Macromolecules **1999,** *32,* 5313−5320

Electrochemical Synthesis and Characterization Studies of Poly[3,3′-dialkylsulfanyl-2,2′-bithiophene] Films

S. C. Ng* and P. Miao

Department of Chemistry, National University of Singapore, Singapore 119260

Received October 9, 1998; Revised Manuscript Received May 17, 1999

ABSTRACT: Of the numerous thiophene derivatives, 3-alkylsulfanylthiophenes (3AST) is one of the few that cannot be readily polymerized electrochemically to afford the corresponding conductive polymer films. We demonstrate in this paper that 3,3′-dialkylsulfanyl-2,2′-bithiophenes are appropriate monomers into polythiophenes incorporating pendant alkylsulfanyl moieties. Facile electrochemical polymerization can be effected by both the potentiostatic and galvatiostatic approach. The resulting polymer films have molecular weighs (M_n) of ca. 3600 and were soluble in common solvents. Characterization by NMR, UV−vis spectroscopy, cyclic voltammetry, and X-ray photoelectron spectroscopy are described. The polymers depicted a low-energy $\pi-\pi^*$ transition despite the high steric effects present in such HH−TT polythiophenes. In direct contrast to poly[3,3′-dialkyl-2,2′-bithiophene]s and poly[3,3′-dialkoxy-2,2′-bithiophene]s, PDASBTs exhibited significant thermochromistic effects. More significantly, the polymer films exhibited facile electrochemical oxidative (p-) and reductive (n-) doping which are of importance in the practical applications of electrically conductive polymers in rechargeable batteries and other electronic devices.

1. Introduction

In the past 25 years, a vast number of substituted polythiophenes have been extensively investigated.[1−3] These studies have shown that the steric and electronic effects of the pendant functional groups have a profound influence on polymer properties. Thus, weakly electron-donating groups such as alkyl pendants have been found to improve both solvent and melt processability[4−6] while strongly electron-donating groups exemplified by alkoxy moieties afforded polythiophenes with greatly diminished oxidation potential as well as low band gap energy and other interesting electronic properties.[7−10] Unfortunately, due to the highly stabilized radical cations of monomers with the latter pendants and their consequent low chemical reactivity, only polymers with low molecular weights are obtainable. These effects were also reported for 3-alkylsulfanyl functionalized thiophenes.[11−18] According to studies from the research group of Reynolds,[13] the spin density of alkylsulfanyl thiophene is localized at pendant sulfur, instead of the α-position of thiophene rings. Accordingly, chemical oxidation and electrochemical polymerization of the monomers were effected only with difficulty using “routine methods”. Previously, although there was a report on the electrochemical oxidation of 3-methylsulfanylthiophene[12] in acetonitrile, nitrobenzene, benzonitrile, or THF using tetraalkylammonium salts as electrolytes, prolong polymerization afforded oligomers with an averaged polymerization degree of only 7.4. While chemical polymerization of alkylsulfanylthiophenes have been reported,[18,19] these approaches are severely limited on account of extensive side reactions involving the alkylsulfanyl pendants.[20] Nevertheless, poly(3-alkylsulfanylthiophene)s prepared by these chemical approaches exhibited excellent properties, suggesting that the alkylsulfanyl group may hold promise in affording polythiophenes with special properties. Hence, we were interested in investigating the preparation, properties, and the applications of these materials, particularly those generated through the electrochemical approach since this invariably has the advantage of facile formation of thin uniform films and a straightforward potentiostatic control of the polymers’ oxidation states.[21,22]

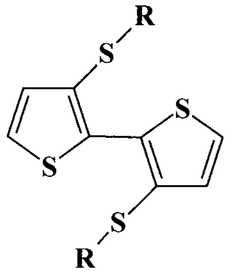
Meanwhile, from an application perspective, materials that are both p- and n-dopable are important for application as light-emitting cells,[23] in electrochemical cells,[24] or for the construction of type III capacitors,[25] whereby one electrode is p-doped and the other is n-doped when the capacitor is charged. Although much work has been done on p-type (oxidative) doping of polythiophenes, n-type (reductive) doping is less well studied on account of the poor stability of the polymer at extreme negative potentials, lower doping levels attainable, poorer doping efficiency, longer activation phase, and accentuated kinetic limitations in n-type doping in comparison to the p-type doping process. In addition, n-type doping is strongly dependent on the nature of the pendant functional group, solvent, and counterions.[26] All these factors combine to make attainment of stable and fully reversible n-type doping a challenge. Successful polymer reduction and/or n-doping in poly[bithiophene],[26] poly[3-methylthiophene],[27] poly[3-hexylthiophene],[28] poly[3-(3,6-dioxaheptyl)thiophene],[29] poly[3-chlorothiophene],[30] poly[4-vinyl-*N*-methylpyridinium iodine],[30] poly[isothianaphthene] with methyl, chloro, and fluoro substituents,[31] bipyridine−bithiophene copolymers,[32] poly[thienylene−vinylene]s,[33] poly[heteroarylene methine]s,[34] poly[3,4-dibutyl-α-terthiophene],[35] polyquinolines,[36] polyanthrazolines,[36] poly[4,4′-dialkyl-2,2′-bithiazole-5,5′-diyl],[37] and polymers containing aromatic-donor and *o*-quinoid acceptor units[38] have been reported. However, to our knowledge, up until now, the electrochemical n-doping process of alkylsulfanyl functionalized polythiophenes has not been studied. This paper, which continues on from our previous short communication,[22] reports in detail on the electropolymerization of a series of 3,3′-dialkylsulfanyl-2,2′-bi-

---

* Author for correspondence.

10.1021/ma981587t CCC: $18.00

thiophenes and their characterization and doping aspects. It was found that, in striking contrast to 3-alkylsulfanylthiophenes, 3,3′-dialkylsulfanyl-2,2′-bithiophenes (DASBT) can be successfully polymerized by the electrochemical approach. Apart from the formation of stable films, the electrochemically derived polymers demonstrated reversible electrochemical p- and n-dopability.



DBuSBT, R= C_4H_9
DOcSBT, R= C_8H_{17}
DDeSBT, R= $C_{10}H_{21}$
DDoSBT, R= $C_{12}H_{25}$

DASBT

2. Experimental Section

Materials. The symmetrical dimers DASBTs were synthesized from 3,3′-dibromo-2,2′-bithiophene as reported previously.[39,40] Electrolyte (n-$Bu_4N^+BF_4^-$) (TCI) was dried under high vacuum at 60 °C for 2 h prior to use. Acetonitrile (J. T. Baker) is reagent grade solvent and was distilled from CaH_2.

Ultraviolet−Visible Absorption Spectroscopy. UV−vis spectra were acquired from dilute solution or thin films of polymer electrochemically deposited on an ITO-coated glass plate. The spectra were obtained with a Perkin-Elmer Lambda 900 UV/vis/NIR spectrometer. The temperature-dependent spectroscopic measurements were carried out using a temperature control unit to allow for measurements from room temperature to 200 °C

Nuclear Magnetic Resonance Spectroscopy. ^1H NMR was recorded on a Bruker ACF300 spectrometer using $CDCl_3$ as solvent and tetramethylsilane as internal reference.

