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Electrically Conducting Polymers Containing Alternating Substituted Phenylene and Bithiophene Repeat Units

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ABSTRACT: Poly(di-2-thienylphenylene) (**2a**), poly(di-2-thienyl-2,5-dimethylphenylene) (**2b**), and poly(di-2-thienyl-2,5-dimethoxyphenylene) (**2c**) have been prepared to examine the effect of substitution on polymer structure and ultimately their physical, optical, electrical, and electrochemical properties. The polymers contain no configurational isomerism due to head to head linkages with fully conjugated structures exclusively composed of α-thienyl couplings. Electrical conductivities for pressed pellets of **2c** of 2 Ω^{-1} cm^{-1} have been measured, while powders of **2a** and **2b** exhibit conductivities of 0.5 and 10^{-6} Ω^{-1} cm^{-1}, respectively. Electronic band gaps (E_g) of 2.2, 2.7, and 2.2 eV are found for polymers **2a–c**, respectively, which are in close correlation with theoretically calculated values of 2.0, 2.6, and 2.2 eV. All of the polymers are electroactive with typical electronic absorption spectral signatures of bipolarons, though **2b** is significantly more difficult to oxidatively dope. Correlation of calculated minimum energy conformations, barriers to rotation, and band structures with experimental results indicates that the methyl-substituted polymer (**2b**), with a high barrier to rotation (i.e., planarity), exhibits a high band gap, narrow bandwidth, and ultimately low electrical conductivity. Conversely, the alkoxy-substituted polymer (**2c**) exhibits a low barrier to rotation, wider bandwidth and energy gap, comparable to the unsubstituted polymer (**2a**), and ultimately a high conductivity in the doped state.

Introduction

Structural modification of conjugated polymer chains has proved useful in the preparation of redox dopable electronically conducting polymers with a broad range of mechanical, electrical, electrochemical, and optical properties.[1,2] Various substituted derivatives of polyacetylene,[3] poly(*p*-phenylene),[4] polypyrrole,[5–7] and polythiophene[8–11] illustrate this. As representative examples, *N*-alkyl- and *N*-aryl-substituted pyrrole/pyrrole copolymers[5] exhibit electrical conductivities that vary from 10^2 to 10^{-5} Ω^{-1} cm^{-1} as a function of composition. Sulfoalkylation of both thiophenes[11] and pyrroles[7] has led to self-doped polymers where the substituent is actively involved in the doping process by providing the charge-compensating counterion. Polythiophenes[6,8–10] and polypyrroles,[6] derivatized at the 3-position with alkyl groups, exhibit both melt and solution processability, allowing fiber, blend, and composite formation. Structural asymmetry in these 3-substituted monomers yields polymers that necessarily contain both head–tail and head–head linkages.[10] This configurational disorder can be expected to limit long-range order in the solid and may ultimately limit crystallinity in oriented systems.

Due to the broad range of substitution possibilities on phenylene rings and the promising electronic properties of both poly(*p*-phenylene) and polythiophene, interest in polymers containing both phenylene and thiophene moieties conjugated along the backbone has developed. A recently reported synthetic route for obtaining these polymers involves the incorporation of sulfur into a poly(1,4-diketone) through a condensation reaction[12] to form perfectly alternating phenylene–thiophene copolymers. A parallel approach was used earlier by Braeke et al.[13] in preparing the same polymer via an alternating copolymer with phenylene and diacetylene repeat units. Since harsh conditions are required for these reactions, the risk of cross-linking is always imminent.

Another route, utilized by Czerwinski et al.,[14] involved the random incorporation of phenylene and thiophene repeat units along the main chain utilizing a Grignard coupling between *p*-dibromobenzene and 2,5-dibromothiophene. By alteration of the thiophene to phenylene feed ratio, the resulting polymers contained different ratios of phenylene to thiophene. Characterization of the electronic structure of the resulting polymers was accomplished by means of electron diffraction and electron energy loss spectroscopy to determine electronic band gaps and π-bandwidths as a function of the copolymer composition. The energy of the lowest energy plasmon, the $\pi \rightarrow \pi^*$ transition, is linearly dependent on the phenylene content. These values lie between 3.0 eV for poly(*p*-phenylene) and 2.0 eV for polythiophene.

Syntheses of alternating copolymers that contain arylene and bithiophene repeat units have also been reported.[15–17] This was accomplished via the electrochemical polymerization of 1,4-di-2-thienylarylenes, which have reactive α (2 and 2′) positions available for coupling. Polymers containing alternating thiophene and substituted phenylene units have recently been reported by using the coupling reaction of a 1,4-di-2-thienylphenylene that had been metalated at the 5 and 5′ positions with zinc chloride.[18] This metallo reagent was reacted with 1,4-dibromo-2,5-disubstituted benzenes via a Grignard coupling to form polymers where the phenylene units contained alkyl, alkoxy, and nitro substituents. The polymers prepared by using the above route were initially insulating but were oxidized by ferric chloride or iodine to yield doped complexes having conductivities between 10^{-5} and 10^{-3} Ω^{-1} cm^{-1}.

In this work, we present the synthesis, characterization, and properties of a series of phenylene-substituted di-2-thienylphenylene polymers, which exhibit doped conductivities on the order of 1 Ω^{-1} cm^{-1}. These polymers demonstrate electrochemical and optical properties very similar to polythiophene, while retaining the synthetic flexibility for substitution found in phenylenes. Symmetric substitution at the 2 and 5 positions on the phenylene ring eliminates the possibility for head to tail coupling and, therefore, configurational disorder along the main chain. This becomes important when considering

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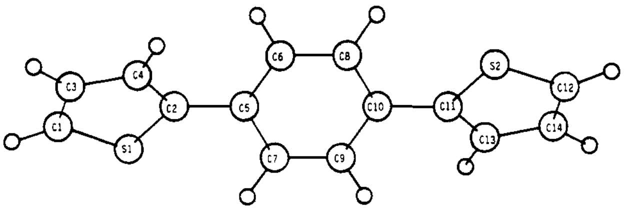
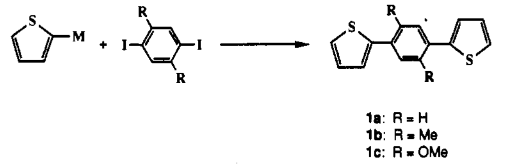


Figure 1. Structure of 1,4-di-2-thienylbenzene (**1a**).

possible long-range order and potential crystallinity in polyheterocycles. The conductivity can be somewhat controlled by altering the planarity of the system through substitution. The optical and electrochemical properties of these polymers are correlated with theoretical calculations, and the structures were verified by using a variety of FT-NMR, FT-IR, and thermoanalytical techniques.

Results and Discussion

Monomer Synthesis. Iodination of *p*-xylene yielded crystalline 1,4-diiodo-2,5-dimethylbenzene.[19] This procedure was not feasible for the iodination of 1,4-dimethoxybenzene since the strongly acidic medium used cleaves ethers. Therefore, the reaction was carried out in peracetic acid to yield 1,4-diiodo-2,5-dimethoxybenzene.[20] The monomers 1,4-di-2-thienylbenzene[12] (**1a**) and 1,4-di-2-thienyl-2,5-dimethylbenzene (**1b**) were prepared from the corresponding 1,4-diiodobenzene derivatives and 2-thienylmagnesium bromide with a nickel catalyst, nickel(II) bis(diphenylphosphino)propane dibromide (NiDPPPBr$_2$), as outlined in eq 1.



