Macromolecules 1993, 26, 2095-2103

Substituent Effects on the Electrical Conductivity and Electrochemical Properties of Conjugated Furanyl Phenylene Polymers

John R. Reynolds* and Andrew D. Child

Center for Macromolecular Science and Engineering, Department of Chemistry, University of Florida, Gainesville, Florida 32611

Jose P. Ruiz, Sung Y. Hong, and Dennis S. Marynick

Center for Advanced Polymer Research, Department of Chemistry, The University of Texas at Arlington, Arlington, Texas 76019

Received June 23, 1992; Revised Manuscript Received December 23, 1992

ABSTRACT: A series of 1,4-bis(2-furanyl)benzenes, substituted at the 2 and 5 positions of the benzene ring with methyl, methoxy, and heptoxy groups, has been synthesized and electropolymerized. Spin density calculations of monomer radical cations show relatively high spin densities on the external α positions of the furan rings. These polymers exhibit conductivities of 10^{-1}–10^{0} S/cm when electrochemically oxidized in the presence of ClO_4^-. Cyclic voltammetry of the polymers has revealed redox states with $E_{1/2}$ potentials ranging from 0.43 to 0.56 V vs Ag/Ag$^+$ (+0.34 V vs SCE) which are dependent on the nature of the substituent. These potentials are not substantially affected by the length of the alkoxy chain. The onset of the π to π^* transition, commonly termed the band gap, of the polymers ranges from 2.3 to 2.5 eV as determined using optoelectrochemical techniques and follows a similar trend. Redox thermodynamic studies, using Nernst plots of each system determined from an optical absorption technique, yield standard electrode potentials that decrease with the donating ability of the substituent. Electrogravimetric studies using a quartz crystal microbalance have demonstrated that the longer chain alkoxy-substituted polymers have a larger amount of mass increase associated with electrochemical oxidation. The doping levels, calculated from mass-transfer and charge-transfer results, increase as the length of the pendant substituent is increased.

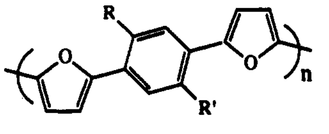
Introduction

Conjugated and electrically conducting polymers have physical, electronic, and electrochemical properties that can be controlled by the attachment of pendant substituents. For example, a variety of highly melt- and/or solution-processable conjugated polymers, which can be redox doped to the highly conducting state, are now available.[1] We have previously shown that the substitution pattern on 1,4-bis(2-thienyl)-2,5-disubstituted-phenylene polymers creates a combination of steric and inductive effects which leads to controllable optical and electrical properties.[2-4] Isoregic polymers with symmetrically substituted repeat units are significantly more crystalline than aregic polymers obtained from asymmetrically substituted monomers. The use of furan in the repeat unit retains many of the advantages observed for the thiophene analogs. The electronic properties of the polyheterocycle are combined with the ease of substitution onto the phenylene ring, ultimately leading to soluble and fusible conducting polymers with high conductivities.

Relative to substituted polythiophenes, little has been reported on the synthesis and properties of polyfurans. This can be attributed to a higher oxidation potential for furan (≥1.7 V vs Ag/Ag$^+$) relative to 3-methylthiophene (1.5 V vs Ag/Ag$^+$) or bithiophene (1.0 V vs Ag/Ag$^+$), and, thus, electrochemical polymerization of furan is hampered by side reactions. Polyfuran has been synthesized by several groups by both electrochemical[5,6] and chemical[7] methods with conductivities up to 80 S/cm reported.[5] In addition, poly(3-alkylfurans), soluble in some organic solvents, have been prepared both chemically and electrochemically.[8,9] Poly(2,5-furlyenevinylene) has been prepared using a soluble precursor method to yield films having onsets of the π to π^* transition (the electronic band gap) at 1.76 eV and conductivities after doping of approximately 30 S/cm.[10,11] In addition, derivatized poly(2,5-furylenevinylenes) have been prepared using metathesis polymerization.[12] In prior work, little has been elucidated concerning the effect of substituents on the electrical, optical, and electrochemical properties of furan-containing conjugated polymers. This is the focus of the present paper.

Previous work with poly[1,4-bis(2-thienyl)phenylenes] has shown that their electronic properties are quite similar to those of polythiophene.[2] The major differences are easily explained by the steric interactions of pendant substituents on the phenylene ring with the thiophene ring, which force nonplanarity of the polymer chain.[3] This suggests that the poly[1,4-bis(2-furanyl)phenylenes] will exhibit electronic and electrochemical properties similar to polyfuran. Due to the smaller size of oxygen, compared to sulfur, the deviations caused by steric strain are expected to be minimized.

In this study, a series of poly[1,4-bis(2-furanyl)phenylenes] (A), symmetrically substituted at the 2 and 5 positions on the phenylene ring with methyl, methoxy, and heptoxy groups and asymmetrically substituted with methoxy and heptoxy groups, have been synthesized.



$R = R' = H, CH_3, OCH_3, OC_7H_{15}$

$R = OCH_3, R' = OC_7H_{15}$

A

Chemical synthesis of these polymers was attempted using an oxidative $FeCl_3$ polymerization, followed by compensation with NH_4OH, and resulted in furan ring opening as evidenced by the presence of carbonyl peaks in the IR spectrum. Electropolymerization on platinum led to doped polymers having conductivities of 10^{-1}–10^{0} S/cm with no apparent ring opening. Electron-donating

0024-9297/93/2226-2095$04.00/0

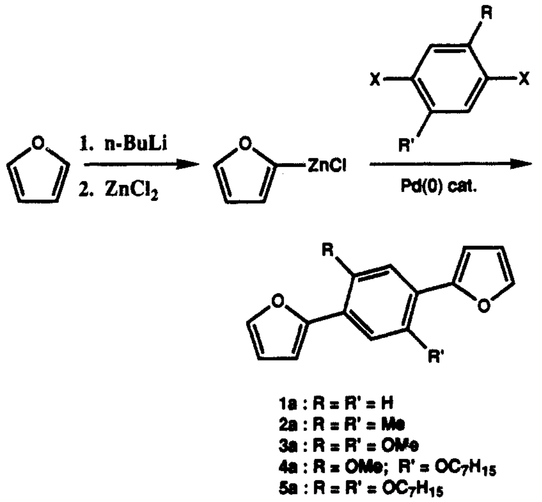
Table I
FT-IR Absorbances and Assignments for the Monomers (cm^{-1})

	arom C–H str			aliphatic C–H str				ring str						arom OOP bends				
compd	α	β	φ					phenyl			furan		CH$_3$ def.	phenyl			furan	
1a	3183	3117	3083					1604	1527	1555	1485	1369		799	833	952	908	833
2a	3165	3118	3037	2972		2860		1612	1511	1553	1492	1380	1354	884	871	942	906	810
3a	3162	3120	3003	2972		2843		1606	1516	1552	1493	1396	1368	887	859	1003	909	811
4a	3189	3115	3001	2955	2932	2865	2853	1623	1516	1549	1493	1388	1370	885	859	1006	912	810
5a	3185	3115	3011	2955	2937	2865	2855	1618	1517	1542	1494	1392	1371	885	862	1009	913	812

alkoxy groups lower the optical band gap and oxidation potential of these polymers, while slightly increasing their electrical conductivities. While the length of the alkoxy pendant substituent has no effect on the oxidation potential, conductivities, or band gaps, the mass transport properties during electrochemical switching are significantly altered. In a concurrent study, PRDDO calculations were utilized to determine the preferred conformation and expected torsional angles of each monomer, and a modified extended Hückel method was used to examine the band structure of each polymer.[13]

Results and Discussion

Monomer Synthesis. The 1,4-bis(2-furanyl)-2,5-disubstituted benzene monomers were prepared as shown in reaction 1. The furan rings were introduced onto the phenylene unit by the coupling of organometallic 2-furanyl intermediates. The use of 2-furanylzinc chloride with a palladium(0) catalyst in the formation of 2-furanylbenzenes has been reported by Pelter et al.[14] Furan was initially lithiated at 0 °C in order to insure that the heat evolved from the reaction did not evaporate the volatile heterocycle. Transmetalation with anhydrous zinc chloride resulted in the preparation of 2-furanylzinc chloride. This reagent was treated with the 1,4-dihalo-2,5-disubstituted benzene derivatives in the presence of Pd(PPh$_3$)$_4$ as catalyst at 50 °C under inert conditions. The 1,4-bis(2-furanyl)-2,5-disubstituted benzene monomers were obtained in excellent yields. The structure and purity of these monomers were confirmed by FT-IR, ^{1}H NMR, and ^{13}C NMR as summarized in Tables I–III, along with elemental analyses shown in the Experimental Section.