X-ray Photoelectron Spectroscopy. XPS analyses of the polymer films on ITO glass were performed by means of a VG ESCA/SIMLAB MKII with Mg Kα radiation. The binding energies were corrected for surface charging by referencing to the designated hydrocarbon C(1s) binding energy as 284.6 eV. Spectra deconvolutions were carried out using Gaussian components with the same full widths at half-maximum (fwhm) for each component in a particular spectrum. Surface elemental stoichiometries were obtained from peak area ratios corrected with the appropriate experimentally determined sensitivity factors.

Molecular Weight. Molecular weight was measured on a Waters 600E HPLC System with Phenogel MXL and MXM columns (300 mm × 4.6 mm i.d.) using polystyrene as standards and THF as eluant.

Electrochemical Polymerization. Electrochemical experiments were performed on an EG&G 273A potentiosat/galvanostat controlled by EG & G M270 electrochemical software in a three-electrode compartment cell comprising a platinum wire as counter electrode, a platinum disk (effective area 0.5 cm^2), or an indium tin oxide (ITO) glass electrode (effective area 0.5 cm^2) as working electrode and a $Ag/AgNO_3$ (0.1 M in dry acetonitrile) electrode as reference electrode. All experimental potentials were corrected with respect to saturated calomel electrode (SCE). Electrochemical polymerization was performed in a reaction medium containing 0.01 M monomer and 0.1 M n-$Bu_4N^+BF_4^-$ in acetonitrile. All solutions were purged with argon prior to the experiment. The polymers were deposited on working electrodes by the galvanostatic method using current densities between 100 and 500 $\mu A/cm^2$ or by the potentiostatic method. After polymerization, the polymer films were electrochemically dedoped in 0.1 M n-Bu_4N^+-BF_4^- in acetonitrile and rinsed in turn with acetonitrile and acetone prior to drying in an argon stream. The cyclic voltammograms of electrochemically deposited films of DASBTs were performed in monomer free acetonitrile- n-$Bu_4N^+BF_4^-$ (0.1 M) in the potential range of 0.30−0.90 V for p-doping and 0 to −2.0 V for n-doping at different potential scan rates.

In-situ solid-state spectroelectrochemical measurements were recorded by immersing and fixing the polymer-coated ITO glass electrodes inside a 1 × 1 cm quartz cell containing 0.1 M n-$Bu_4N^+BF_4^-$ in acetonitrile. A Pt wire was used as counter electrode, and a silver wire was used as reference. Both counter and reference electrodes were placed beyond the path of the optical beam. The cell was sealed with silicone rubber and purged with argon. UV−vis absorbency measurements were then performed at various values of applied potential at 50 mV interval. The polymer films were allowed to equilibrate for at least 20 s at the applied potential before each measurement.

3. Results and Discussion

3.1. Electrochemical Preparation of Poly[3,3′-dialkylsulfanyl-2,2′-bithiophene]. In contrast to alkylsulfanylthiophenes,[11−18] symmetrically functionalized 3,3′-dialkylsulfanyl-2,2′-bithiophenes depicted excellent film formation behavior upon polymerization by both the potentiodynamic and galvanostatic approach. The monomer oxidation potentials of DASBTs in n-$Bu_4N^+BF_4^-$ (0.1 M) at a scan rate of 50 mV s^{-1} were around 1.10 V, which were lower than that for thiophene (+1.65 V),[41,42] bithiophene (+1.2 V),[41,42] and 3,3′-dialkylbithiophenes (1.50 V)[43] but higher than that of 3,3′-dialkoxy-2,2′-bithiophenes (0.75 V).[44] On their first potential sweeping cycle, two cathodic peaks (e.g., 0.69 and 0.82 V in DOcSBT) were observed which increased in intensity with subsequent repeated voltammetric cycling. One main anodic peak with two shoulder peaks was observed from the second cycle. As polymerization proceeds, the peak currents increased with progressive scan cycles, and the anodic peak positions were displaced to higher potentials while the cathodic peak potential was displaced to a lower value, indicative of polymer growth on the surface of electrode. The polymer films can also be readily prepared by the galvanostatic polymerization approach at current density between 100 and 500 $\mu A\ cm^{-2}$.

In our approach, it was found that the quality of the polymer film depended to a large extent on the size of the pendant group. Monomers with long alkyl groups (DOcSBT, DDeSBT, and DDoSBT) could be electrochemically polymerized to afford stable films on both platinum and ITO glass. The obtained films are completely and partially soluble in chloroform and acetone, respectively, but insoluble in acetonitrile, methanol, or ethanol. During polymerization, the electrolyte solution was colorless, indicating that electropolymerized oligomers/products did not dissolve away into the solution. Conversely, electrochemical polymerization of DBuSBT resulted in materials that are partially soluble in acetonitrile and alcohol. Even though a film was obtainable, it was found unstable, dissolving into the electrolyte over a prolong time to afford a deep red solution. Furthermore, unlike the polymerization of DOcSBT, the I_{pa} and I_{pc} of the CV curves in the polymerization of DBuSBT did not increase even after several cycles, indicating that any polymer film formed did not adhere as strongly as in the former case. From these considerations, it can be deduced that solubility of oligomers plays an important role in controlling the formation of good-quality films. Oligomers of DASBTs with long pendant chains have poor solubility in the relatively

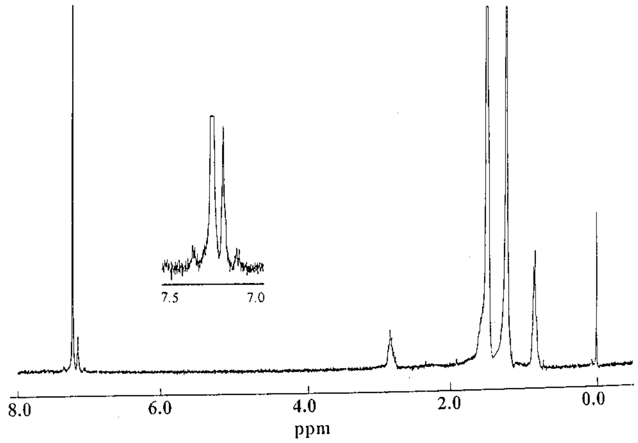


Figure 1. ^{1}H NMR spectra of PDOcSBT.

Table 1. Molecular Weights and Surface Stoichiometries of Derived Polymers

	molecular weight		stoich of polymer surface	
	M_n	M_w/M_n	determined	expected
PDBuSBT	3310	1.54	$C_{18.56}\,S_{4.00}$	$C_{16.00}\,S_{4.00}$
PDOcSBT	3600	1.15	$C_{24.64}\,S_{4.00}$	$C_{24.00}\,S_{4.00}$
PDDeSBT	2303	1.18	$C_{27.68}\,S_{4.00}$	$C_{28.00}\,S_{4.00}$
PDDoSBT	2289	1.21	$C_{31.68}\,S_{4.00}$	$C_{32.00}\,S_{4.00}$

polar acetonitrile, presumably ascribable to steric effects and/or reduced polarity of the polymer with long hydrophobic pendants. Low solubility permits a firm deposition of oligomers on the electrode surface, thus allowing for the propagation of the polymerization process.

