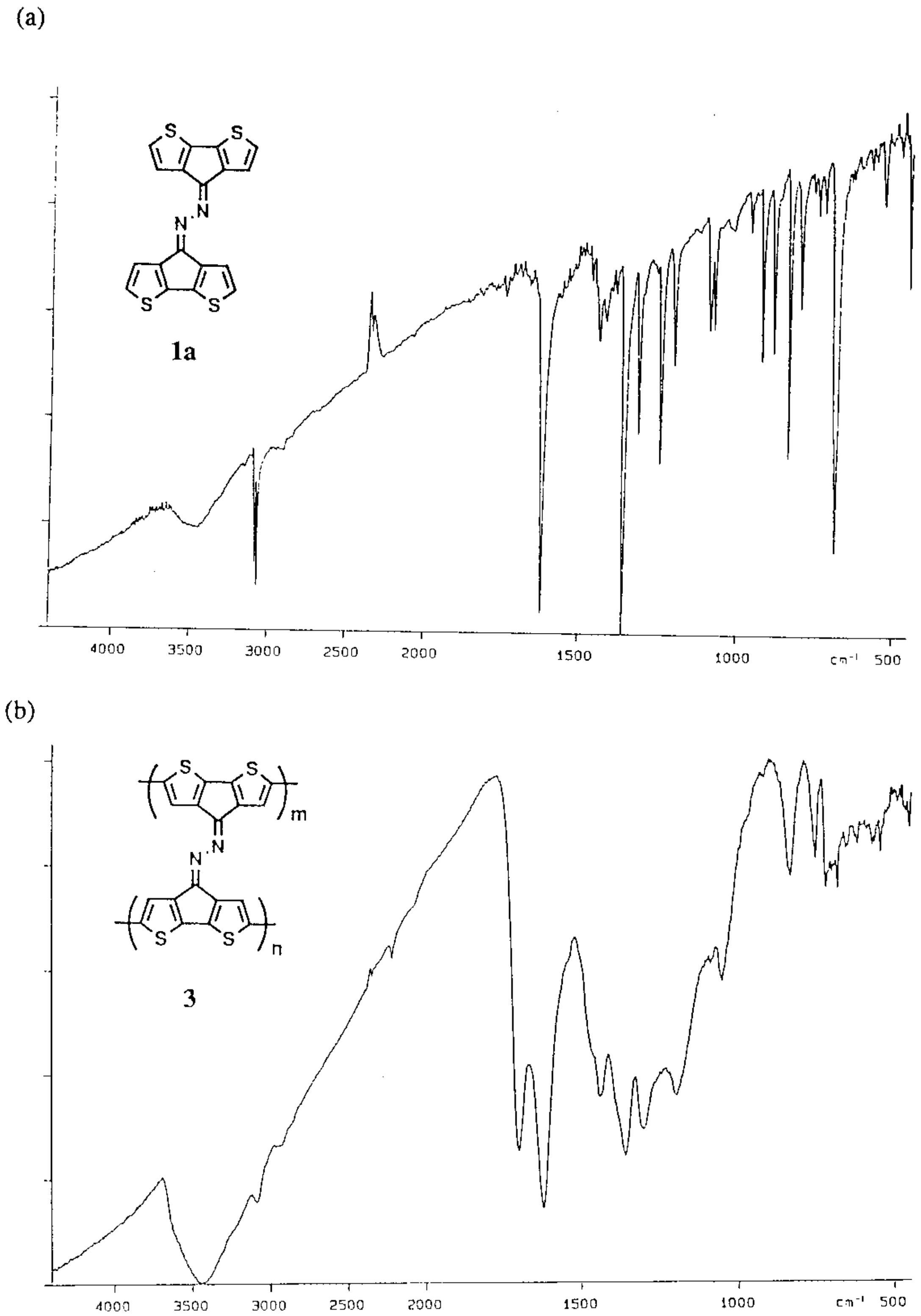


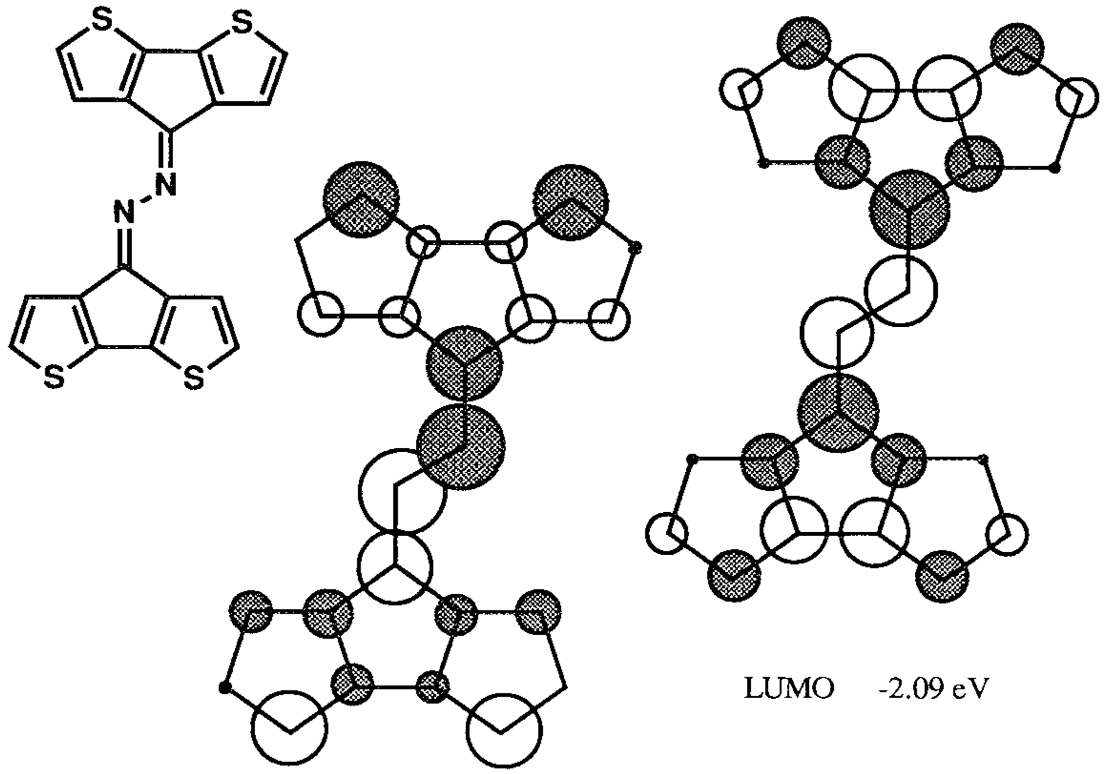
Figure 9. FT-IR spectra of (a) **1a** and (b) **3**.

Molecular Orbital Calculation Results

MNDO-PM3 calculations[14] show that both **1a** and **2** have three almost degenerating orbitals as the HOMOs (Figure 10 and 11, respectively). The calculations for **1a** show a larger atomic orbital (AO) coefficients at the a-positions than at the β-positions in the HOMOs. This result predicts that the polymerization will proceed at α-positions, which was proved by the fact that the polymerization was prevented by the introduction of the substituents on the α-positions of **1a**. Calculated net atomic charges in the dication of **1a** exhibit that the positive charge of the dication was almost localized on the sulfur atoms (Figure 12). These consequences reflect the small on-site Coulombic repulsion and the simultaneous oxidation of **1a** observed in the cyclic voltammogram.