(1)

This technique was unsuccessful for the preparation of **1c** since the electron-donating effect of the methoxy group ortho to the substitution site reduces the electrophilicity at this carbon. The use of a more nucleophilic thiophene derivative, 2-thienylcopper, was necessary.[21] The reaction of 2-thienylcopper with the 1,4-diiodo-2,5-dimethoxybenzene under refluxing pyridine yielded a crystalline product 1,4-di-2-thienyl-2,5-dimethoxybenzene (**1c**), after recrystallization in methanol. 2-Thienylcopper was also used to prepare **1b**; however, lower yields were obtained when compared to the alkoxy-substituted compound as was similarly observed by Nilsson and co-workers.[21]

Electron Spin Density Calculations on Monomer Radical Cations. The oxidative coupling polymerization of heterocycles can be carried out by using both chemical (e.g., FeCl$_3$) and electrochemical methods. The radical cations formed are reactive to polymerization at carbon atoms that contain high electron spin densities. In that this determines the site of polymerization or the linkages between the monomers, it controls the ability to obtain the desired fully conjugated structures. We have carried out a series of calculations to determine the most likely polymerization sites on these di-2-thienylphenylene monomers. Calculations of this sort have proved invaluable in our previous studies of poly(dithienylethylene)[22] and ethylmercapto-substituted thiophenes[23] in directing polymerization studies.

With use of the numbering system of Figures 1–3, the computed spin populations on respective atoms of all monomers studied, **1a–c**, are given in Table I. All three species have significant positive spin densities on the α-carbons, with significant spin density distributed on other sites. These results indicate that all monomers are expected to polymerize under oxidative conditions. In contrast to our previous studies on thiophene[22] in which pure α–α couplings were predicted, due to the presence of highest spin densities at the α-carbon sites, the distribution of significant amounts of spin population at the other sites in these systems suggests that the copolymers may contain some fractions of α–β and/or β–β linkages. The amount of α–β and β–β couplings that form relative to α–α coupling is controlled by other factors in addition to radical-cation spin density. For example, steric interactions decrease reactivity at the β sites, and thus we

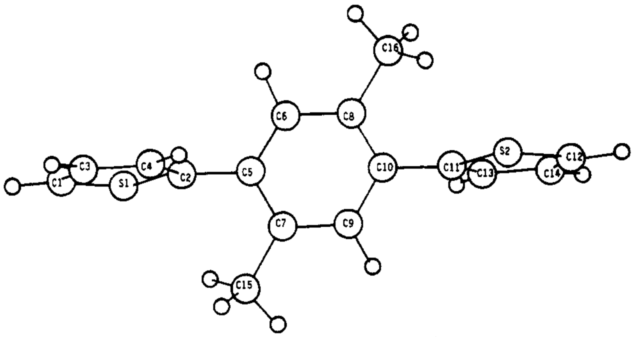


Figure 2. Structure of 1,4-di-2-thienyl-2,5-dimethylbenzene (**1b**). The labeling of the atoms is the same as that of Figure 1 except the methyl group in which the carbons are labeled sequentially as C15 and C16.

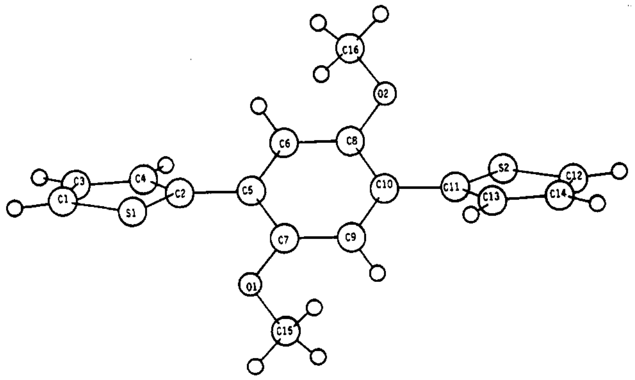


Figure 3. Structure of 1,4-di-2-thienyl-2,5-dimethoxybenzene (**1c**). The labeling of the atoms is the same as that of Figure 1 except the methoxy groups in which the oxygens and carbons are labeled sequentially as O1, C15, O2, and C16.

Table I
PRDDO-Computed Spin Populations

atom	**1a**	**1b**	**1c**
C_1	0.797	0.796	0.697
C_2	0.196	0.512	−0.478
C_3	−0.567	−0.458	−0.593
C_4	0.581	0.434	0.628
C_5	−0.396	−0.629	0.351
C_6	0.641	0.685	−0.321
C_7	0.632	0.671	0.231
C_8	−0.675	−0.679	0.229
C_9	−0.670	−0.703	−0.324
C_{10}	0.691	0.720	0.354
C_{11}	−0.693	−0.669	−0.482
C_{12}	0.744	0.589	0.688
C_{13}	0.725	0.617	0.631
C_{14}	−0.675	−0.539	−0.591
C_{15}		−0.074	−0.001
C_{16}		0.075	−0.011
S_1	−0.193	−0.247	−0.057
S_2	−0.02	0.008	−0.056
O_1			0.082
O_2			0.080

Table II
Infrared Absorption Positions and Assignments for Monomers and Polymers (cm^{-1})

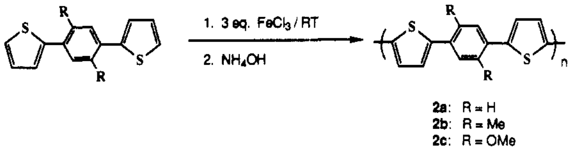
	aromatic C–H					ring stretches			aromatic bends	
material	α(w)[a]	β[a]	φ-H	aliphatic C–H		phenyl	thiophene	methyl deformn	phenyl	thiophene[a]
1a	3100	3065	3029			1598, 1539	1493, 1462, 1426		815, 896	957, 852
2a	3099	3066	3020			1603, 1518	1491, 1459, 1442		829, 870	792
1b	3101	3069	3007	2974	2858	1605, 1531	1491, 1452, 1433	1379	895, 839	959, 848
2b	3098	3066	3009	2965	2859	1603, 1518	1489, 1453, 1442	1380	889, 839	796
1c	3101	3074	2999	2928	2842	1603, 1529	1488, 1453, 1425	1392	866, 830	904, 852
2c	3099	3066	2995	2932	2839	1602, 1528	1486, 1461, 1451	1392	855, 842	788
PT[b]		3063					1491, 1453, 1441			788

[a] The vibrations in this area delineate the 2-substituted versus the 2,5-disubstituted thiophenes. [b] Polythiophene prepared in our laboratory using the Kobayashi method.[46]

expect the polymers to be essentially α coupled. This will be discussed further in the context of polymer structure.

Additional evidence concerning the nature of the molecular orbitals involved in the primary oxidation process is obtained from PRDDO closed-shell calculations on these systems. The ionization potentials (the negative of the eigenvalue of the highest occupied molecular orbital, i.e., the $-E_{HOMO}$) of **1a–c** are estimated to be 6.03, 6.72, and 5.98 eV, respectively. It has been established that there exists an excellent correlation of oxidation potential (E_{pa}) vs the Koopmans' theorem ionization potential.[24] The ordering of ionization potentials as **1c** < **1a** < **1b** shows the same trend determined electrochemically from the cyclic voltammetric peak potentials (E_{pa}) [E_{pa}(**1a**) ≅ 1.65, E_{pa}(**1b**) ≅ 1.75, E_{pa}(**1c**) = 1.05 V] as will be discussed later.