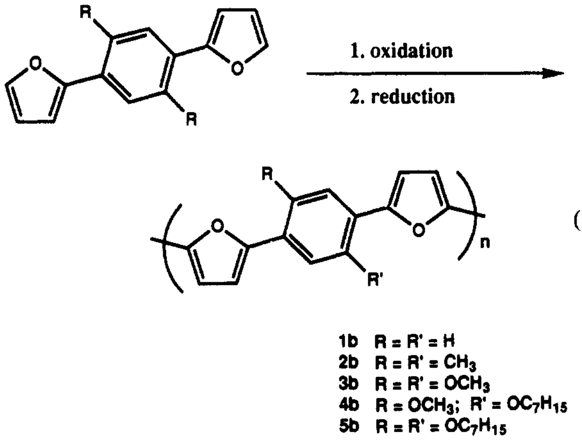


(1)

Oxidative Polymerization. Oxidative coupling polymerization of aromatic heterocycles occurs at sites on the ring where a high spin density resides for the radical ion. This allows both chemical and electrochemical methods to be used to carry out oxidatively activated step-growth polymerizations. We have shown, for a variety of thiophene derivatives, that the existence of a high amount of spin density at the α positions on the rings is conducive to polymerization and the formation of conjugated polymers.[15] Cation-radical spin densities for **1a**, **2a**, and **3a** are shown in Table IV. Comparable to their thiophene analogues,[3] a high probability of spin is present at the 5 and 5′ positions of the terminal furan rings (C-7) in these 1,4-bis(2-furanyl)benzenes, suggesting similar polymerization routes as illustrated in reaction 2. In contrast to the thiophene analogues, the highest spin density is not found at the terminal α positions but is located at C-1 on the phenylene ring. In addition, relatively high spin densities are located on C-5, the β furan carbon closest to the phenylene ring. While little coupling polymerization is expected at C-1 or C-5 due to steric interactions, polymerization through them will lead to defects in the conjugated polymer. Steric considerations suggest reactivity at these sites to be low, and UV–vis–near-IR results, coupled with high electrical conductivities, suggest the number of these defects to be small.

Table II
^{1}H NMR Peak Assignments for the Monomers [ppm (mult.)]

compd	H-1	H-2	H-3	H-4	CH_2	CH_3
1a	7.46 (d)	6.47 (t)	6.66 (d)	7.67 (s)		
2a	7.50 (d)	6.50 (t)	6.56 (d)	7.59 (s)		
3a	7.45 (d)	6.50 (t)	6.99 (d)	7.45 (s)		3.97 (s)
4a	7.43 (d)	6.50 (t)	7.03 (d) 7.00 (d)	7.46 (s)	4.13 (t) 1.92 (q) 1.50 (m)	3.97 (s) 0.90 (t)
5a	7.45 (d)	6.50 (t)	7.02 (d)	7.44 (s)	4.12 (t) 1.90 (q) 1.50 (m)	0.90 (s)



(2)

Based on the fact that FeCl$_3$ serves as a useful oxidant in the synthesis of poly(3-alkylthiophenes)[1] and polymerizes 1,4-bis(2-thienyl)benzenes well,[2–4] we utilized this reagent in chemical polymerization of the 1,4-bis(2-furanyl)benzenes followed by compensation with NH$_4$OH. A significant amount of carbonyl functionality was observed in the FT-IR and ^{13}C NMR spectra of the neutral polymers. This is due to ring opening of the furan during either the polymerization or neutralization steps. A more detailed explanation of these results has been presented

Table III
^{13}C NMR Peak Assignments for the Monomers [ppm]

compd	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-R
1a	142.13	111.75	105.12	153.72	127.06	124.04		
2a	141.63	111.39	108.59	153.25	128.92	129.41	131.83	21.49
3a	141.08	111.97	108.67	150.06	118.73	110.03	149.54	55.91
4a	140.96	111.97	109.40, 108.61	150.23, 150.15	118.76	110.36, 110.19	149.40, 149.07	68.88, 55.91, 31.75, 29.48, 29.08, 26.20, 22.59, 14.07
5a	140.91	111.95	109.31	150.30	118.72	110.20	148.91	68.87, 31.75, 25.49, 29.08, 26.20, 22.09, 14.06

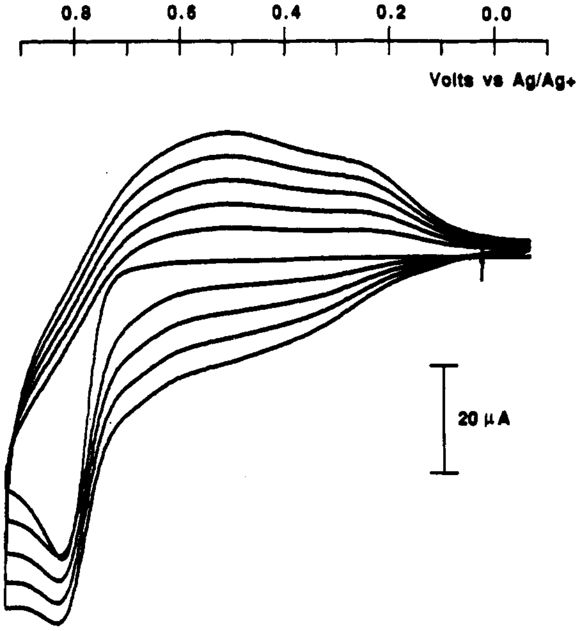
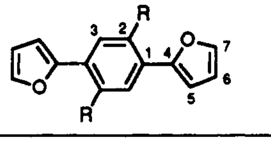


Figure 1. Cyclic voltammograms of 1 mM 1,4-bis(2-furanyl)benzene (**1a**) in 0.1 M $TBAClO_4/CH_3CN$ electrolyte at 50 mV/s. The first five scans are shown.

Table IV
Cation-Radical Spin Densities for Substituted 1,4-Bis(2-furanyl)benzenes



atom position	spin densities R = H	R = CH_3	R = OCH_3
C-1	0.15	0.18	0.16
C-2	0.05	0.06	0.09
C-3	0.04	0.03	0.00
C-4	0.06	0.05	0.05
C-5	0.10	0.08	0.08
C-6	0.01	0.01	0.01
C-7	0.09	0.07	0.07

elsewhere.[16] As a result of this side reaction, electrochemical polymerizations were used to synthesize the polymers for further analysis.