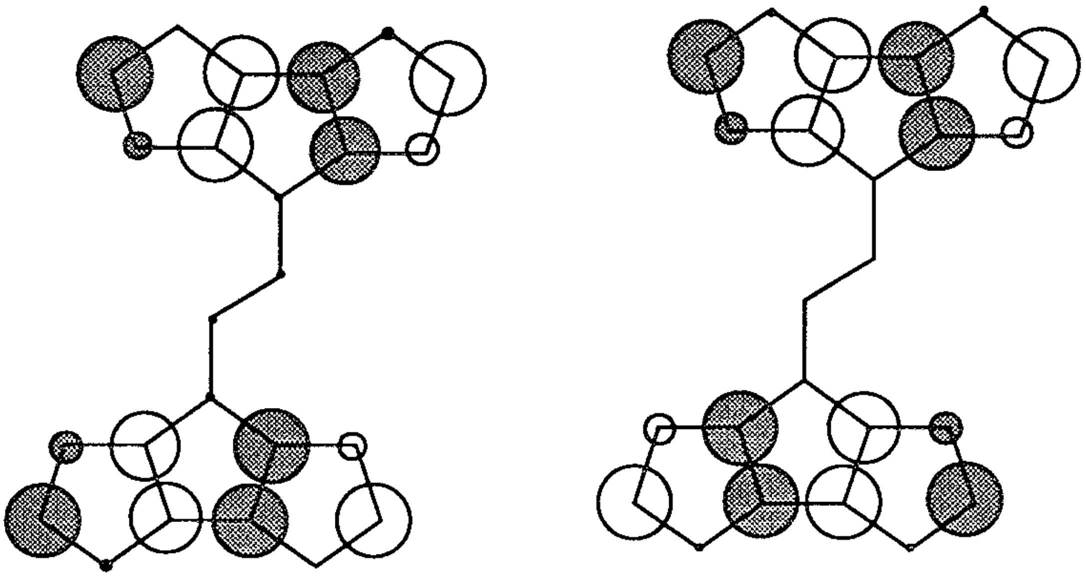
INDO/1-CI calculations[15] were also performed for the investigation of the difference between the absorption spectra of **1** and **2**. The author performed the configuration interaction (CI) calculations up to 100 configuration functions. The simulated spectra indicate that **1a** has π-π^* absorptions with low intensity in a long wavelength region, whereas **2** does not have such absorptions. These facts are consistent with the observation and indicate that the observed weak absorptions of **1a** are not assigned to n-π^* but to π-π^*. There are forbidden transitions at ca. 570 nm on the edge of the longest absorption in the spectrum of **2**. This fact shows that the HOMO-LUMO separation can not be estimated from the observed absorption edge

The HOMO-LUMO gaps of a series of molecules with cyclopentadithiophene skeletons were investigated using the MNDO-PM3 method (Table II). The HOMO-LUMO gaps and substitution effects in type A molecules are similar to those in type B. The molecules with 1,3-dithiol-2-ylidene or azine groups have smaller HOMO-LUMO separation than those of the other molecules. The azine group largely stabilizes the LUMO and gives only a small effect on the HOMO. Other electron-accepting groups lower the energy levels of both the HOMO and LUMO.



LUMO -2.09 eV

HOMO(1) -8.90 eV



HOMO(2) -8.95 eV

HOMO(2') -8.95 eV

Figure 10. AO coefficients in the HOMOs and LUMO of **1a** calculated by the MNDO-PM3 method. The radii of circles are approximately proportional to the magnitude of the coefficients.

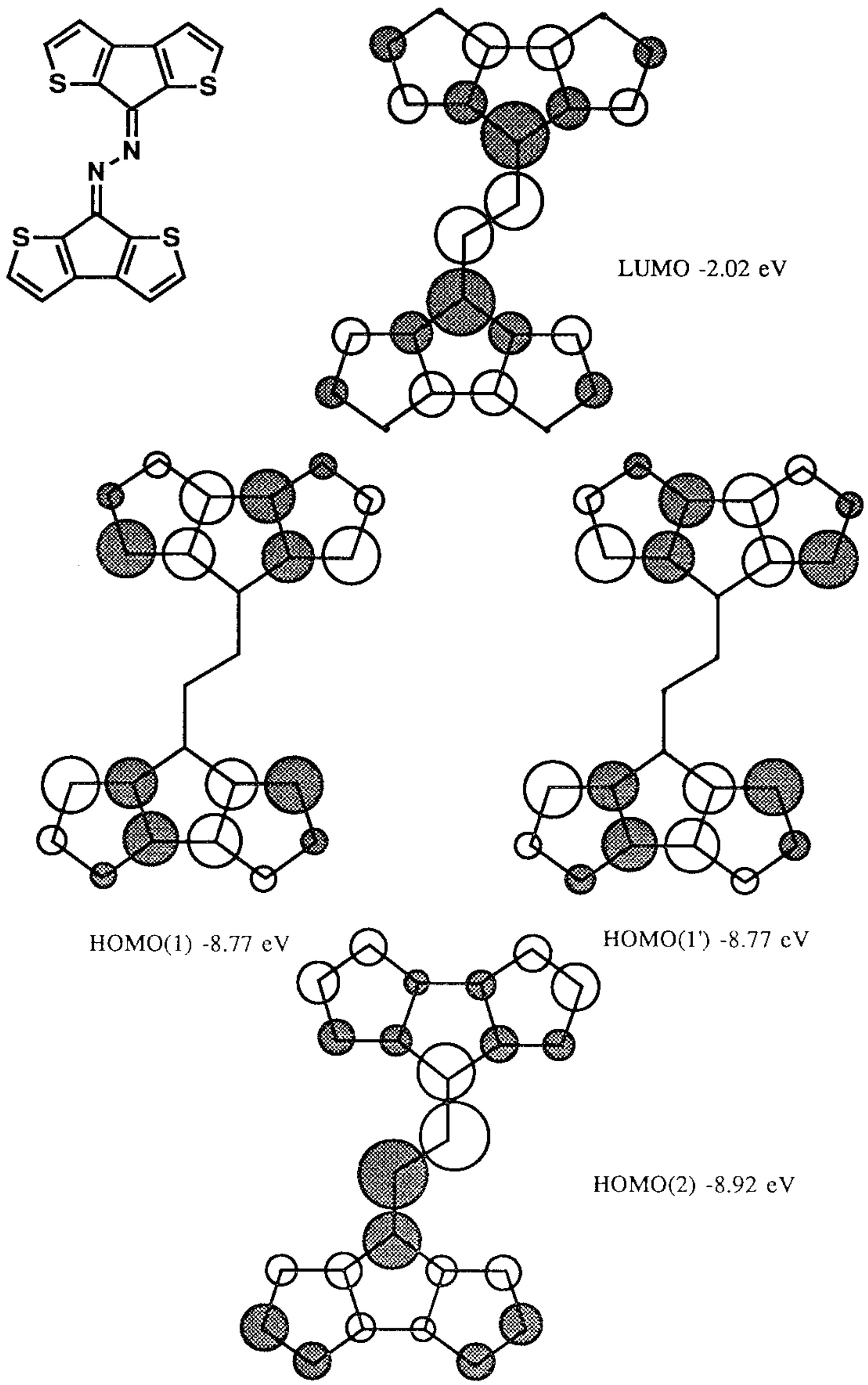


Figure 11. AO coefficients in the HOMOs and LUMO of **2** calculated by the MNDO-PM3 method. The radii of circles are approximately proportional to the magnitude of the coefficients.