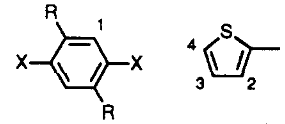
$FeCl_3$ Polymerization. The polymerization of monomers having the general structure 1 has been carried out by using both chemical and electrochemical methods. The high reactivity of the available α (5 and 5′) positions on the thiophene rings affords a significant amount of synthetic flexibility for the various oxidative polymerization methods. The use of ferric chloride as the oxidizing agent in the polymerization of 3-alkylthiophenes has been shown to give exceptionally high molecular weight polymers[25,26] and was chosen for this work as outlined in eq 2. Since it is easier to oxidize the conjugated polymer than the monomer, a minimum of 3 equiv of $FeCl_3$ was used for polymerization to allot enough reagent for the oxidative coupling and to oxidize the polymeric backbone. The resulting polymers, all bluish black, were initially obtained in the oxidized, conductive form as insoluble powders.



(2)

The powders were not analyzed at this point since excess ferric chloride is present. Repeated washings with methanol and water to remove ferric chloride resulted in a color change for the polymers from blue-black to green for **2a** and **2b** and purple-brown for **2c**. It is expected that compensation of these materials occurred as has been similarly reported for poly(3-alkylthiophenes).[26] The polymers, still in the partially oxidized state, were fully dedoped by compensation with aqueous ammonium hydroxide to yield orange, yellow, and brick red powders for **2a–c**, respectively. An ether wash of **2b** and **2c** produced a yellow residue that fluoresced green. Enough ether was used to wash this residue from the insoluble materials. This residue was assumed to be low molecular weight oligomers or decomposition products from overoxidation. The exact structure of this residue was not verified; however, Pelter et al.[18] have reported a similar soluble fluorescing yellow material to be an alternating polymer.

Table III
Proton NMR Chemical Shifts and Assignments for the Monomers [ppm (multiplet)]



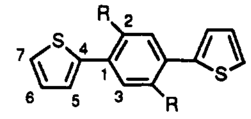
compd						
X	R	H_1	H_2	H_3	H_4	H_R
2-thienyl	H	7.60 (s)	7.30 (d)	7.07 (t)	7.25 (d)	
I	Me	7.63 (s)				2.32 (s)
2-thienyl	Me	7.35 (s)	7.34 (d)	7.10 (t)	7.32 (d)	2.42 (s)
I	OMe	7.19 (s)				3.82 (s)
2-thienyl	OMe	7.24 (s)	7.33 (d)	7.08 (t)	7.51 (d)	3.92 (s)

Structural Properties of Neutral Di-2-thienylphenylene Polymers. The structure and purity of both monomers and polymers were fully analyzed by using FT-IR, ^1H NMR, ^{13}C NMR, and elemental analysis. The relevant results of these studies, as well as IR and NMR assignments, are listed in Tables II–IV.

The principal IR bands for the polymers and their assignments are listed in Table II along with important bands for polythiophene (PT) for comparison. The absorbances due to the thiophene ring vibration at 1500–1420 cm^{-1} and the C–H out of plane vibrations at about 790 cm^{-1} are indicative of 2,5-disubstituted thiophenes.[27] The C–H stretching vibrations due to the β-hydrogens in the thiophene ring are found at 3060 cm^{-1}. A very weak absorption at about 3100 cm^{-1}, due to the residual α-hydrogen of the terminal thiophene ring, is observed in the polymers. The intensity of this absorbance is significantly reduced when compared to the monomers as illustrated in Figure 4 for **1c**. Three aromatic C–H stretches are observed for the monomer (Figure 4a) at 3101, 3074, and 2999 cm^{-1} which are assigned to the thiophene α C–H, the thiophene β C–H, and the phenylene C–H, respectively. After polymerization, it is evident that the thiophene α C–H stretch has essentially vanished (Figure 4b) while the thiophene β C–H and phenylene C–H are unchanged. This indicates that the oxidative coupling polymerization is occurring extensively at the terminal α sites on the thiophene, yielding the fully conjugated polymer as desired. The presence of the ring stretching vibration at 1600 and 1510 cm^{-1} as well as a C–H stretch at around 3000 cm^{-1} supports the presence of the phenyl groups along with the π-substitution pattern of the phenyl component, elucidated by the aromatic out of plane bending modes between 900 and 800 cm^{-1}.

Due to the insolubility of the polymers, ^1H NMR spectra were obtained only for the monomers, as reported in Table

Table IV
Carbon-13 NMR Shifts and Assignments for Monomers and Polymers (ppm)



R	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_R
1a	143.99	128.05		133.61	124.86	126.34	123.10	
2a	140	129		134	121	121	138	
1b	143.00	133.50	132.69	133.34	126.39	127.12	125.15	20.58
2b	140	134	130	135	126	125	135	77.5
1c	122.97	149.95	112.26	139.05	125.45	125.71	126.89	56.39
2c	120	147	106	136	125	124	133	50
PT[a]				134	123			

[a] Prepared in our laboratory using the Kobayashi method.[46]

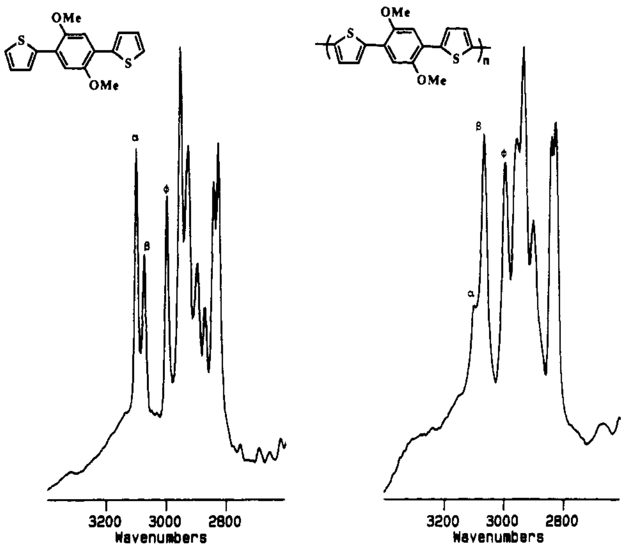


Figure 4. FT-IR spectra of 1,4-di-2-thienyl-2,5-dimethoxybenzene (**1c**) and poly(di-2-thienyl-2,5-dimethoxyphenylene) (**2c**).

III. The spectra of the monomers were consistent with the expected structures.

In order to more fully define the polymerization coupling sites, the structures of both monomers and polymers were analyzed by ^{13}C NMR. These results are detailed in Table IV and show, in agreement with the FT-IR results, that the polymers are forming by essentially α–α coupling. This is illustrated in Figure 5 for 1,4-di-2-thienyl-2,5-dimethoxybenzene (**1c**) and its polymer (**2c**). The aromatic peaks assigned to the dimethoxy and para-linked benzene units (peaks 1–3) are located in essentially the same place in both monomer and polymer, demonstrating low reactivity at these sites. Thus, no polymerization occurs through the phenylene ring. Examination of the resonances assigned to the 2-thienyl ring shows one major change, with a new resonance appearing in the polymer (peak 7) at 133 ppm and the typical line-width broadening due to inequivalent environments for carbon atoms in polymers. Comparison of peak 7 in the monomer and polymer reveals a decrease in intensity, along with a downfield shift, which is expected as the C–H bond in the monomer is converted to the thiophene linking C–C bond in the polymer.[27] Similar results, with 10–15 ppm downfield shifts exhibited for the α-thienyl carbon resonances, are observed in the other polymers. The fact that the NMR spectra of these polymers are well-defined is due to the presence of essentially complete α–α linkages and the absence of configurational isomerism in the form of head–head linkages. The use of symmetrically substituted monomers may prove useful beyond structural identification as there is a regular and ordered repeat unit in these polymers that may ultimately play a role in their physical properties (e.g., crystallinity).