In order to determine the proper conditions for electropolymerization, monomer oxidation potentials were determined by cyclic voltammetry. During the first anodic scan, each monomer exhibited a single peak due to formation of monomer radical cation as illustrated in Figure 1 for **1a**. The cathodic processes and lower potential anodic processes, which increase in intensity with the number of scans, are due to conducting polymer film growth. The monomer oxidation peak potentials ($E_{p,m}$) were found to decrease with the electron-donating ability of the substituent as shown in Table V. Interestingly, all of the alkoxy-derivatized monomers exhibited equivalent $E_{p,m}$ values of 0.65 V. These low oxidation potentials demonstrate the ease of formation of the radical cations and suggest polymerization will occur with a minimum of side reactions. Two of the possible reactions avoided here include the formation of β linkages and overoxidation of the polymer. It is well-known that the electropolymerization of thiophene occurs close to its breakdown potential, thus necessitating electrosynthesis at low temperature or the use of bithiophene.[17] In fact, these oxidation potentials are 100–250 mV lower than that of pyrrole, one of the most highly studied of the electrochemically polymerizable heterocycles.[18,19] Comparison of these oxidation potentials to those for the 1,4-bis(2-thienyl)benzenes[3] shows them to be quite close [$E_{p,m}$(1,4-bis(2-thienyl)-2,5-dimethoxybenzene) = +0.7 V]. These furan-containing monomers are, thus, expected to be extremely useful for the formation of conducting and electroactive polymers.

Table V
Monomer and Polymer Redox Potentials and Electrical Conductivities for Poly[1,4-bis(2-furanyl)phenylenes]

R	R′	$E_{p,m}$ (V)	$E_{1,2,p}$ (V)	σ (S/cm)
H	H	0.78	0.56	2×10^{-1}
CH_3	CH_3	0.76	0.55	1×10^{-1}
OCH_3	OCH_3	0.65	0.48	4×10^{-1}
OCH_3	OC_7H_{15}	0.65	0.48	3×10^{-1}
OC_7H_{15}	OC_7H_{15}	0.65	0.10, 0.43	4×10^{-1}

During repeated potential scanning, thin insoluble films (ca. 100–200 nm) of the poly[1,4-bis(2-furanyl)phenylenes] formed on the electrode surface. After six scans, each electrode was washed with CH_3CN with the film in the oxidized form and placed in a monomer-free electrolyte solution. All polymers studied here are insoluble in the CH_3CN electrolyte employed. Cyclic voltammetry at various scan rates shows the general shape of the voltammograms to be similar for each polymer, with the exception of the diheptoxy-substituted derivative which displays two redox couples. This is illustrated in Figures 2 and 3 for **1b** and **5b**, respectively. The oxidation potentials for these polymers are tabulated in Table V. Again substituent dependencies are observed with half-wave potentials ($E_{1/2,p}$) decreasing with H > $-CH_3$ > $-OCH_3$. The alkoxy-substituted polymers exhibit $E_{1/2,p}$ of 0.48 V for **3b** and **4b** and 0.43 V for **5b**. Not surprisingly, these values are intermediate between those for poly(p-phenylene)[20] and polyfuran[21] which exhibit oxidation potentials of 0.7 and 0.4 V, respectively. For each of the polymers investigated here, the peak current varies linearly with scan rate, which indicates the electroactive species is electrode bound.[22] These poly[1,4-bis(2-furanyl)phenylenes] are found to be relatively electrochemically stable throughout this redox process. The films could be cycled more than 20 times with no observable loss in electroactivity. This is in contrast to polyfuran where we find that, during cyclic scanning polymerization, the platinum electrode tends to passivate.

A comparison of the $E_{1/2,p}$ values for these polymers with the poly[1,4-bis(2-thienyl)phenylenes][4] shows a reduced influence of substitution on the oxidation potential of the furan polymers. The values for the thiophene-containing polymers range from 0.6 to >1.0 V, with the dimethyl-substituted polymer exhibiting the highest ox-

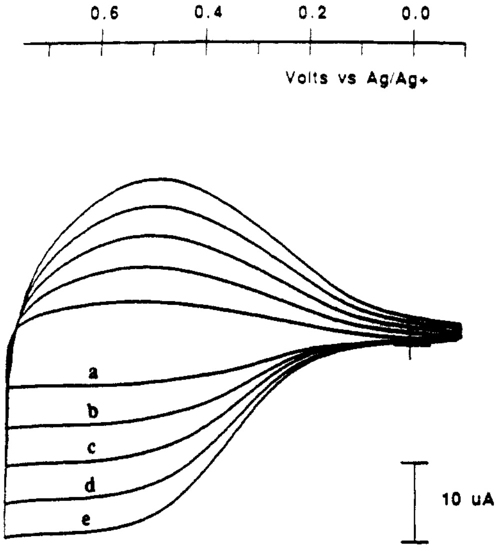


Figure 2. Cyclic voltammograms of poly[1,4-bis(2-furanyl)-phenylene] (**1b**) in 0.1 M $TBAClO_4/CH_3CN$ at (a) 25, (b) 50, (c) 75, (d) 100, and (e) 125 mV/s.

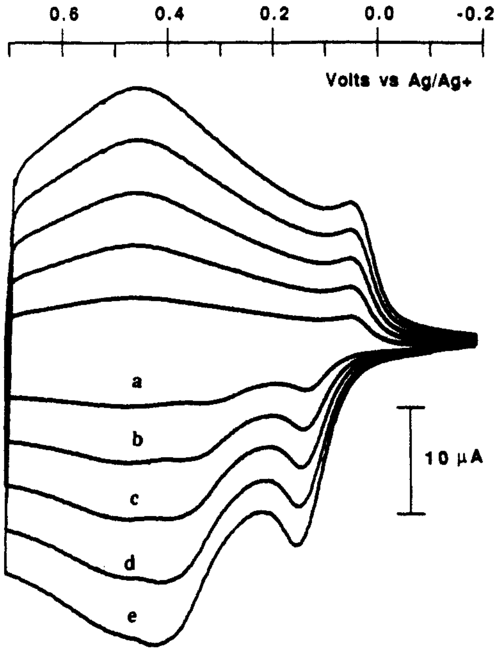


Figure 3. Cyclic voltammograms of poly[1,4-bis(2-furanyl)-2,5-diheptoxyphenylene (**5b**) in 0.1 M $TBAClO_4/CH_3CN$ at (a) 25, (b) 50, (c) 75, (d) 100, and (e) 125 mV/s.

idation potential. This is due to the large steric interaction of the substituent with the conjugated chain, which forces the polymer to be nonplanar. In addition, the long-chain alkoxy-substituted thiophene polymers display a more resolved low-potential, redox process at 0.3–0.35 V.[23] EPR results indicate that this first oxidation leads to the formation of stable polarons which are subsequently converted to bipolarons at about 0.7 V. In the poly[1,4-bis(2-furanyl)phenylenes] studied here, only the diheptoxy-substituted polymer displays a well-defined, low-potential, redox process.

Electrical Conductivity. Relatively thick poly[1,4-bis(2-furanyl)phenylene] films (compared to the ca. 100–200-nm films used in the electrochemical studies) were electrosynthesized using a constant potential method at $E_{p,m}$ on a platinum plate for electrical conductivity measurements. The polymerizations were discontinued after 800 mC had been passed, and the thicknesses of the films, measured by profilometry, varied from 1.5 to 3.0 μm after washing with CH_3CN and drying. These films showed no evidence of carbonyl functionality in either oxidized or reduced forms when characterized by FT-IR, suggesting that little, if any, ring opening of the furan had occurred under the mild electrochemical conditions employed. A minimum of three films of each polymer was subjected to conductivity measurements, and the average results are summarized in Table V.

It can be seen that all of the polymers have conductivities between 10^{-1} and 10^0 S/cm. The presence of electron-donating alkoxy substituents on the phenylene ring increases the room-temperature conductivity slightly, analogous to the slight lowering of $E_{1/2,p}$. In general, these conductivities are close to those measured for the poly[1,4-bis(2-thienyl)phenylenes][3] with the exception of poly[1,4-bis(2-furanyl)-2,5-dimethylphenylene] (**2b**). Here the conductivity of 1×10^{-1} S/cm for **2b** is 5 *orders of magnitude higher* than that of the thiophene analogue poly[1,4-bis(2-thienyl)-2,5-dimethylphenylene].