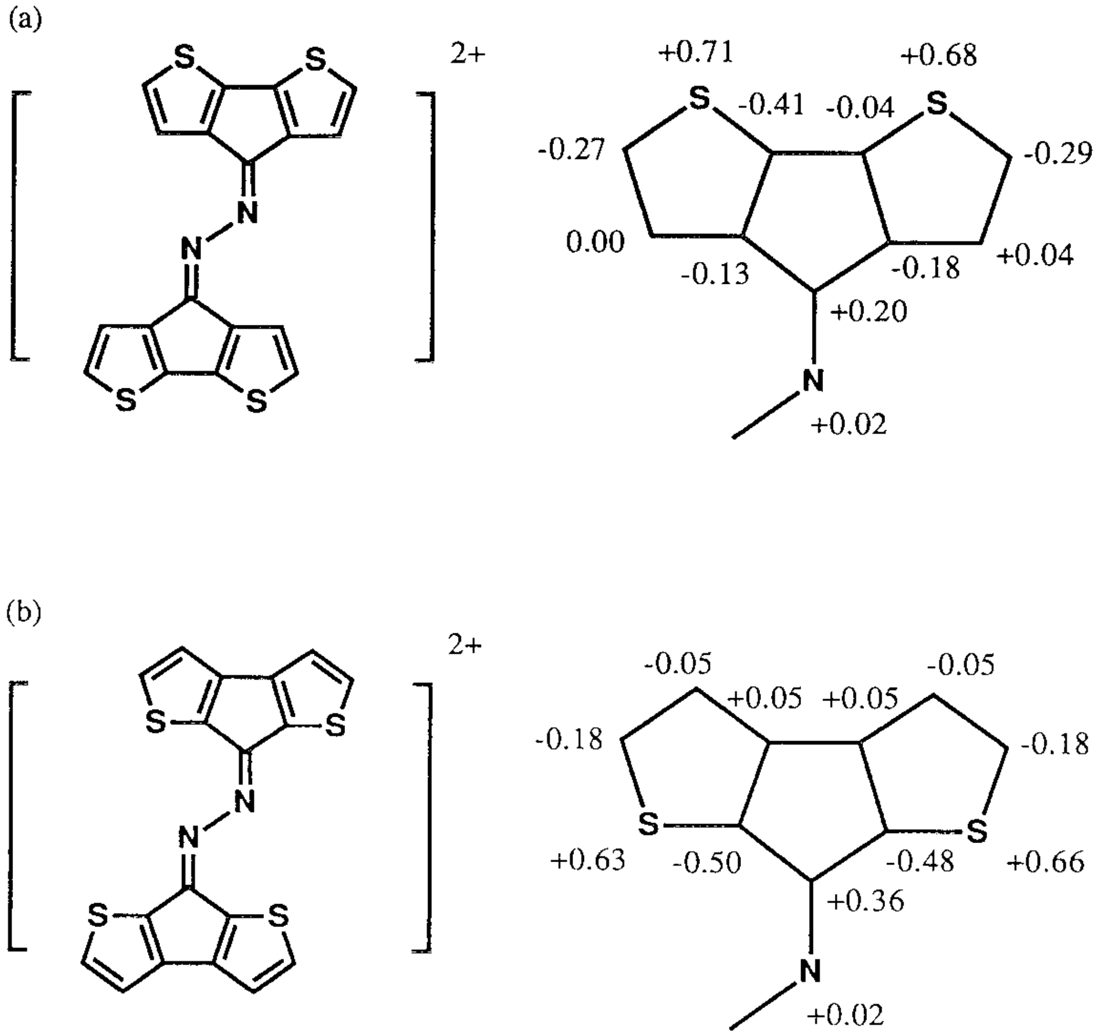
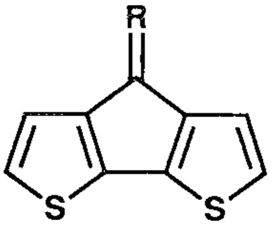
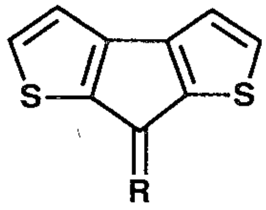


Figure 12. Net atomic charges of the dications derived from **1a** (a) and **2** (b) calculated by the MNDO-PM3 method.

Table II. Energy levels of the HOMOs and the LUMOs and their energy gaps calculated for the molecules with cyclopentadithiophene parts by the MNDO-PM3 method.



Type A



Type B

		Type I			Type II	
R	HOMO[a]	LUMO[a]	E_g[a]	HOMO[a]	LUMO[a]	E_g[a]
methylene	-8.74	-1.35	7.39	-8.66	-1.22	-7.44
ketone (**5** and **6**)	-9.17	-1.74	7.43	-9.03	-1.59	7.44
dicyanomethylene	-9.32	-2.38	6.94	-9.21	-2.34	6.87
1,3-dithiol-2-ylidene	-8.19	-1.67	6.52	-8.19	-1.58	6.61
azine (**1** and **2**)	-8.90	-2.09	6.81	-8.77	-2.02	6.75

[a] eV

Conclusion

The monomers, **1** and **2**, with four α-positions were synthesized to prepare the novel polymers with linked chains. The methyl and thiomethyl derivatives of **1** were also prepared and investigated for the comparison with the other compounds and the interest for the properties of themselves. These compounds show amphoteric multistage redox behavior and absorptions in a longer wavelength region. The blue shifts of the absorption maxima were brought about by the introduction of electron-withdrawing groups into α-positions. Only **1a** gave the corresponding polymer **3** by the electrochemical method. The polymer showed both oxidation and reduction waves in the cyclic voltammograms. The optical band gap estimated from the absorption edge was 1.4 eV. The conductivity of the film so grown was low (< 10^{-3} S cm^{-1}) and the film contained 0.6 anion a monomer unit. Molecular orbital calculations of **1a** and **2** show that both **1a** and **2** have three almost degenerating orbitals as the HOMOs and they have small HOMO-LUMO gaps. The simulated absorption spectra of **1a** and **2** explain the difference in observed ones.

Experimental

General. Melting points are uncorrected. ^1H NMR spectra were recorded at 400 MHz. Infrared spectra were taken in KBr pellets. Mass spectra were obtained in the EI mode at 70 eV unless indicated otherwise.

4H-Cyclopenta[2,1-b;3,4-b']dithiophen-4-one derivatives (5b, c). 4H-Cyclopenta[2,1-b;3,4-b']dithiophen-4-one ethylene acetal (7) was synthesized by the same method used for the preparation of **5a** without treatment with HCl in 58 % yield. **7** was spontaneously decomposed to give **5a** at room temperature. But **7** can be stored in a refrigerator. : brown crystals; mp 146-148 °C (from EtOH); ^1H NMR ($CDCl_3$) δ 4.31 (s, 4 H), 6.96 (d, J = 4.9 Hz, 2 H), 7.12 (d, J = 4.9 Hz, 2 H); IR (KBr) 3102, 1317, 1162, 987, 715 cm^{-1}; UV (EtOH) λ_{max} 234 nm (log ε 4.12), 238 (4.12), 339 (3.91); MS m/z (relative intensity) 236 (M^+, 100), 193 (12), 177 (32). Anal. Calcd. for $C_{11}H_8O_2S_2$: C, 55.93; H, 3.42. Found: C, 55.85; H, 3.57. To a solution of acetal 7 (118 mg, 0.5 mmol) in dry THF (15 ml) was added dropwise n-BuLi in hexane (1.56 mol dm^{-3}, 7.7 ml, 12.0 mmol) at -78 °C under argon. This solution was stirred for 45 min at -78 °C, and then iodomethane (1.0 ml, 16.0 mmol) was added. The solution was stirred for 20 min. After a cooling bath was removed, the solution was stirred for further 1 h. The solution was poured into conc. HCl solution (50 ml) and extracted with ether. The extract was washed with $NaHCO_3$ solution and water, and then dried over anhydrous Na_2SO_4. After evaporation of the solvent, the resulting solid was purified by recrystallization from EtOH to give **5b** (93 mg) as purple crystals in 85 % yield. According to the similar procedure to the previous one, **5c** was prepared from **7** (118 mg, 0.5 mmol), n-BuLi in hexane (1.56 mol dm^{-3}, 7.7 ml, 12.0 mmol), and dimethyl disulfide (1.5 ml, 16.0 mmol) in dry THF in 59 % yield. In this case the resulting oily residue was purified by SiO_2 column chromatography before recrystallization from EtOH.