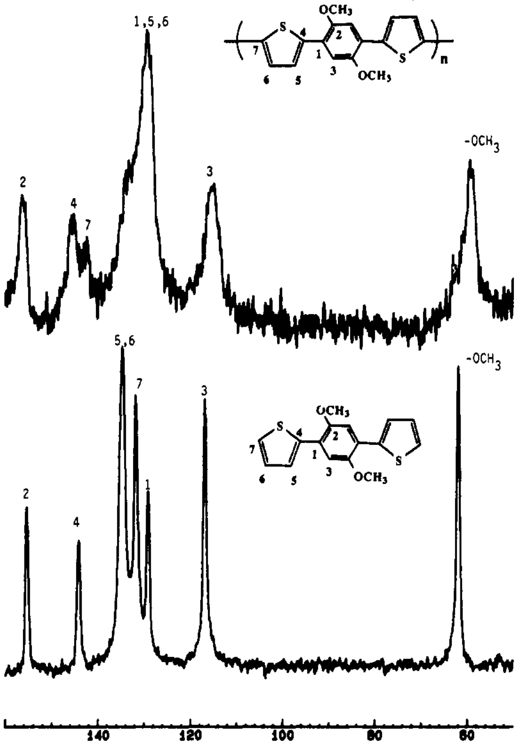


Figure 5. ^{13}C NMR spectra of 1,4-di-2-thienyl-2,5-dimethoxybenzene (**1c**) and poly(di-2-thienyl-2,5-dimethoxyphenylene) (**2c**). Solid-state CP-MAS technique.

The elemental compositions of the polymers were also confirmed by the carbon to hydrogen molar ratios from the elemental analysis, which support the structures depicted for **2a–c** (see the Experimental Section).

Polymer Physical Properties. Similar to the unsubstituted and methyl- and methoxy-substituted polythiophenes, the polymers prepared here are insoluble in common organic solvents.[28] Flexible alkyl and alkoxy substituents are typically used to improve both solution and melt processability of polythiophenes.[8–10,25,26] These same concepts have been employed for these di-2-thienylphenylene polymers where we have recently prepared soluble diheptoxy, didodecyloxy, and mixed substituent polymers. The properties of these polymers are presently under investigation.[29]

The thermal stabilities of polymers **2a–c** were analyzed using thermogravimetry. A thermogram is shown in Figure 6 for **2b**. All three polymers exhibit an onset of

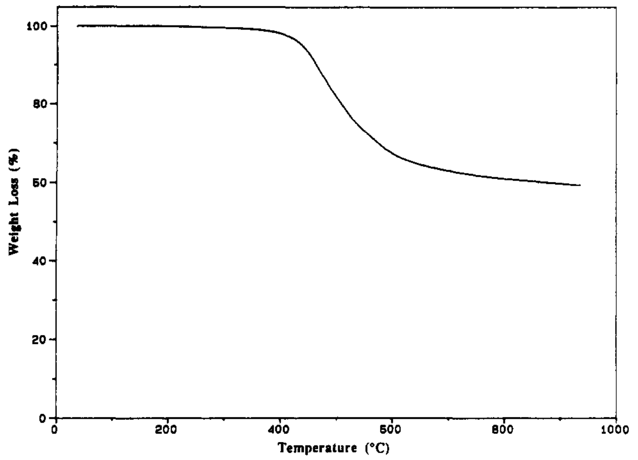


Figure 6. Thermogram of poly(di-2-thienyl-2,5-dimethylphenylene) (**2b**), under nitrogen.

Table V
Thermogravimetric Analysis Data

polymer	onset of degrdn, °C	% char residue
2a	380	65
2b	410	65
2c	430	60
poly(3-hexylthiophene)[a]	410	40

[a] Electrochemically prepared and reduced in our laboratory.

Table VI
Electrical Conductivities for the Neutral and Oxidized Polymers

		oxidized form, Ω^{-1} cm^{-1}	
polymer	reduced form, Ω^{-1} cm^{-1}	$NOPF_6$	I_2
2a	$\leq 5 \times 10^{-9}$	5×10^{-1}	2×10^{-6}
2b	$\leq 4 \times 10^{-9}$	2×10^{-6}	4×10^{-6}
2c	$\leq 2 \times 10^{-9}$	2×10^{0}	2×10^{-3}

degradation of at least 390 °C in the reduced form (see Table V), which is comparable to substituted polythiophenes. The most striking difference is the char residue, with the di-2-thienylphenylene polymers leaving about 60% residue after heating up to 1000 °C. This is larger than the residue left for poly(3-hexylthiophene) prepared and reduced electrochemically in our laboratory.

Electrical Conductivity. The polymers were isolated in their insulating form by treatment of the $FeCl_3$-polymerized product with NH_4OH. As such, pressed pellets of the polymer powders exhibit electrical conductivities $\leq 10^{-9}$ Ω^{-1} cm^{-1}. Though insoluble, the powders could be oxidatively doped, with a concurrent elevation in conductivity, by dispersing the polymer in an oxidizing solution. The results of $NOPF_6$ and I_2 doping experiments are shown in Table VI. Upon oxidation, the color of the polymers changed from the insulating forms of orange, yellow, and brick red for **2a–c**, respectively, to bluish black for the **2a** and **2c** polymers and a very dark green for **2b**.

A conductivity of 2 Ω^{-1} cm^{-1} is observed for the dimethoxy-substituted polymer when oxidized with $NOPF_6$. Significantly lower conductivites are observed when I_2 is used as the dopant, which is most likely due to the lower oxidation power of I_2 when compared to nitrosonium salt in solution. It can be seen that the substituent has a strong effect on the conductivities of these polymers with up to a 6 order of magnitude difference between the dimethoxy- and the dimethyl-substituted polymers. In order to understand this more fully, we have examined the polymers conformational preferences and band structures. These results of theoretical calculations will be compared to the experimental results later.

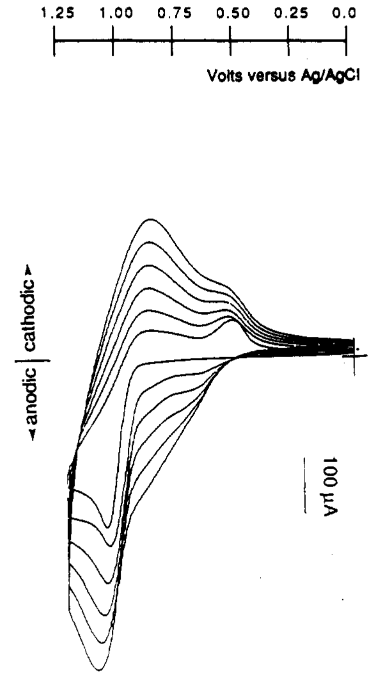


Figure 7. Cyclic voltammogram of 1,4-di-2-thienyl-2,5-dimethoxybenzene (**1c**; 5 mM) in 0.05 M $TBAClO_4$ at 100 mV/s.

Electrochemical Analysis and Polymerization. The insolubility of the polymers prepared by $FeCl_3$ oxidation forced the above conductivity measurements to be made on pressed pellets and precluded any useful analysis of the polymers' electronic spectra. Anodic electropolymerization is useful for the preparation of both electrode-supported and free-standing conducting polyheterocycle films and has been applied here.