3.2. Characterization of Neutral Poly[3,3′-dialkylsulfanyl-2,2′-bithiophene]. As all PDASBT had excellent solubility in common solvents such as THF and chloroform, simple dissolution of electrochemically deposited films into chloroform provides a simple procedure for obtaining adequate amounts of polymers for molecular weight determinations and characterization studies using NMR spectroscopy.

Molecular Weights. The molecular weights estimated using gel permeation chromatography (GPC) in THF eluent with polystyrene standards were investigated (Table 1). The representative polymer PDOcSBT has a molecular weight (M_n) ca. 3600 with a polydispersity index of 1.15, suggesting that the polymer had approximately 16 thiophene units or eight DOcSBT repeating units.

^{1}H NMR Spectroscopy. Figure 1 depicts the solution 300 MHz ^{1}H NMR spectrum of the representative PDOcSBT. In the aliphatic region, four groups of protons arising from the octyl group were clearly evident. The methylene hydrogens adjacent to the pendant sulfur manifested a triplet centered at δ 2.87 ppm, which was of similar chemical shift to that of corresponding hydrogens in the monomer. Over in the aromatic region, the dominant singlet at δ 7.19 ppm was assigned to the thiophene β-protons, indicative of a regioregular HH−TT arrangement in the polymer. Two weak doublets at ca. δ 7.35 and δ 7.10 ppm with same intensity can be ascribable to the terminal thiophene α-H's and β-H's, respectively. The integrated ratio of the two peaks at δ 7.19 and δ 7.35 ppm is ~7, indicating that the degree of polymerization determined is consistent with that from the GPC result.

XPS Analysis. The nature and surface stoichiometry of neutral polymer films were evaluated from XPS studies. In the wide scan for neutral polymer films, photoelectron signals originating from the C(1s) and S(2p) core levels were detected. No signals arising from the N(1s), B(1s), and F(1s) core levels were seen, indicative of the absence of electrolyte and trapped solvent (acetonitrile) in the films. The XPS of bare ITO glass revealed some carbon-containing contaminants, possibly hydrocarbons, through the manifestation of C(1s) signals apart from the expected O(1s), In(3d), and Sn(3d) contributions from ITO. Table 1 depicts the surface stoichiometry of polymers after allowing for the carbon contaminants on bare ITO glass. It can be seen that the resulting empirical formulas for the polymers accorded well with the expected values. The C(1s) envelope in the neutral polymers can be deconvoluted into two carbon environments with binding energy (BE) of 284.6 and 286.1 eV. The main species (284.6 eV) is ascribable to contributions from C−C, C═C, and C−S, while the second species is due to the C−O.[45]

Table 2. XPS S(2p) Data of Neutral PDASBT

	S^c		S^r		$S^{\delta+}$	
	BE	%	BE	%	BE	%
PDBuSBT	163.1	49.9	163.7	38.6	165.1	11.6
PDOcSBT	163.0	50.0	163.7	39.8	165.2	10.2
PDDeSBT	163.0	50.0	163.6	39.4	165.0	10.6
PDDoSBT	163.0	50.1	163.6	41.1	165.0	8.9

The S(2p) envelope was deconvoluted into three environments, each with a pair of bands with intensity ratios $S(2p_{3/2})$:$S(2p_{1/2})$ of 2:1 arising from sulfur spin−orbit couplings. The pair with binding energies (BEs) of 163.1 and 164.1 eV and a full width at half-maximum (fwhm) of 1.3 eV is ascribed to sulfur in the pendant chain (S^c), while the remaining pairs at BEs 163.7/164.7 eV (fwhm = 1.3 eV) and 165.0/166.0 eV (fwhm = 1.8 eV) are attributable respectively to the ring sulfur (S^r) and oxidized sulfur ($S^{\delta+}$) species arising from incomplete dedoping and/or aerial oxidation of the polymers. Table 2 summarizes the respective area percentages under each sulfur environment. These were found to be ca. 50, 40, and 10% respectively for the S^c, S^r, and $S^{\delta+}$ environments for all polymers, suggesting that oxidation had taken place at the ring sulfur instead of the pendant sulfur.

3.3. UV−vis Spectroscopy. *Solution-Phase UV−vis Spectroscopy.* The solution UV−vis spectra of undoped regioregular HH−TT poly[3,3′-dialkylsulfanyl-2,2′-bithiophene]s depicted absorption maxima (λ_{max}) between 420 and 450 nm with onsets at around 550 nm (Figure 2), which is blue-shifted from the regioregular HT−HT poly[3-alkylsulfanylthiophene]s prepared using the "Rieke zinc" method which has absorption maxima at ca. 500 nm.[18] The hyperchromic shift arises from the presence of HH diads in PDASBTs which has the effect of reducing coplanarity and consequently the effective conjugation between adjacent thiophene units. This is consistent with the report of poly[3-alkylsulfanylthiophene]s prepared via the electrochemical approach which have λ_{max} at about 410 nm, blue-shifted by 90 nm from polymers prepared from Grignard and Rieke zinc polymerization.[13,18] In our approach, even though there are apparently higher steric effects arising from a greater occurrence of HH diads, our polymers still exhibited longer conjugation lengths in comparison to poly[3-alkylsulfanylthiophene]s, suggesting that the symmetrical substituted bithiophenes lend themselves