In order for these polymers to exhibit elevated conductivities, a high extent of conjugation is required down the polymer chains. We have shown through theoretical calculations that, while the unsubstituted and dialkoxy-substituted poly[1,4-bis(2-thienyl)phenylenes] exhibit relatively low rotational energy barriers (ca. 3 kcal/mol) to attain a planar conjugated chain, the dimethyl-substituted 1,4-bis(2-thienyl)phenylene polymer has a much higher rotational barrier of about 16 kcal/mol.[2] The conductivity results observed here suggest the conformational preference of the poly[1,4-bis(2-furanyl)-2,5-dimethylphenylene] is significantly different from its thiophene analogue.

As noted previously,[13] the PRDDO method predicts that the coplanar structure is the most stable, and the orthogonal structure the least stable, for the unsubstituted monomer, **1a**, with a rotational barrier of about 14 kcal/mol. The preferred structure of **2a** is predicted to have a 30° torsional angle because of steric hindrance between hydrogens of the methyl groups and oxygens of the furan rings. However, the rotational barrier is quite small, 0.5 kcal/mol, and the planar conformation is highly likely in the polymeric solid. The most stable conformation of **3a** is predicted to be coplanar. This planarity for all of the monomers is in stark contrast to what we observed for the 1,4-bis(2-thienyl)benzenes where we observed minimum-energy torsional angles of 24, 40, and 63° for the unsubstituted, dialkoxy-substituted, and dimethyl-substituted systems, respectively. The most likely explanation for this effect is that the significantly larger van der Waals radius of sulfur (1.85 Å) compared to oxygen (1.40 Å) causes enough steric interaction to force nonplanarity of the monomer and, analogously, the polymer. The fact that **2a** has only a 0.5 kcal/mol energy difference between the planar form and the minimum-energy conformation of 30° indicates that, when polymer **2b** is oxidized, there is essentially no difficulty in forming planar delocalized charge carriers which can have significant mobility.

The electrical conductivities of the alkoxy-substituted poly[1,4-bis(2-furanyl)phenylenes] in Table V are similar. This is in contrast to the poly[1,4-bis(2-thienyl)-phenylenes] where we find asymmetrically substituted, aregic polymers to have about an order of magnitude lower conductivity than symmetrically substituted isoregic polymers.[4] As will be brought out later, this is worth noting as their electrochemical mass transport properties are quite different.

Electronic Structure. In order to elucidate the effect of the substituents on the electronic structure of these polymers, especially on the energies of the π electrons,

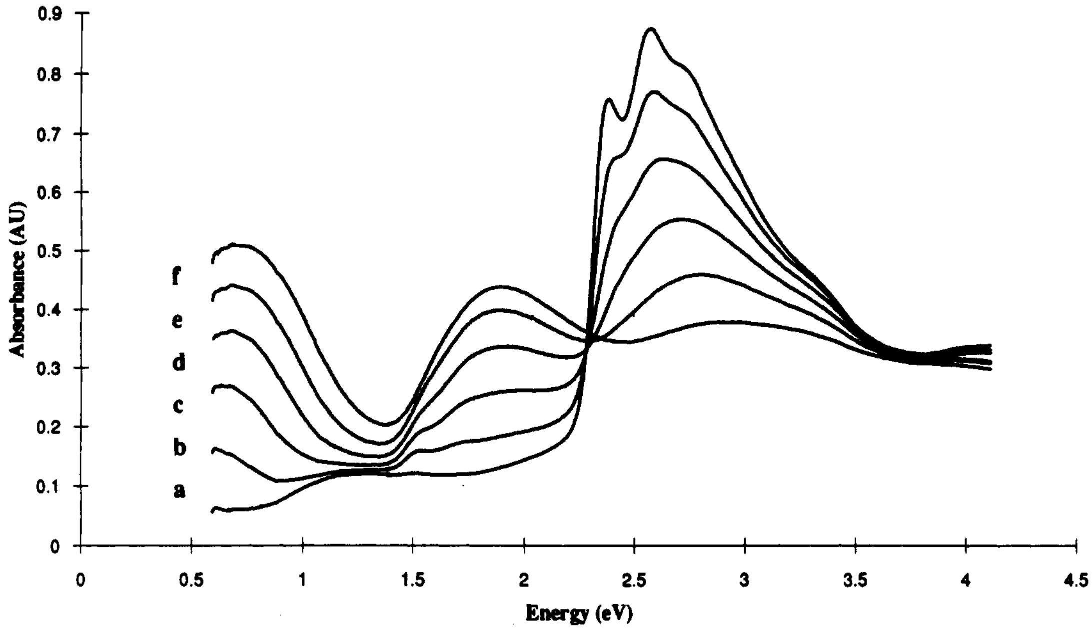


Figure 4. UV–vis–near-IR spectra of poly[1,4-bis(2-furanyl)-2,5-dimethoxyphenylene] (**3b**) during electrochemical doping. Applied potentials [vs Ag wire] (+0.11 V vs SCE) are (a) 0.0, (b) 0.40, (c) 0.45, (d) 0.50, (e) 0.55, and (f) 0.60 V.

optoelectrochemical methods were employed. The polymer's electronic band structure was calculated previously using a modified extended Hückel method.[13] Polymer films for optoelectrochemical analysis were electrosynthesized on ITO glass and subsequently placed in a quartz cuvette with a counter and reference electrode. The polymers were fully reduced at −0.2 V, and an initial spectrum (300–2200 nm) was obtained. The potential was stepped in 50–100 mV intervals, obtaining absorption spectra at each step, until the polymer was completely oxidized. A series of UV–vis–near-IR spectra of the dimethoxy-substituted polymer (**3b**) is shown in Figure 4 and its representative of all of the polymers. The fine structure observed in the neutral form of the polymer is consistent with a carbon–carbon double bond stretch which is coupled to the electronic structure.[24,25] The band gap of each polymer was obtained from the isosbestic point of each set of spectra. The unsubstituted (**1b**) and dimethyl-substituted (**2b**) polymers exhibit band gaps of 2.5 and 2.6 eV, respectively, which are lower than the value for polyfuran (2.7 eV)[5] and poly(*p*-phenylene) (3.0 eV).[26] The band gaps for the alkoxy-substituted polymers are identical to each other and are all significantly lower than any of the above polymers (2.3 eV for **3b**, **4b**, and **5b**). A much larger dependence of band gap on the substitution pattern was observed for the poly[1,4-bis(2-thienyl)phenylenes].[3] The large variance in torsional angles between the thiophene and phenylene rings is responsible for this wide range in band gaps. Upon oxidation, two new mid-gap absorptions emerge which are consistent with the formation of delocalized cationic charge carriers.[27]

The experimentally determined electronic properties are compared to the theoretically predicted electronic properties[13] in Table VI. The one-dimensional frozen band gaps (E_g, calculated) show excellent agreements with the experimental values for π–π^* transitions obtained in this study from the *peaks* of the neutral polymers. Substituents on the phenylene rings do not significantly affect the electronic structures of these furan systems, in stark contrast to the case of the thiophene analogs.[2,3] The π-band structures of all of the poly[1,4-bis(2-furanyl)phenylenes] are quite similar. More detailed descriptions of the theoretical work, including the pyrrole analogs of these systems, have been given elsewhere.[13]

Table VI
Electronic Properties of Poly[1,4-bis(2-furanyl)phenylenes]

	E_g (eV)				bandwidth (eV)	
polymer	isosbestic[a]	peak	calculated	E_f (eV)[b]	valence band	conduction band
1b	2.53	3.2	3.13	−11.06	1.05	1.36
2b	2.63	3.2	3.20	−11.06	1.02	1.33
3b	2.33	3.0	3.01	−10.82	1.08	1.30

[a] E_g = electronic band gap. [b] E_f = Fermi level.