5b: mp 195-198 °C ; ^{1}H NMR ($CDCl_3$) δ 2.42 (d, J = 0.9 Hz, 6 H), 6.62 (d, J = 0.9 Hz, 2 H); IR (KBr) 1707, 1328, 1199, 766, 472 cm^{-1}; UV (EtOH) λ_{max} 265 nm (log ε 4.54), 522 (3.10); MS m/z (relative intensity) 220 (M^+, 100), 219 (74), 191 (18). Anal. Calcd. for $C_{11}H_8OS_2$: C, 59.97; H, 3.66. Found: C, 60.01; H, 3.84.

5c: mp 144-147 °C ; ^{1}H NMR ($CDCl_3$) δ 2.48 (s, 6 H), 7.02 (s, 2 H); IR (KBr) 1699, 1288, 762, 500 cm^{-1}; UV (EtOH) λ_{max} 285 nm (log ε 4.60), 518 (3.32); MS m/z (relative intensity) 284 (M^+, 95), 269 (100), 254 (29). Anal. Calcd. for $C_{11}H_8OS_4$: C, 46.49; H, 2.84. Found: C, 46.50; H, 2.98.

4H-Cyclopenta[2,1-b;3,4-b']dithiophen-4-one azine (3) (General Procedure). To a solution of ketone **6** (384 mg, 2 mmol) in EtOH were added 80 % hydrazine monohydrate (0.4 ml, 6.6 mmol) and *p*-toluenesulfonic acid monohydrate (144 mg, 0.76 mmol). This solution was stirred for 12 hours at 50 °C. The resulting precipitate was filtered off and washed with EtOH. Recrystallization from $CHCl_3$ gave pure **3a** (319 mg) as dark purple crystals in 84 % yield.

1,1',7,7'-Tetramethyl-4H-cyclopenta[2,1-b;3,4-b']dithiophen-4-one azine (**3b**), 1,1',7,7'-tetrathiomethyl-4H-cyclopenta[2,1-b;3,4-b']dithiophen-4-one azine (**3c**) and 7H-cyclopenta[1,2-b;4,3-b']dithiophen-7-one azine (**4**) were similarly prepared from 1,1',7,7'-tetramethyl-4H-cyclopenta[2,1-b;3,4-b']dithiophen-4-one (**5b**), 1,1',7,7'-tetrathiomethyl-4H-cyclopenta[2,1-b;3,4-b']dithiophen-4-one (**5c**), and 7H-cyclopenta [1,2-b;4,3-b']dithiophen-7-one (**6**), respectively.

3a: mp 326-327 °C ; ^{1}H NMR ($CDCl_3$) δ 7.03 (d, J = 4.9 Hz, 2 H), 7.14 (d, J = 4.9 Hz, 2 H), 7.31 (d, J = 4.9 Hz, 2 H), 7.37 (d, J = 4.9 Hz, 2 H); IR (KBr) 3070, 1620, 1362, 840, 687 cm^{-1}; UV (CH_2Cl_2) λ_{max} 269 nm (log ε 4.63), 341 (4.44, sh), 357 (4.50), 373 (4.47), 392 (4.22, sh), 467 (3.32); MS m/z (relative intensity) 380 (M^+, 92), 352 (31), 190 (32), 146 (100). Anal. Calcd. for $C_{18}H_4N_2S_4$: C, 56.85; H, 2.12; N, 7.37. Found: C, 56.69; H, 2.42; N, 7.33.

3b: yield 85 %, dark purple crystals; mp 322 °C (decomp.) (from THF) ; ^{1}H NMR ($CDCl_3$) δ 2.44 (s, 6 H), 2.52 (s, 6 H), 6.95 (s, 2 H), 6.95 (s, 2 H); IR (KBr) 2912, 1624, 1326, 1204, 782 cm^{-1}; UV (CH_2Cl_2) λ_{max} 274 nm (log ε 4.50), 360 (4.36), 374 (4.31, sh), 528 (3.18); MS m/z (relative intensity) 436 (M^+, 100), 408 (23), 218 (34). Anal. Calcd. for $C_{22}H_{16}N_2S_4$: C, 60.55; H, 3.70; N,6.42. Found: C, 60.68; H, 3.83; N, 6.40.

3c: yield 86 %, dark purple crystals; mp 309-310 °C (decomp.) (from THF); ^{1}H NMR ($CDCl_3$) δ 2.49 (s, 6 H), 2.55 (s, 6 H), 7.35 (s, 2 H), 7.43 (s, 2 H); IR (KBr) 2914, 1623, 1351, 728 cm^{-1}; UV (CH_2Cl_2) λ_{max} 292 nm (log ε 4.74), 365 (4.58), 357 (4.58), 380 (4.37, sh), 527 (3.36); MS m/z (relative intensity) 564 (M^+, 100), 549 (36), 267 (53), 220 (33). Anal. Calcd. for $C_{22}H_{16}N_2S_6$: C, 46.82; H, 2.86; N, 4.97. Found: C, 46.64; H, 2.93; N, 5.01.

4a: yield 89 %, dark purple crystals; mp 307 °C (from THF); ^{1}H NMR ($CDCl_3$) δ 6.96 (d, $J = 4.9$ Hz, 2 H), 7.00 (d, $J = 4.6$ Hz, 2 H), 7.44 (d, $J = 4.6$ Hz, 2 H), 7.50 (d, $J = 4.9$ Hz, 2 H); IR (KBr) 3070, 1625, 1500, 1416, 815, 733 cm^{-1}; UV (CH_2Cl_2) λ_{max} 269 nm (log ε 4.03), 347 (3.91), 403 (4.12), 423 (4.18), 445 (4.02); MS m/z (relative intensity) 380 (M^+, 100), 352 (22), 190 (12), 146 (48). Anal. Calcd. for $C_{18}H_4N_2S_4$: C, 56.85; H, 2.12; N, 7.36. Found: C, 56.79; H, 2.40; N, 7.35.