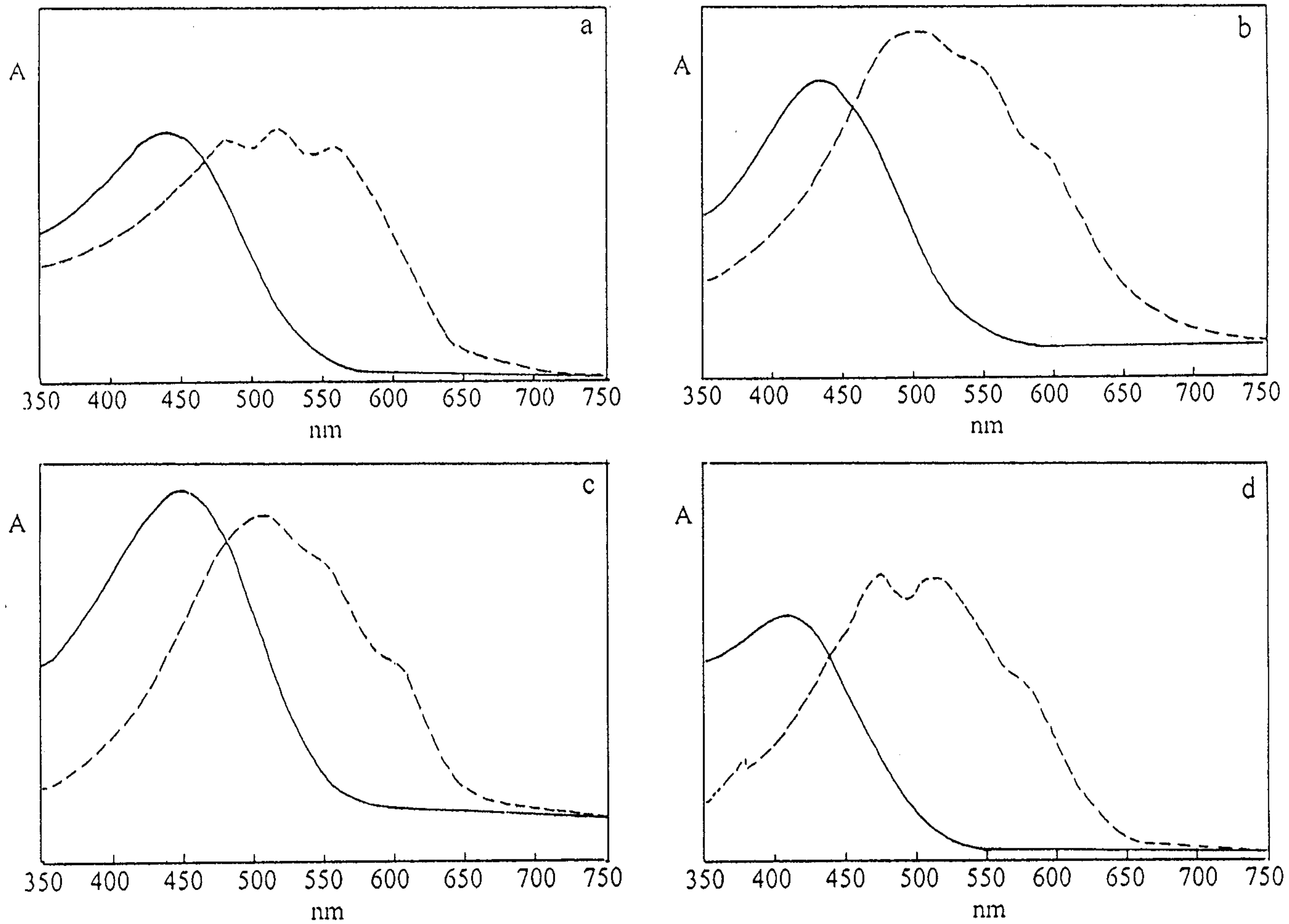


Figure 2. UV−vis spectra of PDASBTs in chloroform solution (—) and solid state (- - -): (a) PDBuSBT, (b) PDOcSBT, (c) PDDeSBT, and (d) PDDoSBT.

to a more favorable electrochemical polymerization. In addition, it is notable that the derived PDASBT exhibited similar $\lambda_{\max}$ as that of HT regioregular poly[3-alkylthiophene]s (ca. 435 nm) but much higher than the ca. 390 nm of poly[3,3′-dialkyl-2,2′-bithiophene]s. This may be ascribable to the electron-donating effects of the pendant sulfur.

Condensed-Phase UV−vis Spectroscopy. As evident from Figure 2, thin films of PDASBT electrodeposited on ITO glass depict $\pi-\pi^*$ absorption maxima in the range 500−510 nm with onset at ca. 700 nm. From the extrapolation of the low-energy absorption edge,[46] the band gaps of these polymers were estimated to be around 1.8−2.0 eV. Apart from the absorption maxima, two vibration bands were seen for all polymers (Figure 2). Similar observations have been reported previously in conjunction to HT−HT regioregular poly[3-alkylthiophene]s and poly[3-alkylsulfanylthiophene]s which depicted absorption maxima at 550 nm and vibrational bands at ca. 520 and 600 nm.[18] This phenomenon is of interest since unlike a comparison between poly[3,3′-dialkyl-2,2′-bithiophene]s and HT−HT regioregular P3ATs, PDOcSBT and PDDeSBT exhibited almost identical absorption behavior as that reported for the HT−HT regioregular P3AST, suggesting the presence of a high degree of conjugation despite the presence of sterically encumbered HH diads. In accordance with earlier theoretical studies on the gas-phase conformation of 3,3′-dimethylsulfanyl-2,2′-bithiophene,[47] the ring torsional angle (θ) of the most stable conformer of DMeSBT in the gaseous phase was 74° with an energy differential (ΔE) between the most stable and the coplanar conformer of merely 2.3 kcal mol^{-1}. In contrast, for 3,3′-diethyl-2,2′-bithiophene which has 3,3′-dialkyl pendants, the corresponding θ and ΔE value were reported to be 102° and a much higher 7.6 kcal mol^{-1}.[47] These contrasting energetics suggest that in the condensed phase the presence of HH-dialkylsulfanyl pendants would not prevent attainment of coplanarity between adjacent rings unlike that of HH-dialkyl pendants where significant deviation from planarity are anticipated at the point of occurrence of the HH-diads.

Thermochromism. In contrast to poly[3,3′-dialkyl-2,2′-bithiophene][48] and poly[3,3′-dialkoxy-2,2′-bithiophene],[47] poly[3,3′-dialkylsulfanyl-2,2′-bithiophene] exhibited interesting thermochromism effects.[49] On the first heating scan of a freshly prepared film of the representative PDOcSBT, the $\lambda_{\max}$ was blue-shifted with significant hypochromic effects at temperatures between 70 and 100 °C. This change was ascribable to irreversible rearrangements of the polymer. In the ensuing cooling scan, a gradual red shift was observed as temperatures decreased with the intensity of three absorption peaks increasing significantly. Upon attaining ambient temperature, the original three absorption peaks recovered, except that the absorption intensities were largely accentuated than from before prior to the first heating cycle.

On the second and subsequent heating−cooling cycle, the polymer displayed good reversibility in thermochro-