Redox Thermodynamics. The complex electrochemical properties of conjugated electroactive polymers can be attributed to changes in electrical conductivity, dopant ion concentration, solvent content and film swelling, and polymer chain conformation during redox switching. A thermodynamic analysis can prove especially useful in comparing similar polymers with minor structural modifications, and their effect on electrochemical properties, such as the series being studied here.

To address this, the effect of electrochemical potential (and thus oxidation state) on the optical absorbance of ITO glass supported polymer films was used to determine the relative concentrations of oxidized ([O]) and reduced ([R]) sites in the polymer. The intensity of the peak absorption energy of the interband transition was measured as a function of the applied potential. A reversible decrease of this absorption occurs as the polymers are oxidized (Figure 4). Starting at one extreme (fully oxidized or fully reduced) the potential was stepped a small amount (ca. 10 mV) with a sufficient delay prior to measurement of the next spectrum to allow the current to decay to a small value and an equilibrium dopant level to be attained at each potential. The ratio of oxidized to reduced sites on the polymer was determined by the expression

$$\frac{[O]}{[R]} = \frac{A_{\text{red}} - A}{A - A_{\text{ox}}} \qquad (3)$$

where A is the absorbance at a given potential, A_{red} is the absorbance at the fully reduced potential, and A_{ox} is the absorbance at the fully oxidized potential. Marque and Roncali used this technique to investigate the redox thermodynamics of polythiophene, poly(3-methylthiophene), and poly(3-nonylthiophene).[28] Figures 5 and

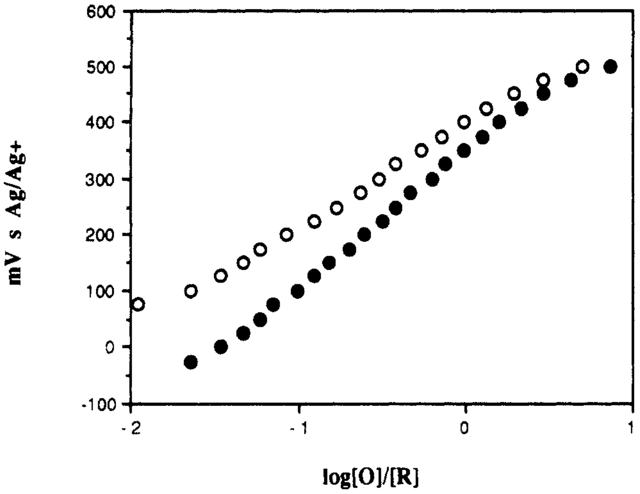


Figure 5. Nernst relationship for poly[1,4-bis(2-furanyl)phenylene] (**1b**): (○) oxidation; (●) reduction).

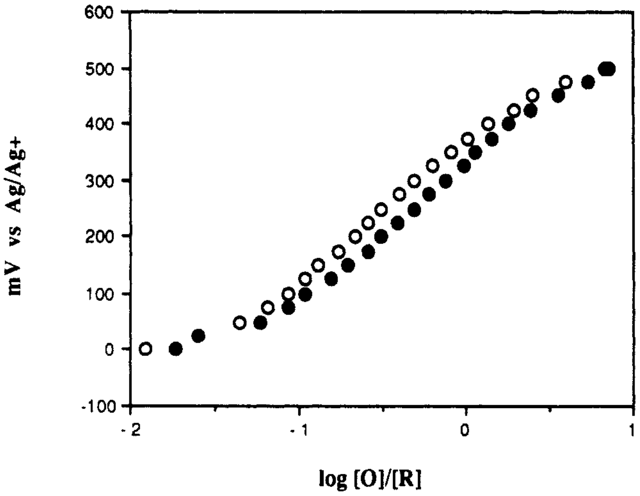


Figure 6. Nernst relationship for poly[1,4-bis(2-furanyl)-2,5-dimethylphenylene] (**2b**): (○) oxidation; (●) reduction.

Table VII
Redox Thermodynamic Results for Poly[1,4-bis(2-furanyl)phenylenes]

polymer	$E°_{(ox)}$ (mV)	$E°_{(red)}$ (mV)	n-values$_{(ox)}$	n-values$_{(red)}$
1b	400	350	0.314	0.241
2b	375	325	0.239	0.234
3b	280	240	0.321	0.277
4b	280	240	0.288	0.249
5b	250	200	0.335	0.253

6 show the result as plots of potential versus log ([O]/[R]) for polymers **1b** and **2b**, respectively. Polymers **3b**, **4b**, and **5b** exhibit Nernst plots quite similar to that for polymer **2b**. Recall the Nernst equation:

$$E = E° + (0.059/n)\log([O]/[R]) \qquad (4)$$

In a Nernstian system a plot of E versus log([O]/[R]) will yield a straight line with a slope of 0.059/n and an intercept of $E°$ (where the concentrations of oxidized and reduced species are equal). It is understood that these conducting polymer systems are not Nernstian, but this technique affords a useful way of comparing the thermodynamic properties of similar polymers.

The redox thermodynamic results from the Nernst plots for polymers **1b**–**5b** are listed in Table VII. It should be noted that this technique is only sensitive to Faradaic electrochemical processes which form oxidized sites. This enables relatively accurate determination of $E°$ values. The apparent standard electrode potentials can be seen to decrease (Table VII) as:

$$E°_{1b} > E°_{2b} > E°_{3b} = E°_{4b} > E°_{5b}$$

This substituent effect on the redox thermodynamics is not surprising as the electron-donating ability of the substituents will increase the ease of formation of the oxidized site (positively charged) from the reduced site (neutral) and follows the same trend as the $E_{1/2,p}$ values determined using cyclic voltammetry. Previous studies of the redox thermodynamics of alkyl- and alkoxy-substituted polythiophenes[28-30] attributed a similarly observed decrease in $E°$ to an increase in the mean conjugation length for the substituted derivative. While this is also possible for the poly[1,4-bis(2-furanyl)phenylenes], the large $\Delta E°$ between **2b** and **3b** make this unlikely since, having short substituents, both are insoluble as electrochemically synthesized, and, thus, there is little possibility of side-group enhanced extended conjugation.

The lower values for $E°$ obtained for the alkoxy-substituted polymers might also be attributed to a combination of mechanical and electronic factors. Marque and Roncali[28] have suggested that the extension of the mean conjugation length in substituted polymers leads to a decrease in the Coulombic interactions between charged sites by facilitating the combination of polarons into bipolarons. Furthermore, a more porous morphology of substituted polymers might decrease the contribution of mechanical strain to the overall electrode potential.[28] It is reasonable to suggest, therefore, that the presence of alkoxy substituents on the phenylene ring of poly[1,4-bis(2-furanyl)phenylenes] decreases the internal pressure of the doped polymer caused by insertion of counterions during electrochemical doping. This allows for a higher doping level and, therefore, greater charge transfer.

The reversibility of the redox processes can be examined by comparing the Nernst results in Figures 5 and 6 obtained during oxidation (open circles) to those obtained during reduction (closed circles). While hysteresis is evident for all of the polymers, deviation from reversibility is quite small except for the unsubstituted polymer **1b**. This is likely due to its high oxidation potential which is closer to the potential for overoxidation than the oxidation potentials of the other polymers. Repetitive scanning leads to a decrease in the overall absorbance of **1b** due to electrochemical instability.