Experimental details of the X-ray crystal structure analysis. A dark purple cubic single crystal with approximate dimensions of 0.20 × 0.20 × 0.15 mm prepared by slow evaporation of $CHCl_3$ was selected for X-ray analysis. Crystal data were as followed. MF $C_{18}H_4N_2S_4$, fw 376.49, orthorhombic, *Pbca*, $a = 13.084$ (5) Å, $b = 7.916$ (2) Å, $c = 15.424$ (6) Å, $V = 1597.8$ (9) Å^3, $Z = 8$, $D_c = 1.57$ g cm^{-3}. The atomic and thermal parameters and bond lengths and angles are presented in appendix at the end of this thesis. Enraf-Nonius CAD4 (40 kV, 32 mA) diffractometer was used with graphite-monochromated Cu Kα radiation (λ = 1.5148 Å); $\theta / 2\theta$ scan technique. Cell parameters were determined from least-squares procedures on 25 reflections (44° < 2θ < 50°). A total of 1770 reflections were measured up to 2θ = 140° at room temperature. No significant variation was observed in intensities of three standards monitored every 7200 s. The structure was solved by the direct method using the MULTAN78 program[16] and refined by the block-diagonal least squares analysis based on F values using the UNICS III program[17] package. All the non-hydrogen atoms of the molecule were refined with anisotropic temperature factors. At the final stage, all hydrogen atoms found in the D maps were included in the refinement with isotropic temperature factors. A final R factor was 0.0450 for 1361 reflections with $|F_o| > 3\sigma|F_o|$. The final difference Fourier synthesis gave the largest peak of 6.3 e Å^{-3}. These calculations were carried out in the Computer Center of Institute for Molecular Science.

Electrochemical Measurements. All cyclic voltammetries were carried out with a three-component cell in distilled PhCN containing 0.1 mol dm^{-3} TBAP at a scan rate of 100 mV s^{-1}. The solution was degassed by argon bubbling before an electrochemical measurement which was performed under an argon atmosphere. A Pt disk, Pt wire, and SCE electrode were used as working, counter, and reference electrode, respectively.

The polymer for cyclic voltammetry was prepared by a cyclic potential-sweep technique using the above conditions. The resulting polymer on the electrode was thoroughly washed with PhCN. Cyclic voltammogram of polymer was then recorded in monomer free electrolyte under the same condition as above except for a scan rate. In order to avoid a shift of the E_{pa} arising from the IR drop across the film, cyclic voltammograms of polymer were measured at a scan rate of 10 mV s^{-1}.

General Procedure for Electrochemical Polymerization. The polymer for the conductivity measurement and elemental analysis was prepared by a constant potential method using an ITO, Pt wire, and SCE as a working, counter, and reference electrode, respectively, in distilled PhCN containing 3-10 mmol dm^{-3} monomer and 0.1 mol dm^{-3} supporting electrolyte. After degassed by argon, the polymerization was performed under an argon atomospher until a current became slight. The film so grown was peeled off from the electrode in MeCN, rinsed with MeCN, and dried. The polymer was yielded as black films. The conductivity measurement was carried out by a four-probe method. SEM was used for both the observation of a superficial morphology of the film and measurement of the thickness of the films.

The film for the elemental analysis was further washed with MeCN using a soxhlet with a glass filter for 24 hours and dried under vacuum at 60 °C for 24 hours. The elemental analysis was performed twice to check homogeneity and these two values agreed in 0.30 %. Inclusion of nitrogen was 0.00%.

The polymer for the measurement of the absorption spectrum was prepared by a cyclic potential-sweep technique under the conditions as described above except for using about 2.0 mmol dm^{-3} monomer solution. After the polymerization, the resulting film was thoroughly washed with PhCN. Then, electrochemical dedoping was carried out in a monomer free electrolyte at the most negative potential which do no serious damage to the film and ITO. Before the measurement of electronic spectrum, the dedoped film was rinsed with MeCN. On the other hand, for FT-IR measurement the dedoped film was peeled off from ITO, washed with MeCN, and dried.

3: black film; IR (KBr) 1699, 1622, 1360, 1302, 1198, 838, 758 cm^{-3}; UV λ_{max} 379 nm. Anal. Calcd. for $C_{18}H_4N_2S_4Cl_{0.62}O_{2.48}$: C, 49.34; H, 0.92; N, 6.39. Found: C, 49.54; H, 2.10; N, 6.39.

Computational Studies. MNDO-PM3 calculations were performed by using version 6.10 of the MOPAC program.[18] INDO/1 calculations were performed by the ZINDO program.[15] These calculations were carried out using the Sony-Tektronix CAChe system

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Conclusion

This thesis described novel three groups of conducting polymers that are poly(2-(2,4-cyclopentadien-1-ylidene)-1,3-dithioles) (in chapter 2), poly(4-(1,3-dithiol-2-ylidene)-4H-cyclopenta[2,1-b;3,4-b']dithiophenes) and poly(7-(1,3-dithiol-2-ylidene)-7H-cyclopenta[1,2-b;4,3-b']dithiophenes) (in chapter 3), and poly(4H-cyclopenta[2,1-b;3,4-b']dithiophen-4-one azine) (in chapter 4).

Chapter 2 involves a novel approach of the modification of poly(heterocycles), in which a carbon atom with a cross conjugation system is introduced instead of heteroatoms. The polymer could not be prepared by a common electrochemical method but the introduction of a methyl substituent was proved to effectively improve the character of the polymer such as the oxidation potential and stability to oxidation. 1,3-Dithiole skeleton was also presented in chapter 2 as a novel building block for conducting polymers. The investigation of the properties of the monomers and polymers revealed some advantages induced by the 1,3-dithiole skeleton, for example the promotion of oxidation and the increase in a polarization.

In chapter 3 additional favorable characters of the 1,3-dithiole skeleton such as the enhancement of intermolecular interactions and structural versatilities are described with investigating the properties of the novel monomers and corresponding polymers containing 1,3-dithiole groups. The polymers discussed in chapter 3 exhibit high conductivities. The best conductivity is as high as that of PITN which is known as one of the most conducting poly(thiophene) derivatives. Theoretical investigations in chapter 3 emphasize the significance of the effective conjugation among monomer units and utility of cyclopentadithiophene derivatives for the prevention of the steric hindrance between successive monomer units.

In chapter 4 cyclopentadithiophene derivatives are used to make novel poly(thiophenes) with two-dimensional structures. Though the polymer prepared here showed a poor conductivity, the investigation of the corresponding monomer and its derivatives revealed their interesting properties such as amphoteric multistage redox behavior and small HOMO-LUMO gaps. Moreover, MO calculations indicate that these molecules have three almost degenerate orbitals.

Throughout this work, it is revealed that the modifications of conducting polymers are very fruitful. Novel two methods for the modification of conducting polymers were proposed. One is the introduction of the carbon atom with cross conjugating system instead of heteroatom. The other is to use cyclopentadithiophene unit, which is more preferable in terms of a steric congestion. Some groups such as 1,3-dithiole rings are proposed as very useful building blocks for the preparation of conducting polymers. This is proved by the successful preparation of highly conducting poly(thiophenes) described in this thesis. These results will serve for the design of new type of conducting polymers.

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The graduate University for Advanced Studies

November 1993

List of Publications

1. Kozaki, M.; Tanaka, S.; Yamashita, Y. "Preparation and Properties of Poly-4-(1,3-dithiol-2-ylidene)-4H-cyclopenta[2,1-b;3,4-b']dithiophene and Its Derivatives," *J. Chem. Soc., Chem. Commun.* **1992**, 1137.
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Other Publications

1. Saito, K.; Kozaki, M.; Takahashi, K. "Reaction of Azepin with Palladium(II) Acetate : Formation of Muconzialdehyde and Dihydroazepine Derivative," *Heterocycles* **1990**, *31(8)*, 1491.
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3. Saito, K.; Kozaki, M.; Takahashi, K. "Aromatization and Hydrogen-Shift of 7-Substituted 1,3,5-Cycloheptatrienes in the Presence of Palladium(II) Acetate," *Chem. Pharm. Bull.* **1993**, *41(12)*, 2187.
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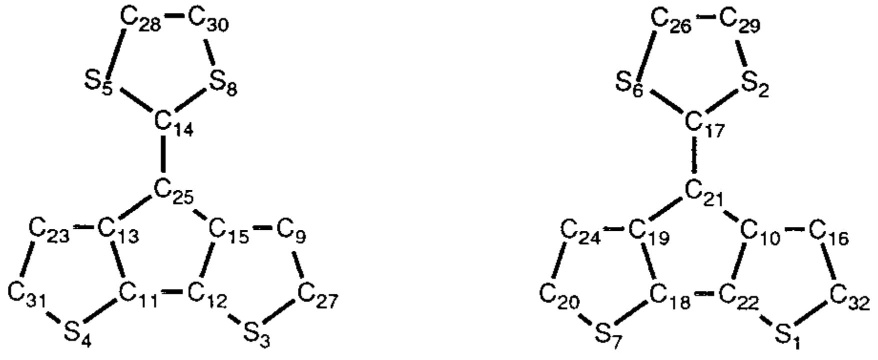
Appendix X-ray Diffraction Data

1. 4-(1,3-dithiol-2-ylidene)-4H-cyclopenta[2,1-b;3,4-b']dithiophene


Molecule I

Molecule II

Figure 1. Atomic numbering system.