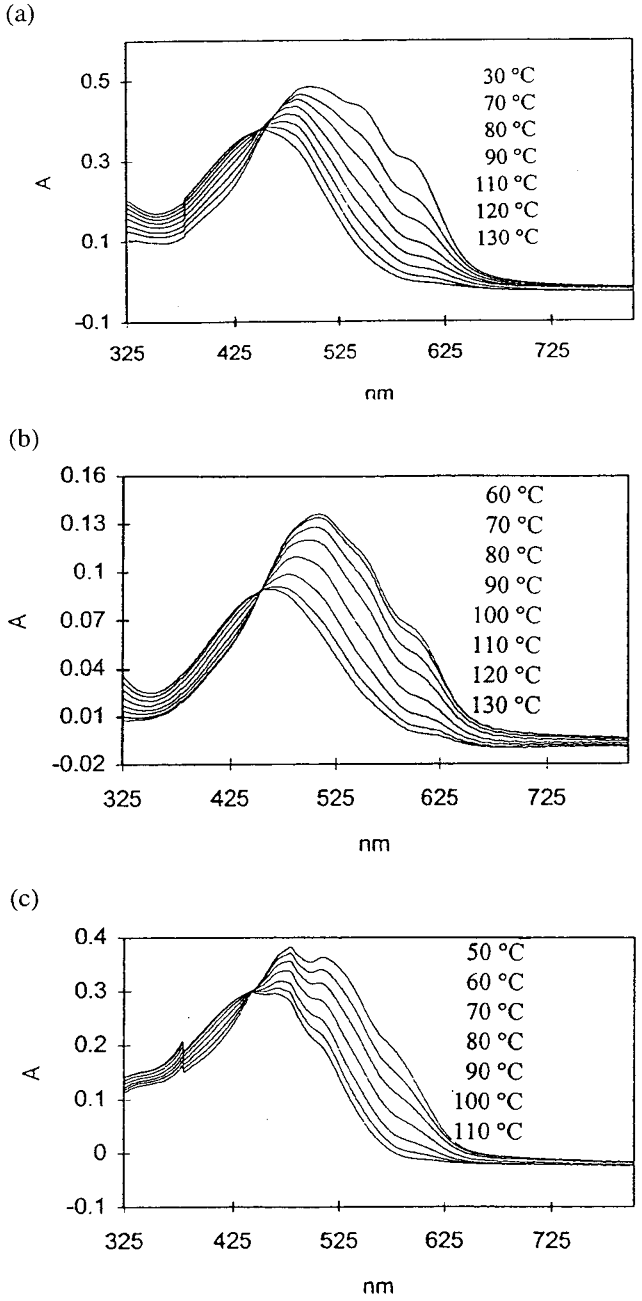


Figure 3. Temperature-dependent UV−vis spectra of (a) PDOcSBT, (b) PDDeSBT, and (c) PDDoSBT.

mistic behavior. A gradual hypsochromic shift of the $\lambda_{\max}$ from 498 to 445 nm was observed upon heating from 30 to 130 °C (Figure 3a). The other two shoulder bands at 538 and 583 nm decreased in intensity, disappearing at ca. 120 °C. There were two isosbestic points for the PDOcSBT film at 467 nm in the 30−80 °C temperature range and another one at 452 nm in the 90−120 °C range. This implies the coexistence of two phases with an intermediate state. Above 120 °C, only a small blue shift was found.

Similar thermochromistic behavior was found for the other electrodeposited poly[3,3′-dialkylsulfanyl-2,2′-bithiophene]s. The rearrangement of freshly prepared polymer films in the first heating scan also takes place in PDBuSBT, PDDeSBT, and PDDoSBT. However, unlike PDOcSBT, only one isosbestic point was observed for these polymers during the thermochromism transition (Figure 3b,c). Again this optical behavior could be related to the coexistence of two different phases without evidence of any other intermediate phase.

3.4. Electrochemistry of Polymers. Cyclic voltammetry (CV) scans revealed a highly reversible p-doping mechanism for all polymer films on both Pt and ITO glass electrode, depicting strong electrochromisms from dark blue in the oxidized to lilac in the neutral dedoped state. Polymer films that were rinsed with acetonitrile or absolute alcohol depicted two oxidative peaks with two corresponding reductive processes. The first oxidation occurred at ca. 0.70−0.80 V ($E_{pa}{}^{1}$) and the second at 0.80−0.90 V ($E_{pa}{}^{2}$) at scan rate of 50 mV/s. With increasing of scan rate, the value of these oxidation potentials increased, while the reduction potentials decreased slightly. In addition, the peak anodic ($I_{pa}{}^{1}$, $I_{pa}{}^{2}$) and cathodic currents ($I_{pc}{}^{1}$, $I_{pc}{}^{2}$) were found to increase linearly with the potential sweep rate. The E_{pa} of PDASBTs are between those of poly(alkoxythiophene) ($E_{pa} \sim 0.1$ V)[8b] and polythiophene ($E_{pa} \sim 1.0$ V)[4,5] and comparable to that of regioregular poly(3-alkylthiophene),[4] poly[3,4-bis(methylthio)thiophene],[15] poly[4,4′-bis(methyl)-2,2′-bithiophene],[15] poly[4,4″-bis(methylthio)-2,2′: 5,2″-terthiophene],[15] and poly[3-ethylthiothiophene].[16] As the scan rate increases, the $I_{pa}{}^{2}$ increased more slowly than the $I_{pa}{}^{1}$. After several scan cycles, the two oxidation processes merged into one broad band. Subsequently, it was found that acetone rinsing of freshly prepared film resulted in only one oxidation process in the range 0.66−0.80 V with a corresponding reduction process between 0.63 and 0.68 V (Figure 4), suggesting that there were small amounts of oligomers present in alcohol/acetonitrile rinsed polymer films. These oligomers could be removed just by simply washing with acetone.

Figure 5 depicts the UV−vis−near-IR absorption spectra of PDDeSBT at electrochemical potential of 0 and +0.70 V. At 0.70 V, the p-doping process was evidenced by the significant change in the absorption spectra. During oxidation, polarons are generated which depict two absorption bands at ca. 730 and >1350 nm. This was accompanied by a simultaneous decrease of the $\pi-\pi^*$ transitions. These changes were reversible upon reduction of the p-doped polymer.

Figure 6 depicts the cyclic voltammograms of thin films of PDASBTs on Pt electrode in the −2.3 to + 1.1 V potential range at the scan rate of 100 mV s^{-1}. Here, two redox cycles exhibit a characteristic wave shape between sharp reduction peaks and the corresponding sharp oxidation peaks. The oxidation potentials (E_{pa}) of PDBuSBT, PDOcSBT, PDDeSBT, and PDDoSBT were 0.71−0.83 V (at a 100 mV s^{-1} scan rate) with onset potentials (E_{on}) of 0.50−0.60 V, respectively. The E_{on} values corresponded to ionization potentials (IP) of 4.90−5.00 eV. These IPs were smaller than or comparable to those of poly(3-alkylthiophene)[50−53] and poly(heteroarylene methines)[36] with varying number of 2,5-thienylene rings. The peak potentials for reduction were between −1.66 and −1.74 V, having onset potentials of ∼−1.50 V with corresponding electron affinities (EA) of ∼2.90 eV, which are higher than those of poly(3-alkylthiophene).[34] The observed electrochemical band gaps evaluated from the differences between IP and EA were 2.0−2.1 eV. In addition, at sweep rates of 50−100 mV s^{-1}, both cathodic and anodic peak currents of reductive cycle of PDDeSBT and PDOcSBT were found to scale linearly with the sweep rate, suggesting that