The third piece of information available from the Nernst relationships is obtained from the slope. In a perfectly Nernstian system with single electron transfer the relationships are linear, with a slope of 59 mV/log unit, and the results can be used to determine the number of electrons transferred per site (n). Examining the results where $0.1 \leq [O]/[R] \leq 10$, we find essentially linear behavior for all of the polymers except **5b**. It is evident from Table VII that there is no correlated substituent effect on the n-values, but all are significantly lower than 1. In all cases, the n-value is less than that predicted for a single electron transfer. This fractional charge transfer has been observed previously in conducting polymers[31-34] and has been attributed to the charge storage mechanism in conjugated materials.[28] Due to the non-Nernstian behavior of these polymers, caused by the potential dependent change in electroactive sites, these n-values should not be construed as an extent of doping. Instead, they are an indication of the sensitivity of doping to potential. A system with a high n-value, then, has more charged sites created per volt. In the case of these poly[1,4-bis(2-furanyl)phenylenes], this parameter is essen-

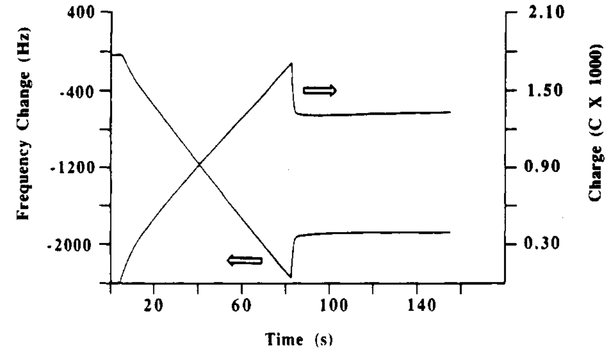


Figure 7. Gravimetric and coulometric responses during the electrosynthesis and immediate reduction of poly[1,4-bis(2-furanyl)phenylene] (**1b**).

tially invariant, indicating they all have a similar susceptibility to doping.

Mass and Charge Transport during Switching. In addition to the electronic effects of the substituents elucidated by redox thermodynamic experiments, they will contribute to electrochemical switching characteristics by partially determining the chemical nature of the space between polymer chains. During redox switching, charge-compensating counterions move in and out of the polymer matrix along with solvent and possibly mobile ion pairs. Coulometric methods allow determination of the number of charged sites created but yield no information on the identity of the mobile species. Application of the electrochemical quartz crystal microbalance (EQCM)[18,19,35,36] to switching in conducting polymers allows this to be addressed. The EQCM simultaneously monitors mass changes at an electrode surface during an electrochemical event by monitoring the change in the resonant frequency of an oscillating quartz crystal. The mass change is related to the measured frequency change by the Sauerbrey equation.[37]

$$\Delta f = \frac{-2f_0^{\,2}\Delta m}{A(u_q\rho_q)^{0.5}} \tag{5}$$

In this relationship, f_0 is the base frequency of the quartz resonator, A is the electrode area, u_q is the shear modulus of the quartz, and ρ_q is the quartz density. It should be noted that a decrease in frequency corresponds to an increase in mass.

The constant-potential electropolymerization of each substituted 1,4-bis(2-furanyl)benzene under investigation was carried out at 50 mV above the monomer oxidation potentials. The current and frequency responses at the EQCM were subsequently monitored as the polymer films were deposited. The polymerization was stopped by stepping the electrode to a cathodic potential where the polymer would reduce. During electrochemical switching the dominant mobile ionic species in these polymers are the dopant ions, and thus frequency changes due to polymer deposition and mass transport during electrochemical doping could be separated.

A typical set of charge and frequency response results are shown in Figure 7 for poly[1,4-bis(2-furanyl)phenylene] (**1b**). The electropolymerization was initiated at $t = 5$ s, and an immediate, and linear, deposition of polymer (frequency decrease) was observed. At $t \cong 85$ s the potential was reversed ($E = -0.2$ V) and the immediate reductive undoping and mass loss (frequency increase) due to dopant anion expulsion is evident. The film was rinsed with CH_3CN to remove residual monomer and placed into a cell containing monomer-free electrolyte. After equilibration in the reduced state ($E = -0.2$ V) the potential was stepped to 50 mV beyond the peak for polymer oxidation and again the charge and frequency responses were monitored. These results are shown in Figure 8 for **1b**. This set of experiments was carried out for each polymer under investigation.

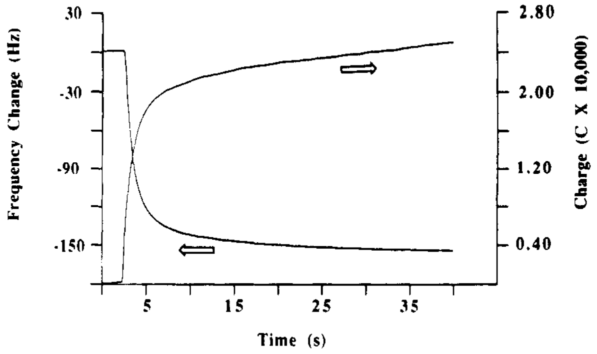


Figure 8. Gravimetric and coulometric responses during electrochemical oxidation of poly[1,4-bis(2-furanyl)phenylene] (**1b**).

The doping level (Y) of a conjugated conducting polymer can be represented by

$$Y = M_d/M_p \tag{6}$$

where M_d is the number of moles of charge compensating dopant anions and M_p represents the moles of polymer repeat units. If the frequency change during oxidation is assumed to be due to the insertion of counterions only, the doping level can be determined by combining eq 6 with the Sauerbrey equation (eq 5)

$$Y = \Delta f_d(\mathrm{MW_p})/\Delta f_p(\mathrm{MW_d}) \tag{7}$$

where Δf_p is the change in frequency due to neutral polymer deposition, Δf_d is the change in frequency due to doping, and $\mathrm{MW_p}$ and $\mathrm{MW_d}$ are the molecular weights of the polymer repeat unit and the mobile dopant anion, respectively.

The doping level can also be determined from the charge passed during each electrochemical process. This method has the advantage of detecting the transport of charged species only, thus eliminating the possible contribution from solvent and ion pairs observed in the gravimetric study. On the other hand, non-Faradaic or background charge effects during doping can interfere here, and comparison of the results from both methods is important. Correlating Faraday's law with eq 6, the following relationship holds when the electrochemical processes are 100% efficient.

$$Y = Q_d(n_p)/Q_p(n_d) \tag{8}$$

In this relationship, Q_d and Q_p are the charge passed during doping and polymerization, and n is the number of electrons transferred during each process. In the generally accepted mechanism for electrochemical oxidative coupling polymerization, two electrons are transferred for each monomer unit incorporated into the polymer chain.[19] Also, since the ClO_4^- ion used as the dopant is monovalent, one electron is transferred for each perchlorate serving as a counterion. Therefore, the value of n_p/n_d is 2 and we obtain

$$Y = 2Q_d/Q_p \tag{9}$$

Doping levels calculated using both the gravimetric and coulometric results are shown in Table VIII. The close agreement of the two methods indicates that solvent and ion-pair movements have a negligible net effect on the overall mass transport as discussed for polybithiophene by Hillman et al.,[38] suggesting that ion pairs and solvent are transferred in opposite directions and are essentially compensatory. It is evident that, as the length of the

Table VIII
Doping Level Determination for Poly[1,4-bis(2-furanyl)phenylenes]

R	R′	doping level: mass change	doping level: charge passed
H	H	0.308	0.410
CH_3	CH_3	0.584	0.560
OCH_3	OCH_3	0.497	0.508
OCH_3	OC_7H_{15}	0.675	0.650
OC_7H_{15}	OC_7H_{15}	0.843	0.840

pendant side chain increases, the amount of dopant and charge removed per ring increases also. This is in agreement with previous reports indicating longer chain alkoxy and alkyl substituents on polythiophenes enable higher doping levels.[28,39] It should be noted that these dopant levels are determined per monomer unit and the number of charges per aromatic ring ranges from about 0.10 to 0.28. These dopant levels are comparable to many polyheterocycles.