All of the di-2-thienylphenylenes studied electropolymerize to form electroactive polymer films. In cyclic voltammetric experiments, when a glassy-carbon working electrode is used, the monomers exhibit an anodic peak due to the formation of radical cations with onset potentials of 1.15, 1.20, and 0.95 V (versus Ag/AgCl) for **1a–c**, respectively. This is shown in the first scan of Figure 7 for the dimethoxy-substituted monomer **1c**, which is representative of all monomers. Two cathodic peaks are observed at 0.90 and 0.50 V on the first return scan due to reduction of oxidized polymer on the electrode surface. Switching potentials were maintained ≤1.4 V in all cases to avoid overoxidation and deactivation of the polymers electroactivity.[30] The second scan shows anodic current beginning at much lower potentials of ca. 0.60 V as the reduced polymer on the electrode surface reoxidizes, followed by a higher current during monomer oxidation. This overall increase in current with repetitive scanning is due to the fact that the depositing conducting polymer is increasing the effective surface area of the electrode.

The electrochemically prepared poly(di-2-thienyl-2,5-dimethoxyphenylene) film was subsequently thoroughly washed with CH_3CN to remove excess monomer and its electroactivity examined in monomer free electrolyte. This is shown in Figure 8 as a function of scan rate and is again representative of all monomers studied, though this polymer (**2c**) exhibited a slightly lower oxidation potential (and better peak resolution) than **2a** or **2b**. The electrochemical behavior of **2c** is quite similar to that of polythiophene.[31] A broad oxidation process is observed between 0.6 and 1.2 V while two reduction processes are observed at 0.9 and 0.5 V, respectively. These two cathodic peaks have been attributed to the sequential reduction of

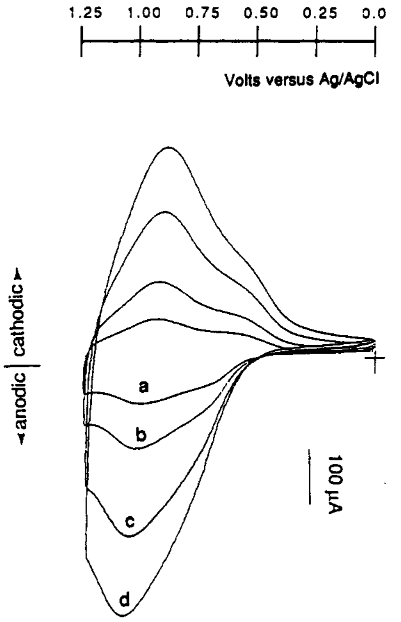


Figure 8. Cyclic voltammogram of poly(di-2-thienyl-2,5-dimethoxyphenylene) (**2c**) thin film in 0.05 M TBAClO$_4$. Scan rate: (a) 25, (b) 50, (c) 100, (d) 150 mV/s.

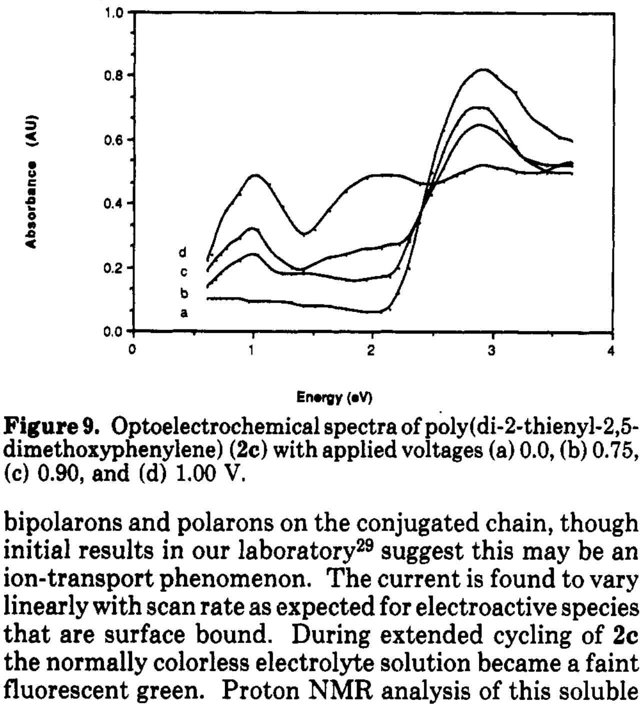


Figure 9. Optoelectrochemical spectra of poly(di-2-thienyl-2,5-dimethoxyphenylene) (**2c**) with applied voltages (a) 0.0, (b) 0.75, (c) 0.90, and (d) 1.00 V.

bipolarons and polarons on the conjugated chain, though initial results in our laboratory[29] suggest this may be an ion-transport phenomenon. The current is found to vary linearly with scan rate as expected for electroactive species that are surface bound. During extended cycling of **2c** the normally colorless electrolyte solution became a faint fluorescent green. Proton NMR analysis of this soluble material revealed a series of unassignable aliphatic signals. Further characteriztion of these products was not pursued.

Optoelectrochemistry. Optoelectrochemical analysis[32] allows the electronic states of the polymers to be probed in situ during electrochemical oxidation and reduction. The polymers were electrochemically synthesized on optically transparent conducting glass (indium tin oxide coated glass) followed by electrochemical reduction to the neutral form. Onsets of absorption, an approximation of the band gap, of 2.2, 2.7, and 2.2 eV were observed for **2a–c**, respectively. The spectrum of **2c** is representative and is shown in Figure 9. The energy gap (E_g) was also obtained for the FeCl$_3$-synthesized polymers by dispersing the powders in polystyrene and measuring the electronic spectra of cast films. In these cases absorption onsets were found at 2.5, 2.7, and 2.5 eV for **2a–c**, respectively. The higher E_g's measured for these polymer dispersions were the result of broad peaks from light-scattered spectra. These polymers, comparable to poly(*p*-phenylene) and contrary to polythiophenes, exhibit differences in their electronic band gaps upon the incorporation of substituent groups. In the case of the polymers where only a thiophene backbone is present, the incorporation of these groups presents no significant effect.

Partial oxidation, using applied potentials less than or equal to that of the polymer oxidation potential, resulted in the emergence of two new low-energy transitions between 0.5 and ca. 2.0 eV for all polymers. This is indicative of the formation of bipolaronic species.[33] In **2a** and **2c**, the decay of the π to π^* transition accompanied the emergence of these midgap absorptions. With **2b**, on the other hand, the intensity of the interband transition did not significantly alter upon oxidation. The high oxidation potential of **2b** causes the polymer oxidation to be difficult, and, to avoid overoxidation, low applied potentials lead to low doping levels.

Correlations with Theoretical Calculations. In order to understand the electronic and optical properties of these polymers, a series of theoretical studies has been carried out. The minimum energy conformations of the polymers were analyzed by examining torsional angles between aromatic rings to gain an understanding about how the substituents affect the planarity of the conjugated backbone. The electronic band structure for each polymer was subsequently calculated using extended Hückel theory and found to correlate well with the measured optoelectronic properties.