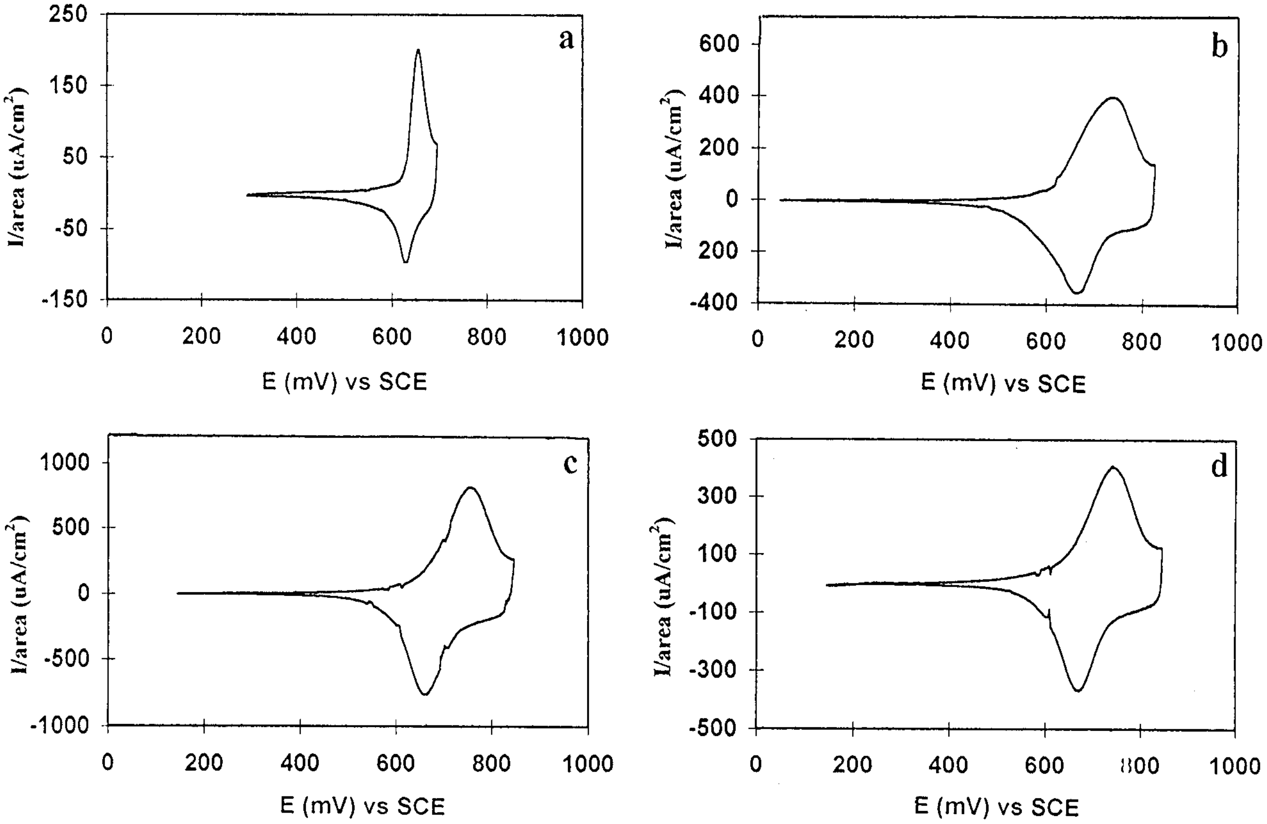


Figure 4. CV of PDASBTs on Pt in an acetonitrile solution of 0.1 M n-Bu$_4$N$^+$BF$_4^-$ (sweep rate = 50 mV s^{-1}): (a) PDBuSBT, (b) PDOcSBT, (c) PDDeSBT, and (d) PDDoSBT.

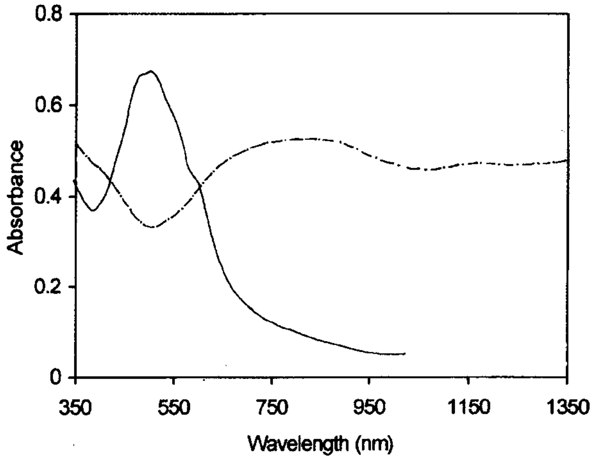


Figure 5. In-situ potential-dependent UV–vis spectra of PDDeSBT on ITO in an acetonitrile solution of 0.1 M n-Bu$_4$N$^+$-BF$_4^-$ at (—) 0.03 V and (- • -) 0.70 V.

kinetic limitations on the electrochemical reduction of these two polymers were not significant.[54]

As reported in other works,[3] the p-doping process for most polythiophenes is more facile and stable than n-doping. In our current work, it was found similarly that p-doping with sweep potential between 0 and 1.0 V was highly stable and reversible with no significant change in CV behavior for all polymer films after more than 100 scan cycles. On the other hand, the polymer films appeared readily degraded at high negative potentials in the course of reduction upon sweeping from 0 to −2.0 V. However, in the experiments whereby the sweep potential was varied from 0 → +1.0 → 0 → −2.0 → 0 V, the reduction of polymers reveals a significant effect on the i/E response during subsequent p-doping as in the case of polythiophene, where a potential excursion into the n-doping region resulted in additional structure on the leading edge of the current peak for subsequent oxidation of neutral polymer.[55] After a number of scans (>80), the film lost most of its p-doping reversibility while still showing good reversibility of the electrochemical reduction process.

In our experiments, the stability of polymer films at high negative potential (−2.0 V) in electrochemical medium was found largely dependent on the size of pendant alkylsulfanyl group as of the electrode type on which the films were deposited. As mentioned above, electrochemical polymerization of DOcSBT, DDeSBT, and DDoSBT readily afforded high-quality films, resulting in little changes in their cyclic voltagrams. In contrast, on account of the poor film-forming ability of PDBuSBT in acetonitrile, any film was found to dissolve in the electrolyte solution when the potential attained −2.0 V. In addition, in comparison to polymer films deposited on Pt electrode, those on ITO glass are less stable at high negative potentials. Here, the polymers appeared to decompose/detach from the ITO glass surface into the electrolyte solution, resulting in irreversibility of the CV behaviors.

Figure 7 depicts the spectroscopic changes accompanying reduction of the representative PDDeSBT deposited on ITO glass. At − 2.0 V, the decrease of the π–π* transitions and the appearance of a small absorption bands at >1350 nm are indicative of an n-doping process with electrochromism from lilac in the neutral dedoped state to dark blue in the reduced state observed. However, presumably on account of the lower film stability on ITO surfaces as of the difficulty of effecting a rigorous exclusion of oxygen/moisture in our experimental setup together with a lower environmental