Conclusions

A family of 1,4-bis(2-furanyl)-2,5-disubstituted benzenes have been polymerized to form electroactive and electrically conductive poly[1,4-bis(2-furanyl)-2,5-disubstituted phenylenes]. All of the polymers exhibit conductivities between 10^{-1} and 10^0 S/cm. The fact that little effect of the substituent on the conductivity is observed is supported by theoretical calculations that show all of the polymer backbones to be essentially planar. The trends in the measured $E°$ and E_g values for these polymers are consistent with the electron-donating ability of the substituents. Electrogravimetry and chronocoulometry show a higher extent of counterion uptake and charge transfer during electrochemical oxidation of the substituted polymers and a corresponding increase in the doping level indicative of side-chain-assisted doping processes in these polymers.

Experimental Section

Diethyl ether and tetrahydrofuran (THF) were freshly distilled after refluxing with benzophenone ketyl. Furan, *n*-butyllithium, palladium tetrakis(triphenylphosphine) ($Pd(PPh_3)_4$), and zinc chloride were used as received from Aldrich Chemicals. All of the 1,4-dihalo-2,5-disubstituted benzenes were prepared according to previously reported procedures.[2,4] All reactions and transfers were performed using inert-atmosphere techniques.

1,4-Bis(2-furanyl)benzene (1a). A solution of *n*-butyllithium (0.113 mol) in hexane (Aldrich Chemicals) was added dropwise into a stirred ice-cooled solution of furan (0.137 mol) in THF. The reaction was warmed to room temperature and stirred for 2 h. The resulting 2-furanyllithium was added to a stirred solution of zinc chloride (0.091 mol) in THF and stirred at room temperature for 1 h. The resulting furanylzinc chloride was added to a stirred solution of 1,4-diodobenzene (0.023 mol) and $Pd(PPh_3)_4$ (60 mg) in THF. The reaction was heated to 50 °C, stirred for 72 h, quenched by aqueous HCl (1 M), and neutralized by washing with water. After solvent removal, recrystallization from ethanol resulted in a white flaky solid (mp = 140–142 °C, 46%). Anal. Calcd for $C_{14}H_{10}O_2$: C, 79.98; H, 4.80. Found: C, 79.05; H, 4.62.

1,4-Bis(2-furanyl)-2,5-dimethylbenzene (2a). Compound **2a** was prepared according to the procedure described for **1a** utilizing furan (0.206 mol), *n*-butyllithium (0.118 mol), zinc chloride (0.080 mol), 1,4-diiodo-2,5-dimethylbenzene (0.020 mol), and $Pd(PPh_3)_4$ (50 mg). Recrystallization from ethanol yielded off-white small needles (mp = 123–124 °C, 86%). Anal. Calcd for $C_{16}H_{16}O_2$: C, 80.63; H, 5.93. Found: C, 80.31; H, 5.66.

1,4-Bis(2-furanyl)-2,5-dimethoxybenzene (3a). Compound **3a** was prepared according to the procedure described for **1a** utilizing furan (0.137 mol), *n*-butyllithium (0.068 mol), zinc chloride (0.069 mol), 1,4-diiodo-2,5-dimethoxybenzene (0.017 mol), and $Pd(PPh_3)_4$ (80 mg). Recrystallization from ethanol produced an off-white solid (mp = 139 °C (dec), 67%). Anal. Calcd for $C_{16}H_{16}O_4$: C, 71.09; H, 5.23. Found: C, 70.96; H, 5.07.

1,4-Bis(2-furanyl)-2-heptoxy-5-methoxybenzene (4a). Compound **4a** was prepared according to the procedure described for **1a** utilizing furan (0.137 mol), *n*-butyllithium (0.080 mol), zinc chloride (0.080 mol), 1,4-dibromo-2-heptoxy-5-methoxybenzene (0.013 mol), and $Pd(PPh_3)_4$ (100 mg). Reprecipitation from methanol resulted in a fluffy off-white solid (mp = 63–64 °C, 53%). Anal. Calcd for $C_{22}H_{26}O_4$: C, 74.54; H, 7.41. Found: C, 74.17; H, 7.21.

1,4-Bis(2-furanyl)-2,5-diheptoxybenzene (5a). Compound **5a** was prepared according to the procedure described for **1a** utilizing furan (0.137 mol), *n*-butyllithium (0.065 mol), zinc chloride (0.065 mol), 1,4-dibromo-2,5-diheptoxybenzene (0.011 mol), and $Pd(PPh_3)_4$ (80 mg). Reprecipitation from methanol resulted in a fluffy off-white solid (mp = 85–86 °C, 78%). Anal. Calcd for $C_{28}H_{38}O_4$: C, 76.66; H, 8.75. Found: C, 76.63; H, 8.98.

Chemical Polymerization of 1a. A solution of ferric chloride (0.0101 mol) in 50 mL of chloroform was added in one portion into a solution of **1a** (0.0031 mol) in 15 mL of chloroform. The mixture was allowed to stir at room temperature with air bubbling through the solution for 20 h. The reaction was filtered and the residue washed with chloroform, methanol, and water. The brown residue was completely dedoped by stirring with 30 mL of concentrated NH_4OH. The yellowish-brown powder was collected by filtration, washed thoroughly with water and methanol until the ammonia odor had dissipated, and finally washed with ether. The resulting yellowish-brown powder was dried in a vacuum dessicator overnight. Anal. Calcd for $C_{14}H_8O_2$: C, 80.75; H, 3.88. Found: C, 70.32; H, 3.80.

Electrochemical Methods. Cyclic voltammetry and electrochemical polymerizations were carried out using an EG&G Princeton Applied Research Model 273 potentiostat/galvanostat. A 0.006-cm² platinum button was used as a working electrode in cyclic voltammetry experiments, and a 1-cm² platinum plate was utilized for the electrosynthesis of films for conductivity measurements. In each case, a platinum strip was used as a counter electrode and a Ag/Ag^+ (Ag wire in 0.01 N $AgNO_3$) was employed as a reference electrode which has a potential +0.34 V vs SCE. All electrochemical potentials will be reported and discussed relative to this reference electrode. CH_3CN was distilled over P_2O_5 and tetrabutylammonium perchlorate (TBAP) was used as received (Fluka). All electrolyte concentrations were 0.1 M, and monomer solutions were 1 mM. The mass transport properties of polymer films during redox switching were investigated using an electrochemical quartz crystal microbalance (EQCM). The change in resonant frequency of a 5-MHz AT cut quartz crystal (Valpey–Fisher) was monitored with a Philips PM6654 frequency counter. The top electrode of the oscillator also serves as the working electrode of an electrochemical cell. The change in frequency is then monitored as a function of potential and converted to mass change. Details of the EQCM are presented in a previous work.[19]

Conductivity Measurements. Film thicknesses were measured on electrode-supported films with a Tencor Instruments Alpha Step 200 profilometer. Thin films of each polymer were removed from the platinum plate using transparent adhesive tape and the conductivities measured via the four probe method utilizing a Keithley Model 224 programmable current source and a Keithley Model 197 autoranging multimeter.

Optoelectrochemical Measurements. The optical spectrum of each polymer, as a function of injected charge, was obtained using indium tin oxide (ITO) coated conducting glass as a working electrode. Films were prepared using a constant-current polymerization of $-30\ \mu A/cm^2$. The polymer-coated electrode was placed in a quartz cuvette with monomer-free electrolyte and the counter electrode described above. A silver wire was employed as a quasi reference electrode. The spectra were obtained on a Varian Cary 5 UV–vis–near-IR spectrophotometer, while the potential at the working electrode was varied. Nernst plots were obtained at the λ_{max} for each neutral polymer π–π^* transition, as outlined below.