Table I. Fractional atomic coordinates of non-H atoms and their equivalent isotropic thermal parameters (Å^2) with estimated standard deviations in parentheses

atom	X	Y	Z	B_{eq}
S(1)	0.7675 (1)	0.0968 (1)	0.1436 (1)	4.29 (4)
S(2)	0.7180 (1)	0.6612 (1)	-0.0237 (1)	4.86 (5)
S(3)	1.0772 (1)	0.1123 (1)	-0.2414 (1)	4.31 (4)
S(4)	0.9440 (1)	0.1400 (1)	-0.5488 (1)	4.66 (4)
S(5)	0.8998 (1)	0.6925 (1)	-0.4055 (1)	4.83 (5)
S(6)	0.8095 (1)	0.6495 (1)	-0.1653 (1)	4.79 (5)
S(7)	0.8968 (1)	0.0878 (1)	-0.0438 (1)	5.14 (5)
S(8)	1.0008 (1)	0.6804 (1)	-0.1871 (1)	4.71 (4)
C(9)	1.0736 (2)	0.3648 (5)	-0.1575 (4)	4.2 (2)
C(10)	0.7663 (2)	0.3396 (5)	0.0442 (3)	3.7 (1)
C(11)	0.9756 (2)	0.2431 (4)	-0.4297 (3)	3.5 (1)

Table I. (Continued)

atom	X	Y	Z	B_{eq}
C(12)	1.0240 (2)	0.2348 (4)	-0.3220 (3)	3.5 (1)
C(13)	0.9480 (2)	0.3776 (5)	-0.4425 (3)	3.6 (1)
C(14)	0.9620 (2)	0.5929 (4)	-0.3143 (3)	3.7 (2)
C(15)	1.0268 (2)	0.3645 (4)	-0.2671 (3)	3.5 (1)
C(16)	0.7214 (2)	0.3537 (5)	0.1127 (3)	4.3 (2)
C(17)	0.7755 (2)	0.5595 (5)	-0.0696 (3)	3.8 (2)
C(18)	0.8413 (2)	0.2019 (5)	-0.0138 (3)	3.8 (2)
C(19)	0.8408 (2)	0.3335 (5)	-0.0657 (3)	3.7 (1)
C(20)	0.9210 (3)	0.2164 (6)	-0.1257 (4)	5.4 (2)
C(21)	0.7925 (2)	0.4254 (4)	-0.0337 (3)	3.6 (2)
C(22)	0.7947 (2)	0.2060 (5)	0.0539 (3)	3.7 (2)
C(23)	0.9015 (2)	0.3974 (5)	-0.5499 (3)	4.3 (2)
C(24)	0.8873 (2)	0.3406 (5)	-0.1314 (4)	4.6 (2)
C(25)	0.9781 (2)	0.4590 (4)	-0.3392 (3)	3.5 (1)
C(26)	0.7680 (3)	0.8088 (5)	-0.1621 (4)	5.4 (2)
C(27)	1.1040 (2)	0.2354 (5)	-0.1333 (4)	4.7 (2)
C(28)	0.9101 (3)	0.8421 (5)	-0.3195 (5)	5.4 (2)
C(29)	0.7270 (2)	0.8144 (5)	-0.0980 (4)	5.4 (2)
C(30)	0.9549 (3)	0.8356 (5)	-0.2208 (5)	5.7 (2)
C(31)	0.8947 (2)	0.2783 (6)	-0.6153 (4)	4.9 (2)
C(32)	0.7177 (2)	0.2296 (5)	0.1711 (4)	4.6 (2)

Table II. Bond lengths (Å) with estimated standard deviations

atom 1	atom 2	dist.	E.S.D.	atom 1	atom 2	dist.	E.S.D.
S(1)	-C(22)	1.7083	0.0045	S(1)	-C(32)	1.7202	0.0051
S(2)	-C(17)	1.7482	0.0046	S(2)	-C(29)	1.7382	0.0054
S(3)	-C(12)	1.7130	0.0038	S(3)	-C(27)	1.7275	0.0046
S(4)	-C(11)	1.7194	0.0039	S(4)	-C(31)	1.7205	0.0049

Table II. (Continued)

atom 1	atom 2	dist.	E.S.D.	atom 1	atom 2	dist.	E.S.D.
S(5)	-C(14)	1.7391	0.0038	S(5)	-C(28)	1.7326	0.0053
S(6)	-C(17)	1.7458	0.0046	S(6)	-C(26)	1.7404	0.0054
S(7)	-C(18)	1.6976	0.0046	S(7)	-C(20)	1.7310	0.0058
S(8)	-C(14)	1.7463	0.0039	S(8)	-C(30)	1.7342	0.0052
C(9)	-C(15)	1.4249	0.0050	C(9)	-C(27)	1.3688	0.0064
C(10)	-C(16)	1.4280	0.0065	C(10)	-C(21)	1.4645	0.0061
C(10)	-C(22)	1.3825	0.0060	C(11)	-S(4)	1.7194	0.0039
C(11)	-C(12)	1.4260	0.0047	C(11)	-C(13)	1.3816	0.0058
C(12)	-S(3)	1.7130	0.0038	C(12)	-C(11)	1.4260	0.0047
C(12)	-C(15)	1.3841	0.0056	C(13)	-C(11)	1.3816	0.0058
C(13)	-C(23)	1.4144	0.0050	C(13)	-C(25)	1.4603	0.0052
C(14)	-S(5)	1.7391	0.0038	C(14)	-S(8)	1.7463	0.0039
C(14)	-C(25)	1.3594	0.0058	C(15)	-C(9)	1.4249	0.0050
C(15)	-C(12)	1.3841	0.0056	C(15)	-C(25)	1.4544	0.0051
C(16)	-C(10)	1.4280	0.0065	C(16)	-C(32)	1.3798	0.0069
C(17)	-S(2)	1.7482	0.0046	C(17)	-S(6)	1.7458	0.0046
C(17)	-C(21)	1.3506	0.0059	C(18)	-S(7)	1.6976	0.0046
C(18)	-C(19)	1.3888	0.0060	C(18)	-C(22)	1.4440	0.0064
C(19)	-C(18)	1.3888	0.0060	C(19)	-C(21)	1.4642	0.0062
C(19)	-C(24)	1.4253	0.0070	C(20)	-S(7)	1.7310	0.0058
C(20)	-C(24)	1.3589	0.0072	C(21)	-C(10)	1.4645	0.0061
C(21)	-C(17)	1.3506	0.0059	C(21)	-C(19)	1.4642	0.0062
C(22)	-S(1)	1.7083	0.0045	C(22)	-C(10)	1.3825	0.0060
C(22)	-C(18)	1.4440	0.0064	C(23)	-C(13)	1.4144	0.0050
C(23)	-C(31)	1.3596	0.0068	C(24)	-C(19)	1.4253	0.0070
C(24)	-C(20)	1.3589	0.0072	C(25)	-C(13)	1.4603	0.0052
C(25)	-C(14)	1.3594	0.0058	C(25)	-C(15)	1.4544	0.0051
C(26)	-S(6)	1.7404	0.0054	C(26)	-C(29)	1.3126	0.0083
C(27)	-S(3)	1.7275	0.0046	C(27)	-C(9)	1.3688	0.0064
C(28)	-S(5)	1.7326	0.0053	C(28)	-C(30)	1.3099	0.0070
C(29)	-S(2)	1.7382	0.0054	C(29)	-C(26)	1.3126	0.0083
C(30)	-S(8)	1.7342	0.0052	C(30)	-C(28)	1.3099	0.0070
C(31)	-S(4)	1.7205	0.0049	C(31)	-C(23)	1.3596	0.0068
C(32)	-S(1)	1.7202	0.0051	C(32)	-C(16)	1.3798	0.0069