Conformational Details. At the PRDDO level, total energy optimizations were performed by using internal bond stretches and angle bend variations in order to determine the equilibrium ground-state geometries of the monomers of the thiophene and phenylene rings. Upon coupling the two units of thiophene to the phenylene moiety at its para positions, geometry optimizations were performed to estimate the inter-ring bond distances and the corresponding torsional angles between the phenylene and thiophene moieties. For comparison, the modified neglect of differential overlap method (MNDO) within the CHEMX program[34] was also employed to obtain minimum energy conformations. The structures of interest are shown in Figures 1–3, respectively. For monomer **1a**, the inter-ring distance (r) and the torsional angle (ϕ) about the inter-ring bond were calculated to be 1.47 Å and 24.3°, respectively, with a barrier to rotation (ΔE) of the order of 3.1 kcal/mol. In the case of system **1b**, it was found that r = 1.48 Å and ϕ = 63°, the increased twist angle clearly being due to the steric interaction of the methyl group with the sulfur atom. This calculation included the optimization of the bond distances C_{15}–C_7 and C_{16}–C_8 and bond angles C_{15}–C_7–C_5 and C_{16}–C_{18}–C_{10} and the orientations of the hydrogens of the methyl groups. The barrier to rotation was of the order of 15.8 kcal/mol. For monomer **1c**, the optimized torsional angle (ϕ) was found to be 40° and r = 1.474 Å with ΔE of the order of 3.5 kcal/mol. Here our calculation also included optimization of the bond distances O_1–C_7, O_2–C_8, C_{15}–O_1, and C_{16}–O_2 and the bond angles C_{15}–O_1–C_7, C_{16}–O_2–C_8, O_1–C_7–C_5, and O_2–C_8–C_{10} and the torsions about O_1–C_7 and O_2–C_8 bonds of the methoxy groups. Thus, it is evident that the di-2-thienyl-*p*-phenylene units do not represent planar systems. In the case of system **1a**, we carried out MNDO calculations within the CHEMX program,[34] which predicted the perpendicular conformation (a rotation of 90° between the phenylene and thiophene units) to be 4.1 kcal/mol more stable than the planar form.

In comparing the PRDDO calculated torsional angles and barrier for rotation, we note an interesting correlation with the band gaps of the polymers. Though there is a significant difference in ϕ between **2a** and **2c**, their calculated rotational barriers are quite close at ca. 3 kcal/mol. At the same time their measured band gaps (ca. 2.2 eV) are approximately the same as are their optoelectrochemical doping spectra. Both polymers dope easily and attain a high conductivity. Polymer **2b**, on the other hand, displays a signficiantly higher barrier to rotation. This high barrier prevents the polymer from attaining planarity; it is difficult to dope and does not attain high levels of conductivity.

Recently a number of studies[35-42] have appeared, leading to a controversy concerning the relative stabilities of the aromatic and quinoid forms of polythiophene and its derivatives. It is thus quite interesting to explore such alternate features in the case of copolymers of the phenylene and bithiophene systems. Initial optimizations of the aromatic monomeric systems suggest that these copolymers do represent essentially nonplanar backbones. Since it is obvious that the aromatic and quinoid structures may coexist, we extended our studies to estimate the stabilities between the aromatic and quinoid forms of these systems using the PRDDO method and the thermodynamic cycle arguments developed earlier.[42] Briefly we define the thermodynamic cycle to estimate the relative stability between the quinoid and aromatic forms (ΔE_{qa}) in the absence of end groups. ΔE_{qa} cannot be defined directly; however, it can be estimated from the relation

$$\Delta E_{qa} = E(H_2\text{–}P_Q\text{–}H_2) - E(H\text{–}P_A\text{–}H) - 2E_H + 2E_{CH}$$

where $E(H_2\text{–}P_Q\text{–}H_2)$ and $E(H\text{–}P_A\text{–}H)$ are the calculated energies of the quinoid form ($H_2\text{–}P_Q\text{–}H_2$) and the aromatic form ($H\text{–}P_A\text{–}H$), respectively. P_Q and P_A are used to refer to the quinoid and aromatic forms, respectively, in the absence of terminating groups. E_H and E_{CH} have the usual meaning as defined elsewhere.[42] Calculations of $\Delta E_{qa}/N$ as a function of N (the chain length) and extrapolations to the infinite system through accurate least-square fits yield an estimate of the relative thermodynamic stabilities of the aromatic and quinoid forms.

Initially the quinoid geometry of the thiophene monomer of thiophene was obtained by terminating C_α's with CH_2 groups. In a similar way the para carbons of a quinoidal phenylene ring were terminated with CH_2 groups. At the PRDDO level total energy optimizations were done including all bond stretches and angle bend variations in order to obtain the ground-state quinoid geometries of the thiophene and phenylene monomers. Finally these quinoid structures of the thiophene and phenylene moieties were coupled together to generate the quinoid structure of the phenylene–bithiophene unit. In order to obtain the quinoid form of system **1a**, the extreme C_α's were terminated with H_2 groups (or a saturated carbon) instead of H as in the case of the aromatic systems. The optimized inter-ring distance between the phenylene moiety and the thiophene units was calculated to be 1.31 Å, typical of C=C bonds. The quinoid structure represents a planar backbone, with sulfur atoms on adjacent units arranged in the transoid geometry. Since the size of the monomeric unit is relatively large, the relative stabilities between the quinoid and aromatic forms of systems up to the oligomeric chain length limit of 2 were calculated. At the limit of $N = 2$, the $\Delta E_{qa}/N$ between the quinoid and conformed nonplanar aromatic geometry of system **1a** was found to be 56.3 (kcal/mol)/chain length, a value substantially higher than the 24.2 (kcal/mol)/chain length obtained in the case of polythiophene.[42] On the basis of our predictions for polythiophene (in which the aromatic form is predicted to be 10.6 (kcal/mol)/chain length more stable than the quinoid form in the infinite chain-length limit), it is clear that the aromatic nonplanar system **1a** is more stable than its quinoid counterpart. Similar conclusions could be drawn for the systems **1b** and **1c**. Because of these findings, investigation of the electronic properties of the quinoid structures of any of these three systems using band structure calculations was not pursued.

Table VII
Extended Hückel Band Structure

compd	ϕ, deg	E_g, eV	E_g (measd), eV	E_{bw}, eV
2a	24.3	2.03	2.2	0.43
2b	63.0	2.58	2.7	0.13
2a	40.0	2.18	2.2	0.36

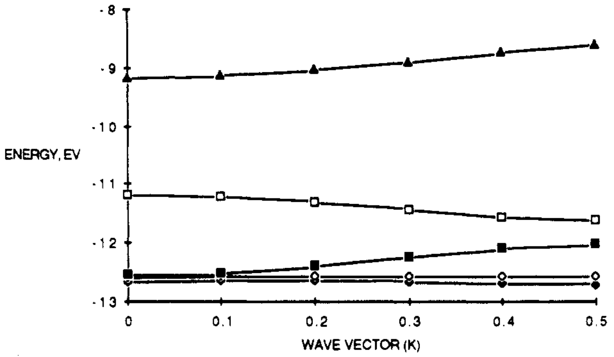


Figure 10. Band structure of poly(di-2-thienyl-*p*-phenylene) (**2a**). The four highest occupied valence bands (HOVB) along with the lowest unoccupied conduction band (LUCB) are displayed.