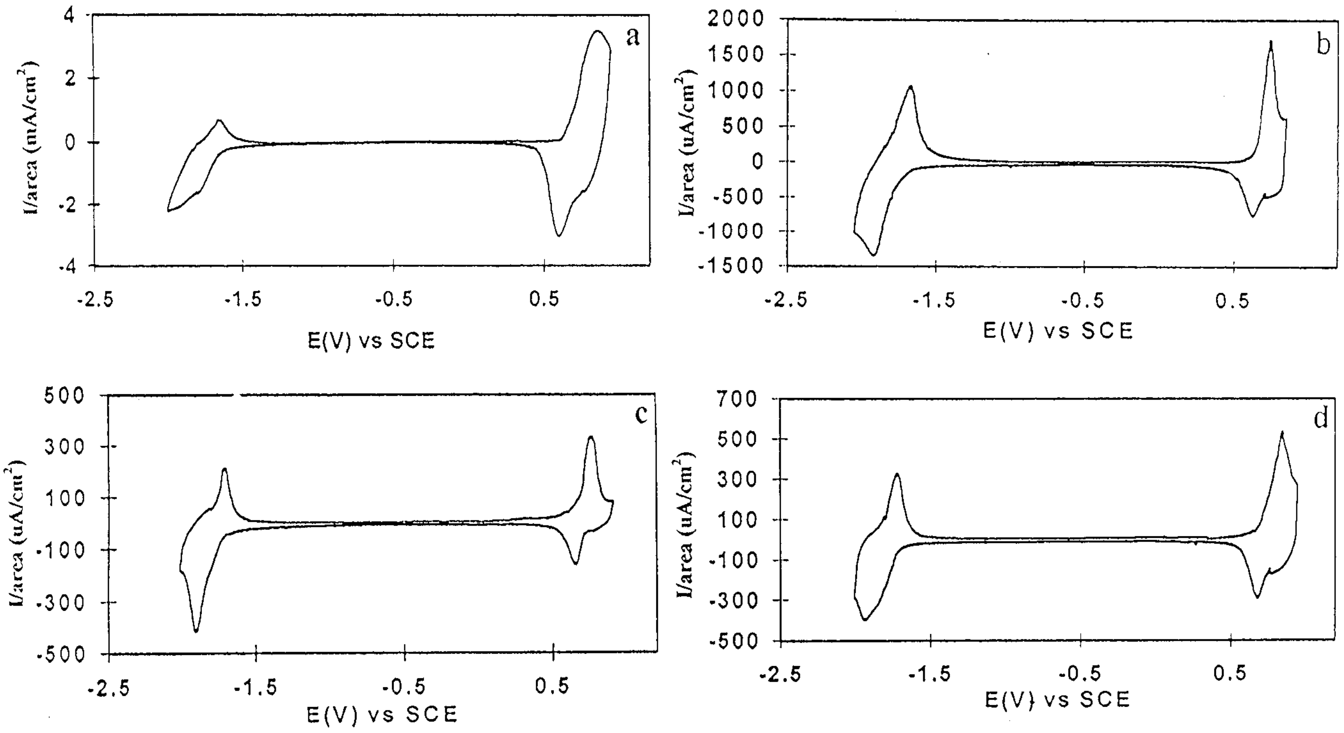


Figure 6. The "p−n"-doping cycle of (a) PDBuSBT, (b) PDOcSBT, (c) PDDeSBT, and (d) PDDoSBT in an acetonitrile solution of 0.1 M n-$Bu_4N^+BF_4^-$. Sweep rate = 100 mV s^{-1}. All polymer films were prepared by electrochemical deposition on a platinum electrode.

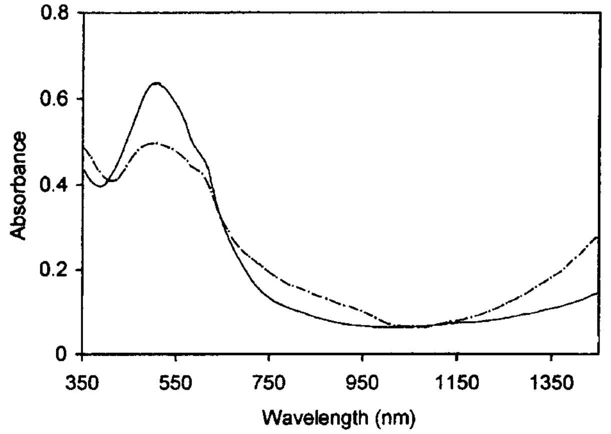


Figure 7. In-situ UV−vis spectra of PDDeSBT on ITO in a 0.1 M acetonitrile solution of n-$Bu_4N^+BF_4^-$ at (—) 0.00 V and (- • -) −2.0 V.

stability of anionic polarons, the anticipated increase of intensity in the polaronic absorption band at longer wavelength during reduction is not as marked as in the oxidation process.

4. Conclusion

Successful electrochemical polymerization of a series of symmetrical 3,3′-dialkylsulfanyl-2,2′-bithiophenes afforded novel and stable electroactive polymer films, which have good solubility in common organic solvents. These films undergo facial electrochemical p- and n-doping under the electrochemical system Bu_4NBF_4−CH_3CN−Pt and exhibit lower π−π^* transition energy, higher conjugation degree, and strong thermochromism effects in comparison to analogous polymers with HH alkyl pendants.

Acknowledgment. We thank the National University of Singapore for financial support through the research grant RP960613. P. Miao is grateful to NUS for the award of a research scholarship.

References and Notes

(1) Tourillon, G. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1986.
(2) Roncali, J. *Chem. Rev.* **1992**, *92*, 711.
(3) Schopf, G.; Kossmehl, G. *Advances in Polymer Science*; Springer: Berlin, 1996; Vol. 129.
(4) (a) McCullough, R. D.; Williams, S. P. *J. Am. Chem. Soc.* **1993**, *115*, 11608. (b) McCullough, R. D.; Tristram-Nagle, S.; Williams, S. P.; Lowe, R. D.; Jayaraman, M. *J. Am. Chem. Soc.* **1993**, *115*, 4910. (c) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson. D. L. *J. Org. Chem.* **1993**, *58* (4), 904. (d) McCullough, R. D.; Jayaraman, M. *J. Chem. Soc., Chem. Commun.* **1995**, 135. (e) McCullough, R. D.; Williams, S. P.; Tristram-Nagle, S.; Jayaraman, M.; Ewbank, P. C.; Miller, L. L. *Synth. Met.* **1995**, *69*, 279.
(5) (a) Mao, H.; Holdcroft, S. *Macromolecules* **1992**, *25*, 554. (b) Mao, H.; Xu, B.; Holdcroft, S. *Macromolecules* **1993**, *26*, 1163.
(6) (a) Chen, T.-A.; Rieke, R. D. *Synth. Met.* **1993**, *60*, 175. (b) Chen, T.-A.; Rieke, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 10087. (c) Chen, T.-A.; O'Brien, R. A.; Rieke, R. D. *Macromolecules* **1993**, *26*, 3462. (d) Chen, T.-A.; Wu, X.; Rieke R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233.
(7) Heywang, G.; Jonas, F. *Adv. Mater.* **1992**, *4*, 116.
(8) (a) Daoust, G.; Leclerc, M. *Macromolecules* **1991**, *24*, 455. (b) Faid, K.; Cloutier, R.; Leclerc, M. *Macromolecules* **1993**, *26*, 2501. (c) Faid, K.; Cloutier, R.; Leclerc, M. *Synth. Met.* **1993,** *55*−*57*, 1272.
(9) Zotti, G.; Gallazzi, M. C.; Zerbi, G.; Meille, S. V. *Synth. Met.* **1995**, *73*, 217.
(10) (a) Hasik, M.; Laska, J. E.; Pron, A.; Kulszewicz-Bajer, I.; Koziel, K.; Lapkowski, M. *J. Polym. Sci., Part A: Polym. Chem.* **1992,** *30*, 1741. (b) Pron, A.; Louarn, G.; Lapkowski, M.; Zagorska, M.; Glowczyk-Zubek, J.; Lefrant, S. *Macromolecules* **1995**, *28*, 4644.
(11) Elsenbaumer, R. L.; Jen, K. Y.; Oboodi, R. *Synth. Met.* **1986**, *15*, 169.
(12) Tanaka, S.; Sato, M.; Kaeriyama, K. *Synth. Met.* **1988**, *25*, 277.