Table III. Bond angles with estimated standard deviations

			angle (degree)	E.S.D.
C(22)	-S(1)	-C(32)	90.95	0.23
C(17)	-S(2)	-C(29)	95.95	0.25
C(12)	-S(3)	-C(27)	90.65	0.20
C(11)	-S(4)	-C(31)	90.79	0.21
C(14)	-S(5)	-C(28)	95.97	0.21
C(17)	-S(6)	-C(26)	95.84	0.25
C(18)	-S(7)	-C(20)	90.66	0.25
C(14)	-S(8)	-C(30)	95.36	0.22
C(15)	-C(9)	-C(27)	111.18	0.37
C(16)	-C(10)	-C(21)	139.06	0.40
C(16)	-C(10)	-C(22)	111.94	0.39
C(21)	-C(10)	-C(22)	108.99	0.38
S(4)	-C(11)	-C(12)	139.32	0.32
S(4)	-C(11)	-C(13)	111.62	0.26
C(12)	-C(11)	-C(13)	108.99	0.34
S(3)	-C(12)	-C(11)	138.84	0.32
S(3)	-C(12)	-C(15)	112.44	0.26
C(11)	-C(12)	-C(15)	108.70	0.33
C(11)	-C(13)	-C(23)	112.78	0.36
C(11)	-C(13)	-C(25)	108.29	0.31
C(23)	-C(13)	-C(25)	138.91	0.40
S(5)	-C(14)	-S(8)	113.50	0.24
S(5)	-C(14)	-C(25)	123.09	0.28
S(8)	-C(14)	-C(25)	123.41	0.27
C(9)	-C(15)	-C(12)	112.39	0.34
C(9)	-C(15)	-C(25)	139.03	0.38
C(12)	-C(15)	-C(25)	108.53	0.30
C(10)	-C(16)	-C(32)	111.24	0.42
S(2)	-C(17)	-S(6)	113.21	0.24
S(2)	-C(17)	-C(21)	123.56	0.35
S(6)	-C(17)	-C(21)	123.22	0.35
S(7)	-C(18)	-C(19)	112.62	0.34
S(7)	-C(18)	-C(22)	138.94	0.34

Table III. (Continued)

	angle (degree)	E.S.D.
C(19) -C(18) -C(22)	108.39	0.38
C(18) -C(19) -C(21)	108.87	0.39
C(18) -C(19) -C(24)	112.17	0.39
C(21) -C(19) -C(24)	138.95	0.40
S(7) -C(20) -C(24)	113.45	0.44
C(10) -C(21) -C(17)	127.62	0.41
C(10) -C(21) -C(19)	105.05	0.35
C(17) -C(21) -C(19)	127.33	0.41
S(1) -C(22) -C(10)	112.87	0.34
S(1) -C(22) -C(18)	138.45	0.34
C(10) -C(22) -C(18)	108.65	0.38
C(13) -C(23) -C(31)	111.56	0.40
C(19) -C(24) -C(20)	111.09	0.45
C(13) -C(25) -C(14)	127.05	0.33
C(13) -C(25) -C(15)	105.45	0.33
C(14) -C(25) -C(15)	127.47	0.33
S(6) -C(26) -C(29)	117.57	0.41
S(3) -C(27) -C(9)	113.34	0.30
S(5) -C(28) -C(30)	117.12	0.39
S(2) -C(29) -C(26)	117.37	0.41
S(8) -C(30) -C(28)	118.02	0.41
S(4) -C(31) -C(23)	113.24	0.30
S(1) -C(32) -C(16)	113.00	0.37

2. 7-(1,3-dithiol-2-ylidene)-7H-cyclopenta[1,2-b;4,3-b']dithiophene

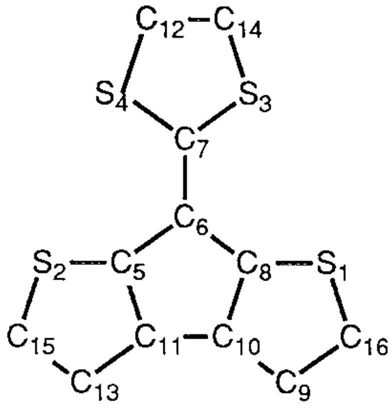


Figure 2. Atomic numbering system.

Table IV. Fractional atomic coordinates of non-H atoms and their equivalent isotropic thermal parameters (Å^2) with estimated standard deviations in parentheses

atom	X	Y	Z	B_{eq}
S1	0.4999 (1)	0.1069 (4)	0.6173 (1)	3.22 (3)
S2	0.6679 (1)	0.0391 (4)	0.9916 (1)	3.21 (3)
S3	0.3906 (1)	-0.2687 (4)	0.7060 (1)	3.23 (3)
S4	0.4752 (1)	-0.2879 (4)	0.8983 (1)	3.31 (3)
C5	0.6242 (3)	0.074 (1)	0.8802 (3)	2.8 (1)
C6	0.5456 (3)	-0.012 (1)	0.8039 (3)	2.6 (1)
C7	0.4792 (3)	-0.169 (1)	0.8036 (3)	2.4 (1)
C8	0.5570 (3)	0.102 (1)	0.7297 (3)	2.7 (1)
C9	0.6475 (3)	0.351 (1)	0.6873 (3)	3.3 (1)
C10	0.6340 (3)	0.239 (1)	0.7582 (3)	2.7 (1)
C11	0.6768 (3)	0.224 (1)	0.8535 (3)	2.7 (1)
C12	0.3763 (3)	-0.456 (2)	0.8438 (4)	3.7 (2)
C13	0.7544 (3)	0.306 (1)	0.9260 (3)	3.4 (1)
C14	0.3378 (3)	-0.448 (2)	0.7574 (4)	3.7 (2)
C15	0.7579 (3)	0.219 (2)	1.0037 (3)	3.8 (2)
C16	0.5810 (4)	0.295 (2)	0.6078 (3)	3.5 (1)