Band Structure Calculations. The band structures of the one-dimensional polymer chain of copolymers of phenylene and bithiophene were calculated by using extended Hückel theory within the tight-binding approximation.[43,44] A repeat unit consisting of a phenylene moiety at the center connected to the thiophene moieties at the para positions was considered for our calculations. The geometric parameters required, such as bond lengths and bond angles, were obtained from our PRDDO calculations. Because of the large size of the unit cell, the lattice sums were carried out only to the first nearest neighbor. The present calculations include all the valence atomic orbitals of H, C, O, and S atoms. The atomic parameters required for the computations were obtained from the literature.[43-45]

The estimated quantities of interest are the band gaps and bandwidths of the highest occupied valence bands of these polymers. The band structures were obtained within the first half of the first Brillouin zone with wave vector κ (where $\kappa = 2\pi/\mathbf{a}$, **a** being the primitive vector) ranging from 0.0 to 0.5k with an increment of 0.1. In the case of system **2a** in its most stable conformational state, the band gap (E_g) and bandwidth (E_{bw}) are found to be 2.03 and 0.43 eV, respectively. The corresponding values of that of pure polythiophene are of the order of 1.73 and 1.17 eV.[23] In the case of system **2b**, the band gap and bandwidths are found to be 2.58 and 0.13 eV, respectively. For the system **2c** the values of E_g and E_{bw} are found to be 2.18 and 0.36 eV, respectively. The band gaps and bandwidths of these systems are reviewed in Table VII and the structures shown in Figures 10–12. In general, the electronic properties of these polymers are found to be intermediate between those of polyparaphenylene and

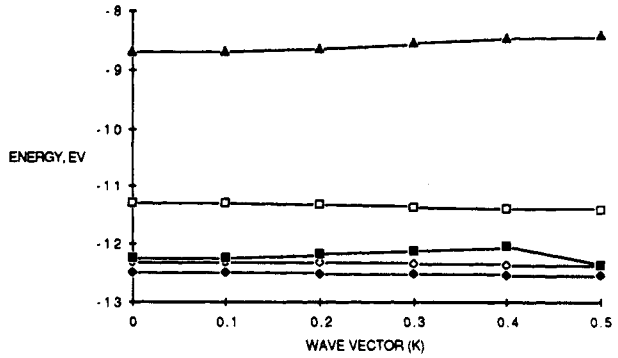


Figure 11. Band structure of poly(di-2-thienyl-2,5-dimethylphenylene) (**2b**). The four HOVB and the LUCB are shown.

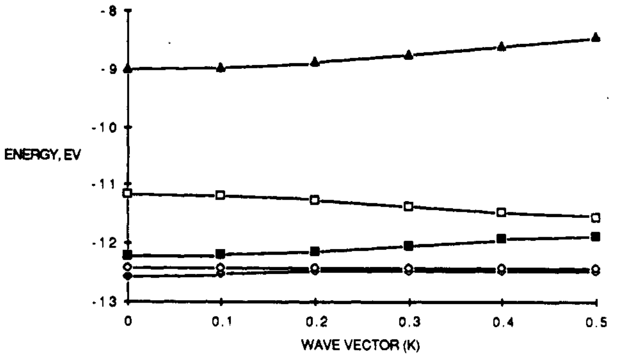


Figure 12. Band structure of poly(di-2-thienyl-2,5-dimethoxyphenylene) (**2c**). The four HOVB and the LUCB are shown.

polythiophene. As we change from the unsubstituted phenylene ring to a bulky substituent, the band gap increases and the bandwidth decreases. From a detailed analysis of the highest occupied valence band (HOVB) of system **2a**, it is found that the HOVB originates from the π orbitals of the phenylene ring and sulfur atoms. In the case of the substituted copolymers, there is loss of conjugation due to the nonplanarity of the backbones and the states in HOVB are localized more to the individual rings. This partly explains the flatness or the nondispersive characteristics of the HOVBs of the methyl-substituted polymer.

In these studies, our calculations correlate quite well with our experimentally observed parameters. In addition, the bandwidth calculations show polymers **2a** and **2c** to be quite similar, with relatively high bandwidths and capable of high conductivities. Polymer **2b**, on the other hand, is nonplanar, poorly delocalized, exhibits a low conductivity, and exhibits a much lower bandwidth.

Conclusions

The polymerization of 1,4-di-2-thienyl-2,5-disubstituted phenylenes lead to fully conjugated polymers linked exclusively at the α-thienyl sites. These polymers are stable up to ca. 400 °C. Due to the symmetry of the monomers, the polymers formed contain no head–head configurational isomerism, making their structures more regular than 3-substituted polyheterocycles. These polymers can be oxidatively doped to yield conducting complexes with conductivities on the order of 1 Ω^{-1} cm^{-1}, and electrochemically synthesized films can be prepared free standing and electrode-supported. The polymer films are electroactive and can be reversibly cycled between the insulating and the conductive forms both electrochemically and chemically. The differences in the electrochemical, electrical, and optoelectrochemical behavior of the polymers can be attributed to the steric effects of substituent groups. These experimental results have been compared with theoretical modeling of the polymers' molecular and electronic properties and found to correlate well.

Experimental Section

General Procedures. THF and ether were distilled after refluxing with sodium benzophenone ketyl. Thiophene, 1,4-diiodobenzene, *p*-xylene, 1,4-dimethoxybenzene, and magnesium bromide etherate were obtained from Aldrich Chemicals and used as received. Iodine from Fisher Scientific was used as received. 1,4-Diiodo-2,5-dimethylbenzenes[19] and nickel bis(diphenylphosphino)propane dibromide[47] (NiDPPPBr$_2$) were prepared according to literature preparations.

1,4-Diiodo-2,5-dimethoxybenzene. 1,4-Diiodo-2,5-dimethoxybenzene was prepared similar to a literature procedure.[20] 1,4-Dimethoxybenzene (0.073 mol), 1 M peroxyacetic acid[48] (0.250 mol), and iodine crystals (0.146 mol) were heated to 60 °C for 24 h. The reaction mixture was cooled and then poured into 10% aqueous Na$_2$HSO$_2$. The product was extracted with CCl$_4$ and then neutralized with water rinses. The organic layer was dried (calcium chloride) and the solvent evaporated. The solid product was recrystallized from ethanol/benzene (3:1) to give a white granular product (45%, mp = 168–170 °C). ^{13}C NMR (75.4 MHz): δ 57.14, 85.42, 121.55, and 153.28. Anal. Calcd for C$_6$H$_8$O$_2$I$_2$: C, 24.64; H, 2.07. Found: C, 24.79; H, 1.90.

1,4-Di-2-thienylbenzene (1a). *tert*-Butyllithium (0.073 mol; Aldrich Chemicals) in pentane was slowly added to a cold solution of thiophene (0.140 mol) in 50 mL of ether at −78 °C (dry ice/acetone bath). The reaction mixture was stirred for 15 min at −78 °C and then for 1 h at room temperature. The 2-thienyllithium formed was transferred to a solution of magnesium bromide etherate (0.078 mol) in ether using inert-atmosphere techniques and stirred at room temperature for 1 h. The 2-thienylmagnesium bromide solution was added to a solution of 1,4-diiodobenzene (0.026 mol), in ether with 50 mg of NiDPPPBr$_2$ and stirred at 35 °C for 50 h. The cooled reaction mixture was poured into 4 M HCl and the aqueous layer extracted with ether. The combined organic layer was neutralized with water washes and dried over calcium chloride and the solvent evaporated. Recrystallization from methanol yielded an orange granular product (78%, mp = 128–131 °C dec). Anal. Calcd for C$_{14}$H$_{10}$S$_2$: C, 68.38; H, 4.17. Found: C, 68.21; H, 3.97.

1,4-Di-2-thienyl-2,5-dimethylbenzene (1b). Compound **1b** was prepared by using the same conditions as **1a** with thiophene (0.112 mol), *tert*-butyllithium (0.068 mol), magnesium bromide etherate (0.069 mol), 1,4-diiodo-2,5-dimethylbenzene (0.022 mol), and NiDPPPBr$_2$ (50 mg). An orange granular product was obtained upon recrystallization from methanol (80%, mp = 90–92 °C). Anal. Calcd for C$_{16}$H$_{14}$S$_2$: C, 71.06; H, 5.23. Found: C, 70.34; H, 5.23.