(13) Reynolds, J. R.; Ruiz, J. P.; Wang, F.; Jolly, C. A.; Nayak, K.; Marynick, D. S. *Synth. Met.* **1989**, *28*, C621

(14) Ruiz, J. P.; Gieselman, M. B.; Nayak, K.; Marynick, D. S.; Reynolds, J. R. *Synth. Met.* **1989**, *28*, C481.

(15) Bauerle, P.; Gotz, G.; Synomczyk, A.; Heinze, J. *Liebigs Ann.* **1996**, 279.

(16) Ruiz, J. P.; Nayak, K.; Marynick, D. S.; Reynolds, J. R. *Macromolecules* **1989**, *22*, 1231.

(17) Tsai, E. W.; Basak, S.; Ruiz, J. P.; Reynolds, J. R.; Rajeshwar, K. *J. Electrochem. Soc.* **1989**, *136*, 3683.

(18) (a) Wu, X.; Chen, T.-A.; Rieke, R. D. *Macromolecules* **1995**, *28*, 2101. (b) Wu, X.; Chen, T.-A.; Rieke, R. D. *Macromolecules* **1996**, *29*, 7671.

(19) Goldoni, F.; Iarossi, D.; Mucci, A.; Schenetti, L.; Zambianchi, M. *J. Mater. Chem.* **1997**, *7*, 593.

(20) Fiandanese, V. *Pure Appl. Chem.* **1990**, *62*, 1987.

(21) Ng, S. C.; Chan, H. S. O.; Miao, P.; Tan, K. L. *Synth. Met.* **1997**, *90*, 25.

(22) Ng, S. C.; Miao, P.; Chan, H. S. O. *Chem. Commun.* **1998**, 153.

(23) Pei, Q. B.; Yu, G.; Zhang, C.; Yang, Y.; Heeger, A. J. *Science* **1995**, *269*, 1086.

(24) Onoda, M.; Nakayama, H.; Morita, S.; Yoshino, K. *J. Appl. Phys.* **1993**, *73* (6), 2859.

(25) King, G.; Higgins, S. J. *J. Mater. Chem.* **1995**, *5* (3), 447.

(26) Mastragostino, M.; Soddu, L. *Electrochim. Acta* **1990**, *35*, 463.

(27) (a) Visy, C.; Lukkari, J.; Kankare, J. *Synth. Met.* **1993,** *55*, 1620. (b) Visy, C.; Lukkari, J.; Kankare, J. *J. Electroanal. Chem.* **1991**, *319*, 85.

(28) Onoda, M.; Manda, Y.; Morita, S.; Yoshino, K. *Jpn J. Appl. Phys.* **1992**, *31*, 2265.

(29) Garnier, F.; Dalabouglise, D.; Roncali, J.; Korri, H.; Li, H. *Polym. Mater. Sci. Eng.* **1991**, *64*, 334.

(30) Osaki, Y.; Mori, T. *Jpn. Kokai Tokkyo Koho*, JP 02272066, 4 pp, 1990.

(31) Onoda, M.; Nakayama, H.; Morita, S.; Yoshino, K. *J. Electrochem Soc.* **1994**, *141*, 338.

(32) Jenkins, I. H.; Rees, N. G.; Pickup, P. G. *Chem. Mater.* **1997**, *9*, 1213.

(33) Eckhardt, H.; Shacklette, L. W.; Jen, K. Y.; Elsenbaumer, R. L. *J. Chem. Phys.* **1989**, *91* (2), 1303.

(34) Chen, W.-C.; Jenekhe, S. A. *Macromolecules* **1995**, *28*, 465.

(35) Glenis, S.; Benz, M.; LeGoff, E.; Kanatzidis, M. G.; DeGroot, D. C.; Schindler, J. L.; Kannewurf, C. R. *Synth. Met.* **1995**, *75*, 213.

(36) Agrawal, A. K.; Jenekhe, S. A. *Chem. Mater.* **1996**, *8*, 579.

(37) Yamamoto, T.; Suganuma, H.; Maruyama, T.; Inoue, T.; Muramatsu, Y.; Arai, M.; Komarudin, D.; Ooba, N.; Tomaru, S.; Sasaki, S.; Kubota, K. *Chem. Mater.* **1997**, *9*, 1217.

(38) Kitamura, C.; Tanaka, S.; Yamashita, Y. *Chem. Mater.* **1996**, *8*, 570.

(39) (a) Ng, S. C.; Chan, H. S. O.; Huang, H. H.; Seow, R. S. H. *J. Chem. Res., Miniprint* **1996**, 1285. (b) Ng, S. C.; Chan, H. S. O.; Huang, H. H.; Seow R. S. H. *J. Chem. Res., Synop.* **1996**, 232.

(40) Khor, E.; Ng, S. C.; Li, H. C.; Chai, S. *Heterocycles* **1991**, *32*, 1805.

(41) Inganas, O.; Liedberg, B.; Wu, C. R.; Wynberg, H. *Synth. Met.* **1985**, *11*, 239.

(42) Tourillon, G.; Garnier, F. *J. Electroanal. Chem.* **1984**, *161*, 51.

(43) Tanaka, S.; Kumei, M. *J. Chem. Soc., Chem. Commun.* **1995**, 815.

(44) Roncali, J.; Garreau, R.; Yassar, A.; Marque, P.; Garnier, F.; Lemaire, M. *J. Phys. Chem.* **1987**, *97*, 6706.

(45) Morea, G.; Malitesta, C.; Sabbatini, L.; Zambonin, P. G. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 3769.

(46) Johnson, E. G. In *Semiconductors and Semimetal*; Willardson, R., Beer, A. C., Eds.; Academic: New York, 1967; Vol. 3, p 153.

(47) Cesare, D. N.; Belletete, M.; Durocher, G.; Leclerc, M. *Chem. Phys. Lett.* **1997**, *275*, 533.

(48) Roux, C.; Bergeron, J. Y.; Leclerc, M. *Makromol. Chem.* **1993**, *194*, 869.

(49) Raymond, F.; Cesare, N. D.; Belletete, M.; Durocher, G.; Leclerc, M. *Adv Mater.* **1998**, *10*, 599.

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

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

(52) Leclerc, M.; Diaz, F. M.; Wegner, G. *Makromol. Chem.* **1989**, *190*, 3105.

(53) Yassar, A.; Roncali, J.; Garnier, F. *Macromolecules* **1989**, *22*, 804.

(54) Genies, E. M.; Bidan, G.; Diaz, A. F. *J. Electroanal. Chem.* **1983**, *149*, 101.

(55) Hillman, A. R.; Mallen, E. F. *J. Electroanal. Chem.* **1990**, *281*, 109.

MA981587T