Table V. Bond lengths (Å) with estimated standard deviations

atom 1	atom 2	dist.	E.S.D.	atom 1	atom 2	dist.	E.S.D.
S1	-C8	1.7134	0.0046	S2	-C5	1.7010	0.0051
S3	-C7	1.7460	0.0039	S4	-C7	1.7325	0.0057
C5	-S2	1.7010	0.0051	C5	-C11	1.3848	0.0087
C6	-C7	1.3662	0.0079	C7	-S3	1.7460	0.0039
C7	-C6	1.3662	0.0079	C8	-C6	1.4616	0.0083
C9	-C10	1.4273	0.0090	C10	-C9	1.4273	0.0090
C11	-C5	1.3848	0.0087	C11	-C13	1.4201	0.0060
C12	-C14	1.3143	0.0082	C13	-C11	1.4201	0.0060
C14	-C12	1.3143	0.0082	C15	-S2	1.7187	0.0067
C16	-C9	1.3571	0.0062	S1	-C16	1.7387	0.0073
S2	-C15	1.7187	0.0067	S3	-C14	1.7412	0.0075
S4	-C12	1.7368	0.0057	C5	-C6	1.4621	0.0056
C6	-C5	1.4621	0.0056	C6	-C8	1.4616	0.0083
C7	-S4	1.7325	0.0057	C8	-S1	1.7134	0.0046
C8	-C10	1.3704	0.0073	C9	-C16	1.3571	0.0062
C10	-C8	1.3704	0.0073	C10	-C11	1.4487	0.0065
C11	-C10	1.4487	0.0065	C12	-S4	1.7368	0.0057
C13	-C15	1.3555	0.0091	C14	-S3	1.7412	0.0075
C15	-C13	1.3555	0.0091	C16	-S1	1.7387	0.0073

Table VI. Bond angles with estimated standard deviations

			angle (degree)	E.S.D.
C8	-S1	-C16	91.01	0.26
C5	-S2	-C15	91.03	0.28
C7	-S3	-C14	95.20	0.26
C7	-S4	-C12	95.29	0.28
S2	-C5	-C6	137.38	0.49
S2	-C5	-C11	112.28	0.32
C6	-C5	-C11	110.33	0.46

Table VI. (Continued)

			angle (degree)	E.S.D.
C5	-C6	-C7	127.55	0.49
C5	-C6	-C8	103.17	0.46
C7	-C6	-C8	129.27	0.37
S3	-C7	-S4	114.38	0.31
S3	-C7	-C6	122.02	0.39
S4	-C7	-C6	123.60	0.31
S1	-C8	-C6	136.85	0.39
S1	-C8	-C10	112.24	0.45
C6	-C8	-C10	110.91	0.39
C10	-C9	-C16	112.17	0.55
C8	-C10	-C9	112.44	0.40
C8	-C10	-C11	107.89	0.52
C9	-C10	-C11	139.68	0.48
C5	-C11	-C10	107.70	0.40
C5	-C11	-C13	111.85	0.48
C10	-C11	-C13	140.43	0.59
S4	-C12	-C14	117.95	0.57
C11	-C13	-C15	111.84	0.56
S3	-C14	-C12	117.17	0.46
S2	-C15	-C13	112.99	0.36
S1	-C16	-C9	112.14	0.51

3. 4H-cyclopenta[2,1-b;3,4-b']dithiophen-4-one azine

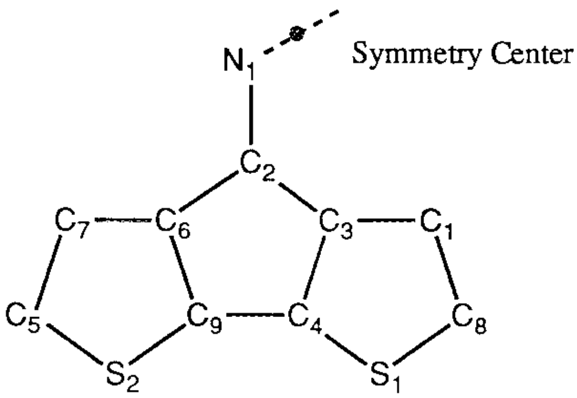


Figure 3. Atomic numbering system.

Table VII. Fractional atomic coordinates of non-H atoms and their equivalent isotropic thermal parameters (Å^2) with estimated standard deviations in parentheses

atom	X	Y	Z	B_{eq}
S1	0.6178 (1)	0.1066 (1)	0.0550 (1)	3.95 (3)
S2	0.7698 (1)	0.2997 (1)	0.2570 (1)	3.73 (3)
N1	1.0023 (2)	0.0402 (3)	0.0402 (1)	3.2 (1)
C1	0.7612 (2)	-0.0156 (4)	-0.0412 (2)	3.4 (1)
C2	0.9125 (2)	0.0816 (3)	0.0681 (2)	2.8 (1)
C3	0.8093 (2)	0.0571 (3)	0.0320 (2)	2.7 (1)
C4	0.7400 (2)	0.1263 (3)	0.0900 (2)	2.8 (1)
C5	0.8975 (3)	0.3094 (4)	0.2817 (2)	4.5 (1)
C6	0.8977 (2)	0.1690 (3)	0.1516 (2)	3.1 (1)
C7	0.9569 (2)	0.2344 (4)	0.2199 (2)	4.1 (1)
C8	0.6581 (2)	0.0038 (4)	-0.0380 (2)	4.2 (1)
C9	0.7949 (2)	0.1957 (3)	0.1628 (2)	3.0 (1)

Table VIII. Bond lengths (Å) with estimated standard deviations

atom 1	atom 2	dist.	E.S.D.	atom 1	atom 2	dist.	E.S.D.
S1	-C4	1.6953	0.0025	S1	-C8	1.7318	0.0031
S2	-C5	1.7162	0.0034	S2	-C9	1.7015	0.0026
N1	-C2	1.2925	0.0032	C1	-C3	1.4147	0.0036
C1	-C8	1.3583	0.0042	C2	-N1	1.2925	0.0032
C2	-C3	1.4742	0.0035	C2	-C6	1.4746	0.0034
C3	-C1	1.4147	0.0036	C3	-C2	1.4742	0.0035
C3	-C4	1.3875	0.0034	C4	-S1	1.6953	0.0025
C4	-C3	1.3875	0.0034	C4	-C9	1.4414	0.0035
C5	-S2	1.7162	0.0034	C5	-C7	1.3661	0.0044
C6	-C2	1.4746	0.0034	C6	-C7	1.4078	0.0040
C6	-C9	1.3727	0.0036	C7	-C5	1.3661	0.0044
C7	-C6	1.4078	0.0040	C8	-S1	1.7318	0.0031
C8	-C1	1.3583	0.0042	C9	-S2	1.7015	0.0026
C9	-C4	1.4414	0.0035	C9	-C6	1.3727	0.0036
N1	- N1'	1.3951	0.0029				

Table IX. Bond angles with estimated standard deviations

			angle (degree)	E.S.D.
C4	-S1	-C8	91.14	0.14
C5	-S2	-C9	91.35	0.14
C3	-C1	-C8	111.52	0.25
N1	-C2	-C3	132.32	0.22
N1	-C2	-C6	121.96	0.22
C3	-C2	-C6	105.71	0.20
C1	-C3	-C2	139.73	0.23
C1	-C3	-C4	112.64	0.23
C2	-C3	-C4	107.62	0.21
S1	-C4	-C3	111.98	0.19
S1	-C4	-C9	138.86	0.20
C3	-C4	-C9	109.16	0.21
S2	-C5	-C7	112.32	0.24
C2	-C6	-C7	138.92	0.24
C2	-C6	-C9	108.20	0.21
C7	-C6	-C9	112.86	0.24
C5	-C7	-C6	111.65	0.27
S1	-C8	-C1	112.69	0.22
S2	-C9	-C4	138.88	0.20
S2	-C9	-C6	111.82	0.19
C4	-C9	-C6	109.30	0.22