1,4-Di-2-thienyl-2,5-dimethoxybenzene (1c). 2-Thienyllithium was prepared as described above using thiophene (0.088 mol) and *tert*-butyllithium (0.075 mol). The resulting 2-thienyllithium was added to a suspension of cuprous bromide in ether to produce a yellow precipitate. The precipitate was filtered under nitrogen to obtain 2-thienylcopper powder (0.068 mol). The 2-thienylcopper and 1,4-diiodo-2,5-dimethoxybenzene (0.023 mol) was refluxed in 50 mL of pyridine for 40 h. The cooled reaction mixture was poured into ether and filtered to remove the precipitate. The filtrate was washed with acidic (4 N HCl) solution, the organic layer was neutralized with water and dried over calcium chloride, and the solvent was evaporated. Recrystallization from methanol yielded a yellow granular product (85%, mp = 130–132 °C). Anal. Calcd for C$_{16}$H$_{14}$O$_2$S$_2$: C, 63.54; H, 4.68. Found: C, 63.31; H, 4.52.

Poly(di-2-thienylphenylene) (2a). A solution of ferric chloride (0.01 mol) in 50 mL of chloroform was added in one portion to a solution of **1a** (0.003 mol) in 15 mL of chloroform. The mixture was stirred at room temperature with air bubbling through the solution for 20 h. The reaction was filtered and the residue was washed with chloroform, methanol, and water. The green residue that was isolated was completely dedoped by stirring with 30 mL of concentrated NH$_4$OH for 20 h. The orange polymer was finally collected by filtration and washed thoroughly with water and methanol until the ammonia odor had dissipated and finally with ether. The powder was dried in a vacuum desiccator overnight. Anal. Calcd for $C_{14}H_8S_2$: C, 69.96; H, 3.36. Found: C, 70.01; H, 2.79.

Poly(di-2-thienyl-2,5-dimethylphenylene) (2b). Compound **1b** (0.002 mol) was polymerized as described for **1a** utilizing ferric chloride (0.007 mol). A yellow-green solid was collected before completely dedoping with concentrated ammonium hydroxide solution to obtain a yellow polymer powder. Anal. Calcd for $C_{16}H_{14}S_2$: C, 71.05; H, 5.22. Found: C, 70.77; H, 4.33.

Poly(di-2-thienyl-2,5-dimethoxyphenylene) (2c). Compound **1c** (0.002 mol) was polymerized as described for **1a** utilizing ferric chloride (0.007mol). A dark green solid was collected before completely dedoping with concentrated ammonium hydroxide solution to obtain a red-orange polymer powder. Anal. Calcd for $C_{16}H_{14}O_2S_2$: C, 63.54; H, 4.68. Found: C, 62.36; H, 3.98.

Electrochemical Polymerization. Electrochemical polymerization was carried out by using an EG&G Princeton Research Model 273 potentiostat/galvanostat. A constant current density of 1.0 mA/cm^2 was employed to conduct electropolymerization on a glassy-carbon working electrode, with a platinum strip counter electrode and a silver/silver chloride reference electrode. Acetonitrile, distilled over P_2O_5, and tetrabutylammonium perchlorate, recrystallized from methanol, were used as the supporting electrolyte.

Structural Identification of Monomers and Polymers. FT-IR spectra were obtained with a Digilab FTS-40 FT-IR spectrophotometer utilizing the DRIFT (diffused reflectance infrared spectroscopy) technique on samples in a powdered KBr dispersion. Since the polymer samples were highly opaque, this method was preferred over more conventional methods (KBr pressed pellets) in order to compare the spectra of the monomeric materials with the polymers.

^{1}H NMR spectra in deuterated chloroform were recorded on Varian EM-360 or Bruker 300 MSL-FT-NMR spectrometers for all monomers. ^{13}C NMR for the monomers was carried out on a Bruker 300 MSL-FT-NMR using the $CDCl_3$ triplet at 77 ppm as an approximate internal reference. ^{13}C NMR spectra on the polymeric materials were recorded by using a solid-state CP-MAS technique on the Bruker 300 instrument.

Elemental analyses for carbon and hydrogen were obtained on a Perkin-Elmer 2400 CHN Analyzer.

Theoretical Methods. We employed the PRDDO (partial retention of diatomic differential overlap) method, an approximate ab initio type molecular orbital technique, to estimate the equilibrium ground-state geometries of the polymers. The theoretical details of the method can be found elsewhere.[49-52] and will not be reiterated here. PRDDO has been shown to be a useful tool for obtaining geometries of reasonably large molecules.[22,23,25,53] Open-shell calculations were performed within the unrestricted Hartree-Fock (UHF) approximations.[54] Mulliken population analyses were done to calculate the spin densities of the constituent atoms in order to predict the polymerization sites. In order to explore the electronic properties of the polymers, we used the extended Hückel technique[43,44] for band structure calculations within the framework of the one-electron tight-binding approximation.

Electrochemistry. Cyclic voltammetry was carried out by using an EG&G Princeton Applied Research Model 273 potentiostat/galvanostat employing a 0.07-cm^2 glassy-carbon working electrode, a platinum strip counter electrode, and a Ag/AgCl reference electrode. The monomer concentration was 5 mM in each case, and the electrolyte was 0.05 M tetrabutylammonium perchlorate in acetonitrile.

Optoelectrochemistry and Oxidative Doping of the Polymers. Films were electropolymerized onto indium tin oxide (ITO) conducting glass using constant current conditions. The ITO-supported films were washed with acetonitrile and placed in a cuvette with a platinum counter electrode and silver wire quasi reference. The electronic properties were examined by using a Varian 2300 UV-vis-near IR spectrophotometer. Electrode potentials were controlled by using the EG&G potentiostat/galvanostat.

Chemically synthesized polymers were oxidized as suspensions by nitrosonium hexafluorophosphate ($NOPF_6$) or iodine (I_2). The oxidation was done in dry (refluxed and distilled over P_2O_5), degassed solvent under a blanket of nitrogen. Solvents used were acetonitrile for $NOPF_6$ and chloroform for I_2. $NOPF_6$ and I_2 were used as received from Strem Chemicals and Fisher Scientific, respectively. The reaction mixture was allowed to stir for 1 h. Filtration under a blanket of nitrogen was followed by washing with fresh solvent. The conductive oxidized powders obtained were then dried under vacuum and subsequently used for pressed-pellet conductivity measurements.

Thermal Analysis. Thermal gravimetric analyses (TGA) were run on each of the polymers in the reduced state using a Du Pont 951 instrument. The program included an equilibration temperature of about 60 °C for 1 min and then a 20 °C/min ramp to a temperature of 1000 °C. The samples were run under a purge stream of nitrogen or air.

Conductivity Measurements. Measurements were made by using a Keithley 610C electrometer or a Keithley 197 autoranging microvolt digital multimeter. Samples were prepared as pressed pellets or were pressed between two wires in a capillary tube. The Van der Pauw technique[55] was used to determine conductivity for pressed pellets, the two-probe technique was employed for capillary samples, and the four-point method was used for free-standing films.

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Registry No. **1a**, 23354-94-1; **1b**, 67061-72-7; **1c**, 129607-89-2; **2a** (homopolymer), 109612-00-2; **2b** (homopolymer), 129607-88-1; **2c** (homopolymer), 129607-90-5; thiophene, 110-02-1; 1,4-diiodobenzene, 624-38-4; 1,4-diiodo-2,5-dimethylbenzene, 1124-08-9; 1,4-diiodo-2,5-dimethoxybenzene, 51560-21-5.