Theoretical Calculations. In a concurrent study, conformational analyses and electronic structure calculations were carried out on these poly[1,4-bis(2-furanyl)phenylenes].[13] Band structures of the polymers were calculated using a modified extended Hückel method.[40] The partial retention of diatomic differential overlap (PRDDO) method[41,42] was employed to optimize inter-ring distances and angles as a function of torsional angle. PRDDO has been shown to be a useful tool for predicting the conformations as well as geometries of relatively large molecules[2,3,43,44] while semiempirical methods such as MNDO and CNDO are often unrealistic in indicating the perpendicular conformations to be of minimum energy.[41,42] Open-shell calculations were performed within the restricted open-shell Hartree–Fock approximations, using a 4-31G basis set and the program GAMESS.[45,46] Mullikan population analyses were done to calculate the spin densities of the constituent atoms in order to predict the polymerization sites.

Acknowledgment. Financial support from grants from the Defense Advanced Research Projects Agency, monitored by the Office of Naval Research, the Robert A. Welch Foundation (Y-743), and Rockwell International is gratefully acknowledged. J.R.R. thanks Mr. and Mrs. James A. Knight for their hospitality during the preparation of this manuscript.

References and Notes

(1) Reynolds, J. R.; Pomerantz, M. P. In *Electroresponsive Molecular and Polymeric Systems*; Marcel Dekker, Inc.: New York, 1991; pp 187–256.
(2) Ruiz, J. P.; Child, A. D.; Nayak, K.; Marynick, D. S.; Reynolds, J. R. *Synth. Met.* **1991**, *41–43*, 783.
(3) Reynolds, J. R.; Ruiz, J. P.; Child, A. D.; Navak, K.; Marynick, D. S. *Macromolecules* **1991**, *24*, 678.
(4) Ruiz, J. P.; Dharia, J. R.; Reynolds, J. R.; Buckley, L. F. *Macromolecules* **1992**, *25*, 849.
(5) Tourillon, G.; Garnier, F. *J. Electroanal. Chem.* **1982**, *135*, 173.
(6) Oshawa, T.; Kaneto, K.; Yoshino, K. *Jap. J. Appl. Phys.* **1984**, *23*, L663.
(7) Yoshino, K.; Hayashi, S.; Sugimoto, R. *Jap. J. Appl. Phys.* **1984**, *23*, L899.
(8) Wang, S.; Kawai, T.; Yoshino, K.; Tanaka, K.; Yamabe, T. *Jap. J. Appl. Phys.* **1990**, *29*, L2264.
(9) Nishioka, Y.; Wang, S.; Yoshino, K. *Synth. Met.* **1991**, *41–43*, 815.
(10) Jen, K.-Y.; Jow, T. R.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1987**, 1113.
(11) Jen, K.-Y.; Jow, T. R.; Shacklette, L. W.; Maxfield, M.; Eckhardt, H.; Elsenbaumer, R. L. *Mol. Cryst. Liq. Cryst.* **1988**, *160*, 69.
(12) Hamilton, J. G.; Marquess, D. G.; O'Neill, T. J.; Rooney, J. J. *J. Chem. Soc., Chem. Commun.* **1990**, 119.
(13) Hong, S. Y.; Marynick, D. S. *Macromolecules* **1992**, *25*, 3591.
(14) Pelter, A.; Maud, J. M.; Jenkins, I.; Sadeka, C.; Coles, G. *Tetrahedron Lett.* **1989**, *30*, 3461.
(15) Reynolds, J. R.; Marynick, D. S. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1992**, *33* (1), 1158.
(16) Ruiz, J. P. Dissertation, August 1990, The University of Texas at Arlington, Arlington, TX.
(17) Marque, P.; Roncali, J.; Garnier, F. *J. Electroanal. Chem.* **1987**, *218*, 107.
(18) Baker, C. K.; Qiu, Y.-J.; Reynolds, J. R. *J. Phys. Chem.* **1991**, *95*, 4446.
(19) Baker, C. K.; Reynolds, J. R. *J. Electroanal. Chem.* **1988**, *251*, 307.
(20) Aboulkassim, A.; Pelous, Y.; Chevrot, C.; Froyer, G. *Polym. Bull.* **1988**, *19*, 595.
(21) Distefano, G.; Jones, D.; Guerra, M.; Favaretto, L.; Mengoli, G. *J. Phys. Chem.* **1991**, *95*, 9746.
(22) Abruna, H. D. *Coord. Chem. Rev.* **1988**, *86*, 135.
(23) Child, A. D.; Reynolds, J. R. *J. Chem. Soc., Chem. Commun.* **1991**, 1780.
(24) Daoust, G.; Leclerc, M. *Macromolecules* **1991**, *24*, 455.
(25) Rughooputh, S. D. D. V.; Hotta, S.; Heeger, A. J.; Wudl, F. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 1071.
(26) Froyer, G.; Maurice, F.; Goblot, J. Y.; Fauvarque, J. F.; Petit, M. A.; Digua, A. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 267.
(27) Bredas, J. L.; Street, G. B. *Acc. Chem. Res.* **1985**, *18*, 309.
(28) Marque, P.; Roncali, J. *J. Phys. Chem.* **1990**, *94*, 8614.
(29) Roncali, J.; Shi, L. H.; Garreau, R.; Garnier, F.; Lemaire, M. *Synth. Met.* **1990**, *36*, 267.
(30) Roncali, J.; Garreau, R.; Delabouglise, D.; Garnier, F.; Lemaire, M. *Synth. Met.* **1989**, *28*, C341.
(31) Kaner, R. B.; Porter, S. J.; Nairns, D. P.; MacDiarmid, A. G. *J. Chem. Phys.* **1989**, *90*, 5102.
(32) Diaz, A. F.; Castillo, J. I.; Logan, J. A.; Lee, W.-Y.; *J. Electroanal. Chem.* **1981**, *129*, 115.
(33) Genies, E. M.; Pernaut, J. M. *Synth. Met.* **1984/85**, *10*, 117.
(34) Nechtshien, M.; Devereux, F.; Geroud, F.; Vieil, E.; Pernaut, J. M.; Genies, E. M. *Synth. Met.* **1986**, *15*, 59.
(35) Deakin, M. R.; Buttry, D. A. *Anal. Chem.* **1989**, *61*, 1147A.
(36) Ward, M. A.; Buttry, D. A. *Science* **1990**, *249*, 1000.
(37) Sauerbrey, G. *Z. Phys.* **1959**, *155*, 206.
(38) Hillman, A. R.; Swann, M. J.; Bruckenstein, S. *J. Electroanal. Chem.* **1990**, *291*, 147.
(39) Colaneri, N.; Nowak, M.; Speigel, D.; Hotta, S.; Heeger, A. J. *Phys. Rev. B* **1987**, *36*, 7964.
(40) Hong, S.; Marynick, D. S. *J. Chem. Phys.* **1992**, *96*, 5497.
(41) Halgren, T. A.; Lipscomb, W. N. *J. Chem. Phys.* **1973**, *58*, 1569.
(42) Marynick, D. S.; Lipscomb, W. N. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 1341.
(43) Martinez, M.; Reynolds, J. R.; Basak, S.; Black, D.; Marynick, D. S.; Pomerantz, M. *J. Polym. Sci., Polym. Phys. Ed.* **1988**, *26*, 911.
(44) Ruiz, J. P.; Nayak, K.; Marynick, D. S.; Reynolds, J. R. *Macromolecules* **1989**, *22*, 1231.
(45) Ditchfield, R.; Hahre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.
(46) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Jensen, J. H.; Koseki, S.; Gordon, M. S.; Nguyen, K. A.; Windus, T. L.; Elbert, S. T. *QCPE Bull.* **1990**, *10*, 52.